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Review

Ozone oxidation for the alleviation of membrane fouling by natural organic matter: A review

Steven Van Geluwe[a,*], Leen Braeken[a,b], Bart Van der Bruggen[a]

[a] Laboratory of Applied Physical Chemistry and Environmental Technology, Department of Chemical Engineering, K.U. Leuven, W. de Croylaan 46, B-3001 Leuven (Heverlee), Belgium
[b] Department of Industrial Sciences and Technology, KHLim, Universitaire Campus Gebouw B, Bus 3, B-3590 Diepenbeek, Belgium

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ABSTRACT

Membrane fouling by natural organic matter is one of the main problems that slow down the application of membrane technology in water treatment. O_3 is able to efficiently change the physico-chemical characteristics of natural organic matter in order to reduce membrane fouling. This paper presents the state-of-the-art knowledge of the reaction mechanisms between natural organic matter and molecular O_3 or $^{\bullet}OH$ radicals, together with an in-depth discussion of the interactions between natural organic matter and membranes that govern membrane fouling, inclusive the effect of O_3 oxidation on it.

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* Corresponding author. Tel.: +32 16 322 341; fax: +32 16 322 991.
E-mail addresses: steven.vangeluwe@cit.kuleuven.be (S. Van Geluwe), leen.braeken@khlim.be (L. Braeken), bart.vanderbruggen@cit.kuleuven.be (B. Van der Bruggen).

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Abbreviations

AOP	advanced oxidation process
BOD_5	biological oxygen demand after 5 days
COD	chemical oxygen demand
DBP	disinfection by-product
DOC	dissolved organic carbon
FTIR	Fourier transform infrared
HAA	haloacetic acid
IEP	isoelectric point
MF	microfiltration
MWCO	molecular weight cut-off
NF	nanofiltration
NMR	nuclear magnetic resonance
NOM	natural organic matter
PVDF	polyvinylidene fluoride
RO	reverse osmosis
SBH	Staehelin, Bühler and Hoigné
THM	trihalomethane
TOC	total organic carbon
UF	ultrafiltration
USEPA	United States Environmental Protection Agency
UVA	absorbance (optical density) of UV irradiation

1. Introduction

Membrane technology has become well established in water treatment, and the demand for membranes increases yearly by 8% (Leiknes, 2009). The most important type of membrane processes are pressure-driven, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Typical values of the main membrane characteristics, i.e. water permeability, operating pressure, pore size and retention characteristics for these four membrane types are listed in Table 1. Because of the large pores of the MF and UF membranes, the water flux is high while the transmembrane pressure is low. MF is used for the removal of suspended particles, turbidity and various micro-organisms (Yuan and Zydney, 1999), while UF removes viruses (van Voorthuizen et al., 2001), colloids and the high-molecular mass fraction of natural organic matter (NOM) as well (Siddiqui et al., 2000; Lee et al., 2005a; Kennedy et al., 2005). NF membranes have smaller pores, but still maintain a fairly high flux at a reasonable pressure. NF is very effective in the removal of the medium- and lower-molecular mass fraction of NOM (Siddiqui et al., 2000; Shon et al., 2004; Meylan et al., 2007; de la Rubia et al., 2008), and emerging micropollutants such as pesticides, pharmaceuticals and endocrine disrupting chemicals (Kimura et al., 2003; Nghiem et al., 2004; Yoon et al., 2006; Verliefde et al., 2007). The retention of inorganic ions by NF membranes is strongly dependent on the charge of the ions. The retention of divalent ions ranges between 50 and 100%. It is much higher than the retention of monovalent ions, which is usually lower than 40%, because of Donnan exclusion (de la Rubia et al., 2008; Ouyang et al., 2008). RO is commonly used for desalting brackish water and seawater, but operates under very high transmembrane pressures and a low permeate flux compared to the other pressure-driven membranes. However, RO shares about 45% of the global production capacity of desalinated water, because of its lower energy consumption compared to multistage flash evaporation (Darwish and Al-Najem, 2000; Eltawil et al., 2009).

In spite of the excellent retention characteristics of membrane filtration in water treatment, there are still problems that slow down its growth. The best known problem is fouling of the membrane, which results in a reduction in water flux, and thus leads to higher operating costs. Over time, fouling and subsequent cleaning of the membranes causes deterioration of membrane materials, resulting in a compromised permeate water quality and ultimately, a shorter membrane lifetime (Košutić and Kunst, 2002; Seidel and Elimelech, 2002; Al-Amoudi and Lovitt, 2007). Membrane fouling is usually minimized by an excessive pretreatment or else a very conservative membrane flux needs to be used. Consequently, the capital cost is high, which makes membrane filtration less competitive against conventional water treatment technologies (such as coagulation or activated carbon) in certain cases (Pianta et al., 2000).

The emerging use of O_3 oxidation in water treatment offers new opportunities, because O_3 is able to decompose certain membrane foulants very efficiently. The present paper is a critical review of literature concerning the fouling potential of NOM in water purification and the use of O_3 oxidation for the alleviation of membrane fouling by NOM. The effect of O_3 oxidation on membrane fouling is difficult to predict due to the complex nature of NOM, the strong variability of the NOM characteristics and the water matrix with location, season and weather (Lowe and Hossain, 2008), and the major effect of the water matrix on the conformation of NOM and the decomposition of O_3. This review paper presents the reaction

Table 1 – Comparison between the four pressure-driven membrane processes with respect to permeability, applied pressure, pore size and rejection characteristics.

	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse osmosis (RO)
Pure water permeability (L m^{-2} h^{-1} MPa^{-1})	>>500	100–500	15–150	0.5–15
Transmembrane pressure (kPa)	10–100	100–500	500–2000	2000–4000
Pore size (nm)	100-10,000	2–100	0.1–2	< 1
Molecular weight cut-off (g mol^{-1})		1000–100,000	150–1000	
Retention:				
Suspended particles	+	+	+	+
Macromolecules	−	+	+	+
Small organic molecules	−	−	−/+	+
Multivalent salts	−	−	+	+
Monovalent salts	−	−	−/+	+

mechanisms and its products when NOM solutions are treated by O_3 or $O_3 + H_2O_2$, and the various interactions that exist between NOM components and the membrane surface. The relation between the complex fouling behavior of NOM, before and after its reaction with O_3, is discussed in a systematic and detailed way, in order to better understand the mechanisms behind the fouling reduction in water treatment by O_3 treatment.

2. The chemical composition of different NOM fractions

NOM is a complex heterogeneous mixture of organic material, such as humic substances, polysaccharides, aminosugars, proteins, peptides, lipids, small hydrophilic acids, and others (Frimmel et al., 2002). In a first approach to separate the different components in NOM, it is divided into two major classes. The first class, i.e. autochthonous NOM, is derived from extracellular macromolecules of micro-organisms in the water body and carbon fixation by algae and aquatic plants. The second class, allochthonous NOM, is derived from the decay of plant and animal residues in the watershed (Frimmel et al., 2002). It is usually referred to as humic substances, and this term will be used in the remaining text.

Although the correct chemical structure of humic substances still remains unknown, they consist of a skeleton of alkyl and aromatic units, cross-linked by a variety of functional groups. Humic substances are high in aromatic carbon and have a negative charge. This charge is primarily contributed by their three main functional groups, namely carboxylic acids, methoxyl carbonyls and phenolic functional groups (Thurman, 1986). The chemical properties of humic substances are succinctly explained by McDonald et al. (2004) and Sutzkover-Gutman et al. (2010). The humic substances present in natural waters are traditionally divided into two categories, namely humic and fulvic acids. Humic acids have a higher molecular mass (2000–5000 g mol^{-1}) than fulvic acids (500–2000 g mol^{-1}) (Her et al., 2003). They have a lower oxygen content and are more hydrophobic than fulvic acids (Thurman, 1986).

The knowledge of the structural chemistry of humic substances is somewhat like that of proteins in the middle of the last century. Although the main building blocks are known, there are no conclusive studies about the long-range conformational structure of humic substances. This is probably because of the difficulty of obtaining reliable structural data, due to the size and number of stereochemical isomers (Jansen et al., 1996). In addition, the conformation of humic substances may vary significantly due to changes in pH (humic substances are highly deprotonated is most aquatic environments), cation concentration (humic substances form strong complexes with metals and other cations) and the great stabilization effect on the electrostatic energy by the presence of water molecules (Kubicki and Apitz, 1999). Therefore, the complexity of humic substances in its natural environment is too high for the application of modeling techniques on an atomic scale.

Autochthonous NOM includes a large number of relatively simple compounds of known structures: carbohydrates, aminosugars, proteins, peptides, small organic acids, etc. The main functional groups in autochthonous NOM are carboxylic acids, alcohols and amines, which make these compounds hydrophilic, in contrast to the more hydrophobic humic substances. The molecular mass of these hydrophilic compounds shows a great variety. The simple organic molecules have a molecular mass of a few 100 g mol^{-1}, and thus have an apparently smaller molecular size than humic substances, while the biopolymers, such as polysaccharides and proteins, have a molecular mass between 10,000 and 30,000 g mol^{-1} (Lee et al., 2004), which is about one order of magnitude higher than the molecular mass of humic substances. Polysaccharides present in surface water have a diameter in the range between 2 and 20 nm. They have a linear molecular structure and can be hundreds of times longer than wide and can be branched (Leppard, 1997).

3. The decomposition of NOM by ozone and hydroxyl radicals

3.1. *Ozone reacts selectively with certain functional groups in NOM*

O_3 is a powerful oxidant and its high reactivity can be attributed to the electronic configuration of this molecule. The O_3 molecule represents a hybrid, formed by the two possible resonance structures shown in Fig. 1. The positive formal charges on the central oxygen atom in both resonance structures explains the electrophilic character of O_3.

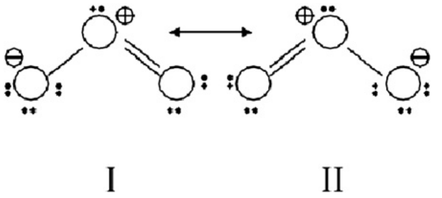

Fig. 1 – Resonance forms of the O_3 molecule. Adapted from Beltrán (2004).

Conversely, the excess negative charge present in one of the terminal atoms imparts a nucleophilic character to O_3. These properties make O_3 an extremely reactive compound (Beltrán, 2004).

The electrophilic character of O_3 accounts for the very fast reaction of O_3 with unsaturated bonds (von Gunten, 2003a). The fast reaction of O_3 with double bonds and aromatic rings present in NOM molecules, is manifested by a sharp decrease of the optical density at 254 nm (UVA_{254}) during ozonation. For instance, Song et al. (2010) reported a UVA_{254} reduction of 71% in surface water treatment, at a O_3 dosage of 3.0 mg L^{-1} (oxidation time: 10 min). Wang and Pai (2001) reported a reduction of 40% for biologically treated wastewater effluents, and Lee et al. (2009) observed a reduction of 55% for RO concentrates in wastewater reclamation, at the same O_3 dosage and oxidation time. Although O_3 oxidation is able to efficiently remove unsaturated bonds, it shows only a minor dissolved organic carbon (DOC) removal under acceptable economic conditions. Typical reductions of DOC achieved by ozonation in drinking water plants, with O_3 doses between 2 and 5 mg L^{-1}, is only about 10–20% (Can and Gurol, 2003). The DOC removal in the experiments of Song et al. (2010) was approximately 10%. Wang and Pai (2001) reported 15% DOC removal, while Lee et al. (2009) observed 5% DOC removal, for the same O_3 dosage and oxidation time as mentioned above.

von Gunten (2003a) reports that O_3 preferentially reacts with unsaturated bonds to oxygenated saturated functional groups, such as aldehydic, ketonic and especially carboxylic groups. This can be demonstrated by the results of different spectroscopic techniques. Nuclear magnetic resonance (NMR) spectroscopy by Westerhoff et al. (1999), used for investigating the oxidation of surface waters by O_3, found a depletion of aromatic against aliphatic moieties. The O_3 consumption was positively correlated with aromatic carbon content, especially electron enriched aromatics, and inversely correlated with aliphatic carbon content. Fluorescence spectra of NOM solutions, before and after O_3 oxidation (Świetlik and Sikorska, 2004; Zhang et al., 2008), revealed a reduction of the number of aromatic rings and conjugated bonds, and the decomposition of condensed aromatic moieties to smaller molecules. The number of electron withdrawing groups, such as carboxyl, carbonyl, hydroxyl, alkoxyl and amino groups, increased during ozonation. Mass spectrometry analysis of Suwannee River fulvic acids, by These and Reemtsma (2005), showed that O_3 removes preferentially molecules with a low oxidation state (low O/C ratio) and a high degree of unsaturation (low H/C ratio). They also observed that molecules with a more extended carbon skeleton and less carboxylate substituents showed higher reactivity, whereas some highly unsaturated molecules did not show measurable removal up to a specific O_3 dose of 2.5 mg per mg DOC. The reaction products were characterized by a very high number of carboxylate groups, i.e. the O/C ratio increased from 0.2 to 0.7.

Ozonation products can generally contain alcoholic, carbonyl and carboxyl groups (von Gunten, 2003a). The main reaction products after ozonation mainly consist of short-chain (<C5) carboxylic acids, such as formic, acetic and particularly oxalic acid, and aldehydes, such as formaldehyde,

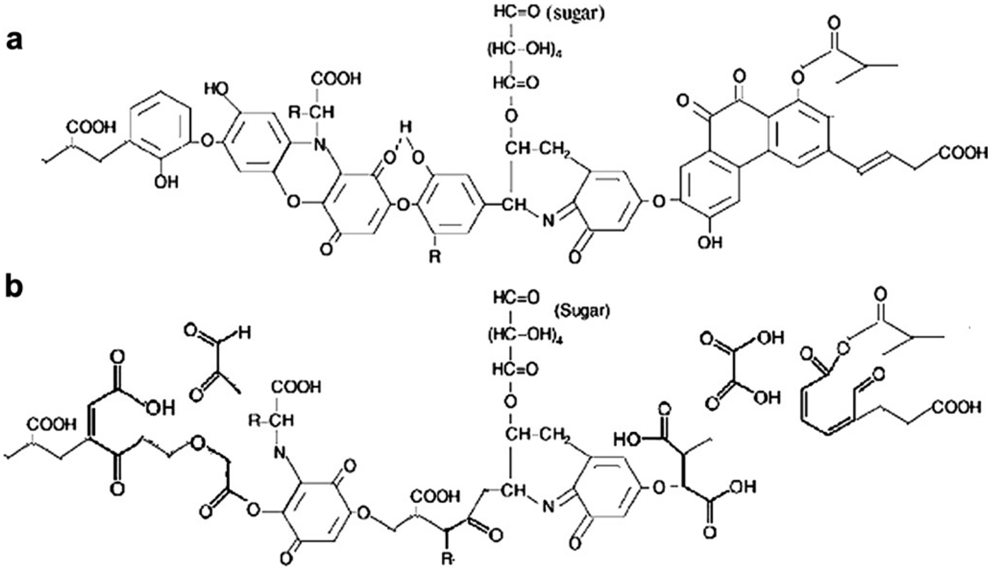

Fig. 2 – A hypothetical structure of humic substances (a) before and (b) after O_3 oxidation. O_3 reacts selectively with electron-rich sites (double bonds, aromatic rings) by cycloaddition and electrophilic substitution, and can even breakup aromatic rings. O_3 transforms them to carbonyl and carboxyl groups, which adsorb less on hydrophobic membranes. Adapted from Song et al. (2004).

acetaldehyde, glyoxal and methylglyoxal (Xiong et al., 1992; Nawrocki et al., 2003; Hammes et al., 2006; Wert et al., 2007). Oxalic acid is formed mainly by the destruction of aromatic rings by O_3 (Kusakabe et al., 1990). The amounts of carboxylic acids generated upon ozonation are usually much higher, i.e. approximately one order of magnitude, than those of aldehydes and ketones (Nawrocki et al., 2003; Xie, 2004). Can and Gurol (2003) observed that a high O_3 dose results in a decline in the concentration of aldehydes, due to their oxidation to carboxylic acids. The saturated reaction products accumulate in the solution and are not mineralized, even after long oxidation times (Oh et al., 2003; von Gunten, 2003a; Van Geluwe et al., 2010, Van Geluwe et al., in press). The inefficient reaction between O_3 and the saturated reaction products can be demonstrated by the low rate constants between O_3 and these molecules, which are given in Table 2. With the exception of formate, which reacts relatively well with O_3, the rate constants range between 10^{-5} and 10^1 M^{-1} s^{-1}, while rate constants with olefins and aromatic rings can reach values of 10^6 and 10^9 M^{-1} s^{-1}, respectively (Williamson and Cvetanovic, 1970; Hoigné and Bader, 1983b). This explains why O_3 oxidation can only achieve a small DOC removal, as mentioned above.

The vast abundance of unsaturated bonds in humic substances facilitates the efficient decomposition of these compounds by O_3 (Van Geluwe et al., 2009; Van Geluwe et al., 2010). The unsaturated bonds in these molecules are transformed to oxygenated saturated bonds. This is schematically represented in Fig. 2, where a model structure of a humic acid molecule is drawn, before and after O_3 oxidation. The decomposition of proteins and polysaccharides by O_3 was investigated by Cataldo (2003) and Wang et al. (1999), respectively. Cataldo (2003) found that only the aromatic amino acids tryptophan, tyrosine and phenylalanine are oxidized, as well as cysteine. The most reactive amino acid is tryptophan, followed by tyrosine while phenylalanine appears much less reactive toward O_3. The reaction schemes between the former two amino acids and O_3 are presented in Fig. 3. Histidine and methionine should probably react quite well with O_3, but there is no direct spectral evidence for this claim. Concerning cysteine, O_3 oxidates the thiol group, with the consequent formation of disulfide bonds and crosslinks between proteins containing cysteine residues (Fig. 3). The polyamide bond of the main chain of the protein is not degraded by the action of O_3, even after prolonged exposure. However, O_3 causes denaturation of proteins, i.e. introduces changes in their secondary and tertiary structure (Cataldo, 2003). Wang et al. (1999) showed that O_3 depolymerizes polysaccharides by reacting with the glycosidic linkages in those molecules. It selectively oxidates β-D-glycosidic linkages to aldonic esters, as shown in Fig. 4. Ozonolysis proceeds under strong stereo-electric control. However, the oxidation of α-D-glycosidic linkages during O_3 oxidation is also possible, but slow, and is caused by several side reactions with radicals and acid hydrolysis.

Table 2 – Rate constants (at 298 K) for the reaction of O_3 and $^{\bullet}OH$ radicals with the main reaction products after O_3 oxidation of NOM. Sources: [a] Hoigné and Bader, 1983(a), [b] Hoigné and Bader, 1983(b), [c] Buxton et al., 1988.

	k_{O_3} (M^{-1} s^{-1}) [a,b]	$k_{^{\bullet}OH}$ (M^{-1} s^{-1}) [c]	$k_{^{\bullet}OH}/k_{O_3}$
Formaldehyde	0.1	$2.0 \cdot 10^9$	$2.0 \cdot 10^{10}$
Acetaldehyde	1.5	$7.3 \cdot 10^8$	$4.9 \cdot 10^8$
Acetone	0.032	$6.6 \cdot 10^7$	$2.1 \cdot 10^9$
Formic acid	5	$1.3 \cdot 10^8$	$2.6 \cdot 10^7$
Formate	100	$2.8 \cdot 10^9$	$2.8 \cdot 10^7$
Acetic acid	$<3.0 \cdot 10^{-5}$	$1.6 \cdot 10^7$	$>5.3 \cdot 10^{11}$
Acetate	$<3.0 \cdot 10^{-5}$	$8.5 \cdot 10^7$	$>2.8 \cdot 10^{12}$
Oxalate	$4.0 \cdot 10^{-2}$	$7.7 \cdot 10^6$	$1.9 \cdot 10^8$

3.2. *Which functional groups in the NOM can act as a promoter or inhibitor of O_3 decomposition?*

O_3 may react directly with dissolved substances in water, or it may decompose to form radical species, which themselves react with these substances. This corresponds to direct oxidation by molecular O_3 and indirect oxidation, respectively. The most important radical species is the $^{\bullet}OH$ radical, because of its high standard reduction potential (2.80 V), which is even higher than the standard reduction potential of O_3 (2.07 V) (Beltrán, 2004). In contrast to O_3, $^{\bullet}OH$ is believed to be a non-selective oxidant, which reacts very fast with the vast majority of organic and inorganic compounds in water (von Gunten, 2003a).

The decomposition of O_3 in pure water is well-described in literature. The SBH (Staehelin, Bühler, Hoigné) model is widely used for predicting the lifetime of O_3 in natural waters (Beltrán, 2004). This model is represented in Fig. 5 and a brief discussion is given below.

The decomposition of O_3 in water is a radical-type chain reaction, where various solutes can act as initiators, promoters or inhibitors (Staehelin and Hoigné, 1985).

Initiation step: The decomposition of O_3 is initiated by OH^- ions (reaction 1), and this leads to the formation of one superoxide anion ($^{\bullet}O_2^-$) and one hydroperoxyl radical ($^{\bullet}HO_2$), which are in an acid–base equilibrium ($pK_a = 4.8$):

$$O_3 + OH^- \rightarrow {}^{\bullet}O_2^- + {}^{\bullet}HO_2 \quad (k = 70\ M^{-1}\ s^{-1}) \tag{1}$$

In addition, the reaction of unsaturated bonds in NOM with O_3 can lead to the consumption of O_3 (reaction 2), or the production of an ozonide ion radical ($^{\bullet}O_3^-$) by an electron transfer reaction (reaction 3):

$$O_3 + NOM \rightarrow NOM_{OX} \tag{2}$$

$$O_3 + NOM \rightarrow {}^{\bullet}NOM^+ + {}^{\bullet}O_3^- \tag{3}$$

The direct reactions (2) and (3) between O_3 and NOM are generally attributed to double bonds, electron-rich aromatic systems, amines and sulphides (von Gunten, 2003a). These direct reactions control the decomposition of O_3 during the initial phase of ozonation ($t < 20$ s), in which very high amounts of $^{\bullet}OH$ radicals are generated, i.e. the concentration $^{\bullet}OH$ is about 10^{-6} to 10^{-8} times the concentration of O_3 (von Gunten, 2003a), and the presence of radical scavengers does not exert any significant effect on the O_3 consumption (Xiong et al., 1991). During the second phase ($t > 20$ s), when the most reactive parts of NOM have already reacted with O_3, the O_3 decomposition is mostly controlled by radical chain reactions instead of direct reaction with NOM, and the $^{\bullet}OH$ concentration is about ten times lower than during the initial phase of ozonation (Buffle and von Gunten, 2006).

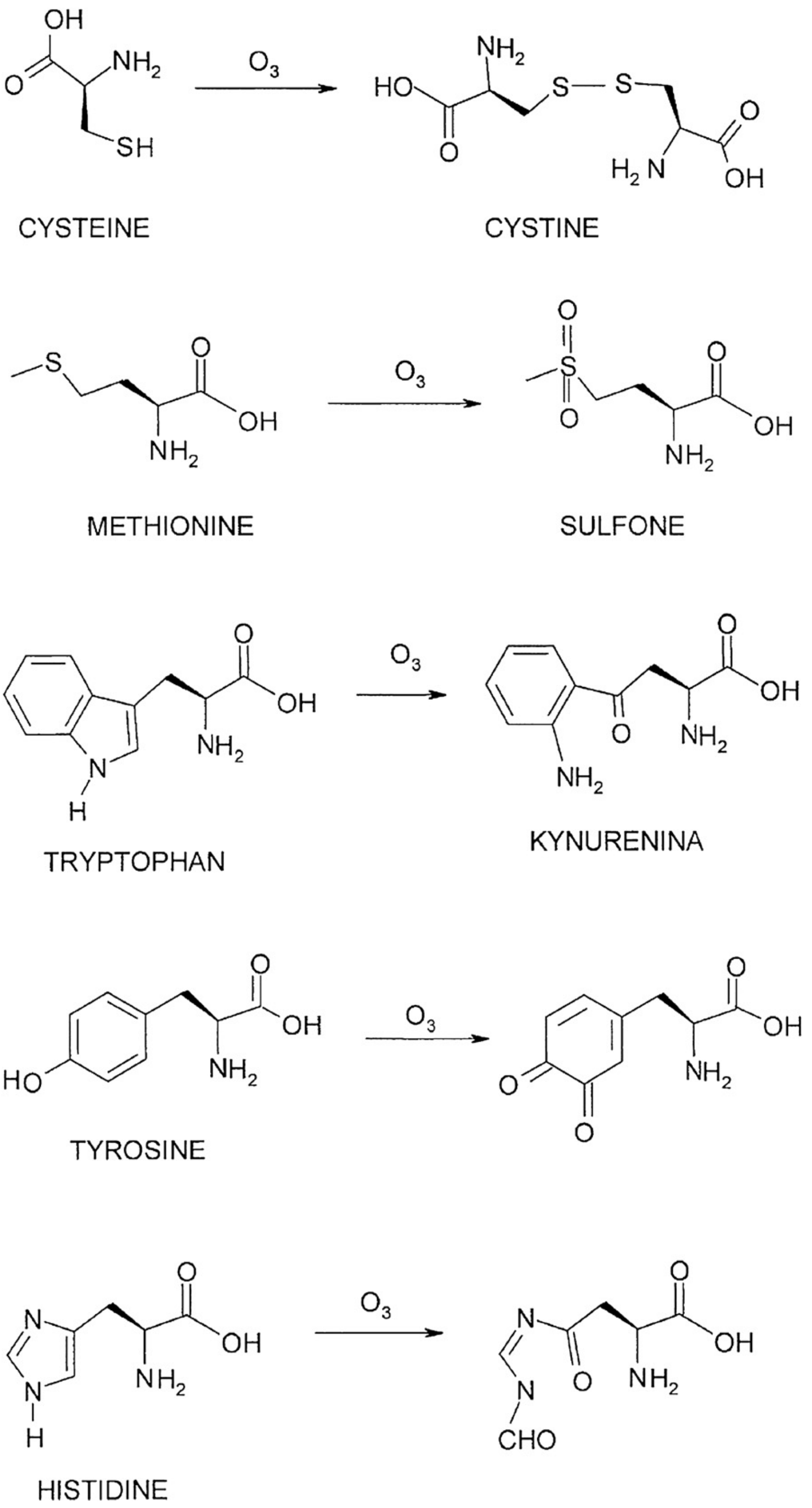

Fig. 3 – Mechanism for the reaction between amino acids and O_3. Only the aromatic amino acids tryptophan, tyrosine and the much less reactive phenylalanine (not shown) are oxidized, as well as cysteine. Probably histidine and methionine should react quite well with O_3, but there was no direct evidence of this. Concerning cysteine, O_3 oxidates the thiol groups with the consequent formation of disulfide bonds. Adapted from Cataldo (2003).

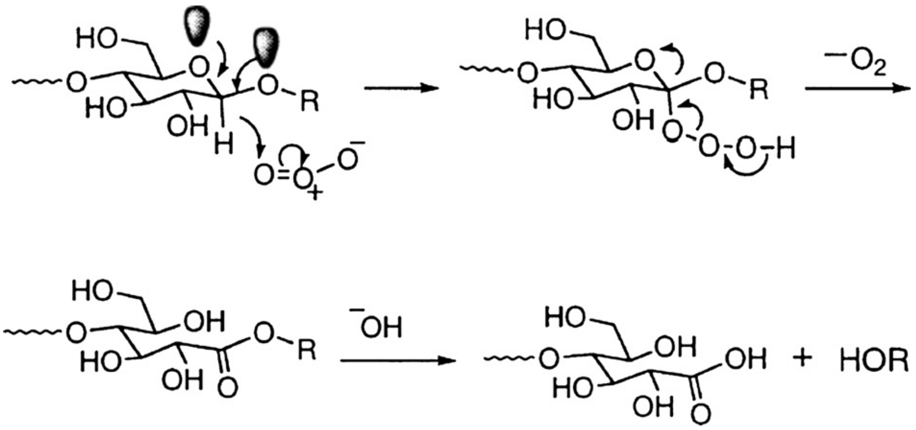

Fig. 4 – Mechanism for the reaction between polysaccharides and O_3. O_3 is very selective in cleaving β-D-aldosidic linkages. Ozonolysis proceeds only if the aldoside can assume a conformation in which the acetal function at the anomeric center has two of its lone-pair electron orbitals oriented trans-antiperiplanar (antiperiplanar: describing an angle between 150 and 210°) to the alkylidene C–H bond (stereo-electric control). However, non-selective degradation is possible as well, due to the presence of ˙OH radicals and organic acids in the ozonated solution. Adapted from Wang et al. (1999).

Propagation step: $^{\bullet}O_2^-$ is a highly selective catalyst for the decomposition of O_3 in water. The rate constant with which $^{\bullet}O_2^-$ reacts with O_3 molecules is very high and results in the formation of $^{\bullet}O_3^-$:

$$^{\bullet}O_2^- + O_3 \rightarrow {}^{\bullet}O_3^- + O_2 \quad (k = 1.6\cdot 10^9\ M^{-1}\ s^{-1}) \tag{4}$$

$^{\bullet}O_3^-$ decomposes upon protonation into ˙OH radicals:

$$^{\bullet}O_3^- + H^+ \rightarrow {}^{\bullet}HO_3 \quad (k = 5\cdot 10^{10}\ M^{-1}\ s^{-1}) \tag{5}$$

$$^{\bullet}HO_3 \rightarrow {}^{\bullet}OH + O_2 \quad (k = 1.4\cdot 10^5\ M^{-1}\ s^{-1}) \tag{6}$$

Even in solutions where the DOC concentration is low, such as drinking water, the ˙OH radicals react with a solute before they encounter another radical (Staehelin and Hoigné, 1985). Typical rate constants for reactions of ˙OH radicals with organic solutes are in the range 10^6–$10^{10}\ M^{-1}\ s^{-1}$ (Buxton et al., 1988; Lal et al., 1988; Mao et al., 1991).

Some functional groups present in NOM are known to react with ˙OH, and this can lead to the formation of carbon-centered radicals (see Fig. 5, reaction 7). The reaction of these carbon-centered radicals with O_2 (see Fig. 5, reaction 8) subsequently leads to the elimination of $^{\bullet}HO_2/^{\bullet}O_2^-$ in a base

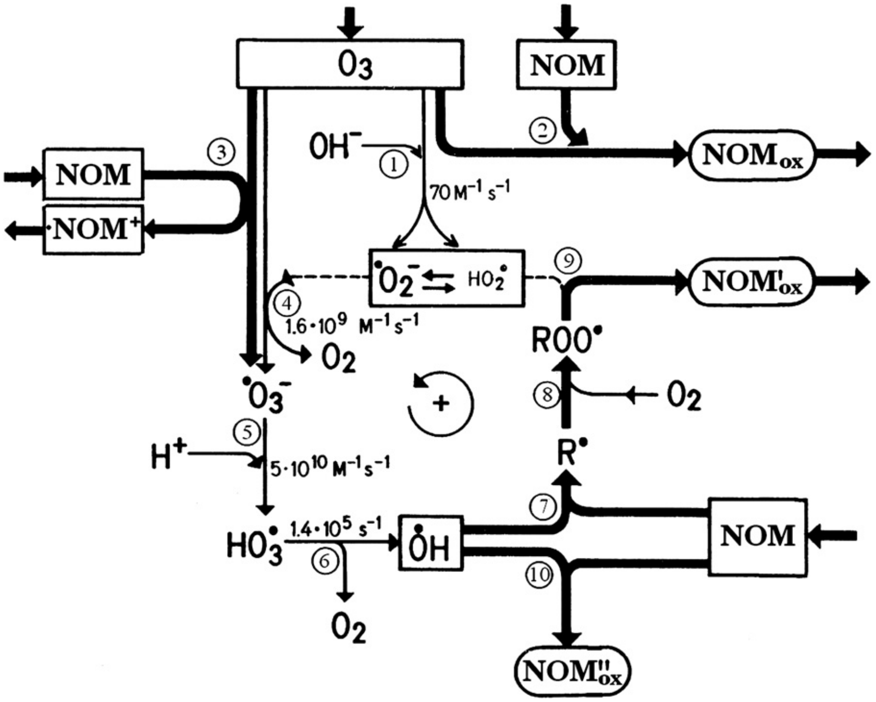

Fig. 5 – Reactions of aqueous O_3 in the presence of NOM, which reacts with O_3 or with ˙OH radicals (scavenging or converting ˙OH into $^{\bullet}HO_2$). Adapted from Staehelin and Hoigné (1985).

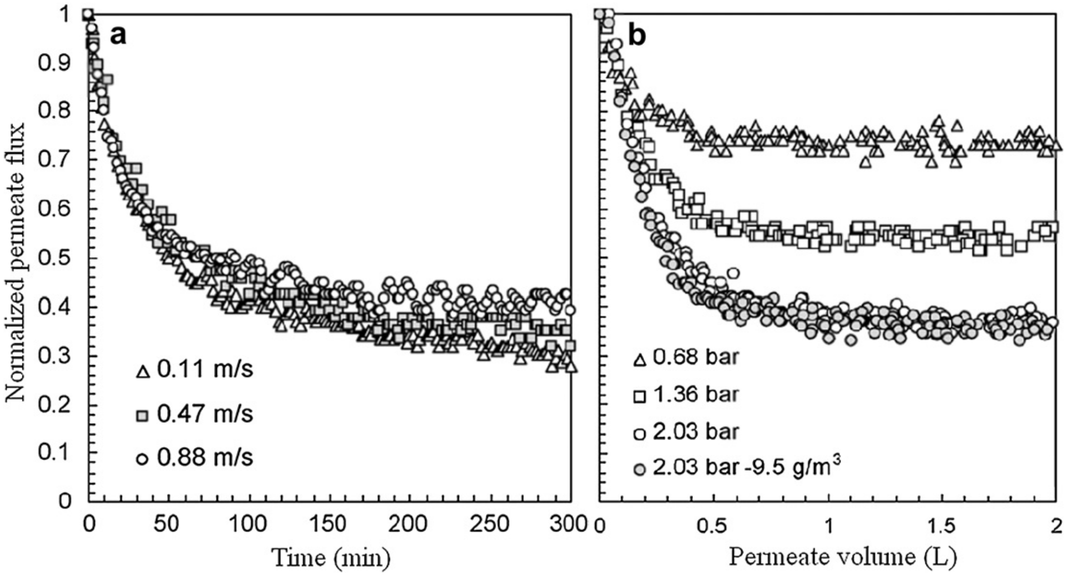

Fig. 6 – (a) Effect of cross-flow velocity on the permeate flux of a ceramic UF membrane treating surface water. The transmembrane pressure is 0.136 MPa and the O_3 concentration in the gas phase is 1.5 g m^{-3} (b) Effect of transmembrane pressure on permeate flux at an O_3 concentration in the gas phase of 5.5 g m^{-3} (except if otherwise mentioned) and a cross-flow velocity of 0.47 m s^{-1}. Adapted from Kim et al. (2008).

catalyzed reaction (see Fig. 5, reaction 9). Due to the high selectivity of $^{\bullet}O_2^-$ for O_3, the conversion of the less ozone-selective $^{\bullet}OH$ radical into $^{\bullet}O_2^-$ promotes the chain reaction. This explains how certain functional groups of NOM act as promoters for the O_3 decomposition (Staehelin and Hoigné, 1985).

Termination step: Many other solutes do not liberate $^{\bullet}O_2^-$ radicals after reaction with $^{\bullet}OH$ (see Fig. 5, reaction 10). These substances are called inhibitors or radical scavengers.

The question that remains is "which functional groups of NOM promote the decomposition of O_3, and which functional groups act as inhibitors?" Primary alcohols (such as methanol, glycol, glycerine, or present in glucose and other carbohydrates) promote the decomposition of O_3, although their direct reaction with O_3 is rather slow, due to the absence of unsaturated bonds (Staehelin and Hoigné, 1985). Aromatic rings can also be regarded as promoters for O_3 decomposition, because the attack of O_3 and $^{\bullet}OH$ cleave aromatic rings into olefins, which immediately react with O_3, with the subsequent formation of H_2O_2 (Pi et al., 2005). Glyoxalate can act both as a promoter and initiator (Staehelin and Hoigné, 1985). Alkyl groups and carboxylic acids (with the exception of formic acid, which is a promoter) are inhibitors (Staehelin and Hoigné, 1985). $^{\bullet}OH$ can also subtract a H atom from higher alkyl alcohols than methanol, such as tert-butyl alcohol, that is not in a position α to the –OH group. These reactions are not followed by the formation of $^{\bullet}O_2^-$ radicals, so these compounds act as scavengers. The relative importance of scavenging to promotion for aliphatic alcohols increases with the length of the alkyl chain in these compounds, relative to the amount of H atoms in a position α to the –OH group (Staehelin and Hoigné, 1985).

3.3. *Reaction mechanisms of NOM with $^{\bullet}OH$ radicals*

Although the $^{\bullet}OH$ radical is thought to be an unselective oxidant, organic molecules with unsaturated bonds react faster with $^{\bullet}OH$ radicals than saturated C–C bonds or C–H bonds (Westerhoff et al., 1999). Reactions of $^{\bullet}OH$ radicals with olefins and aromatic molecules occur at nearly diffusion-controlled limits (10^{10} M^{-1} s^{-1}), whereas the slowest reaction rates with $^{\bullet}OH$ radicals were observed for aliphatic polyhalogenated compounds such as haloacetic acids (HAA) and trihalomethanes (THM) (10^7–10^8 M^{-1} s^{-1}) (Buxton et al., 1988; Lal et al., 1988; Mao et al., 1991). $^{\bullet}OH$ can be regarded as an electrophilic oxidant like O_3, because electron donating groups, such as hydroxyls and amines, enhance the reactivity of adjacent carbon bonds, while electron withdrawing groups, such as carboxyl groups, lessen its reactivity (Song et al., 2008). A few researchers determined the second rate constant of $^{\bullet}OH$ reaction with NOM ($3.6 \cdot 10^8$ M^{-1} s^{-1} (Westerhoff et al., 1999)) or humic acids ($1.9 \cdot 10^7$ M^{-1} s^{-1} (Liao and Gurol, 1995), $8.1 \cdot 10^8$ M^{-1} s^{-1} (Westerhoff et al., 1999), 2.3–$3.2 \cdot 10^9$ M^{-1} s^{-1} (Goldstone et al., 2002)), at which the concentration of organic matter is expressed as mol C per liter.

Reactions of $^{\bullet}OH$ radicals with organic compounds fall into two basic mechanisms, i.e. addition, generally to an aromatic ring (hydroxylation), or abstraction of a H atom. Both mechanisms can lead to the formation of low-molecular mass acids. Hydroxylation of aromatic moieties in NOM, followed by ring opening, can produce both mono- and dicarboxylic acids (Gopalan and Savage, 1994). Abstraction of $^{\bullet}H$ from an unsaturated C–C bond leads to the formation of a carbon-centered radical, followed by reaction with O_2 to form a peroxyl radical, and subsequent decomposition to a carboxylic acid (Goldstone et al., 2002).

3.4. The addition of H_2O_2 slightly improves the mineralization of organic matter during ozonation

The contribution of the radical pathway can strongly be enhanced by adding H_2O_2 to the solution. In this case, the main O_3 decay path is the reaction between O_3 and the conjugated base of H_2O_2, i.e. HO_2^- ($pK_a = 2.24 \cdot 10^{-12}$ (Paillard et al., 1988)), leading to a higher production rate of $^{\bullet}OH$ radicals (Staehelin and Hoigné, 1982):

$$O_3 + HO_2^- \rightarrow {}^{\bullet}OH + {}^{\bullet}O_2^- + O_2 \quad (k = 2.8 \cdot 10^6\ M^{-1}\ s^{-1}) \tag{7}$$

This leads to an advanced oxidation process (AOP). Indeed, in pure water systems, two $^{\bullet}OH$ radicals are formed per three O_3 molecules consumed, while in the presence of H_2O_2, one $^{\bullet}OH$ radical is formed per O_3 molecule consumed (Acero and von Gunten, 2001). The main advantages of AOPs are the oxidation of ozone-resistant compounds. However, the higher formation rate of $^{\bullet}OH$ is at the cost of a higher O_3 consumption, i.e. the decomposition of O_3 is accelerated in the presence of H_2O_2 at pH values higher than 5 (Staehelin and Hoigné, 1982). In addition, $^{\bullet}OH$ reacts rather unselective, and thus only a small fraction of these radicals reacts with the target pollutant, which severely reduces the efficiency of AOPs (von Gunten, 2003a).

Several researchers reported that $O_3 + H_2O_2$ systems remove DOC better, because of the ability of $^{\bullet}OH$ radicals to react with the unsaturated reaction products formed during O_3 oxidation. The effectiveness of $^{\bullet}OH$ radicals for the mineralization of these compounds can be assessed by comparing the rate constants with O_3 and $^{\bullet}OH$ radicals (see Table 2). The rate constants for the reaction with $^{\bullet}OH$ radicals is evidently higher than for the reaction with molecular O_3. However, the concentration of $^{\bullet}OH$ radicals is typically 10^7–10^9 times lower than the dissolved O_3 concentration (von Gunten, 2003a). If the proportion of the two rate constants is lower than 10^8, an increase of the $^{\bullet}OH$ concentration will not be able to improve the decomposition of these saturated compounds. This proportion is calculated for each compound in the last column of Table 2, and it can be seen that it is higher than 10^8 for all compounds, with the exception of formate, which already reacts relatively well with O_3. Goldstone et al. (2002) reported that reactions between humic substances and $^{\bullet}OH$ radicals produced CO_2 with a high efficiency of ~0.3 mol CO_2 per mole $^{\bullet}OH$. This efficiency remained approximately constant from the early phases of oxidation until complete mineralization of the DOC, and was not significantly altered within the range of pH values found in natural waters (pH 4–10). However, they reported that the CO_2 production from $^{\bullet}OH$ reaction with low-molecular mass acids is an insignificant fraction of the overall CO_2 formation rate, indicating that most of the mineralization of humic substances does not occur via low-molecular mass acid intermediates.

Acero and von Gunten (2001) reported that, when the organic matter content in the water is low (<1 mg L^{-1} DOC), the addition of H_2O_2 considerably enhances the oxidation capacity by $^{\bullet}OH$ radicals. However, if the NOM concentration in natural waters is higher than 3 mg L^{-1} DOC, O_3 decomposition is controlled by the promoting or inhibiting effect of certain functional groups in the DOC on the O_3 decomposition. Therefore, the effect of H_2O_2 addition in order to raise the $^{\bullet}OH$ concentration, will be negligible in that case. This was also observed by the following researchers, who observed that $O_3 + H_2O_2$ performed well, but only slightly better than pure O_3 oxidation. Irabelli et al. (2008) reported for surface water (DOC > 3 mg L^{-1}) a DOC removal of 61% by $O_3 + H_2O_2$ (0.7 mg H_2O_2 was added prior to oxidation) compared to 53% by O_3 (O_3 dosage: 2.0 mg L^{-1}, reaction time: 13.2 min). Van Geluwe et al. (2010) found that the continuous addition of H_2O_2 between 10 and 30 min oxidation time (0.25 mol H_2O_2 per mole O_3), could enhance the removal of UV absorbing compounds at 280 nm, from 42% (if no H_2O_2 was added) to 54%, for the treatment of humic acid solutions. If the same experimental conditions were applied to NF concentrates, obtained after filtration of surface water, a reduction of 74% could be achieved by $O_3 + H_2O_2$, compared to 68% by O_3 (Van Geluwe et al., in press).

3.5. Guidelines for finding the optimal dose of H_2O_2 in water treatment

The dosage of H_2O_2 has a significant effect on the mineralization of organic compounds. There exists an optimal H_2O_2 dosage because this compound not only acts as a generator of $^{\bullet}OH$ radicals, but also as a scavenger of $^{\bullet}OH$ radicals at high H_2O_2 concentrations. This is attributed to the formation of much less powerful $HO_2^{\bullet}$ radicals by the reaction between H_2O_2 and $^{\bullet}OH$ (reaction 8), and the subsequent reaction of $HO_2^{\bullet}$ with $^{\bullet}OH$ (reactions 9 and 10) (Weinstein and Bielski, 1979; Buxton et al., 1988):

$$H_2O_2 + {}^{\bullet}OH \rightarrow H_2O + HO_2^{\bullet} \quad (k = 2.7 \cdot 10^7\ M^{-1}\ s^{-1}) \tag{8}$$

$$HO_2^{\bullet} + {}^{\bullet}OH \rightarrow H_2O + O_2 \quad (k = 6.0 \cdot 10^9\ M^{-1}\ s^{-1}) \tag{9}$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \quad (k = 7.6 \cdot 10^5\ M^{-1}\ s^{-1}) \tag{10}$$

Multiple additions of H_2O_2 at different stages is better for DOC removal than a single addition of H_2O_2 at the inlet of the reactor only (Kosaka et al., 2001). Higher H_2O_2 doses are required at later stages, in which low reactivity compounds with $^{\bullet}OH$ radicals are predominant (Kosaka et al., 2001). It is also important to maintain a low concentration of dissolved O_3 for efficient DOC removal, because O_3 is required for the rapid formation of $^{\bullet}OH$ radicals (Kosaka et al., 2001). Once H_2O_2 is completely consumed, the AOP comes to a halt, achieving a similar COD conversion as with pure O_3 oxidation (Rivas et al., 2009).

The optimal H_2O_2/O_3 ratio depends on the composition of the water solution, such as the type and concentration of the solutes (Kosaka et al., 2001), and the alkalinity of the water (Rosal et al., 2009). In most full-scale plants, the optimal ratio of the H_2O_2 dosage to the O_3 dosage, appeared to lie between 0.25 and 1.0. There are no formulas available yet for predicting the optimal value, so it should be determined experimentally for each raw water and O_3 installation (Acero and von Gunten, 2001). Paillard et al. (1988) determined the optimal conditions for removal of oxalic acid by $O_3 + H_2O_2$. Oxalic acid is a major reaction product that accumulates during O_3 oxidation of natural waters. The continuous introduction of H_2O_2 improved the degradation of oxalic acid, compared to single addition of H_2O_2 at the start of the experiment. The optimal pH was equal to 7.5 and the optimal dosage of H_2O_2 ranged between 0.6 and 0.7 · 10^{-4} M, for an initial oxalic acid concentration of 2 · 10^{-4} M. This corresponded to a ratio of 0.5 mol H_2O_2 consumed per mole O_3. The presence of bicarbonates did not influence the optimal conditions, but if the solution contained bicarbonates, a significant reduction of the degradation rate for oxalic acid was observed.

3.6. *A short note on the health hazard of O_3 in water treatment*

3.6.1. *Bromate formation*

The formation of the suspected carcinogenic bromate (BrO_3^-) in waters containing Br^- is a serious concern in O_3 oxidation. Br^- is a constituent of all natural waters and its concentration mainly depends on the geochemistry of the watershed (Magazinovic et al., 2004). It ranges from 10 to 1000 μg L^{-1} (von Gunten, 2003b). Currently, the U.S. Environmental Protection Agency (USEPA) and the European Union have set a maximum contaminant level of 10 μg L^{-1} for BrO_3^- in drinking water (Agus et al., 2009). At Br^- concentrations as low as 50 μg L^{-1}, excessive BrO_3^- formation can already become a problem. Details about the formation mechanisms of bromate and strategies to control it can be found in von Gunten, (2003b).

A reduction of the O_3 dose by a factor of two could reduce the formation of BrO_3^- by a factor of more than ten (Meunier et al., 2006). However, the reduction of O_3 doses decreases the inactivation of resistant protozoa, such as *Cryptosporidium parvum* and *Giardia lamblia*. The lower residual O_3 concentration in AOPs and the reduction of HOBr by H_2O_2 reduce BrO_3^- formation in O_3-based AOPs in comparison to conventional O_3 oxidation (von Gunten, 2003b). BrO_3^- formation is noticeably higher in highly alkaline waters than in waters with lower alkalinity. This is due to the reaction of carbonate radicals with OBr^-. Therefore, the application of O_3 oxidation has to be carefully evaluated for high-alkalinity waters in order to avoid excessive BrO_3^- formation (von Gunten, 2003b). Another decisive factor is the temperature of the treated water: BrO_3^- formation increases with increasing temperature (von Gunten, 2003b).

3.6.2. *Trihalomethanes and haloacetic acids*

The reaction of NOM with chlorine causes the formation of a variety of potentially carcinogenic DBPs such as THMs and HAAs. The USEPA has currently set maximum contamination levels of total THMs and HAAs at 80 μg L^{-1} and 60 μg L^{-1}, respectively. The European Union has only a limit for THMs, namely 100 μg L^{-1} (see Agus et al., 2009 for more details).

The hydrophobic NOM fraction is the main precursor of DBP formation, because it has the highest tendency to react with chlorine (Chang et al., 2002). In Section 4.1, it will be shown that O_3 is able to transform these hydrophobic components into hydrophilic products, so that O_3 oxidation will decrease the formation potential of THMs and HAAs quite efficiently (Chang et al., 2002; Gallard and von Gunten, 2002; Chin and Bérubé, 2005; Li et al., 2008). Kleiser and Frimmel (2000) and Meunier et al. (2006) found that even a small O_3 dose of 1.5 and 2.5 mg per mg DOC respectively, reduced the THM formation potential by about 70% in surface water, whereas almost no DOC was removed.

4. The structural changes of NOM by O_3 oxidation

NOM fouling is attributed to the accumulation of molecules which are retained on the membrane surface, forming a cake or gel layer, and the adsorption of non-retained molecules in the inner pores of the membrane, leading to constriction and blocking of the inner pores of the membrane. The fouling potential of NOM is defined by different types of chemical and physical interactions between the NOM and the membrane surface, such as hydrophobic interactions, hydrogen bridges and electrostatic interactions, besides the size and conformation of the NOM molecules. NOM fouling in membrane filtration is already reviewed by several authors: Zularisam et al., 2006; Al-Amoudi and Lovitt, 2007; Amy, 2008; Al-Amoudi, 2010; Sutzkover-Gutman et al., 2010. Therefore, this section will only discuss the effect of O_3 oxidation on the different fouling mechanisms. A summary of recent studies on the effect of O_3 oxidation on membrane fouling, both in surface water applications and municipal wastewater treatment, is given in Table 3.

4.1. *Hydrophobic interactions between NOM and membrane surfaces*

The electrophilic nature of O_3 results in the transformation of unsaturated bonds in aromatic moieties, into hydrophilic reaction products, such as carboxylic acids, as stated in the previous section. This could be confirmed by several researchers. Świetlik and Sikorska (2004) treated sand-filtered groundwater with 1.0 mg O_3 per mg DOC, for 10 min, and observed that the hydrophobic DOC (i.e. the DOC fraction retained by the Amberlite XAD 8 resin or a similar resin) decreased from 54 to 5% of the total DOC. Song et al. (2010) reported that a O_3 dose of 0.5 mg O_3 per mg DOC, applied for 10 min, to surface water, reduced the hydrophobic DOC by ~45%, while the total DOC dropped by only 10%. Van Geluwe et al. (in press) showed that the hydrophobic fraction of the chemical oxygen demand (COD) decreased by 86%, while the overall COD decreased by only 22%, while treating the concentrate stream after NF of surface water, with 2.0 mg O_3 per mg COD for 20 min. The transformation of the hydrophobic part of NOM into hydrophilic reaction products is schematically shown in Fig. 2, where a model structure of a humic acid molecule is drawn, before and after O_3 oxidation. Most of the aromatic rings in the humic acid molecule are cleaved by O_3, and the molecule is enriched in oxygenated functional groups. The hydrophilic reaction products have a lower propensity for adsorption on membrane surfaces. This is an important reason for the increase of the membrane flux after O_3 oxidation.

4.2. *Molecular size and (dis)aggregation of NOM*

4.2.1. *Results obtained by high-performance size exclusion chromatography (HPSEC)*

The size of NOM is a critical parameter for membrane fouling. The occurrence of different modes of fouling is related to foulants size relative to membrane pore size (Katsoufidou et al., 2005; Huang et al., 2008; Lin et al., 2009). Substances close to

Table 3 – Experimental results of hybrid ozone-membrane systems.

Reference	Raw water composition	Oxidation features	Membrane features	Results
Karnik et al. (2005)	Michigan lake water (US) pH: 7.7–8.6 TOC: 8.6–11.6 mg L^{-1} Alkalinity: 145–157 mg L^{-1} $CaCO_3$ UVA (254 nm): 0.160–0.180 cm^{-1}	C_{O_3} (g): 1–12.5 mg L^{-1} Gas flow rate: 6 L h^{-1} Batch volume: 3.5 L	UF (TiO_2) MWCO: 15 kDa Constant flux of 1820 L m^{-2} h^{-1} MPa^{-1} Transmembrane pressure: 17 kPa	Without O_3 treatment, flux reduced 40% in 12 h. Stable fluxes of more than 95% of the pure water flux can be maintained if the dissolved O_3 concentration at the membrane surface is greater than 0.05 mg L^{-1}. Continuous O_3 injection was not necessary. Intermittent O_3 injection for 1 min per 5 min gave the same results. Improved permeate flux recovery at lower pH due to higher dissolved O_3 concentration
Kim et al. (2007)	Sewage water TOC: 163 mg L^{-1} BOD_5: 85 mg L^{-1} Suspended solids: 203 mg L^{-1}	C_{O_3} (g): 58 mg L^{-1} Gas flow rate: 2 or 4 L h^{-1}, respectively Backwashing time (per 60 min): 2 or 1 min, respectively	Metallic MF membrane Mean pore size: 1 μm Pure water flux: 5000 L m^{-2} h^{-1} MPa^{-1} Transmembrane pressure: 50 kPa	The effect of air backwashing and O_3 backwashing on the filtration flux was compared. The mean membrane flux (for 25 h filtration) was higher in the case of O_3 backwashing, i.e. 60 L m^{-2} h^{-1} instead of 20 L m^{-2} h^{-1}, in the case of 1 min backwashing per hour, and 75 L m^{-2} h^{-1} instead of 45 L m^{-2} h^{-1}, in the case of 2 min backwashing per hour
Kim et al. (2008)	Michigan lake water (US) TOC : 11.8 mg L^{-1}	C_{O_3} (g): 1.5/5.5/9.5 mg L^{-1} Gas flow rate: 12 L h^{-1}	UF (α-$Al_2O_3 + TiO_2$) MWCO: 5 kDa Pure water flux: 1430 L m^{-2} h^{-1} MPa^{-1} Transmembrane pressure: 68/136/204 kPa	At a gaseous O_3 concentration of 1.5 mg L^{-1}: no improvement of permeate flux, flux reduced to 40% of initial value after collecting 1 L permeate At an O_3 concentration of 5.5 mg L^{-1}: flux reduced to 75% of initial value after collecting 1 L permeate and stayed stable afterward Effect of cross-flow velocity and transmembrane pressure is illustrated in Fig. 6.
Lee et al. (2005b)	Municipal wastewater, influent pH: 6.8–7.2 TOC: 8.89–9.91 mg L^{-1} COD: 105–218 mg L^{-1} BOD_5: 50–86 mg L^{-1}	For an O_3 dose of 2.3 mg L^{-1}, there is a residual O_3 concentration of 0.1 mg L^{-1} in the permeate	MF (PVDF) Mean pore size: 0.22 μm Pure water flux: 414 L m^{-2} h^{-1}	After 20 min, the flux reduced to 20% of the pure water flux without O_3 pretreatment against 40% with O_3 pretreatment. Due to ozonation, the thickness of the foulant layer was reduced by about 50% (1.4 μm instead of 3.2 μm) TOC increased through O_3 pretreatment from 9.6 mg L^{-1} to 14.5 mg L^{-1}. TOC of permeate with O_3 treatment (15.6 mg L^{-1}) was higher than without O_3 treatment (12.5 mg L^{-1})

(continued on next page)

Table 3 (*continued*)

Reference	Raw water composition	Oxidation features	Membrane features	Results
Lehman and Liu (2009)	Municipal wastewater, secondary effluent pH: 6.8 TOC: 3.8–5.9 mg L^{-1} Alkalinity: 140 mg L^{-1} $CaCO_3$	O_3 doses ranged between 2.7 and 6 mg L^{-1}	MF (ceramic) Mean pore size: 0.1 µm Constant flux of 170 L m^{-2} h^{-1} Inline direct coagulation (1 mg L^{-1} Al in PACl) to the ozonated water prior to membrane filtration	Membrane flux can be stabilized for long-term operation at an O_3 dose that is slightly above the instantaneous O_3 demand. The results are summarized in Fig. 7. O_3 dose (mg L^{-1}) 2.7 3.5 5 6 C_{O_3} in permeate (mg L^{-1}) <0.05 0.15 0.61 0.89 Normalized permeate flux after 5 days (%) 36 70 82 98
Sartor et al. (2008)	River water (Thailand) pH: 7.2–9.3 TOC: 10.0–46 mg L^{-1} Conductivity: 263–1781 µS cm^{-1}	C_{O_3}(g): 0.3–3.1 mg L^{-1} Gas flow rate: 500 L h^{-1} Ozonation was carried out using a by-pass flow (2 m^3 h^{-1}) into which gaseous O_3 was fed via a venturi injector	MF (ceramic) Mean pore size: 200 nm UF (ceramic) Mean pore size: 80 nm Transmembrane pressure: 30.0 kPa	The membranes were backflushed by O_3 at intervals of 150 min for 2 min, at 0.600 bar (MF) or 0.900 bar (UF) excess pressure. The main results are illustrated in Fig. 8. Without O_3 treatment, the fouling layer is tightly fixed to the membrane, which is the reason why backflushing without chemicals is unsuccessful (black points). However, if the surface is continuously ozonated during filtration with an O_3 residual in the permeate, simple backflushing is successful in controlling fouling (gray points).
Schlichter et al. (2004)	Saar river water (Germany) pH: 6.8–7.3 TOC: 3.5–4.5 mg L^{-1} COD: 2.7–3.7 mg L^{-1}	O_3 dose: 1.7/2.8/4.5 g O_3 g^{-1} TOC Raw water feed flow: 1 m^3 h^{-1} Gas flow rate: 300 L h^{-1}	UF (ceramic) MWCO: 20 kDa Pure water flux: 2100 L m^{-2} h^{-1} MPa^{-1}	An O_3 concentration of 0.05 mg L^{-1} (1.7 g O_3 g^{-1} TOC) in the permeate is required to maintain stable and high permeate fluxes. O_3 dose (g O_3 g-1TOC) 0.0 1.7 2.8 4.5 C_{O_3} in permeate (mg L^{-1}) 0.00 0.05 0.10 0.40 Membrane permeability (L m^{-2} h^{-1} bar^{-1}) 80 128 149 194 Similar results for the ceramic MF membrane (0.1 µm)
Song et al. (2010)	Huangpu river water (China) pH: 7.2–7.6 TOC: 5.1–6.6 mg L^{-1} UVA (254 nm): 0.128–0.157 cm^{-1}	O_3 doses ranged between 0.5 and 3.0 mg L^{-1} Oxidation time: 10 min	MF (PVDF) Pore size: 0.1 µm Hollow fiber	Maximal membrane flux at a dose of 1.5 mg O_3 L^{-1}. At the end of the filtration (after collecting 800 mL permeate), the membrane flux was 37% of the pure water flux, with O_3 oxidation, while only 20% without O_3 oxidation of the feed.

Van Geluwe et al. (in press)	NF concentrate after filtering Dijle river water (Belgium) pH: 7.7–8.4 COD: 43.7 ± 2.2 mg L^{-1} UVA (254 nm): 0.222 ± 0.008 cm^{-1}	C_{O_3} (g): 12.2 ± 0.4 mg L^{-1} Gas flow rate: 1 L min^{-1} Oxidation time: 10 min Batch volume: 3 L	Four NF membranes (NF 90, NF 270, Desal 51 HL, NF-PES 10)	The average permeability of the concentrate solution throughout the filtration (40 h), increased from 23 to 74% of the pure water permeability with NF 90 due to O_3 oxidation, from 73 to 88% with NF 270, from 63 to 76% with NF-PES 10, and from 69 to 77% with Desal 51 HL.
Wang et al. (2007)	Secondary effluent TOC: 8–10 mg L^{-1} COD: 10.8–41.2 mg L^{-1} BOD_5: 6–12 mg L^{-1} UVA (254 nm): 0.106–0.163 cm^{-1} Suspended solids: 10–20 mg L^{-1}	C_{O_3} (g): 20 mg L^{-1} Gas flow rate: 1 L min^{-1} Oxidation time: 1–20 min Batch volume: 0.5 L	UF (PVDF) MWCO: 30 kDa Transmembrane pressure: 100 kPa	The membrane flux is shown in function of the O_3 oxidation time. The membrane flux increased from 80 to 140 L m^{-2} h^{-1}, for a O_3 contact time of 1 min. When the O_3 contact time increased, the membrane flux did not change appreciably.
You et al. (2007)	Tertiary effluent from industrial wastewater plant in Taiwan (mostly dying and electronic wastewater) pH: 6.53 TOC: 6.51 mg L^{-1}	O_3 dose: 1.76 mg L^{-1} min^{-1} residual aqueous O_3 concentration in permeate: 4.02 mg L^{-1}	UF (PVDF) MWCO: 50 kDa Pure water flux: 675 L m^{-2} h^{-1} Transmembrane pressure: 0.1 MPa	Without O_3 oxidation, the permeate flux dropped to 60% after 1 h, but with O_3 oxidation, it could be maintained at 90% throughout the test of 2 h. TOC did not decrease during O_3 oxidation.

the size of the membrane pores can cause pore blocking, which provokes a severe increase of the filtration resistance (Lohwacharin and Takizawa, 2009). This is the case for the high-molecular mass molecules, such as polysaccharides and proteins, constricting and blocking the pores in loose membranes (MF and UF). Substances much larger than the membrane pores lead to cake formation, that is more readily removed. This is the case for the vast majority of the NOM components with tight membranes (NF and RO). In this case, substances with a high-molecular mass that are retained by the membrane, have a small back diffusion rate during cross-flow filtration, so that a thicker cake or gel layer is formed on the membrane surface (Ang et al., 2006).

Various researchers observed that ozonation is able to decompose NOM molecules into smaller fragments. HPSEC analysis before and after ozonation, shows a clear shift toward longer retention times, corresponding to a decrease in the average molecular mass. This is observed for synthetic solution of humic substances (Kerc et al., 2004; These and Reemtsma, 2005; Van Geluwe et al., 2009), as well as for natural waters and wastewater effluents (Nissinen et al., 2001; Nawrocki et al., 2003; Lehman and Liu, 2009; Song et al., 2010). Similar observations were made in studies where the NOM reacted with $^{\bullet}OH$ radicals instead of molecular O_3 (Le-Clech et al., 2006; Liu et al., 2008). The cross-flow operation can flush away loose fragments of the cake layer. This decreases the thickness of the foulant layer and thus reduces the flux decline (Karnik et al., 2005; Lee et al., 2005b).

Jansen et al. (2006) investigated the molecular mass distribution of concentrated solutions of humic substances with a low polydispersity (1.23) during O_3 oxidation. The average molecular mass shifted from 2600 to 1500 g mol^{-1} and the polydispersity of the peak decreased remarkably from 1.23 to 1.09, after a O_3 consumption of 0.65 mol O_3 per mol C. Another peak emerged at longer retention times, because small compounds were formed during the ozonation process. The size of the reaction products was restricted to only two distinct peaks throughout the reaction. In almost all experiments, the shape of the original peak did not broaden toward longer elution times. This indicates that no random splitting of the humic molecules occurs, since that would result in a very broad range of molecular sizes. Only small molecular fragments are split off from the periphery of the larger humic molecules. The main structure is reduced in size during ozonation, but remains intact. Cleavage occurs mainly at the periphery of the molecules. Steric obstruction related to the coiled structure of the humic substances, prevents O_3 and $^{\bullet}OH$ radicals from cleaving bonds in the core of the molecules (Jansen et al., 2007; Nawrocki, 2007).

4.2.2. *Aggregation of humic substances by calcium and magnesium*

The size of the humic substances is also influenced by aggregation/disaggregation forces, which in turn depend on the pH of the solution. For a long time, humic substances have been regarded as polymeric molecules, having a relatively high-molecular mass. Molecular masses of several 10,000 g mol^{-1} have been reported (Sutton and Sposito, 2005). Nowadays, humic substances are regarded as supramolecular associations of many, relatively small (<1000 g mol^{-1}) and chemically diverse bio-organic molecules, that are hold together by different kinds of weak interactions, such as Van der Waals forces and hydrogen bridges (Piccolo, 2002; Sutton and Sposito, 2005; Ahn et al., 2008). Therefore, it is appropriate to study the aggregation kinetics of humic substances, and the effect of O_3 oxidation on it.

Aggregation is promoted by the presence of divalent inorganic cations, such as calcium and magnesium. These ions can bind to carboxylate groups present in certain fractions of the NOM (Hong and Elimelech, 1997; Ahn et al., 2008). Charge screening by the adsorbed cations decreases the net negative charge of the NOM molecules, and thus the electrostatic repulsions with the membrane surface (Engebretson and von Wandruszka, 1998). This phenomena can be observed even at low concentrations of divalent ions, i.e. lower than $0.5 \cdot 10^{-3}$ M (Shao et al., 2011).

If the concentration of divalent ions is higher than $0.5 \cdot 10^{-3}$ M, these cations act as bridges between carboxylic groups of two adjacent molecules, increasing the attractive forces between them (Shao et al., 2011). This bridging function of divalent cations has been proven with atomic force microscopy (AFM) (Li and Elimelech, 2004; Nguyen and Chen, 2007). This phenomenon was observed for all NOM fractions, but was especially significant in the presence of hydrophobic NOM, i.e. humic substances (Makdissy et al., 2002). Due to the formation of complexes between NOM and divalent ions, the size of the humic aggregates becomes larger (Shao et al., 2011). It is important to note that these conclusions are all obtained without the effect of O_3 treatment on NOM. The impact of divalent ions on the complexation of ozonated NOM is not investigated yet, but it is an important issue for further study. An increase of the number of carboxylic acids in NOM after O_3 oxidation provides more ligands for complexation, and consequently the negative charge of NOM decreases. A decrease in NOM charge is expected to promote the adsorption of NOM on negatively charged membranes. However, Song et al. (2004) reported that the calcium content of foulants from oxidized surface waters (with UV + H_2O_2) is lower than that from raw water (0.3% vs. 0.8%).

Presently, there is little agreement on the effect of complexation on membrane fouling. Shao et al. (2011) stated that the porous character of the flocculated aggregates enhances the permeability of the cake layer formed on the membrane surface, and a smaller flux decline was observed as the calcium concentration increased from 0 to 0.5 mM (see Fig. 9). The aggregate porosity (ϵ_{agg}) is related to the primary particle radius (r_{prim}), aggregate radius (r_{agg}), and the fractal dimension D (Jiang and Logan, 1991):

$$\epsilon_{agg} = 1 - \left(\frac{r_{agg}}{r_{prim}}\right)^{D-3}$$

Fractal dimensions are related to the aggregate structure, e.g. $D = 3$ for a sphere, $D = 2$ for a flat sheet, $D \approx 1.8$–2.4 for typical aggregates (Waite et al., 1999). Indeed, the equation shows that, for any other shape than perfect spheres, the aggregate porosity increases as r_{agg}/r_{prim} becomes larger. However, this trend is reversed at higher calcium concentrations (see Fig. 9). Shao et al. (2011) suggested that the higher flux decline is caused by the formation of calcium bridges between the NOM and the membrane surface. This explanation is questionable, because the authors observed the same trend for neutral membranes.

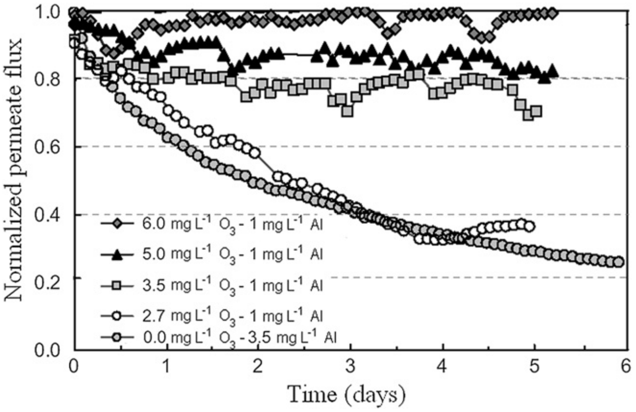

Fig. 7 – Influence of the O_3 dose on the flux of a ceramic membrane (nominal pore size: 0.1 μm) treating secondary wastewater effluent. The pure water flux of the membrane is 12,800 L m^{-2} h^{-1} Mpa^{-1}. The feed water was ozonated and 1–3.5 mg L^{-1} Al of polyaluminiumchloride was added to the ozonated water before it entered the membrane module. Adapted from Lehman and Liu (2009).

In addition, the aggregates can act as a secondary membrane, which removes a significant portion of the small particles, before they reach the polymeric membrane surface. The removal of the small particles prevents the obstruction of membrane pores or the formation of a tightly packed cake layer on the membrane surface (Kuberkar and Davies, 2000). Membrane fouling will be strongly alleviated if NOM aggregation causes a change of the fouling mechanisms, i.e. from internal pore constriction to the formation of a permeable cake on the membrane surface (Lohwacharin and Takizawa, 2009).

Other researchers stated that the complexation causes severe flux decline, because the cross-linked aggregates form a dense, compact cake layer on the membrane surface, with a high fouling resistance (Hong and Elimelech, 1997; Yuan and

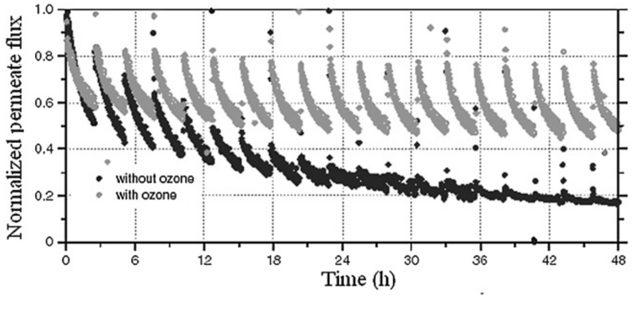

Fig. 8 – Permeate fluxes for a ceramic UF membrane (mean pore size: 80 nm) treating surface water. The pure water flux of the membrane is 1600 L m^{-2} h^{-1} MPa^{-1}. Fouling is essentially caused by the formation of a biofilm. The membrane flux can be increased considerably by adding O_3 (20–100 mg L^{-1} O_3) prior to the membrane module. The suction pressure is 30.0 kPa. Membrane fouling can be largely removed with each backflushing cycling (gray points), in contrast to the case without O_3 pretreatment (black points). Adapted from Sartor et al. (2008).

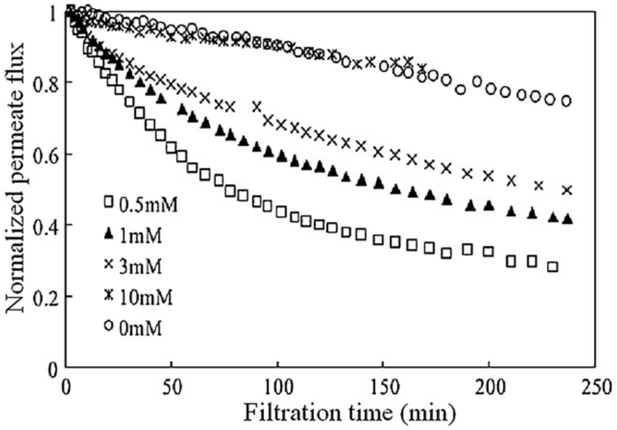

Fig. 9 – Influence of the calcium concentration on the membrane flux during filtration of surface water. Adapted from Shao et al. (2011).

Zydney, 1999; Cho et al., 1999, 2000; Schäfer et al., 2002; Costa et al., 2006; Tang et al., 2007; Katsoufidou et al., 2008; Mattaraj et al., 2008; Zhu et al., 2010), or internal deposition of aggregates reduces the pore size of the membrane (Aoustin et al., 2001).

4.3. *Electrostatic interactions and hydrogen bridges*

The surface of many membranes carries a negative charge at neutral pH, because of the presence of carboxylic and amine groups (Childress and Elimelech, 1996). Electrostatic repulsions between the negatively charged groups in NOM and the membrane surface decreases the fouling tendency. For instance, Shao et al. (2011) observed a lower flux decline when humic acids were filtered by a charged regenarated cellulose membrane, in comparison to a neutral membrane of the same material.

Due to the absence of ionizable groups in polysaccharides, electrostatic interactions do not play a role for these molecules. Proteins are nearly all negatively charged at neutral pH, because of the preponderance of weakly acid residues in almost all proteins. The isoelectric point (IEP) of natural proteins lies in many cases between 5 and 6 (Scopes, 1994). The presence of carboxylic ($pK_a \sim 3–5$) and phenolic ($pK_a \sim 8–11$) acid groups in humic substances, make them anionic at neutral pH (Buffle, 1991; Milne et al., 2001). The mole fractions of either carboxylic or phenolic sites in humic substances are usually markedly unequal, with carboxylic acids typically dominating (Buffle, 1991). For instance, Suwannee River humic acids contain 7.85 mol carboxylic groups per kg (dry weight), while only 1.86 mol phenolic groups per kg (IHSS, 2001).

The number of carbonyl and carboxyl groups increases after O_3 oxidation, as stated previously. Carbonyl compounds carry a negative charge at neutral pH, which is repulsed by the negatively charged membrane. However, carboxyl groups can form strong hydrogen bridges with hydrophilic membranes, such as polyamide and regenerated cellulose membranes.

Van Geluwe et al. (in press) recorded Fourier transform infrared (FTIR) spectra of the NF 270 membrane, after 40 h filtration of concentrated surface water. He observed that carbonyl compounds were able to adsorb onto the membrane, if the solution was treated with O_3 (O_3 dosage: 1.0 mg O_3 per mg COD; oxidation time: 10 min). However, the membrane had a significant lower fouling rate after O_3 oxidation, although the COD of the solution did not decrease. The mean water flux, during the first 40 h filtration, increased from 73 to 88% of the pure water flux.

An estimation of the strength of these hydrogen bridges is provided by Nie et al. (2005). They calculated the strength of hydrogen bridges between the carboxyl group (of butyric acid) and methanol, via ab initio methods. The methanol molecule can be considered as an alcoholic group on the membrane surface. Table 4 shows the dissociation energies of several hydrogen bridges, with water as solvent. The notation, H**O**–C=O, represents that the hydroxyl O atom of the carboxyl group forms a hydrogen bridge with an alcoholic group on the membrane surface.

The strength of the hydrogen bridges is compared to the electrostatic repulsion energy between two negative charges, e.g. a carboxylate group in the NOM and a negative charge on the membrane surface. The calculated hydrogen bridge strengths strongly depend on the specific type of hydrogen bridges. The formation of hydrogen bridges between carboxyl groups and alcoholic groups are all exothermic, with the exception of H**O**–C=O. The hydrogen bridges are relatively weak, and weaker than those formed between water molecules (11 kJ mol^{-1}). The strongest hydrogen bridges are formed with the acid hydrogen of the carboxyl group (**H**O–C=O). This type of bond does not occur frequently at neutral pH, because most

Table 4 – Dissociation energies, bond lengths and the distance dependence of the dissociation energies, for hydrogen bridges and electrostatic bonds of a COOH group in water. Adapted from Nie et al. (2005).

	Dissociation energy in water (kJ mol^{-1})	Bond length (pm)	Dependence of the dissociation energy on the separation distance r
No interaction	0	Infinity	N/A
Type of H bridge			
H**O**–C=O	−5.6	294	$1/r^3$
HO–C=**O**	1.5	287	$1/r^3$
HO–C=O	6.7	275	$1/r^3$
HO–C=**O**	2.4 × 2	265/275	$1/r^3$
Electrostatic repulsion between two elementary charges	3.9	275	$1/r$

carboxyl groups are dissociated at this pH. The other hydrogen bridges are weaker than the electrostatic repulsion forces between two elementary negative charges. These results show that the hydrogen bridges between the carboxylate groups in the NOM, formed during O_3 oxidation, with the membrane surface are in most cases relatively weak, and are of comparable strength as the electrostatic repulsion forces between charges with the same sign. Whether the increase of the number of carboxylic groups by O_3 oxidation promotes the adsorption of NOM on the membrane surface or not, is an open question at this moment, and it would be interesting to study this in the future.

5. Conclusion

The electrophilic character of O_3 accounts for the fast reaction of O_3 molecules with unsaturated bonds. The possible reaction pathways between NOM and O_3 were described within the framework of the SBH model (Staehelin, Bühler, Hoigné). The direct reaction of unsaturated bonds in NOM with O_3 can lead to the consumption of O_3, or the production of an ozonide ion radical ($^{\bullet}O_3^-$), which decomposes upon protonation into a hydroxyl ($^{\bullet}OH$) radical. The $^{\bullet}OH$ radical is a strong oxidizing agent that can react with NOM molecules. This is referred to as the indirect oxidation pathway. Although the $^{\bullet}OH$ radical is thought to be an unselective oxidant, it can be regarded as electrophilic oxidant.

These direct reactions between NOM and O_3 control the decomposition of O_3 during the initial phase of ozonation ($t < 20$ s), in which very high amounts of $^{\bullet}OH$ are generated, i.e. the concentration $^{\bullet}OH$ is about 10^{-6} to 10^{-8} times the concentration of O_3, and the presence of radical scavengers does not exert any significant effect on the O_3 consumption. During the second phase ($t > 20$ s), the most reactive moieties of NOM have reacted with O_3, so that O_3 decomposition is mostly controlled by a radical chain reaction, and the $^{\bullet}OH$ concentration is about ten times lower than during the initial phase. During the second phase, some functional groups in the NOM, such as aromatic rings and primary alcohols (abundant in polysaccharides), act as promoters for the decomposition of O_3. Alkyl groups and carboxylic acids act as scavengers of $^{\bullet}OH$ radicals.

Although O_3 oxidation without addition of H_2O_2 is not considered as an AOP, the concentration of $^{\bullet}OH$ radicals during ozonation of NOM solutions, can be as high as in AOPs at neutral pH ($>>10^{-12}$ M). The contribution of the radical pathway can strongly be enhanced by adding H_2O_2 to the solution. The addition of H_2O_2 improves the mineralization of the saturated reaction products, mostly carboxylic acids, that are formed during O_3 oxidation.

Several researchers proved that the application of O_3 oxidation of the feed water prior to membrane filtration, resulted in a significant decrease in membrane fouling, although only a minor DOC removal (10–20%) could be achieved. This is explained by the fact that O_3 causes substantial structural changes to the NOM present in the feed water, of which the most important are:

- An efficient removal of aromatic rings, which decreases the adsorption of NOM by hydrophobic interactions.
- A significant increase of the number of carboxylic functions, which are repelled by the negative membrane surface. These repulsion forces have a comparable strength as the hydrogen bridges that carboxylic groups can form with the membrane surface.
- Decomposition of molecules into smaller fragments, whereby small molecular fragments are split off from the periphery of the larger molecules that remain intact.
- A higher propensity for complexation of humic substances with divalent ions, if the concentration of divalent ions is larger than $0.5 \cdot 10^{-3}$ M. However, it is important to note that this figure is obtained with non-ozonated NOM.

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