

OZONATION OF HUMIC SUBSTANCES IN A
MEMBRANE CONTACTOR
MASS TRANSFER, PRODUCT CHARACTERIZATION AND
BIODEGRADABILITY

Ronald Jansen

The research described in this thesis was carried out at Van Hall Institute , Leeuwarden, the Netherlands, under the departments of Sustainable Technology and Membrane Technology, University of Twente and Wetsus, Centre for Sustainable Water Technology, Leeuwarden, The Netherlands.

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Ozonation of Humic Substances in a Membrane Contactor

Mass Transfer, Product Characterization and Biodegradability

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PROEFSCHRIFT

ter verkrijging van
de graad van doctor aan de Universiteit Twente,
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en de assistent promotor:

Dr. A. Zwijnenburg

In memory of

Prof.dr.ing Marcel Mulder 1951-2002

Voorwoord

En hier zit je dan. Je legt de laatste hand aan het proefschrift en je overdenkt de afgelopen periode die je hebt gehad als promovendus in Leeuwarden. Een periode waarin veel gebeurde en alles in zich had. Met de pieken, vervolgens de dalen en dan weer de pieken die een echte promotietijd hoort te hebben.

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Begin 2004 kwam de grote verandering met de komst van het waterkenniscentrum. Toen werd duidelijk dat Wetsus opgezet ging worden in Leeuwarden en STMT op zou gaan in het nieuwe onderzoeksinstituut. Met de komst van Wetsus werd er meteen geïnvesteerd in de broodnodige analyseapparatuur. In hoog tempo werd de groep uit gebouwd met enthousiaste medewerkers uit alle richtingen, met de officiële opening in september 2004.

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I

Humic Substances: General Information, Removal and Research Outline

In this chapter the objective and possibilities for the removal of humic substances (HS) from drinking water is given. The chapter starts with the origin and general properties of humic substances. Further a brief overview is given of the characterization and of the several possibilities to remove HS from drinking water used in drinking water production. A distinction was made between destructive and non-destructive removal techniques. The outline of the research is explained in Section 5.

1 Humic Substances

1.1 Drinking water

Despite treatment many drinking water production stations produce drinking water that has a yellow/brown colour that is not removed by the purification process. In many cases this yellow/brown colour can be ascribed to so-called humic substances (HS) dissolved in the water.

Drinking water is produced from groundwater or surface water (mainly fresh water). Depending on the raw water quality it undergoes a series of purification steps, consisting usually of treatment processes like sand bed filtration, air oxidation, disinfection, coal filtration, softening etc. After this treatment process the water is qualified as drinking water.

1.2 Definitions of humic substances and related organic constituents in water found in literature

Several terms describing the organic matter in natural waters circulate in literature. The lot of them refer to the same matter, where sometimes a distinction is made based on characteristics concerning solubility and biodegradability. Below follows a summary of the most frequently used terms.

Natural organic matter. - The most general reference is the term Natural Organic Matter (NOM) describing the total content of soluble and not soluble dead organic matter in the water.

Dissolved organic matter (DOM) - Dissolved Organic Matter (DOM) is that part of Natural Organic Matter that is soluble in water consisting of humic and non-humic material.

BDOM - Biodegradable Dissolved Organic Matter (BDOM) is the part of dissolved organic matter that is biodegradable in some degree and therefore removable by some biodegradation process.

AOM/AOC - Assimilable Organic Matter/Carbon seems to refer to the same material as BDOM.

HS - The term Humic Substances (HS) seems to refer to the same matter as Natural Organic Matter does in literature and is used

throughout this thesis to refer to the dissolved organic matter in drinking water.

Humuszuren (Dutch) - Humuszuren is literally translated as humic acids and although humic acids are a fraction of HS (see below), humuszuren usually seem to represent the same compounds as the term HS.

1.3 Origin of HS

The term HS refers to a category of naturally occurring materials found in soils, sediments and natural waters. HS are formed when living matter, especially plants (but not exclusively), dies and is broken down by micro-organisms [1, 2]. The end product of the total microbial degradation tree is a cocktail of organic molecules that has lost its value as energy source for the majority of the living organisms. Many of the substances are formed in soils and find their way through groundwater to lacustrine, riverine and estuarine waters [3]. HS can also be formed directly within aquatic systems. The brown water of swamps is a good example of HS formed in the water and in the soil.

A large fraction (60-70%) of the soil organic matter and 30-50% of the surface water organic matter is represented by HS and they are believed to be the most abundant of naturally occurring organic macromolecules on the earth [1, 2].

Depending on the source the drinking water the HS content can be different. This content usually ranges from 0 up to 8 mg/L TOC. A few Dutch ground water pumping stations withdraw their water from old peat soils. These waters may have a yellow colour caused by the presence of HS. Tap water from pumping station Spannenburg (The Netherlands) usually contains up to 8 mg/L TOC with a colour value of around 20 mgPt-Co/l.

Three HS fractions

Natural organic matter can be divided in humic and non-humic material. The classic soil extraction procedure of HS yields three main fractions based on solubility and pH: humic acid (HA), fulvic acid (FA) and humin [2]. These fractions are defined operationally in terms of their solubility in aqueous media as a function of pH or in terms of their extractability from soils as a function of pH of the extraction medium. Humic acid is the fraction of HS that is not soluble in water

under acidic conditions ($\text{pH} < 2$). They become soluble (and extractable from soil) at higher pH values. Fulvic acid is that fraction that is soluble in water under all pH values. Humic acid is that fraction that is soluble in water under all pH values. Humin represents the fraction that is not soluble in water, and as such not extractable with an aqueous medium under all pH values. Figure 1 gives a presentation of the humic composition in NOM.

The adjective humic (or humic acid) is commonly used in a generic way to describe all three fractions. In the case of drinking water virtually only soluble HS are found hence the humic substance content only consists of fulvic and humic acids. In this thesis the term humic substances (HS) is used to refer to the (soluble) mixture of fulvic and humic acids.

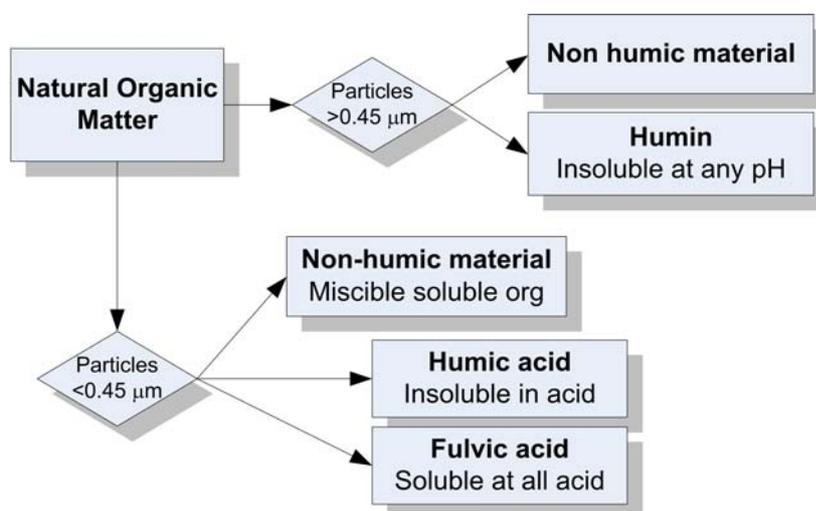


Figure 1: Schematic presentation of the composition of Natural Organic Matter in water with emphasis on humic material.

1.4 General characteristics

1.4.1 Chemical Elements in humic substances

Humic substances are typical organic molecules. An elemental analysis usually yields Carbon, hydrogen and oxygen in relatively high quantities, nitrogen in low quantities and traces of sulphur and phosphorus [4-7]. The atomic mass quantities taken from various analyses in literature lay in the range of: C: 45-55%, H: 3.3-6%, O:39-43%, N: 0.69-5.5% [4-7].

1.4.2 Molecular structure

It is important to emphasize that there is no actual molecular structure known of "a humic substance". Being a supermixture, humic substances cannot be separated into pure chemicals [2]. Determining the molecular structure of humic substances would ultimately mean determining each molecule in the system, which is not feasible. Most studies that are performed to understand the chemical behaviour by means of spectroscopic techniques yield, at the highest, qualitative information on types of functional groups present in the HS molecules. Analyses with several techniques (see Section 3 in this chapter) have given some clues on the molecular structures and functional groups that may be present in HS molecules. Those analyses indicate that almost any type of group that is thinkable in organic chemistry might be present in a HS molecule. The carbon structure may consist of aliphatic chains, (poly-)aromatic and furanic groups. Ester and ether bonds may be found throughout the structure as well as carboxyl, carbonyl and alcoholic groups. Nitrogen can be located in pyrrole and pyridine groups and amines in the molecular structure.

Westerhoff et al. [4] characterized a number of humic substances of different origin within the United States. From C^{13} -NMR analysis they derived that of the total carbon content on average 49% was situated in aliphatic structures, 21% in aromatic structures, 20% in carboxylic groups and 4.8% in ketonic groups

Several researchers [2, 8] (and references herein) have proposed pseudo humic substance structures as hypothetical molecular constructs. Those structures have the elemental, structural and functional group features consistent with some or all the observed properties of a given HS mixture. By no means should these structures be taken as representations of real molecules. They only account for general compositional features of a HS mixture. Figure 2 shows a structural concept (pseudo structure) of a humic substance according to Schulten and Schnitzer [8]. Such a conceptual structure is useful to give an insight into what molecular structures and functional groups one might expect to find in humic substances.

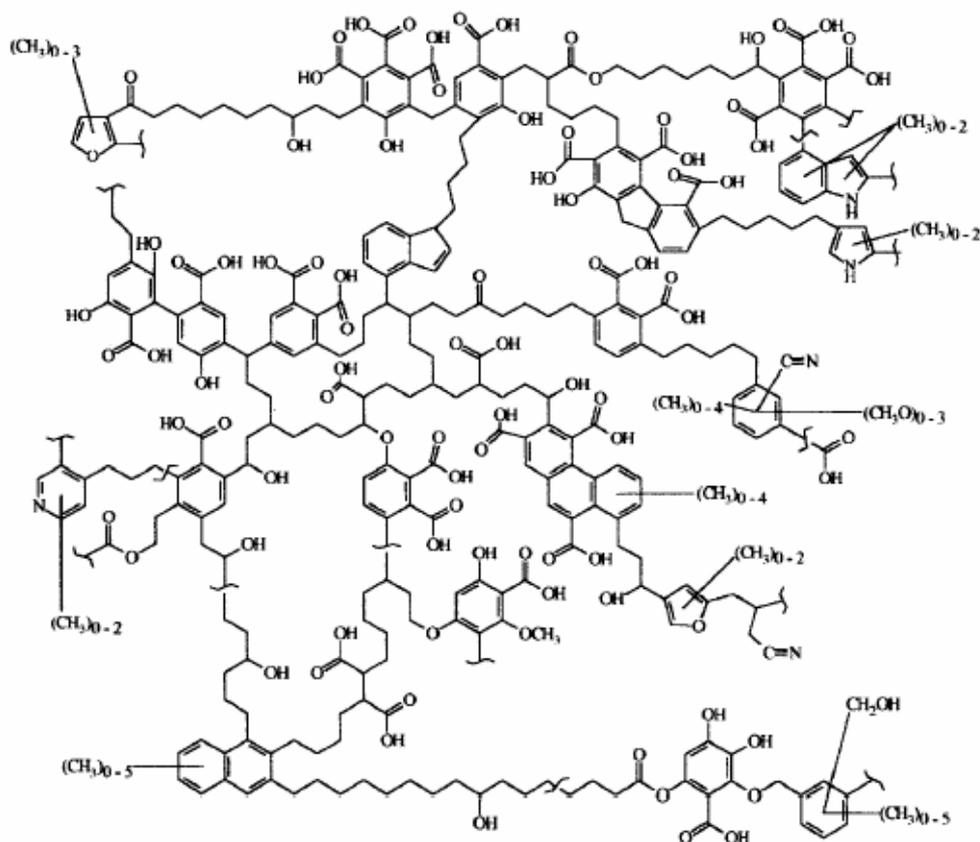


Figure 2: Structural concept of a humic substance molecule, adapted from Schulten and Schnitzer [8].

1.4.3 Molecular weight

The molecular weight of humic substances is a value that is difficult to grasp. Several techniques have been applied to estimate the molecular weight and it is thought that the molecular weight can vary from 10^2 to 10^5 Dalton [9, 10]. There are two major problems associated with the mass determination of humic molecules. The first is the mass distribution of the molecules as humic substances are a cocktail of organic molecules of various type and size. Secondly, the possible association of humic molecules, which is dependent on concentration and water conditions, makes it difficult to distinguish between intrinsically high mass molecules and aggregations of masses [1].

1.4.4 Colloidal Properties

Water conditions

Humic substances are refractory anionic macromolecules. They contain aromatic and aliphatic components with carboxylic, alcoholic

and ketonic functional groups. As a result of the presence of a large amount of carboxylic groups humic substances are negatively charged in the pH range in natural waters. Besides hydrophilic functional groups humic substances also contain hydrophobic parts. These properties and being flexible macromolecules, make that the behaviour of humic substances is depending on the conditions of the environment that it is present in. Investigations in the field of membrane filtration (membrane fouling) [11], size exclusion chromatography [12, 13] and adsorption on minerals and metal oxides confirm this. The shape or size of humic substances in aqueous solution may be dependent on the conditions of the water. At high pH a large part of the carboxylic and phenolic groups are deprotonized [1]. As a result the molecules tend to stretch out because of the electrostatic repulsing forces of the negative charges and because the carboxylic sites become more hydrophilic. At low pH more carboxylic groups are protonized and the molecules tend to get a smaller configuration due to the reduced electrostatic repulsion and increasing hydrophobicity. Hong and Elimelech [11] investigated the fouling behaviour of natural organic matter (NOM) at several ionic strengths. At high ionic strength the charges of the humic molecules are reduced due to double layer compression and charge screening thus lowering the zeta-potential of the molecules. This leads to a lower electrostatic repulsion which leads to a more compact molecular structure [14]. The reduced electrostatic repulsion between molecules at higher ionic strengths can lead to coagulation of the humic molecules (see also Section 4.3). The higher the charge of the cations present in the solution the stronger the reduction of the zeta potential and the stronger the coagulating effect. At low ionic strength the zeta potential of the molecules is higher and the electrostatic repulsion forces stronger cause the humic molecules to stretch out and prohibit coagulation of humic molecules [11]. Wall and Choppin [15] investigated the influence of divalent cations (Ca^{2+} and Mg^{2+}) on the coagulation of humic acids and found that the coagulation increased with ionic strength and cation charge density and decreased with increasing pH.

Binding with metals

Humic substances are known to interact strongly with cations and with that also metals. The presence of the negative potential around the humic molecule will cause cations to be attracted towards

the surface. This attraction of cations creates the electrostatic double layer around the molecule. Double layers are very dependent on the ionic strength, which explains the ionic strength dependence of metal binding [1]. Calcium-ions can form complexes with humic substances. From observations Hong and Elimelech [11] suggested that at pH 8 each Ca^{2+} binds two carboxylic groups. At high Ca^{2+} concentrations they observed that humic substances become insoluble when maximum complexation is attained. From the perspective of metals it is a subject of interest since it may affect the mobility of (heavy) metals in the environment [1, 16]. Humics can bind almost all transition metals [1]. The strength of the binding depends strongly on the type of metal ion. Humic substances may also be redox active towards metals [1] reducing metals in oxidized state.

Interaction with biocides

The widespread use of biocides in agriculture has led to studies on the interaction and retention of these materials by soil components and the mechanisms of their interaction with components such as humic substances [1, 17]. The binding of biocides to soil components is considered to be a major cause of biocide deactivation once in soil. This deactivation can be caused by inhibition of their toxic properties and by restriction of the transport of these compounds into water systems [1]. Various binding mechanisms have been proposed for the formation of biocide-humic complexes. Ionic interaction, interaction by charge transfer bonds with complementary electron donor or acceptor structural residues in the humics and hydrogen bond interactions are mentioned as possible binding mechanisms [1] .

Humic substances as carrier of toxic compounds

From environmental health point of view there is interest in the binding of certain organic chemicals and metals by humic substances. Humic substances can have the potential to fix or retain organic molecules [17]. By this way it may enhance the solubility of low soluble anthropogenic organic chemicals and with that the mobility of these compounds in soil and surface water [18].

1.4.5 Biodegradability

The biodegradability of HS is known to be low to extremely low. The reason for this might be the size and complexity of the

molecules. Further, being already a product of microbial degradation it has lost its value as an energy source for micro organisms. When one considers, in the case of groundwater, the fact that the layers from which the drinking water is drawn are peat soil layers which have been formed thousands of years ago, one can imagine that these organic compounds had every chance to be broken down over the years; first aerobically, later anaerobically deeper in the soil. The fact that these organic compounds despite a long residence time remain in the water is a sign on itself that its biodegradability may be very low.

2 Hazards and legislation

2.1 Health hazards of HS

HS themselves are not hazardous for public health. They can have however an adverse effect on the drinking water quality in three ways [19]:

- HS can transport and distribute organic and inorganic micro pollutants such as heavy metals and biocides. (see Section 1.4.3)
- They can act as precursor for hazardous compounds [17]. A specific side-effect of the disinfection of HS containing water with halogenated disinfectants is the formation of trihalomethanes (THM). THM's such as chloroform, dibromochloromethane are suspected to be carcinogenic. Rook [20] investigated the possibility for fulvic acids to form trihalomethanes when chlorine is added. It was demonstrated that a few micrograms THF's could be formed out of a few milligrams chlorine and/or bromine in HS containing waters.
- They can serve as a substrate for undesired biological growth in transport and process systems.

2.2 Drinking water legislation on colour

Among the demands for drinking water quality the colour is defined specifically. This colour demand is mainly for aesthetic reasons: people demand colourless water. The current Dutch government regulations on drinking water allow a colour level equivalent to 20 mgPt-Co/l [21]. At this moment the amount of

colour found in tap water from pumping station Spannenburg (The Netherlands) is more or less at the edge of the permitted colour level. However, this colour demand becomes more stringent and will force drinking water companies to remove colour from their drinking water, either by a treatment that lowers the colour but leaves the HS carbon content more or less unaffected or by (partial) removal of the HS that cause the yellow/brown colour.

3 Characterization of humic substances

Being a cocktail of various complex organic compounds HS are hard to characterize. To make things worse: HS show generally the same characteristics [2] but differ depending on their origin. Almost every analysis technique known in science has been used to characterize HS. Most of these techniques are only able to estimate general characteristics such as molecular size distribution, qualitative indication of functional groups, colloidal properties etc. The outcome of these techniques, in general, only results in a "fingerprint" of the concerned HS sample.

3.1 Water Quality parameters

In many studies the treatment of HS is evaluated by measuring some standard water quality parameters. None of these parameters can exactly quantify amounts or indicate something about the molecular structure of the compounds, but following these parameters during treatment might indicate the effectiveness of the processes that are going on.

TOC - To quantify the humic substance mass in a solution usually the amount is expressed as Total Organic Carbon (TOC) (mg/l). This measure is also used throughout this thesis to express the HS content in the solutions.

Colour - The yellow/brown colour of water that is caused by the presence of HS is usually expressed as equivalent of the Pt concentration in a Pt/Co complex solution (mgPt-Co/l).

UV-Vis/SUVA - Also UV absorbance is used as a measure. The standard wavelengths that are used are usually 254 nm (unsaturated bonds) and 455 nm (colour). SUVA stands for Specific Ultra Violet Absorption and is calculated as

$$\text{SUVA} = \frac{A}{\text{TOC}} \left(\frac{1}{\text{mg} \cdot \text{cm}} \right) \quad (1)$$

The measurement is officially performed at 253.7 nm, but often rounded of at 254 nm. The SUVA is often considered as a measure of the aromaticity and hydrophobicity of organic compounds. Westerhoff et al [4] characterized a large number of humic substances of different origin. They found a strong correlation between the SUVA, molecular weight and aromaticity of the humic substances. The SUVA of drinking water from pumping station Spannenburg in The Netherlands is 0.026 l/mg/cm. Humic substances concentrated by ion exchange absorption and used throughout this research has a SUVA of 0.036 l/mg/cm.

COD - Chemical Oxygen Demand (COD) (mg/l) represents the oxygen needed for complete mineralization of the (organic) compounds by chemical oxidation.

BOD₅ - Biochemical Oxygen Demand (BOD) (mg/l) refers to the amount of oxygen needed for biodegradation of the compounds in solution in five days. When the BOD₅ is equal to the COD it means that all compounds are completely biodegradable (provided that all components have been mineralized during the COD measurement).

3.2 Chromatographic Techniques

Several studies are published on of chromatographic methods or their use in research concerning humic substances. Janoš [22] summarized a number of chromatographic methods and studies on the separation of HS.

(HP-)LC – (High Performance) Liquid Chromatography. The separation in liquid chromatography is based on chemical interaction with the stationary and mobile phase and therefore differences in adsorption characteristics. Depending on the column that is used a separation can be made on hydrophobicity/hydrophilicity, acidity, ionic characteristics etc. In the chromatogram the HS fractions are characterized on these properties. It is clear that the conditions (ionic strength, pH, temperature etc.) of the mobile phase strongly influence the result of this technique.

(HP-)GPC/SEC – The separation in (High Pressure) Gel Permeation Chromatography/Size Exclusion Chromatography is based on molecular size and therefore as chemical interaction with the

stationary phase should be avoided. The separation column is filled with particles containing pores. The separation occurs through intrusion probability of compounds in the pores: large compounds cannot enter the pores because of their size and are eluted fast whereas small compounds have a higher probability of entering the pores and have a longer travelling path, or residence time before elution. A number of studies have been performed on humic substances by GPC/SEC. It is mainly used to determine molecular weight and weight distributions [12, 13, 23]. An important factor in GPC/SEC is the calibration of the system with reference compounds. In case of humic substances the problem is that no reference compounds are available that exactly match the behaviour of humic substances. In Chapter V this is handled further in more detail.

(Capillary) Electrophoresis – is a separation technique based on the migration of electrically charged or ionic particles in solution due to an applied electric field between an anode and a cathode. To prevent migration through convection stabilizing media such as a gel, a membrane, or on paper are used. These methods are usually operated as zone electrophoresis. In a review by Janoš [22] several types of electrophoreses are described which were used for characterization of humic substances. As in many characterization techniques used for humic substances also electrophoretic techniques give a fingerprint of the analysed humic substances, which might change with each HS origin and/or treatment.

3.3 Spectrometry

NMR – The nuclei of many atoms possess a magnetic moment. Placed in a magnetic field the nuclei can point only in two directions relative to the field and none in between. Radio radiation of the right frequency can raise a nucleus from the ground state (aligned along the magnetic field) to the excited state (aligned against the magnetic field). Nuclear Magnetic Resonance Spectroscopy is based on the moment of energy absorption of these nuclei in a magnetic field when with a certain frequency (i.e. energy) is radiated. The specific frequency (resonance frequency) depends on the magnetic field strength and the identity of the nucleus. However depending on the chemical environment of a nucleus a so called chemical shift occurs of the resonance frequency: the chemical environment shields the nucleus from the magnetic field. Since in a molecule the chemical

environment for several nuclei of the same type can differ, different chemical shifts can be observed during a NMR test. A nucleus in a functional group has its own specific chemical shift. Therefore the chemical shifts observed at an NMR analysis of a compound might reveal (partly) the molecular structure of a compound. There are a few nuclei suitable for NMR analysis of which ^1H and ^{13}C are the most well known. For analysis of humic substances ^{13}C NMR is most common. To reveal the complete molecular structure of humic substances is virtually impossible due to the size and complexity of the structure. However, the technique may be useful to give an insight in the type of functional groups present in the molecules and with that it may also be useful in following the change in functional groups during a specific treatment.

IR / RS – Infrared spectrometry (IR) and Raman spectrometry both are used to probe the characteristic vibrations or rotations of molecules, crystals and glasses or chemical bonds in molecules. In IR the absorption of light in the infrared region is measured at several frequencies. The light absorption at a specific wavelength corresponds to stretching or bending of specific atomic bonds. The vibration of bonds is dependent on the type of atoms, type of bond and the functional group (or molecule) that contains them. This way each compound has its own IR absorption spectrum that can give some information on the molecular structure. In Raman spectrometry a sample is irradiated with light of a certain wavelength. The energy levels of molecules are explored by examining the frequencies present in the radiation scattered by molecules. In a typical experiment the scattered radiation is monitored perpendicular to the incoming beam. Here photons may collide with molecules, give up some energy and emerge with a lower energy (lower frequency). Other photons may collect energy from (excited) molecules and emerge with a higher energy (higher frequency). The shift in frequency is a measure for the vibration and rotation energy of atomic bonds and molecules. Also here each compound has its own characteristic spectrum. The different compounds in humic substances make that an IR or Raman spectrometric analysis yields a fingerprint of that specific humic substance. As in NMR analysis the technique is useful to trace some functional groups in the HS molecules. Treatment with for example ozone, yields a different spectrum with changes for specific functional groups so the effects of ozonation on the molecular structure might be estimated.

Mass Spectrometry (MS) - Mass spectrometry is a name for a collection of techniques to measure the masses of ions and their abundances in the gas phase. In general all techniques consist out of the following steps: 1. Generation of the gas-phase molecules (and molecular fragments and atoms), 2. Their ionization, 3. Their separation based on mass, 4. detection of the ion beam. The difference between the techniques is how they procure one or more of these steps. In principle ionized gas-phase molecules are accelerated (in a broad sense) in an electromagnetic field. The driving force for acceleration is depending on the field force and the charge of the ions. The mass of the ions is counteraction the acceleration (mass inertia). The separation is than based on the m/z ratio of the ions, where m is the mass of the ion and z the charge. For humic substances mass spectrometry had its limitations initially. One is because of the destructive nature of the ionization techniques. Through this only fragments of molecules can be detected and for large molecules it becomes hard to puzzle the pieces back together to the original molecule. In the case of humic substances this becomes worse being already a cocktail of molecules of different shape and size. This can be overcome partially by using a separation technique, like gas chromatography (GC), prior to MS. The problem with GC analysis is that it is not easily applicable for polar and macromolecular substances, of which humic substances contains a great portion. However, in the last years soft ionization techniques have developed together with the development of new interface designs and mass analyzers [24]. Techniques like ESI, APCI and MALDI have caused significant progress in characterization of macromolecules and can look forward to an increasing interest for use in research on humic substances [24, 25].

3.4 Combinations of characterization methods.

Often a combination of analysis techniques is used to characterize humic substances either on molecular weight or structure. Combinations of GPC and electrophoresis [26], GPC and mass spectrometry [27], pyrolysis with gas chromatography followed by mass spectrometry [8] can be found in literature. Also membrane fractionation is used prior to an analysis technique [23]. These combinations offer a more extensive insight in the structural and chemical properties of humic substances and during a possible

treatment. But even with a combination of such analysis techniques it remains virtually impossible to reveal the molecular structure of the cocktail of organic compounds existing in the group of humic substances.

4 Removal of humic substances

4.1 Introduction

For several reasons there is a demand for removal of the HS. This may be aesthetic (giving colour to water) and/or health hazard (see Section 2.1 in this chapter) reasons. The removal of HS does not seem to give much technical problems as can be seen by the large amount of successful results published in literature. In some cases a waste stream consisting out of concentrated HS (in solution) may result from the removal process. Disposal of this concentrate to the surface water, land or in the sewage may not be desirable.

Considering the removal techniques a division can be made between destructive and non-destructive techniques. In destructive processes the HS are treated directly by chemical and/or biodegradation processes. In non-destructive processes the HS are removed in concentrated form or adsorbed on an adsorption medium.

4.2 Waste water disposal demands

Considering the several non-destructive techniques it is relatively easy to remove HS from aqueous systems and concentrate them. Own experience with ion-exchange for example shows that HS concentration up to 30 gC/l can be obtained, with a salt content (from regeneration) of 1 M. The COD of such a HS solution can run up to $5 \cdot 10^4$ mg/L. As stated earlier the biodegradability of these humic substances is very low. Disposal of this brine on the land or surface water is not desirable. However, the legislation on waste water discharge is not univocal and depends on the environmental region in which the waste water is discharged. Table 1 shows the limiting values for BOD₅, COD and undissolved components in urban wastewater for discharge on surface water, ordered by Dutch legislation [28].

Table 1: Dutch legislative demands for discharge of urban wastewater on surface water [28].

Parameters	Max. level
BOD ₅ without nitrification (20 °C)	20 mg/l
COD	125 mg/l
Total amount undissolved components	30 mg/l

4.3 Non-destructive removal

4.3.1 Adsorption

The most common adsorption technique used in drinking water treatment is activated carbon adsorption. Usually granular activated carbon (GAC) is used where granulates of different sized can be applied. The grains may contain pores which increase the contact area considerably. Several physical and chemical parameters affect the HS adsorption. The adsorption capacity seems to be based on the surface charge, the pore structure and size, the size of the HS and with that the conditions of the water such as pH and ionic strength [29]. The size of the pores may even cause a fractionation of compounds with different molecular sizes. GAC has limited abilities for regeneration. Changing the water condition may result in some regeneration of GAC, but for complete regeneration more extensive measures are needed like pyrolysis or treatment with a strong oxidant like ozone.

4.3.2 Ion exchange adsorption

An adsorption technique based on charge is ion exchange adsorption. Because of their negative charge at normal pH, HS may effectively be removed by anion exchangers. An extensive research with a number of ion exchange resins has been done by Bolto et al. [30]. They compared ion exchange resins with different characteristics on their ability to remove NOM from several sources. Ion exchange processes have already been applied in drinking water production to remove colour in Norway [31, 32].

4.3.3 Coagulation/flocculation

An important aspect concerning the stability of colloids in solution is the existence of an electric charge on their surfaces. Ions of opposite charge tend to cluster nearby and an ionic atmosphere is formed. There is a fairly immobile layer of ions that stick closely to the surface of the colloid (which may include water molecules). The electric potential at the radius of this sphere relative to its value in the distant, bulk medium is called the zeta potential. The inner shell of charge and the outer atmosphere is called the electric double layer. At high ionic strengths the atmosphere is dense and the potential of the colloid falls to its bulk value in a short distance. In this situation there is little repulsion among equally charged colloids. As a result coagulation and flocculation occurs as a consequence of Van der Waals forces. The ionic strength is increased by addition of ions and as such they can act as flocculating agents when they are of opposite charge compared to the colloids zeta potential. The flocculating potential increases strongly with higher charge numbers. Al^{3+} and Fe^{3+} are well known flocculating agents, but also Ca^{2+} and Mg^{2+} have proven their use. Next to inorganic coagulants also cationic polymers (polyelectrolytes) are used as coagulant. Besides their coagulating qualities they also have the ability of binding already formed flocs into larger particles. Many studies have been reported on the removal of humic substances and the use of several coagulants [15, 33, 34]. Coagulation processes are sometimes combined with membrane filtration [35, 36].

4.3.4 Membrane filtration

Drinking water treatment by membrane filtration becomes increasingly widespread. In principle membrane filtration can be effective in removal of natural organic matter from water [37]. However, fouling of the membranes may result in major operational problems causing reduced filtration rates and high operation costs [37, 38]. In some cases membrane filtration is used in combination with adsorption or coagulation techniques [35, 36, 39]. Basu and Huck [40] investigated the combination of a biofilter and an immersed membrane (UF) and concluded that the biofilter should be placed ahead of the membrane for improved TOC removal from humic waters and lower membrane fouling.

4.4 Destructive removal

One of the simplest ways to break down humic substances is to evaporate the water and to incinerate the dry humic substances. However, this is not a very energy and/or cost effective method. There are some ways to treat humic substance in the water phase. A few oxidative methods are described below.

4.4.1 Ozone oxidation

Ozone is one of the strongest oxidants and is used widely in treatment processes for drinking water and (industrial) wastewater. Also in processes where ultra clean water is used ozone is applied for disinfection and oxidation of pollutants. Ozone has the property to decompose in water in a self sustaining radical chain reaction, initiated by hydroxide ions (see Chapter II). For effective use this may be a disadvantage. It is however a great advantage in the water treatment field since hardly any ozone resides long in the water after the treatment process due to its auto-decomposition. The ozonation mechanism can act in two ways: the direct reaction, where ozone reacts directly with the other compound and the indirect reaction where the reactions occur through a radical pathway of which ozone stands on the beginning of the radical chain reaction. The radical reaction is very fast, however the radical formation is relatively slow and depends on the reaction surroundings and circumstances. The efficiency for ozone use differs depending on its utilization. Ozone oxidation is extensively handled in Chapter II.

4.4.2 Wet (air) oxidation

Wet oxidation involves the liquid phase oxidation of organics or oxidizable inorganic compounds at elevated temperatures (125 – 230 °C) and pressures (0.5 – 20 MPa) using a gaseous source of oxygen [41]. When the oxygen source is air the process is referred to as wet air oxidation (WAO). The elevated temperature and pressure enhance the driving force for oxidation. WAO can completely mineralize organic compounds depending on the extent of oxidation. Carbon is oxidized to CO₂ and nitrogen to NH₃, NO₂ or elemental nitrogen. The operating costs are almost entirely for power to compress air and high pressure liquid pumping. However, WAO becomes self-sustaining when the COD is above 20·10³ mg/l [41]. WAO can become more efficient when using a suitable catalyst (Cu²⁺, Fe²⁺, CuO/ZnO etc.).

Wet oxidation of HS has not been widely reported yet. Some results in the Netherlands were published on the investigation of the combination of ion exchange and wet oxidation for removal of colour from drinking water [42]. The TOC amount of the ion-exchange regenerate can be up to $30 \cdot 10^3$ g/l. Complete mineralization of the organic compounds in this solution may clean the brine so that it is suitable again for regenerating the ion-exchange column again. According to the authors this combination results in a removal against relatively low costs per cubic meter of drinking water. Wet oxidation is also used as combustion process for (dissolved) carbon analysis in water.

4.4.3 Photolysis

Photolysis refers to photo-activated chemical reactions which are characterized by a free radical mechanism initiated by the interaction of photons of a proper energy level with the molecules of chemical species present in the solution, with or without the presence of a catalyst [43]. The radicals can be produced using UV radiation by the homogeneous photochemical degradation of oxidizing compounds like hydrogen peroxide and ozone (also referred to as Advanced Oxidation Processes, AOPs). Another way is the photo catalytic mechanism occurring at the surface of a semiconductor (like TiO_2). This enhances the rate of generation of free radicals. Several publications report research on the photocatalytic degradation of HS [44-46]. Also a number of studies have been reported that handle the influence of humic substances on photocatalytic processes for treatment of compounds in aqueous solutions [47, 48].

4.4.4 Hydrogen peroxide oxidation/Fenton oxidation

Hydrogen peroxide is a strong oxidant and is applied in the treatment of various inorganic and organic pollutants. However, reactions occur at a much lower rate. Like the indirect ozone reaction, the reaction takes place by hydroxyl radicals. A low reaction rate is mostly due to a low dissociation rate of hydrogen peroxide into radicals. Therefore hydrogen peroxide is usually applied in AOPs or in combination with a catalyst which enhances the production of hydroxyl radicals. The combination of hydrogen peroxide and ferrous salts is referred to as Fenton's reagent [49]. Ferrous ions enhance the decomposition of hydrogen peroxide producing hydroxyl ions and radicals, making the oxidation efficiency pH dependent. Fenton

oxidation is widely used in water treatment [43, 49]. Not much research has been published recently on the treatment of HS by Fenton oxidation. Murray et al [50] studied the NOM-removal by Fenton oxidation and combined with UV irradiation. Other studies monitor the influence of HS on the oxidation process [51].

4.4.5 Advanced Oxidation Processes (AOP's)

The hydroxyl radical is one of the most oxidizing compounds known. It reacts very fast and virtually non-selective with organic components. In situations where oxidation with ozone is not sufficient or economically feasible, oxidation by OH radicals becomes preferable. Processes that aim for the enhanced formation of hydroxyl radicals are called "Advanced Oxidation Processes" or AOPs. An AOP usually involves the combination of two or more separate oxidation processes optionally with a catalyst [52, 53]. O₃/H₂O₂, O₃/UV, H₂O₂/UV, O₃/UV/H₂O₂ and UV/Fenton oxidation are examples of well known combinations [17, 53, 54]. Also these processes are often followed by biological treatment [54-57]. More detailed information on AOP reactions is given in Chapter II.

4.4.6 Chlorine/ chlorine dioxide oxidation

From the early beginning of water disinfection chlorine has been used as an effective disinfectant. Chlorine is usually applied as OCl⁻/HOCl. For a few decades it is known that a side effect of chlorination in drinking water treatment is the formation of potentially harmful disinfection by-products like trihalomethanes (THMs) and haloacetic acids (HAAs) and others [20, 58]. Studies have shown that many parameters influence the formation of these products such as chlorine dose, concentration and type of natural organic matter (NOM), the presence of bromide and ammonia, pH and temperature [59-61]. In more recent work of Gallard et al [62] the THM formation was studied for NOM of different origin and pre-treatment and for model compounds. Gang et al [63] studied the relationship between the size of NOM fractions and THM formation. They found an increasing amount of THM's formed per amount of Cl₂ with decreasing molecular size of the NOM fractions.

Oxidation with chlorine dioxide (ClO₂) is said to produce less THMs and HAAs in water treatment [64-66]. However, concern does exist in the formation of by-products including chlorite and chlorate [66]. About the formation of halogenated by-products different

results are reported. Li et al found no THMs after oxidation of humic acid with ClO, but in presence of chlorine or bromide also oxidation with chlorine dioxide yielded substantial THMs and HAAs [65]. Chang et al [67] reported formation of THM and HAAs with only ClO₂ as oxidant and addition of bromide only resulted in a shift of THM types but not in total concentration. Based on distinguished NOM fractions Świetlik et al [68] studied the NOM composition and products after treatment with ClO₂ (and ozone) but focussed mainly on molecular size distribution of the products.

4.4.7 Biodegradation

Bacterial

The biodegradability of HS is known to be low to extremely low. Being already a product of microbial degradation it has lost its value as an energy source for micro organisms. They may be biodegradable in at least some extend but because of the molecular size biodegradation is not expected to be rapid. [69]. The biodegradability may differ with the origin and type of the humic substance. The biodegradability may well be site-specific and some functionalities within a molecule are more easily biodegraded than others [69].

Fungi

Some authors report some success in breaking down HS by fungi. Blondeau demonstrated the degradation of humic acids by a white rot fungus by its decolourization and shift in molecular weight [70]. More recently Yanagi et al. [71] compared the decolourization of several humic substances with different structural properties by microorganisms among which a few fungi. The decolourization depended on the molecular structure of the humic acids. A high carbohydrate content and a low aromaticity appeared to be conditions for relatively fast degradation.

4.4.8 Chemical oxidation and biodegradation

Total chemical oxidation of humic substances to complete mineralization (CO₂ and H₂O) is economically not favourable and the biodegradability of humic substances is very low. A possible solution for a successful destructive removal of humic substances is the combination of a partial chemical oxidation followed by biodegradation. The products of the chemical oxidation of humic substances should be biodegradable. Possible types of products from

ozone oxidation of humic substances are discussed in Chapter III. A few studies have shown the success of this combined treatment [72-75]. In some places a full scale drinking water treatment plant has been put into operation using ozone oxidation followed by biofiltration to remove humic substances from the drinking water [31].

For an optimal treatment it is important to know the extend of ozone oxidation that is needed for a successful biodegradation. Usually this is expressed in the amount of ozone needed per amount of TOC or DOC. Melin et al [72] found that an amount of 1.0 to 1.7 mgO₃/mgTOC was sufficient for 73 to 84% colour removal (TOC = 8 mg/l) in an ozonation/biofiltration treatment plant. In a review on the removal of HS by oxidation/biofiltration Graham [75] listed the findings of several ozonation/biofiltration experiments on the performance of oxidation of HS followed by biofiltration (slow sand filtration). Depending on the ozone dose colour removals up to 80% were achieved and DOC removals up to 55%. Unfortunately the ozone dose was not always expressed in the specific ozone consumption (mgO₃/mgDOC) but in the ozone concentration applied. In the cases where the specific ozone consumption was given, a DOC removal of 30-35% was reported after an ozone consumption of 1 mgO₃/mgDOC. Usually, an increased ozone dose results in an increased colour and DOC removal. However the source of HS seems to be an important factor in the ozone expenditure [74, 75].

5 Outline of the research

5.1 Problem

Drinking water companies are forced into active removal of the colour of the drinking water by legislation. The substances responsible for this colour are so-called humic substances (HS) and are not removed by the conventional drinking water treatment processes.

5.2 Choice of treatment

Among several options an ozonation/biofiltration process is a possible way to treat humic substances in the removal of colour. This process has already proven its success in drinking water treatment

(see Section 4.4.8). In these applications ozonation is applied for colour removal and biofiltration is used to remove any biodegradable ozonation by-products that may cause biofouling in the drinking water system.

There are two choices of operation to treat these HS:

1. In-line in the drinking water process.
2. Removal of HS from the drinking water and treat them separate from the drinking water production line.

In-line treatment means focus on colour reduction, large process equipment, risk of hazardous products from treatment in a clean drinking water production process and possible low effective use of ozone. Separate treatment means the installation of an extra step for the removal of humic substances, focus on substrate removal, small process equipment, effective ozone use and no hazards for the drinking water quality.

Since the quality of the drinking water is the most important factor in this decision, the choice is made to remove the humic substances from the drinking water process and treat the humic substances separately from the drinking water process.

5.3 Research aim

The goal of the research is to investigate the degradation of concentrated humic substances by an ozonation/biofiltration system. The humic substances are concentrated by ion-exchange adsorption and the research is mainly focused on the ozonation of humic substances. To bring the ozone into contact with the HS solution an ozone resistant membrane module is developed to serve as gas-liquid contactor. The research is divided in a number of research topics of interest:

- *Ozone mass transfer in a PVDF hollow fibre membrane contactor.* Testing of a membrane hollow fibre module suitable as gas-liquid contactor for ozone applications. The membranes and module components are made out of ozone resistant materials. The performance was measured during mass transfer experiments. (Chapter III)
- *Reaction kinetics of the ozonation of humic substances in a membrane contactor.* Based on its specific features the membrane contactor is applied as a tool to study the reaction kinetics of the ozonation of humic substances at several ozone concentrations,

humic substance concentrations and as function of the oxidation level of the humic substances. (Chapter IV)

- *Products from ozonation of humic substances.* Identification and product characterization on molecular size (distribution) of humic substances during ozonation. (Chapter V)
- *Ozonation of humic substances at several humic substance concentrations.* Influence of different humic substance concentrations on colour, TOC reduction and the change in molecular size (distribution) of humic substances and ozonation products during ozonation. (Chapter VI)
- *Biodegradation of humic substances after ozonation.* The ultimate goal is the enhancement of the biodegradability of humic substances by ozonation. Experiments in Norway and in the laboratory were conducted to investigate the biodegradability of pre-oxidized humic substances. (Chapter VI)

6 Nomenclature

Abbreviations

AOM/AOC	Assimilable Organic Matter/Carbon
AOP	Advanced Oxidation Process
COD	Chemical Oxygen Demand
DOC	Dissolved Organic Carbon
DOM/BDOM	Dissolved Organic Matter/Biodegradable Dissolved Organic Matter
FA	Fulvic Acids
GAC	Granular Activated Carbon
HA	Humic Acids
HAA	Halo-Acetic Acids
HS	Humic Substances
NOM	Natural Organic Matter
THM	Tri-Halo-Methane
TOC	Total Organic Carbon
WAO	Wet Air Oxidation

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II

Properties of ozone in water

Literature overview on properties of ozone in water. The overview concerns the molecular structure and thermodynamics and general properties. The solubility, and diffusivity of ozone in gas and water is discussed involving several correlations to estimate these properties. Further, the reactions concerning the ozone (self-)decomposition in water and considerations on ozone reactions with organic compounds, chloride and bromide in water are described. In the end possible products of ozonation and advanced oxidation processes (AOP's) of some organic compounds are briefly summarized.

1 Introduction

Ozone is well known with the general public as the gas that forms the ozone layer in the stratosphere that filters a large part of the harmful UV radiation from the sun. In the world of water treatment ozone is known to be a strong oxidant used as disinfectant or as a reactant for the degradation of undesired compounds. In this capacity ozonation is used in many countries as part of drinking water processes and in waste water treatment. Next to being a strong oxidant, ozone itself has the quality that in water it slowly decomposes by an auto catalytic reaction into oxygen initiated by hydroxide ions. This way any residual ozone disappears after sufficient time in the water without causing any harm to consumers or in following processes.

2 Ozone properties

2.1 Identity

Ozone (CAS number [100028-15-6]) as a gas was discovered in 1839 by the Swiss chemist Schönbein. The gas was named "ozone" which is derived from the word "ozo", Greek for smell. Later it was found that the molecule is an allotrope of oxygen. It is built from three oxygen atoms (O_3). Under standard conditions ozone is a gaseous compound with a pale blue colour. It is a relatively unstable compound and due this instability ozone is mostly found as a mixture of oxygen and ozone.

2.2 Structure and bonding

Ozone has a bent structure of C_{2v} symmetry with an angle of $116^{\circ}49'$ and equal oxygen bond distances of 0.128 nm. The bonds have a double bond character. The resonance structures of ozone are presented in Figure 1. These forms are consistent with the 1,3-addition chemistry of ozone to double bonds. The π -electrons are almost evenly distributed over the molecule but the exterior atoms have a slight excess of electron density over the central atom. This results in a low dipole moment of $\mu_D = 0.53$ D [1].

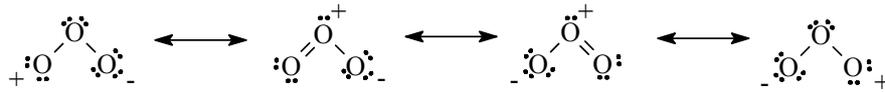
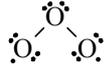


Figure 1: Resonance structures of ozone

Molecular orbital and valence bond calculations suggest that a 1,3-singlet diradical structure like ,



may contribute significantly to the ground state of ozone. This could explain the reaction of ozone with saturated C–H bonds [1].

2.3 Thermodynamics

Ozone is a stronger oxidizing agent than oxygen or hydrogen peroxide. It reacts with most substances at room temperature. In acid solution the oxidizing power of ozone is exceeded only by a few other compounds like fluoride, atomic oxygen, OH radicals and a few others of such species [1]. The potentials in aqueous solutions are [2]:



Ozone is thermodynamically unstable and its decomposition $\text{O}_3 \rightarrow 3/2\text{O}_2$ is exothermic. This is reflected in the standard free energy of formation of ozone [2]:

$$\Delta G_{298}^0 = 163 \text{ kJ mol}^{-1} \quad (\Delta H_{298}^0 = 142 \text{ kJ mol}^{-1}, \Delta S_{298}^0 = 239 \text{ kJ mol}^{-1})$$

Under atmospheric pressure the melting point of ozone is 80.45 K (-192.7 °C) and the boiling point is 161.3 K (-111.9 °C). The critical temperature is at 261.1 K (-12.0 °C) [2].

2.4 Ozone solubility in water

Ozone is moderately soluble in water. The solubility of ozone in pure water at 1 atm and 273 K is 1.1 g/L and is strongly dependent on any salt concentration in the water. Many publications can be

found on the study of the ozone solubility in water. In these publications a number of values for the equilibrium concentration of ozone in water are reported. Kosak-Channing and Helz [3] suggest a Henry's law constant K_H , depending on temperature T and ionic strength μ :

$$\ln K_H = -\frac{2297}{T} + 2.659\mu - \frac{688\mu}{T} + 16.808 \quad (3)$$

Based on reports of several reports in literature Morris [4] suggested that a linear correlation between the solubility ratio of ozone (s) and the temperature can be used as a first estimate for the solubility of ozone in water:

$$\log_{10}(s) = 3.302 - 0.013T \quad (4)$$

As a result of self decomposition (see Section 3) the gas/liquid partitioning can be influenced not only by temperature and ionic strength, but pH as well. In situations where ozone decomposition is significant compared to the mass transfer over the gas-liquid interface the apparent partitioning coefficient K_H^* can deviate strongly from the Henry's law constant. Roth and Sullivan suggest a model (Equation (5)) with the apparent Henry's law constant as a function of the pH and temperature only [5].

$$K_H^* = 3.89 \cdot 10^{12} [\text{OH}^-]^{0.035} \cdot \exp\left(-\frac{2428}{T}\right) \quad (5)$$

Sotelo et al. [6] published an extensive research on the influence of the presence of several salts on the ozone solubility. They developed equations for the Henry's law constant as a function of temperature, pH and ionic strength which agreed with the experimental values within 15 %. Table 1 gives an overview of a several general equations for the Henry's Law constant K_H (kPa (mol fr.)⁻¹).

Table 1: General equations for the Henry's Law constant K_{Henry} (kPa (mol fr.)⁻¹) [6]

Salt solution	K_{Henry} (kPa(mol fr.) ⁻¹)	T (°C)	pH (-)	ionic strength μ (mol·l ⁻¹)
Na ₃ PO ₄	$1.03 \cdot 10^9 e^{\left(\frac{-2.118}{T}\right)} e^{(0.961\mu)} \cdot [\text{OH}^-]^{0.012}$	0-20	2-8.5	$10^{-3} - 10^{-1}$
Na ₃ PO ₄ and Na ₂ CO ₃	$4.67 \cdot 10^7 e^{\left(\frac{-1.3645}{T}\right)} e^{(2.98\mu)}$	0-20	7.0	$10^{-2} - 10^{-1}$
Na ₂ SO ₄	$1.76 \cdot 10^6 e^{(0.033\mu)} \cdot [\text{OH}^-]^{0.062}$	20	2-7	$4.9 \cdot 10^{-2} - 4.9 \cdot 10^{-1}$
NaCl	$4.87 \cdot 10^5 e^{(0.48\mu)} \cdot [\text{OH}^-]^{0.012}$	20	6.0	$4.0 \cdot 10^{-2} - 4.9 \cdot 10^{-1}$
NaCl and Na ₃ PO ₄	$5.82 \cdot 10^5 e^{(0.42\mu)}$	20	7.0	$5.0 \cdot 10^{-2} - 5.0 \cdot 10^{-1}$

2.5 Ozone diffusion in air and water

The diffusivity of ozone through a medium is a determining factor in mass transfer studies. In the transport of ozone from a gaseous phase into a water phase the transport kinetics depend directly on the diffusion rates of ozone in gas and water.

Ozone diffusion in air

Experimental results on the diffusion of ozone in air were not found in literature and have to be estimated. Several empirical models are proposed to estimate the diffusion coefficient of compounds in gases. Massman [7] presented a review in which the diffusion coefficients of several gases in air, calculated according to a few models known in literature, are discussed and re-analyzed. The diffusion coefficient for ozone in air is 1.44×10^{-5} m²/s according to the model proposed by Chen and Othmer [8] and 1.30×10^{-5} m²/s according to the Chapman-Enskog/Lennard-Jones model [9]. These values however could not be verified by experimental data.

Ozone diffusion in water

Johnson and Davies [10] calculated the ozone diffusion experimentally by measuring the rate at which ozone was absorbed in a laminated jet, using the penetration theory (more details on the penetration theory in Chapter VI) and Roth and Sullivan's relationship [5] for the Henry's law constant. They suggested equation (6) as relation between temperature and the ozone diffusion coefficient in water.

$$D_{O_3, \text{water}} = 1.1 \cdot 10^{-6} e^{\left(\frac{-1896}{T}\right)} \quad (6)$$

Several methods of estimating the diffusion coefficient of a gas in water have been proposed. A well known method is that of Wilke and Chang equation (7):

$$D_{\text{water}} = \frac{7.4 \cdot 10^{-8} \sqrt{\phi M_2 T}}{\eta \cdot V_{M,1}^{0.6}} \quad (7)$$

where ϕ is the interaction coefficient with a value of 2.6 for water. Table 2 presents values for the diffusion coefficient at different temperatures according to the Wilke-Chang estimation.

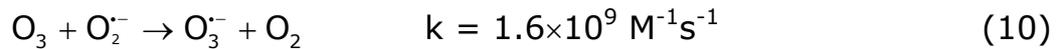
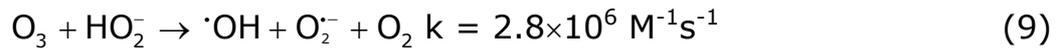
Table 2: Diffusion coefficients of ozone in water based on experimental values and suggested models [11].

T (°C)	$D_{O_3, w}$ ($10^{-9} \text{m}^2 / \text{s}$) Johnson and Davies (experimental)	$D_{O_3, w}$ ($10^{-9} \text{m}^2 / \text{s}$) Johnson and Davies (model)	$D_{O_3, w}$ ($10^{-9} \text{m}^2 / \text{s}$) Wilke and Chang (model)
10	Not available	1.35	1.29
15	1.50	1.53	1.50
20	1.76	1.71	1.74
30	2.14	2.11	2.25

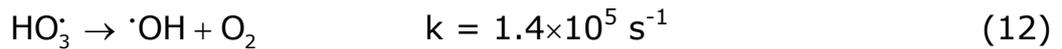
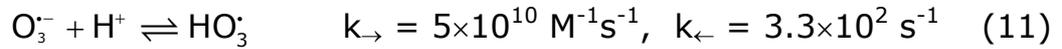
3 Ozone Reactions

3.1 Ozone (self-)Decomposition

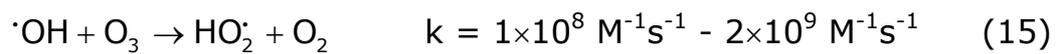
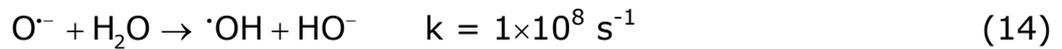
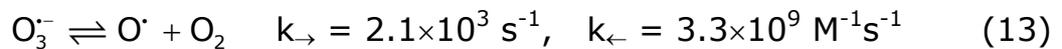
Ozone is an unstable gas and decomposes in gas atmosphere and solved in water. The stability of ozone in water depends strongly on the water matrix. Especially the pH of the water is important because hydroxide ions initiate the ozone decomposition process. Further the alkalinity and the type and content of other components such as natural organic matter (NOM) play an important role. From its initiation the decomposition of ozone in water occurs through a complex radical chain mechanism [12]:



For pH < ≈8:



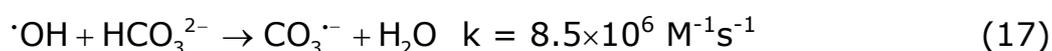
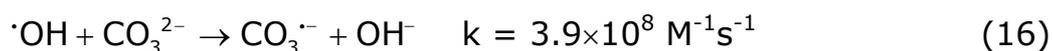
For pH > ≈8:



The net conversion is $\text{O}_3 \rightarrow 2/3\text{O}_2$

Reaction (15) is very fast, but the rate of reaction is controversial in literature [12].

Another important oxidant formed during the decomposition of ozone in water is the hydroxyl (OH) radical, see Reactions (9), (12) and (14). OH radicals have a strong oxidizing capacity themselves (see Section 3.2). The initiation of ozone decomposition can be enhanced by increasing the pH or by addition of hydrogen peroxide (see Section 3.4). On the other hand, low pH and radical scavengers may decrease the decomposition rate considerably. These compounds act as inhibitors of the radical chain mechanism. An example of a radical scavenger is carbonate/bicarbonate [12]:



Another potential radical scavenger in natural waters is the group of humic substances (or natural organic matter (NOM)). They can affect the decomposition in more ways as will be discussed in Section 3.2. Eventually many substances can initiate, promote or terminate the chain reaction [13]. Table 3 lists some possible compounds in water that influence the ozone decomposition.

Table 3: Some initiators, promoters and scavengers for decomposition of ozone in water (Steahelin Hoigne 1983, Xiong graham 1992).

Initiator	Promotor	Scavenger
		HCO ₃ ⁻ /CO ₃ ²⁻
OH ⁻	Humic acid	PO ₃ ⁴⁻
H ₂ O ₂ /HO ₂ ⁻	aryl-R	humic acid
Fe ²⁺	primary/seconda	alkyl-R
	ry alcohols	tert-butyl alcohol.

The delicate mechanism of the ozone decomposition is reflected in the number of investigations that have been performed on the reaction kinetics. In literature many studies can be found on measurements of the order of reaction with respect to ozone regarding its self-decomposition. Comparing the results (Table 4) it

shows that the determination of ozone decay in clear water is rather complicated.

Table 4: Reaction orders reported in several studies on ozone decay in phosphate buffered solutions of demineralized water. ⁽¹⁾

Reference	T in °C	pH	order in O ₃
Stumm, 1954	0.2- 19.8	7.6- 10.4	1
Kilpatrick et al, 1956	25	0-6.8	1.5
		8-10	2
Rankas, 1962	5-25	5.4-8.5	1.5
		2-4	2
Hewes and Davis, 1971	10-20	6	1.5-2
		8	1
Kuo et al, 1977	15-35	2.2-11	1.5
Sullivan, 1979	3.5-60	0.5-10	1
Gurol and Singer, 1982	20	2.2-9.5	2
Staehelin and Hoigné, 1982	20	8-10	1
Sotelo et al, 1987	10-40	2.5-9	1.5-2
Minchews et al, 1987		6.65	2
Grasso and Weber, 1989		5-9	1
Gottschalk, 1997	20	7	1-2

(1) Table adapted from Gottschalk et al. [13]

Considering the radical reaction chain process (Equations (8)-(15)) the ozone decay is mainly a function of the OH⁻ concentration and consequently the pH. A systematic dependence of the reaction order on temperature and pH is not visible. The order seems to vary between one and two. Different experimental conditions and different analytical methods make a comparison between these results very difficult [13].

For various parts in the radical chain process the reaction rate constants have been measured. Also many attempts have been made to determine the overall reaction rate constant of the decomposition of ozone. Qiu [14] performed the measurements in two ways and compared the outcome to findings of other researchers. He found that the data obtained at 25 °C could best be fitted by first order kinetics. Figure 2 was adapted from Qiu [14] and presents the first order kinetics researches against the pH of the solution found in various reports. It seems that under acidic conditions the decomposition rate is very low: 0.0001 s^{-1} at pH 2. Increasing the pH seems to result in an increasing rate constant: approximately 0.001 s^{-1} at pH 7 to almost $1 \times 10^3 \text{ s}^{-1}$ at pH 13.5. As the alkalinity increases the dependence of the pH seems to be getting stronger. Qiu [14] correlated the decomposition rate by the following two formulas:

$$k = 0.267 [\text{OH}^-]^{0.314} \quad 2.0 \leq \text{pH} \leq 7.0 \quad (18)$$

with a correlation coefficient of 0.885.

$$k = 325 [\text{OH}^-]^{0.751} \quad 7.0 \leq \text{pH} \leq 13.5 \quad (19)$$

with a correlation coefficient of 0.963.

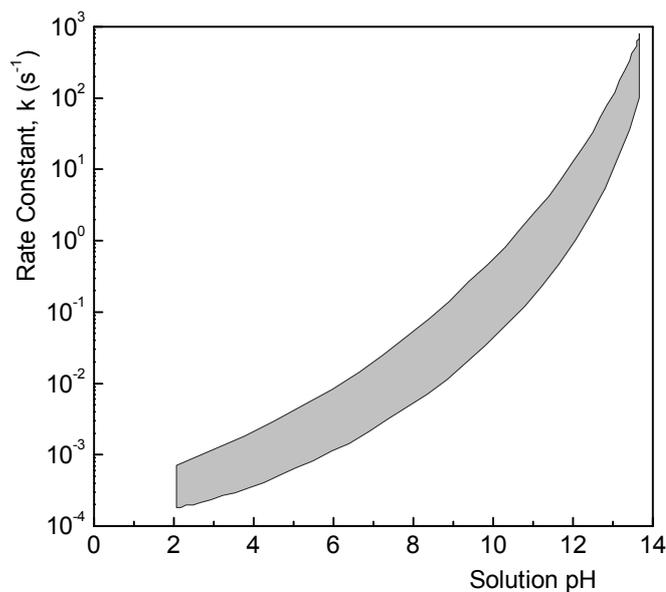


Figure 2: First order rate constants for the self-decomposition of ozone. Adapted from Qiu [14]

3.2 Reactions of ozone with humic substances.

Reactions of ozone with organic compounds in aqueous solutions imply complex reaction mechanism following several possible pathways (Figure 3).

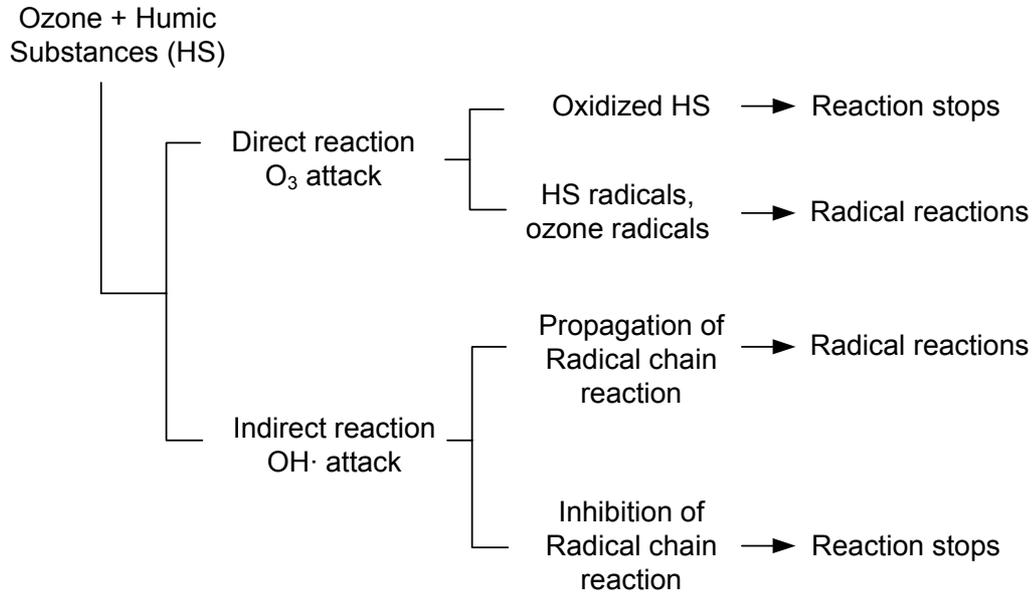


Figure 3: Pathways for the reaction of ozone with humic substances in aqueous solution.

The reactions of humic substances with ozone in water can be two-fold. They can react directly with ozone (O_3 attack) (i) or indirectly through reaction with OH radicals (ii) that are generated by reaction of ozone with constituents in the solution [12, 15]. In the first case ozone can react with humic substances to form oxidized compounds (Reaction (20)) or to form an HS cation radical and an ozonide anion radical (Reaction (21)).



These reactions are generally attributed to double bonds, activated aromatic systems, amines and sulfides [12].

In the second case where the humic substances react with OH radicals again two options are possible. The first: propagation of the radical chain reaction. Here OH radicals react with HS which leads to

a carbo-radical that reacts with oxygen to form a superoxide ion and a carbo cation. The superoxide ion reacts quickly with ozone (Reaction (10)) with which the radical chain mechanism is supported (Reaction (22)-(23)).



or $\rightarrow \text{HS}^{\cdot+} + \text{OH}^-$



The second option is the role of HS as scavenger and acting that way as inhibitor of the ozone decomposition. Here, a reaction between HS and OH radicals does not result in the formation of superoxide ions which terminates the radical chain reaction (Reaction (24)-(25)).



Considering the promoting/inhibiting abilities of humic substances the HS concentration might be an important factor for its own degradation. A high concentration of HS with inhibiting tendencies may result in a relatively low degradation rate of these humic substances. On the other hand, a high concentration of HS with a strong promoting quality may oxidize relatively faster than when treated in low concentrations. Due to the complexity and the indistinctness of the structure of humic substances it is virtually impossible to determine the propagating or inhibiting character of humic substances (that may be different for HS of different origin) in the oxidation process.

3.3 Reactions of ozone with chloride and bromide

A possible way to treat humic substances is to remove them from the water flow and then treat the (concentrated) humic substances separately. Removing humic substances by ion-exchange absorption may have the consequence that after regeneration the concentrate may contain a large quantity of regeneration salt (see Chapter I). In this research the pyrolite A860S resin was used for ion-

exchange absorption and regenerated with a 10% NaCl solution. As a consequence the amount of Cl^- ions in the concentrate can be substantial. In Section 2.4 the influence of a salt solution on the solubility of ozone is handled. It is known that ozone can react with inorganic compounds in aqueous solution. Hoigne et al. [16] investigated the reaction of chloride (Cl^-) with ozone and found an apparent rate constant of only $0.003 \text{ M}^{-1}\text{s}^{-1}$ ($23 \text{ }^\circ\text{C}$) above pH 2. They state that this value must be considered as an upper limit since trace impurities present in the chloride reagents could have interfered. Yeatts and Taube [17] proposed the reaction as



This is followed by a rapid protonation to HOCl and conversion to Cl_2 . Considering the rate constant the reaction of ozone with Cl^- is an extremely slow process even when Cl^- is present in high concentrations.

One of the main concerns of the ozonation of waters containing bromide is the formation of bromate (BrO_3^-). Bromate is formed in ozonation and AOP processes through a combination of ozone and OH radical reactions [18]. In a mechanism in which the bromine atom goes through a number of oxidation stages bromate is formed. The reaction rate constant of bromide with ozone is $160 \text{ M}^{-1}\text{s}^{-1}$ [19] and with OH radicals $1.1 \cdot 10^9$ [20] For a more detailed description is referred to Von Gunten [18].

Bromate is found to be a genotoxic carcinogen [21]. Depending on treatment goals, bromate formation can become a serious problem. The world health organisation (WHO) issued a guideline value of $25 \text{ } \mu\text{g/L}$ and both the European Union and the USEPA set a maximum contaminant level of $10 \text{ } \mu\text{g/l}$. The Dutch drinking water law handles a standard of $1 \text{ } \mu\text{g/L}$ for bromate [22]. However, the Dutch drinking water companies use a standard of $0.5 \text{ } \mu\text{g/l}$ of bromate in drinking water. In many waters low levels of bromide ($<20 \text{ } \mu\text{g/l}$) are found that pose little problems involving for bromide-derived by-products. Bromide levels in natural water can vary considerably in the range of 10 to $1000 \text{ } \mu\text{g/l}$ [12]. For bromide levels in the range of $50 - 100 \text{ } \mu\text{g/l}$ excessive bromate formation may already become a problem [18]. The bromide level in tap water from pumping station Spannenburg (The Netherlands) contains less than $200 \text{ } \mu\text{g/l}$ of

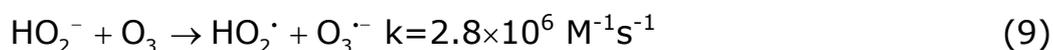
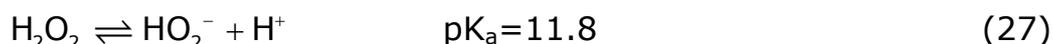
bromide [23], which implicates that the formation of bromate should be monitored if the drinking water should be treated by an ozonation process.

When treating a (waste) stream outside the drinking water process by ozonation the bromate standards for drinking water do not apply. Here, demands for disposal should be applied. Although there seems to be no clearly defined standard in Dutch discharge demands for bromate [24], discharge of bromate in the environment is undesirable.

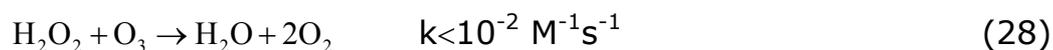
3.4 Advanced Oxidation Processes: O₃/H₂O₂

Processes in which the generation of OH radicals as an oxidant is stimulated are generally referred to as advanced oxidation processes (AOPs) [12, 13]. In contrast to ozone OH radicals react fast and non-selective. AOPs are applied when "simple" ozonation is not sufficient. Generating extra OH radicals may reduce the reaction time. This may result in a shorter residence time that is needed or larger amounts of ozone that can be applied without the danger of high ozone concentrations in the effluent of the reactor. AOPs are usually a combination of two or three of the following methods/compounds: ozone, hydrogen peroxide and UV radiation. Also the application of ozone in an environment with high pH can be qualified as an AOP.

In an AOP involving ozone and hydrogen peroxide the hydrogen peroxide reacts with ozone when present as anion [25]:



With Reaction (9) the radical chain process of the ozone decomposition is joined. The direct reaction of ozone with undissociated hydrogen peroxide is negligible [13]:



Comparing the initiation reaction with HO₂⁻ (Reaction (9)) and OH⁻ (Reaction (8)) it is clear that in the O₃/H₂O₂ system the initiation

step by OH^- is negligible. Whenever the concentration of hydrogen peroxide is above 10^{-7} M and the $\text{pH} < 12$, HO_2^- has a larger effect than OH^- on the decomposition of ozone and with that on the generation of OH radicals.

For oxidation of humic substances the advantage of an AOP above standard ozonation depends on the nature of the humic substances regarding their promoting/inhibiting properties in the radical chain mechanism.

4 Oxidation products of ozonation and AOPs

Ozone attacks nucleophilic centres in organic compounds [1]: points of high electron density, for example olefinic bonds. The reactivity of potential reaction sites is enhanced by the presence of electron donating groups, such as CH_3 and decreases by electron-withdrawing substituents such as $\text{C}=\text{O}$, COOH , Cl and NO_2 . Reaction products of ozone with organic compounds in aqueous solutions are often difficult to predict. This is especially the case with humic substances that consist out of large organic compounds with different bonds and functional groups.

Aliphatics, alcohols, aldehydes, ketones and carboxylic acids

Ozone shows little tendency to react directly with saturated hydrocarbons under water treatment conditions. However, via radical and ionic mechanisms it can react with hydrocarbons containing secondary or tertiary hydrogen atoms [1]. Isolated methylene groups are oxidized to carbonyl [26]. The reaction rates of aliphatic carboxylic acids are rather low when the compounds do not contain other chemical groups which may react [27]. Formate is an exception on this. This compound reacts fast with ozone to form carbon dioxide ozone and a hydroxide ion [12]. Primary alcohols are oxidized to carboxylic acids, H_2O_2 and aldehydes. Secondary alcohols form ketones, which are cleaved by ozone. Ethers are cleaved by ozone yielding alcohols, aldehydes, ketones and esters [1, 12].

Small compounds of the types above are formed as oxidation products with humic substances. Their oxidation rate is usually lower than their formation rate and will therefore accumulate during the reaction.

Table 5: Products of the ozonation organic compounds based on some functional groups.

Compound/functional group	Product (groups)	Comments
Aliphatics	Alcohols, aldehydes	Mostly through radical reactions
Primary alcohols	Carboxylic acids, H ₂ O ₂ , aldehydes	
Secondary alcohols	Ketones	
Aldehydes	Esters	
Ethers	Cleavage, alcohols, aldehydes, ketones, esters	
Carboxylic acids	Unreactive	Exceptions: formic acid (CO ₂ , O ₂) Malonic acid (oxalic acid, ketomalonic acid, H ₂ O ₂)

Olefins

One of the best known ozone reactions is the oxidation of olefins. The generally accepted mechanism for this reaction is the so called Criegee mechanism [12, 27]. The reaction of ozone with olefins is shown schematically in Figure 4. First an unstable ozonide is formed which falls apart into a carbonyl compound and a peroxidic dipolar ion. The latter then decomposes in water into a carbonyl compound and hydrogen peroxide [28].

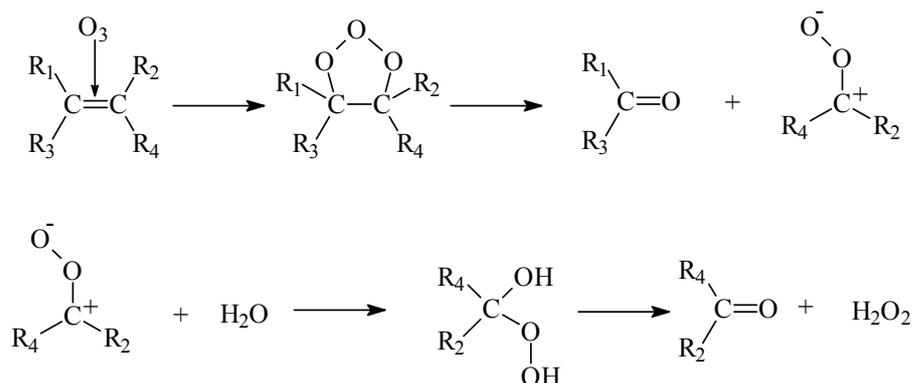


Figure 4: Ozonation reaction of olefins

This oxidation is strongly dependent on substitution and the second-order reaction rate constants vary over 8 orders of magnitude [12]. Electron withdrawing substituents may cause a strong decrease in reactivity of adjacent olefinic bonds [27]. Such groups can be Cl, COOH, C=O and NO₂. Carboxylic acids seem to decrease reaction rates with which adjacent aryl or alkene groups react with ozone.

Aromatic compounds

Aromatic ring structures are attacked much slower than olefinic bonds. Also here reactions are inhibited by electron withdrawing substituents and enhanced by electron donating groups such as CH₃ [12, 15]. The oxidation of benzene is a relatively slow process [12, 15], therefore under standard ozonation conditions the oxidation occurs most likely with OH radicals.

The oxidation product of benzene and OH radicals is in first instance phenol [12]. Ring cleavage may also occur under formation of muconic acid. The unsaturated bonds may then be oxidized as olefinic bonds (see Figure 5)

Other sources [1] report that ozonation of benzene leads to the formation of catechol, hydroquinone and resorcinol. The first two compounds can further be oxidized to *o*- and *p*-benzoquinone. Further oxidation leads to the formation of aliphatic diacids as well as glyoxal, glyoxylic acid and CO₂ (see Figure 5). The reaction of ozone with naphthalene is faster than with benzene [15]. Initially the oxidation leads to products with an intact aromatic ring [12]. Further oxidation yields the same products as mentioned above.

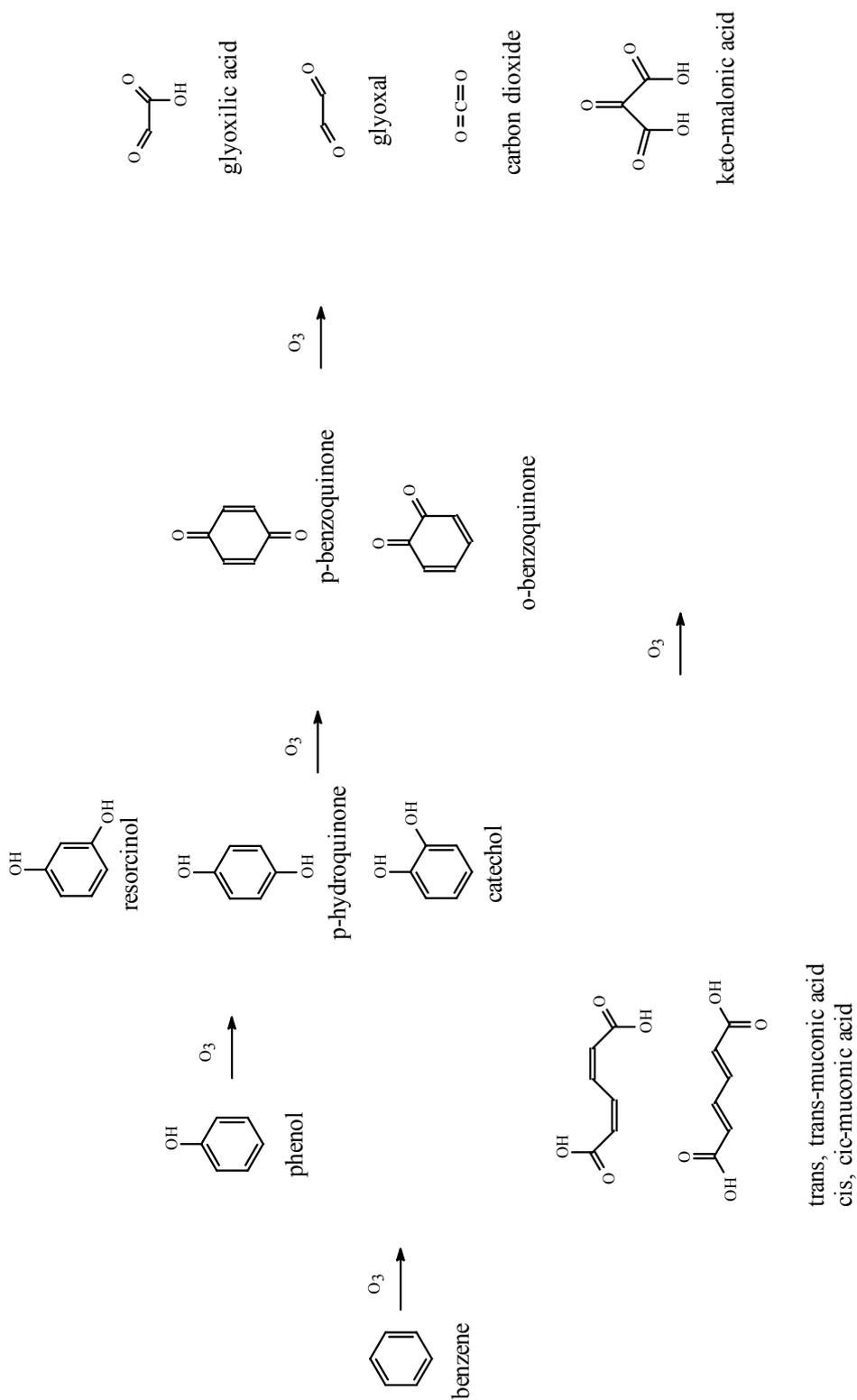


Figure 5: Possible ozonation (intermediate) products of some aromatic compounds [12, 26].

Identified ozonation products

Characterization of reaction products from ozonation of humic substances show the formation of low molecular weight compounds consisting of aldehydes, ketones, ketoacids and carboxylic acids [29-32]. Some specific compounds that were identified are pyruvic acid, glyoxylic acid, mesoxalic acid, propanal, glyoxal, methylglyoxal and acetaldehyde [29, 33]. This subject is further handled in Chapter V.

5 Nomenclature

Symbols

C	concentration	mol/l or M
D	diffusion coefficient	m ² /s
G	Gibbs enthalpy	J/mol
H	Heat enthalpy	J/mol
K _H	Henry's coefficient	-
K _{Henry}	Henry's coefficient	kPa(molfr) ⁻¹
k	reaction rate constant	M ⁻¹ s ⁻¹
M	Molecular weight	g/mol
s	solubility ratio	mol _{in liquid} /mol _{in gas}
S	Entropy	J/mol/K
T	Temperature	K
V _M	Molar volume	m ³ /mol
μ	ionic strength	-
μ _D	dipole moment	D (Debye unit)
φ	interaction coefficient	-
η	dynamic viscosity coefficient	Pa·s

indices

1, 2 component indicator

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III

Ozone Transport in a PVDF Membrane Contactor.

This chapter handles the use of a hollow fibre membrane module as gas-liquid contactor for the transfer of ozone to a liquid phase. For this purpose ozone resistant membrane modules with PVDF hollow fibre membranes were made. The modules were tested on mass transfer performance. The mass transfer data are compared to theoretical Graetz-Lévèque mass transfer correlations for bore side mass transfer and some considerations on the mass transfer resistance of the membrane are discussed. The modules performed well as gas-liquid contactors for the absorption of ozone to a water phase. The experimentally determined mass transfer data show a deviation of approximately 30% with respect to the theoretically calculated mass transfer coefficient for the liquid k_L by the mass transfer correlation according to Kreulen et al [1] which is a deviation of the well known Graetz-Lévèque correlation for mass transfer in tubes. Through experiments with sodium sulphite and humic substances in the water phase the mass transfer coefficient of the membrane was estimated to be at least $3.8 \cdot 10^{-4}$ m/s. However, a significant contribution of the gas phase resistance could be possible. The contribution of the resistance due to the presence of membrane to the total mass transfer resistance was estimated to be at the most 3% in physical mass transfer processes, i.e. in absence of reaction in the liquid phase. This resistance however could become significant in processes where the mass transfer of ozone is enhanced by a reaction in the liquid phase.

1 Introduction

A rather new technology that has attracted increasing attention in process engineering in the last few decades is the application of membranes as contacting medium between phases offering a wide range of applications [2, 3]. It offers gas-liquid or liquid-liquid mass transfer without dispersion of one phase within another. The technical advantages of using membrane contactors are [2, 3]:

- Potentially large surface area and control of the surface area. Depending on the dimensions of the membranes a large exchange area can be achieved per unit of process volume. This is beneficial in processes where mass transfer is a limiting factor.
- Separation of phases. Membrane contactors can be very useful where mixing of phases is undesirable e.g. oxygenation of blood, aeration of liquids with surfactants (foaming problems), phases with identical densities etc.
- Hydrodynamic decoupling. The flow rates can be varied independently, in speed but also in direction (co- or counter-current processes). Because the phases are separated there are no loading and flooding limitations. Also the modules are insensitive to orientation or motion.
- Easy scale up. This is often mentioned as being an advantage. Membrane contactors are modular in design: increasing the capacity means simply applying more contactors.

Challenges in applying membrane contactors are:

- Addition of extra mass transfer resistance. In conventional gas-liquid contactors the number of resistances to mass transfer is equal to the number of mixed phases. In membrane contactors the membrane provides an additional resistance. For microporous membranes the membrane resistance depends on membrane properties like thickness, porosity and tortuosity.
- Usually the mass transfer coefficients of the phases in a membrane contactor are lower than in conventional contactors. This is reinforced by laminar flow in and around fibres.
- Maldistribution. The problem of inefficient distribution counts mainly for flow around the fibres. This problem is counteracted by using transversal flow, baffles and preparing a hollow fibre fabric to improve contacting around the fibres.

- Trans-membrane pressure (TMP) limitations. This is mainly a potential problem for microporous membranes since too high TMP's may cause accidental flow through the membrane pores leading to unwanted mixture of phases. Such flow can be controlled by applying a higher pressure on the phase that does not wet the pores.
- Fouling of the membranes. Although this is much less a problem than for membrane filtration processes, fouling can cause problems. Presence of particles may result in plugging of pores or in altering the membrane surface activity by adsorption, e.g. turning a hydrophobic surface into a more hydrophilic one.
- Availability of construction material. Many processes require special materials resistant to aggressive chemicals, solvents and temperatures. In membrane processes the construction materials also need to have good membrane properties, including interaction with (one of) the phases for efficient mass transfer.
- Costs. Although a strong reduction in membrane costs can be seen over the past years, the construction of membrane equipment is still relatively costly compared to the conventional process equipment, which is usually older technology with a longer history of optimization and cost reduction through production volume. Additional is the finite lifetime of the membrane modules for which replacement should be taken into the cost account.

Several investigations involving the use of membrane contactors for ozone transport have been reported. Shanbhag et al. investigated the ozone mass transfer application of silicone hollow fiber membranes and their application for ozonation of wastewaters [4-6]. Guha et al. tested both silicone and microporous Teflon tubes and polypropylene hollow fibers in investigating a multiphase ozonation reactor [7]. Janknecht et al. [8, 9] and Picard et al. [10] developed hydrophobic and hydrophilic ceramic membranes for ozonation purposes. Also a few companies, such as Gore (DISSO₃LVE contactors [3]) and Pall (Infuzor contactors) offer membrane ozone contactors for several applications.

For ozone applications the module housing and membranes need to be chemically resistant. Furthermore, the membranes need to be hydrophobic with pores small enough to prevent wetting of the membrane at the applied pressure difference over the membrane to obtain the best mass transfer properties. Comparing suitable membranes only few types of polymer membranes meet the above requirements. Currently polytetrafluorethylene (PTFE) and

polyvinylidenedifluoride (PVDF) meet the criteria for ozone applications. In an application with ozone, fouling of the membrane may not be a problem since ozone, being a powerful oxidant, might keep the membranes clean.

2 Mass transfer theories

2.1 Mass transfer in gas-liquid systems with an interfacial medium

The molar flux of a gas A, into a liquid can be described by the general equation

$$J_A = K_{ov,A} (c_{A,L,i} - c_{A,L}) \quad (1)$$

with $K_{ov,A}$ being the overall mass transfer coefficient for A concerning the liquid concentration of A.

The absorption of a gas in a liquid with a membrane interface is a multiphase system. The transport of gas to the liquid consists of basically three steps: transport in the gas phase to the contact area with the membrane, through the membrane to the contact surface with the liquid phase and finally transport in the liquid phase.

The overall mass transfer can be described by a resistances-in-series model [3]. The overall mass transfer coefficient is related to the sum of the partial resistances in the system. These are the reciprocal values of the mass transfer coefficients k_G , k_L and k_M of the gas, the liquid and the membrane phase respectively. Depending on the wetting of the membrane the mass transfer coefficient in the resistance model can be described by Equation (2) and (3).

Non wetted membrane:

$$\frac{1}{dm_{M,L} \cdot K_{ov,A}} = \frac{1}{dm_{M,G} \cdot s_A \cdot k_{G,A}} + \frac{1}{dm_{M,lm} \cdot s_A \cdot k_{M,A}} + \frac{1}{dm_{M,L} \cdot k_{L,A}} \quad (2)$$

Wetted membrane:

$$\frac{1}{dm_{M,G} \cdot K_{ov,A}} = \frac{1}{dm_{M,G} \cdot s_A \cdot k_{G,A}} + \frac{1}{dm_{M,lm} \cdot k_{M,A}} + \frac{1}{dm_{M,L} \cdot k_{L,A}} \quad (3)$$

In this case the driving force is based on the solute (A) concentration in the liquid and s_A is applied to account for the discontinuous concentration difference between the gas phase and the liquid phase. Here, s_A is a (dimensionless) partitioning coefficient concerning the equilibrium ratio between the concentration of A in a gas phase and a liquid phase that are in contact with each other. In the case of gas filled pores (non wetted membrane) s_A is concerning the mass transfer in the gas phase and in the membrane (Equation (2)). In the case of liquid filled pores (wetted membrane) the driving force for mass transfer in the membrane is based on liquid concentrations of A and s_A only concerns the mass transfer in the gas phase (Equation (3)).

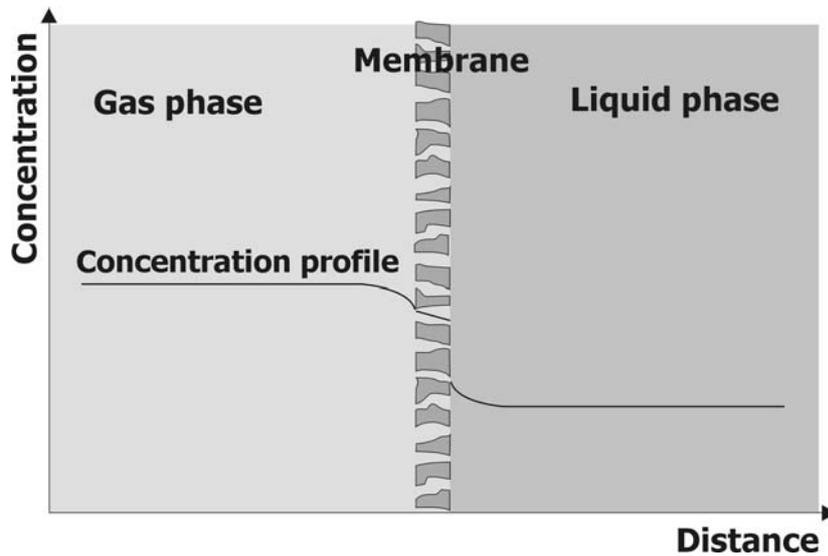


Figure 1: Schematic representation of transfer of a compound from a (mixed) gas phase to a liquid phase with a non-wetted porous membrane as interface.

Inside the structure of a microporous membrane convection can be neglected and the mass transfer coefficient of the membrane can be described by Equation (4) [11].

$$k_{M,A} = \frac{D_A}{0.5(dm_{M,out} - dm_{M,in})} \cdot \frac{\varepsilon_M}{\tau_M} \quad (4)$$

The mass transfer coefficient depends on the membrane thickness and a diffusion coefficient. The porosity of the membrane and tortuosity of the pores affect the diffusion coefficient, D_A , resulting in an effective diffusion coefficient, $D_{A,eff}$. When the membrane is wetted the pores are filled with liquid and the diffusion coefficient D_A in Equation (4) is concerning the diffusion coefficient of A in the liquid phase. In the case of a non-wetted membrane the pores are filled with gas and the D_A is concerning the diffusion coefficient in the gas phase.

Transport of gases through microporous membranes is mainly determined by the pore size. In case of large pore sizes ($r > 10 \mu\text{m}$) viscous flow occurs in which the molecules mainly collide with each other. The existence of the membrane seems to be negligible. When pores are small ($r < 0.1 \mu\text{m}$) or when the pressure of the gas is reduced, the mean free path of the diffusing molecules becomes comparable or larger than the pore size of the membrane and Knudsen diffusion occurs. Collisions with the pore wall now occur more frequently than collisions between gas molecules.

In the intermediate region where both types of diffusion play a role the diffusion coefficient can be related to the continuum and the Knudsen diffusion coefficient. In the case of a binary mixture, D_i is calculated from Equation (5) [12]

$$\frac{1}{D_A} = \frac{1}{D_{A,j}} + \frac{1}{D_{K,A}} \quad (5)$$

The continuum diffusion coefficient can be calculated from the kinetic gas theory. The Knudsen diffusion can be calculated by Equation (6) [12]:

$$D_{K,A} = \frac{4}{3} Q \sqrt{\frac{8RT}{\pi M}} \quad (6)$$

Q is a constant depending on the geometry of the pores and the interaction between the molecules and the pore wall. For cylindrical pores Q is equal to the pore diameter d_p [11].

The membrane mass transfer coefficient k_M for porous membranes is around 10^{-3} - 10^{-2} m/s [13, 14].

The mass transfer coefficient of a gas phase (or liquid phase) on the shell side depends on the fluid hydrodynamics around the fibres. These hydrodynamics are dependent on the packing (density) of the fibres in the module and therefore module specific [3]. Correlations of the form of

$$Sh = ARe^\alpha Sc^\beta \quad (A, \alpha \text{ and } \beta \text{ are constants}) \quad (7)$$

can be found in literature to predict k_G [3]. Typical values for the gas phase mass transfer coefficient, k_G , are around 10^{-2} - 10^{-1} m/s [15]. In Appendix A the shell side mass transfer coefficient of the gas phase is estimated according to some mass transfer correlations found in literature.

2.2 Liquid side mass transfer in tubes

In this absorption process the liquid flows through the bore of the non-wetted membrane. For the mathematic approach of the transport of a gas into a liquid several models have been developed. The most well known basic models are the film, penetration and surface renewal model. The film model assumes a stagnant liquid film near the interface and a well mixed bulk behind it. The mass transfer coefficient of the liquid is then determined by the thickness of the layer and the diffusion coefficient of the compound in the liquid (Equation (8)). The penetration model (also known as Higbie-penetration model) assumes that a liquid-package is transported from the bulk to the interface, remains there for a certain time and then turns back to the bulk. During the time at the interface non-stationary mass transfer occurs. The mass transfer coefficient can be calculated by Equation (9). The penetration depth of the compound in the package depends on the contact time, τ and thus the length of the membrane and the liquid velocity. This penetration depth should be small with respect to the thickness of the dimensions of the medium ($\ll 0.5 \cdot d_{m_{in}}$). The Danckwerts surface renewal model is a modification of the penetration model and assumes a surface age distribution with a replacement probability, s . The mass transfer coefficient can be calculated by Equation (10). In contrast to the

Higbie model this model also covers the case that the bulk concentration differs from zero.

$$k_L = \frac{D_{A,L}}{\delta} \quad (\text{film model}) \quad (8)$$

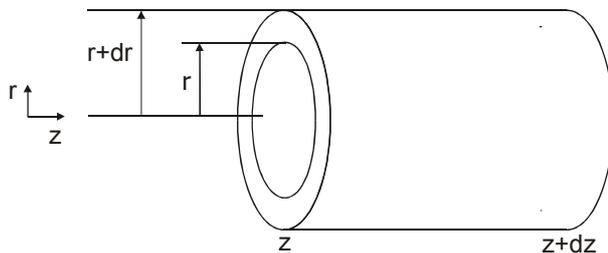
$$k_L(\tau) = 2\sqrt{\frac{D_{A,L}}{\pi\tau}} \quad \text{and} \quad \delta_{\text{penetration}} = 2\sqrt{D_{A,L}\pi\tau} \quad (\text{Higbie pen. model}) \quad (9)$$

$$k_L = \sqrt{D_{A,L}s} \quad (\text{sur. ren. model}) \quad (10)$$

The basic assumption of all these models is the presence of a well mixed bulk nearby the gas-liquid interface. In the case of laminar flow through small tubes the well mixed bulk is however absent. Due to the laminar flow in the bore there is a velocity profile in the liquid phase. For a fully developed laminar flow in a tube the velocity profile can be described by Equation (11).

$$v_r = 2v_m \left(1 - \left(\frac{r}{r_{\text{total}}} \right)^2 \right) \quad (11)$$

The concentration profiles in the liquid can be described by the differential mass balance that describes diffusion and convection in a medium that flows through a circular pipe.



Assuming negligible axial diffusion the simplified differential mass balance for any solute in the liquid becomes:

$$v_r \frac{\partial c}{\partial z} = D \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial c}{\partial r} \right) \quad (12)$$

with boundary conditions

$$c_{r=R} = c_w = s \cdot c_G, \quad 0 \leq z \leq Z$$

$$\left(\frac{\partial C}{\partial r} \right)_{r=0} = 0, \quad 0 \leq z \leq Z$$

The analogous differential equation for heat transfer was solved by Graetz [16, 17] and extended by L ev eque [18]. For a (liquid) phase flowing through the bore of a fibre the Graetz-L ev eque (G-L) correlation gives two asymptotic correlations for the dimensionless mass transfer coefficient, the Sherwood-number, Sh.

$$Sh_L = 1.62 \left(Re_L \cdot Sc_L \cdot \frac{d_{m,in}}{Z} \right)^{1/3} = 1.62 \left(\frac{v_L d_{m,in}^2}{D_{A,L} Z} \right)^{1/3} = 1.62 Gz_L^{1/3} \quad Gz_L > 20 \quad (13)$$

$$Sh_L = 3.67 \quad Gz_L < 10 \quad (14)$$

Kreulen et al. [1] proposed a fit correlation derived from the G-L correlation that should be valid over the whole range of Graetz numbers (Gz)

$$Sh_L = \sqrt[3]{3,67^3 + 1.62^3 Gz_L} \quad (15)$$

With the Sherwood number being the ratio between convective and stagnant layer mass transfer resistance, the mass transfer coefficient of the liquid $k_{L,A}$ can be calculated from

$$Sh_L = \frac{k_{L,A} d_{m,in}}{D_{A,L}} \quad (16)$$

Deviations from the G-L correlation in practice might be due to:
 1. High gas phase resistance. 2. High membrane resistance. 3. non-uniform flow distribution, depending on manifold configuration, packing density, dimensional variation in (inner) fibre diameter, tube length and Reynolds number [3, 19].

2.3 Methods for measuring the mass transfer resistance of the membrane

In a system where the resistance for mass transfer is determined by the resistances of a number of phases in series one can estimate the resistance of a phase by reducing the resistances for mass transfer in the other phases. A method to determine the membrane mass transfer resistance is to make a so-called Wilson-Plot. This method was originally developed for heat transfer processes [20] but can easily be applied for mass transfer processes as well. With a gas phase on one side and a liquid phase on the other the overall mass transfer, K_{ov} , for the gas is determined at several liquid flow rates. The reciprocal value of the overall mass transfer K_{ov}^{-1} is plotted against $(Re_L)^{-y}$ where y is a constant with a value chosen such that the best linear relation is obtained. For mass transfer without reaction this value should theoretically be 1/3 (see Equation (13)). Extrapolation of the data and considering Equation (2), the intercept represents the reciprocal overall mass transfer resistance at infinite Reynolds number. At this point the liquid mass transfer resistance is negligible and the overall mass transfer resistance is equal to the mass transfer resistance in the membrane and in the gas phase. Assuming that the gas phase resistance is negligible compared to the resistance in the membrane the overall mass transfer resistance resembles the mass transfer resistance in the membrane:

$$\frac{1}{dm_{M,L} \cdot K_{ov,A}} \approx \frac{1}{dm_{M,lm} \cdot s_A \cdot k_{M,A}} \quad (17)$$

In the case where the gas phase resistance is not negligible equation (17) becomes

$$\frac{1}{dm_{M,L} \cdot K_{ov,A}} \approx \frac{1}{dm_{M,G} \cdot s \cdot k_{G,A} + dm_{M,lm} \cdot s \cdot k_{M,A}} \quad (18)$$

and the mass transfer resistances in the gas and membrane are taken together.

Another method to reduce the liquid side mass transfer resistance is to add a reactant to liquid that reacts with the transferring compound. When the reaction is fast enough it creates a stronger concentration gradient in the liquid near the interface thus enhancing the mass transfer in the liquid and giving the suggestion of

a reduced mass transfer resistance of the liquid. The mass transfer resistance in the liquid could then be expressed as

$$\frac{1}{E_A \cdot k_{L,A}} \quad (19)$$

where E represents the so-called “enhancement factor” by which the mass transfer coefficient is enhanced compared to mass transfer in absence of reaction. This method can be performed in combination with the Wilson-plot method. In Chapter IV the subject of mass transfer enhancement by reaction in the liquid phase is discussed more extensively.

2.4 Ozone (self) decomposition in water

Characteristic for ozone is that it decomposes in water through a radical chain reaction, initiated by hydroxide ions. This is explained in more detail in Chapter II. At certain conditions the self decomposition of ozone can affect the mass transfer properties: the conversion reaction is then fast enough to speed up the gas to liquid transfer of ozone. These conditions depend on the pH, temperature and the residence time in the module. As can be seen from Figure 2 in Chapter II the first order decomposition rate constant at values from pH 5 to pH 7 ranges from approximately 0.0002 to approximately 0.003 s⁻¹ [21]. Hence, it depends on the physical mass transfer of the gas in the liquid and the residence time in the contactor whether ozone self decomposition is affecting the mass transfer measurements. When the liquid rate is high enough the residence time is short compared to the rate of decomposition and the decomposition of ozone can be neglected in that time period.

3 Materials, methods and experiments

3.1 Contactor module

The membrane modules were constructed with hydrophobic PVDF hollow fiber membranes supplied by EMI Twente (The Netherlands). The outer diameter of the fibres is 1.1 mm. The inner diameter of 0.6 mm creates a specific surface area of 6.7·10³ m²/m³ in the bore of the membranes. Figure 1 shows a SEM-photo of the

cross sectional area of a membrane hollow fibre. More features of the membrane fibres are presented in Table 1. Polydimethylsiloxane (PDMS, General Electric RTV 615) was used as potting material for its ozone resistant character. Two membrane modules were constructed: one with a stainless steel housing and 375 fibres potted inside and one with a glass housing and with 200 membrane fibres inside. Technical specifications of both modules are presented in Table 1. During the experiments no significant change was observed in mass transfer under equal operational conditions. This showed that the membrane module was operating stable for the duration of the experimental period.

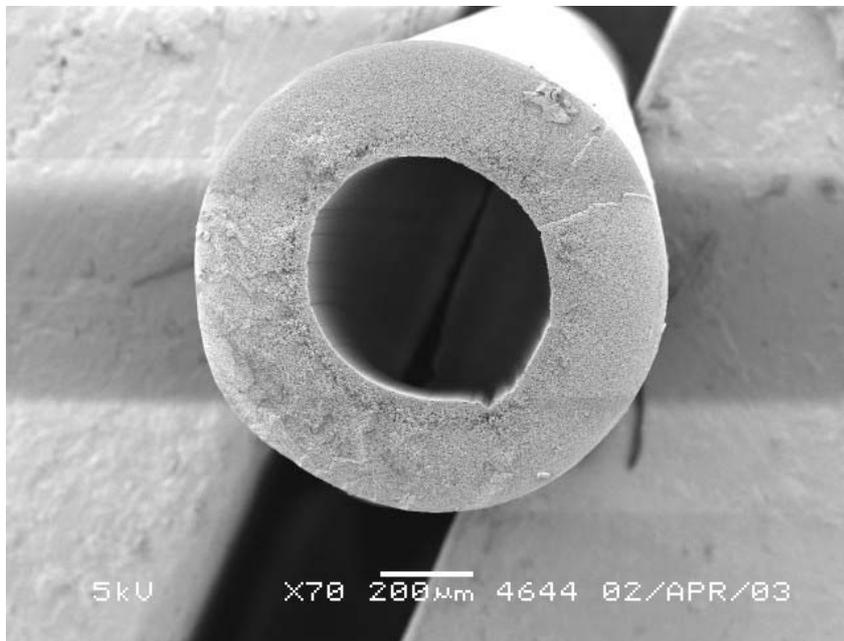


Figure 2: SEM photo of a cross section of the PVDF hollow fiber membrane.

3.2 Experimental setup and measuring methods

The setup for the ozone mass transfer measurements is presented in Figure 3. Air is led through an ozone generator (Ozone Generator Peripheral Com, Anseros Klaus Nonnenmacher GmbH) in which a part of the oxygen is converted to ozone. The ozone enriched air flowed into the contactor module on the shell side of the membranes. The ozone concentration both in the gas feed and outlet

was measured spectrophotometrically at a wavelength λ , of 253 nm with a Pharmacia LKB Ultrospec Plus double beam spectrophotometer. The ozone concentration was calculated according to Equation (20). The extinction coefficient, e , of ozone at $\lambda=253$ nm is $3000 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ [22].

$$A_{\text{ozone}} = c_{\text{ozone}} \cdot e_{\text{ozone}} \cdot d_{\text{cuvette}} \quad (20)$$

The water phase was led through the bore of the membranes by a displacement pump. The ozone concentration in the water phase was measured by the indigo colorimetric method [23].

The ozone concentration in the liquid near the interface, $c_{\text{O}_3,\text{L},i}$ was calculated from the concentration in the gas phase using Henry's law for the equilibrium between a compound in the gas and the liquid phase: $K_{\text{H},\text{A}} = p_{\text{A}}/x_{\text{A}}$. At 21 °C and very low ionic strength the dimensionless value for K_{H,O_3} , the dimensionless partitioning coefficient, s_{O_3} is equal to 3.30 for ozone in water with very low ionic strength. (see Equation (2) [24] in Chapter II). The liquid interface concentrations then calculated with

$$c_{\text{O}_3,\text{L},i} = \frac{c_{\text{O}_3,\text{G}}}{s_{\text{O}_3}} \quad (21)$$

The interface concentrations in the liquid were calculated separately for the liquid inlet and liquid outlet out of the ozone concentration in the gas outlet and inlet respectively. Since the average ozone concentrations in the liquid and in the gas phase change over the length of the membrane module due to mass transfer, the driving force was calculated as the log mean driving force over the module:

$$J = k_{\text{L}} a \cdot \Delta c_{\text{lm}} \quad (22)$$

$$\Delta c_{\text{lm}} = \frac{\Delta c_{\text{e}} - \Delta c_{\text{b}}}{\ln\left(\frac{\Delta c_{\text{e}}}{\Delta c_{\text{b}}}\right)} \quad (23)$$

where $\Delta c = (c_{\text{O}_3,\text{L},i} - c_{\text{O}_3,\text{L}})$. The diffusion coefficient of ozone in water, $D_{\text{O}_3,\text{L}}$ is equal to $1.80 \cdot 10^{-9} \text{ m}^2/\text{s}$. The diffusion coefficient of

ozone in air is $1.30 \cdot 10^{-5} \text{ m}^2/\text{s}$ according to the Chapman-Enskog/Lennard-Jones model [25] (see also Section 2.5 in Chapter II). The pore diameter in the skin layer is approximately 20 nm. Knudsen diffusion has a significant effect in these pores. According to Equation (6) $D_{K,O_3} = 7.2 \cdot 10^{-6} \text{ m}^2/\text{s}$ and with Equation (5) the overall diffusion coefficient D_{O_3} in the skin pores is $4.6 \cdot 10^{-6} \text{ m}^2/\text{s}$.

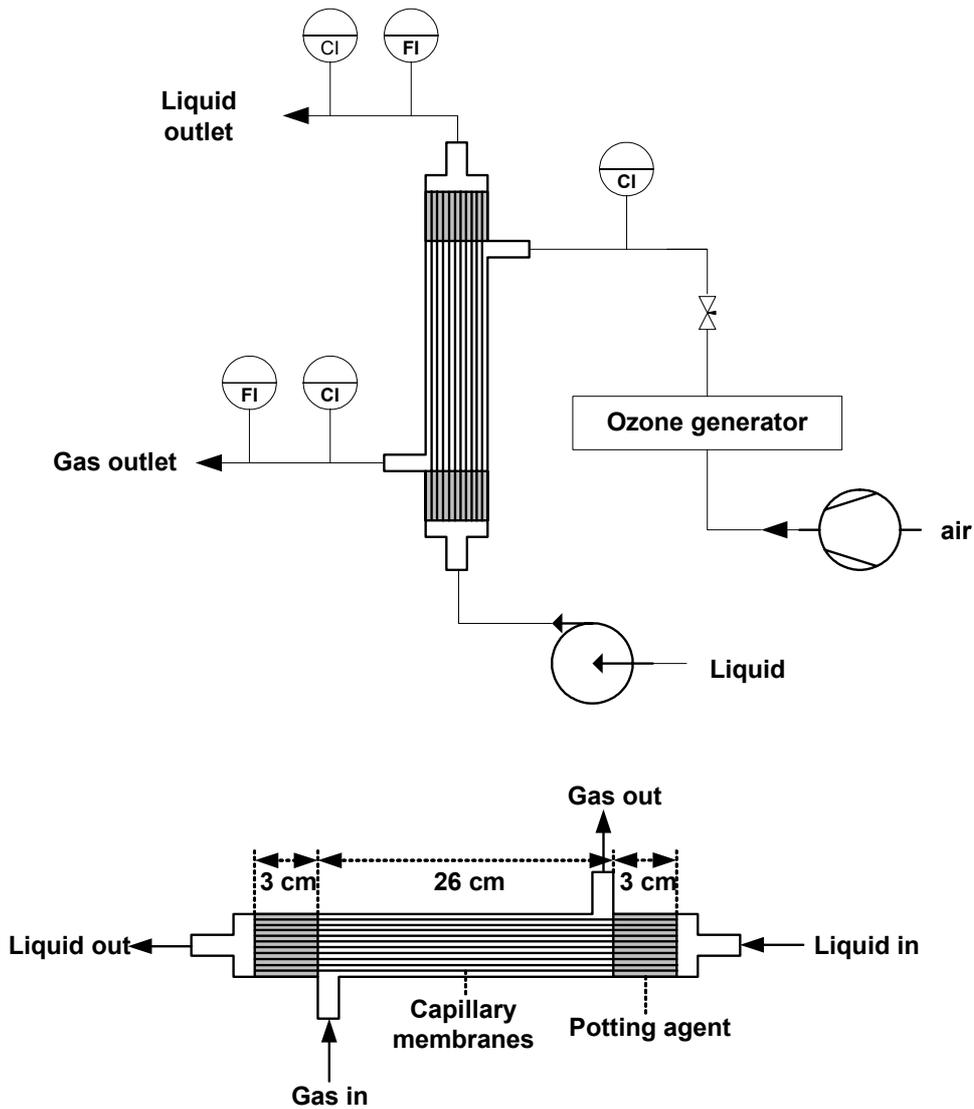


Figure 3: Schematic presentation of the experimental setup for ozone mass transfer measurements.

Table 1: Features of the membrane contactor module.

Membrane			
Material	PVDF	Position skin	shell side
Hollow fiber OD	1.1 mm	Skin thickness	unknown
Hollow fiber ID	0.6 mm	Pore size shell side (skin)	~ 20 nm
		Pore size bore	0.1–1.0 μm
Module 1			
Module housing	Stainless steel	Potting material	PDMS
Housing Diameter	0.0256 m	# membranes	375
Contact length	0.26 m	Packing density	65%
Spec. area bore	$6.7 \cdot 10^3 \text{ m}^2/\text{m}_i^3$	Spec. area shell side	$6.8 \cdot 10^3 \text{ m}^2/\text{m}_o^3$
	$1.3 \cdot 10^3 \text{ m}^2/\text{m}_m^3$		$2.4 \cdot 10^3 \text{ m}^2/\text{m}_m^3$
Module 2			
Module housing	Glass	Potting material	PDMS
Housing Diameter	0.0256 m	# membranes	200
Contact length	0.26 m	Packing density	34%
Spec. area bore	$6.7 \cdot 10^3 \text{ m}^2/\text{m}_i^3$	Spec. area shell side	$1.8 \cdot 10^3 \text{ m}^2/\text{m}_o^3$
	$0.69 \cdot 10^3 \text{ m}^2/\text{m}_m^3$		$1.3 \cdot 10^3 \text{ m}^2/\text{m}_m^3$

Indices:

i) volume inside fibres o) volume outside fibres m) volume module

3.3 Mass transfer experiments

3.3.1 Mass transfer in water without reaction

Mass transfer experiments concerning the absorption of ozone in water without reaction were performed with demineralised water and both modules 1 and 2. Conditions for experiments with module 1: Ozone concentration in the feed gas: 0.34 and 0.60 mol/m³, gas flow rate 5.8 ml/s (0.031 m/s), liquid flow rate 0.0018 to 0.16 m/s ($Re_L = 0.89$ to 94). Experiments with module 2: ozone concentration in gas feed: 0.36 and 0.29 mol/m³, gas flow rate 4.9 ml/s (0.014 m/s), liquid flow rate 0.072 to 0.55 m/s ($Re_L = 36$ to 324). The highest pressure drop at these flow rates over both modules is 0.15 bar.

3.3.2 Mass transfer with reaction

Mass transfer experiments in presence of reaction in the liquid phase were performed with sodium sulphite and humic substances solutions.

Sodium sulphite solution

According to Hoigne et al. [26] the rate of reaction of sulphite with ozone is a fast reaction of first order in both reactants and the reaction rate constant is approximately $1 \cdot 10^9 \text{ M}^{-1}\text{s}^{-1}$. The measurements were performed with module 2 with sodium sulphite concentrations of 0.1, 0.2 and 0.4 g/l (1.3, 2.5, 5.0 mol/m³). According to Equation (2) in Chapter II these concentrations have no significant influence on the solubility of ozone in water. Experiments with 0.1 and 0.2 g/l sodium sulphite: ozone concentration in gas feed: 0.35 mol/m³, gas flow rate 5.3 ml/s (0.015 m/s), liquid flow rate 0.055 to 0.53 m/s ($Re_L = 28$ to 265). Experiments with 0.4 g/l of sodium sulphite: ozone concentration in gas feed: 0.26 mol/m³, gas flow rate 9.4 ml/s (0.026 m/s), liquid flow rate 0.055 to 0.34 m/s ($Re_L = 28$ to 170).

Solution with humic substances

For mass transfer experiments with humic substances two HS concentrations were used: $1.7 \cdot 10^3 \text{ molDOC/m}^3$, which was taken undiluted from a stock solution and 33 molDOC/m^3 (20 gDOC/l and 0.40 gDOC/l respectively). These experiments were performed in module 1. As a result of the concentration step of the humic

substances by ion exchange adsorption (see Chapter IV, Section 3.2) the NaCl concentration of the stock solution is approximately 1 M. The high ionic strength of the solution at this concentration has a strong effect on the solubility of ozone. The dimensionless partitioning coefficient s_{O_3} at that ionic strength is 4.38 at 20°C. The partitioning coefficient of the 33 molDOC/m³ solution was taken as 3.30, the same value as for water with very low ionic strength. It should be noted that the presence of ionic humic substances in high concentrations also may have a major contribution in the total ionic strength of the solution. The ionic content of the humic substances is unknown however, and therefore not taken into account.

Considering the high reaction rates in the liquid phase the reaction regime was considered to be at least fast and consequently the ozone concentration in the bulk was considered to be zero (See Chapter IV Section 2.3).

4 Results and discussion

4.1 Gas- liquid mass transfer without reaction

The mass transfer experiments in demineralised water in module 1 showed mass transfer fluxes of $7.2 \cdot 10^{-8}$ to $3.1 \cdot 10^{-6}$ mol/m²/s from the gas to the liquid phase. Experiments in module 2 showed mass transfer rates of $1.2 \cdot 10^{-6}$ to $3.1 \cdot 10^{-6}$ mol/m²/s. The overall mass transfer coefficients K_{ov,O_3} that were calculated for both modules were comparable and show an increase of $8.3 \cdot 10^{-7}$ to $3.3 \cdot 10^{-5}$ m/s over the Re_L range of 0.89 to 276 (Figure 4). The measured K_{ov,O_3} values stay significantly below the theoretical mass transfer coefficients for k_L calculated by Kreulen's adjusted Graetz-Lévêque correlation (Equation (15) and (16)). A fit that was calculated through the measured data points yielded: $K_{ov,O_3} = -5.4 \cdot 10^{-6} + 5.7 \cdot 10^{-6} Re_L^{0.33}$. The difference between K_{ov,O_3} of the data fit and the G-L correlation is approximately 30 % compared to the theoretical k_{L,O_3} .

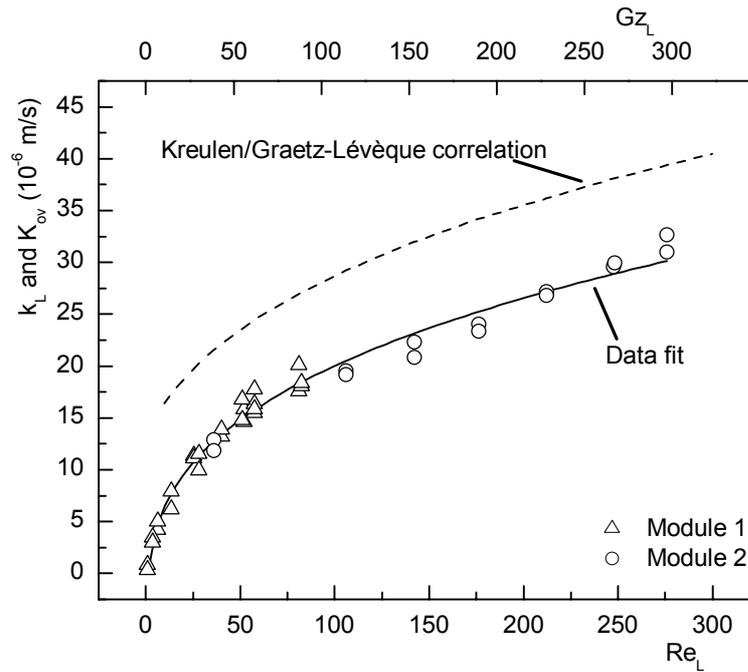


Figure 4: Liquid mass transfer coefficient k_L according to adjusted Graetz-Lévêque correlation according to Kreulen et al [1] (Equation (15)). Experimental overall mass transfer coefficient K_{ov,O_3} as function of the Reynolds number Re_L and the Graetz number of the liquid Gz_L flowing through the fibres. The data fit is a function according to $K_{ov,O_3} = -5.4 \cdot 10^{-6} + 5.7 \cdot 10^{-6} Re_L^{0.33}$. The measurements were performed with module 1 (375 fibres) and module 2 (200 fibres).

4.2 Membrane resistance

4.2.1 Mass transfer with reaction in the liquid phase.

Sodium sulphite

The ozone transfer was greatly enhanced with sodium sulphite in the water. An increase in sulphite concentration led to an increase in the mass transfer coefficient of ozone. In Figure 5 the overall mass transfer coefficient K_{ov,O_3} is presented as function of Re_L for mass transfer experiments with different sulphite concentrations in the water. As can be observed the mass transfer coefficient at a liquid flow speed of 0.35 m/s ($Re_L = 176$) is enhanced by a factor of 3.2, 12 and 47 at sulphite concentrations of 0.1, 0.2 and 0.4 g/l respectively. The maximum overall mass transfer coefficient that was reached is $1.1 \cdot 10^{-3}$ m/s. Using the resistance in series model (Equation (2)) the

resistance in the gas phase plus the membrane is at least equal or smaller than the maximum overall mass transfer resistance:

$$\frac{1}{dm_{M,G} \cdot s_A \cdot k_G} + \frac{1}{dm_{M,lm} \cdot s_A \cdot k_M} \leq \frac{1}{1.1 \cdot 10^{-3}} = \frac{1}{dm_{M,L} \cdot K_{ov,max}}$$

Several empirical correlations for shell side mass transfer are reported in literature [3]. In Appendix A some mass transfer coefficients for the gas phase are estimated according several correlations for shell side mass transfer. Under the experimental conditions the average estimated mass transfer coefficient is in the order of around $10^{-3} - 10^{-2}$ m/s in both modules. So, the gas phase resistance is not negligible with respect to the resistance in the membrane. The measured mass transfer coefficient is the sum of the membrane and the gas phase the mass transfer coefficient and with $s_{O_3} = 3.30$ at least $3.3 \cdot 10^{-4}$ m/s. In this situation it is only safe to state that the mass transfer coefficient in the membrane is at least $2.4 \cdot 10^{-4}$ m/s for module 2. It is then assumed that all resistance is situated in the membrane.

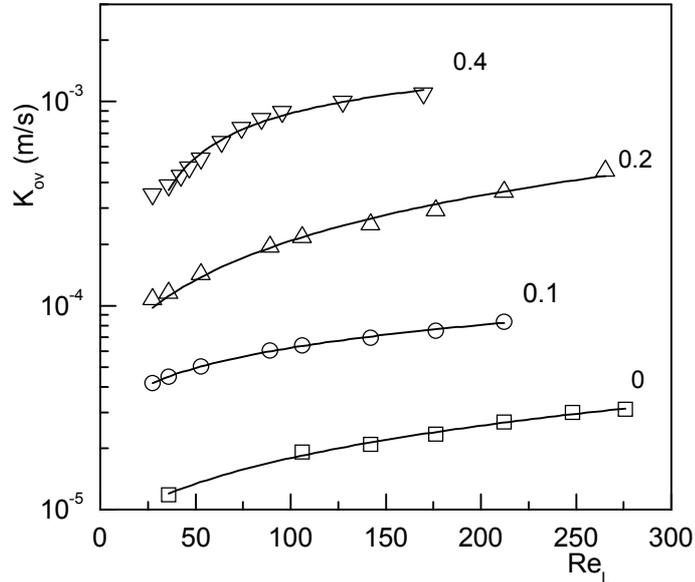


Figure 5: Overall mass transfer coefficient K_{ov,O_3} as function of the Reynolds number of the liquid phase Re_L and sodium sulphite concentration. Sodium sulphite concentrations: 0, 0.10, 0.20 and 0.40 g/l (0, 0.8, 0.16 and 0.32 mol/m³). The figures at the data points indicate the sodium sulphite concentration (g/l). Experiments were performed with module 2 (200 fibres).

Humic substances

Mass transfer experiments with concentrated humic substances also resulted in a strong enhancement of the overall mass transfer (Figure 6). The highest HS concentration in the reaction solution resulted in the highest overall mass transfer coefficient. At a flow rate of 0.12 m/s ($Re_L = 61$) the overall mass transfer coefficient $K_{ov} = 1.83 \cdot 10^{-3}$ m/s. With respect to mass transfer without reaction K_{ov} was enhanced by a factor of $1.2 \cdot 10^2$. With the resistance in series model (Equation (2)) and $s_{O_3} = 4.38$ the mass transfer coefficient of the membrane k_M is at least $3.1 \cdot 10^{-4}$ m/s for module 1.

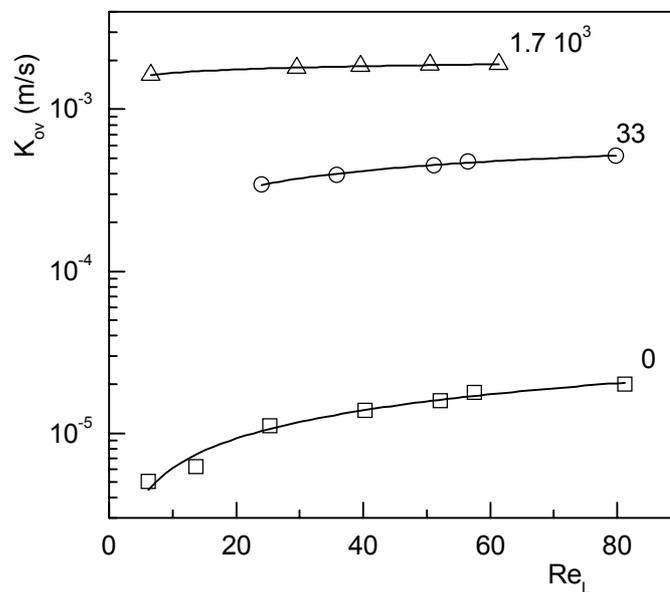


Figure 6: Overall mass transfer K_{ov,O_3} as function of the liquid flow rate (expressed as Re_L) and the humic substance concentration (0, 33 and $1.7 \cdot 10^3$ molDOC/m³). The figures near the data points indicate the humic substance concentration (molDOC/m³). The experiments were performed with module 1 (375 fibres).

4.2.2 Wilson plot

A Wilson-Plot is drawn for the mass transfer data for ozone in demineralised water as shown Figure 7 is the result. A linear fit yields a negative y-axis intercept, which makes these data unsuitable to determine the resistance for mass transfer in the membrane.

In Figure 8 Wilson-plots are presented which were drawn with the mass transfer data of the experiments with the presence of a

reaction in the water. Here the overall mass transfer resistance K_{ov}^{-1} is plotted against Re_L^{-y} where y was chosen to make the optimum linear fit possible through the data points. By extrapolation of the data the intercept was calculated, which represents the reciprocal overall mass transfer coefficient K_{ov}^{-1} at infinite Re_L . The Wilson-plot from mass transfer data of the experiments with the $1.7 \cdot 10^3$ molDOC/m³ HS solution yielded $K_{ov, \text{intercept}} = 2.27 \cdot 10^{-3}$ m/s. Using Equation (17) with the same assumptions regarding the mass transfer resistance in the gas phase as earlier and with $s_{O_3} = 4.38$ the membrane mass transfer coefficient k_M is calculated to be at least $3.8 \cdot 10^{-4}$ m/s.

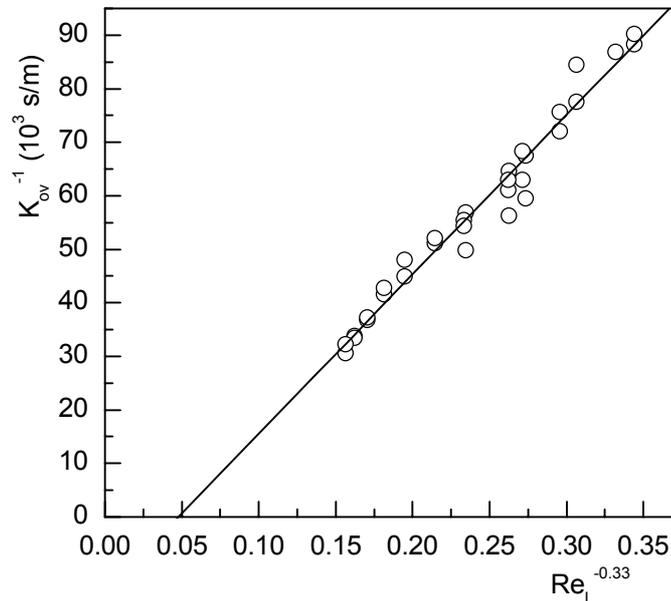


Figure 7: Wilson plot drawn with the data from mass transfer experiments with ozone in demineralised water (see Figure 4).

The Wilson-plot from the data of the experiments with 0.4 g/l sodium sulphite was more difficult to interpret. A linear fit through the data points over a large range of Re_L yielded a negative intercept. A fit through data points associated with the highest Re_L that was measured at yielded $K_{ov, \text{intercept}} = 3.2 \cdot 10^{-3}$ m/s. With $s_{O_3} = 3.30$ k_M is calculated to be at least $7.0 \cdot 10^{-4}$ m/s. However, it may be clear that the estimated mass transfer coefficients of the membrane are highly speculative due to the inaccuracy of the results.

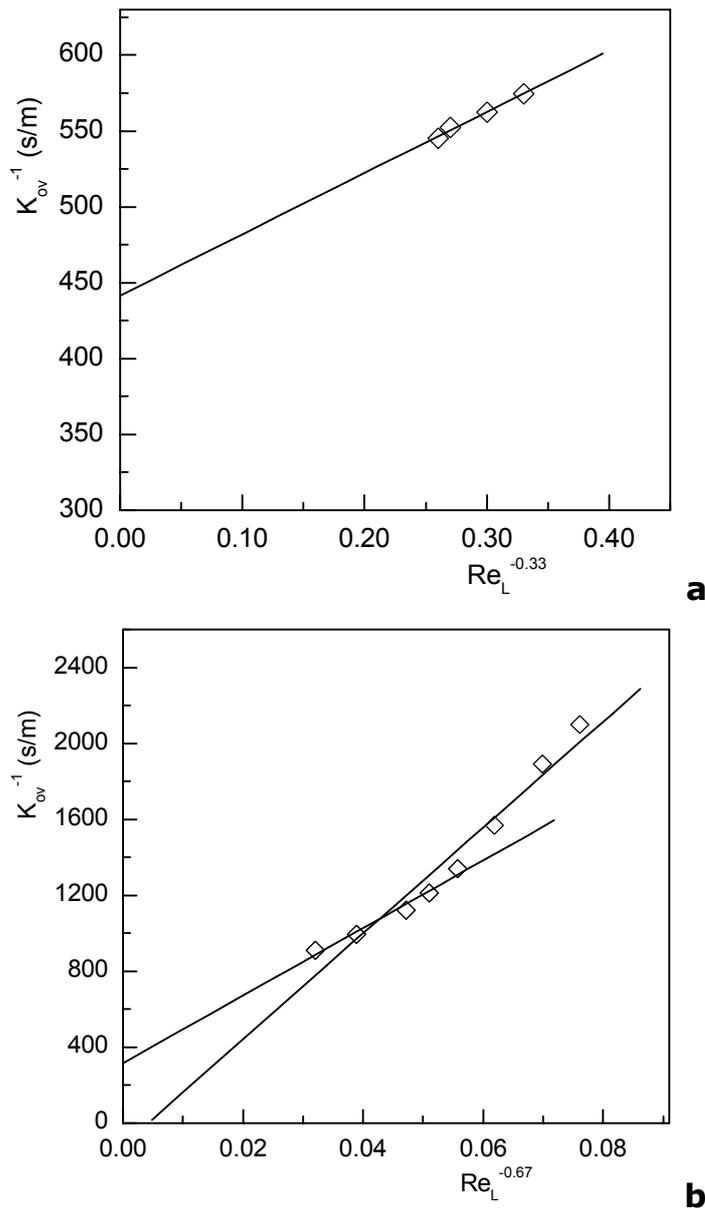


Figure 8: Wilson plots of a PVDF membrane module. a. With a solution of $1.7 \cdot 10^3$ molDOC/m³ (20 gDOC/l) humic substances in water, Module 1. b. With solution of 3.2 mol/m³ (0.4 g/l) sodium sulphite. The solid lines are linear fits through the data points.

4.3 Membrane properties from the estimated mass transfer resistances

Since the pore diameter in the skin layer is approximately 20 nm Knudsen diffusion has a significant effect in these pores. According to Equation (6) $D_{K,O_3} = 7.2 \cdot 10^{-6}$ m²/s and with Equation (5)

and $D_{O_3,air} = 1.30 \cdot 10^{-5} \text{ m}^2/\text{s}$ the overall diffusion coefficient D_{O_3} in the skin pores is $4.6 \cdot 10^{-6} \text{ m}^2/\text{s}$. The porosity to tortuosity ratio, ε/τ_m can be calculated with Equation (4). The membrane fibre wall has a thickness of 0.25 mm. However it is likely that the main resistance for mass transfer is situated in the skin layer. Unfortunately, it is difficult to estimate the exact skin thickness, so any estimation on ε/τ_m is virtually impossible.

The contribution of the membrane resistance to the total resistance for mass transfer seems to be small under the experimental conditions compared to the coefficient for mass transfer without reaction: $K_{ov,O_3} = 3.3 \cdot 10^{-5} \text{ m/s}$ and the contribution in the transport process due to the presence of the membrane, $s_{O_3} \cdot k_M(dm_{M,lm}/dm_{M,L}) \geq 1.1 \cdot 10^{-3} \text{ m/s}$, which is $\geq 3\%$.

Table 2: Values of mass transfer coefficients for the membrane used in modules 1 and 2. $(s_{O_3} \cdot k_M(dm_{M,lm}/dm_{M,L}))^{-1}$ represents the contribution to the total resistance for mass transfer in the membrane modules due to the presence of the membrane.

$(s_{O_3} \cdot k_M(dm_{M,lm}/dm_{M,L}))^{-1}$ ¹ (s/m)	k_M (m/s)	Method
$\leq 0.91 \cdot 10^3$	$\geq 2.4 \cdot 10^{-4}$	Max K_{ov} SO_3^{2-} solution
$\leq 0.55 \cdot 10^3$	$\geq 3.1 \cdot 10^{-4}$	Max K_{ov} HS solution
$\leq 0.44 \cdot 10^3$	$\geq 3.8 \cdot 10^{-4}$	Wilson plot K_{ov} HS solution

Reflecting on the difference between the theoretical mass transfer based on the G-L correlation and the experimental overall mass transfer coefficient it may be stated that this difference is most likely not caused by the resistance in the gas phase or membrane but probably by the non-ideal flow conditions in the membrane module. Although the membrane resistance is low compared to the mass transfer without reaction, it is still relatively high and can contribute largely to the mass transfer resistance in processes where a fast reaction takes place in the liquid phase and the mass transfer rate in the liquid increases.

5 Conclusions and outlook

The modules with PVDF hollow fibre membranes are suitable in performing as gas-liquid contactor for ozone. The overall mass transfer coefficients measured with the two membrane modules seem to coincide well. The experimentally determined mass transfer data show a deviation of approximately 30% with respect to the theoretically calculated mass transfer coefficient for the liquid k_L by the adjusted Graetz-Lévêque correlation according to Kreulen et al [1] (Equation (15)).

The contribution of the mass transfer resistance in the membrane to the overall resistance in the mass transfer processes is small under the experimental conditions without reaction in the liquid. According to experiments with substances in the water that are highly reactive towards ozone the mass transfer coefficient of the membrane is at least $3.8 \cdot 10^{-4}$ m/s. A Wilson-plot drawn from the mass transfer data from experiments without reaction did not give useful results. Wilson-plots drawn with the mass transfer data from experiments with reaction of ozone with humic substances and sodium sulphite in the water yielded a mass transfer coefficient of $5.2 \cdot 10^{-4}$ m/s and $9.6 \cdot 10^{-4}$ m/s. Although the roughness of the Wilson-plot method gives reason to suspicion it may be, considering the direct mass transfer findings, just to assume that the mass transfer coefficient of the membrane is at least $3.8 \cdot 10^{-4}$ m/s.

Although the mass transfer resistance in the membrane + gas phase is relatively small compared to overall mass transfer resistance in experiments without reaction in the water (3% of the total resistance) it can be of significant importance in mass transfer processes with a fast reaction in the liquid phase.

6 Nomenclature

Symbols

A	absorption	(-)
a	interfacial area	(m ²)
c	concentration	(mol/l)
d	thickness	(m)
dm	diameter	(m)
e	extinction coefficient	(l/mol/cm)
D	diffusion coefficient	(m ² /s)
J	mass transfer rate	(mol/s/m ²)

K_{ov}	overall mass transfer coefficient	(m/s)
K_H	Henry's constant	(kPa)
k	mass transfer coefficient	(m/s)
M	Molar mass	(g/mol)
p	Partial pressure	(kPa)
R	gas constant	(8.31 J/K)
r	radius / radial coordinate	(m)
s	dimensionless partitioning coefficient	(-)
s	Replacement probability	(1/s)
T	temperature	(K)
v	velocity	(m/s)
x	fraction	(-)
z	axial coordinate	(m)
ε	porosity	(-)
τ_m	tortuosity of the membrane	(-)

Indices

A	compound
b	module inlet
e	module outlet
eff	effective
G	gas phase/ gas side
k	Knudsen
L	liquid phase/ liquid side
lm	log mean
M	membrane
m	middle, $r = 0$
r	on place r on the radius
w	water

Dimensionless numbers

Gz_L	Graetz $\left((d_{m,in}/Z) Re_L Sc_L \right)$
Ha	Hatta number for (1,1)-reaction $\left(\sqrt{k_{1,1} c_{B,L} D_{A,L} / k_L^2} \right)$
Re_L	Reynolds $\left(\rho_L v_L d_{m,in} / \eta_L \right)$
Sc_L	Schmidt $\left(v_L / D_{A,L} \right)$
Sh	Sherwood $\left(k_L d_{m,in} / D_{A,L} \right)$

Abbreviations

DOC	Dissolved Organic Carbon
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidenedifluoride
PDMS	Polydimethylsiloxane

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Appendix A

Correlations for shell side mass transfer behaviour in tubular contactors

Inefficient flow hydrodynamics like maldistribution of flow around the fibres has a negative influence on the mass transfer. Variations in packing density, spacing and type of membranes, as well as feed entry influence the fluid hydrodynamics and make the prediction of the mass transfer behaviour more complicated. A number of researchers have attempted to find a correlation between the configuration and fluid hydrodynamics for shell side mass transfer in tubular contacting modules. All correlations that can be found in literature are relations of the type:

$$Sh = A Re^\alpha Sc^\beta$$

Where A , α and β are constants, sometimes related to some module feature. Unlike the standard equation of Graetz-L ev eque for the theoretical description of bore side mass transfer all these equations are obtained empirically. In Table 3 a number of correlations are presented that were found in literature. Some correlations include the packing density of the modules for the estimation of the Sherwood number (Equations (24), (25) and (26)). All correlations predict different values for k_G but on average, both $k_{G,module 1}$ and $k_{G,module 2}$ are in the order of $7 \cdot 10^{-4}$ - $3 \cdot 10^{-2}$ m/s.

Table 3: Several correlations proposed in literature for shell side mass transfer. The mass transfer coefficient in the gas is calculated with parameters from the experimental conditions for both modules. The figures represent the minimum and maximum mass transfer coefficient that was calculated.

nr	Equation	Comments	k_G (10^{-3} m/s) (module nr.)
(24) [27]	$Sh = \beta (d_h (1 - \phi) / Z) Re^{0.6} Sc^{0.33}$	$\beta = 5.8$ (hydrophobic fibres) $0 < Re < 500$, $0.04 < \phi < 0.4$	0.78 – 1.2 (1) 1.84 – 2.76 (2)
(25) [28]	$Sh = (0.53 - 0.58\phi) Re^{0.53} Sc^{0.33}$	$21 < Re < 324$, $0.32 < \phi < 0.76$	26 – 39 (1) 21 – 30 (2)
(26) [29]	$Sh = 0.09 (1 - \phi) Re^{(0.8-0.16\phi)} Sc^{0.33}$	$Re < 2.6$, $0.35 < \phi < 0.79$	5.6 – 9.4 (1) 4.3 – 7.2 (2)
(27) [30]	$Sh = 1.25 (Re \cdot d_h / Z)^{0.6} Sc^{0.33}$	$0.5 < Re < 500$, $\phi = 0.03$	0.78 – 1.6 (1) 0.72 – 1.2 (2)
(28) [31]	$Sh = 8.71 (d_h / Z) Re^{0.74} Sc^{0.33}$	$0.16 < Re < 7.30$, $\phi = 30$	3.38 – 5.89 (1) 4.6 – 7.6 (2)

IV

Ozonation of Humic Substances in a Hollow Fibre Membrane Contactor: Reaction Kinetics

This chapter describes the use of membrane contactors to investigate the reaction kinetics of the ozonation of humic substances (HS). A methodology based on theoretical mass transfer considerations was used to evaluate and interpret results from ozonation experiments. Mass transfer experiments were conducted in a hollow fibre membrane contactor in order to allow stationary ozonation conditions. Theoretical considerations on mass transfer with and without reaction and experimental mass transfer data indicate that the initial ozonation reactions occur instantaneously compared to the diffusive ozone mass transfer. During the oxidation process the reaction rate shifts from instantaneous to fast, compared to the physical ozone mass transfer in absence of reaction. Even when the ozone consumption is $0.25 \text{ molO}_3/\text{molDOC}$ the enhancement factor is >2 and no ozone is found in the liquid bulk. This indicates that the reaction is at least fast. The HS diffusion coefficient is calculated to be $6.1 \cdot 10^{-11} \text{ m}^2/\text{s}$ during the initial ozonation reactions and seems to increase along the ozonation process to $3.3 \cdot 10^{-10} \text{ m}^2/\text{s}$ at an ozone consumption of $0.15 \text{ molO}_3/\text{molDOC}$.

1 Introduction

Most investigations focusing on the effect of ozonation on HS mainly address the characterization of the ozonation products. Few results however have been reported on the process technology involving mass transfer and reaction kinetics of the ozonation of HS. Xiong et al. [1] describe the ozone consumption rate in presence of aquatic fulvic acids at different pH values with and without the presence of radical scavengers. They found a total rate constant of 215 l/mol/s for fulvic acids under acidic conditions (pH = 2) at 15 °C. Between pH 2 and 8 the reaction was found to be first order in the ozone concentration. Their results indicate that fulvic acid does not participate in the radical type ozone consumption and that at increasing pH it acts as promoter of the ozone decomposition in water. Staehelin et al. [2] investigated the effect of pre-ozonated HS on the radical chain reactions during the ozone decomposition and found that HS acted as promoter of the radical chain reactions. This effect depended strongly on pH. Langlais et al. [3] discuss in their book a few studies on the ozonation of humic substances.

The molecular structure of HS is usually very complex and hard to reveal, which makes HS a subject for many studies for the characterization of the molecular structure. The fact that quantity and type of varying potentially reactive sites, each with its own reactivity, are hardly known has consequences for reaction kinetic studies. In batch-wise experiments the reaction kinetics may change during the ozonation period making a qualitative evaluation of reaction experiments a difficult task. For this purpose an experimental setup which can be operated stationary may be desirable.

In recent years the use of membranes as gas-liquid contactors has advanced rapidly. As described in Chapter III they may offer several technical advantages over conventional G-L contactors. Due to the low solubility of ozone in water a high contact area would be very beneficial to enhance the ozone transfer from the gas to the liquid phase. Several investigations involving the use of membrane contactors for ozone transport have been reported. Shanbhag et al. investigated the ozone mass transfer application of silicone hollow fibre membranes and their application for ozonation of wastewaters [4-6]. Guha et al. tested both silicone and microporous Teflon tubes and polypropylene hollow fibres in investigating a multiphase

ozonation reactor [7]. Janknecht et al. [8, 9] and Picard et al. [10] developed hydrophobic and hydrophilic ceramic membranes for ozonation purposes.

A beneficial feature of the hollow fibre membrane contactor is that its surface area is known accurately. Also the fluid dynamics and mass transfer description of a phase flowing through the hollow fibres is very accurate. Furthermore, the gas/liquid adsorption processes can be operated stationary so that the chosen experimental conditions remain constant throughout the experiments. This makes the membrane contactor a potentially useful tool for measurements in mass transfer and reaction kinetics. Based on the considerations mentioned above Kumar et al. [11] suggested the use of a single fibre membrane contactor as model gas-liquid contactor. Proceeding on this work Dindore et al. [12] investigated the use of a single fibre membrane contactor as model-gas liquid contactor in carbon dioxide (reactive) absorption in a NaOH solution. They compared experimental results with simplified asymptotic approximation solutions and a numerical approximation method. They found that for a simple reaction scheme and high Graetz numbers simplified asymptotic solutions can be used to estimate properties like diffusivity, solubility and reaction rate constants. At lower Graetz-numbers and complex reaction schemes the numerical model should be applied. They found that using simplified asymptotic solutions at sufficiently high Graetz-numbers the calculated diffusivity of CO₂ in water and diffusivity ratio of CO₂ and OH⁻ in water and the second order reaction rate constant at was in good agreement with values reported in literature. With this they showed that the membrane contactor can be used as model gas-liquid contactor to estimate physical and chemical properties in absorption processes.

In this paper the results and evaluation of mass transfer measurements in a PVDF membrane contactor are reported which were conducted to investigate the reaction kinetics of the ozonation of HS.

2 Theory

2.1 Mass transfer without reaction

The molar flux of a gas A, into a liquid can be described by the general equation

$$J_A = K_{ov,A} (c_{A,L,i} - c_{A,L}) \quad (1)$$

For a non-wetted porous membrane, the overall mass transfer coefficient for a substance A, $K_{ov,A}$, can be described by a resistance-in-series model:

$$\frac{1}{dm_{M,L} \cdot K_{ov,A}} = \frac{1}{dm_{M,G} \cdot s_A \cdot k_{G,A}} + \frac{1}{dm_{M,lm} \cdot s_A \cdot k_{M,A}} + \frac{1}{dm_{M,L} \cdot E_A \cdot k_{L,A}} \quad (2)$$

Here E_A is the so-called enhancement factor which accounts for an apparent acceleration of the mass transfer coefficient due to a reaction in the liquid phase. Details on the enhancement factor are further elaborated in Section 2.3. For details on mathematical models for (physical) mass transfer in tubes is referred to Chapter III, Section 2.2.

2.2 Reaction of ozone with humic substances

The reaction of ozone with humic substances is very complex. Humic substances contain many potential reactive sites with different reactivity and concentration. Furthermore the ozonation can occur by direct ozone reactions or through a radical chain mechanism with the indirect ozone reaction depending on reaction conditions such as pH. In case of indirect reactions, HS can act as initiator, promoter and inhibitor of the radical chain mechanism depending on its concentration [3, 13]. The exact molecular structure of humic substances is generally not known. It is therefore impossible to quantify the number of reactive sites and due to the variety of reactive sites it is virtually impossible to quantify the reaction kinetics for each type. This only leaves the possibility to measure overall reaction kinetics. Considering that, it might be expected that during a batch-wise ozonation reaction with HS the reaction rate decreases because of two effects: The first is the decrease of concentration of

reactive sites due to conversion. The second is that sites with high reactivity will convert faster than sites with lower reactivity. The overall reaction rate constant therefore also decreases during the ozonation period.

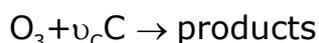
2.3 Enhancement of mass transfer by chemical reaction in the liquid

To simplify the problem the overall reaction of ozone is considered to be a (1,1)-reaction:



Ozone reacts with a humic substance molecule with a stoichiometric constant ν_{HS} .

The concentration of humic substances is usually expressed in dissolved organic carbon (DOC). From that point of view the reaction can be written as



Ozone reacts with a carbon atom with a stoichiometric constant of ν_C . Here $\nu_C = \chi \cdot \nu_{HS}$ where χ is the number of carbon atoms in a HS molecule.

The following considerations on mass transfer in presence of a reaction were adapted from Westerterp et. al. [14].

The mass transfer of a compound from a gaseous phase to a liquid phase can be enhanced when the compound reacts in the liquid with another compound or with itself. This causes a lower concentration in the liquid giving a larger driving force and hence a greater mass transfer. When the reaction is fast enough with respect to the mass transfer without reaction the latter is accelerated by a certain multiplying factor. The enhancement factor, E_A is a measure for this multiplying factor and is defined as the ratio between the mass transfer with reaction and the physical mass transfer (in absence of reaction) at the same driving force. The driving force is the difference between the concentration in the liquid bulk and the concentration in the liquid near the interface.

$$E_A = \frac{J_{A, \text{reaction}}}{J_{A, \text{physical}}} \quad (3)$$

With the mass transfer rates normalized for the driving force, which is the concentration difference of A in the liquid near the interface and in the liquid bulk, E_A can be defined as

$$E_A = \frac{k'_L}{k_L} \quad (4)$$

where k'_L is the liquid mass transfer coefficient in presence of reaction. When the mass transfer resistance in the gas and membrane phase is negligible compared to the resistance in the liquid phase the enhancement factor can be calculated by Equation (5).

$$E_A = \frac{K_{\text{ov},A,\text{reaction}}}{K_{\text{ov},A,\text{physical}}} \quad (5)$$

Considering the rate of reaction compared to the mass transfer of A without reaction three limiting cases are distinguished: Slow reaction, fast reaction and instantaneous reaction (see Figure 1 for a schematic representation of the three distinguished reaction regimes explained by the film model). A reaction is regarded as "slow" in case the mass transfer is not enhanced by the reaction ($E_A = 1$). The reaction takes place in the liquid bulk. The reaction is considered a "fast reaction" in case the rate of reaction is so high, compared to the rate of mass transfer, that A is completely converted near the interface: the mass transfer is limited by the diffusion of A in the water. The concentration of A in the bulk liquid is 0. This causes a larger concentration gradient near the interface and therefore a stronger driving force for mass transfer hence the mass transfer rate is enhanced. The definition of an instantaneous reaction is in fact an asymptotic situation of the case for a fast reaction. Now, the reaction is so fast that the conversion rate is completely limited by diffusion of reactants A and B into the reaction zone. A and B do not occur in the same location. The place where A and B meet each other is known as the reaction plane (near the gas-liquid interface) in which the concentrations of both A and B are zero. In this case the enhancement factor reaches its maximum value: an even higher reaction rate does not enhance the mass transfer rate any further.

It should be emphasized that the terms slow, fast and instantaneous reaction do not concern absolute values of reaction rates but are merely definitions for the rate of reaction compared to the diffusive mass transfer of a compound A in the liquid.

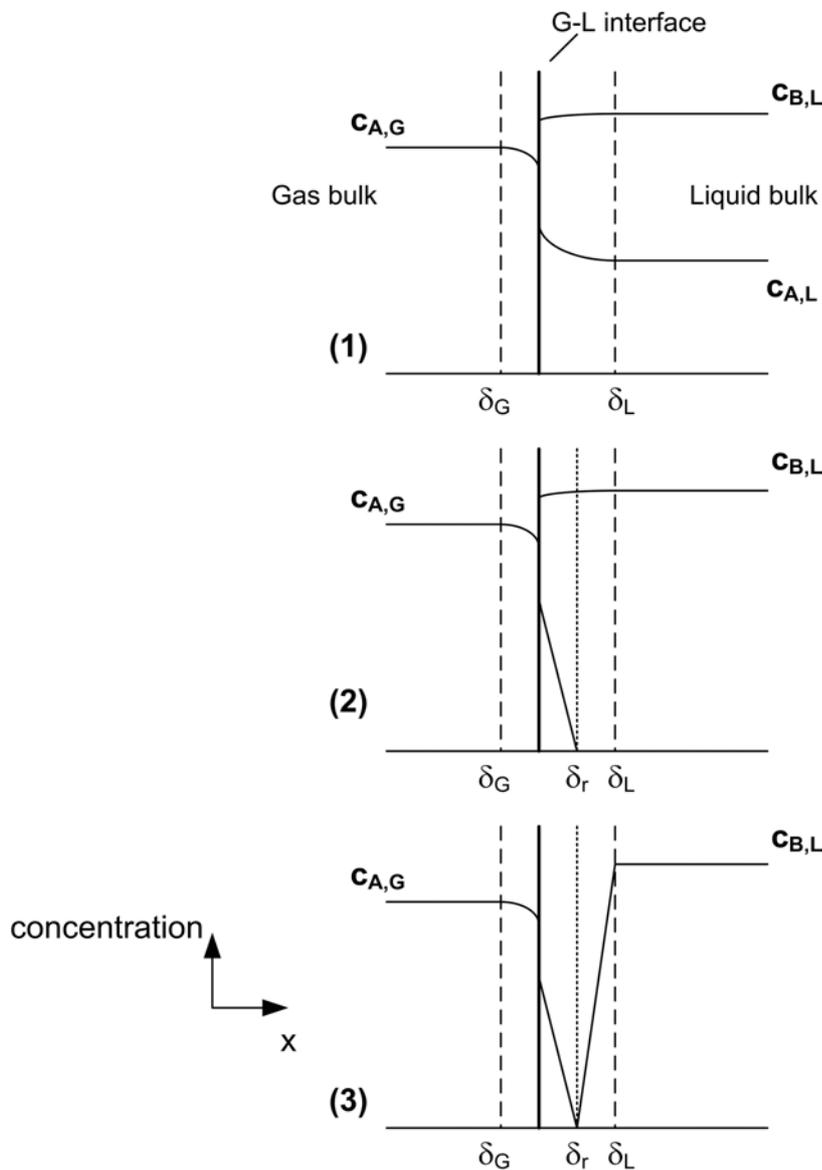


Figure 1: Three regimes for mass transfer explained by the film model.

- (1) Slow reaction. No mass transfer limitations in A or B. Reaction occurs in liquid bulk**
- (2) Fast reaction. Mass transfer limitation in A. Reaction occurs in reaction zone near G-L interface: $0-\delta_r$.**
- (3) Instantaneous reaction. Transfer limitation in A and B. Reaction occurs in the reaction plane at δ_r .**

For mass transfer in presence of reaction two dimensionless numbers are of importance: The Hatta number (Ha) and the

maximum enhancement factor $E_{\infty,A}$. The Hatta-number for a substance A, Ha_A , in a first order reaction in A and B is defined as:

$$Ha_A = \sqrt{\frac{k_{1,1}c_{B,L}c_{A,L,i}\delta}{D_{A,L}(c_{A,L,i} - 0)}} = \sqrt{\frac{k_{1,1}c_{B,L}D_{A,L}}{k_L^2}} \quad (6)$$

where

$$Ha_A^2 = \frac{\text{maximum conversion of A in a film per m}^2 \text{ of film}}{\text{maximum flux of A through the film in absence of reaction}}$$

The maximum enhancement factor, $E_{\infty,A}$, represents the maximum enhancement possible when the transport of the reactants is the limiting factor in a relatively fast reaction regime.

$$E_{\infty,A} = \left(1 + \frac{D_{B,L}c_{B,L}}{v_B D_{A,L}c_{A,i,L}}\right) \left(\frac{D_{A,L}}{D_{B,L}}\right)^n \quad (7)$$

The factor n is 0.5 according to the penetration model and 0.33 according to the film model. It is the limiting case where the reaction is so fast that the conversion rate is limited by the diffusion of the reactants, as mentioned above for the instantaneous reaction. The enhancement factor is completely determined by the diffusion properties and concentrations of both reactants and the stoichiometric factor of the reaction equation, v_B .

The value of the enhancement factor E_A , depends on the value of Ha_A , the Hinterland factor AL and $E_{\infty,A}$. The Hinterland ratio, AL, is the ratio between the liquid volume and the volume of the liquid film near the interface. Table 1 shows the asymptotic solutions for the enhancement factor and the accompanying conditions. In case of a fast reaction the enhancement factor is equal to Ha_A and the mass flux is independent of the mass transfer coefficient of the liquid, k_L . Measurements at different $c_{A,L,i}$ might yield the reaction rate constant. In the case of an instantaneous reaction E_A is equal to the maximum possible enhancement factor $E_{\infty,A}$ and the mass flux is dependent on the mass transfer resistance in the liquid. Under instantaneous reaction conditions compared to physical mass transfer, the intercept of the linear graph of E_A plotted against $c_{B,L}$ or $(c_{A,L,i})^{-1}$ represents $(D_{A,L}/D_{B,L})^n$ and the stoichiometric constant v_B can be calculated.

Table 1: Conditions for the asymptotic approximate solutions for the enhancement factor, E_A for a (1,1) reaction.

Ha_A	$(AI-1)Ha_A^2$	$c_{A,L}$	E_A	J_A
<0.3 (slow reaction)	$<<1$	$\approx c_{A,L,i}$	1	$J_A = k_L (c_{A,L,i} - c_{A,L}) \approx \frac{k_1 c_{A,L,i} c_{B,L} V_L}{a_i}$
<0.3 (slow reaction)	$>>1$	0	1	$J_A = k_L c_{A,L,i}$
>2 and $<< E_{A,\infty}$ (fast reaction)	All values	0	Ha_A	$J_A = Ha_A k_L c_{A,L,i} = \sqrt{k_{1,1} c_{B,L} D_{A,L}} (c_{A,L,i})$
$>> E_{A,\infty}$ and >2 (instantaneous reaction)	All values	0	$E_{A,\infty}$	$J_A = E_{A,\infty} k_L c_{A,L,i} = k_L \left(\left(1 + \frac{D_{B,L} c_{B,L}}{v_B D_{A,L} c_{A,L,i}} \right) \left(\frac{D_{A,L}}{D_{B,L}} \right)^n \right) \cdot c_{A,L,i}$

$n = 1/2$ film model

$n = 1/3$ penetration model

Some notifications should be made on the applicability of the approximate solutions on mass transfer processes. The Hatta number and maximum enhancement factor are based on the concentration of B at the liquid inlet, assuming that the concentration of B at the axis remains constant. However, during the reaction process B is converted by which the concentration in the bulk changes over the length of the reaction module. Therefore the actual bulk concentration of B should be used in calculation of the Hatta number and the maximum enhancement factor. The error that is made by the approximation solutions in absorption process in hollow fibres in presence of reaction was investigated by Kumar [11]. They compared the results from the approximation solutions with the results from numerical approximations. From the results he concluded that approximate solutions fail at low Gz_L . For irreversible (1,1) reactions with $v_B = 1$ the use of the approximate solutions is limited to

$$Gz_L > 120(D_B/D_A) \quad (8)$$

due to depletion of reactant B in the liquid phase at lower Gz numbers. In the case where humic substances and ozone are the reactants the ratio D_B/D_A can be substantial. The diffusion coefficient of ozone is estimated to be $1.80 \cdot 10^{-9} \text{ m}^2/\text{s}$ and the diffusion coefficient of HS can be in the order of 10^{-11} to $10^{-10} \text{ m}^2/\text{s}$ [15-17]. D_B/D_A may be in the order of 10^{-3} to 10^{-2} . In an ozone/HS reaction most likely $\nu_B \neq 1$. In the case where $\nu_B > 1$ the depletion rate of HS is higher than when $\nu_B = 1$ and the approximate solutions are limited to higher Gz numbers than in Equation (8). If $\nu_B < 1$ the depletion rate is lower and approximate solutions are limited to lower Gz numbers than in Equation (8).

Another factor of potential importance is the fact that humic substances consist of reactive sites with different reactivity's as mentioned in Section 2.2. This means that the overall reaction rate constant may change over the contact time in the module. The actual reaction rate constant should than be incorporated in the Hatta number. This is important in the case of a moderate to fast reaction. If the reaction rate remains in the instantaneous regime during the contact time in this situation is not significant.

3 Experimental

3.1 Contactor module

Hydrophobic PVDF membranes supplied by EMI Twente (The Netherlands) were applied in the membrane contactor. The membrane features can be found on Chapter III, Section 3.1. The features of the contactor module are presented in Table 2. PDMS was used as potting material for its ozone resistant character. 375 PVDF membranes were potted in the contactor module. This created a specific surface area of $6.8 \cdot 10^3 \text{ m}^2/\text{m}^3$ on the shell side of the membranes. During the experiments no significant change was observed in mass transfer under equal operation conditions. This showed that the membrane module was operating stable for the duration of the experimental period.

Table 2: Features of the membrane contactor module.

Module 1			
Module housing	Stainless steel	Potting material	PDMS
Housing Diameter	0.0256 m	# membranes	375
Contact length	0.26 m	Packing density	65%
Specific area bore side	$6.7 \cdot 10^3 \text{ m}^2/\text{m}_i^3$ $1.3 \cdot 10^3 \text{ m}^2/\text{m}_m^3$	Specific area shell side	$6.8 \cdot 10^3 \text{ m}^2/\text{m}_o^3$ $2.4 \cdot 10^3 \text{ m}^2/\text{m}_m^3$

Subscripts: i) volume bore side, o) volume shell side, m) volume module

3.2 Humic substance solution

The humic substances were obtained from tap water from pumping station Spannenburg (The Netherlands). The HS molecules were concentrated by an anion exchange adsorption process. Purolite A806S acted as ion exchange resin on which the HS molecules absorb. According to the manufacturers prescription the column was regenerated by a 10% NaCl solution in water. The HS concentration obtained in the regenerate reached up to 30 gDOC/l. The concentrated HS solution was diluted to a solution with 20 gDOC/l to form the stock solution. The NaCl concentration in the stock solution was kept below 1 M so that the influence of NaCl on the mass transfer is kept to a minimum during the reaction experiments. The HS solutions for the experiments were prepared out of the stock solution. TOC amounts in the experimental solutions ranged from 3.3 to 33 molDOC/m³ (40 to 400 mgDOC/l). In these dilutions the highest NaCl concentration in the HS solutions is 0.02 M. At these low concentrations the ionic strength of the reaction solutions is considered to have an insignificant effect on the ozone solubility in water. Experimental considerations on the effect of NaCl on the ozone mass transfer during the ozonation reactions are handled in Appendix A.

3.3 Experimental Setup

The experiments were performed on the same setup as described in Chapter III, Section 3.2. During the experiments the applied ozone concentrations in the gas phase were varied from 0.16 to 0.60 mol/m³. The mass transfer processes were performed

counter-currently with the liquid flowing through the fibers. The ozone concentration in demineralized water without humic substances was measured spectrophotometrically with the indigo-method [18]. The ozone concentration in HS solutions was measured with a GLI Accuzone™ 53 ozone sensor, model 5920Z0. The ozone sensor was calibrated in demineralized water with the indigo method. A blank test with HS solution showed that humic substances do not seem to interfere in the ozone detection.

The ozone concentration in the liquid near the interface, $c_{O_3,L,i}$ was calculated from the concentration in the gas phase using Henry's law for the equilibrium between a compound in the gas and the liquid phase: $K_{H_A} = p_A/x_A$. At 21 °C and very low ionic strength the dimensionless value for K_{H,O_3} , expressed as s_{O_3} , is equal to 3.30, and 4.38 for an ionic strength of 1 (1 M NaCl) (see Equation (2) [19] in Chapter II). The ozone concentration near the liquid interface was calculated from the ozone gas concentration:

$$c_{O_3,L,i} = \frac{c_{O_3,G}}{s_{O_3}} \quad (9)$$

The driving force for ozone transport from the gas phase to the liquid phase was calculated as described in Chapter III, Section 3.2. The ozone flux is calculated by the ozone concentration in water at the outlet or by the ozone loss in the gas phase.

3.4 Experiments

First the ozone mass transfer from air to demineralized water in absence of humic substances was measured. The ozone concentration in the gas inlet and outlet was measured as well as the ozone concentration at the liquid outlet. The experiment was performed at several liquid flow rates ranging from $7.4 \cdot 10^{-3}$ to $16 \cdot 10^{-3}$ m/s and ozone concentrations of 0.34 and 0.60 mol/m³ in the gas phase. These experiments are also reported in Chapter III.

For ozone mass transfer measurements with HS in the solution of the experiments described below were performed. All experiments were performed at 20 °C. The initial pH of each HS solution was 9.5. No pH adjustments were made prior or during the ozonation period.

3.4.1 Ozone transport in HS solution at different liquid flow rates and ozone concentrations

Mass transfer experiments with untreated HS at different liquid flow rates ranging from 0.05 to 0.17 m/s and at several ozone gas concentrations ranging from 0.16 to 0.47 mol/m³ with flow rates of 5.8 and 11 ml/s. The HS concentration was 33 molDOC/m³ (400 mgDOC/l).

3.4.2 Ozone transport in untreated HS solutions at different liquid flow rates and HS concentrations

Mass transfer experiments with four HS solutions with different concentrations at two liquid flow rates (0.08 and 0.12 m/s). The HS concentrations were: 3.3, 8.3, 17 and 33 molDOC/m³ (40, 100, 200, 400 mgDOC/l). The ozone feed concentration in the gas phase was held constant at 0.31 mol/m³ and a gas flow rate of 12 ml/s.

3.4.3 Ozone transport in HS solutions at different oxidation levels

As the ozonation is in process the oxidized state of the humic substances changes. This oxidized state is called the oxidation level ω expressed in molO₃/molDOC, and is the ozone consumption at a certain moment. The ozone mass transfer in a HS solution changes with the increasing oxidation level of the humic substances in the solution during the ozonation process. During these experiments the transfer behaviour of ozone at different oxidation levels of the humic substances is monitored.

In preparation five HS solutions were run batch wise through ozonation module, at a low liquid flow rate ($7.8 \cdot 10^{-3}$ m/s, contact time 33 s), an ozone concentration in the gas of 0.38 mol/m³ and a gas flow of 6.1 ml/s. The ozone consumption was monitored during each circulation and the number of circulations was different for each solution. In this way each HS solution reached a certain oxidation level of 0 to 0.75 molO₃/molDOC

Ozone transfer at different liquid flow rates for HS solutions of several oxidation levels

Each of the oxidized HS solutions was then ozonated at a flow rate of 0.23 m/s through the column (contact time 1.2 s) at which the ozone mass transfer was determined. The ozone gas feed

concentration at the inlet was around 0.36 mol/m^3 with a flow rate of 6.1 ml/s .

Ozone transfer experiments with HS with $\omega = 0.15$ molO₃/molDOC at different HS concentrations.

The HS solution with an oxidation level ω of $0.15 \text{ molO}_3/\text{molDOC}$ was diluted to four different HS concentrations, ranging from 3.3 to 33 molDOC/m^3 (40 to 400 mgDOC/l). These solutions were ozonated at two different liquid flow rates of 0.11 and 0.20 m/s during which the ozone mass transfer was measured. The ozone concentration in the feed gas was 0.34 mol/m^3 with a gas flow rate of 6.1 ml/s .

3.5 Method for evaluating mass transfer measurements for analysis of the reaction kinetics

From the ozone mass transfer behavior it is possible to determine the details of the reaction kinetics. The first step is to distinguish whether the reaction is slow or at least fast. This is done using Table 1. The enhancement factor E_{O_3} is calculated by Equation (5). The overall mass transfer coefficients were calculated using Equation (1) where the driving was calculated using. If $c_{\text{O}_3,\text{L}} \neq 0 \text{ mol/m}^3$ and/or $E_{\text{O}_3} = 1$ the reaction is slow. If $c_{\text{O}_3,\text{L}} = 0 \text{ mol/m}^3$ and $E_{\text{O}_3} > 2$ then the reaction is fast or instantaneous. Whether the reaction is fast or instantaneous can be deduced by investigating the dependence of the ozone mass transfer rate, J_{O_3} on the liquid flow rate v_{L} , during the ozonation reaction. When the reaction is instantaneous the ozone mass transfer rate, J_{O_3} is dependent on the mass transfer coefficient of the liquid, k_{L} and therefore dependent on the liquid flow rate, v_{L} in the case of convective transport (see Table 1). When the reaction is fast J_{O_3} is independent of k_{L} and consequently independent of v_{L} . If the reaction is fast then $E_{\text{O}_3} = \text{Ha}_{\text{O}_3}$ and using the equation in Table 1 the reaction rate constant, $k_{1,1}$ can be calculated. When the reaction is instantaneous then $E_{\text{O}_3} = E_{\infty,\text{O}_3}$ and the HS diffusion coefficient, $D_{\text{HS,L}}$ and the stoichiometric constant, ν_{C} can be calculated.

Since the actual HS mol concentration is not known the HS concentration, c_{HS} is expressed in molDOC/m³ or mgDOC/l in the calculations.

4 Results and discussion

4.1 Ozone mass transfer without presence of humic substances

The experimental results of the mass transfer experiments with demineralized water in the membrane module 1 with 375 hollow fibers is shown in Figure 2. Over the range of Re_L numbers the overall mass transfer coefficient increases from $0.4 \cdot 10^{-5}$ to $1.8 \cdot 10^{-5}$ m/s. The applied difference in ozone gas phase concentration does not seem to have a significant effect on the mass transfer coefficient. In the figure the overall mass transfer coefficient is compared to the theoretical liquid mass transfer coefficient calculated with Equation (12) in Chapter III, the correlation according to Kreulen et al [20] derived from the Graetz-Lévèque (G-L) correlation. The experimental data follow the same trend but remain well below the theoretical G-L correlation. The difference might be explained by non-ideal flow conditions as mentioned in the theory but might also be caused by a significant membrane or gas phase resistance. According to Figure 2 this possible membrane or gas phase resistance should then be of the same order of magnitude as the mass transfer resistance in the liquid. In Chapter III the mass transfer resistance of the membrane was investigated. According to the result of the experiments the mass transfer coefficient of the membrane + gas phase together is at least $3.3 \cdot 10^{-4}$ m/s. The contribution of the resistance in the gas phase and the membrane is small compared to the overall resistance during mass transfer in absence of reaction in the liquid phase: $K_{ov,O_3,physical} \approx 10^{-5}$ m/s. However, the resistance in the gas phase or membrane can become significant when the mass transfer resistance in the liquid phase is reduced by a fast reaction.

A mathematical fit with a power function of the type $y = a + b x^c$ was calculated through the data points. Out of this Equation (10) was derived and describes the fitted line in Figure 2.

$$K_{ov,O_3,physical} = -6.7 \cdot 10^{-6} + 6.1 \cdot 10^{-6} (v_L)^{0.32} \quad (10)$$

This equation is used to describe the physical mass transfer coefficient for ozone in the module and is used to calculate enhancement factors for ozone mass transfer in the Re_L range that is applied in the mass transfer experiments.

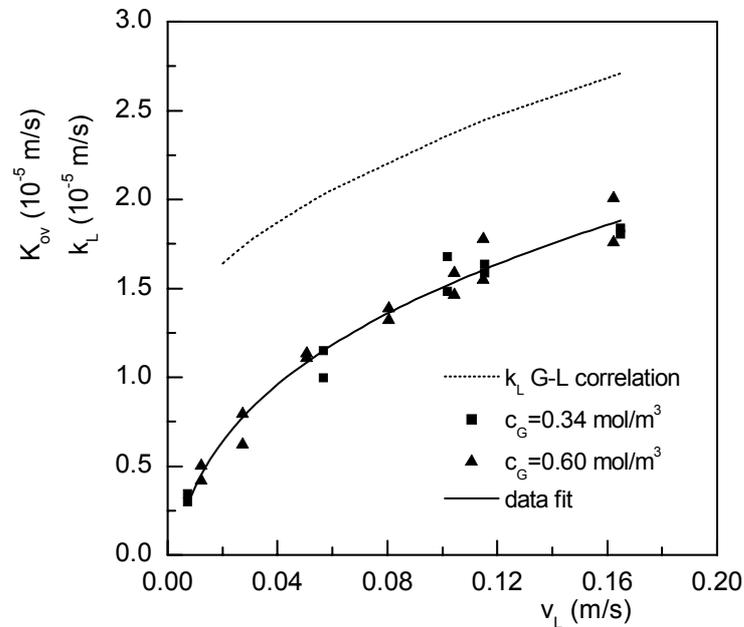


Figure 2: Physical ozone transport in the PVDF membrane module: Overall mass transfer coefficient against the flow rate of the liquid phase v_L . Ozone concentration in the gas phase: 0.34 and 0.60 mol/m³. Performed in module 1 (375 membrane fibres). The G-L correlation represents the derivation according to Kreulen et al [20] (Equation (12) in Chapter III) from the Graetz-Lévêque correlation for mass transfer.

When dealing with the mass transfer of ozone to water the ozone decomposition in pure water should be considered as well. Qiu [21] investigated the reaction rate constants for ozone decomposition under different pH conditions in water and compared the results with result from other investigations. Although the reaction rate deviates among the different studies it can be assumed that the first order reaction rate constant of ozone self decomposition varies from approximately 0.0001 s^{-1} at pH=2 to 0.001 s^{-1} at pH=7. These reaction rates are too low for the decomposition to have a significant effect on the mass transfer at the residence times of the liquid that were applied in the module. Experimentally there was no significant difference found between the ozone loss in the gas phase over the

module and the ozone concentration in the water. This supports that no significant amount of ozone was lost, which is in turn an indication that the decomposition of ozone in water under these conditions may be neglected.

4.2 Ozone consumption and enhancement factor during the ozonation process

The result of successive ozonation of humic substances is given in Figure 3. It shows an example of the ozone consumption and enhancement factor of the ozone mass transfer during the ozonation reaction of humic substances at successive oxidation levels.

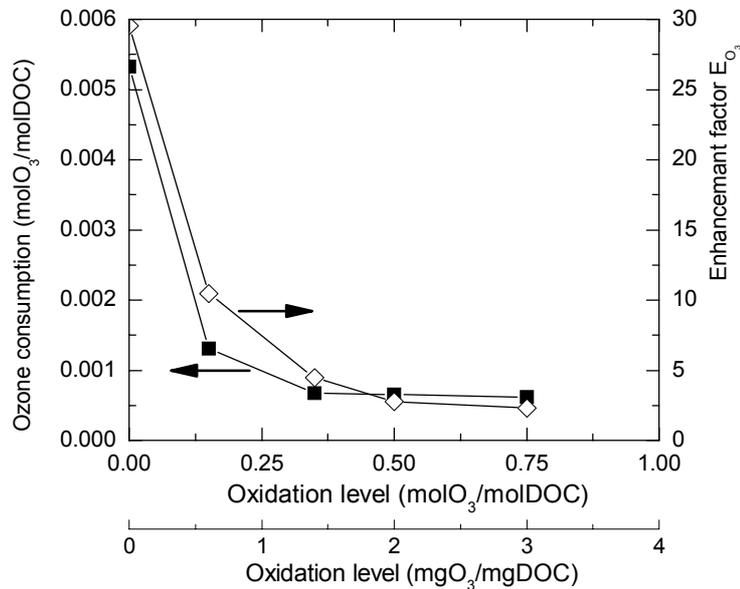


Figure 3: Enhancement factor of the ozone mass transfer and the ozone consumption at that moment at several levels of oxidation. The levels are expressed in molO₃/molDOC, the level of 0 molO₃/molDOC is an untreated HS solution. The ozone mass transfer was measured at a liquid flow rate of 0.23 m/s (Re_L=114, contact time 1.2 s), the ozone concentration in the feed was 0.36 mol/m³. Initial HS concentration: 33 molDOC/m³.

The oxidation level, ω of the different solutions is defined by the amount of ozone that has been consumed per amount of the initial HS concentration (molO₃/molDOC). According to this definition five solutions were prepared with oxidation levels of 0.15, 0.35, 0.50

and 0.75 molO₃/molDOC respectively. As illustrated in Figure 3 it seems that under the experimental conditions the ozonation reaction may start as a fast or as an instantaneous reaction compared to the diffusive ozone mass transfer. Indications for this are the high enhancement factor of 29 ($\gg 2$) and the fact that no ozone was detected in the liquid bulk: $c_{O_3,L} = 0 \text{ mol/m}^3$ (see also Table 1). At the stage where $\omega = 0.15 \text{ molO}_3/\text{molDOC}$ the enhancement factor has dropped to a value of around 10.

As the ozonation continues, the ozone mass transfer decreases and subsequently the enhancement factor seems to decrease asymptotically to $E_{O_3} = 2$. Although the enhancement factor is low at this point, still no ozone was detected in the liquid bulk indicating that the ozonation reaction at that point is still fast compared to the diffusive ozone mass transfer.

4.3 Initial ozonation reaction at different liquid flow rates, ozone concentrations and HS concentrations.

To have a closer look at the mass transfer behaviour during the initial ozonation reaction of these humic substances, experiments were conducted at several ozone gas concentrations, liquid flow rates and HS concentrations in the solution. Experiments where the ozone mass transfer is measured at several liquid flow rates at constant liquid interface concentration show that the mass transfer rises clearly with an increasing liquid flow rate (Figure 4a), whereas the enhancement factor hardly changes (Figure 4b). These results suggest that the reactions at this point are instantaneous compared to the physical mass transfer. Another indication for an instantaneous reaction is the decrease of the overall mass transfer coefficient $K_{ov,O_3,reaction}$, and consequently the enhancement factor, with every increase of the ozone concentration in the liquid interface.

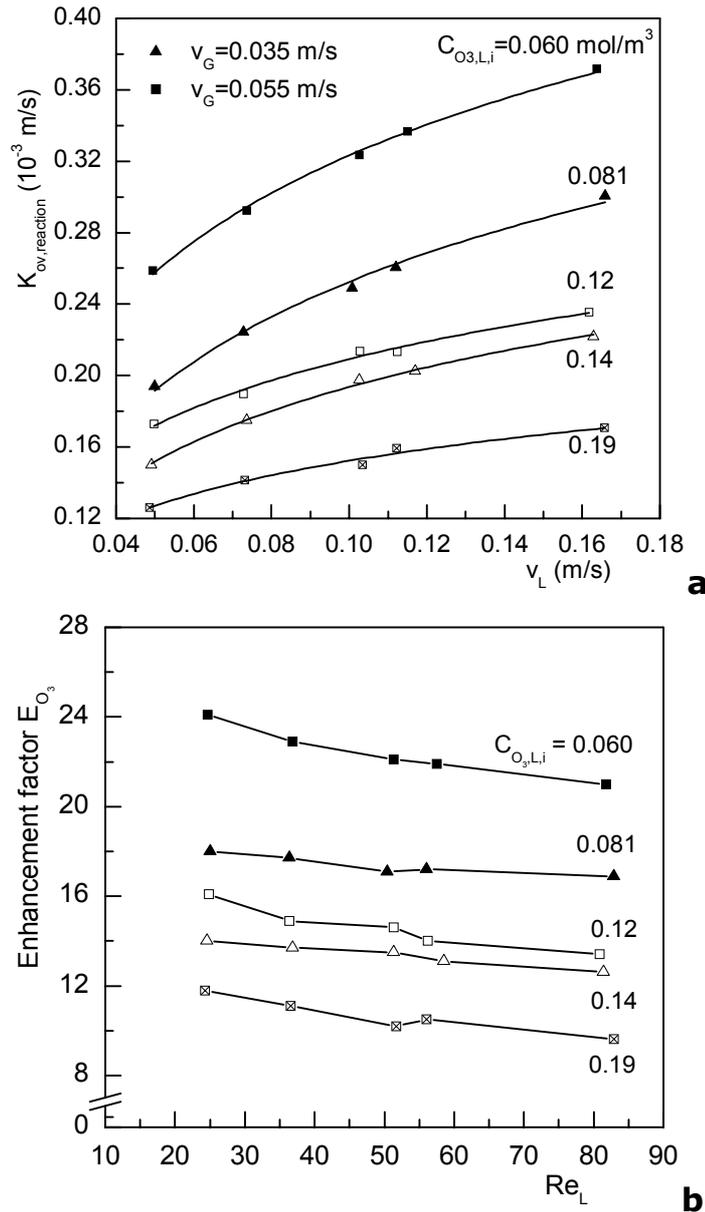


Figure 4: Overall mass transfer coefficient (a) and the enhancement factor (b) against the liquid flow rate. Experiments were performed at several ozone liquid interface concentrations, $c_{O_3, L, I}$ (mol/m^3) by varying the ozone concentration in the gas phase. $c_{HS} = 33$ molDOC/m^3 .

4.4 Ozonation at other oxidation levels

As mentioned in Section 4.3 a number of HS solutions were ozonated for different periods under the same conditions to obtain HS solutions of different levels of oxidation (expressed in $\text{molO}_3/\text{molDOC}$, see Figure 3). For each solution, again the ozone mass transfer was measured at different liquid flow rates. These experiments show again that no ozone was found in the bulk liquid ($c_{O_3, L} = 0$ mol/m^3)

for all solutions. Figure 5 shows that a higher oxidation level results in a lower ozone mass transfer. It is reasonable to relate this to the decrease of available reactive sites during the ozonation period. More interesting is the trend of the curves. The data points were mathematically fit with a power function of the type $y = a + b x^c$. From Figure 5 it can be seen that with increasing oxidation level the dependence of the mass transfer on the liquid flow rate decreases. To stress this out linear line-fits were made through the data points which clearly show the decreasing slope of the curves.

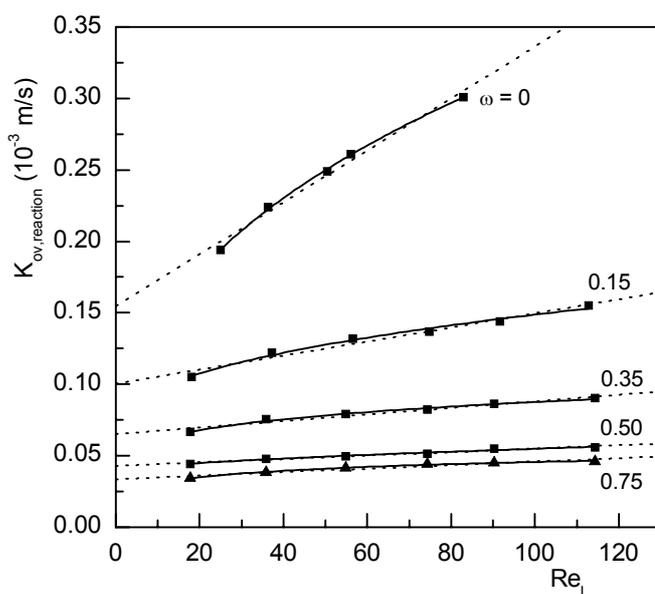


Figure 5: Mass transfer coefficient against the liquid flow rate. The experiments were performed with HS solutions of different oxidation level, ω expressed as the ozone consumption per amount of HS ($\text{molO}_3/\text{molDOC}$) and indicated by the values accompanying the curves.

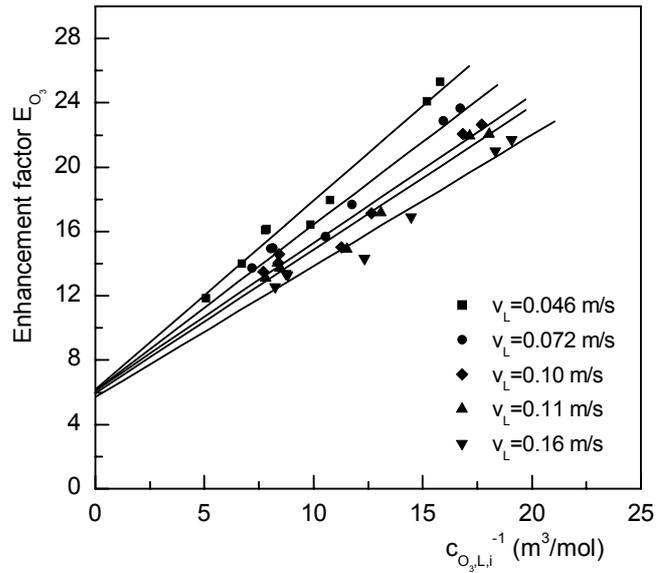
According to the mass transfer considerations (Table 1) the ozone flux during an instantaneous reaction should be dependent on the physical mass transfer coefficient of the liquid k_L , which is in turn dependent on the liquid flow rate. In contrast, during a fast reaction the ozone flux should be independent of the physical mass transfer coefficient of the liquid, k_L and thus independent of the liquid flow rate. Ideally the curve of the ozone flux against the liquid flow rate is then horizontal (factor $c = 0$ or $b = 0$). A flattening curvature and slope as function of the oxidation level of the humic substances might indicate that the reaction shifts from an instantaneous towards a fast reaction compared to mass transfer through diffusion. Shifting to a

fast reaction means that the value of the reaction rate is a determining factor in the mass transfer since the enhancement factor now becomes equal to the Hatta number which in turn is dependent on the reaction rate constant (see Table 1). A completely flat curve is not reached, although the enhancement factor approaches 2 (see Figure 3) which is the lower limit where it can be stated that a reaction is at least fast.

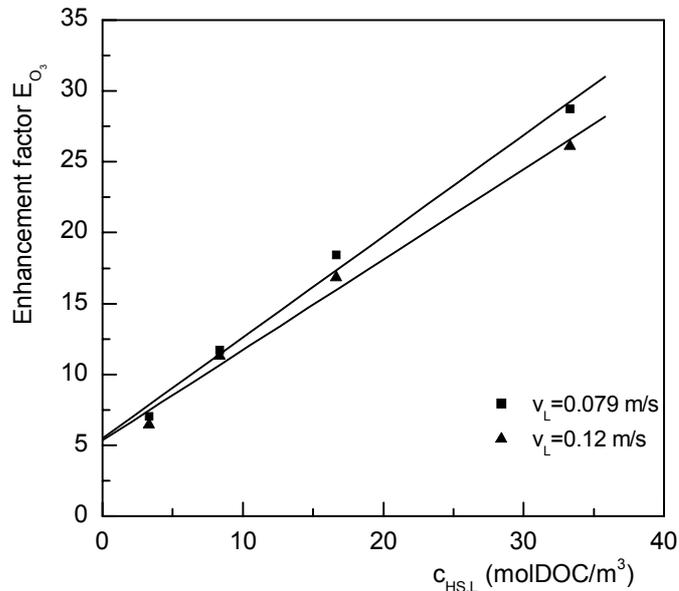
4.5 HS diffusion coefficient and stoichiometric constant from mass transfer measurements.

Plotting the enhancement factor against the reciprocal ozone concentration in the liquid interface, $(c_{O_3,L,i})^{-1}$ or the HS concentration, $c_{HS,L}$ yields Figures 6a and 6b respectively for the initial ozonation reaction. It shows that the enhancement factor is a linear function of the ozone concentration in the liquid interface and the HS concentration. From the intercepts of the linear fits of both graphs and Equation (7) (see also Table 1) the apparent average overall diffusion coefficient of the humic substances was calculated to be $6.1 \cdot 10^{-11} \text{ m}^2/\text{s}$ (also in Table 3). The calculated diffusion coefficient is comparable with diffusion coefficients that were found in literature, measured with different methods [22-25]. From the intercepts and the slopes of Figures 6a and 6b the average overall stoichiometric constant, ν_C was calculated (Table 3). According to this factor one ozone molecule reacts with, on average, one reactive site on every 3.4 carbon atoms in the initial ozonation stage.

At the point where the oxidation level of the humic substances is $0.15 \text{ molO}_3/\text{molDOC}$ the ozone mass transfer still significantly depends on the liquid flow rate (Figure 5). It can not be determined with certainty whether the reaction is instantaneous or fast with respect to the diffusive mass transfer. Despite this fact the ozonation reaction is treated as though it was an instantaneous reaction for the calculation of the diffusion coefficient and the stoichiometric constant, ν_C . At this level of oxidation hardly any DOC loss was found. So the initial DOC concentration was used for the calculations. The ozone mass transfer was again measured at different HS concentrations.



a



b

Figure 6: Enhancement factor for ozone mass transfer as function of (a) the reciprocal ozone liquid interface concentration. $c_{HS} = 33 \text{ molDOC/m}^3$ (b) the HS concentration. $c_{O_3,G} = 0.31 \text{ mol/m}^3$.

In Figure 7 the enhancement factor E_{O_3} is plotted against the HS concentration of the reaction solution. The enhancement factor is a linear function of the HS concentration in the solution, an indication that the reaction is still instantaneous compared to diffusive mass transfer. When the reaction would have been fast the dependence

should be linear with the square root of the HS concentration (see Table 1).

Table 3: Overall HS diffusion coefficient in water and stoichiometric constant of the ozonation reaction. Calculated according to the penetration model from the experimental results shown in Figure 5 and 7.

Total specific ozone consumption (molO₃/molDOC)	0	0.15
D _{HS,L,overall} (m ² /s)	6.1·10 ⁻¹¹	3.3·10 ⁻¹⁰
ν _C	3.4	1.3·10 ²

From the intercepts and slopes of the linear fits again the HS diffusion coefficient and stoichiometric constant, ν_C were calculated. The results are presented in Table 3. The diffusion coefficient was calculated to be 3.3·10⁻¹⁰ m²/s, a factor of 5 higher than calculated for the initial ozonation in Section 4.3. Still, also this value falls within the range of values for diffusion coefficients of humic substances that is found in literature. The calculated stoichiometric constant, ν_C has increased to a value of 1.3·10². Now, apparently one ozone molecule interacts with, on average, one reactive site on 1.3·10² carbon atoms.

The increase of calculated diffusion coefficient may be caused by a decrease in size of the HS molecules as they are broken down by ozonation. In Chapter V a clearly decreasing size of the HS molecules was measured as a result of ozonation. Other effects however also may take place that affect the diffusion coefficient of the HS molecules. Creation of new functional groups on molecules as a result of the reactions may change the molecular interaction with the aqueous environment and may influence the configuration of the molecules and with that the diffusion coefficient. Another effect that has to be taken into account is the changing water conditions during ozonation: a lower pH and a possible higher ionic strength due to formation of carboxylic acids might cause a change in the configuration of the (ozonated) HS molecules.

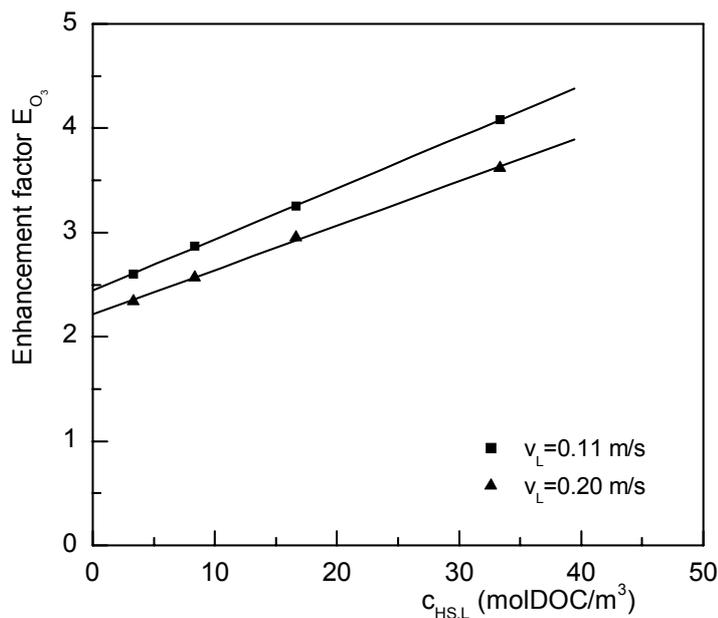


Figure 7: Enhancement factor of ozone mass transfer as function of the HS concentration in the reaction solution. The ozone consumption due to the reaction is at this point 0.15 molO₃/molDOC. $c_{O_3,G} = 0.34$ mol/m³

The stoichiometric constant ν_C is involved with the HS concentration expressed in molDOC/m³. ν_{HS} is the stoichiometric constant when the HS concentration is expressed in molHS/m³. The relation between the two stoichiometric constants is $\nu_C = \chi \cdot \nu_{HS}$, where χ is the number of carbon atoms in a HS molecule. Considering the size of an average HS molecule the number of carbon atoms can be considerable. The carbon weight content of an average HS molecule is approximately 50% (Chapter I, Section 1.4.1). A HS molecule with a weight of $2.5 \cdot 10^3$ Dalton (Chapter V, Section 3.3) then contains approximately 100 carbon atoms. During the initial reactions ν_C was calculated to be 3.4. ν_{HS} would then be 0.034: one HS molecule would react with around 30 ozone molecules. At an ozone consumption of 0.15 molO₃/molDOC the average M_w of a HS molecule is $2.3 \cdot 10^3$ Dalton. Assuming the same carbon content one ozone molecule would now react with 1.5 HS molecule.

4.6 Industrial application

In the experimental cases in this research the ozone concentration in the gas feed is relatively low: 0.36 mol/m^3 and also the HS concentration is far below the concentration that can be achieved with ion-exchange adsorption: 400 mgDOC/l (33 molDOC/m^3). With industrial ozone generators concentrations of 15 mol\% (7 mol/m^3) can be obtained, depending on the process conditions and using oxygen as feed gas [26, 27]. HS concentrations may reach up to 30 gDOC/l ($2.5 \cdot 10^3 \text{ molDOC/m}^3$) in the concentrated solutions. Furthermore the NaCl concentration will be much higher when treating humic substances concentrated by ion-exchange adsorption. As discussed in Appendix A the salt concentration has little influence on the reactions but will have a major influence on the ozone mass transfer since the solubility of ozone in water decreases with increasing ionic strength (Chapter II, Section 2.4). The reaction kinetics therefore may not be completely comparable, but the above described situation gives a good idea of what can be expected.

5 Conclusions and outlook

The ozone membrane contactor is suitable for the ozonation of humic substances (HS) solutions. During ozonation of a 33 molDOC/m^3 HS solution the ozone mass transfer decreases while the HS content of the solution hardly decreases.

The initial ozonation reaction can be considered instantaneous compared to the diffusive ozone transport. During the ozonation the reaction seems to shift from an instantaneous to a fast reaction. At the point where the reaction has consumed $0.15 \text{ molO}_3/\text{molDOC}$ the reaction still seems instantaneous considering the linear dependence of the enhancement factor on the HS concentration. The ozone flux is however less dependent on the liquid flow rate than during the initial ozonation reactions.

It will be difficult to measure the reaction rate constant at the initial ozonation stage. A low HS concentration and a high ozone concentration in a batch reactor might be sufficient; however the most reactive sites are probably relatively few and might have reacted before an adequate measurement could have been made.

The HS diffusion coefficient is calculated to be $6.1 \cdot 10^{-11} \text{ m}^2/\text{s}$ during the initial ozonation reactions and seems to increase during

the ozonation process to $3.3 \cdot 10^{-10} \text{ m}^2/\text{s}$ at an ozone consumption of $0.15 \text{ molO}_3/\text{molDOC}$. It is not justified to attribute this only to a decreasing average size of the HS molecules. Although it is shown in Chapter V that the average molecular weight of the humic substances indeed decreases during the ozonation process, other circumstances, such as changing water conditions during ozonation may result in a different configuration of the HS molecules and result in a size change in the solution not caused by degradation alone.

Also the stoichiometric constant seems to increase during ozonation which indicates that fewer reactive sites per amount of C atoms are involved in the reaction as the ozonation process continues.

6 Nomenclature

Symbols

a	contact area	(m^2)	
Al	Hintenland ratio $\left(= \frac{\text{total liquid volume}}{\text{liquid film volume}} \right)$	(-)	
c	concentration	mol/m^3	
D	diffusion coefficient	(m^2/s)	
dm	diameter	(m)	
E	enhancement factor	(-)	
E_∞	maximum enhancement factor		
e	extinction coefficient	($\text{l}/\text{mol}/\text{cm}$)	
J_A	molar flux	($\text{mol}/\text{s}/\text{m}^2$)	
K_H	Henry's law constant	($\text{kPa} \cdot \text{l}/\text{mol}$)	
K_{ov}	overall mass transfer resistance	(m/s)	
k	mass transfer coefficient	(m/s)	
$k_{1,1}$	second order reaction rate constant	($\text{l}/\text{mol}/\text{s}$)	
m	amount (mol) or mass	(mg)	
n	power factor, 1/2 for the fim model, 1/3 for the penetration model		
p	partial pressure	(Pa)	
r	radius	(m)	
s	dimensionless partitioning coefficient	(-)	
V	volume	(m^3)	
v	superficial velocity	(m/s)	
x	mole fraction	(-)	
Z	fiber length	(m)	
ω	oxidation ($\text{molO}_3/\text{molDOC}$)		level

δ	film thickness	(m)
$\delta_{\text{penetration}}$	penetration depth	(m)
ε	porosity	(-)
η	dynamic viscosity	(N·s/m ²)
ν	kinematic viscosity	(m ² /s)
τ	contact time	(s)
τ_m	membrane tortuosity	(-)
ν	stoichiometric constant	(-)
χ	number of C atoms in a HS molecule	(-)

indices

A, B	compound indication
i	near interface
in, out	inside, outside
G, L, M	gas, liquid, membrane phase
m	membrane
p	pore

Dimensionless numbers

Gz_L	Graetz $((d_{m,in}/Z)Re_L Sc_L)$
Ha	Hatta number for (1,1)-reaction $(\sqrt{k_{1,1}c_{B,L}D_{A,L}/k_L^2})$
Re_L	Reynolds $(\rho_L v_L d_{m,in}/\eta_L)$
Sc_L	Schmidt $(v_L/D_{A,L})$
Sh	Sherwood $(k_L d_{m,in}/D_{A,L})$

Abbreviations

DOC	Dissolved Organic Carbon
HS	Humic substances
PVDF	Polyvinylidenedifluoride

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Appendix A

Influence of sodium chloride on the ozone mass transfer during the ozonation of humic substances

The concentrated humic substances (HS) are collected by an ion-exchange adsorption process. The HS concentrate is obtained by regeneration of the resin with a NaCl solution. Consequently the concentrate (DOC=20 g/l) contains a substantial amount of NaCl. For experimental use this amount was kept below 1 M. The solution with the highest HS concentration contained approximately 1 g/l which implies a dilution factor of 20 with respect to the concentrate. All other HS solutions that were used were obtained from the concentrate by a higher dilution factor. The NaCl concentration in these solutions is therefore at the highest 0.05 M.

Hoigne et al [28] found that the apparent rate constant of chloride ions and ozone was only $0.003 \text{ M}^{-1}\text{s}^{-1}$ (23 °C) above pH 2. They state that this value must be considered as an upper limit since trace impurities present in the chloride reagents could have interfered. From this it can be assumed that chloride does not affect the ozone mass transfer through reaction during the ozonation process of the humic substances. However, the NaCl concentration can have a strong effect on the solubility of ozone in water (see Section 2.8 in Chapter II). As expressed in Equation 3 in Chapter II: the higher the ionic strength in the solution the lower the solubility of ozone. As a consequence the driving force for mass transfer is decreasing, thus affecting the transport of ozone from the gas to the liquid phase. Table 4 summarizes a few solubility ratios calculated with Equation (3) in Chapter II. The solubility of ozone in water is seriously affected when the ionic strength of a solution is higher than 0.1 mol/l.

Table 4: Henry's law constant K_H and the dimensionless distribution coefficient s of ozone in an air/water system. The values were calculated with Equation (3) in Chapter II. $T=294\text{ K}$

Ionic strength, μ (mol/l)	$K_{H_{O_3}}$ (kPa l/mol)	s_{O_3} (-)
0	8063	3.30
0.01	8089	3.31
0.1	8325	3.41
1	11092	4.54

To investigate the effect of NaCl on the mass transfer during the ozonation of humic substances three HS solutions with $DOC=33\text{ mol/m}^3$ were prepared. The dilution factor of these solutions is 50 with respect to the concentrate. So, the NaCl concentrate is at the highest 0.02 M ($\mu=0.02\text{ mol/l}$). To two of the solutions NaCl was added with concentration of 0.1 M and 1 M respectively. According to the experimental conditions in Section 3.4 mass transfer experiments were performed on these three solutions. The results of these experiments (Figure 8) show that the mass transfer is decreasing as a function of the NaCl concentration. There is no clear effect of the NaCl concentration on the overall mass transfer coefficient of ozone during the reaction. On these observations it is assumed that the NaCl concentration has a negative effect on the mass transfer but not on the reaction of ozone with humic substances.

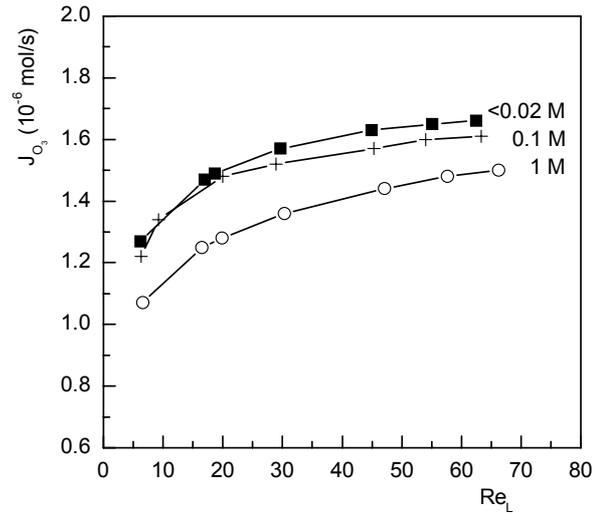
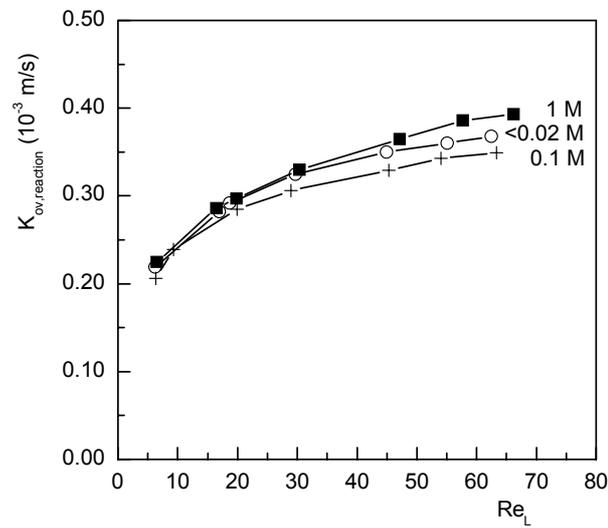
**a****b**

Figure 8: Ozone mass transfer J_{O_3} (a) and the ozone mass transfer coefficient $K_{ov,reaction}$ (b) plotted against the Reynolds number of the liquid (Re_L) during ozonation of a HS solutions ($c_{HS}=33\text{ molDOC/m}^3$) containing <math><0.02\text{ M}</math>, 0.1 M and 1 M NaCl respectively.

V

Ozonation of Humic Substances: Ozonation Products

This chapter handles the change of the molecular size distribution of humic substances (HS) during ozonation as well as the characterization and identification of some small ozonation products. The molecular size distribution was followed by gel permeation chromatography (GPC). Characterization and identification of small ozonation products was performed by membrane filtration and high performance liquid chromatography (HPLC). The weight average molecular weight of the humic substances was estimated to be between $2.5 \cdot 10^3$ and $2.9 \cdot 10^3$ Dalton with a polydispersity of approximately 1.15. Measurements on molecular size distribution and ozonation products identification indicate that during the ozonation process the size of the HS molecules decreases slowly and only small highly oxidated compounds are being split of the larger molecules. This suggests that HS molecules consist of a relatively stable backbone network structure and that the HS molecule degrade according to an outside-in trimming mechanism. The larger part of the DOC loss during ozonation can be attributed to the formation of carbon dioxide that leaves the solution.

1 Introduction

The ozonation of humic substances is a subject of major interest in drinking water treatment. In some cases ozonation is followed by biodegradation to prevent biofouling of the process systems [1-6]. However, the ozonation/biofiltration process may be a possible way to accomplish total removal of humic substances. The low biodegradability of humic substances is generally explained by the size and complex composition of the humic molecules. The goal of ozonation is the degradation of humic substances into smaller and less complex compounds that are biodegradable [5, 6]. The biodegradability of ozonated humic substances depends on the products that have been formed after ozonation. In this, the effect of ozonation on the biodegradability can be different for humic substances for different origin [4, 7, 8]. The enhanced biodegradability lies in the conversion of the large complex molecular structures into smaller less complex molecules. It is therefore of interest to investigate the change in molecular size distribution of the compounds in the solution during the ozonation process. Even more interesting is the identification of products of ozonation of humic substances.

1.1 Reactions of ozone with organic compounds in water

Typical humic substance molecules can have sizes that range from 10^3 to 10^5 Dalton [9, 10]. For aquatic humic substances molecular weights of 10^3 to 10^4 Dalton are common [11]. The carbon structure may consist of aliphatic chains, (poly-) aromatic groups, furanic groups (see Chapter I, section 1.4). These contain various organic functional groups. Ester and ether bonds may be found throughout the structure as well as carboxyl, ketone, aldehyde and alcohol groups. Through this variety in humic structures it is evident that the products of oxidation also show a wide variety in size and structure. One can make some estimation on ozonation products with the help of the information that is gathered over the years of reactions of known organic compounds and functional groups with ozone. In a review article Von Gunten [12] discusses the possible products from the ozonation of drinking water for both the direct and

indirect ozonation reaction. The discussion reflects on organic compounds and several functional groups that can be found in drinking water. Generally ozonation products can contain functional groups like alcoholic, carbonyl and carboxyl groups. Also esters can be formed in the ozonation process. Splitting of bonds yields smaller compounds and complete oxidation yields water and carbon dioxide.

1.2 Ozonation products

Ozonating the coloured humic substances results in decoloration and a certain DOC loss that depends on the amount of ozone that has been utilized. Characterization of reaction products from ozonation of humic substances show the formation of low molecular weight compounds consisting of aldehydes, ketones, ketoacids and carboxylic acids [13-16]. Some specific compounds that were identified are pyruvic acid, glyoxylic acid, mesoxalic acid, propanal, glyoxal, methylglyoxal and acetaldehyde [2, 13].

1.3 Gel permeation chromatography

Gel permeation chromatography (GPC) is a useful technique to follow the molecular size distribution. The separation is based on size exclusion and preferably as little as possible on affinity with the stationary phase. However, one can never avoid any chemical interaction with either phase. GPC has been practised on humic substances in several studies [17-20].

Two main problems exist in the determination of the molecular size distribution of humic substances. The first is lack of reference compounds. There are no reference compounds available with a known molecular weight that can act as model compounds for humic substances concerning the chemical interactions [11]. Instead, calibration of the GPC column is usually done by polymer standards. By choosing a number of different compounds as reference a good estimation of the separation curve may be possible. The second problem is the effect of the water conditions on the shape of the molecules. Ionic strength and pH can affect the configuration of the molecules severely (see also Chapter I, section 1.4). The result is that the molecular size distribution is never an absolute value but merely an apparent molecular size distribution [17]. Despite these problems GPC may be used to follow at least qualitatively the

(apparent) molecular size distribution of humic substances during a treatment.

1.4 Research strategy

The research was focussed on the investigation of the products that result from ozonation of humic substances. With GPC and fractionation by membrane filtration the molecular size (distribution) of the humic substances and ozonation products during the ozonation process was studied.

HPLC analysis was used to identify some of the small ozonation products.

From the results of the molecular size measurements, product identification and measurements of some water quality parameters like DOC, colour and COD, a mechanism was suggested for the degradation of humic substances by ozonation.

2 Materials, Methods and Experiments

2.1 HS collection

The humic substances were obtained from tap water from pumping station Spannenburg (The Netherlands). The HS molecules were concentrated by an anion exchange adsorption process, where Purolite A806S was used as ion exchange resin on which the HS molecules adsorb. According to the manufacturers prescription the column was regenerated by a 10% NaCl solution in water. The HS concentration obtained in the regenerate reached up to 30 gDOC/l. The concentrated HS solution was diluted to a solution with 20 gDOC/l to form the stock solution. The NaCl concentration in the stock solution was kept below 1 M. According to Hoigne et al [21] chloride ions do not react significantly with ozone and it is assumed that chloride ions do not take part in the reactions. HS solutions for the experiments were prepared out of the stock solution. The amount HS in the experimental solution was 3.3 molDOC/m³ (40 mgDOC/l). In these dilutions the NaCl concentration in the HS solutions is 0.002 M. At these low concentrations the ionic strength of the reaction solutions is considered to have no significant effect on the ozone solubility in water.

2.2 Experimental setup

The ozonation experiments were performed in a setup as presented in Figure 1. A membrane module with hollow fibre membranes was used as gas-liquid contactor for the ozonation experiments. The module is constructed with PVDF capillary membranes in a glass housing. The membranes were supplied by EMI University of Twente, The Netherlands. For detailed information on the membrane module is referred to Chapter 3, Section 3.1.

Air was led through an ozone generator (Ozone Generator Peripheral Com, Anseros Klaus Nonnenbacher GmbH). The ozone enriched air flowed into the contactor module on the shell side of the membranes. The ozone concentration both in the gas feed and outlet was measured spectrophotometrically at a wavelength (λ) of 253 nm with a Pharmacia LKB Ultrospec Plus double beam spectrophotometer. The concentration was calculated according to $A = c \cdot e \cdot d_c$. The extinction coefficient (e) for ozone, was taken as $3000 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$.

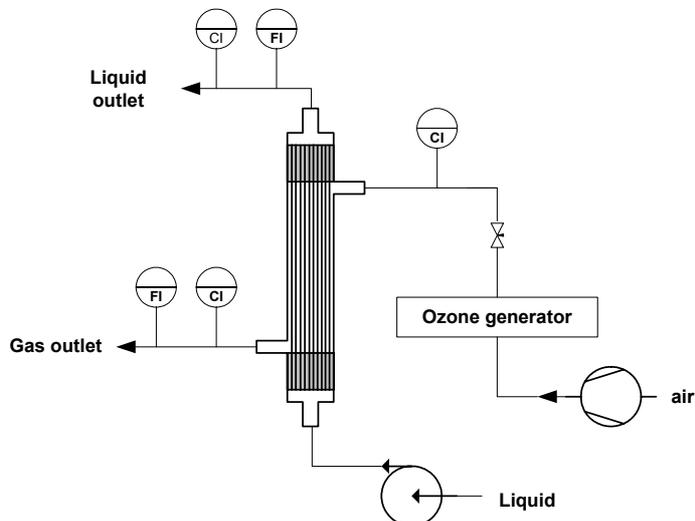


Figure 1: Experimental setup for the ozonation of humic substances in a membrane contactor.

During the experiments the applied ozone concentration was approximately 0.38 mol/m^3 at a flow of 20 l/h . The liquid flow was approximately 1 l/h . The mass transfer processes were performed counter-currently with the liquid flowing through the fibres. The

ozone consumption was calculated from the difference in ozone concentration between the gas feed and the gas outlet. The benefit of using a membrane contactor in this process is that the operating conditions can be controlled easily. The phases can flow through the reactor independent of each other and the gas/liquid adsorption process can be operated stationary so that the chosen experimental conditions remain constant throughout the experiments. This is essential for measuring the ozone consumption during the oxidation process accurately.

2.3 HS characterization

The HS solutions were characterized by DOC (molDOC/m³ or mgDOC/l), by GPC analysis and HPLC analysis. The DOC was measured on a Shimadzu TOC-V CPH Total organic carbon analyzer. The GPC analysis was performed on a Metrohm HPLC 761 compac IC setup with a PSS MCX-1000Å GPC column. A Bisschoff Lambda 1010 was used as UV-VIS detector. The eluents consisted of an aqueous solution of 0.1 M Na₃PO₄ running at 1 ml/min. The organic acids were also measured on a Metrohm HPLC 761 compac IC setup with a Metrosep Organic acids 6.1005.200 column, a suppressor with 50 mM LiCl and a Metrohm 1006 conductivity detector. The eluents was 0.5 mM H₂SO₄ running at 0.7 ml/min.

2.4 GPC and HPLC calibration

Several organic compounds were used as reference standard and for calibration of the GPC system. These compounds were several types of polymers with different molecular weights. Further, low molecular weight acidic and non-acidic organic compounds were used, summarized in Table 1. Also for reference purposes, several small ketones and carboxylic (keto-) acids were analyzed on the HPLC IC column.

Table 1: Compounds for calibration of the GPC column and HPLC column.

Polymers (# of standards)	Non-acidic compounds		Acidic compounds	
Dextrans (2)	Ethanol	Lactose	Formic acid	Oxalic acid
Pullulans (4)	Ethylene glycol	Acetaldehyde	Acetic acid	Adipic acid
PEG (8)	Glycerol	Propion-aldehyde	Malic acid	Ascorbic acid
PSS (2)	Glucose	Glyoxal	Mesoxalic acid	Citric acid
	Sucrose	Methyl glyoxal	Glyoxalic acid	Gluconic acid
	Hydrogen peroxide		Pyruvic acid	Salicylic acid

2.5 Detection wavelength of the UV-vis detector for GPC

In research for water treatment usually the UV absorption is measured at a wavelength of 253.7 nm (254 nm rounded off). It is also often used as a measure for the DOC or COD value of the solution using a certain conversion factor typical for that water. It is known that olefinic bonds, common in compounds found in natural waters and waste waters, have an absorption band at 254 nm. During ozonation exactly these double bonds are very likely to be converted. This means that detection at 254 nm only has sense when one wants to have a measure for the conversion of double bonds to other bonds. Compounds that do not contain olefinic bonds have little absorption at 254 nm. Preliminary experiments show that HS solutions before and after ozonation show absorption on a broad spectrum ranging from 200 nm to over 300 nm (Figure 2). However, during the ozonation process products are formed that have an absorption over a smaller spectrum ranging from 200 nm to 240 nm. It appears that all observed peaks during the analyses of humic substances and

ozonated humic substance solutions have their maximum at a wavelength of 223 nm (Figure 2). For that reason this wavelength was chosen for detection in the GPC analysis procedure.

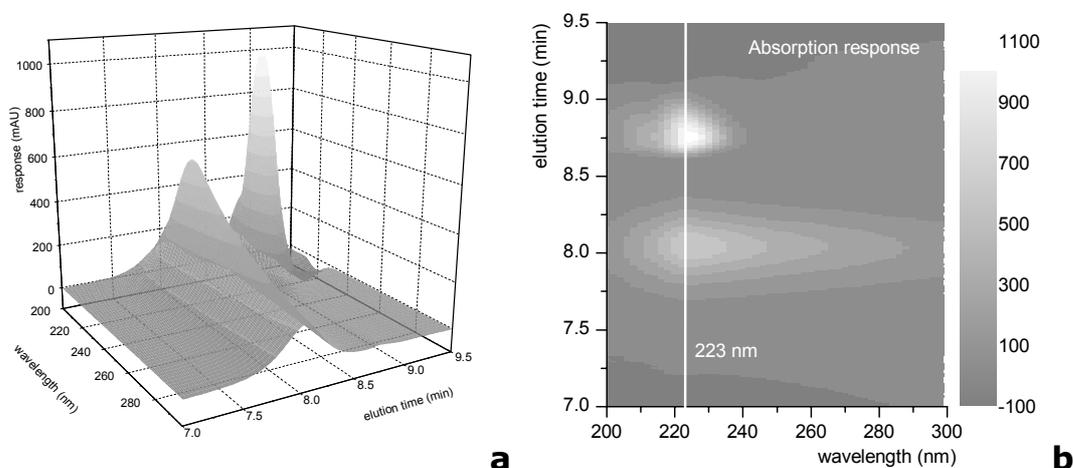


Figure 2: a. Typical 3D chromatogram resulting from GPC analysis of an ozonated HS solution where the UV-vis detector was set to scan at a range between the wavelengths of 200 and 300 nm. b. Chromatographic map of the response against the elution time and the detection wavelength. The maxima of the peaks are measured at 223 nm.

O'Loughlin and Chin [22] showed that the detector wavelength is of influence on the calculation of the molecular weight of the humic substances. They measured at wavelengths in the range of 220 to 380 nm and found some clear variations in the calculated molecular weights. For humic substances from three different water sources the number average molecular weight M_n , showed a larger variety than the weight average molecular weight M_w at different wavelengths. The variety in molecular weights was less pronounced in the range 220 to 280 nm for both M_n (2.3-13.8%) and M_w (-2.0-6.5%). For the analyses in this research the molecular weights are calculated with the absorptive response at a wavelength of 223 nm.

2.6 Molecular weight distribution

With the help of the non-acidic reference compounds a calibration curve of the molecular weight against the elution time was calculated with a logarithmic fit. This curve was used to determine the molecular weight M_i at i -th time fraction, at an eluted volume i of the sample. The number average molecular weight M_n and the weight

average molecular weight M_w , were determined with equations (1) and (2) respectively. r_i is the detector response at elution volume i .

$$M_n = \frac{\sum_{i=1}^N r_i}{\sum_{i=1}^N r_i / M_i} \quad (1)$$

$$M_w = \frac{\sum_{i=1}^N r_i \cdot M_i}{\sum_{i=1}^N r_i} \quad (2)$$

The polydispersity D is calculated as the ratio between M_n and M_w : $D = M_w / M_n$.

For these calculations it is assumed that the specific light absorption is independent of the molecular size of the humic molecules: the amount of light absorbing groups is equal per molecular weight unit for every humic molecule.

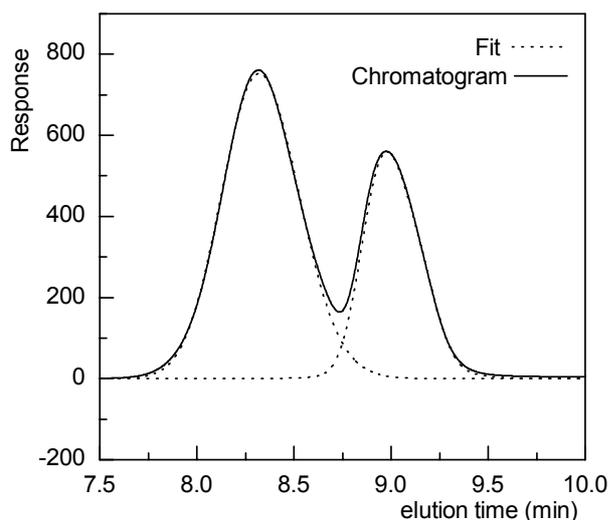


Figure 3: Example of a gel permeation chromatogram of an ozonated HS solution and its fit made by an Edgeworth-Cramer Peak Function.

The peaks that are observed may be overlapping. To calculate the molecular weight distribution for each peak they are fit by an Edgeworth-Cramer Peak Function to deconvolute them. The molecular weight distributions are then calculated with the separate fit functions. An example is shown in Figure 3. It is important to analyse the molecular weight distribution generated for symmetrical and unsymmetrical (skewing) band broadening that may result in

non-negligible errors in the calculated average molecular weights. A procedure to correct for these possible errors is calculating the symmetrical and unsymmetrical broadening factors and correct the calculated molecular weights with these parameters [23]. The symmetrical broadening factor Λ is calculated according to

$$\Lambda = 1/2 \left(\frac{M_n(t)}{M_n(u)} + \frac{M_w(u)}{M_w(t)} \right) \quad (3)$$

t and u refer to the true and uncorrected moments. The skewing or unsymmetrical factor, sk is calculated as

$$sk = \frac{\Phi - 1}{\Phi + 1} \quad (4)$$

where

$$\Phi = \frac{M_n(t) \cdot M_w(t)}{M_n(u) \cdot M_w(u)} \quad (5)$$

Under ideal conditions $\Lambda=1$ and $sk=0$ and no corrections are necessary, however practically this is never the case. If these values are 1.05 and 0.05 or less respectively then the resulting corrections are small. If they are larger, the samples distribution moments may be corrected according to

$$M_n(t) = M_n(u)(1 + sk)\Lambda \quad (6)$$

$$M_w(t) = \frac{M_w(u)}{(1 - sk)\Lambda} \quad (7)$$

The correction factor f_D for the dispersity would then be

$$f_D = ((1 - sk)(1 + sk)\Lambda^2)^{-1} \quad (8)$$

A major restriction however is the fact that peak broadening is very dependent on the type of reference that is used. Different kinds of compounds give diverse results on peak broadening and skewing. Again also here a number of reference compounds may give an idea of the "general" deviations in the peaks.

As a reference to measure peak broadening caused by the GPC system a citric acid sample ($M_w=192.2$ Dalton), a lactose sample ($M_w=338$ Dalton) and two polystyrenesulfonate samples (Polymer Standard Service, Germany. $M_w=1360$ and 2220) were run through the system. Citric acid and lactose are pure compounds, hence their number average molecular weight is equal to the weight average molecular weight: $M_n = M_w$. The molecular weight of lactose is situated exactly on the calibration line (see Figure 4) according to its elution time. However citric acid and the PSS samples tend to shift towards lower elution times than expected on account of their molecular weight. For citric acid the molecular weight according to the calibration line at the peak maximum (M_p) was used to represent $M_w(t)$ and $M_n(t)$. Almost the same procedure was followed for the PSS standards with the difference that $M_w(t)$ and $M_n(t)$ were calculated from M_p by the ratios in Table 2.

Table 2: Molecular weight characteristics of the polystyrene sulfonate standards given by the supplier (Polymer Standards Service, Germany).

Type	M_p	M_n/M_p	M_w/M_p
PSS 8072	1260	0.99	1.08
PSS 1048	2290	0.94	0.97

Tests for measuring the peak broadening and skewing with lactose, citric acid and PSS showed a fairly constant symmetrical peak broadening factor (Λ) of around 1.04. The skewing factor sk varies with each reference compound from 0.011 (PSS 1048) to 0.13 (PSS 8072) (Table 3). According to these factors the calculated average molecular weights of the humic substance should be corrected by a factor of 0.98 to 1.1 for M_w and by a factor of 1.05 to 1.17 for M_n .

Table 3: Symmetrical peak (Λ) and asymmetrical (skewing, sk) peak broadening factor calculated for the GPC system from reference samples citric acid and lactose.

		Λ	sk	$((1 - sk)\Lambda)^{-1} (1 + sk)\Lambda$		f_D
se	Lacto	1.0	0.0	0.99	1.0	0.9
		4	33	8	2	
acid	Citric	1.0	0.0	1.04	1.1	0.9
		3	69	1	5	
8072	PSS	1.0	0.1	1.1	1.1	0.9
		4	3	7	4	
1048	PSS	1.0	0.0	0.98	1.0	0.9
		4	11	5	3	

2.7 Experiments for sequential ozonation of a humic substance solution

A HS solution with a concentration of 3.3 molDOC/m³ (40 mgDOC/l) was subjected to sequential ozonation, which means that the solution was run through the ozonation module for several times. The liquid flow rate was 1.0 l/h (0.28 ml/s) and the gas flow rate was 14.9 l/h (4.14 ml/s) at an ozone concentration of 0.378 mol/m³.

To investigate the molecular size of the ozonation products a part of the ozonated HS solution was fractionated by nanofiltration after each run. The fractionation was performed in a stirred dead-end cell with a SpectraPor type C cellulose ester membrane with a MWCO of 500 Dalton (given by manufacturer). Solutions were filtered until half the feed volume had permeated. For reference purposes also a solution of glucose and sucrose was filtered by the membrane. The filtration test with lactose (Mw = 342.3 Dalton) showed that 93% of the lactose was retained. The same test with a glucose (Mw = 180) solution showed that 50% of the feed concentration was found in the permeate.

GPC and HPLC (IC) analysis was performed to characterize the samples or identify specific compounds. GPC was also used to monitor the performance of the ion-exchange process that is used to concentrate humic substances from the tap water. These results are discussed in Appendix A.

3 Results and discussion

3.1 Calibration line for the GPC system and peak alterations

GPC on the set of organic compounds presented in Table 1 yielded Figure 4. Non-ionic compounds show a clear trend where the elution time depends on the molecular size of the compounds. They show an elution time of around 6 minutes for compounds with a molecular weight of approximately 10^5 Dalton, around 8.7 minutes for compounds of approximately 10^3 Dalton and 9.5 minutes for compounds with a molecular weight of around 10^2 Dalton. For acidic low molecular weight compounds the situation is completely different. Compared to the non-acidic compounds the elution time is shorter: they all appear at elution times between 8.5 and 9.0 minutes. The elution time is more dependent on the number of acidic groups associated with these compounds than their molecular weight. For example formic acid (Mw = 46 Dalton), salicylic acid (Mw = 138 Dalton) and gluconic acid (Mw = 195 Dalton), all with a single carboxylic group, appear roughly at the same elution time (around 8.9 minutes). Hydrogen peroxide (Mw = 34 Dalton) has an elution time of around 9.9 minutes. Considering the molecular weight of hydrogen peroxide compared to the non-acidic organic compounds this elution time is relatively short. The results with the reference compounds show that the GPC results are strongly sensitive for the hydrophilicity of the compounds. Acidic groups associated with organic compounds highly contribute to shorter elution times.

The question remains however whether the reference samples are suitable to calculate the peak shifts caused by the system for humic substances. A non-ionic and ionic compounds have been used however all compounds are hydrophilic and do not contain large hydrophobic parts as may be expected for humic substances. On the other hand it may be expected that in the environment of the ionic

and high pH conditions of the eluent (0.1 M Na₃PO₄) the hydrophilic and ionic parts of the humic substances may be dominant in the behaviour of the molecules. In that case the peak shifts for humic substances may lie somewhere between the values calculated for the reference samples.

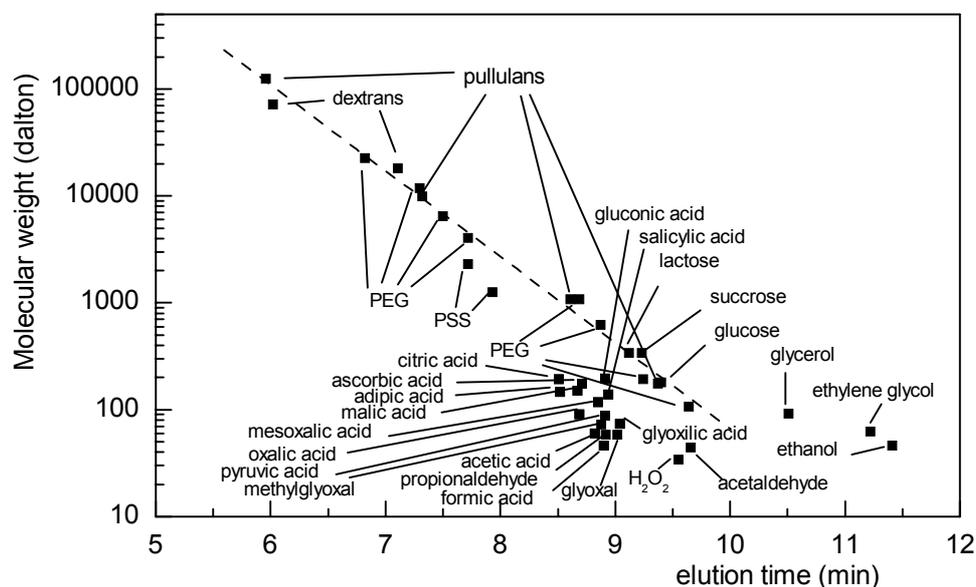


Figure 4: The molecular weight of several organic compounds (Table 1) plotted against the elution time of the Gel Permeation Chromatography setup (column: PSS MCX 1000Å). The data are based on the absorption peaks of the separate compounds. The solid line represents the logarithmic fit through the points associated with the non-acidic compounds.

3.2 Reference chromatogram HPLC

Figure 5 represents the reference chromatogram of the elution times of several acidic and non-acidic compounds that were run through the HPLC (IC) setup. Here, several compounds are presented with their specific elution times. This chromatogram is used to identify some of the products of ozonation of humic substances. Compounds like pyruvic acid, glyoxylic acid, mesoxalic acid, propanal, glyoxal, methylglyoxal and acetaldehyde were already identified as ozonation products in some studies on ozonation products from humic substances [13-16].

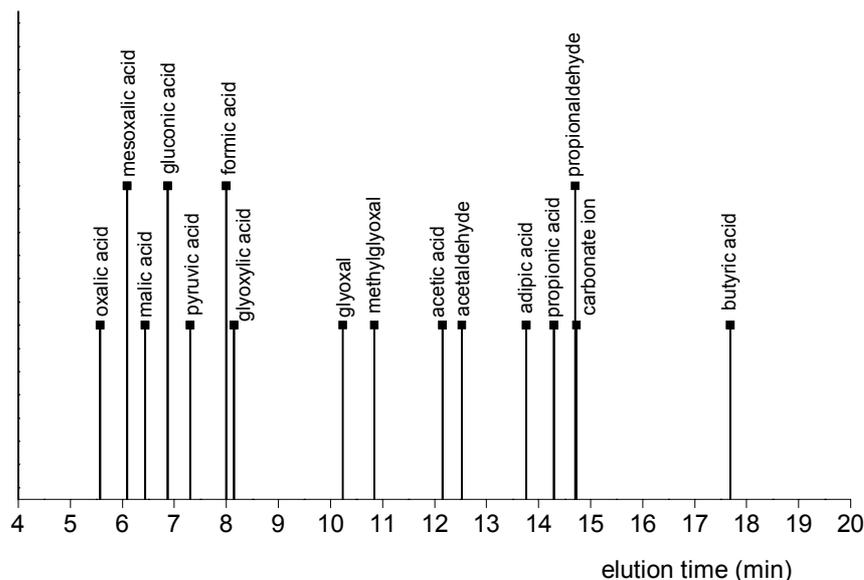


Figure 5: Reference chromatogram for the HPLC (organic acids) analysis representing several compounds and their specific elution times (column: Metrohm 761 compac IC)

3.3 GPC analysis of humic substances

Analysis of concentrated humic substances shows chromatograms that are in good proportion with each other regarding the DOC content of the samples (Figure 6). When referring to the calibration line in Figure 4 the molecular weight of the compounds in the samples seem to vary from approximately 10^4 to $0.5 \cdot 10^2$ Dalton. The weight average molecular weight M_w is calculated as $2.6 \cdot 10^3$ Dalton and the number average molecular weight M_n as $2.1 \cdot 10^3$ Dalton. With these figures the polydispersity is 1.23. These weight averages have not been corrected for the skewing and peak broadening caused by the GPC system. According to the findings in Section 3.1 the corrected molecular weights would be: $M_w = 2.5 \cdot 10^3 - 2.9 \cdot 10^3$ Dalton and $M_n = 2.2 \cdot 10^3 - 2.5 \cdot 10^3$ Dalton. The polydispersity would be between 1.15 and 1.16, which would imply that the molecular weight distribution of these humic substances is relatively narrow.

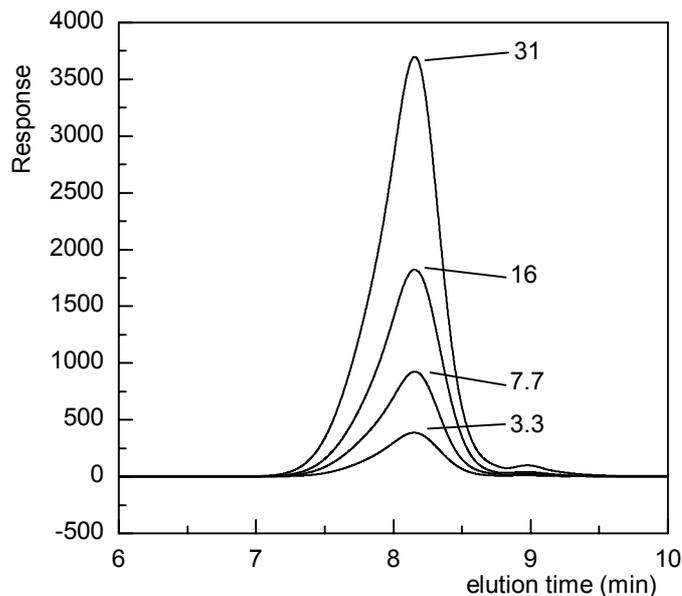


Figure 6: GP chromatogram of humic substances in several dilutions. According to the GPC calibration line (Figure 4) the molecular weight ranges from approximately $1 \cdot 10^4$ to $0.5 \cdot 10^2$ Dalton. The figures at the curves indicate the DOC content of the solutions in molDOC/m³.

3.4 DOC, colour and COD of a HS solution during ozonation

During the ozonation process a strong colour decrease of the reaction solution can be observed visually. This is also expressed in the specific colour (colour/DOC) of the solution, which decreases considerably during the ozonation process resulting in a low colour/DOC ratio (Figure 7). Meanwhile, the DOC content of the solution is lowering slowly. Apparently volatile compounds are leaving the reaction solution that may have been formed during the ozonation process. Together with the DOC the chemical oxygen demand (COD) of the solution is also slowly decreasing however the COD/DOC ratio is reducing as the solution undergoes the ozone treatment. This is an indication that the humic substances are being oxidized.

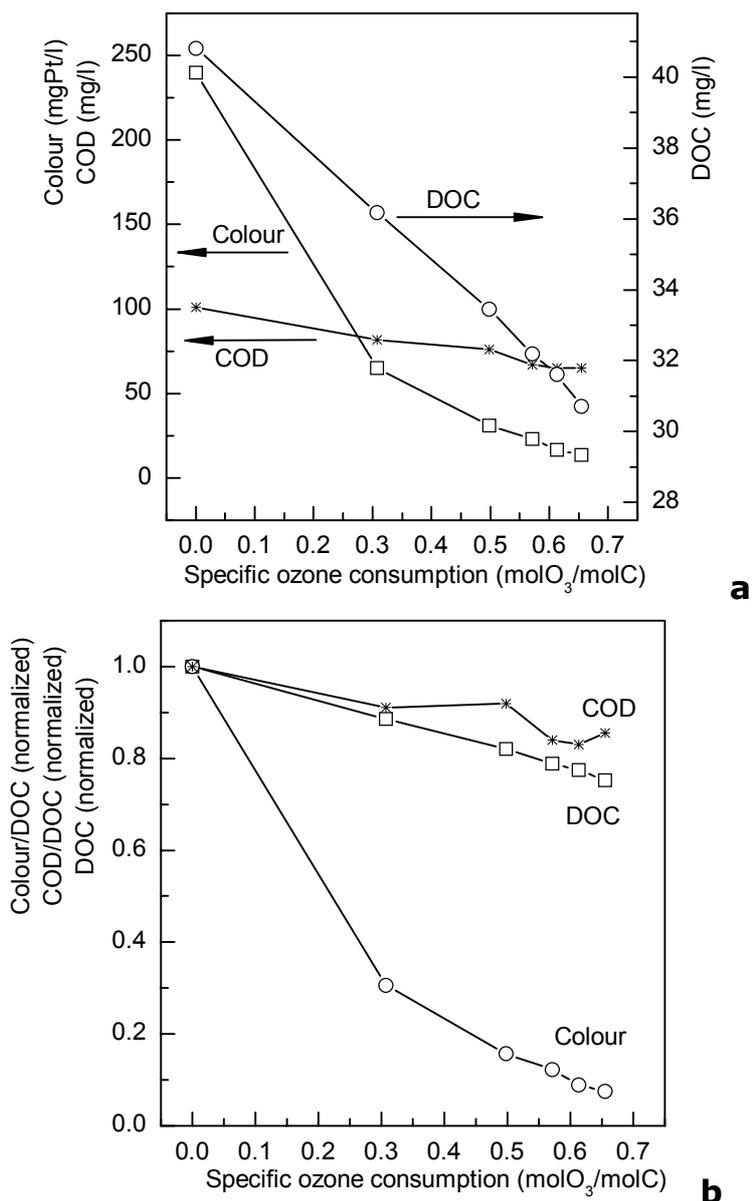


Figure 7: a. Course of the DOC content, colour and COD of a HS solution during sequential ozonation. b. Normalized DOC content, specific colour and COD of the HS solution during sequential ozonation. Initial HS concentration 40 mgDOC/l (3.3 molDOC/m³). The parameters are plotted against the specific ozone consumption. An ozone consumption of 0 molO₃/molDOC indicates an untreated HS solution.

The pH of the solution is dropping rapidly from 7.75 to 3.19 (Figure 8). This indicates the formation of acidic groups during the ozonation process. These groups could either be formed on the HS molecules or be part of (acidic) compounds that are split from HS molecules as a result of the oxidation.

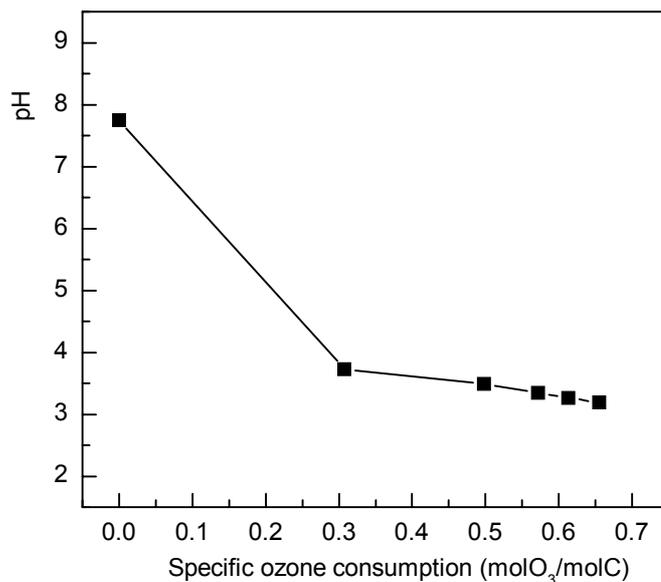


Figure 8: pH of a HS solution as function of the specific ozone consumption during sequential ozonation. HS concentration: 3.3 molDOC/m³.

3.5 GPC and HPLC analysis of HS during ozone oxidation. Course of the molecular size of large compounds.

During the ozonation of humic substances one might expect a wide range of ozonation products of different size and structure, because of the diversity of the humic substance content. Therefore it might be expected that the large peak around 8 minutes elution time becomes smaller in surface and is "smeared out" towards higher elution times, indicating the gradual formation of small compounds. Figure 9 presents the GPC results of samples taken during the sequential ozonation of a HS solution. The large peak around 8 minutes is clearly decreasing and a shift of the peak can be observed. After an ozone consumption of 0.65 molO₃/molC the weight average molecular weight M_w has appeared to shift from $2.6 \cdot 10^3$ to $1.5 \cdot 10^3$ Dalton (Figure 10). Remarkable is a decreasing apparent polydispersity during the ozonation process: from 1.23 to 1.09. The spreading in molecular weight of the larger molecules seems to become smaller during ozonation.

As the ozonation sequence goes on, another peak emerges around 9 minutes elution time indicating that small compounds are being formed during the ozonation process. The apparent M_w is calculated to be around $4.3 \cdot 10^2$ Dalton with a polydispersity D_p of 1.07. This low polydispersity indicates that products are being formed within a small range of size. However, since it is likely that these ozonation products contain acidic groups and considering the outcome of the GPC analysis of the organic compounds (Section 3.1) conclusions on molecular size of the small ozonation products should be made carefully.

It is remarkable to observe that the size of the ozonation products seems to be restricted as only two distinct peaks can be observed throughout the ozonation process. This observation applies to the whole wavelength range between 200 and 300 nm of the detector, which, as an example, can be seen in Figure 2. It indicates that during ozonation only small molecular fragments are split off from the large HS molecules and that the main structure is disintegrating slowly during ozonation. This may indicate that the HS molecules consist of relatively stable network structure instead of a chain structure.

The DOC content of the ozonated solutions decreases considerable as is shown in Figure 7. This indicates that compounds that may have been formed during the ozonation process leave the reaction solution. These could be volatile low molecular weight organic compounds among which carbon dioxide. Batch experiments where the carbon dioxide concentration was measured in the off gas of the reactor revealed that a substantial amount of carbon dioxide is formed during the ozonation process. This is reported in Appendix A. The amount of carbon dioxide that was measured appears to be comparable with the measured DOC loss. It is however not clear in what ratio the CO_2 is formed by further oxidation of small compounds that were already a product of oxidation of HS or by direct oxidation of the large HS molecules.

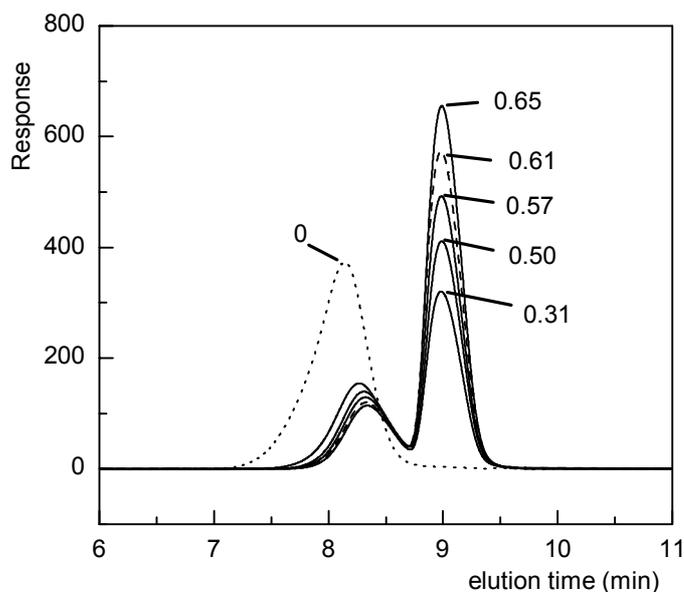


Figure 9: GP chromatogram of a humic substance solution after sequential ozonation in a membrane contactor. The solution is repeatedly sent through the membrane contactor. Initial HS concentration: 3.3 molDOC/m³ (40 mgDOC/l). The figures indicate the specific ozone consumption (molO₃/molDOC).

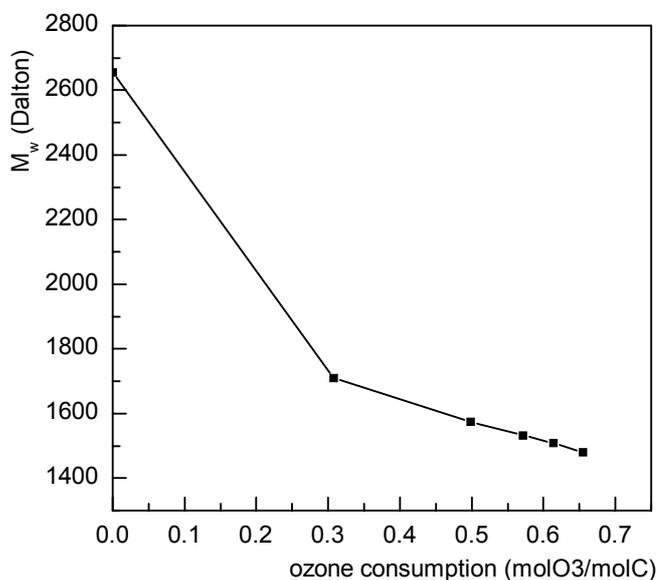


Figure 10: Course of the calculated average Mw (weight average molecular weight) of the large compounds of a HS solution (represented by the left peak in Figure 9) against the specific ozone consumption. HS concentration: 3.3 molDOC/m³ (40 mgDOC/l).

3.6 Molecular size characterization and identification of small ozonation products

Nanofiltration was used to fractionate the ozonated HS solutions to investigate the molecular size of the small ozonation products that are eluted around 9 minutes. With this fractionation the small compounds could be separated from the larger compounds. This was demonstrated by GPC analysis, illustrated in Figure 11.

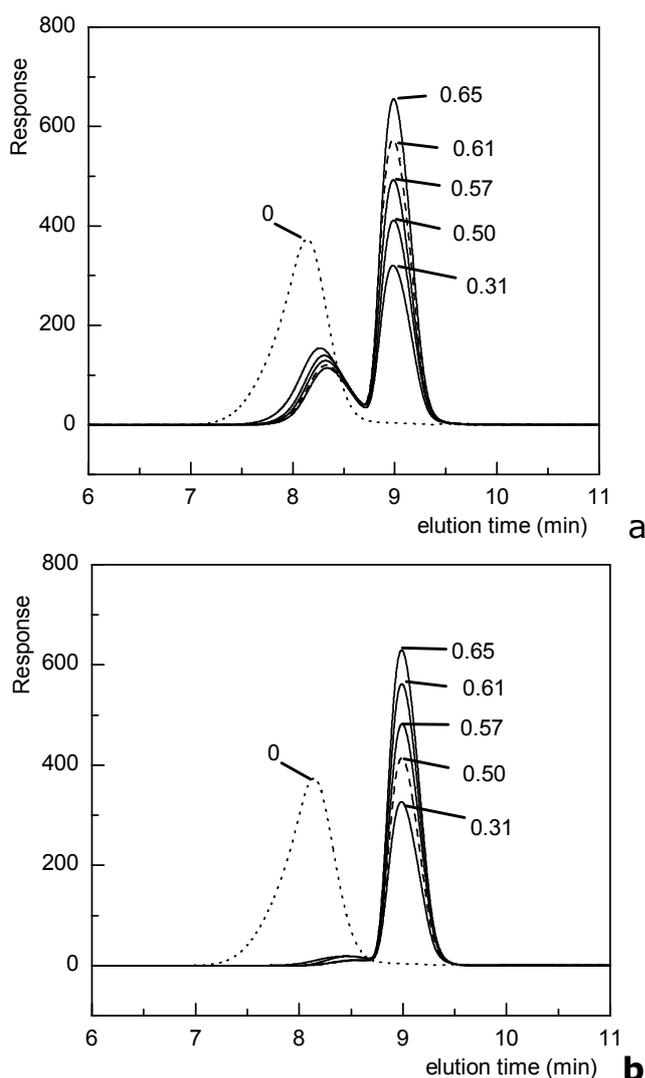


Figure 11: a. GP chromatograms of a HS solution (3.3 molDOC/m³) after ozonation as function of the specific ozone consumption (same as Figure 9). b. GP chromatograms of the permeate of the same samples after membrane fractionation by a NF membrane with MWCO 500 Dalton. The figures near the graphs indicate the specific ozone consumption (molO₃/molDOC)

The chromatogram of the permeate only shows a peak around 9.0 minutes indicating the presence of small compounds and the absence of larger compounds. The area of the peaks in the all permeate samples have the same size as the areas of the corresponding peaks in the unfractionated solutions. This indicates that all compounds associated with the peak at 9.0 minutes have permeated. Since the molecular weight cut off of the membrane appears to be approximately around the molecular weight of lactose (338 Dalton) it can be assumed that the compounds are much smaller in size than lactose. However, as also glucose was partly retained by the membrane it is plausible that the molecular sizes of these compounds are even smaller than that of glucose.

Figure 12 shows the result of HPLC (IC) analysis of samples that were subjected to sequential ozonation. It can be seen that peaks emerge during the ozonation process that can be associated with ozonation products. The size of these compounds is then still unknown. HPLC analysis on the fractionated samples of an ozonated HS solution showed that the same compounds were found in the permeate as in the unfractionated solution (Figure 13). Also this indicates that ozonation products are relatively small (<180 Dalton).

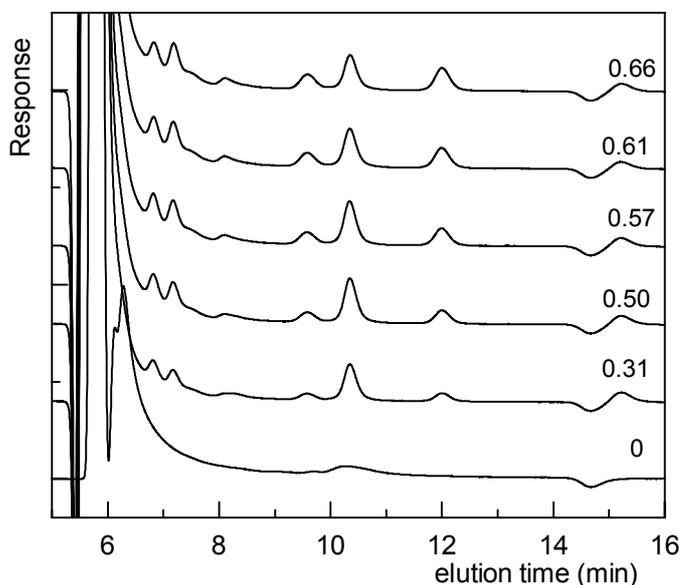


Figure 12: HPLC (organic acids) diagram of humic substances after sequential ozonation in a membrane contactor. Initial HS concentration: 3.3 molDOC/m^3 . The figures at the chromatograms indicate the specific ozone consumption in $\text{molO}_3/\text{molDOC}$ indicates an untreated sample.

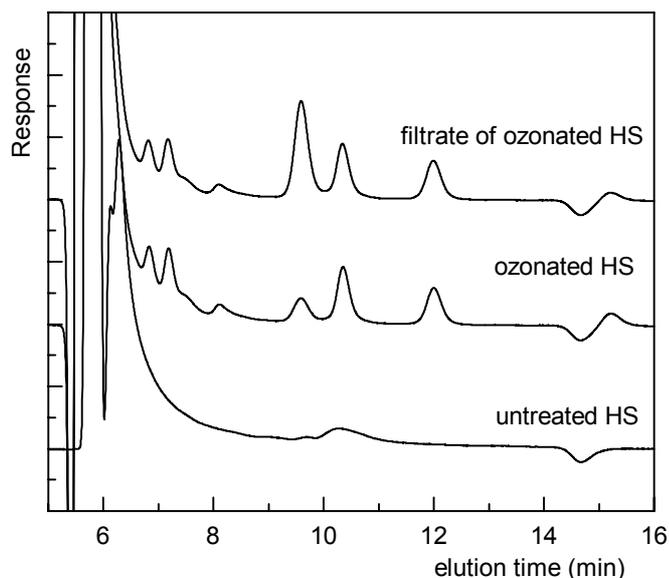


Figure 13: HPLC diagram of an ozonated HS solution (32 molDOC/m³) and the permeate of the same solution after membrane filtration (MWCO 500 Dalton).

With the help of the reference diagram (Figure 5) a number of peaks in HPLC diagram could be identified Figure 14. Mesoxalic acid, Pyruvic acid, methyl glyoxal and acetaldehyde could be identified by substantial peaks. Glyoxilic acid and formic acid were identified by less distinct peaks. The peak at 14.4 minutes was suspected to correspond with carbonate. This peak is found in most water samples and is due to dissolved carbon dioxide present in the water.

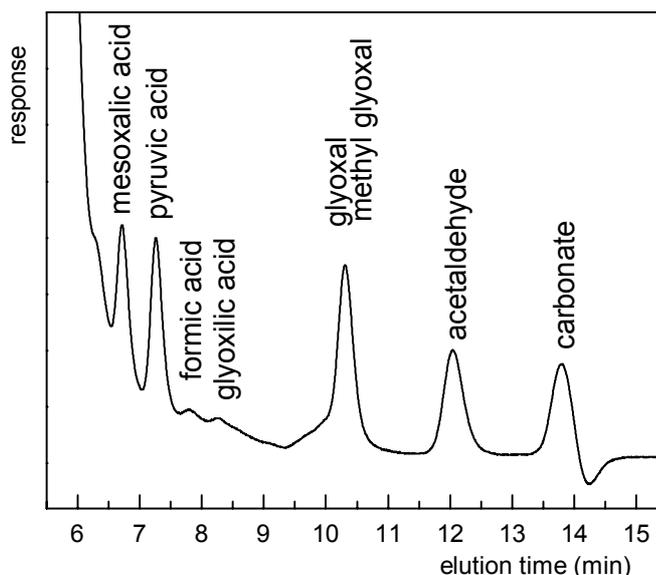


Figure 14: Identification of ozonation products of a HS solution (3.3 molDOC/m³) by HPLC. The ozone consumption was 0.61 molO₃/molDOC

The largest molecular size of these compounds is 88 Dalton (pyruvic acid). It is most likely that not all small compounds that result from ozonation have been identified. However, considering the membrane filtration tests it may be justified to assume that all small compounds have a molecular size smaller than 180 Dalton as stated previously. Regarding the course of the molecular weight and polydispersity of the large compounds during ozonation and the fact that size of the small ozonation compounds is assumed to be smaller than glucose ($M_w=180$) it appears that ozonation of humic substances yields products in two size regions: small compounds (<200 Dalton) and large compounds (> 1000 Dalton) residue from the original HS structure that became smaller only gradually. This indicates that there occurs no random splitting of HS molecules, because that would result in a very broad range of molecular sizes. Apparently only small molecules are split off from the large humic substances. A possibility is that the splitting of bonds occurs mainly on the periphery of the molecules. On first instance the thought might be that steric obstruction or the possibly coiled structure of the humic substance molecules prevents ozone (or the OH radical) from splitting bonds in the mid section of the molecules. However, considering the colour decrease during ozonation and assuming that the colour-causing sites are spread throughout a HS molecule indicates that the oxidation reactions occur generally all over the molecule. Another explanation is that the backbone structure branched throughout the HS molecules is relatively stable and keeps the molecular structure together even though some bonds are broken randomly in the molecule. Bonds on the periphery that are cut have a higher chance in being split off of a molecule from the HS structure.

4 Conclusions and outlook

The weight average molecular size of the humic substances M_w used in this study was estimated to be between $2.5 \cdot 10^3$ and $2.9 \cdot 10^3$ Dalton. Tests with reference compounds showed that M_w and M_n values should be corrected for peak broadening and skewing deviations. Lack of suitable reference compounds obstructs a reliable conclusion on the true molecular weight. However after any correction the polydispersity of the HS seems to be relatively low: approximately 1.15, which indicates a relatively narrow molecular size distribution.

The ozonation of humic substances follows such a mechanism that the molecular size decreases slowly and only relatively small ozonation products are being formed. The size of these small molecules appears to be smaller than at least 180 Dalton. The average apparent molecular size (M_w) of the HS molecules seems to decrease gradually from $2.6 \cdot 10^3$ to $1.6 \cdot 10^3$ Dalton instead of breaking up into big compounds with lower molecular weight. The polydispersity of the large compounds seemed to decrease from 1.23 to 1.09 during the ozonation process, which indicates that the spreading in molecular size of the large compounds becomes smaller as the ozonation process proceeds.

All this indicates that the HS molecules consist out of a relatively stable cross-linked network structure. Breaking of some bonds does not lead to a rapid disintegration of the molecule, but only to formation of relatively small molecules (with molecular weight <200 Dalton) that are split from the original HS molecules. This mechanism may be called "outside-in trimming mechanism". With the help of HPLC analysis a number of ozonation products could be identified. Pyruvic acid, formic acid, methyl glyoxal and acetaldehyde could be identified by substantial peaks. Glyoxilic acid and glyoxal were identified by less distinct peaks.

According to the loss in DOC during ozonation it can be assumed that volatile components like carbon dioxide are formed during the ozonation process, which is confirmed by carbon dioxide measurements during an ozonation process. It could not be determined whether the CO_2 formation was mainly due to further oxidation of small ozonation products or by oxidation reactions with the large HS compounds.

Considering the goal of ozonation (to enhance the biodegradability of humic substances) and the observations done concerning the ozonation products it may be concluded that the ozone is not utilized in an efficient way: complete oxidation of parts of HS molecules occurs while large molecules still remain, that are probably not biodegradable.

5 Nomenclature

Symbols

A	Light absorption	(-)
c	Concentration	(mol/l)
COD	Chemical Oxygen Demand	(mgO/l)
Colour	Colour equivalent to a Pt/Co solution	(mgPt/l)
D_p	Polydispersity	(-)
d	Path length	(cm)
DOC mgDOC/l)	Dissolved organic carbon	(molDOC/m ³ or
e	Molar extinction coefficient	(l/mol/cm)
f_D	Correction factor for polydispersity	
M_w	Weight average molecular weight	(Dalton)
M_n	Number average molecular weight	(Dalton)
Mw	Molecular weight	(Dalton)
sk	unsymmetrical peak broadening factor	(-)
r	detector response	(-)
Λ	symmetrical peak broadening factor	(-)

Abbreviations

GPC	Gel permeation chromatography
HPLC (IC)	High performance liquid chromatography (ion chromatography)
HS	Humic substances
PSS	Polystyrenesulfonate
PVDF	Polyvinylidenedifluoride

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Appendix A

Humic substances from Ion-Exchange adsorption

In the ion exchange setup a part of the organic compounds in the drinking water is adsorbed. With GPC analysis an insight is obtained in which range of molecular weights the substances in drinking water is concentrated by the ion-exchange step. Therefore GPC analysis was performed on a drinking water sample, a sample from the ion exchange effluent and a sample of the solution resulting from the regeneration of the ion exchange column. The results are shown in Figure 15.

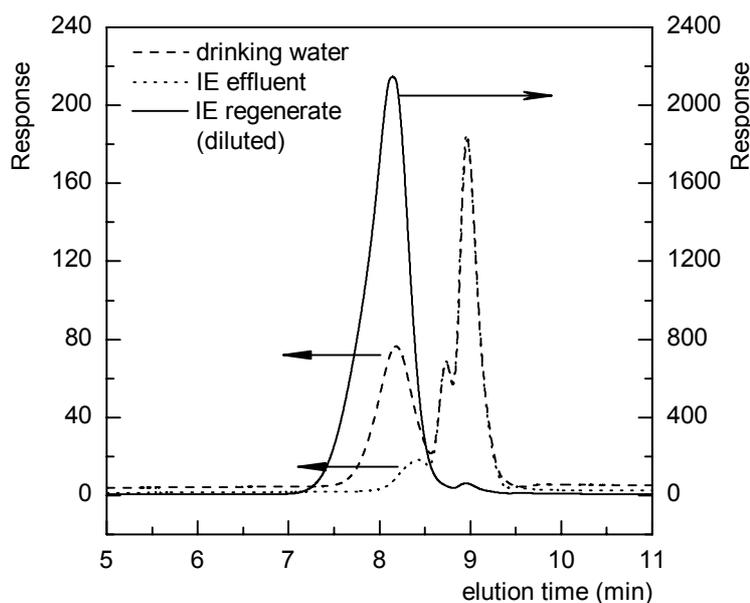


Figure 15: GP chromatogram of humic substances concentrated by the ion-exchange column, drinkingwater, effluent from the ion-exchange column and milli-Q water. The regenerate from the ion exchange setup was diluted 50 times (concentration of diluted sample: 33 molDOC/m³). IE = Ion-exchange.

It seems that the ion-exchange resin mainly adsorbs substances associated with an elution time of around 8 minutes, which corresponds to an average molecular weight (M_w) of $2.6 \cdot 10^3$

Dalton on the GPC calibration line. Small compounds (appearing at 8.6 minutes and later) seem to be hardly adsorbed on the ion exchange resin and pass the adsorption column untouched.

The colour of the drinking water was measured to be 21 mgPt-Co/l, with a DOC content of 7.8 mg/l. The colour of the ion-exchange effluent was <2 mgPt-Co/l (below detection limit) with a DOC content of 2.2 mg/l. With a DOC removal of 72% and a colour removal of >89%, this indicates that the majority of the DOC content consists of large compounds that are responsible for most of the colour in the drinking water.

Appendix B

Carbon dioxide formation during ozonation of humic substances

The formation of carbon dioxide during the ozonation process of humic substances could be monitored in a batch operation. A HS solution of 2 l with $c_{\text{HS}} = 8.3 \text{ molDOC/m}^3$ was ozonated for 12 hours in a closed bubble column with a gas outlet connected to a Servomex 1410 B infrared CO_2 analyzer. The ozone concentration in the feed and off-gas was measured spectrophotometrically according to specifications described in Section 2.2.

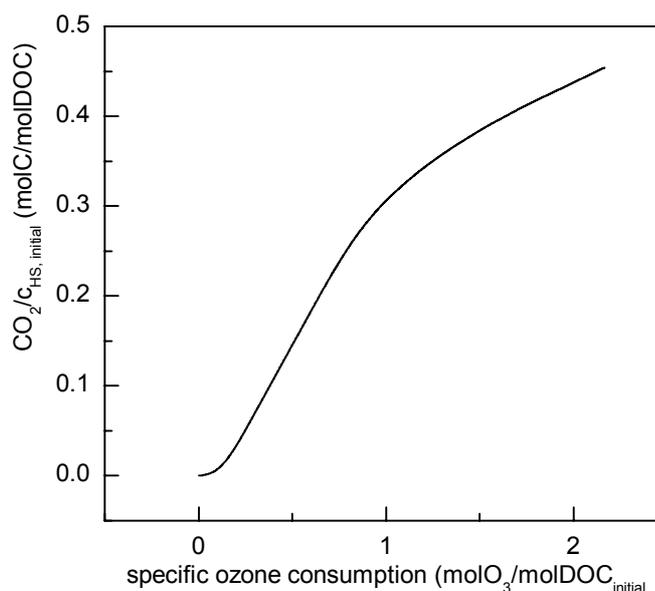


Figure 16: Carbon dioxide formation relative to the initial HS concentration as function of the ozone consumption during the batch-wise ozonation of a HS solution. Carbon dioxide is expressed in molC. $c_{\text{HS,initial}} = 8.3 \text{ mol/m}^3$. $c_{\text{HS,after}} = 4.4 \text{ mol/m}^3$. Reaction volume: 2 l, gas flow rate: 20 l/h, $c_{\text{O}_3, \text{gas}} = 0.11 \text{ mol/m}^3$.

Figure 16 shows the carbon dioxide formation relative to the initial HS concentration in the solution (expressed in $\text{molC/molDOC}_{\text{initial}}$) as a function of the specific ozone consumption. The DOC content of the solution after the ozonation period was 4.4

molDOC/m³, which means a DOC loss of approximately 50%. The carbon content in the total amount CO₂ that was measured was 45% compared to the initial DOC content. This indicates that the DOC loss occurring during the ozonation process can be attributed almost entirely to the formation of CO₂. It is not clear in what ratio the CO₂ formation is due to further oxidation of small compounds or that it is formed directly by oxidation of the large HS molecules.

VI

Effect of HS Concentration on the Ozonation Efficiency

This chapter handles the result of ozonation at different humic substance (HS) concentrations. The influence of ozonation on several water quality parameters of the solutions and change in molecular weight of the HS molecules is presented. The emphasis is on whether the HS concentration has any influence on the ozonation efficiency. The overall conclusion is that the efficiency of ozonation is not dependent on the HS concentration that is applied in the process. For all used HS solutions it seems to apply that the DOC loss is 45% and the colour decreases 95% after a specific ozone consumption of 0.6 molO₃/molDOC. A relatively slow decrease of the specific COD (20%) compared to a relatively large DOC decrease (50%) indicates that the complete oxidation of C-atoms occurs in a stronger extent than partial oxidation of residual HS components. The results of the experiments indicate that at the used HS concentration ranges there are no differences between the results of ozonation of the applied HS concentrations. The water quality parameters (DOC, colour, COD, pH and light absorption at 254 nm) seem to change in the same extend for all HS concentrations per amount of consumed ozone. The same is observed for the average molecular weight M_w of the large HS compounds, decreasing from $2.6 \cdot 10^3$ to $1.5 \cdot 10^3$ Dalton after an ozone consumption of 0.6 molO₃/molDOC, during ozonation and the area of the peak in the GPC diagrams.

1 Introduction

The main target of ozonation of humic substances (HS) is to reduce the colour caused by humic substances, or to remove humic substances before a disinfection step that may yield halogenated by-products [1]. For this purpose large ozonation setups have been installed in drinking water processes to treat the drinking water with ozone [2, 3].

The ozonation of HS has some side effects that can not be ignored. Until now there are no clear indications that humic substances themselves pose a threat to public health, although they are suspected to be a potential carrier of some hazardous organic and inorganic compounds (see Chapter I, Section 1.4.4). The products that are being formed during the ozonation process however, may contain compounds that pose a health risk [2-4]. Another problem in this process is that a part of the ozonation products are biodegradable components, which may cause undesired biofouling in the pipes of the water system. A biofilter, possibly combined with membrane filtration or granular activated carbon (GAC) adsorption may then be applied for removal of any (biodegradable) components to prevent excessive biofouling in the drinking water system and to minimize health risks [1]. Considering these side effects, drinking water companies with colour problems that provide water from resources that hardly need any disinfection may not be eager to install a treatment step in their drinking water process that may potentially pose a health risk to their drinking water or risk pollution of their drinking water distribution system. In those cases they may remove humic substances from drinking water by some non-destructive process in stead of treating them in-line in the production process. Ion-exchange adsorption, for example, has already proven to be a useful and potentially cost effective technique [5, 6]. The humic substances are then retrieved in a concentrated form after regeneration of the ion-exchange column.

When discharge of the HS concentrate in the environment is not desired also here a possible treatment is an ozonation/biofiltration system. When only colour removal is the objective, the DOC loss or increased biodegradability is not the main target but just a (undesired) side effect. In this project however, the main target is sufficient removal of organic compounds or at least to

meet discharge demands and colour removal is then only one of the demands. This difference is of major significance for the ozonation/biofiltration process. It means that the ozonation needs to be such that a sufficient amount of the humic substances are converted into biodegradable compounds. Further, the HS concentration in the regenerate can be up to 30 gDOC /l which is a factor of $4 \cdot 10^3$ to $7 \cdot 10^3$ times higher than found in drinking water. This may have some consequences for the reaction kinetics of the ozonation process. Ozonation reactions with organic components can be very complex following a radical chain mechanism involving OH radicals [7] (See Chapter II). The role of humic substances in this process can be ambiguous. They can potentially act as initiator, promoter and terminator of the radical chain reaction [7, 8]. Which of the three mechanisms is dominant may be different for each type of humic substance and it may determine the efficiency of the ozonation process, where the concentration of reaction initiators, promoters and inhibitors play an important role. This makes the concentration of humic substances in the reaction solution possibly an important factor for the efficiency of the process. Another consequence concerns the result of the concentration step of the humic substances in case of the use of ion-exchange adsorption. The ion-exchange adsorption material is regenerated by a 10% NaCl solution. As a result the regenerate may also contain a large amount of NaCl. Since the solubility of ozone in water is dependent on the ionic strength of the water the NaCl concentration in the solution can have a significant influence on the ozone transfer from the gas to the liquid phase. Hoinge et al. measured that the reaction of chloride with ozone is negligible [9] (see also Section 2.2). Investigation on the influence of the presence of NaCl on the mass transfer of ozone to the reaction solution (Chapter IV) showed that the ozone mass transfer is decreasing with higher NaCl concentrations, but there were no indications that NaCl has any influence on the ozonation reaction.

Most studies on ozonation of HS involve HS concentrations in drinking water or concentrations similar to those found in natural waters [10-13]. This is mainly because in drinking water treatment most ozone applications involve processing of all drinking water. Gilbert [14] and Takahashi et al. [15] studied the effect of ozonation of humic acids (HA) solutions on several water quality parameters (DOC, colour, COD, BOD₅, UV absorbance, conductivity and pH). Both articles report decreasing values for DOC, colour, COD, UV

absorbance and pH and an increase in conductivity and biodegradability (BOD₅). Gilbert used humic acids of two sources (HA from groundwater and surface water) in concentrations up to 600 mg/l (≈ 270 mgDOC/l). Generally no strong differences were found comparing the water quality parameters during the ozonation of solutions with different HA concentrations. Small differences in BOD₅/COD ratio were found between the two types of humic substances when the pH conditions were varied. Takahashi et al. used commercial humic acids originating from coal. HA concentrations in their experimental solutions reached up to 274 mgDOC/l. The HA concentration had no significant effect on the relative colour decrease of the solutions.

This chapter reports the results of experiments conducted to investigate the effect of the HS concentration on the ozonation of HS. The result is measured by water quality parameters (DOC, colour, COD, pH and UV absorbance) and the molecular size distribution of the compounds in the reaction solution.

2 Ozonation reaction and ozone gas-liquid mass transfer

2.1 Role of humic substances in the ozonation reactions

In water ozone can potentially react with HS in two ways. It can react directly with HS (i) or it can react indirectly through the formation OH radicals in the reaction solution (ii). In the first case ozone can react with humic substances to form oxidized compounds (Reaction (1)) or to form an HS cation radical and an ozonide anion radical (Reaction (2)).



These reactions are generally attributed to double bonds, activated aromatic systems, amines and sulfides [7].

In the second case where HS react with OH radicals again two options are possible. The first is propagation of the radical chain reaction. Here OH radicals react with HS which leads to a carbon centred radical that reacts with oxygen to form a superoxide ion (Reaction (4)). The superoxide ion reacts quickly with ozone and with interaction of H₂O to form radicals again (see Chapter II, Section 2.6) and the radical chain mechanism is supported (Reactions (3) and (4)).



or $\rightarrow \text{HS}^{+\cdot} + \text{OH}^-$



The second option in the reaction of HS with OH radicals is the role of HS as scavenger and therefore as inhibitor of the radical chain mechanism. Here, a reaction between HS and OH radicals does not result in the formation of superoxide ions and terminates the radical chain reaction (Reaction (5) and (6)).



Considering the initiating/promoting/inhibiting abilities of humic substances the HS concentration might be an important factor for its own degradation. A high concentration of HS with inhibiting tendencies may result in a relatively low degradation of these humic substances. On the other hand, a high concentration of HS with strong promoting or initiating properties may oxidize relatively faster than when treated in low concentrations. Due to the complexity and the indefiniteness of the molecular structure of humic substances it is virtually impossible to determine the propagating or inhibiting character of humic substances in the water beforehand.

2.2 Influence of chloride on the ozonation reaction

Usually ion exchange adsorbers are regenerated by a salt solution. In this case a NaCl solution is used. Consequently the

regenerate contains, apart from humic substances, a certain amount of NaCl, of which chloride might be involved in the ozonation reactions. Yeatts and Taube [16] proposed the reaction between ozone and chloride to be as



This is followed by a rapid protonation to HOCl and conversion to Cl_2 . Hoigne et al. [9] investigated the reaction rate of chloride (Cl^-) with ozone. They found an apparent rate constant of only $0.003 \text{ M}^{-1}\text{s}^{-1}$ (23 °C) above pH 2. They state that this value must be considered as an upper limit since trace impurities present in the chloride reagents could have interfered. Considering the rate constant the reaction of ozone with Cl^- is an extremely slow process even when Cl^- is present in high concentrations. For this reason the reaction of ozone with chloride can be neglected.

3 Experimental

3.1 HS collection

Humic substances were obtained as described in Chapter V, Section 2.1. The HS solutions for the experiments were prepared out of the stock solution. DOC amounts in the experimental solutions ranged from approximately 3.3 molDOC/m^3 to 83 molDOC/m^3 (40 mgDOC/l to 1 gDOC/l). In these dilutions the highest NaCl concentration in the HS solutions is 0.05 M. At these low concentrations the ionic strength of the reaction solutions is considered to have an insignificant effect on the ozone solubility in water.

3.2 Experimental setup

The experiments were performed on the experimental setup described in Chapter V, Section 2. Membrane module 2 (see Chapter III, Section 3.1) was used as gas-liquid contactor for the ozonation experiments.

The ozone concentration both in the gas feed and outlet was measured spectrophotometrically at a wavelength of 253 nm with a

Pharmacia LKB Ultrospec Plus double beam spectrophotometer. The concentration was calculated according to $A = c \cdot e \cdot d_c$. The extinction coefficient e , was taken as 3000 l/mol/cm. During the experiments the ozone concentration in the gas feed was approximately 0.38 mol/m³ at a flow of 20 l/h. The liquid flow was approximately 1 l/h. The ozonation process was performed counter-currently with the liquid flowing through the fibres. The ozone consumption was determined from the difference in ozone concentration between the gas feed and the gas outlet.

3.3 HS characterization

The HS solutions were characterized on water quality parameters ((mgDOC/l), colour (mgPt-Co/l), specific light absorption at 254 nm (m³/molDOC), pH and chemical oxygen demand (COD)) and by GPC analysis. The DOC was measured on a Shimadzu TOC-V CPH Total organic carbon analyzer. The colour was determined by spectrophotometrical comparison with Pt/Co solution standards at a wavelength of 455 nm. The Pt-standards were prepared according to the Visual Comparison Method (Standard Methods 2120 B) [17]. The light absorption at 455 nm and 254 nm was measured on a Shimadzu double beam spectrophotometer. The COD was determined by Dr Lange COD kits. GPC analysis was performed on a Metrohm HPLC setup with a PSS MCX-1000Å GPC column. A Bisschoff Lambda 1010 was used as UV-VIS detector. The mobile phase consisted of water with 0.1 M of Na₂HPO₄.

The methods used for GPC and analysis of the chromatograms for calculation of the average molecular weights are described in Chapter V, Section 2.5.

3.4 Experiments

HS solutions of different concentrations ranging from 3.3 to 78 molDOC/m³ (40 to 975 mgDOC/l) were repeatedly led through the ozonation module. The liquid flow rate was held constant at 1.0 l/h (0.28 ml/s) and the gas flow rate was 14.9 l/h (4.14 ml/s) at an ozone concentration of 0.378 mol/m³. During each run the ozone consumption was measured and after each run samples were taken for analysis on water quality parameters (DOC, colour, COD, pH, UV

absorption) and GPC. For GPC analysis first four HS solutions of concentrations of 3.3, 7.1, 16 and 31 molDOC/m³ were analysed.

4 Results and discussion

4.1 Ozone consumption

The ozone consumption shows a clear relation with the HS concentration in the reaction solution: a high HS concentration in the solution results a high ozone consumption rate. This indicates that the reaction rate increases with increasing HS concentration. Matters on the reaction rate are discussed more extensively in Chapter IV.

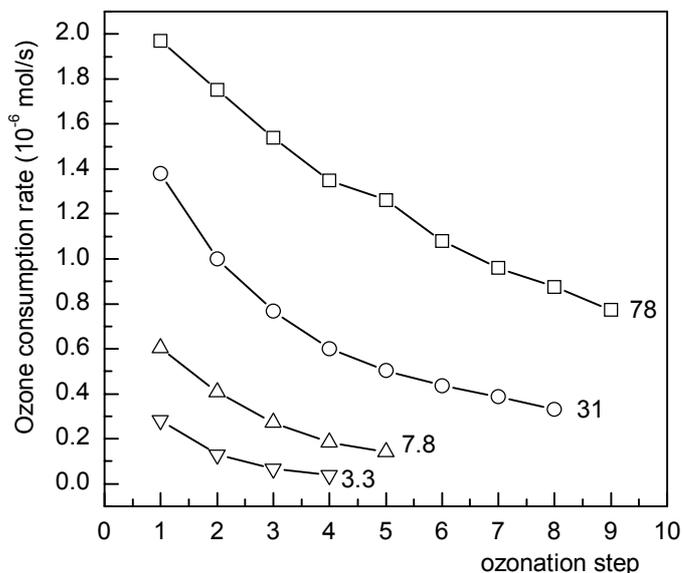


Figure 1: Ozone consumption rate (mol/s) during each step in the sequential ozonation process. Ozone feed gas concentration: 0.38 mol/m³, gas flow 4.1 ml/s, liquid flow 0.28 ml/s. The figures near the lines indicate the HS concentration in the reaction solution.

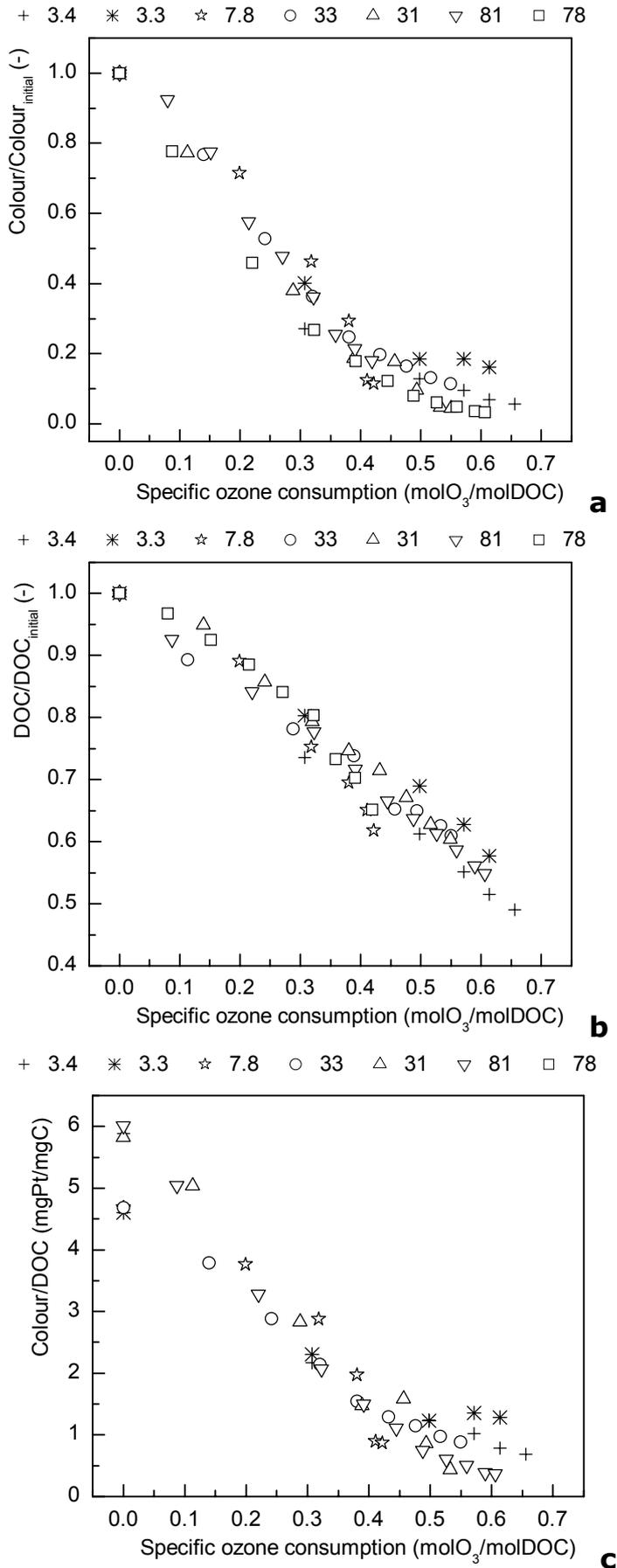


Figure 2: Effect of ozonation on colour and DOC of HS solutions with different HS concentrations. The figures at the labels in the agenda represent the initial DOC concentration of the solutions (mol/m³) a) Colour relative to the initial colour of the solutions. b) DOC content relative to the initial DOC content of the solutions. c) Colour relative to DOC content.

4.2 Effect of HS concentration on water quality parameters during ozonation

Plotted as function of the specific ozone consumption ($\text{molO}_3/\text{molDOC}$) the HS concentration does not seem to have a significant influence on the relative colour and DOC decrease during the ozonation process (Figure 2). It seems that the concentration of humic substances at these levels is of no influence on the effectiveness of the ozonation. For all solutions roughly the same amount of ozone per unit of DOC is needed for the decrease rate of the relative DOC and colour values.

For all solutions a DOC decrease of 40 to 50% and a colour decrease of 80 to 95% is observed for all solutions with a specific ozone consumption between 0.4 and 0.65 $\text{molO}_3/\text{molDOC}$. The average DOC loss in the solution was 45% with a colour loss of 95% at 0.6 $\text{molO}_3/\text{molDOC}$. The colour/DOC ratio decreases from a factor of 6 to less than 1 after extensive ozonation. During the ozonation the light absorption at 254 nm per amount of DOC decreases with approximately 60% (Figure 3a). The light absorption at 254 nm may be connected to the double bond character of organic compounds [18] and is often used as a measure for the aromaticity of the organic compounds [19]. A strongly decreasing light absorption at this wavelength may indicate destruction of such unsaturated bonds in the HS molecules. The COD of the solutions decreases clearly during the ozonation process (Figure 3b). However, the specific COD decreases slowly with approximately 20% while the DOC concentration has dropped with 40 to 50%. This may indicate that while small volatile components are split of the HS molecules and leave the reaction solution, the oxidation of the remaining molecules proceeds relatively slow. In these cases no clear difference in behaviour was observed as a result of ozonating humic substances of different concentration. The decreasing pH of the solutions during ozonation indicates that carboxylic groups are formed during the ozonation process. Here it can be observed that the pH is decreasing faster as lower HS concentrations are being used in the ozonation process (Figure 3c). For the present this is not attributed to a higher concentration of carboxylic groups in the solution, but to the lower pH buffering capacity of solutions with low HS concentration.

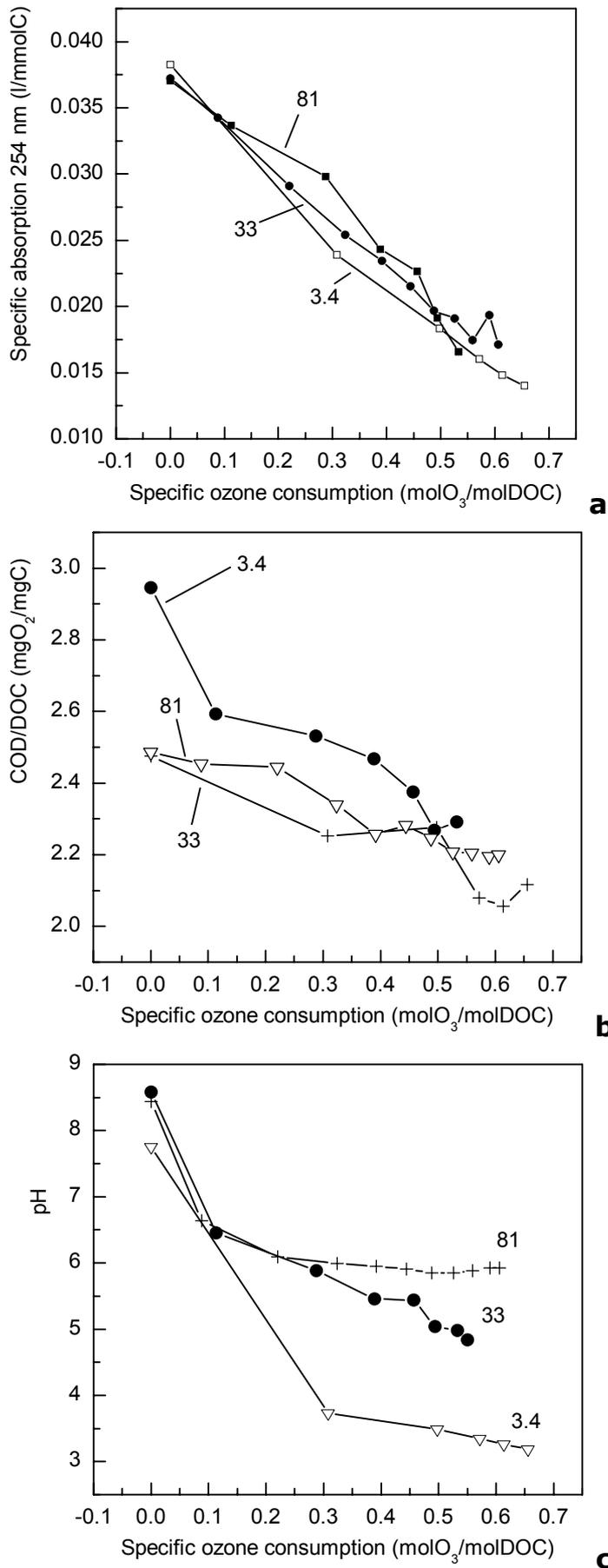


Figure 3: Several water quality parameters as function of the specific ozone consumption for three HS solutions (3.4, 33 and 81 molDOC/m³). The figures in the plot indicate the HS concentration (molDOC/m³). a) Specific absorption (254 nm) of the HS solutions b) Specific COD. c) pH of the solutions.

4.3 Change of the molecular weight (distribution) of humic substances during ozonation

The GP chromatogram of untreated humic substances shows a distinct peak at an elution time of around 8.1 minutes. This peak will be referred to as the "humic substances-peak" (HS-peak). The peak indicates a molecular weight distribution ranging from approximately $5 \cdot 10^2$ to 10^4 Dalton. From the chromatograms (Figure 4) the average molecular weight of the humic substances were calculated according to equations (1) and (2) in Chapter V. Calculations on the average molecular weight show that there are hardly any differences between the solutions. The calculated average molecular weight parameters are: $M_w = 2.6 \cdot 10^3$ Dalton, $M_n = 2.1 \cdot 10^3$ and the polydispersity $M_w/M_n = 1.24$. These values for the molecular weight are not corrected for the dispersion caused by the chromatography system (See Chapter V). The fact that the same M_w and M_n was calculated with the chromatograms of all HS solutions indicates that the GPC analysis is reproducible and that the peak width at the basis is not depending on the HS concentration at these loads (no sample overload in the system).

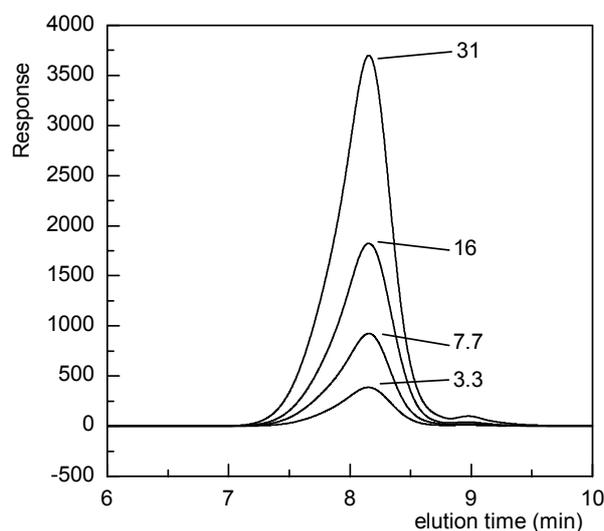
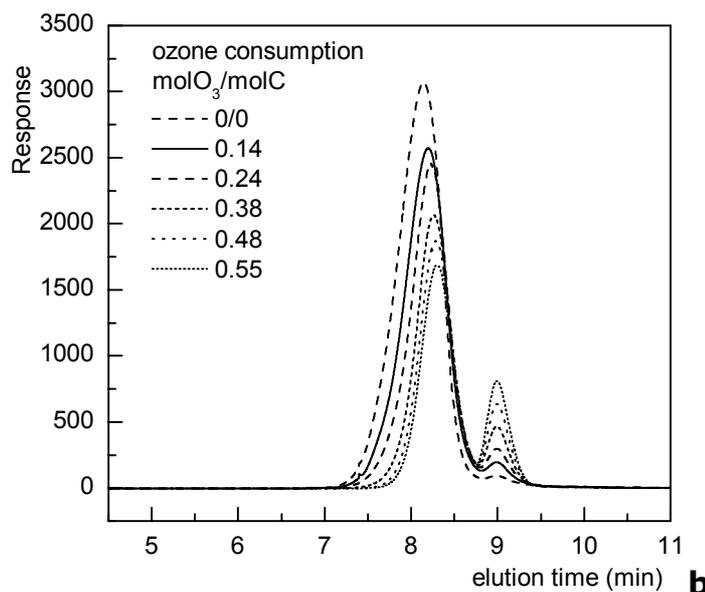
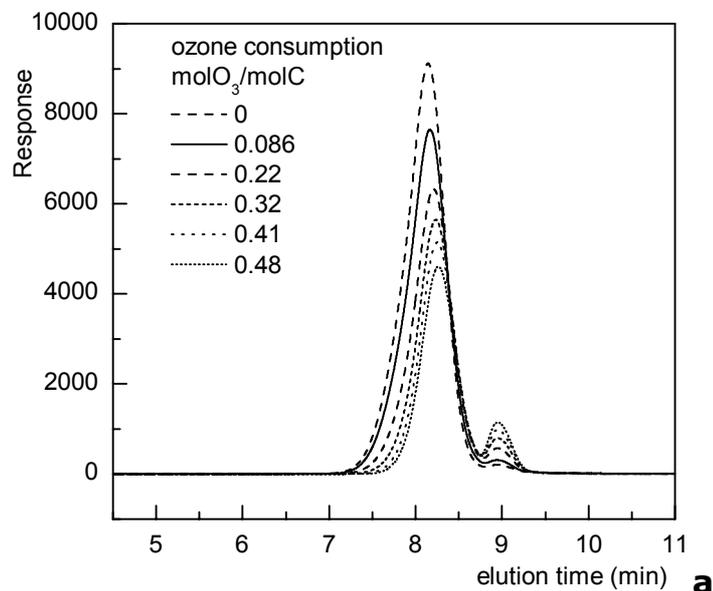


Figure 4: Gel permeation chromatograms of HS solutions of four different concentrations. HS concentrations are indicated by the figures at the curves (molDOC/m³).

During the ozonation process the area of the HS-peak becomes smaller and the top shifts to higher elution times (Figure 5). This was

already described in Chapter III and the peak shift indicates that the average molecular size of the HS compounds decreases during ozonation. A decreasing area does not necessarily mean a decrease in the amount of compounds but more exactly a decrease in light absorbing components that may be caused by DOC reduction and changes in functional groups. Due to the oxidation process functional groups in the molecular structure may be added or change. Because of this the molar light absorption may change. Consequently, the ratio between the amount of compounds and the light absorption changes during ozonation of the HS molecules. It is therefore not justified to assume that the ratio between the peak height and the DOC content remains constant as the oxidation process proceeds.



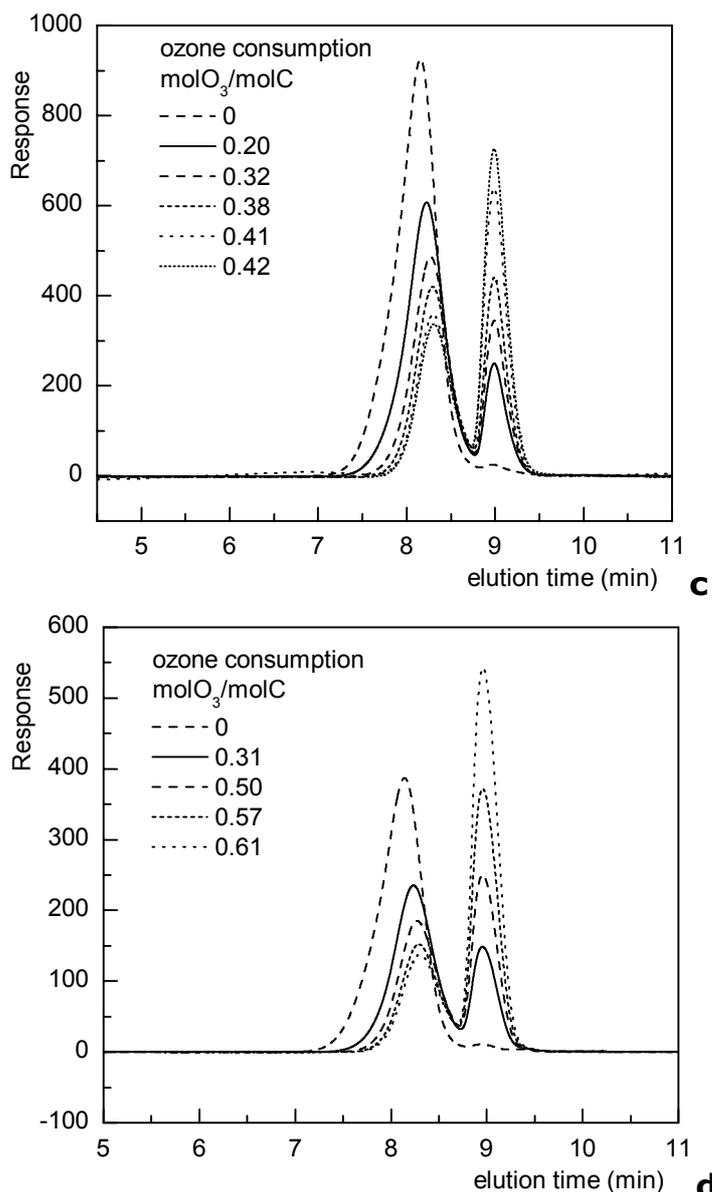


Figure 5: Gel permeation chromatograms of four HS solutions with different concentrations during sequential ozonation. Initial HS concentrations: a: 78, b: 32, c: 7.8, d: 3.3 molDOC/m³ (934, 374, 93, 40 mgDOC/l). The figures in the chromatograms indicate the specific ozone consumption of the HS solution (molO₃/molDOC).

Calculations based on the left peaks (“HS-peaks”) in the chromatograms show that the weight average molecular weight, M_w , of the large compounds is decreasing during the ozonation process (Figure 6). The equal decrease in M_w 's as function of the specific ozone consumption for all solutions indicates that the HS concentration is of little influence on the decrease of the molecular weight of the large components. The decrease of the M_w is equally

dependent on the specific ozone consumption for all HS concentrations.

As the ozonation process continues another peak emerges in the GP chromatograms at an elution time of around 9 minutes. Analysis showed that the components associated with this elution time are most likely small compounds, identified as typical products of the ozonation of humic substances (Chapter V). The peak is therefore referred to as "product peak". These compounds are most likely split of the larger molecules due to the oxidation reaction with ozone.

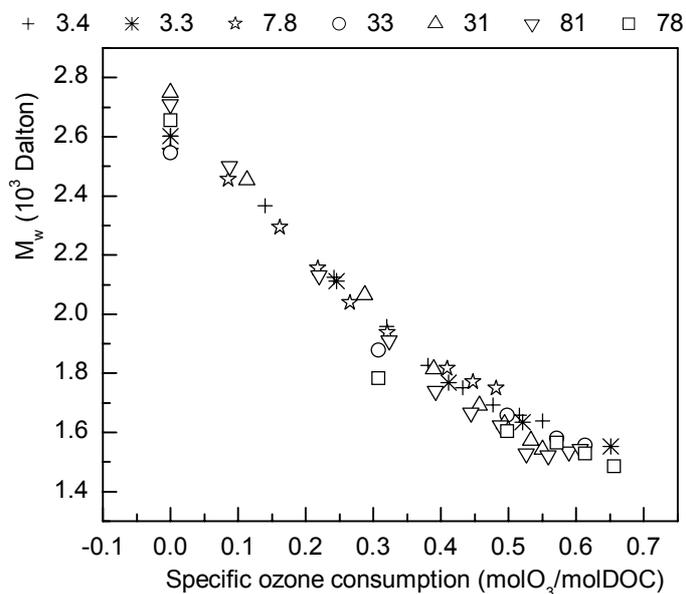


Figure 6: Average molecular weight, M_w , of humic substances during the ozonation of HS solutions with different initial DOC concentrations. HS concentrations range from 3.3 to 78 mol DOC/m³ (40 to 975 mg DOC/l). The molecular weight is not corrected for the dispersion of the GPC system.

The small ozonation products were identified to be small carboxylic acids, ketoacids and aldehydes with an average molecular weight smaller than 100 Dalton. Also in other studies reported in literature these compounds were found to be products of ozonation of humic substances [12, 20-23]. Calculation of the molecular weight of the "product peaks" yields a M_w of approximately 430 Dalton. This is, according to the results in Chapter V, an overestimation of the real molecular weight. Considering the calculated molecular weights it

appears that the average molecular weight hardly changes during the ozonation process and that the polydispersity is approximately 1.06 representing a very narrow molecular weight distribution. Although the analysis showed that several small compounds are being formed during the ozonation process (Chapter V), [12, 20-23], it is possible that the distinct peak may be associated with just a single compound with a prevailing molar absorption at 223 nm, the wavelength used for detection in the GPC system. It may also indicate that the molecular weights of the compounds associated with the product-peak lie closely together. If the latter is the case and regarding the fact that the calculated average molecular weight associated with the product peak hardly changes this may indicate that the type of compounds that are being formed remain the same throughout the whole ozonation process and that the ratio in which these compounds are formed is also constant during the time span of the ozonation process. It is therefore assumed that the overall specific light absorption of the small ozonation products remains the same throughout the ozonation time. With this assumption the peak surfaces associated with small ozonation compounds can be compared and be used to estimate the relative increase of the amount of small ozonation products.

Figure 7 shows the surfaces of the GPC peaks associated with the large compounds and the small ozonation products relative to the peak surfaces the starting solutions. The area of the HS peak decreases with increasing ozone consumption. This happens for all HS concentrations in the same extent. From this point of view the HS concentration has no significant influence on the speed of degradation of the HS components. On the other hand, when observing the area of the peaks associated with the small ozonation products it can be seen that the relative increase is higher when ozonating low concentrations of humic substances. Here, after a certain specific ozone consumption the peak seems to increase exponentially indicating a more rapid production of small ozonation products. It seems that the production of small compounds is larger per amount of consumed ozone when a low HS concentration is used. However, this difference can not be observed when considering the course of the specific peak area associated with the large compounds. Here the decreasing factor is equal for all different HS concentrations.

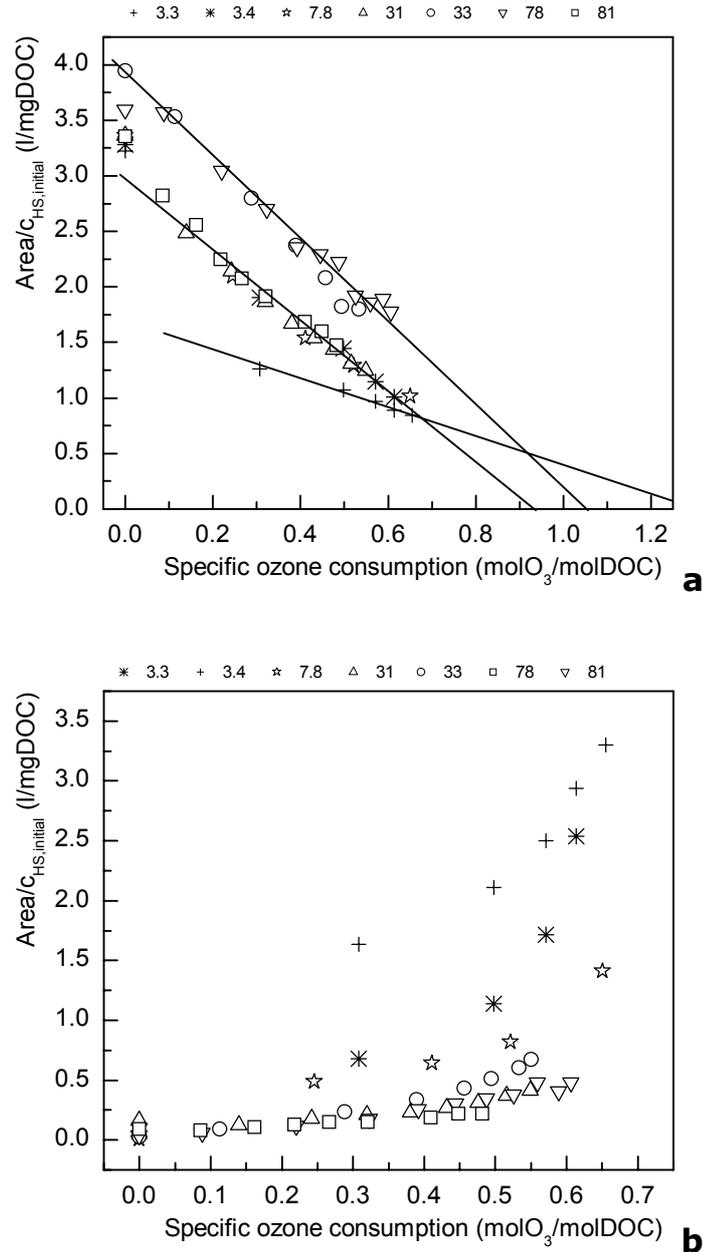


Figure 7: Peak areas calculated out of the gel permeation chromatograms plotted against the ozone consumption for ozonated HS solutions. Solutions of different initial HS concentrations were analysed. The areas are set out relative to the initial HS concentration ($DOC_{initial}$) of the reaction solution. The figures in the agenda indicate the initial HS concentration in the reaction solution ($molDOC/m^3$) a) From the HS peak (large compounds). b) From the product peak (small compounds).

When the ozonation is continued long enough all large HS molecules will be degraded. The peak area associated with the large compounds in a GPC diagram will then be approaching 0. This x-axis intercept in a graph where the peak area is plotted as function of the

ozone consumption is then point where there are no detectable large HS molecules present in the solution. When extrapolating the data points from Figure 1a with a linear fit to where the peak area is 0 the value of the intercept may be taken as estimation for the amount of ozone that is needed for full degradation of the large HS molecules. For most solutions this intercept seems to lie between 0.9 and 1.1 molO₃/molDOC (3.6 and 4.4 mgO₃/mgDOC) (Figure 1a). Caution should be taken in drawing conclusions on this matter since the reaction behaviour in these far stages of ozonation is not explored yet. For this fit a linear relation was assumed. However it may very well be possible that there are some refractory compounds that are virtually resistant to further oxidation. An asymptotic extrapolation would then be more appropriate and the ozone demand for complete removal of the large compounds would then be somewhat higher.

It should be noted that at the point where all large HS molecules are broken down the DOC loss due to complete mineralization of compounds will be substantial. This may have some major consequences for the evaluation of the ozonation efficiency in the ozonation/biofiltration process.

5 Conclusions and outlook

For all used HS solutions it seems to apply that the DOC loss is 45% and the colour decreases with 95% after a specific ozone consumption of 0.6 molO₃/molDOC. Overall, the concentration of the HS solutions seems to have no significant influence on the efficiency of the ozonation reaction considering the course of the water quality parameters (DOC, Colour, COD and absorption 254 nm), the molecular weight of the humic substances and the area of the peak associated with the large HS compounds: the parameters seem to change with the specific ozone consumption in the same ratio for every HS concentration that was used in the experiments. On the other hand the production rate of small ozonation products, identified as small carboxylic acids, keto-acids and aldehydes, seems to be dependent on the concentration of humic substances that was applied. When using lower HS concentrations more small compounds are being formed per amount of specific ozone consumption considering the relative increase in peak area when a lower HS concentration is used in the ozonation experiments. It is however, not safe to conclude that the efficiency of ozonation increases with a

lower HS concentration since the relative increased formation of small compounds could not be related to the decrease of the amount and size of the large compounds.

A relatively slow decrease of the specific COD (20%) compared to a relatively large DOC decrease (50%) indicates that the complete oxidation of C-atoms occurs in a stronger extent than partial oxidation of residual HS components. This strengthens the idea that small molecular structures of highly oxidized state are split of the large HS molecules while that the backbone structure of the humic substances is relatively stable.

On the basis of the decrease of the peak area as function of the ozone consumption it is estimated that full degradation of the large HS molecules is reached at an ozone consumption of approximately 1 molO₃/molDOC (4 mgO₃/mgDOC). This estimation is to be taken with caution since the ozonation behaviour in the final ozonation stages is not explored yet. It should be noted that at the point where full decay is reached of the large HS molecules the DOC loss will be substantial.

Considering the conclusions above the HS concentration does not seem to influence the ozonation efficiency. This means that for the design of a treatment process there are no restrictions in a HS concentration that may desirable for the process. Using high HS concentrations means smaller process volumes to treat. However, apparently always the same amount of ozone is needed per amount of HS for the desired level of degradation.

6 Nomenclature

Symbols

A	Light absorption	(-)
BOD ₅	Biochemical Oxygen Demand (over 5 days)	(mg/l)
c	Concentration	(mol/l)
COD	Chemical Oxygen Demand	(mg/l)
DOC	Dissolved organic carbon	(molDOC/m ³) or (gDOC/l)
e	Molar extinction coefficient	(l/mol/cm)
d _c	Path length of cuvette	(cm)
M _w	Weight average molecular weight	(Dalton)
M _n	Number average molecular weight	(Dalton)
M _w	Molecular weight	(Dalton)

Abbreviations

GPC	Gel permeation chromatography
HA	Humic acids
HS	Humic substances

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Appendix A

Ozonation of drinking water

During the ozonation of a drinking water batch the ozone uptake was $0.75 \text{ molO}_3/\text{molDOC}$ ($3 \text{ mgO}_3/\text{mgDOC}$). The DOC content decreased from 7.8 to 5.7 mg/l and the colour of the sample decreased from 20 to 3 mgPt-Co/l. The colour decrease was similar as found in experiments with concentrated humic substances, but the DOC decrease is smaller compared to the DOC loss that was found after ozonation of stronger concentrated HS solutions with the same specific ozone consumption.

Figure 8 shows the GPC chromatogram of a drinking water sample before and after ozonation. It can be seen that drinking water contains some small organic compounds (elution time 9 min) and large organic compounds (elution time 8.2 min) that are related with humic substances. After ozonation the peak at an elution time of 8.2 minutes in the GPC diagram has become much smaller in area while the peak area associated with the large compounds has increased strongly, similar to what is observed during experiments with concentrated humic substances. It should be noted that the substances associated with an elution time of 9 min in the untreated drinking water sample do not necessarily have to be the same compounds resulting from ozonation of humic substances.

Figure 9 is the result of HPLC analysis of drinking water before and after ozonation. The peaks that emerge after ozonation are the result of degradation of the humic substances into small compounds and were as such identified in Chapter V.

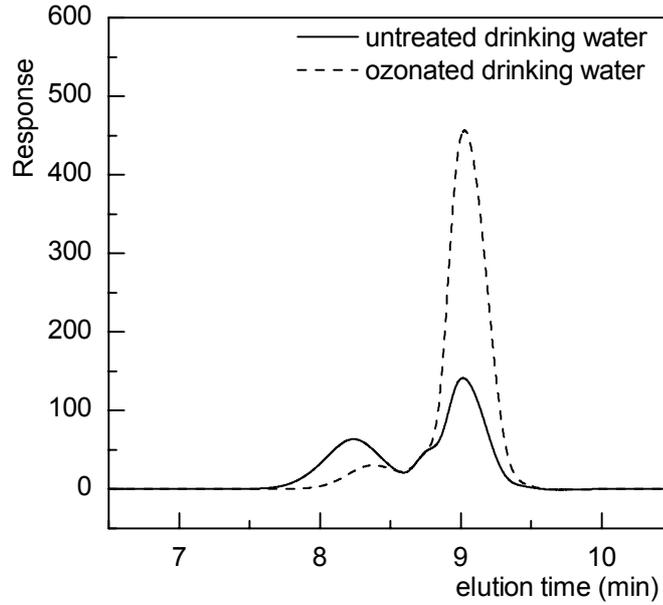


Figure 8: Example of a GPC diagram of untreated and ozonated drinking water. Specific ozone consumption: 0.75 molO₃/molDOC (3 mgO₃/mgDOC). The peak decrease at 8.2 min and the peak increase at 9 min is a result of the degradation of the humic substances into small compounds.

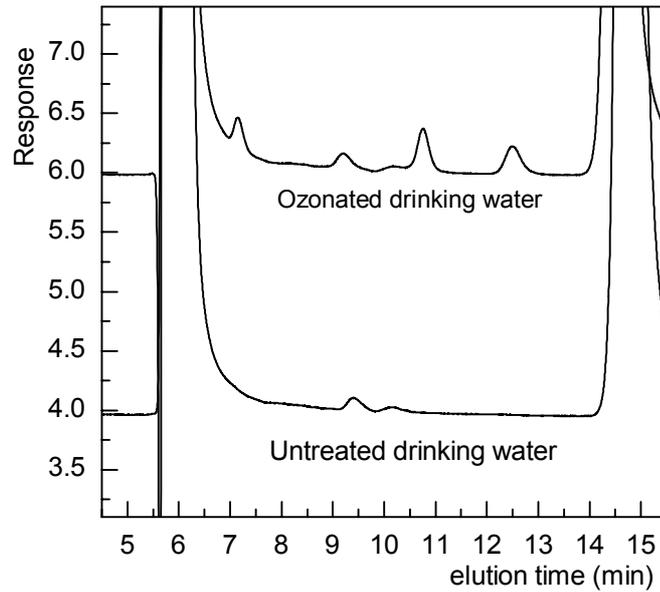


Figure 9: HPLC diagram of untreated and ozonated drinking water. Specific ozone consumption: 0.75 molO₃/molDOC (3 mgO₃/mgDOC). The peaks that emerge after ozonation are identified as products of ozonation of humic substances in Chapter V. The large peaks at 6 and 15 min result from salt and carbonate ions respectively.

VII

Biodegradation of Products from Ozonation of Humic Substances

This chapter handles the biodegradation of products resulting from ozonation of humic substances. A lab-scale biofilter was used to investigate the biodegradability of ozonation products (OP's). The research comprised biofiltration experiments with a synthetic solution composed out of several known OP of HS and a biofiltration experiment on "freshly" ozonated drinking water. Samples before and after passing the biofilter were examined on DOC content, COD, HPLC and GPC.

For the synthetic OP solutions removal ratios of 90% DOC and 80% COD were achieved and 60-90% DOC and 51% COD depending on the exact OP composition. HPLC and GPC analysis indicated substantial removal of compounds by the biofilter. GPC analysis of samples in a continuous ozonation/biofiltration process of drinking water indicated the degradation of large HS molecules and an increase in small compounds as a result of ozonation. The analysis indicated that the biofilter was able to remove some small compounds but not the residual large compounds from the ozonated solution.

1 Introduction

The ultimate goal of this research is to investigate the removal of humic substances by an ozonation/biofiltration process. The ozonation step is applied to enhance the biodegradability of humic substances. Several researchers have reported the formation of degradation products that were biodegradable after ozonating humic substances in (drinking) water [1-5]. The occurrence of these biodegradable ozonation by-products (OP's) may cause problems with growth of biomass in the distribution net. This problem can be overcome by placing biologically active filters after the ozonation step.

In most of these studies ozone is used for disinfection and for colour removal purposes [6]. The formation of biodegradable compounds is then merely an undesired side-effect of the ozonation process. When the emphasis lies on HS removal in the sense of DOC and COD reduction, enhancement of biodegradability may become a goal instead of a side effect. Also in this case an ozonation/biofiltration process may be effective in removing humic substances. The process was proposed as a side-stream treatment. First the humic substances are to be removed from the drinking water stream by some concentration step (e.g. ion-exchange adsorption) and subsequently be treated as a concentrated HS flow by an ozonation/biofiltration process as schematically pictured in Figure 1.

On basis of known ozonation products in literature [7, 8] and ozonation products identified in Chapter V a synthetic OP solution was composed to resemble a solution of ozonation products. With this solution experiments were performed with a lab scale packed biofilter. The samples before and after biofiltration were characterized to investigate the effect of the biofilter on the OP solution. In the end a test was run where drinking water was treated in a continuous process by ozonation followed by a biofiltration step.

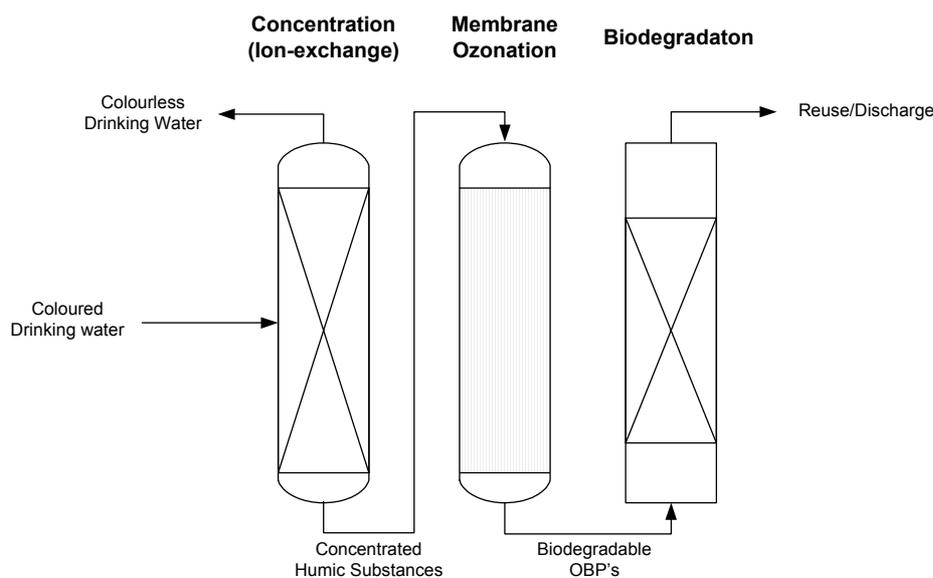


Figure 1: Schematic overview of the presumed removal process of humic substances from drinking water.

2 Experimental

2.1 Materials

Solution synthetic ozonation by-products

For the experiments with synthetic OP's a concentrated solution of several small organic compounds and standard nutrients was composed. The organic solutes consist of several aldehydes and keto-carboxylic acids (Table 1). In several studies [7, 8] and in Chapter V in this thesis these organic compounds were identified as products of the ozonation of humic substances.

A nutrient solution was prepared for the biofiltration setup consisting of several salts composed according to a typical elemental composition of bacteria cells [9] and standard nutrient solutions [10]. The nutrients composition in the feed solution that was used in the biofiltration experiments is shown in Table 2.

Table 1: Contents and data of the synthetic OP solution used for biofiltration experiments.

Compounds	Concentrate I (g/l)	Concentrate II (g/l)
formaldehyde	0.58	0.58
acetaldehyde	0.081	0.083
acetone	0.18	0.19
glyoxal	0.38	0.38
methyl glyoxal	0.14	0.33
glyoxilic acid	3.1	3.0
pyruvic acid	1.6	2.0
mesoxalic acid	0.59	4.5
Total COD (mg/l)	4.5·10 ³ (theoretical) 4.1·10 ³ (experimental)	6.1·10 ³ (theoretical) 4.5·10 ³ (experimental)

Table 2: Nutrients and contents added to the OP concentrate I and concentrate II for biofiltration experiments.

Nutrients	
Compounds	Content (g/l)
K ₂ HPO ₄	0.5
NH ₄ Cl	1.0
MgSO ₄ ·7H ₂ O	0.2
CaCl ₂ ·2H ₂ O	0.0785
Yeast extract	0.1
Trace elements	1 ml/l

2.2 Experimental setup and operation

2.2.1 Setup biofiltration experiment with synthetic OP solution

The synthetic OP solution is diluted with drinking water. The mixture flows with a rate of approximately 1 l/h upwards into a packed biofilter column. The features of the process are presented in Table 3 and a schematic flow sheet is presented in Figure 2. Without aeration the oxygen concentration in the biofilter was 0-1 mg/l. The biofilter was therefore aerated softly to prevent aggressive turbulence that may cause the biofilm to detach too much from the packing material. The biofilter was inoculated with drinking water, surface water and various samples of effluent from small wastewater treatment setups for household water.

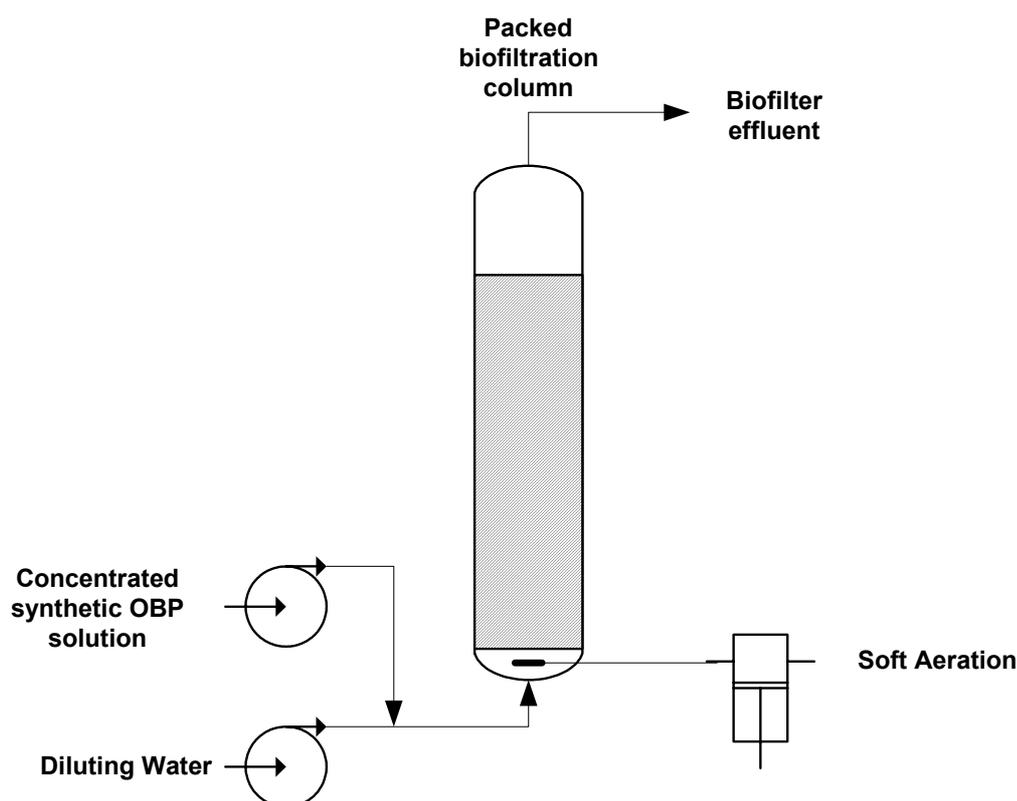


Figure 2: Setup for the biofiltration experiments with synthetic OP solutions. The biofiltration unit consisted of a packed bed reactor (Table 3).

Table 3: Features of the biofiltration setup and process.

Height packed bed	0.44 m	Volume (empty)	0.0014 m ³	
Diameter column	0.063 m	Packing material	Plastic Rings	D = 1.5 cm L = 1.5 cm W = 0.1 cm
Flow rate diluting medium	1 l/h	Flow rate Concentrate	6-30 ml/h	
EBCT	80 min.			

2.2.2 Ozonation/biofiltration setup for drinking water treatment

A membrane contactor was used as gas-liquid contactor for the ozonation of the drinking water. The membrane contactor was constructed with PVDF capillary membranes in a stainless steel housing. The membranes were supplied by EMI University of Twente, The Netherlands. Air was led through an ozone generator (Ozone Generator Peripheral Com, Anseros Klaus Nonnenbacher GmbH) from there ozone enriched air flowed into the contactor module on the shell side of the membranes. Water containing humic substances ran through the bore side (1 l/h) of the membranes and was than led into a buffer reservoir (2 L) with enough residence time to get rid of any residual ozone. From here the water was led into the bottom of a packed biofilter column (column features see Table 1) flowing upwards through the column. The biofiltration setup is the same as shown in Figure 2.

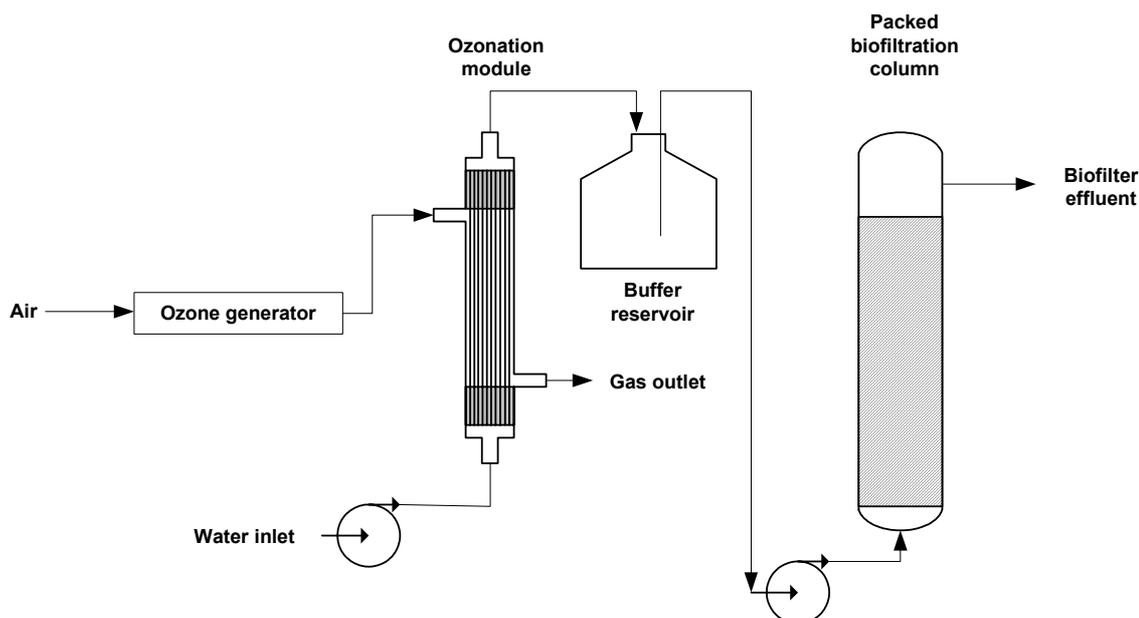


Figure 3: Experimental setup for the continuous ozonation/biofiltration system. The ozonation of the drinking water was performed in membrane contactor 2 (see Chapter III). The biofilter is the same as used for the biofiltration experiments with the synthetic OP solutions shown in Figure 2 .

2.3 Analysis

Oxygen measurement

The oxygen concentration in the biofilter was measured with a WTW 321i Oxygen meter.

Sample characterization

All samples were filtered with a 0.45 μm filter. The biofilter influent (BFI) and effluent (BFE) was characterized by DOC (mg/l), colour (mgPt-Co/l) and COD (mg/l). Further the samples were analyzed by GPC and by HPLC (organic acids).

DOC was measured on a Shimadzu TOC-V CPH Total Organic Carbon analyzer. The colour was determined by spectrophotometrical comparison with Pt-Co standard solutions at a wavelength of 455 nm. The Pt-Co standards were prepared according to the Visual Comparison Method [11]. The COD was determined with Dr Lange kits. GPC analysis was performed on a Metrohm HPLC setup with a PSS MCX-1000Å GPC column, with a Bisschoff Lambda 1010 as UV-VIS detector. The mobile phase consisted of water with 0.1 M of

Na₂HPO₄. The organic acids were also measured on a Metrohm HPLC 761 Compac IC setup with a Metrosep Organic Acids 6.1005.200 column, a suppressor running with 50 mM LiCl and a Metrohm 1006 conductivity detector. The eluent was 0.5 mM H₂SO₄ running at 0.7 ml/min.

2.4 Experiments

2.4.1 Synthetic solution

While the flow rate of the diluting medium (drinking water) remained constant at 1 l/h (16.7 ml/min), the following experiments were performed with the synthetic solution:

Experiments with different OP concentrations in the biofilter feed. Two concentrate solutions were used in these tests (see Table 1). The flow rate of the concentrate was varied between 0.1 and 0.5 ml/min (dilution factor between 168 and 29).

Blank experiment with drinking water. While the biofilter is running the concentrate supply was shut. The aim was to investigate the biodegradability of components in drinking water to use as blank determination.

Demineralised water as diluting medium. Drinking water was replaced by demineralised water as diluting medium. The aim was to run the tests without any biodegradable components that may be present in the drinking water. This experiment was also used as adsorption test to investigate whether any adsorption takes place of substrate to the micro-organisms.

2.4.2 Ozonation/biofiltration

Tap water was led through the system with a constant flow rate of 1.0 l/h (0.28 ml/s). The gas flow rate was 20 l/h (5.6 ml/s). During the experiments samples were taken for analysis on GPC. The ozone concentration in the gas phase was 0.37 mol/m³. A nutrient solution (composition as in Table 2) was added to the ozonated tap water before entering the biofilter. The flow rate of the nutrient solution was 0.05 ml/min.

3 Results and discussion

3.1 Synthetic solution

3.1.1 Startup

After start up of the biofilter with the synthetic OP concentrate as feed, with nutrients, a substantial growth of white/yellow coloured biomass could be observed.

It appeared that there was no growth of biomass without the addition of nutrients to the feed flow: there was no significant difference between the COD and DOC values of the biofilter influent (BFI) and biofilter effluent (BFE) without addition of nutrients to the OP feed solution.

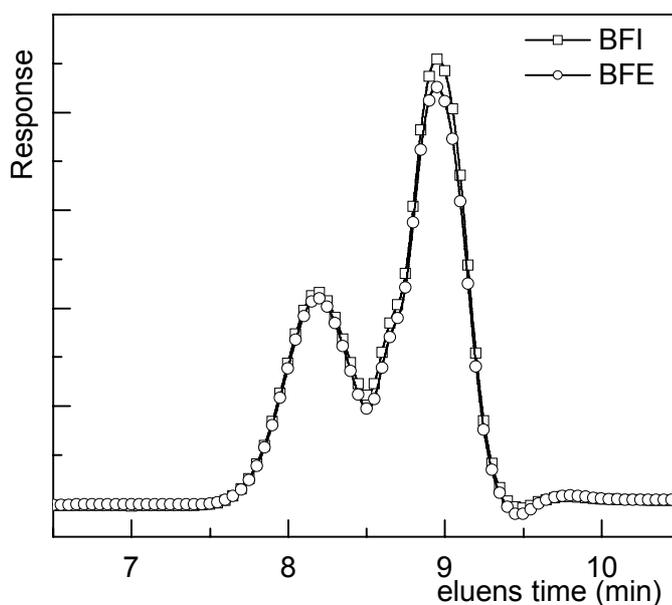


Figure 4: GPC diagram of drinking water before (BFI) and after (BFE) passing the biofiltration column. Flow rate: 1 l/h. Empty bed contact time: 84 min.

3.1.2 Effect of biofiltration on drinking water.

The COD and DOC values of drinking water were 20 mg/l and 7.7 mg/l respectively. During a test with an active biofilter where no concentrate was added to the diluting medium (drinking water) the COD and DOC values of the BFI and BFE were similar (Table 4). Figure 4 shows a chromatogram of gel permeation analysis of a

drinking water sample before (BFI) and after (BFE) passing the active bio filter. The chromatograms of both samples do not show any significant difference. Apparently the substances in this sample are not consumed. These findings indicate that the drinking water has a low biodegradability in this biofilter. It may therefore be justified to calculate the COD and DOC removal of the OP's with subtraction of the COD and DOC values of drinking water.

3.1.3 Effect of biofiltration on OP concentrate solutions

The results of the experiments with OP concentrate with different loading rates are shown in Table 4. According to measurements the gross COD and DOC removal is about 73% and 74% respectively for concentrate I and 53% and 47% respectively for concentrate II. When assuming zero biodegradability for the drinking water components, the COD and DOC removal of OP's is around 83% and 91% for concentrate I and 62% and 51% respectively for concentrate II. The lower removal percentages for concentrate II may be explained by the higher concentration of mesoxalic acid. Melin et al [7] found that mesoxalic acid (named ketomalonic acid in their report) showed the lowest biodegradability of all OP's.

Table 4: COD and TOC values of the biofilter influent (BFI) and effluent (BFE) during biofiltration experiments. Empty bed contact time: 84 min. Diluting medium: Drinking water. Flow rate diluting medium: 1 l/h. Samples were taken at stationary conditions.

Concentrate flow (ml/min)	BFI		BFE		COD ^a removal (%)	DOC ^a removal (%)
	COD (mg/l)	DOC (mg/l)	COD (mg/l)	DOC (mg/l)		
Concentrate I						
0	21	7.7	22.6	9.0	-10	-17
0.2	71	33	30	10	58 / 80	70 / 91
0.4	127	59	35	13	73 / 85	78 / 90
Concentrate II						
0.1	45		22		51 / 92	56 / 74
0.3	110	70	54	38	51 / 62	45 / 51
0.5	170	102	76	53	55 / 62	48 / 52

^a absolute removal / removal using drinking water DOC and COD as blank.

HPLC analysis shows that the majority of the OP components are removed from the solution after passing through the biofilter. This is shown in Figure 5 for concentrate I and Figure 6 for concentrate II. All peaks associated with OP compounds in the solution show a decrease when analyzed after passing the biofilter. This indicates removal of the associated compounds. Analysis by GPC of a BFI and BFE sample from a dilution of concentrate II (Figure 7) shows a decrease in small compounds (elution time approximately 8.8 min) after passing the biofilter. The large compounds (elution time 8.1 min) originate from drinking water (as diluting medium) and are associated with humic substances in the drinking water (see Chapter V). These compounds leave the biofiltration column untouched.

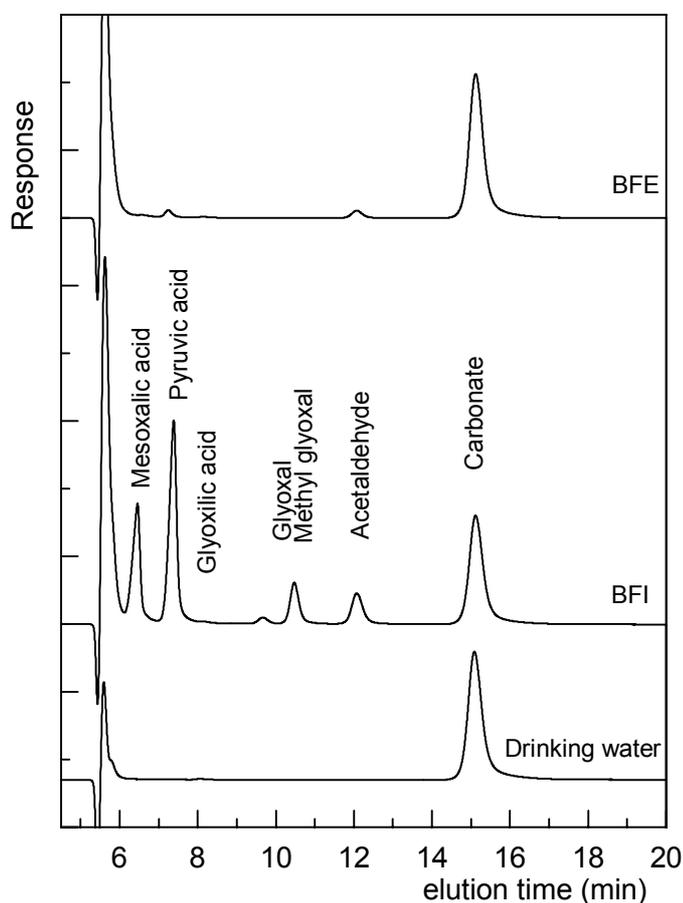


Figure 5: Result of HPLC analysis on drinking water, BFI and BFE. OP source: Concentrate I. BFI: COD = 121 mg/l, DOC = 61 mg/l. BFE: COD = 47 mg/l, DOC = 18 mg/l.

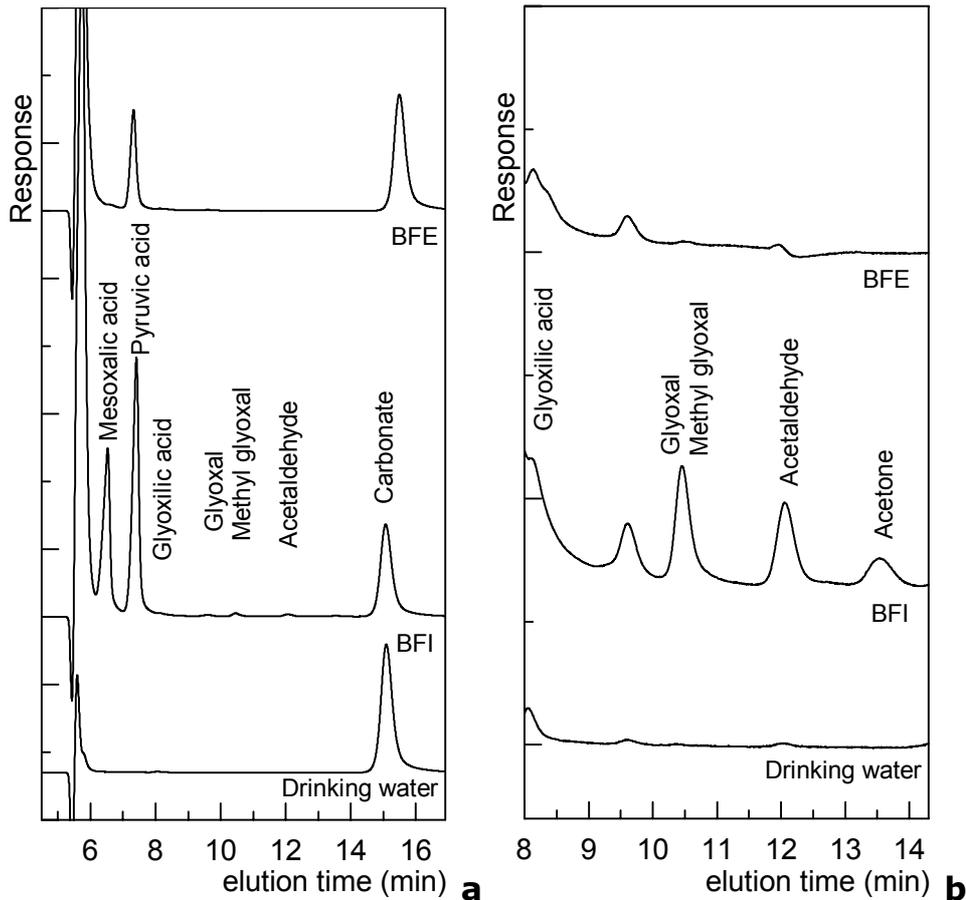


Figure 6: Result of HPLC analysis on drinking water, BFI and BFE. OP source: Concentrate II. a. Total chromatograms. b. Magnification of the chromatograms of Figure a between 8 and 14.5 minutes elution time.

At one point, while the biofilter was running under steady state conditions, the drinking water as diluting medium was replaced by demineralised water. After this replacement there was no activity measured in the biofilter: COD and DOC values in BFI and BFE were equal. This was probably caused by the low pH of the influent. When drinking water was used as diluting medium the influent pH was 6.5. Using demineralised water as diluting medium the pH dropped to 3.5, which is probably due to the low pH buffering capacity of demineralised water. This also indicates that under the experimental circumstances the adsorption of substrate on the biofilter packing material or biomass is not significant and removal probably occurs through metabolism by the biomass.

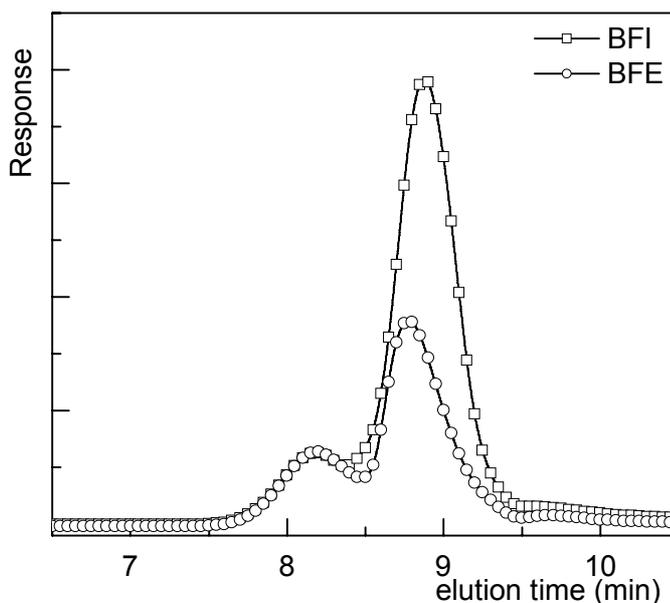


Figure 7: GPC diagrams of a sample from biofilter influent (BFI) and biofilter effluent (BFE). OP source: Concentrate II. Flow rate concentrate 0.50 ml/min. Flow rate diluting medium 1 l/h (16.7 ml/min). BFI: COD = 169 mg/l, DOC = 104 mg/l BFE: COD = 78.7 mg/l, DOC = 51.3 mg/l.

3.2 Ozonation/biofiltration of drinking water.

The effect of continuous ozonation/biofiltration of tap water can be seen by the GPC diagram in Figure 8. After ozonation the peak associated with the large HS compounds (8.2 min elution time) has decreased considerably. The peak area at 9 min elution time, associated with small organic compounds has increased after ozonation. After biofiltration the latter peak shows some reduction, indicating the removal of small compounds. The reduced peak associated with large HS compounds showed no change before and after biofiltration. This indicates that the large HS compounds are not removed by the biofilter. The reason is most likely the low biodegradability of these large compounds.

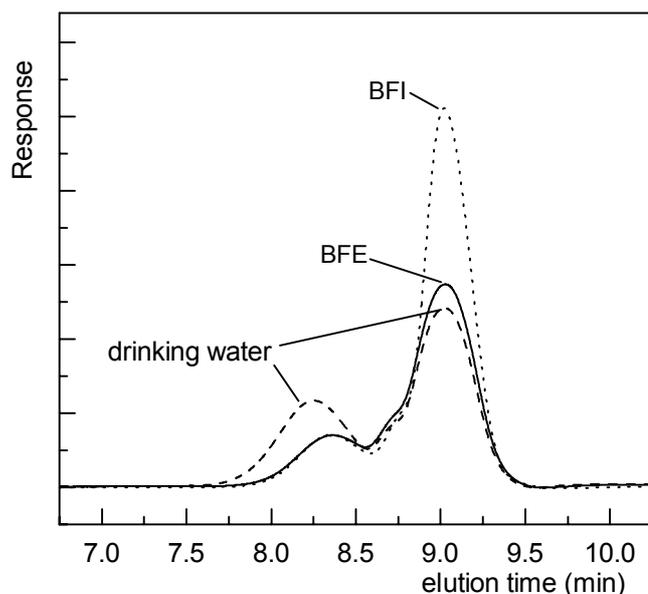


Figure 8: GPC diagrams of sample of drinking water, drinking water after ozonation (BFI) and after biofiltration (BFE).

4 Conclusions

It appears that the biofilter is able to remove small OP's under the experimental conditions. This was confirmed by DOC, COD and HPLC analysis. Removal by adsorption of substrate on the biomass or packing material is probably negligible. Components in rinking water (the diluting medium) showed no biodegradation over the biofilter on basis of analysis. When this is taken into account removal ratios of 90% DOC and 80% COD were achieved when using concentrate I and 60-90% DOC and 51% COD using concentrate II. The differences between the removal rates of concentrate I and II is attributed to a higher concentration of mesoxalic acid.

GPC analysis of samples of drinking water and ozonated drinking water indicate a clear reduction of HS compounds and an increase in ozonation products after ozonation. After passing the biofilter GPC analysis indicated a reduction in small ozonation products, but not in large compounds. However it could not be made clear whether the large ozonated compounds have a low biodegradability or that the biofilter had not adapted yet to these compounds at the time of the measurements.

The biofilter seems to become inactive at low pH values. With drinking water as diluting medium the biofilter was active and the pH

of the biofilter influent was 6.5. With demineralised water the pH of the influent was 3.5 and the biofilter showed no activity. When designing a biofiltration process after ozonation this fact should be recognized and some pH adjustments may be necessary.

Acknowledgement

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5 Nomenclature

symbols

A	Light absorption	(-)
c	concentration	(mol/m ³)
DOC	Dissolved organic carbon	(molC/l or mgC/l)
e	Molar extinction coefficient	(l/mol/cm)
D	Diameter	(cm)
d _c	Path length of cuvette	(cm)
COD	Cemical oxygen demand	(mg/l)

Abbreviations

BFI	Biofilter influent
BFE	Biofilter effluent
GPC	Gel permeation chromatography
HS	Humic substances
OP's	Ozonation products

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VIII

Evaluation and Outlook

In this chapter a brief evaluation of the ozonation/biofiltration process is made based on the experimental observations in this research. Some considerations on in-line treatment and side-stream treatment are made. In the end the use of a membrane contactor in this application is discussed based on mass transfer considerations. Considering the high conversion rate and the reaction kinetics a membrane contactor may be suitable as contacting medium in which the reaction takes place. However, it may be doubtful to use ozone oxidation to enhance the biodegradability of humic substances for complete removal. The process is probably unfavourable considering the effort and complete mineralization of a large part of the reaction products before all HS compounds have been converted into biodegradable products. High ozone demands and probably long residence times in the reactor might make the ozonation process economically unattractive. A good economic comparison with other destruction techniques (e.g. advanced oxidation processes or wet oxidation) should be made to draw final conclusions.

1 Discussion: side-stream/in-line treatment, energy-input (ozone)

Pumping station Spannenburg has an annual production of 25 million m³ of drinking water. The drinking water contains 7.8 mgDOC/l with a colour of 20 mgPt-Co/l. According to colour and DOC measurements and GPC analysis of samples taken during an ion-exchange adsorption process approximately 5 mg of the DOC amount is responsible for the colour and can be removed by ion-exchange adsorption (Chapter V, Appendix A).

When deciding to use an ozonation/biofiltration process for the removal of colour from drinking water there are two options of operation which both have their advantages and disadvantages (Table 1): 1. In-line treatment and 2. Side-stream treatment. The choice is based on which process is most cost effective or by other overruling priorities, such as environmental and public health matters.

1. In-line treatment.

Since the colour is the principle problem the aim may be only colour removal in stead of complete removal of humic substances. This demands less ozone per amount of DOC then complete removal of HS. The humic substances are not removed from the drinking water before treatment. Consequently all drinking water is processed; hence large process equipment is needed. In principle a potential health risk is introduced when ozonating organic compounds in drinking water (e.g. organic OP's and bromate formation), although ozonation of drinking water is common practice in many countries for several purposes [1].

2. Side-stream treatment.

The humic substances are first removed from the drinking water flow and then treated as a concentrated stream separately. In this way there is no potential health risk is created in the drinking water system. An important draw back however is that the concentrated HS stream is to be considered as wastewater and has to obey legal wastewater demands.

An advantage is that because the humic substances are concentrated (concentration factors of 5000 to 7000 are possible in ion-exchange adsorption) the necessary process volume is much smaller, so smaller process equipment is required. Removing the humic substances from the drinking water line and treating them separately leaves a guaranteed safe drinking water process Ødegaard et. al. reported in [2] a full scale plant of 200 m³/day in Nes, Norway where an ozonation/biofiltration process is in operation for colour removal. The humic substances are treated in line of the drinking water process using single medium sand filters for biodegradation. The costs for this treatment were estimated to be 0.5 NOK/m³ drinking water (0.06 €/m³) [3]. It cannot be prevented that some heterotrophic bacteria from the biofilter pass the sand filter. They now investigate the use of a membrane bioreactor as biodegradation step after ozonation [4, 5].

In the Netherlands drinking water company Vitens started the removal of humic substances from drinking water by an ion-exchange process [6]. The ion-exchange resin shows excellent removal ratios for humic substances. The resin is regenerated with a 10% NaCl solution. The resulting concentrate, the regenerate, is then concentrated by dead-end nanofiltration, where a concentration factor of 10 is achieved (recovery of 90% of the NaCl solution and a colour retention of 99%). The permeate can be reused for regeneration of the ion-exchange columns. The colour concentration of the concentrate after filtration is 140.000 mgPt-Co/l. The removal costs, including nanofiltration were estimated to be 0.04 €/m³ drinking water, of which 0.006 €/m³ (14% of the costs) is for discharge of the HS concentrate after nanofiltration [6].

Siegers et. al. [7] suggested to use wet oxidation (WO) (see Section 4.4.2, Chapter I) as a destructive treatment to remove humic substances after concentration by ion-exchange adsorption. WO becomes self-sustaining when the COD is above 20·10³ mg/l [8]. This figure is easily met by high HS concentrations from ion-exchange adsorption. Siegers et. al. estimated the total costs for such operation to be 0.05 to 0.06 €/m², although practical tests have not been done yet.

Table 1: Advantages and disadvantages in using an ozonation/biofiltration process for the removal of colour from drinking water.

	Advantages	Disadvantages
In-line treatment	<p>Aim: colour removal → "low" ozone demand</p> <p>No extra concentration step needed.</p>	<p>Large process volumes: $7 \cdot 10^4$ m³/day. Large process equipment.</p> <p>Undesired reactions with other components in drinking water</p> <p>Introduction potential health risks through OP's</p>
Side-stream treatment	<p>Small process volume 10 – 14 m³/day : small process equipment</p> <p>Only HS is treated</p> <p>No undesired effects in the drinking water process</p>	<p>Aim: DOC/COD removal → "high" ozone demand</p> <p>Extra process step needed: HS removal from drinking water</p> <p>In case of ion-exchange adsorption as removal step: salty waste stream</p>

2 Evaluation of ozone utilization for the (partial) oxidation of humic substances to enhance the biodegradability

2.1 Technical evaluation

In this research the removal of concentrated humic substances was investigated assuming a side-stream treatment, where the humic substances are concentrated by an ion-exchange adsorption process.

For the technical evaluation of the ozonation step the two main process criteria are:

1. Ozone demand for degradation of humic substances and efficiency. How much ozone is needed for sufficient enhancement of the biodegradability to meet at least the discharge criteria and how efficiently is the ozone utilized. This determines largely the energy demand and the sense in using an ozonation/biofiltration for degradation of humic substances.
2. Process speed. How much time does it take to ozonate the humic substances sufficiently so all humic substances are converted into biodegradable compounds? Parameters like mass transfer properties, ozone demand and reactant concentration are important here. These determine the reactor volume and residence time of a HS solution in the oxidation process.

Ozone demand and ozonation efficiency

Analysis of the molecular size distribution of humic substances during ozonation indicates that the degradation of the HS molecules occurs through split off of small molecules containing with a molecular weight smaller than 200 Dalton (Chapter V). These small components are easily biodegradable (Chapter VII). The large residual HS components probably show a low biodegradability. This means that for complete removal of humic substances all large components have to be converted into small compounds to reach full biodegradability.

In Chapter VI it is estimated that for complete degradation (although refractory compounds always remain) of the large compounds the ozone demand is at least 4 - 5 mgO₃/mgDOC. This

appears to be independent of the HS concentration. By this time the major part of the DOC content will be completely mineralized regarding the high DOC loss that was measured during the experiments. Considering the intended purpose of ozonation to partially oxidize the humic substances into biodegradable components, complete mineralization of humic substances is beyond the objective and probably economically undesirable. It is therefore questionable whether the ozonation/biofiltration is an efficient process for complete removal of humic substances. Considering the high DOC loss as a result of thorough ozonation one may even question whether it is still worth to install a biodegradation process after the ozonation step and instead extend the ozonation process a little further to complete mineralization of all organic components in the solution. It could not be determined whether the CO₂ formation was mainly due to reactions of ozone with the HS compounds or by further oxidation of the small ozonation products. If the latter is the case then the ozonation process may become more efficient when the small compounds that are formed are removed from the reaction solution (e.g. by an extraction or filtration process). This way, more ozone might be utilized for the oxidation of the large HS molecules instead of the complete oxidation of small compounds.

Ozone transfer during the ozonation process

Observing the results of reaction kinetics experiments that are reported in Chapter IV it can be concluded that during the initial stage the ozone uptake in the reaction solution occurs relatively fast (instantaneous) because fast reactions in the solution enhance the ozone transfer in the liquid phase. After this initial stage the ozone uptake decreases rapidly because the most reactive sites have then depleted. Further oxidation processes occur at a lower reaction rates and as the ozonation continues the ozone transfer to the HS solution approaches the rate of physical mass transfer (mass transfer in absence of reaction).

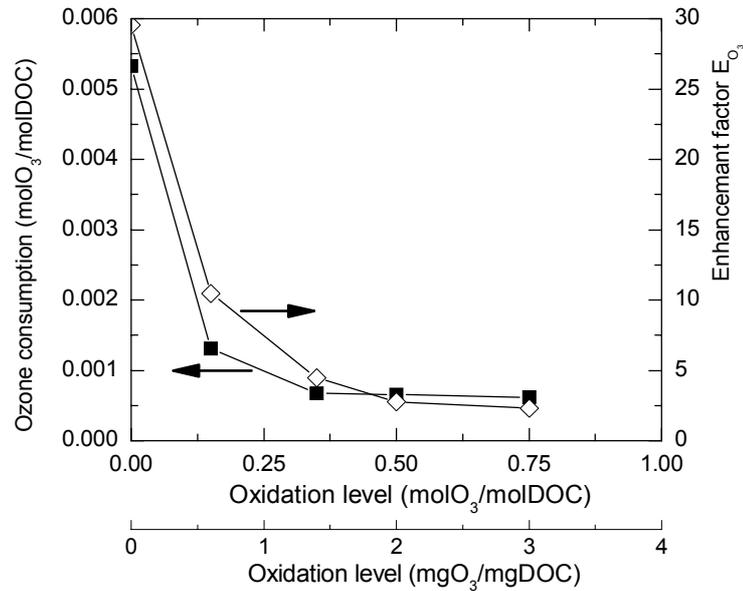


Figure 1: Enhancement factor of the ozone mass transfer and the ozone consumption of a HS solution, measured at several levels of ozone consumption. The ozone mass transfer was measured at a liquid flow rate of 0.23 m/s ($Re_L=114$, contact time 1.2 s), the ozone concentration in the feed was 0.36 mol/m³. Initial HS concentration: 33 molDOC /m³. Adapted from Chapter IV, Figure 3.

The physical mass transfer of ozone to a water phase is relatively slow due to the low solubility of ozone in water (see Chapter II). The decreasing ozone transfer to the reaction solution is illustrated in Figure 1 for an experimental case (see Chapter IV). It should be noted that in Figure 1 the ozone consumption and enhancement factor are presented as function of the oxidation level and not as function of the number of sequence steps or the total contact time in the membrane contactor. It can be assumed that for a specific ozone consumption of 1 molO₃/molDOC a much longer contact time is needed for the last 0.5 molO₃/molDOC than for the first 0.5 molO₃/molDOC since during the last oxidation stages, where the humic substances are already in an oxidized state, reactions are slow and the rate of mass transfer approaches the rate of physical mass transfer. This means that a high residence time may be required in a reactor especially when the ozone concentration in the gas phase is limited and implies that large reactor volumes are needed.

Translation to industrial conditions

In the experimental cases in this research the ozone concentration in the gas feed is relatively low: 0.36 mol/m^3 and also the HS concentration is far below the concentration that can be achieved with ion-exchange adsorption: 400 mgDOC/l (33 molDOC/m^3). With industrial ozone generators concentrations of 15 mol\% (7 mol/m^3) can be obtained, depending on the process conditions and using pure oxygen as feed gas [9, 10]. HS concentrations may reach up to 30 gDOC/l ($2.5 \cdot 10^3 \text{ molDOC/m}^3$) in the concentrated solutions. Furthermore the NaCl concentration will be much higher when treating humic substances concentrated by ion-exchange adsorption. As reported in Chapter IV, Appendix A the salt concentration has little influence on the reactions but will have a major influence on the ozone mass transfer since the solubility of ozone in water decreases with increasing ionic strength (Chapter II, Section 2.4). The reaction kinetics therefore may not be completely comparable, but the above described experimental situation gives a good idea of what may be expected.

2.2 Energy costs for ozonation production according to the demand

Modern ozone generators achieve an efficiency of 0.05 to 0.125 kgO_3/kWh . This is dependent on whether air or pure oxygen is used as feed gas [11]. In Table 2 an estimation of the energy costs for ozone production is presented based on the estimated ozone demand for sufficient oxidation of humic substances and the daily amount of humic substances that has to be treated. The ozone demand is based on the experiments that are reported in Chapter VI. The costs are calculated for the case where only colour removal and where complete removal of humic substances is the objective. From the point of view of energy costs the complete removal of HS is twice as costly as HS treatment for colour removal only. The costs per cubic meter of drinking water seem relatively low, however these are purely the energy costs for production of ozone and any process equipment and other maintenance costs are not taken into account here.

Table 2: Ozone demand and energy cost estimations for the situation of colour removal and complete HS removal. Ozone generation efficiency: 0.125 kgO₃/kWh (from pure oxygen) [10]. Energy costs taken at 0.05 €/kWh (Netherlands).

	Colour removal	HS removal
Ozone demand (mgO ₃ /mgDOC)	1.6 – 2.0 (90% removal)	3.5 – 4.5
Total ozone demand (kg/day)	0.6·10 ³ – 0.7·10 ³	1.2·10 ³ – 1.5·10 ³
Energy costs for ozone production (€/day)	2·10 ² – 3·10 ²	5 ·10 ² – 6·10 ²
Energy costs for ozone production (€/m ³ drinking water)	0.003 – 0.004	0.007 – 0.009

The capacity of a big modern ozone generator is up to 100 kg/h (2.4·10³ m³/day) and with modern technology ozone can be produced for less than 2 US\$/kg [12]. With the highest estimated ozone demand (1.5·10³ kg/day) the costs would then be 0.002 US\$/m³ drinking water. Considering the costs for discharge of the concentrated HS flow mentioned in Section 1 (0.006 €/m²), it will depend on the costs for investment, maintenance etc. whether the treatment is worth installing.

3 Is there sense in using a membrane contactor as ozonation reactor?

A membrane contactor with a reaction occurring in one of the phase can be considered as a reactor. In stead of “membrane contactor” the designation for such a system could then also be “membrane reactor”.

In Chapter III the advantages and disadvantages are described for using a membrane contactor in (industrial) processes. Whether it makes sense to use a membrane contactor depends on the mass

transfer benefits and costs. High mass transfer performances of membrane contactors are usually achieved by offering a high contacting area per unit of volume. However, also as reactor type a membrane module may have some advantages.

Membrane material

An important factor in ozone applications is that the process equipment needs to be highly chemically resistant. Furthermore, for best mass transfer performance the membranes need to be hydrophobic and porous with sufficiently small pores to prevent wetting at low trans-membrane pressures (see Chapter III). For membranes only a few materials seem to meet these demands: Teflon (PTFE), PVDF, PVC, silicone rubber (PDMS) and some ceramic materials (PDMS is sometimes used as dense layer on a porous support for ozone applications) [13-19]. Of the polymeric materials PTFE shows the highest resistance towards ozone.

These few choices in membrane materials hamper the successful development of a membrane with the desired mass transfer properties (highly porous membranes, small dimensions of hollow fibres). Materials like Teflon and PVDF are not easy to handle in membrane manufacturing. However, progress in membrane manufacturing show good promises for membranes with the desired properties.

Mass transfer considerations in gas-liquid contactors for ozone. Choice for a membrane contactor/reactor?

For complete HS removal high conversion rates are required. The oxidation starts off as a very fast reaction and reduces to a slow reaction as the most reactive sites deplete. The thorough ozonation of organic compounds is usually a slow process. Therefore, to meet the required ozone consumption for sufficient oxidation of the humic substances a long residence time in the reactor may be required.

Various ozone contactors are available to bring ozone in a gas phase into contact with a liquid [20]. The conventional bubble diffuser is the most widely used technology for ozone transfer because of its relatively simple operation and low energy input. It is a (baffled) container in which the ozone containing gas is bubbled. For higher ozone doses a turbine contactor can be used. Here turbines cause strong gas dispersion and liquid circulation. The power demand in this type of contactor is higher than in a simple bubble diffuser. In

systems with gas injectors very fine gas-liquid emulsions are generated permitting a high ozone transfer. A static mixer can be installed after a injection point to enhance gas-liquid mixing. These types of contactors can be installed in pipelines. In Table 3 some geometrical features important for mass transfer are presented for various types of contactors. Membrane contactors have a relatively low liquid hold up, but can offer a large interfacial area.

Table 3: Geometrical parameters of different contactors. All parameters, except for membranes adapted from Bin and Roustan [20]

Type of contator	Liquid hold up (%)	Interfacial area (m²/m³)
Bubble column	80-99	10-200
Agitated vessel	75-95	50-400
Static mixer	90-97	100-500
Packing or plate column	5-20	50-300
Spray column	5-10	
Membrane contactor	5-20 ^a	1500-20000 ^a

^a Own calculations based on dimensions of available membranes

When dealing with slow reactions ($Ha < 0.3$) the reaction takes place in the liquid bulk and the oxidation is limited by the low reaction rates. High concentrations of ozone are then desired to speed up the conversion rate. In systems where the mass transfer is slow due to a relatively high liquid side resistance or low driving forces, membrane contactors could be beneficial, provided that a substantially larger interfacial area is present per unit of process volume compared to other contactors. High ozone concentrations can then be supplied to speed up the conversion.

When reactions are fast compared to the physical mass transfer ($Ha > 2$) the conversions become controlled by mass transfer of the reactants and reactions take place near the gas-liquid interface (see Chapter IV). Ozone has depleted near the interface before it reaches

the liquid bulk. Here, a large interfacial area is desired to situate as much liquid near a gas-liquid interface as possible.

A drawback in using membrane contactors for this purpose is that they add an extra resistance for mass transfer that could become significant when operating at low liquid side mass transfer resistances, i.e. at high flow rates and/or a fast reaction in the liquid phase. It is then the value of $k_m \cdot a$ that determines the efficiency of the membrane as gas-liquid contactor.

In terms of model reactors a membrane reactor can be regarded as a tube reactor or plug-flow reactor (PFR). These types of reactors are suitable when high conversions are required [21]. It is however very likely that long residence times are required to obtain the desired oxidation of the humic substances. A long residence time means a large reactor volume, which could mean very long reaction tubes with technical and economical disadvantages [21]. The final reactor design depends on the HS concentration, ozone demand, ozone supply (flow rate and concentration in the gas phase), and the mass transfer resistances in each phase (determined by flow rates, solutes etc).

4 Overall conclusion

Based on mass transfer considerations a membrane contactor is technically a suitable reactor for the ozonation of concentrated humic substances. The potentially large contact area enhances the mass transfer of ozone to the water and speed up the conversion of humic substances and reduce the time for treatment.

Based on the overall considerations on ozone demand and ozonation products it is doubtful that the ozonation/biofiltration process is an economically favourable method for complete removal of concentrated humic substances in water. This is mainly due to the high ozone demand and probably long time that is required for sufficient oxidation to convert all large humic molecules into biodegradable compounds. High DOC losses indicate that complete mineralization of the small compounds or small parts of the molecule occurs substantially while large, not biodegradable components, are still present in the solution. This would imply that ozonation will be responsible for the major part of the removal of humic substances and biofiltration would remove only a small part. This degradation technique should be compared with other oxidation techniques like

AOP's or wet oxidation to estimate which technique is more cost effective.

5 Nomenclature

Symbols

a	contact area/interfacial area	m^2
k_m	mass transfer coefficient of the membrane	m/s

Abbreviations

AOP	Advanced Oxidation Process (see chapter II)
DOC	Dissolved organic carbon
GPC	Gel permeation chromatography (see Chapter V)
Ha	Hatta-number (see Chapter IV)
PVC	Polyvinylchloride
PDMS	Polydimethylsiloxane
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene difluoride

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Summary

Stringent legislation on drinking water quality force drinking water companies into active removal of the colour of the drinking water. The compounds responsible for this colour are so-called humic substances (HS). Humic substances comprise large, complex organic molecules in soil and surface water originating from microbial decay of dead organisms and give an undesirable yellow colour to (drinking) water. Coloured drinking water occurs when e.g. it is drawn from peat soils. They are not removed by the conventional drinking water treatment processes due to their high resistance for biodegradation.

For the treatment of these humic substances there are two choices: 1. In-line treatment, where the humic substances are treated in the drinking water process line. 2. Side stream treatment. Here, the humic substances are first removed from the drinking water line and may then be broken down by some destructive method.

The goal of the research was to investigate the degradation of concentrated humic substances by an ozonation/biofiltration system in a side-stream process. The humic substances were concentrated by ion-exchange adsorption and the research was mainly focused on the ozonation of humic substances. To bring the ozone into contact with the HS solution an ozone resistant PVDF membrane module was constructed to serve as gas-liquid contactor.

The main topics in this research were:

- Ozone mass transfer in a PVDF hollow fibre membrane contactor and investigate the module performance.
- Investigation of the reaction kinetics of the ozonation of concentrated humic substances by means of a hollow fibre membrane contactor. It can be as model gas-liquid contactor on account of some characteristic features like a well known contact

area and well described mass transfer properties for transport inside the fibres.

- Characterization and identification of reaction products from the ozonation of humic substances.
- Investigation of the influence of the HS concentration on the efficiency of the ozonation process.
- Investigation of the biodegradability of the ozonation products of humic substances.

From experiments and mass transfer considerations it may be concluded that a membrane contactor with sufficiently large contact area per unit of volume and sufficiently low resistances for mass transfer in the membranes could be beneficial in these kinds of ozonation processes.

Because of its well known contact area, the well described mass transfer behaviour in the fibres and the ease to operate under steady state conditions the membrane contactor was used as a means to study the reactions kinetics of the ozonation of humic substances. According to the mass transfer experiments in the membrane contactor the ozonation reactions start off as instantaneous reactions compared to the physical mass transfer resulting in high mass transfer enhancement factors. As the ozonation process continues the reaction speed decreases down to a fast regime and from there towards a slow reaction regime. However, the mass transfer seems to be enhanced even by the relatively slow reactions where oxidation processes have slowed down due to a strong degree of oxidation of the organic compounds.

The (average) diffusion coefficient of humic substances was calculated to be $6.1 \cdot 10^{-11}$ m²/s which lies in the range of diffusion coefficients found by other methods reported in literature.

Through analysis with gel permeation chromatography (GPC) and high performance liquid chromatography (HPLC) a number of compounds that are known as products of ozonation of humic substances could be identified in the samples from ozonated HS solutions. Measurements of the molecular size distribution and calculation of average molecular weight of the humic substances indicated that the molecular size of the humic substances decreases gradually during the ozonation process from approximately $2.5 \cdot 10^3$ Dalton to $1.5 \cdot 10^3$ Dalton at an ozone consumption of 0.65 molO₃/molC. The polydispersity of the humic compounds is relatively low with a value of 1.23 for untreated humic substances and 1.09 for

ozonated humic substances, indicating that the molecular size distribution decreased during ozonation. Meanwhile, only small compounds (< 200 Dalton) are being split of the large molecules during the ozonation process according to an outside-in trimming mechanism. A large DOC loss, mostly attributed to formation of carbon dioxide, indicates a high degree of complete oxidation of carbon atoms, while large molecules are still present in the solution. This indicates that the ozonation process, as supposed to being a treatment step prior to biodegradation to enhance the biodegradability, is not efficiently utilized.

Analysis of samples from ozonation experiments with different concentrations of humic substances in the reaction solutions indicated that the ozone efficiency does not change when different HS concentrations are applied. To reach the same degree of change in water quality parameters (DOC, colour, COD) and change in molecular size the specific ozone demand (ozone consumption per amount of HS) is similar for different HS concentrations. The DOC loss was 45% and the colour decreases with 95% after a specific ozone consumption of 0.6 molO₃/molDOC. A relatively slow decrease of the specific COD (20%) compared to a relatively large DOC decrease (50%) at the same ozone consumption indicates that the complete oxidation of C-atoms occurs in a stronger extent than partial oxidation of residual HS components. Extrapolation of the peak area in GPC diagrams against the specific ozone consumption indicates that for full degradation of the large compounds an ozone demand of at least 4 to 5 mgO₃/mgDOC is required.

Biofiltration tests with synthetic solutions of ozonation products were run to investigate the biodegradability. These synthetic solutions were composed out of compounds identified as products of ozonation, like acetaldehyde, ketomalonic acid, pyruvic acid, glyoxal, glyoxilic acid etc. The tests showed that these products are relatively easy biodegradable. It seems that drinking water contained no significantly biodegradable compound. A continuous ozonation/biofiltration experiment with drinking water showed that the humic substances were broken down partially after ozonation while the amount of small compounds increased. After passing the biofilter there was some reduction observed of small compounds but no reduction of large residual compounds that are associated with large HS compounds.

The large amount of ozone that is probably needed for full conversion of the humic compounds into biodegradable products, could make the ozonation process a costly undertaking. Furthermore, far going oxidation of humic substances may take a long period since the oxidation in the far stage is a very slow process. Therefore, long residence times will be needed for sufficient conversion, which implies the need of large reactors.

For an economic evaluation the ozonation/biofiltration process should be compared with other strong destructive methods like wet oxidation or the application of advanced oxidation processes. In these kinds of processes a membrane contactor could be very beneficial if a large contact area per volume can be provided. If ozone reactions run fast then the reactions occur near the interface and ozone has depleted before it reaches the liquid bulk. It is then important to bring the liquid close to the interface, hence large contact area per volume of liquid would be beneficial. If reactions run slow the conversion can be enhanced by high ozone concentrations. However, physical mass transfer is slow due to the low solubility of ozone in water. A large contact area is then beneficial to enhance the ozone mass transfer to achieve high ozone concentrations in a short time.

Samenvatting

Striktere wetgeving op het gebied van drinkwaterkwaliteit nopen drinkwaterbedrijven tot actieve verwijdering van de kleur uit drinkwater. De stoffen in drinkwater die verantwoordelijk zijn voor deze kleur zijn zogenaamde humuszuren (HZ). Deze humuszuren bestaan uit natuurlijke grote complexe organische moleculen die zich in de grond en in het oppervlakte water bevinden. Ze zijn ontstaan door microbiologische afbraak van dode plantaardige en dierlijke organismen en geven het (drink-)water een ongewenste gele kleur.. Gekleurd drinkwater komt bijvoorbeeld voor wanneer dit gewonnen wordt uit veengronden. Humuszuren worden niet door het conventionele drinkwaterzuiveringsproces verwijderd door hun hoge weerstand tegen biodegradatie.

Voor de behandeling van de humuszuren in drinkwater bestaan twee keuzemogelijkheden: 1. In-line behandeling, waarbij de humuszuren behandeld worden in de proceslijn van de drinkwaterzuivering. 2. Side-stream behandeling, waarbij de humuszuren eerst uit het drinkwater worden verwijderd om vervolgens eventueel afgebroken te worden door een destructieve methode.

Het doel van het onderzoek was om de afbraak van geconcentreerde humuszuren in een ozonisatie/biofiltratie systeem als side-stream proces te bestuderen. Het onderzoek was voornamelijk gefocuseerd op de ozonisatie van humuszuur. Voor deze toepassing werd een ozon resistente membraanmodule geconstrueerd met PVDF holle-vezelmembranen. Deze module fungeerde als gas-vloeistofcontactor om het ozon met de humuszuuroplossing in contact te brengen. Geconcentreerd

humuszuur werd verkregen door middel van een ion-wisseling adsorptie proces

De voornaamste onderzoeksthema's waren:

- Stof transport van ozon in een PVDF holle-vezelmembraancontactor en het onderzoeken van de eigenschappen van de module.
- Onderzoek naar de reactiekinetiek van de ozonisatie van geconcentreerde humuszuren. Dit werd gedaan met behulp van een holle-vezelmembraancontactor die gebruikt werd als model gas-vloeistofcontactor op basis van zijn karakteristieke kenmerken zoals een nauwkeurig bekend contact oppervlak en een goede beschrijving van de stofoverdrachtsverschijnselen binnen in de vezels.
- Karakterisering en identificatie van reactieproducten voortkomend uit de ozonisatie van humuszuren.
- Onderzoek naar de invloed van de humuszuurconcentratie in de reactieoplossing op de efficiëntie van het ozonisatieproces.
- Bestudering van de biodegradeerbaarheid van de ozonisatieproducten.

Om zijn nauwkeurig bekende contactoppervlak, de goed beschreven stofoverdrachtsverschijnselen in de vezels en het gemak van het opereren onder steady-state omstandigheden is membraancontactor aangewend als hulpmiddel om de reactiekinetiek van de ozonisatie van humuszuren te bestuderen. Volgens de stofoverdrachtsexperimenten in de membraancontactor begint de ozonisatiereactie als een instantane reactie vergeleken met het fysieke stoftransport (zonder reactie). Dit resulteert in hoge versnellingsfactoren voor stofoverdracht. Terwijl het ozonisatieproces voortgaat daalt de reactiesnelheid tot een "snelle reactie" en van daar uit naar een "langzame-reactieproces", waar de oxidatie processen trager worden door een hoge oxidatiegraad van de organische componenten. Echter, het lijkt erop dat ook bij relatief langzame reacties de stofoverdracht versneld nog wordt. De berekende (gemiddelde) diffusiecoëfficiënt voor humuszuren is $6.1 \cdot 10^{-11} \text{ m}^2/\text{s}$. Dit ligt in het bereik van diffusiecoëfficiënten van humuszuren in water berekend volgens andere methoden die vermeld zijn in de literatuur.

Met behulp van gel permeation chromatografie (GPC) en high performance vloeistof chromatografie (HPVC) konden een aantal bekende producten van humuszuurozonisatie worden geïdentificeerd.

Bepaling van de molecuulgewichtsverdeling en berekening van het gemiddelde molecuulgewicht van de humuszuren wezen op een verlaging van het molecuulgewicht van de humuszuren tijdens het ozonisatieproces van $2.5 \cdot 10^3$ Dalton tot $1.5 \cdot 10^3$ Dalton bij een ozonopname van $0.65 \text{ molO}_3/\text{molC}$. De polydispersiteit van de humuszuurmoleculen is relatief laag met een waarde van 1.23 voor onbehandeld humuszuur en een waarde van 1.09 voor geozoniseerd humuszuur. Dit betekent dat de molecuulgewichtsverdeling van de overgebleven gedeeltelijk geoxideerde humuszuren nauwer wordt tijdens het ozonisatieproces. Ondertussen worden slechts relatief kleine componenten (< 200 Dalton) van de grote moleculen afgesplitst door de oxidatiereacties. Dit lijkt te gebeuren volgens een zogenoemd outside-in trimming mechanisme.

Een hoog DOC verlies, vooral door vorming van kooldioxide, wijst op complete oxidatie van koolstofatomen, terwijl er nog steeds grote HZ moleculen met een lage oxidatiegraad aanwezig zijn in de oplossing. Dit geeft aan dat het ozonisatieproces, wat bedoeld is als voorbehandeling om de biodegradeerbaarheid te verhogen, niet efficiënt wordt angewend.

Analyse van oplossingen uit ozonisatie-experimenten met verschillende HZ concentraties in de reactieoplossing wees uit dat de ozonisatie-efficiëntie niet wijzigt bij veranderende HZ concentraties. Het specifieke ozonverbruik in de oplossingen die nodig is om een bepaald niveau van verandering te bereiken in de waterkwaliteitsparameters (DOC, Kleur, CZV) en in molecuulgrootte is gelijk bij gebruik van verschillende HZ concentraties. Het DOC-verlies was 45% en de hoeveelheid kleur verlaagde met 95% na een specifieke ozonconsumptie van $0.6 \text{ molO}_3/\text{molDOC}$ ($2.4 \text{ mg O}_3/\text{mgDOC}$). Een relatief langzame afname van de specifieke CZV (20%), vergeleken met een relatief hoog DOC verlies (50%) bij dezelfde ozonconsumptie wijst erop dat volledige oxidatie van koolstofatomen in een sterkere mate plaatsvindt dan de partiële oxidatie van grote HZ moleculen die aanwezig zijn.

Extrapolatie van het piekoppervlak in de GPC-diagrammen tegen de specifieke ozonconsumptie geeft aan dat een ozonconsumptie van ten minste 4 tot 5 $\text{mgO}_3/\text{mgDOC}$ vereist is voor volledige afbraak van de grote componenten in de HZ oplossing tot.

Om de biodegradeerbaarheid van ozonisatieproducten te onderzoeken werden biofiltratie-experimenten uitgevoerd met synthetische oplossingen van bekende kleine producten van

humuszuurozonisatie. De experimenten wezen uit dat deze producten relatief gemakkelijk biodegradeerbaar zijn.

Het lijkt erop dat drinkwater geen significante hoeveelheden biodegradeerbare producten bevat. Een experimenteel continue ozonisatie/biofiltratieproces met drinkwater liet zien dat de humuszuren gedeeltelijk waren afgebroken na de ozonisatiestap, terwijl de hoeveelheid kleine organische componenten toenam. Na het passeren van de biofilter werd een afname gemeten van kleine componenten, maar niet van grote overgebleven componenten die geassocieerd worden met de grote (overblijfselen van) humuszuren.

De grote hoeveelheid ozon die waarschijnlijk nodig is om alle humuszuren om te zetten in biodegradeerbare componenten kan het ozonisatie proces vanuit energieoogpunt een kostbare onderneming maken. Tevens maakt een vergaande oxidatie van humuszuren een lange verblijftijd in de reactor noodzakelijk, omdat de oxidatiesnelheid sterk afneemt bij toenemende oxidatiegraad van de componenten. Dit betekent dat relatief grote reactoren nodig zijn om deze lange verblijftijd mogelijk te maken.

Voor een economische evaluatie zou het ozonisatie/biofiltratieproces vergeleken moeten worden met andere sterk destructieve methoden zoals natte oxidatie of de toepassing van zogenaamde Advanced Oxidation Processen (combinatie van ozon, UV straling en/of waterstofperoxide).

In dit soort processen zou een membraancontactor goed toepasbaar zijn wanneer een groot contactoppervlak per volume-eenheid mogelijk is. Wanneer de reactiesnelheid hoog is dan vinden de reacties voornamelijk dicht bij het contactoppervlak plaats. In dit geval is een groot contactoppervlak per volume-eenheid vloeistof nuttig. Wanneer reacties langzaam gaan dan wordt de omzetsnelheid verhoogd door hogere ozonconcentraties in de oplossing. Echter, de fysieke stofoverdracht van ozon van gas naar vloeistof is langzaam door de lage oplosbaarheid van ozon in water. Een groot contact oppervlak is dan nuttig om de overdracht van ozon te vergroten in een korte tijd.

