Eightfold increased membrane flux of NF 270 by O₃ oxidation of natural humic acids without deteriorated permeate quality

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Abstract

BACKGROUND: Membrane fouling by humic acids limits the water recovery of nanofiltration in drinking water production. This article investigates if membrane fouling can be reduced by decomposition of humic acids in the concentrate stream by O₃ oxidation.

RESULTS: At a specific O₃ dose of 2.11 g O₃ per g COD (17.0 g m⁻³ O₃ (g) for 20 min), a COD reduction of 38% and a hydrophobic COD reduction of 69% is achieved. The membrane permeability of the ozonated solution by NF 270 membranes is higher ($20.6 \times 10^{-9} \text{ L s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$) than the permeability if the untreated solution is filtered ($2.4 \times 10^{-9} \text{ L s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$). The COD retention of the ozonated solution was similar to the retention of the untreated samples. The addition of H₂O₂ allows a better mineralization degree, i.e. UVA removal increased from 53% to 66% if H₂O₂ was added as from 10 min oxidation at the same molar flow rate as O₃.

CONCLUSION: O₃ oxidation can substantially alleviate membrane fouling by humic acids in nanofiltration systems and the addition of H₂O₂ can slightly improve its decomposition.

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Keywords: nanofiltration; ozone; advanced oxidation; humic acids

INTRODUCTION

Nanofiltration (NF) is an effective and reliable method for the combined removal of a broad range of pollutants in surface water.^{1,2} However, fouling of the membrane limits the water recovery for this application to about 80%.³ As problems with water scarcity are expected to grow worse in the coming decades, even in regions currently considered water-rich,⁴ a 20% waste of the feed water cannot be tolerated. Therefore, this article will investigate if membrane fouling can be reduced by decomposition of organic matter in the concentrate stream by O₃ oxidation.

O₃ oxidation is often chosen for the decomposition of humic acids because it is a powerful oxidant that reacts selectively with double bonds and aromatic rings with a high electron density, which are abundant in humic acids. In addition, O₃ decomposes into reactive radicals, including hydroxyl radicals ([•]OH). In contrast to O₃, [•]OH is a non-selective oxidant which reacts very fast with the vast majority of inorganic and organic compounds in water. Generation of these [•]OH radicals can be artificially accelerated by the addition of H₂O₂ (perozonation). This leads to an advanced oxidation process (AOP). The main advantages of ozone-based AOPs are the oxidation of O₃-resistant compounds and the shorter reaction time. However, the higher formation rate of [•]OH is at the cost of a higher O₃ consumption. In addition, [•]OH reacts rather unselectively and thus only a small fraction of these radicals reacts with the target pollutant, which makes AOPs quite inefficient processes.⁵

Although both subjects, membrane fouling mitigation and O₃ oxidation, are extensively studied in literature, only a few researchers have investigated the process where O₃ oxidation and membrane filtration are combined. Most researchers^{6,7,8,9,10,11,12} investigated the effect of O₃ on fouling of microfiltration (MF) and ultrafiltration (UF) membranes. Researchers showed that the combination of O₃ pre-oxidation and membrane filtration is effective for the prevention of membrane fouling. The membrane performance was highly correlated with the residual aqueous O₃ concentration in the permeate.^{6,7,12} A higher membrane flux is obtained if the aqueous O₃ concentration at the membrane surface increases, without changing the O₃ dose. Karnik *et al.*⁷ and Lehman *et al.*¹² showed that stable fluxes of more than 95% of the

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pure water flux can be maintained if the aqueous O₃ concentration at the membrane surface is greater than 0.05 mg L⁻¹. Thus, if the O₃ dose is slightly above the instantaneous O₃ demand of the feed water, a substantial recovery of the permeate flux could be observed; the larger the O₃ concentration, the larger the flux recovery. Evidently, beyond a certain value, the O₃ concentration does not affect the permeate flux any more, which in some cases can become equal to the pure water flux.

There is no thorough study reported of O₃ oxidation combined with NF or reverse osmosis. This is not surprising, because the literature on membrane cleaning focuses on MF and UF. A second explanation is that O₃ resistant membrane materials, such as ceramics and fluorinated plastics, are only available for MF and UF. If other membrane materials are used, O₃ has to be removed before it reaches the membrane surface. This can be done easily by an additional aeration step after the ozonation reactor.

This paper investigates the decomposition of humic acids by O₃ and O₃ + H₂O₂ oxidation and its effect on flux and retention of the membrane NF 270. Humic acids are high in aromatic carbon and contain primarily carboxylic acids, methoxyl carbonyls and phenolic functional groups.¹³ They represent between 50 and 75% of the DOC content in surface waters.¹⁴ Their fouling potential is defined by their molecular size and the chemical interactions between humic acids and the membrane, i.e. hydrogen bonding, electrostatic and hydrophobic interactions. They are often claimed as the most important membrane foulants of natural waters.^{15,16,17,18} Therefore, the humic acids were deliberately separated from the other organic fractions in the feed water.

Most researchers that investigated the fouling behaviour or oxidation of humic acids, used commercial humic acids, such as supplied by Fluka or Aldrich, as analogues of natural humic acids.¹⁹ Malcolm and MacCarthy²⁰ and Marshall *et al.*²¹ demonstrated that humic acids from streams and soils differ significantly from commercial humic acids. Commercial humic acids were found to have a lower nitrogen content and a higher ash content. In addition, the difference in the numbers of resonance peaks revealed by ¹³C-nuclear magnetic resonance (NMR) implied that natural humic acids contain a markedly more diverse range of functional groups than commercial humic acids. The NMR spectra of commercial humic acids indicated low carboxyl group contents, low contents of carbon atoms bonded to either oxygen or nitrogen, high saturated aliphatic carbon contents and very intense signals at 32 ppm indicative of repeating alkyl chain units. Commercial humic acids have a much higher average molecular mass than typical aquatic humic acids,^{19,22} because they are usually derived from soils and peat. The molecular mass of humic substances in water streams is estimated from 1500–5000 g mol⁻¹, and from 50 000–500 000 g mol⁻¹ for terrestrial humic acids.¹⁴

As a result of these differences, commercial humic acids are not representative of true aquatic humic acids, especially in research on membrane filtration and O₃ oxidation, where the physicochemical nature of the foulants and their reactivity are important. In this research, natural humic acids were isolated from Dijle river water in Belgium by adsorption on Amberlite XAD 7 HP resin (Rohm & Haas, USA).

MATERIALS AND METHODS

Determination of the organic constituents in water samples

The chemical oxygen demand (COD) and UV absorption (UVA) were used as surrogate measures to detect organic constituents in

water. COD was determined by the decrease in chromate concentration after 2 h boiling at 148 °C, which is spectrophotometrically measured (Nanocolor test tubes; Macherey-Nagel, Germany). All COD tests were done in duplicate. UVA was measured by a Shimadzu UV-1601 double beam spectrophotometer (Shimadzu, Japan) at a wavelength of 254 nm, as frequently used in the literature. Because absorptivity varied with solution pH, each sample was adjusted to pH 8 before measurement. Owing to the disturbance of COD measurements by interference from H₂O₂,²³ only UVA could be determined for the peroxonated samples. For the peroxonated samples, UVA at 280 nm instead of 254 nm is shown because of the lower interference from H₂O₂ at this wavelength. It is well known that $\pi-\pi^*$ electron transitions occur between wavelengths from 270–280 nm. For this reason, the application of UVA within 270–280 nm is also suitable for describing aromatic carbon moieties.²⁴

Hydrophobic and hydrophilic fractions of oxidized humic acids were obtained by passage through a nonionic macroreticular resin (Amberlite XAD 7 HP, Rohm & Haas, USA). Before use, the resin was rinsed thoroughly following the procedure of Thurman and Malcolm.²⁵ All samples were acidified to pH 1.5 with HNO₃ before fractionation. The samples were passed through a glass column with 200 mL resin at a constant flow rate of two bed volumes per hour by a peristaltic pump. It was necessary to filter at least 200 mL to obtain stable COD values for the effluent. The COD of the effluent collected between 250 and 300 mL was measured and the hydrophobic COD was determined by the difference between the COD of the column feed and this effluent COD.

Preparation of humic acid solutions

The COD of NF concentrates is dependent on the COD of the raw water source, the water recovery of the membrane module and the COD rejection value of the membrane. The surface water in Flanders, used as the raw water, may be polluted by discharges such as treated and untreated municipal waste-water. Although the situation has improved since 1990, 28% of the municipal waste-water is not treated today and is discharged into the Flemish surface waters.²⁶ For the majority of the monitoring sites, the water quality still does not meet the standards. According to the Flemish Environment Agency (VMM, Vlaamse Milieumaatschappij), which monitors the physico-chemical and biological quality of the natural waters in Flanders, the average COD is 42.7 mg L⁻¹, nitrate concentration 3.9 mg N L⁻¹, ammonia concentration 3.1 mg N L⁻¹, orthophosphate concentration 0.5 mg P L⁻¹ and the mean dissolved O₂ concentration is 7.2 mg L⁻¹ (2006). In conclusion, the overall quality of Flemish surface waters can be considered slightly polluted. A recent incident is the disposal of untreated waste-water from the city of Brussels into the Zenne river for 10 days. The water purification plant in Brussels was shut down as a result of a conflict between the operator Aquiris and the Brussels Region.²⁷

The feed water used in the experiments was taken from the river Dijle, Leuven (Belgium). The raw water was prefiltered using MN 713 1/4 (Macherey-Nagel, Germany) and Whatman Grade No. 4 filters (pore size: 20–25 µm) (Whatman, USA). After lowering the pH to 1.5 with HNO₃, the water was pumped through a glass column (internal diameter: 40 mm) with 400 mL Amberlite XAD 7 HP resin (Rohm & Haas) at a flow rate of two bed volumes per hour by a peristaltic pump. According to certain hydrophobic–hydrophilic interactions between organic solutes and the non-ionic sorbing solid at a given preadjusted acidity, the relatively most hydrophobic macromolecular organic acids (i.e. humic acids) were retained on the resin. The adsorbed matter

was desorbed by pumping 0.1 mol L^{-1} NaOH, in counter-current direction, through the resin, at one bed volume per hour. The sample was acidified immediately to avoid oxidation of humic acids. It was filtered by Whatman Grade No. 50 filters (pore size $2.5 \mu\text{m}$) before use.

The pH of the feed samples was set to 8.0. The mean COD of the samples was 83 mg L^{-1} with a standard deviation of 7 mg L^{-1} . The mean UVA value at 254 nm was 1.023 cm^{-1} and the standard deviation 0.177 cm^{-1} . Carbonate/bicarbonate is also an important parameter since it is a well-known scavenger of $\bullet\text{OH}$ radicals.⁵ A typical value of the alkalinity in NF concentrates is 5 mmol L^{-1} . Therefore, 420 mg L^{-1} NaHCO_3 was added to each feed solution, except where otherwise mentioned. During the experiments, the pH did not change appreciably. The mean pH difference observed was 0.3 units and its maximum 0.9 units.

Ozonation experiments

The feed gas to the O_3 generator (OZ 500) (Fischer, USA) was pure O_2 . The gas flow rate was fixed at 60.0 L h^{-1} at standard temperature and pressure (STP). The glass reactor vessel had an inner diameter of 115 mm and contained 1.90 L humic acid solution. A gFFOZ Process Ozone Sensor (IN, USA) measured the O_3 concentration in the gas flow by UV absorption at 254 nm . The aqueous O_3 concentration was measured by AccuVac ampoules (Hach, USA) which are based on the indigo method. The O_3 – O_2 mixture was introduced from the bottom of the reactor through a pyrex fritted glass diffuser, with a mass transfer coefficient of $89.2 \pm 4.5 \text{ h}^{-1}$ in our experimental conditions. The solution in the vessel was mixed by a magnetic stirrer. For the $\text{O}_3/\text{H}_2\text{O}_2$ experiments, H_2O_2 solution was added at the bottom of the vessel at a constant flow rate by a peristaltic pump. After oxidation, the O_3 generator was turned off and pure O_2 was injected for 5 min to remove residual O_3 in the solution.

Membrane filtration experiments

NF experiments were performed in a cross-flow set-up (Amfilter, the Netherlands) at laboratory scale. The equipment consists of two modules with a flat sheet membrane that has an effective surface area of 0.00415 m^2 . The flow channel is rectangular with a hydraulic diameter of 4.2 mm . The total channel length is 293 mm . The temperature in all experiments was maintained at 293 K by a cooling water circuit. The cross-flow velocity was at least 4.0 m s^{-1} , which corresponds to a Reynolds number of 26 500 (turbulent flow), in order to minimize concentration polarization. NF experiments were carried out with the NF 270 membrane (FilmTec, USA). This is a polyamide membrane with a relatively low molecular weight cut-off (MWCO) of 300 g mol^{-1} .²⁸

Before each experiment, the membrane was kept in deionized water for 24 h to remove the protective coating layer. Afterwards, the membrane was pressurized at 12 bar for 2 h using deionized water (compaction). The pure water flux of the membrane was determined at the end of the compaction process. The feed reservoir was subsequently emptied. It was then refilled with 5 L test solution and diluted by the remaining deionized water in the system (less than 1 L). The applied pressure was 12 bar and both permeate and retentate were recycled to the feed reservoir.

The retention data in Fig. 3 were determined by filtering 125 mL feed solution in a dead-end module (Sterlitech HP4750 Stirred Cell; Kent, USA) pressurized to 0.80 MPa with N_2 gas. The FTIR spectra of the fouled membranes in Fig. 4 were recorded on an Alpha FTIR spectrometer (Bruker, Germany) equipped with a platinum

diamond for single reflection attenuated total reflectance (ATR), in the range 4000 – 400 cm^{-1} with a resolution of 1.43 cm^{-1} , at room temperature with an average of 16 scans.

Determination of the molecular mass fractions

The high molecular mass fractions of the organic matter was measured by the UVA retention for three different membranes, namely UP020, UP010 and UP005 (Microdyn-Nadir, Germany) with MWCO of 20, 10 and 5 kg mol^{-1} respectively. The retention data were determined by filtering 125 mL feed solution in a dead-end module (Sterlitech HP4750 Stirred Cell; Kent) pressurized to 0.80 MPa with N_2 gas at a water recovery of 80%. For each sample, the UVA of the UF permeates was divided by the residual UVA, to calculate the percentage of organic matter with a molecular mass lower than the MWCO of the membrane. Thus, the term ' $\text{UVA} < 20 \text{ kg mol}^{-1}$ ' represents the fraction of the UV absorbing compounds with a molecular mass lower than 20 kg mol^{-1} . The data for the feed solution is the mean of three different samples.

Experimental error

For each O_3 concentration, two different humic acid solutions were used, and the duration between the preparation of these solutions was at least two months. Thus, the composition of the two solutions can be regarded as independent and in this way, season and weather changes of the surface water have been taken into account. However, the same solution was used for the data at 10 and 20 min oxidation time, so that a comparison between different oxidation times can easily be drawn.

The data in Fig. 1 are presented as follows. The reported COD and UVA values are the mean for the two solutions. They are represented, respectively, by diamonds or triangles and connected by a continuous line. The separate measurements for the two solutions are represented by the ends of the error bars, which give a general idea of the accuracy of the measurements. The same strategy was followed for the data of the hydrophobic COD in Fig. 2 and the COD retention of NF 270 membranes in Fig. 3.

The COD measurements were done in duplicate and the mean value was calculated. The mean difference between two replicated COD measurements was 2.4 mg L^{-1} for the solutions before oxidation, 2.1 mg L^{-1} for the solutions after 10 min oxidation and 2.2 mg L^{-1} for the solutions after 20 min oxidation. The maximal tolerated difference between two replicated COD measurements was 4 mg L^{-1} . The UV absorption of the samples was only measured once, because of the small difference between two replicated measurements ($\sim 0.0020 \text{ cm}^{-1}$).

The perozonation experiments, for which the UVA results are shown in Figs 5 and 6, were not replicated, but the same feed solution was used, thus no error was made due to compositional variations of the feed solutions. The UVA differences between the ozonation and perozonation experiments (10–15%) is much higher than the mean experimental error of the UVA measurements shown in the Fig. 1 (4.3%), and thus statistically significant.

RESULTS AND DISCUSSION

Ozone oxidation does not reduce the COD sufficiently

The influence of the O_3 concentration in the gas flow on the residual COD and UVA after 10 min oxidation is shown in Fig. 1. At a gaseous O_3 concentration of 17 g m^{-3} STP in a constant gas flow of 60.0 L h^{-1} , which corresponds to a specific O_3 dose

Figure 1. Influence of O₃ concentration on the removal of humic acids (feed solution: COD: $83 \pm 7 \text{ g m}^{-3}$, UVA(254 nm): $1.023 \pm 0.177 \text{ cm}^{-1}$). The oxidation time was set to 10 min (10') or 20 min (20'). The horizontal axis shows the O₃ concentration in the gas flow. In all experiments, the gas flow was set to 60 L h^{-1} . The vertical axis shows the COD and UVA of the ozonated samples divided by the COD and UVA of the feed solution.

Figure 2. Comparison between the hydrophobic COD and total COD after oxidation. The hydrophobic COD of the feed solutions is equal to their total COD.

Figure 3. COD of the permeate after filtration of an ozonated solution by the NF 270 membrane. The horizontal bars represent the limits of the permeate COD after filtering untreated solutions.

of $1.03 \text{ g O}_3 \text{ g}^{-1} \text{ COD}$, a substantial COD decrease of about 35% could be achieved. The COD was further reduced at higher O₃ concentrations. However, it can be seen in Fig. 1 that the COD could not be reduced by more than 60%. For example, at a

gaseous O₃ concentration of 89 g m^{-3} , which corresponds to a specific O₃ dose of $5.28 \text{ g O}_3 \text{ g}^{-1} \text{ COD}$, the COD reduced by 56%. The small COD reductions at higher O₃ concentrations cannot be justified by the higher treatment costs. The O₃ dose, expressed in $\text{mg L}^{-1} \text{ O}_3$, required per unit COD removed, decreases from 4.02 at $6.3 \text{ g m}^{-3} \text{ O}_3$ to 3.09 at $17 \text{ g m}^{-3} \text{ O}_3$, but increases then steadily to 9.45 at the highest O₃ concentration (89 g m^{-3}).

UVA reductions are higher than COD reductions due to the selective reaction of O₃ with aromatic rings and double bonds. It is reduced by 48% for an O₃ concentration of 17 g m^{-3} , after which it reaches a fairly constant value between 50 and 60% for higher O₃ concentrations. If the ozonation time was increased from 10 to 20 min, COD and UVA showed no further reduction except at O₃ concentrations lower than $12 \text{ g m}^{-3} \text{ O}_3$ in the gas phase (Fig. 1). Therefore, it can be concluded that low O₃ concentrations are to be recommended in order to diminish treatment costs, as higher O₃ concentrations cannot improve humic acid removal appreciably.

The relationship between the O₃ concentration in the liquid phase ($[\text{O}_3]_{\text{L}} (\text{g m}^{-3})$) and in the gas phase ($[\text{O}_3]_{\text{g}} (\text{g m}^{-3})$ (STP)) was $[\text{O}_3]_{\text{L}} = 0.155 + 0.223 [\text{O}_3]_{\text{g}} - 6.0 \times 10^{-4} [\text{O}_3]_{\text{g}}^2$ ($R^2 = 0.996$) for pure water at pH 3 and 297 K, where the decomposition of O₃ can be neglected. Under these circumstances, the steady-state concentration is 2.62 g m^{-3} at a gas phase O₃ concentration of 11.5 g m^{-3} . The steady-state concentration in pure water with

Figure 4. FTIR spectra of (a) a clean NF 270 membrane; (b) after 24 h filtration of an untreated humic acid solution; (c) after 24 h filtration of a humic acid solution after O₃ oxidation (9.0 g m⁻³ O₃, 30 min).

Figure 5. Effect of H₂O₂ addition on the residual UVA at 280 nm. H₂O₂ was added from 10 min at a constant flow rate of 0.98 ± 0.03 mol H₂O₂ mol⁻¹ O₃. The total oxidation time was set to 20 min.

Figure 6. Influence of the molar ratio of H₂O₂ to O₃ dosage on the UVA removal at 280 nm. H₂O₂ was added from 10 min. The O₃ dose stayed constant at 0.25 mmol O₃ min⁻¹, which corresponded to an O₃ concentration in the gas phase of 12 g m⁻³.

pH = 8, i.e. the same acidity as the concentrate solution, is lower, namely 1.79 g m⁻³, due to the self-decomposition of O₃. During the ozonation of humic acid solutions (11.5 g m⁻³ O₃ in the gas phase), the aqueous O₃ concentration increased to only 0.39 g m⁻³ after 19 min, following the second-order polynomial equation $[O_3]_l = 1.4 \times 10^{-3}t - 1.1 \times 10^{-3}t^2$ ($R^2 = 0.986$), where t represents the oxidation time in minutes.

Ozone oxidation changes the hydrophobicity and the molecular mass of humic acids

Although it is not possible to achieve an extensive degree of mineralization with O₃ oxidation, O₃ greatly alters the structure of the humic acids, as can be seen from the effect of O₃ oxidation on the hydrophobicity and the molecular mass of the organic matter.

Hydrophobic interactions are the most important between humic acids and the membrane surface and thus greatly influence membrane fouling. Aromatic rings in humic substances can adsorb on polymeric membranes, such as the aromatic polyamide layer of NF 270, to provide a large van der Waals stabilization. The interaction between two aromatic rings via π - π bonds is also a possible mechanism for adsorption.²⁹ Such π - π bonds are weak dative bonds between adjacent delocalized π systems (usually aromatic rings) that adopt a parallel-planar geometry.³⁰

The hydrophobic COD is measured by the difference of the influent and effluent COD after passage through a XAD 7 resin. The hydrophobic COD of the feed solutions is equal to the total COD, as explained in the Materials and methods section. After O_3 oxidation, the hydrophobic COD is substantially smaller than the total COD. Figure 2 shows the residual COD and residual hydrophobic COD after 10 and 20 min ozonation. Although the total COD was reduced by only 34% at 17 g m^{-3} O_3 , the hydrophobic COD was reduced by 62% after 10 min. The hydrophobic COD could be removed by more than 80% at higher O_3 concentrations.

This is caused by the preferential oxidation of electrophilic aromatic groups by O_3 . O_3 transforms these hydrophobic moieties into aldehydic, ketonic and especially carboxylic groups.^{5,31} O_3 is thus able to transform the hydrophobic groups of humic acids, responsible for severe fouling onto polymeric membranes, into more hydrophilic substances. However, these saturated compounds react typically very inefficiently with O_3 , so they are not further mineralized into CO_2 and H_2O , which explains the difficulties in achieving an extensive COD removal with O_3 oxidation, as discussed in the previous subsection. Similar to the total COD, the hydrophobic COD is only slightly reduced if the reaction time is increased to 20 minutes. The commercial humic acids previously studied¹⁹ showed a similar behaviour concerning the removal of COD and in both cases there was a selective removal of hydrophobic COD. The UVA decrease was higher in the case of the commercial humic acids.

Beside the changes in chemical structure, the size of humic acids is also a paramount parameter in membrane fouling. Several researchers found that the high molecular mass fraction causes severe membrane fouling.^{15,32,12} This fraction can constrict and block the pores of the membrane and have a small back diffusion rate, so a cake or gel layer is formed on the membrane surface. Table 1 shows the distribution of the high molecular mass fractions of the humic acids before and after O_3 oxidation. It is measured by retention data for three UF membranes with different MWCO. It is observed that the high molecular mass fractions of the humic acids ($>10\text{ kg mol}^{-1}$) represent a lower portion of the UV absorbing compounds after O_3 oxidation than before O_3 oxidation. Beside the fact that the high molecular mass chains comprise a lower percentage of the UVA in the ozonated solutions, the amount of high molecular mass components is also decreased by the substantial reduction of the total UVA (40–60%) by O_3 oxidation. This conclusion could also be drawn for the commercial humic acids previously studied.¹⁹ The efficient decomposition of the high molecular mass fraction by O_3 is favourable because the cross-flow operation in the membrane module can flush away loose fragments of the cake layer, which decreases the thickness of the foulant layer and thus flux decline.⁶

Because O_3 is able to decompose organic molecules into smaller fragments, it is possible that the rejection of humic acids by NF membranes is lower after oxidation. Therefore, the retention of the oxidized humic acid solutions has been investigated as well. The reaction products are mainly saturated compounds and are

preferably measured by COD instead of UV absorption. Figure 3 shows the COD of the permeate by the NF 270 membrane, after filtration of solutions oxidized at various O_3 concentrations for 10 min. The horizontal bars represent the limits of the permeate COD after filtering (three) untreated solutions. Similar results were obtained if the oxidation time was increased to 20 min. It can be seen that the CODs of the permeates after O_3 oxidation lie within the range of those measured with the untreated solutions. There are thus no concerns that the reaction products with a low molecular mass will pass through the membrane.

The effect of ozone oxidation on membrane fouling of NF 270 membranes

Membrane filtration experiments with a cross-flow system were carried out in order to investigate the effect of O_3 oxidation on the permeability of the NF 270 membrane. The pure water permeability of the membrane is equal to $27.5 \times 10^{-9}\text{ L s}^{-1}\text{ m}^{-2}\text{ Pa}^{-1}$. Severe membrane fouling during filtration of an untreated humic acid solution caused a rapid decrease of the membrane permeability to a stationary value of $2.4 \times 10^{-9}\text{ L s}^{-1}\text{ m}^{-2}\text{ Pa}^{-1}$. The membrane permeability after O_3 oxidation of the humic acid solution (9 g m^{-3} O_3 (g) for 30 min) is substantially higher than the untreated solution. The mean permeability during the filtration test, which lasted for 24 h, was equal to $20.6 \times 10^{-9}\text{ L s}^{-1}\text{ m}^{-2}\text{ Pa}^{-1}$, which is eight times higher than for the untreated solution, although the residual aqueous O_3 was removed to protect the membrane surface for corrosion.

FTIR spectra were taken of the membranes after 24 h filtration to obtain more information about the chemical structure of the membrane foulants. The FTIR spectrum shown in Fig. 4(a) is taken from the bare NF 270 membrane. The small peaks between 3000 cm^{-1} and 2800 cm^{-1} are caused by stretching vibrations of aliphatic C–H bonds in $-CH_3$ and $-CH_2$ units. The fact that there are no peaks at wavenumbers higher than 3000 cm^{-1} indicates that unsaturated hydrocarbons, such as aromatic rings, are not abundant. The spectrum contains several strong absorption peaks at wavenumbers smaller than 1585 cm^{-1} . Most are associated with functional groups of the polysulfone support layer of the membrane. The peaks at 1585 cm^{-1} and 1470 cm^{-1} correspond to aromatic in-plane ring bend stretching vibrations of polysulfone. The two small peaks around 1280 cm^{-1} are caused by the asymmetric SO_2 stretching vibration, the high peak at 1240 cm^{-1} by the C–O–C asymmetric stretching vibration of the aryl–O–aryl group, the two peaks at 1150 cm^{-1} by the symmetric SO_2 stretching vibration and the peak at 830 cm^{-1} by in-phase out-of-plane hydrogen deformations of para-substituted phenyl groups.³³ The other peaks in the fingerprint region (1200 – 400 cm^{-1}) are mainly due to various bending vibrations of carbon–carbon bonds. The top layer of the NF 270 membrane is a poly(piperazinamide) based semi-aromatic polyamide. However, the amide I band for poly(piperazinamide) at 1630 cm^{-1} is hardly visible, which is in agreement with the results of Tang *et al.*³³

The FTIR spectrum of the membrane fouled by an untreated humic acid solution is shown in Fig. 4(b). The spectrum consists of several broad absorption bands. The broad region between 3600 cm^{-1} and 3000 cm^{-1} corresponds to hydrogen-bonded OH-stretching vibrations from phenolic and aliphatic–OH groups. The small peaks around 2900 cm^{-1} represent stretching vibrations of aliphatic C–H bonds. The broad band between 1750 and 1600 cm^{-1} is assigned to C=O stretching of carboxyl and carbonyl groups. The peak at 1540 cm^{-1} is caused by aromatic C=C stretching vibrations. Amide II stretching at this wavenumber

Table 1. The effect of O₃ oxidation on decomposition of the high molecular mass fraction in the humic acid solutions

Reaction time	Feed	10 min					20 min		
O ₃ -concentration in the gas phase (g m ⁻³)	–	17.0	39.3	74.5	90.0	17.5	39.3	75.0	91.0
Residual UVA (254 nm) (cm ⁻¹)	1.044	0.491	0.608	0.498	0.634	0.472	0.583	0.468	0.565
UVA of permeate after filtration with UP020 membrane (cm ⁻¹)	0.872	0.452	0.578	0.459	0.619	0.420	0.540	0.392	0.510
	±0.008	±0.008	±0.010	±0.002	±0.010	±0.006	±0.005	±0.003	±0.008
UVA of permeate after filtration with UP010 membrane (cm ⁻¹)	0.807	0.449	0.565	0.433	0.616	0.415	0.534	0.395	0.500
	±0.012	±0.015	±0.018	±0.013	±0.009	±0.009	±0.010	±0.004	±0.011
UVA of permeate after filtration with UP005 membrane (cm ⁻¹)	0.613	0.345	0.488	0.432	0.500	0.306	0.467	0.337	0.499
	±0.077	±0.025	±0.073	±0.017	±0.024	±0.023	±0.070	±0.027	±0.021
Fraction of the UV absorbing compounds with a molecular mass lower than the indicated value									
UVA < 20 kg mol ⁻¹	83.6%	92.1%	95.1%	92.2%	97.6%	89.0%	92.6%	83.8%	90.3%
UVA < 10 kg mol ⁻¹	77.5%	91.4%	93.3%	86.9%	97.2%	88.0%	91.8%	84.4%	88.5%
UVA < 5 kg mol ⁻¹	59.1%	70.3%	80.3%	86.7%	78.9%	64.8%	80.1%	72.0%	88.3%

is not likely because of the low nitrogen content of humic acids. The small peak at 1380 cm⁻¹ is associated with O–H bending vibrations of alcohols, carboxylic acids and phenols. The small peak at 1240 cm⁻¹ is caused by C–O stretching and O–H deformation of –COOH groups. The broad region around 1025 cm⁻¹ corresponds to O–H deformation and C–O stretching in aliphatic alcohols. None of the peaks of the bare membrane could be observed. This indicates that the thickness of the cake layer on the membrane surface is larger than the penetration depth of the IR rays, which is between 0.4 and 2.0 µm for ATR.

The FTIR spectrum of the membrane fouled by humic acids after O₃ treatment is shown in Fig. 4(c). It is remarkable that all the absorption peaks of the membrane are again visible, which indicates that the thickness of the fouling layer is much lower if O₃ oxidation is applied. However, there are some differences with the spectrum of the bare membrane in Fig. 4(a). The broad region associated with H bonds (3600–3000 cm⁻¹), the peak of C=O stretching of carboxyl and carbonyl groups (1650 cm⁻¹) and the broad region of aliphatic alcohols between 1150 and 900 cm⁻¹ are reduced compared to the spectrum of the untreated humic acid solution, but still clearly visible.

Improved decomposition of humic acids by advanced ozone oxidation

The major drawback of O₃ oxidation is the too low degree of decomposition that can be achieved. The humic acids are oxidized to saturated organic molecules which react typically very inefficiently with O₃, so they are not further mineralized. Therefore, it is investigated if the formation of •OH radicals could enhance the mineralization of the ozone-resistant reaction products. The formation of •OH is enhanced by the addition of H₂O₂ to the solution during O₃ oxidation. The conjugated base of H₂O₂, HO₂⁻, initiates O₃ decomposition by electron transfer through a reaction that can be written as:

However, the higher formation rate of •OH is at the cost of a higher O₃ consumption. Therefore, it is chosen to add no H₂O₂ during the first 10 min of the oxidation treatment. During this first phase, O₃ is able to change the hydrophobic nature of the humic acids and achieve a reasonable reduction of COD and UVA and a

very efficient reduction of the hydrophobic COD. After 10 min, the carboxylic reaction products have accumulated in the solution. From this moment, H₂O₂ is added to the solution with the aim of increasing the concentration of •OH radicals, which can possibly lead to more efficient decomposition of the carboxylic reaction products.

Figure 5 compares the residual UVA after 20 min O₃ oxidation, with or without the addition of H₂O₂ after 10 min, for O₃ concentrations between 18 and 90 g m⁻³. The flow rate of H₂O₂ was constant at 1.00 mole per mole O₃ injected. The data prove that the UVA reduction can increase by 10–15% in this way. The residual UVA is 30–35% of the UVA of the untreated solution. An increase of the oxidation time to more than 20 minutes could further improve UVA reduction, but not significantly. For instance, at 18 g m⁻³ O₃, UVA was reduced by 64% and 72% after 20 and 30 min, respectively.

The H₂O₂ dosage can be optimized further because there is an optimal H₂O₂ to O₃ ratio, due to scavenging of •OH radicals by excess H₂O₂.³⁴ Excessive amounts of H₂O₂ act as a scavenger for •OH radicals, which is attributed to the formation of much less powerful HO₂• radicals by the reaction between H₂O₂ and •OH (reaction 2), and the subsequent reaction of HO₂• with •OH (reaction 3):

Figure 6 shows the UVA reduction for different H₂O₂ dosages whereby the O₃ dose stayed constant at 0.25 mmol O₃ min⁻¹, which corresponded to an O₃ concentration in the gas phase of 12 g m⁻³. During the first 10 min of the experiment, the UVA removal was equal for all samples because no H₂O₂ was added yet. As expected, the addition of H₂O₂ afterwards improved the UVA reduction by about 10%, but the dependence of the flow rate of H₂O₂ is small. Therefore, it is recommended to use the lowest H₂O₂ dosage, in order to limit its purchase cost, the concentration of H₂O₂ in the permeate of the membrane and possible degradation of the membrane material.

Finally, the influence of the alkalinity on the UVA removal efficiency was investigated. (Bi)carbonate is a well-known •OH radical scavenger, deteriorating the performance of the O₃/H₂O₂

system in this way. NF concentrates have a high alkalinity due to the rejection of monovalent ions. A typical value of the alkalinity in NF concentrates is 5 mmol L^{-1} . Therefore, $420 \text{ mg L}^{-1} \text{ NaHCO}_3$ was added to the sample before each experiment. However, if no NaHCO_3 was added, the UVA reduction was higher than in the case with addition of $420 \text{ mg L}^{-1} \text{ NaHCO}_3$. The UVA reduction at 280 nm was measured with and without the addition of NaHCO_3 at various O_3 concentrations, namely 20, 55, 87 mg L^{-1} . As in previous experiments, the solution was ozonated for 20 min, with the addition of 1.0 mol H_2O_2 per mol O_3 in the last 10 min. UVA reduced by 60%, 60% and 59% respectively if no NaHCO_3 was added to the feed solutions, and by 66, 66 and 69% for the same O_3 concentrations with the addition of NaHCO_3 .

This result is in contrast to what is expected in view of the possible scavenging effect of (bi)carbonates. However, this effect must not be overestimated. Humic acids can also act as a radical promotor or an inhibitor, and its effect in high DOC solutions ($>3 \text{ mg L}^{-1}$) is much greater than that of the carbonate species.³⁷ It is not known which functional groups of humic acids might promote the formation of $\bullet\text{OH}$ radicals, and which functional groups act as inhibitors. Therefore, it is impossible to predict what will be the combined and overall effect of both (bi)carbonate species and humic acids on the concentration of $\bullet\text{OH}$ radicals.

CONCLUSIONS

The decomposition of humic acids by O_3 and $O_3 + H_2O_2$ oxidation was assessed. Humic acids are a major fraction of the organic matter in NF concentrates and cause severe membrane fouling. Fouling of the membranes is known to be caused mainly by hydrophobic organic matter with a high molecular mass.

A specific O_3 dose of $2.11 \text{ g O}_3 \text{ g}^{-1} \text{ COD}$ ($17.0 \text{ g m}^{-3} \text{ O}_3$ (g) for 20 min), achieves a COD reduction of 38%. O_3 changes the hydrophobic humic acids into hydrophilic organic compounds, i.e. the hydrophobic COD reduced by 69% at the same reaction conditions. It decomposes the high molecular mass fraction as well, i.e. the components with a molecular mass higher than 10 kg mol^{-1} represented 8.6% of the UVA absorbing compounds instead of 22.5% without O_3 oxidation.

The water permeability during filtration of the oxidized humic acid solution by NF 270 membranes is consequently higher ($20.6 \times 10^{-9} \text{ L s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$) than the permeability of the untreated solution is filtered ($2.4 \times 10^{-9} \text{ L s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$). Although O_3 decomposes humic acid molecules into smaller fragments, the permeate quality did not deteriorate: the COD retention of the ozonated solution by NF 270 was similar to the retention of the untreated samples.

The UVA residual could be reduced from 47% to 34% if H_2O_2 is added after 10 min O_3 oxidation ($17.0 \text{ g m}^{-3} \text{ O}_3$ (g)), while UVA reduced only to 48% if no H_2O_2 is added and the solution is ozonated for 20 min. The presence of (bi)carbonates, which are well-known $\bullet\text{OH}$ radical scavengers, did not deteriorate the performance of the O_3/H_2O_2 system. This shows that the effect of the humic acids in these concentrated solutions as promotor or inhibitor is much stronger than the inhibiting effect of (bi)carbonates.

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