Kinetic Study and Scaleup of the Oxidation of Nanofiltration Retentates by O₃

Steven Van Geluwe,^{*,†} Jan Degève,[†] Chris Vinckier,[‡] Leen Braeken,^{†,§} Claude Creemers,[†] and Bart Van der Bruggen[†]

[†]Laboratory of Applied Physical Chemistry and Environmental Technology, Department of Chemical Engineering, K.U. Leuven, W. de Croylaan 46, 3001 Leuven, Belgium

[‡]Laboratory of Molecular Design and Synthesis, Department of Chemistry, K.U. Leuven, Celestijnenlaan 200F, 3001 Leuven, Belgium

[§]Department of Industrial Sciences and Technology, KHLim Universitaire Campus, Gebouw B Bus 3, 3590 Diepenbeek, Belgium

S Supporting Information

ABSTRACT: This paper reports on the upscaling of an O₃ reactor for the oxidation of natural organic matter. Natural organic matter is responsible for fouling of nanofiltration membranes used for drinking water production. The proposed concept is to feed the retentate stream of a nanofiltration module (400 m³ h⁻¹) to an O₃ reactor (bubble column) and subsequently recycle it to a second nanofiltration module. The O₃ oxidation of the retentate stream in the bubble column is analyzed in terms of the two-film theory with mass transfer and chemical reaction. The kinetic regime of the ozonation process, i.e., the chemical reaction rate relative to the mass-transfer rate, is determined using data from laboratory-scale experiments. This information is used for the calculation of the reactor volume and the required O₃ dose on an industrial scale. An economic assessment of the integrated nanofiltration–O₃ oxidation process also is given.

INTRODUCTION

Nanofiltration (NF) is an effective and reliable method for the combined removal of a broad range of pollutants in surface water, such as natural organic matter (NOM)¹ and several micropollutants.² This makes NF an appropriate technology for the production of drinking water from surface water. However, fouling of the membranes results in a reduction in water flux, which leads to higher treatment costs. Membrane fouling also limits the water recovery, i.e., the ratio of the permeate (potable water) flow rate to the feed flow rate. A water recovery of ~80% is typically achieved in the drinking water industry. The remaining fraction, the retentate stream, is usually discharged into surface water bodies.³ Since problems with water scarcity are expected to grow worse in the coming decades, even in regions that are currently considered to be water-rich,⁴ wasting 20% of the feedwater is questionable.

O₃ oxidation of the retentate stream is proposed as a possible way to resolve this problem. It is well-known that O₃ oxidation decomposes the NOM, which is an important membrane foulant, that is present in the retentate stream.⁵ The effect of O₃ oxidation of the retentate on the flux of several commercial NF membranes (NF 270, Desal 51 HL, NF-PES 10, and NF 90) has been studied in one of our previous publications.⁶ The results of these experiments are summarized in Table 1, where the membrane permeabilities for retentate solutions after O₃ oxidation are compared to the membrane permeabilities for untreated retentate solutions. The permeability of a membrane is calculated as the permeate flow rate (given in liters, L) per square meter membrane (m⁻²), per hour (h⁻¹), and per unit pressure difference across the membrane (bar⁻¹). A comparison between different membranes can be made easier by calculating the relative permeability of each membrane (see the figures

between the brackets in Table 1). The relative permeability is equal to the membrane permeability divided by the pure water permeability of the membrane in question, so that a figure between 0% (no flux) and 100% (no fouling) is obtained. Concerning the experimental conditions in the O₃ reactor, the residence time of a retentate solution in this reactor ranged between 6 min and 20 min, while the O₃ concentration in the gas phase was kept constant (12.2 ± 0.4 mg L⁻¹). In this way, the specific O₃ dose ranged between 24 and 80 g O₃ per m³ retentate, assuming that the transfer efficiency of O₃ from the gas phase to the liquid is 100%. The pH of the retentate solutions ranged between 7.7 and 8.4, and it did not change appreciably during the ozonation experiments.

The results in Table 1 show that O₃ oxidation is able to alleviate membrane fouling for all investigated membranes. The increase of the relative membrane permeabilities after O₃ oxidation (see the bottom line in Table 1) was quite similar at the different O₃ doses: 18.1 ± 1.9% for the membrane NF 270, 15.3 ± 6.3% for Desal 51, and 16.5 ± 2.8% for NF-PES 10. For the NF 90 membrane, the variation was higher (31.1 ± 17.2%), but also here, no clear trend could be observed when changing the O₃ dose. These observations were explained in terms of the hydrophobicity and the molecular mass of the NOM.^{5,6} It could be shown that O₃ reacts very efficiently with unsaturated C–C bonds (measured by the UV absorbance) that are abundant in the hydrophobic fraction of the NOM (measured by the hydrophobic COD). These hydrophobic

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Table 1. Membrane Permeabilities after 40 h of Filtration of the NF Retentate Streams, before and after O₃ Oxidation

NF membrane	Membrane Permeability (L m ⁻² h ⁻¹ bar ⁻¹) ^a			
	NF 270	Desal 51 HL	NF-PES 10	NF 90
treated with O ₃	11.09 (82.3%)	10.92 (72.7%)	9.37 (73.7%)	6.66 (69.6%)
untreated	9.27 (64.2%)	8.61 (57.4%)	7.77 (57.2%)	3.89 (38.5%)
flux increase	18.1 ± 1.9%	15.3 ± 6.3%	16.5 ± 2.8%	31.1 ± 17.2%

^aThe percentages shown in parentheses are the ratios of the respective permeability to the pure water permeability of the membrane in question (100% means no membrane fouling).

Figure 1. Simplified process flow diagram of the full-scale plant.

components readily adsorb on the membrane surface (mostly a semiaromatic polyamide). They are transformed to saturated bonds by O₃ (mostly carbonyl and carboxyl groups), which are relatively hydrophilic, making the adsorption of NOM onto the membrane surface more difficult. A lower thickness of the fouling layer if O₃ oxidation is applied to the retentate solution confirms this explanation. In addition, O₃ oxidation shifts the molecular mass distribution of the NOM to smaller fragments, but this effect is small, compared to the effect of O₃ on the hydrophobic COD and the UV absorbance. Further details can be found in other work by Van Geluwe et al.⁶

Concerning the full-scale plant, suppose that surface water (2000 m³ h⁻¹) is prefiltered and fed into a first NF module. Assume that the water recovery of this module is 80%. The retentate stream (400 m³ h⁻¹) is fed into an O₃ reactor where an O₃ containing gas stream is introduced at the bottom of the reactor and bubbles through the liquid solution. The ozonated retentate stream subsequently flows to a second NF module (see Figure 1). The O₃ oxidation of the retentate stream in the bubble column is a heterogeneous process, i.e., O₃ gas can react with the target pollutant(s) after it is absorbed into the liquid phase. The kinetic equations of the ozonation process are based on the two-film theory proposed by Lewis and Whitman.⁷ This is discussed in the Supporting Information. The kinetic equations involve not only chemical reaction rate constants, but also mass-transfer coefficients. Therefore, the physical parameters (such as the volumetric mass-transfer coefficient ($k_L a$) and the gas holdup (ϵ)) and the chemical parameters (such as the apparent reaction rate constant k_{app} between O₃ and NOM, the Hatta number (M_H) and the enhancement factor (E)) of the ozonation process must be determined. The purpose of this article is to use the information obtained by laboratory-scale experiments for the determination of the kinetic regime and the dimensioning of the O₃ reactor on an industrial scale. An economic evaluation of membrane fouling alleviation by O₃ oxidation also is presented.

The literature concerning engineering of O₃ units focuses on the ozonation of waters which contain no organic matter ("pure water")^{8–10} and O₃ disinfection of waters with a low organic content.^{11–13} The O₃ oxidation of water streams with a relatively high NOM concentration has hardly been investigated from an engineering point of view. The results of this study will allow understanding of fundamental effects related to scaleup and practical application of O₃ oxidation for membrane fouling alleviation.^{5,6}

MATERIALS AND METHODS

2.1. Preparation of the Nanofiltration Retentate

Solutions. Surface water was taken from the Dijle river in Leuven, Belgium. The Dijle water was prefiltered by the cellulose filters MN 713 1/4 (Macherey-Nagel, Germany), S&S 595 and S&S 589/3 (both from Schleicher & Schüll, Germany). These three paper filtrations minimized the concentration of suspended particles with a size larger than 2.5 μ m in the feed solution. These paper filtrations were carried out to simulate the pretreatment of the feedwater in full-scale plants, e.g., the Méry-sur-Oise plant in France, where the number of particles >1.5 μ m passing through the membranes was kept to less than 100 per mL.¹⁴

The retentate solution was obtained by filtering the prefiltered Dijle water with the NF 270 membrane (FilmTec, USA). This was performed in a cross-flow setup on laboratory scale (batch operation) (Amfilter, The Netherlands). The experimental setup is shown in Figure 2. The equipment

Figure 2. Schematic representation of the cross-flow NF unit (Amfilter, The Netherlands). Legend: (1) module 1, (2) module 2, (3) feed tank, (4) pump, and (5) flow meter.

consists of two modules, containing a flat sheet membrane with an effective surface area of 41.5 cm². The flow channel is rectangular with a hydraulic diameter of 0.43 cm. The total channel length is 29.3 cm. No spacer was used. The cross-flow velocity was in the range of 2.7–3.3 m s⁻¹. This corresponds to a Reynolds number of 11 400–14 200 (turbulent regime). In this way, concentration polarization could be minimized. However, the cross-flow velocity is much higher than what is typically used in spiral-wound modules in full-scale plants (0.1–0.5 m s⁻¹).¹⁵ The high cross-flow velocity did not cause any deformation of the membrane coupons. The transmembrane

pressure was kept constant at 10 bar. The temperature in all experiments was maintained at 293 K (by a cooling water circuit). The permeate was collected in a separate tank and discarded, while the retentate was recycled to the feed tank. The filtration was stopped when a water recovery of 78% was reached, i.e., until the volume of the feed solution was reduced to 22% of its initial value. The remaining retentate solution was used for further experiments. This figure is similar to the operational conditions in full-scale NF plants, where drinking water is produced at water recoveries of 75%–85%.³

2.2. Ozone Reactor. Three liters of retentate solution was kept in a glass reactor vessel that had an inner diameter of 160 mm. All solutions were ozonated at room temperature. The O₃–O₂ mixture was introduced from the bottom of the reactor, through a porous fine-bubble Pyrex diffuser. The rotation of a magnetic stirrer at the bottom of the reactor improved the mixing of the aqueous solution. The feed gas to the O₃ generator (Model OZ 500, Fischer, USA) was pure O₂. The gas flow rate was fixed at 60.0 L h⁻¹ at standard temperature and pressure (STP). A gFFOZ Process Ozone Sensor (IN USA, USA) measured the O₃ concentration in the gas flow entering the aqueous solution, by UV absorption at 254 nm. The O₃ concentration in the gas phase was kept constant (12.4 mg L⁻¹ O₃; 5.78 × 10⁻³ atm (STP)). The O₃ concentration in the aqueous phase was monitored with an electrochemical sensor (i.e., Model Orbisphere 3660, Orbisphere, The Netherlands).

2.3. The Decomposition of NOM and Its Kinetics. The direct reaction between O₃ and NOM can be simplified in the following way:^{16–18}

Literature data show that the reaction order for both O₃ and its coreactant is 1 for the ozonation of all types of organic compounds.^{19,20} It is assumed that this also holds for the reaction between O₃ and NOM.^{18,21,22} Thus, the chemical reaction rate for the disappearance of NOM is

$$\frac{dC_{\text{NOM}}}{dt} = -k_{\text{app}} C_{\text{O}_3} C_{\text{NOM}} \quad (2)$$

where k_{app} is the apparent rate constant between O₃ and NOM. k_{app} can be considered as

$$k_{\text{app}} = \frac{\sum k_i C_i}{C_{\text{NOM}}} \quad (3)$$

k_i is the rate constant between O₃ and the functional group i that is present in the NOM with a concentration C_i .

The rate constant for the direct reaction of O₃ with NOM shows the best correlation with the UV absorbance at 254 nm.^{23–25} π – π^* transitions of electrons in unsaturated bonds occur at this wavelength, but also between 270 nm and 280 nm.²⁶ Therefore, the application of spectrophotometric measurements at a wavelength of 254 nm as well as 275 nm is suitable for describing unsaturated C–C bonds. The UV absorbance was measured by a Model UV-1601 double beam spectrophotometer (Shimadzu, Japan).

The dimension of the UV absorbance is m⁻¹. However, the NOM concentration should be expressed in mol (carbon) m⁻³ (or mg L⁻¹, in which 1 mol m⁻³ = 12 mg L⁻¹). The specific UV absorbance (SUVA) is the ratio of the UV absorbance to the dissolved organic carbon (DOC) value of the water sample. The values of SUVA at 254 nm are widely used and provide a

specific insight into the nature of NOM. As a general rule, natural waters with high SUVA values (>4 L mg⁻¹ m⁻¹) have a relatively high content of macromolecules rich in aromatics, whereas waters with low SUVA values (<2 L mg⁻¹ m⁻¹) contain predominantly low molecular mass compounds, poor in aromatics.²⁶ The UV absorbance of the NF retentate solutions at 254 nm (27.67 ± 3.89 m⁻¹) was divided by an assumed SUVA value¹ of 2.22 L mg⁻¹ m⁻¹ in order to compute the DOC value of 12.5 mg L⁻¹ = 1.04 mol m⁻³. Therefore, it is assumed that the initial NOM concentration in the NF retentate stream is 1.04 mol m⁻³ and that

$$C_{\text{NOM}}(t) = \frac{A(t)}{A(0)} \times (1.04 \text{ mol m}^{-3}) \quad (4)$$

where A is the UV absorbance of the NF retentate at 275 nm.

2.4. Economic Assessment. The economic evaluation of the integrated process where NF and O₃ oxidation are combined (see Figure 1) should take into account the initial capital costs and the maintenance costs. All values are expressed in euros (€). An exchange rate of 1 € = 1.30 US\$ is assumed for literature data found in U.S. dollars. All items are adjusted for inflation to represent 2011 values, using the CPI (consumer price index) inflation calculator.²⁷ The loans to cover the investment costs are paid back in equal annual parts and the annual interest rate is 6%. The total number of operating hours is 8000 per year.

2.4.1. NF Unit. The design flow rate of the NF unit is represented by F [m³ h⁻¹] and the total membrane area is A [m²]. The following equations are based on the data of Van der Bruggen et al.²⁸

Capital costs:

- Civil investment costs (buildings where the installation is housed): 1350 F + 64.6 A . Depreciation period for these investments is 30 years.
- Mechanical investment costs (pumps, filters, piping, etc.): 5640 $F^{0.85}$ + 47.4 A . Depreciation period is 15 years.
- Electrotechnical investment costs (energy supply (e.g., transformers), control equipment and all electronic components): 2 190 000 + 2.815 $F\Delta P$. ΔP is the applied pressure across the membranes [bar].
- Purchase costs of membranes: 80 A . This loan is paid back in 30 years.

Maintenance costs:

- Energy costs: the installation consumes 0.040 kWh per m³ feed per bar feed pressure. The electricity cost is assumed to be 0.0762 €/kWh (estimation based on local costs of utilities in The Netherlands).²⁹
- Membrane replacement costs: the membrane lifetime is estimated at 4 years, so 25% of the membranes need to be replaced annually.
- Chemical costs: cost of chemicals is 0.030 € per m³ feed.
- Replacement of miscellaneous parts: annually 2% of the total investment costs.

2.4.2. O₃ Oxidation Unit.

Capital costs:

- O₃ generator: a generator with a capacity of 8.50 kg O₃ h⁻¹ can be purchased for 375 000 €. The expected lifetime of the generator is 20 years (= depreciation time).³⁰
- Contacting equipment: 1224 V_r , in which V_r is the volume of the O₃ reactor [m³].³¹ This equation is

applicable for reactor volumes between 3.2 m³ and 51.3 m³.

Maintenance costs:

- O₃ generator: the required power and O₂ consumption will be calculated in section 3.2. The electricity costs and the purchase costs of O₂ are assumed to be 0.0762 €/kWh and 60.96 €/ton O₂, respectively (estimation based on local costs of utilities in The Netherlands).²⁹
- Replacement of miscellaneous parts: annually 1% of the total investment costs.

RESULTS AND DISCUSSION

3.1. Determination of the Kinetic Regime. **3.1.1. Calculation of the Diffusion Coefficients.** Diffusion coefficients of compounds in water can be determined from different empirical correlations.³² The concentration of the dissolved species in the retentate stream is very small ($\sim 1 \text{ g L}^{-1}$), so that the diffusion coefficients at infinite dilution can be used. The Stokes–Einstein equation is a purely theoretical method for estimating D_1 , i.e., the binary diffusion coefficient of solute 1 in water [$\text{m}^2 \text{ s}^{-1}$]:

$$D_1 = \frac{k_B T}{3\pi\mu_2 d_1} \quad (5)$$

k_B is the Boltzmann constant ($k_B = 1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$), μ_2 the dynamic viscosity of water [10^{-3} Pa s at 293 K], and d_1 the hydrated diameter of the diffusing molecule [m]. The relationship is valid only if the molecules of the diffusing species are very large, compared to the water molecules.³³

The equation of Wilke and Chang³⁴ is a well-known semiempirical correlation for the calculation of D_1 :

$$D_1 = 7.4 \times 10^{-12} \left(\frac{\sqrt{\phi_2 M_2 T}}{\mu_2 V_1^{0.6}} \right) \quad (6)$$

ϕ_2 is the association factor for water ($\phi_2 = 2.26$),³⁵ M_i the molecular mass of species i [g mol^{-1}], and V_i the molar volume of species i at its normal boiling point [$\text{cm}^3 \text{ mol}^{-1}$]. The use of the Wilke and Chang equation in aqueous systems leads to an average error of $\sim 10\%$ – 15% .²¹ Since the equation is not dimensionally consistent, the specified units must be employed. Other correlations similar to that of Wilke and Chang can also be used to determine the diffusion coefficient: King et al.,³⁶ Hayduk and Laudi,³⁵ Nakanishi,³⁷ Hayduk and Minhas,³⁸ and Siddiqi and Lucas.³⁹ For the specific case of O₃ as the solute, some other empirical correlations are available, such as Matrosov et al.⁴⁰ and Johnson and Davis.⁴¹ All these correlations are listed in Table 2.

The diffusion coefficient of O₃ is calculated with the help of these correlations and the computed values are listed in Table 3. The estimated values for D_{O_3} range between $11.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $17.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. The diffusion coefficient of O₃ is set equal to the average of these estimated values, i.e., $(15.0 \pm 1.2) \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

The diffusion coefficient of NOM is calculated mainly from the Wilke and Chang equation, because NOM molecules are large, compared to the water molecules (0.2 nm), fulfilling the requirement for using this correlation. One peculiar problem when using this equation is the determination of the hydrodynamic diameter of the NOM molecules. This is the diameter of a sphere having the same hydrodynamic properties

Table 2. Correlations for the Diffusion Coefficient D_1 of Species 1 in Water (Species 2) at Infinite Dilution [$\text{m}^2 \text{ s}^{-1}$]^a

reference	expression
Hayduk and Laudi ³⁵	$D_1 = 13.26 \times 10^{-9} \left(\frac{1}{\mu_2^{1.14} V_1^{0.589}} \right)$
Hayduk and Minhas ³⁸	$D_1 = 1.25 \times 10^{-12} (V_1^{-0.19} - 0.292) \mu_2^{(9.58/V_1) - 1.12} T^{1.52}$
Johnson and Davis ^{41b}	$D_1 = 5.9 \times 10^{-12} \left(\frac{T}{\mu_2} \right)$
King et al. ³⁶	$D_1 = 4.4 \times 10^{-12} (V_2/V_1)^{1/6} (\Delta H_2/\Delta H_1)^{1/2} T / \mu_2$
Matrosov et al. ^{40b}	$D_1 = 4.27 \times 10^{-12} \left(\frac{T}{\mu_2} \right)$
Nakanishi ³⁷	$D_1 = 10^{-9} \left(\frac{2.9726}{\mu_2 V_1^{1/3}} + \frac{0.716 \phi_2 V_2}{\mu_2 V_1} \right)$
Siddiqi and Lucas ³⁹	$D_1 = 9.89 \times 10^{-12} \left(\frac{V_2^{0.265} T}{V_1^{0.45} \mu_2^{0.907}} \right)$

^aNotations and units: V is the molar volume at the normal boiling point [$\text{cm}^3 \text{ mol}^{-1}$], ΔH the latent heat of vaporization at the normal boiling point [any consistent units], T the temperature ($T = 293 \text{ K}$), μ the dynamic viscosity [$\text{cP} = 10^{-3} \text{ Pa s}$], and ϕ the association factor ($\phi = 2.26$ for water). ^bThis correlation can only be used for O₃ as solute (species 1).

Table 3. Calculated Values for the Diffusion Coefficient of O₃ in Water at 293 K. The equations of the used correlations can be found in Table 2. The molar volume and the heat of vaporization of O₃ is 35.50 cm³ mol⁻¹ (Medard⁵⁵) and 15.18 kJ mol⁻¹ (Perry and Green⁴⁷), respectively. The viscosity of water is 1 cP at 293 K

Reference	$D_{\text{O}_3} (\times 10^{-10} \text{ m}^2 \text{ s}^{-1})$
Hayduk and Laudi ³⁵	16.2
Hayduk and Minhas ³⁸	13.6
Johnson and Davis ⁴¹	16.1
King et al. ³⁶	17.7
Matrosov et al. ⁴⁰	11.7
Nakanishi ³⁷	17.6
Siddiqi and Lucas ³⁹	11.8
Wilke and Chang ³⁴	15.1
average value	15.0 ± 1.2

as the actual particle in Brownian diffusion. Thorsen⁴² proposed the following equation for the hydrodynamic diameter of NOM particles:

$$d_1 = (0.88 \text{ nm}) \left[0.85 \left(\frac{M_{\text{NOM}}}{200 \text{ g mol}^{-1}} \right)^{1/3} + 0.15 \left(\frac{M_{\text{NOM}}}{200 \text{ g mol}^{-1}} \right)^{5/6} \right] \quad (7)$$

However, the molecular mass of NOM is not a fixed number, but NOM does have a continuous mass distribution. The value of d_1 should be weighted by the molecular mass distribution of the NOM. The results of Her et al.⁴³ for the Barr–Lake surface water (see Figure 6b in that article) are representative for other surface waters and are used in the following calculation. Only the molecular mass distribution between 610 g mol⁻¹ and 3680 g mol⁻¹ was considered, because that part comprises most of the UV-absorbing compounds, i.e., the NOM fraction that is the most reactive to O₃.^{5,17} The size exclusion chromatogram

with a DOC detector for Barr-Lake water between 610 and 3680 g mol⁻¹ was normalized and fitted by a cubic spline curve $S(x)$ with natural end points,⁴⁴ in which $x = {}^{10}\log(M_{\text{NOM}})$ (because the chromatogram has a logarithmic abscissa). The weighted average of the hydrodynamic diameter of NOM is then calculated by the following expression:

$$\bar{d}_1 = \frac{\int_{610}^{3680} d_1(M_{\text{NOM}}) S({}^{10}\log M_{\text{NOM}}) dM_{\text{NOM}}}{3680 - 610} \quad (8)$$

This results in $\bar{d}_1 = 2.95$ nm, so that the hydrodynamic diameter of the NOM molecules is more than 10 times larger than the size of water molecules. The use of the Wilke and Chang equation is thus justified, and this results in $D_{\text{NOM}} = 1.45 \times 10^{-10}$ m² s⁻¹.

3.1.2. The Solubility of O₃ in Pure Water. The dissolved O₃ concentration, as a function of time in pure water buffered at pH 7, is shown in Figure (3a). After a lag of ~20 s, the

Figure 3. (a) Dissolved O₃ concentration in pure water at pH 7. The O₃ concentration in the gas phase was kept constant at 12.4 mg O₃ L⁻¹ (STP). (b) The data in Figure 3a could be fitted by a straight line if the vertical axis is transformed to $\ln((C_{\text{O}_3}^{\infty} - C_{\text{O}_3}(t))/(C_{\text{O}_3}^{\infty} - C_{\text{O}_3}(0)))$.

concentration of O₃ steadily increases until it reaches a constant value of 1.60 mg L⁻¹ after 380 s. The pseudo-Henry constant H^* can be calculated from this plateau value, $C_{\text{O}_3}^{\infty}$, using eq S4 in the Supporting Information, if $C_{\text{O}_3}^{\infty} = C_{\text{O}_3}^*$ (the decomposition rate of O₃ is negligible, compared to the mass transfer rate). The justification of this assumption will be given in section 3.1.3. The calculated value of the Henry constant for O₃ in

water is $H^* = 5.78$ mol m⁻³ atm⁻¹ (pH 7, 290 K). This value lies within the range 3–7 mol m⁻³ atm⁻¹, reported by De Smidt et al.⁴⁵ for a pH value between 6.5 and 7.5 at 289 K.

In order to calculate $k_L a$, the help variable $\ln[(C_{\text{O}_3}^{\infty} - C_{\text{O}_3}(t))/(C_{\text{O}_3}^{\infty} - C_{\text{O}_3}(0))]$ was introduced, and its values between 20 and 360 s are shown in Figure 3b. According to eq S21 in the Supporting Information, this should be a straight line through the origin with slope $-[k_L a + k_d(1 - \varepsilon)]/(1 - \varepsilon)$. The absolute value of the slope of this straight line is 0.0102 ± 0.0010 s⁻¹. k_d is set equal to $(8.67 \pm 2.35) \times 10^{-4}$ s⁻¹ at pH 7 (see Table S1 in the Supporting Information). The gas holdup ε is determined by eq S6 in the Supporting Information. For a gas flow of 60.0 L h⁻¹: $h_{L+G} = 14.3$ cm and $h_L = 13.7$ cm (three observations), so that $\varepsilon = 0.04$. The value of $k_L a$ is thus 0.0089 ± 0.0010 s⁻¹. The regression line in Figure 3b does not cross the horizontal axis in the origin, but it does cross at $t = 39$ s. This lag period is due to the response time of the O₃ sensor. The deviation between the observed values of $\ln[(C_{\text{O}_3}^{\infty} - C_{\text{O}_3}(t))/(C_{\text{O}_3}^{\infty} - C_{\text{O}_3}(0))]$ and the regression line is higher at the far right of the curve in Figure 3b, because of the very steep slope of the logarithmic function for $x \rightarrow 0+$.

The specific interfacial area a is calculated from eq S5 in the Supporting Information. To do this, the mean diameter of the gas bubbles should be known. It was estimated by visual inspection of a photograph of the bubble cloud in the O₃ reactor: $d_b = 2$ mm. The calculation of the value for a results in 120 m⁻¹. This agrees with typical values of a for gas diffusers (with mechanical mixing), ranging from 30 m⁻¹ to 500 m⁻¹, according to Benefield et al.,⁴⁶ and between 50 m⁻¹ and 600 m⁻¹, according to Perry and Green.⁴⁷ The liquid-phase mass-transfer coefficient (k_L) cannot be determined experimentally, but is calculated by dividing $k_L a$ by a : $k_L = 7.4 \times 10^{-4}$ m s⁻¹. This value lies somewhat above the range given by Perry and Green,⁴⁷ i.e., $(1-4) \times 10^{-4}$ m s⁻¹, but is acceptable in view of the uncertainty on the value of a .

3.1.3. The Hatta Number for the Decomposition of O₃ in Pure Water. In order to determine the pseudo-Henry constant, it was assumed that $C_{\text{O}_3}^* = C_{\text{O}_3}^{\infty}$. The validity of this assumption is investigated by calculating $C_{\text{O}_3}^{\infty}$ from eq S17 in the Supporting Information and comparing it with $C_{\text{O}_3}^*$. If k_d is set equal to $(8.67 \pm 2.35) \times 10^{-4}$ s⁻¹ at pH 7 (see Table S1 in the Supporting Information), then $M_{\text{H1}} = 0.00153$ (see eq S15 in the Supporting Information). The low value of M_{H1} indicates that the kinetic regime of O₃ decomposition in pure water corresponds to a very slow reaction ($M_{\text{H}} < 0.03$),²¹ and hence the concentration profile of O₃ is nearly uniform throughout the film layer (see eq S14 in the Supporting Information). The concentration of O₃ in the bulk liquid is almost equal to the O₃ concentration at the gas/liquid interface: $C_{\text{O}_3}^{\infty} = 0.0330$ mol m⁻³ versus $C_{\text{O}_3}^* = 0.0333$ mol m⁻³. This justifies the kinetic treatment in section 3.1.2 to determine the pseudo-Henry constant.

3.1.4. Apparent Reaction Rate Constant between O₃ and NOM. The residence time of the solution in the O₃ reactor ranges from 2 min to 20 min in large-scale applications, so that only this period will be investigated in the following discussion. The concentration of dissolved O₃ was lower than 0.020 mg L⁻¹ in the bulk of the liquid phase throughout the first 20 min of the experiment (see Figure 5 in the work of Van Geluwe et al.⁶). The value of the apparent reaction constant k_{app} between

O₃ and NOM is calculated by solving the system of eqs 9 and 10:

- First, a mass balance is set up for the agitated batch tank used in the laboratory-scale experiments. At any instant, the rate of the decrease of the NOM concentration in the liquid is equal to the absorption rate of O₃ (quasi steady-state approximation):

$$-(1 - \varepsilon)V_r \frac{dC_{\text{NOM}}}{dt} = -r_{\text{O}_3}V_r \quad (9)$$

V_r is the volume of the laboratory-scale reactor [m³]. C_{NOM} was calculated according to the data of Van Geluwe et al.⁶ (see Figure 3 in that article) by eq 4. The derivative $(dC_{\text{NOM}})/(dt)$ was approximated numerically by central differences (with the exception of the derivative at $t = 0$, for which a forward difference formula was used).⁴⁴

- Second, assume that $M_H < 0.3$ (slow reaction with respect to mass transfer),²¹ so that $E \approx 1$. According to eq S8 in the Supporting Information, the overall rate of O₃ consumption is then equal to

$$-r_{\text{O}_3} = \frac{k_L a k_{\text{app}} C_{\text{NOM}} (1 - \varepsilon)}{k_L a + k_{\text{app}} C_{\text{NOM}} (1 - \varepsilon)} C_{\text{O}_3}^* \quad (10)$$

The apparent rate constant k_{app} , as a function of the oxidation time, is shown in Figure 4. The apparent rate constant is not a

Figure 4. Apparent rate constant (k_{app}) for the reaction between NOM and O₃, as a function of the oxidation time.

constant: it decreases at higher oxidation times. At the start of the experiment, k_{app} has a value of $0.830 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$, but after 2 min, its value has decreased to $0.063 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$. It subsequently reaches a fairly constant value of $0.036 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$, after which it again decreases to a second plateau ($0.018 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$). Note that these values (except for k_{app} at $t = 0$) are in agreement with those reported in the literature, which range from 0.0132 to $0.0954 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (see section S.3 in the Supporting Information). The evolution of k_{app} is caused by the change of the chemical composition and conformation of the NOM.^{48,49} It is not unexpected that the reaction rate is higher at the beginning of the ozonation experiment, since the easily oxidizable species can react now rapidly with O₃.^{18,50}

3.1.5. The Hatta number and the Enhancement Factor for the Reaction between O₃ and NOM. When the apparent rate constant k_{app} is known, the Hatta number M_H can subsequently

be calculated (see eq S10 in the Supporting Information), as a function of the oxidation time, as shown in Figure 5. The

Figure 5. Hatta number M_H , as a function of the oxidation time.

results show that the Hatta number ranges from 0.0484 to 0.0045. Consequently, the kinetic regime of the reactions between NOM and O₃ is slow ($M_H < 0.3$) and the reactions occur only in the bulk liquid, not in the liquid film. M_H is also a monotonously decreasing function and its value is 3–30 times higher than the Hatta number for O₃ decay in pure water ($M_{H1} = 0.00153$). Thus, the decomposition reaction of O₃ will not interfere with the reaction between O₃ and NOM.

At low values of the Hatta number, the enhancement factor E is independent of E_i ($E_i = 8.19$ at $t = 0$). It is asymptotically equivalent to $1 + (M_H^2/3)$ (see Figure S1 in the Supporting Information) and does not reach values higher than 1.001. The necessary assumption for the use of eq 10 is thus valid. In case the value of E is significantly different from 1, the same procedure for the determination of k_{app} and E can be applied, but in an iterative way. The fact that the enhancement factor E is ~ 1 means that the O₃ fluxes for the NOM solution are very close to the fluxes for pure water. Low enhancement factors for O₃ oxidation of the NOM solution are attributed to the relatively low NOM concentration ($\sim 1 \text{ mol C m}^{-3}$), together with the low value for the maximal amount of O₃ dissolved in the liquid ($0.0333 \text{ mol m}^{-3}$).⁵¹

3.2. Calculation of the Reactor Volume on an Industrial Scale. Bubble columns are commonly used as O₃ contactors in water treatment, because of their simple construction, operation, and maintenance.²¹ Bubble columns are typically constructed with a water depth of $\sim 6 \text{ m}$ to achieve 85%–95% O₃ transfer efficiency.⁵² Figure 6 shows a sketch of the reactor. O₃-containing gas is introduced at the bottom of the column. The flow direction of the liquid is from top to bottom. The flow scheme assumes plug flow for both the liquid and the gas phase. Assume that the flow rate of the NF retentate is $400 \text{ m}^3 \text{ h}^{-1}$. The design flow rate of the installation is 20% higher, to accommodate for peaks in the water demand: $F = 480 \text{ m}^3 \text{ h}^{-1} = 7.41 \times 10^{-3} \text{ mol s}^{-1}$.

First, the partial pressure of O₃ in the inlet and outlet gas was determined. The O₃ concentration in the inlet gas is a tradeoff between the energy costs of the O₃ generator and the purchase costs of pure O₂. Figure 7a shows the performance characteristics of a large-scale O₃ generator.⁵³ The dotted line represents

Figure 6. Sketch of the countercurrent bubble reactor.

Figure 7. (a) Oxygen consumption (kg O₂ per kg O₃) and energy consumption (kWh per kg O₃), as a function of the O₃ concentration in the gas stream after passage through the O₃ generator. (Adapted from Rakness and Hunter.⁵³) (b) Specific cost of O₃ generation as a function of the O₃ concentration in the gas stream.

the O₂ consumption [kg O₂ per kg O₃] and the dashed line is the energy consumption [kWh per kg O₃] for various O₃ concentrations in the gas stream after passage through the

generator. The specific cost of the generation of O₃ can now be calculated, as shown in Figure 7b. It was assumed that the electricity cost is equal to 0.0762 € per kWh and the purchase cost of pure O₂ is 60.96 € per ton O₂.²⁹ Figure 7b shows that there exists an optimal O₃ concentration, so that the total production cost of O₃ is minimal. There is a broad minimum at ~10 wt % O₃ and this corresponds to a partial pressure of 0.0685 atm O₃ in the gas inlet of the reactor. The partial pressure of O₃ in the outlet gas is taken to be 10% of the partial pressure in the inlet gas. The specific O₃ cost then amounts to 1.3145 € per kg O₃.

The stoichiometrically required gas flow rate G [mol s⁻¹] can be calculated from a mass balance over the entire column:

$$G \frac{(P_{O_3}^2 - P_{O_3}^1)}{1 \text{ atm}} = F \frac{(C_{NOM}^1 - C_{NOM}^2)}{55600 \text{ mol m}^{-3}} \quad (11)$$

The partial pressure of O₃ in the inlet and outlet gas are fixed, so the gas flow rate is increased if more O₃ is needed. The NOM concentration in the feed stream is fixed ($C_{NOM}^1 = 1.04 \text{ mol m}^{-3}$) and the reactor volume V_r [m³] is calculated for different values of the outlet concentration of NOM (C_{NOM}^2) by the following equation:

$$V_r = \frac{G}{1 \text{ atm}} \int_{P_{O_3}^1}^{P_{O_3}^2} \left(\frac{dP_{O_3}}{-r_{O_3}} \right) \quad (12)$$

where $-r_{O_3}$ is calculated by eq S8 in the Supporting Information. The term $-r_{O_3}$ depends on P_{O_3} , C_{NOM} , k_{app} , k_{La} , and E . Assume that the value of k_{La} of the bubble diffuser is the same as for the laboratory-scale equipment. The value of P_{O_3} and C_{NOM} can be calculated at various places in the reactor by applying eq 11 from point 1 to point i in the reactor, in which the value of k_{app} depends on C_{NOM} . The value of the enhancement factor E is ~1 at every point in the reactor.

The reactor volume can be calculated by approximating the integral in eq 12, using the trapezoidal rule.⁴⁴ The results are shown in Figure 8, and the specific O₃ consumption is shown in Figure 9. The reactor volume increases from 8.2 m³ for a decrease of the UV absorbance of the NOM by 26%, to 27.6 m³ for a decrease of the UV absorbance of the NOM by 60%. A higher NOM removal also implies that the gas flow must increase, and thus the specific O₃ consumption, which ranges

Figure 8. Required reactor volume as a function of the NOM removal (measured by the decrease in UV absorbance at 275 nm).

Figure 9. Specific O₃ consumption (averaged over the entire reactor volume), as a function of the NOM removal (measured by the decrease in UV absorbance at 275 nm).

from 14.6 to 33.5 g O₃ per m³ retentate stream. The specific O₃ consumption increases linearly at higher NOM removal, because it was assumed that the stoichiometry of the reaction between O₃ and NOM (eq 1) remains constant.

3.3. Water Recovery of the Second NF Module. The recovery that can be achieved in the second NF module is estimated from the relative membrane permeabilities shown in Table 1. At the maximal recovery of the second NF module, the retentate obtained in this module (treated by O₃) fouls the membranes as severely as the retentate obtained in the first NF module (not treated by O₃). More precisely, the maximal recovery of the second NF module is achieved when the permeability of the last membranes in the second NF module is equal to the permeability of the last membranes in the first NF module.

Van Geluwe et al.⁶ showed that the alleviation of membrane fouling by O₃ treatment is mainly caused by the selective decomposition of unsaturated C–C bonds (measured by the UV absorbance) that are abundant in the hydrophobic fraction of the NOM. As a first-order approximation, assume that membrane fouling is proportional to the UV absorbance of the filtered stream. In that case, the maximal recovery of the second NF module is achieved if the ratio of C_{R2} (the UV absorbance of the retentate obtained in the second NF module) to C_{R1} (the UV absorbance of the retentate obtained in the first NF module) is equal to

$$\frac{C_{R2}}{C_{R1}} = \frac{1 - U}{1 - T} \quad (13)$$

where U represents the relative membrane permeability without O₃ oxidation and T represents the relative membrane permeability with O₃ oxidation (see Table 1). The ratio C_{R2}/C_{R1} depends on the recovery R of the second NF module and the retention r of the UV absorbing compounds by the membranes:⁵⁴

$$\frac{C_{R2}}{C_{R1}} = \frac{1 - R(1 - r)}{1 - R} \quad (14)$$

The retention r is calculated on the data in Figure 7 in the work of Van Geluwe et al.:⁶ $r = 94.5\%$ for NF 270, $r = 97.6\%$ for Desal 51 HL, $r = 85.5\%$ for NF-PES 10, and $r = 91.2\%$ for

NF 90. The maximal recovery R in the second NF module can now be calculated by equating eqs 13 and 14:

$$R = \frac{T - U}{T - U + r(1 - T)} \quad (15)$$

This results in $R = 52.0\%$ for NF 270, $R = 36.5\%$ for Desal 51 HL, $R = 42.3\%$ for NF-PES 10, and $R = 52.9\%$ for NF 90.

3.4. Economic Evaluation. The feasibility of fouling alleviation of NF membranes by O₃ oxidation strongly depends on its economic assessment. An increase of the membrane flux due to O₃ oxidation of the NOM decreases the capital and maintenance costs of the subsequent NF module. These cost reductions (savings) should be higher than the total costs of the O₃ installation (costs). This is investigated for an integrated NF + O₃ installation with a flow rate of 400 m³ h⁻¹ that removes 34% of the NOM. The design flow rate of the installation is 20% higher, to accommodate peaks in the water demand.

The required NF membrane area is calculated with the help of the permeabilities listed in Table 1. In order to calculate the required membrane area, it is assumed that the pressure difference across the membranes (ΔP) is 5 bar. The average temperature of the feedwater is assumed to be 10 °C (instead of 20 °C during the laboratory-scale experiments). The flux of the NF membranes decreases at lower temperatures and it is assumed that the membrane flux decreases 2.5% per °C temperature difference.²⁸ A flux decline of 10% per membrane during the lifetime of the membranes is also taken into account.²⁸ The required membrane area in the second NF module of the full-scale plant reduces from 14 100 m² to 11 000 m² (for the NF 270 membrane), from 15 100 m² to 11 900 m² (Desal 51), from 16 800 m² to 13 000 m² (NF-PES 10), and from 33 500 m² to 18 500 m² (NF 90), if the retentate solution of the first NF module is oxidized by O₃ before it is fed to the second NF module (see Figure 1). The required volume of the O₃ reactor and the specific O₃ dose can be read out from Figures 8 and 9 (i.e., 10.9 m³ and 18.61 g O₃ per m³, respectively).

The savings and costs are listed in Table 4 (see section 2.4 for more details of the economic computations) and expressed in € per m³ permeate in the second NF module. The permeate flow rate in the second NF module is equal to the product of the feed flow rate (400 m³ h⁻¹) and the recovery R of this module, which is estimated in section 3.3. The figures in Table 4 show that the cost reductions in the second NF module are higher than the total costs of the O₃ installation. This conclusion can be drawn for every investigated membrane and it is especially clear with the NF 90 membrane. This membrane has a rather low permeability, so that a high membrane area is needed, and the flux increases by 31% after O₃ oxidation, which is quite high compared to the other membranes, where a flux increase of 15%–18% could be achieved (see Table 1). The highest amount of money can be saved because less membranes have to be replaced. Concerning the O₃ oxidation unit, the capital costs of the contacting equipment are negligible. The capital costs are determined by the purchase costs of the O₃ generator and are roughly half of the maintenance costs. The energy cost of the O₃ installation is higher than the purchase cost of O₂. The total costs of the O₃ installation are ~90%–93% of the expected cost reductions in the NF installation, if the membranes NF 270 or Desal 51 are used, 77% with NF-PES 10, and <20% with NF 90. This shows that the building of an O₃ installation is recommended if the NF-PES 10 or NF 90 membranes are used, although the

Table 4. Comparison of the Cost Reductions (Savings) of the NF Installation and the Costs of the O₃ Oxidation Unit^a

membrane	NF 270	Desal 51	NF-PES 10	NF 90
Cost Reduction: NF				
civil investments	0.0112	0.0165	0.0167	0.0533
mechanical investments	0.0111	0.0164	0.0166	0.0531
electrotechnical investments	0	0	0	0
purchase of membranes	0.0139	0.0204	0.0206	0.0660
energy costs	0	0	0	0
replacement of membranes	0.0371	0.0547	0.0553	0.1769
chemical costs	0	0	0	0
replacement of miscellaneous parts	0.0071	0.0105	0.0106	0.0340
Total savings	0.0805	0.1186	0.1198	0.3833
Costs: O ₃ Oxidation				
investment O ₃ generator	0.0248	0.0353	0.0305	0.0244
investment contacting equipment	0.0009	0.0013	0.0011	0.0009
O ₂ consumption	0.0218	0.0311	0.0268	0.0214
energy consumption	0.0252	0.0359	0.0310	0.0248
replacement of miscellaneous parts	0.0023	0.0033	0.0029	0.0023
Total costs	0.0750	0.1069	0.0923	0.0738
Total savings – total costs	0.0054	0.0117	0.0275	0.3095

^aThe design flow rate is 400 m³ h⁻¹ (+20% for peaks in water demand). The required NF membrane area is calculated with the help of the permeabilities listed in Table 1. The O₃ oxidation unit removes 34% of the NOM. All figures are expressed in € per m³ permeate in the second NF module.

difference is small (<20%) for the NF 270 and Desal 51 membranes. More elaborate calculations are necessary in order to assess whether the investment in an O₃ installation is worth considering.

CONCLUSIONS

Laboratory-scale experiments were performed to locate the regime of the reaction between NOM and O₃ and to determine the enhancement factor *E*, which is necessary to calculate the volume of a reactor on an industrial scale. The O₃ reactor is a countercurrent bubble reactor, with plug flow for both the liquid phase and the gas phase. The decomposition of NOM is measured by the UV absorbance at 275 nm, because this is a measure for the concentration of the organic matter that is reactive toward O₃ and it is an important factor related to membrane fouling. The first 20 min of the laboratory-scale experiments are relevant, with regard to upscaling. During this period, the residual O₃ concentration in the bulk of the NOM solutions approaches zero when it is compared to the O₃ concentration at the gas/liquid interface. It is shown that the Hatta number decreases monotonously as a function of time, from 0.0484 to 0.0045. The kinetic regime of the reaction between NOM and O₃ is slow (*M_H* < 0.3) and the reaction occurs only in the bulk liquid, not in the liquid film. At no time is there an enhancement of the O₃ absorption by the chemical reaction in the liquid phase: *E* = 1. The reactor volume and the required O₃ dose are calculated as a function of the desired decrease of the UV absorbance. For a design flow rate of 480 m³ h⁻¹, the reactor volume was 8.2 m³ if the UV absorbance is to be decreased by 26%, and 27.6 m³ if the UV absorbance must decrease by 60%. The specific O₃ consumption is 14.6

and 33.5 g O₃ per m³ retentate, respectively. The economic assessment shows that the cost reductions in the second NF module are higher than the total costs of the O₃ installation. This conclusion can be drawn for every investigated membrane (NF 90, NF 270, Desal 51, and NF-PES 10), although the difference is small (<20%) for the NF 270 and Desal 51 membranes, for which more-detailed calculations are necessary.

ASSOCIATED CONTENT

Supporting Information

A Supporting Information section is available separately that presents the mathematical development of the two-film theory with mass transfer and chemical reaction.⁷ The two-film theory for the reaction between O₃ and NOM is studied in Section S.1, while Section S.2 reports on the self-decomposition reaction of O₃. An overview of literature values for the apparent rate constant *k_{app}* is also given (Section S.3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*Tel.: +32 16 322 340. Fax: +32 16 322 991. E-mail: euler-mascheroni@hotmail.be.

Notes

The authors declare no competing financial interest.

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NOMENCLATURE

- ε = gas holdup (m_g³ m_r⁻³)
- 1 – ε = liquid holdup (m_l³ m_r⁻³)
- μ_2 = dynamic viscosity of water; $\mu_2 = 10^{-3}$ Pa s
- φ_2 = association factor for water; $\varphi_2 = 2.26$
- a* = specific interfacial area (m_l² m_r⁻³)
- A* = required membrane area (m²)
- A(t)* = UV absorbance at 275 nm at time *t* (m⁻¹)
- b* = ratio of the stoichiometric coefficient of NOM to O₃ (assumed to be 1)
- C_{NOM}* = NOM concentration in the liquid bulk (mol m_l⁻³)
- C_{O₃}* = O₃ concentration in the liquid phase (mol m_l⁻³)
- C_{O₃}^{*}* = O₃ concentration at the gas/liquid interface (mol m_l⁻³)
- C_{O₃}[∞]* = O₃ concentration in the bulk liquid at saturation (mol m_l⁻³)
- C_{O₃}^b* = O₃ concentration in the bulk liquid (mol m_l⁻³)
- d_b* = diameter of the gas bubbles (m)
- D_i* = diffusion coefficient of solute *i* in water at infinite dilution (m² s⁻¹)
- E* = enhancement factor
- E_i* = enhancement factor for instantaneous reactions
- F* = liquid flow rate of the O₃ reactor (m_l³ h⁻¹)
- G* = gas flow rate of the O₃ reactor (m_g³ h⁻¹)
- H^{*}* = pseudo-Henry constant (mol m_l⁻³ atm⁻¹)
- ΔH_i = latent heat of vaporization of *i* at its normal boiling point (J mol⁻¹)
- h_L* = liquid height without gas bubbling (m)
- h_{L+G}* = liquid height with gas bubbling (m)

k_{app} = apparent reaction rate constant between O_3 and NOM ($\text{mol m}_i^{-3} \text{s}^{-1}$)
 k_B = Boltzmann constant; $k_B = 1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$
 k_d = self-decomposition rate constant of O_3 (s^{-1})
 K_L = overall mass-transfer coefficient of O_3 ($\text{m}_i^3 \text{ m}_i^{-2} \text{s}^{-1}$)
 k_L = mass-transfer coefficient of O_3 in the liquid phase ($\text{m}_i^3 \text{ m}_i^{-2} \text{s}^{-1}$)
 k_{La} = volumetric mass-transfer coefficient of O_3 in the liquid phase ($\text{m}_i^3 \text{ m}_r^{-3} \text{s}^{-1}$)
 M_H = Hatta number for the reaction between O_3 and NOM
 M_{H1} = Hatta number for the decomposition reaction of O_3 in pure water
 M_i = molecular mass of i (g mol^{-1})
 N_{O_3} = flux of O_3 transferred per square meter interfacial area ($\text{mol m}_i^{-2} \text{s}^{-1}$)
 ΔP = transmembrane pressure (atm)
 $P_{O_3}^*$ = partial pressure of O_3 at the gas–liquid interface (atm)
 P_{O_3} = partial pressure of O_3 in the gas bulk (atm)
 r_{O_3} = flux of O_3 transferred per cubic meter reactor volume ($\text{mol m}_r^{-3} \text{s}^{-1}$)
 T = temperature (K)
 V_i = molar volume of i at its normal boiling point ($\text{cm}^3 \text{ mol}^{-1}$)
 V_r = volume of the O_3 reactor (m^3)

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