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Ozonation and perozonation of humic acids in nanofiltration concentrates

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ABSTRACT

Nanofiltration is an attractive technology to treat surface water for the production of drinking water. Due to scaling and fouling of the membranes, the water recovery in nanofiltration is generally limited to about 80%. This paper is part of a project which elaborates the concept where the concentrates are treated, so they can return to the feed side of the membrane, without increased membrane fouling, in order to reduce the water loss. The efficacy of ozonation and perozonation to remove humic acids in the concentrate is evaluated in this paper. In particular, the degree of mineralization, the amount of hydrophobic components and the destruction of high molecular mass fractions are considered. Chemical oxygen demand (COD) decreases fast with increasing ozone concentrations but reaches an asymptotic value of 40% of the initial COD, which is too high for this case. There is a selective removal of hydrophobic COD and high molecular mass chains are decomposed efficiently. The process could not be improved by changing the pH or by simultaneous adding hydrogen peroxide to the solution.

Keywords: Nanofiltration; Concentrate treatment; Water conservation; Humic acid; Ozone; Hydrogen peroxide; Advanced oxidation

Introduction

Nanofiltration (NF) is an effective and reliable method for the combined removal of a broad range of pollutants in surface water. However, fouling of the membrane limits the water recovery for this application to about 80% [1,2]. As problems with water scarcity are expected to grow worse in the coming decades, even in regions currently considered water-rich, it cannot be tolerated that 20% of the feed water is wasted [3]. Therefore, it is necessary to develop technologies that make the discharge of concentrate streams superfluous. The general concept of this study is to remove specific pollutants so that the concentrate can be returned to the feed side of the membrane without increased membrane fouling. In this way, a closed cycle with a recovery of almost 100% may be obtained.

Natural organic matter (NOM) is often claimed as the most important fouling agent in membrane filtration of natural waters [4-7]. Several researchers have shown that the extent of NOM fouling is greatly influenced by the adsorption of hydrophobic components of NOM on the membrane surface [8-10]. The hydrophobic fraction of NOM consists of humic and fulvic acids. The molecular mass of NOM plays an important role too: Nilson and DiGiano [8] concluded that only the large molecular

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mass fraction (<30 kg/mol) contributed to the formation of a fouling layer.

Ozone is a powerful oxidant which reacts with double bounds and aromatic rings with a high electron density. But beside these direct reactions with ozone, ozone decomposes into reactive radicals, including hydroxyl radicals ($^{\cdot}$OH). In contrast to ozone, $^{\cdot}$OH is a non-selective oxidant which reacts very fast with the vast majority of inorganic and organic compounds in water. Generation of these $^{\cdot}$OH radicals can be artificially accelerated by increasing the pH, the addition of hydrogen peroxide (perozonation) or the use of UV irradiation. This leads to an advanced oxidation process (AOP) [11]. The main advantages of ozone-based AOPs are the oxidation of ozone-resistant compounds and the shorter reaction time. However, the higher formation rate of $^{\cdot}$OH is at the cost of a higher ozone consumption. In addition, $^{\cdot}$OH reacts rather unselective and thus only a small fraction of these radicals reacts with the target pollutant, which makes AOPs quite inefficient processes [11].

Both in surface water applications [12-14] and wastewater treatment [15-19], several researchers proved that the application of ozonation of the feed water prior to filtration resulted in significant decreases in membrane fouling. Schlichter et al. [12] reasoned that ozone transforms hydrophobic aromatic groups to more hydrophilic groups, which tends to adsorb less on the membrane material. A second mechanism is the decomposition of organic foulants by ozone into smaller molecules, so the cross-flow could flush away loose fragments of the cake layer, which decreases the thickness of the foulant layer and thus flux decline [13,17]. Ozone treatment could not only reduce reversible fouling that formed mostly from cake deposition, but also irreversible fouling formed from pore blockage, which cannot be removed by physical cleaning methods [18].

The disadvantages of ozonation of NF concentrates is the possible lower rejection of organic matter by the membranes [17], the formation of the carcinogen bromate and brominated organics in waters containing bromide ion [20], the high biodegradability of the reaction products which increases the risk of biofouling of the membranes [21] and the accelerated degradation of the NF membranes by ozone and hydrogen peroxide.

The work presented in this paper is a first assessment of ozonation and perozonation for the transformation of humic acids in the concentrate in order to reduce fouling of the NF membranes. In particular, the degree of mineralization, the change in hydrophobicity and the degradation of high molecular mass chains are measured.

Materials and methods

Preparation of feed solutions

Humic acid powder was purchased from Fluka (Sigma–Aldrich). Fluka humic acid (FHA) contains a great number of impurities. The ash content is about 20 wt% [22,23]. Therefore, FHA was purified by the procedure of Zaccone et al. [24]: after treatment with KOH (0.2 M) and KCl (0.3 M), the resulting solution was agitated for 4–5 h and centrifuged to remove insoluble material (humin); the supernatant was then acidified with HCl to pH 1.5 in order to coagulate the humic acid and centrifuged. The partly purified humic acid (sediment) was washed with deionized water + HCl (pH 3) and again centrifuged; deionized water was added to the sediment and agitation was carried out for 3 h. This stock solution of purified Fluka humic acid (PFHA) was stored in the dark at 4 °C. PFHA working solutions were prepared from the stock solution and prefiltered by a cellulose-acetate membrane with a nominal pore size of 0.45 μm in order to remove particles. Carbonates and bicarbonates are well-known scavengers of $^{\cdot}$OH [11]. A typical value of the alkalinity in NF concentrates is 5 mM. Therefore, 420 mg/L $NaHCO_3$ was added to each feed solution. pH was adjusted with HNO_3 and NaOH.

Ozonation experiments

The feed gas to the ozone generator (Fisher model OZ 500) was pure oxygen from a gas cylinder (Praxair). The gas flow rate was fixed at 60.0 L/h at standard temperature and pressure (STP). The glass reactor had an inner diameter of 115 mm and contained 1.00 L humic acid solution. The ozone–oxygen mixture was introduced from the bottom of the reactor through a Pyrex fritted glass diffuser with a mass transfer coefficient of 89.2 ± 4.5/h in our experimental conditions. The relationship between the ozone concentration in the liquid phase ($[O_3]_l$ (mg/L)) and in the gas phase ($[O_3]_g$ (mg/L)(STP)) is $[O_3]_l = 0.155 + 0.223\ [O_3]_g + 6.0 * 10^{-4}\ [O_3]_g^2$) ($R^2 = 0.996$) for pure water solutions at pH 3. The ozone concentration in the gas phase was measured by a sensor (Model gFFOZ™, IN, USA, MA, USA) based on UV absorption (UVA) at 254 nm. H_2O_2 solution is added at the bottom of the vessel at a constant flow rate by a peristaltic pump. The solution in the vessel is mixed by a magnetic stirrer. The solution was ozonated for 10 min, except otherwise stated. After ozonation, the ozone generator is turned off and pure oxygen is injected to remove residual ozone in the solution. The use of a reductant (e.g. $Na_2S_2O_3$) to quench dissolved ozone, was inappropriate due to the subsequent COD analyses.

Water analysis

Since the cost of total organic carbon (TOC) determination is high, it was decided to use COD and UVA as surrogate measures to detect organic constituents in water. COD was determined by the decrease in chromate concentration after two hours boiling at 148 °C, which is spectrophotometrically measured (Nanocolor test tubes, Macherey-Nagel). All COD tests were done in duplicate. UVA was measured by a Shimazu UV-1601 double beam spectrophotometer. Due to the disturbance of the COD measurements by interference of H_2O_2 [25] and the difficulties to measure the H_2O_2-concentration accurately, only UVA could be determined for the perozonated samples. Due to the lower interference of H_2O_2 at this wavelength, the UVA data at 280 nm instead of 254 nm are shown for the perozonated samples. It is well known that Π–Π^* electron transitions, specific for phenolic arenes, benzoic acids, aniline derivatives, polyenes and polycyclic aromatic hydrocarbons with two or more rings, occurs between the wavelengths approximately from 270 to 280 nm. For that reason, the application of UVA within 270–280 nm is also suitable for describing aromatic carbon moieties [26].

Hydrophobic and hydrophilic fractions of oxidized humic acids were obtained by passage through a non-ionic macroreticular resin (Amberlite XAD 7 HP, Rohm & Haas). Before use, the resin was extensively rinsed following the procedure of Thurman and Malcolm [27]. All samples were acidified to pH 1.5 with HNO_3 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 in order 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. Following this procedure, the hydrophobic COD of the PFHA solutions was estimated at 88 mg/L at a total COD of 91 mg/L.

The amount of organic matter with high molecular mass was determined by ultrafiltration using a membrane with a molecular weight cutoff (MWCO) of 20 kg/mol (UP020) (Microdyn-Nadir GmbH, Wiesbaden, Germany). A 150 mL sample was filtered in a dead-end module (Sterlitech HP4750 Stirred Cell, Kent, WA, USA) pressurized to 300 kPa with nitrogen gas. Permeate was collected nine times with 15 mL at a time. The first 15 mL was discarded. The amount of organic matter in the permeates was measured by UVA. Size distributions were calculated using the permeation coefficient model of Logan and Jiang [28].

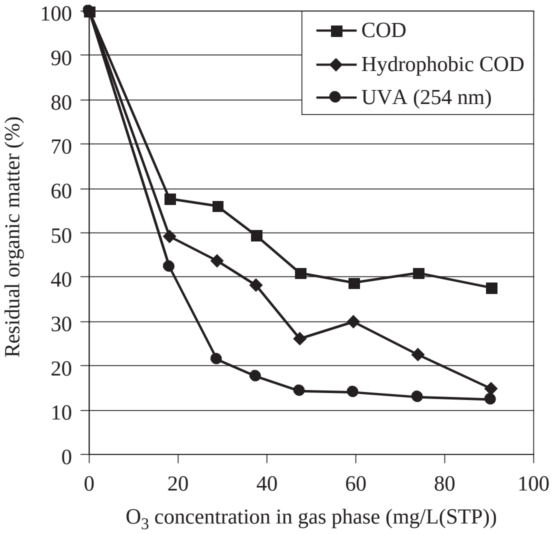

Fig. 1. Influence of the O_3 concentration on the removal of Fluka humic acids (reaction time: 10 min, 84–97 mg/L COD, pH: 7–8, alkalinity: 420 mg/L $NaHCO_3$).

Results and discussion

Fig. 1 shows the influence of the ozone concentration on the residual COD, hydrophobic COD and the UVA at 254 nm at neutral pH. After a rapid decrease with increasing ozone concentrations, the COD reaches an asymptotic value as from 50 mg/L O_3 in the gas phase. This asymptotic value amounts to 40% of the initial COD. The occurrence of residual COD at high ozone dosages is explained by the fact that ozone preferentially oxidizes electrophilic aromatic groups to oxygenated functional groups, such as aldehydic, ketonic and especially carboxylic groups. These saturated compounds react typically very inefficiently with ozone, so they are not further mineralized into carbon dioxide and water [11]. However, in order to prevent accumulation of organic matter in the closed cycle, COD has to be removed by almost 80%, which is not possible by ozonation. There is a selective removal of hydrophobic COD, which is in agreement with the literature, and the hydrophobic COD decreases gradually with increasing ozone concentrations. An increase of the reaction time to 20 min did not improve the removal of COD, UVA or hydrophobic COD for a given ozone concentration (data not shown). The decomposition of high molecular mass chains is presented in Fig. 2. Almost all humic acids in the feed

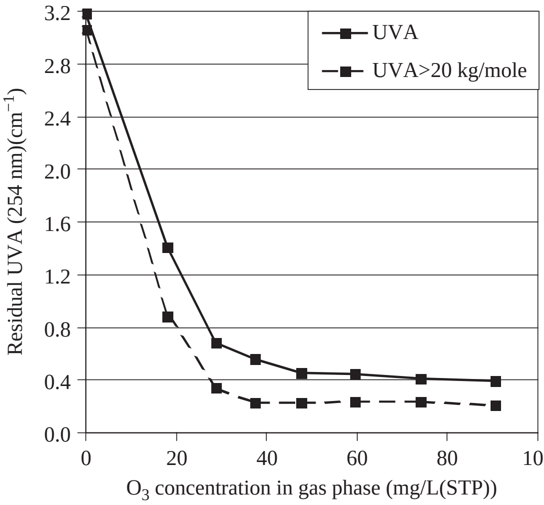

Fig. 2. Influence of the O_3 concentration on total UVA and UVA after filtration through an UP020 membrane (MWCO: 20 kg/mol) (same reaction conditions as in Fig. 1).

solution are retained by the UP020 membrane with a MWCO of 20 kg/mol. After ozonation, only about half of the organic matter is retained by this membrane. Thus, it is concluded that ozone is effective in the destruction of high molecular mass chains into smaller fragments. In literature, it is shown that ozonation is indeed able to reduce the UVA of the entire molecular mass range of the organic matter [17,29].

In ozonated solutions, organic contaminants can either be oxidized by ozone itself or by radicals, corresponding to direct and indirect or advanced oxidation. The direct oxidation pathway has the advantage to be very selective for aromatic organic matter, which is thought to foul the membrane severely due to its hydrophobic nature. The indirect pathway can accelerate the decomposition of organic matter, but this is at the cost of a higher ozone consumption. The relative importance of the direct and indirect oxidation pathway largely depends on the water matrix, especially its pH, the type and content of NOM and its alkalinity [30]. The pH of the water is important because hydroxide ions initiate ozone decomposition. It is known that at low pH (<5.0), the rate of production of $^{\cdot}OH$ is greatly reduced and that the direct oxidation pathway dominates. The reverse is true at high pH (>11.0) [30]. Therefore, the ozonation experiments were repeated at acidic pH and basic pH. The results in Table 1 prove that the removal of COD and UVA is higher at neutral pH than at acidic or basic pH. The lower efficiency at low pH can be attributed by two effects. First of all, protonation of the carboxylic and phenolic acids in the humic acids decreases the rate of direct oxidation significantly. This is due to a decrease in nucleophilicity by protonation [11]. Second, the lower efficiency can be caused by the absence of $^{\cdot}OH$ at low pH. However, except at very high ozone concentrations, the hydrophobic COD is removed to the same extent at low pH as at neutral pH. The lower efficiency at basic pH is caused by the fact that bicarbonates are more effective radical scavengers than carbonates [30]. The direct pathway is less dominant with increasing pH, and thus also the destruction of hydrophobic COD. There is an efficient removal of high molecular mass chains at every pH.

The major sticking point is the too low organic carbon reduction that can be achieved with ozonation. Therefore, it was investigated if the addition of H_2O_2 could enhance the mineralization of the ozone-resistant reaction products. Fig. 3 shows the effect of H_2O_2 on the UVA, before and after filtration with the UP020 membrane. The mineralization of organic matter and the decomposition of high molecular mass chains did not improve in this case. These results suggest that the concentration of $^{\cdot}OH$ is already high at neutral pH without addition of H_2O_2. Because H_2O_2 acts as a scavenger for $^{\cdot}OH$ radicals, an excessive H_2O_2 dose will hinder the radical degradation. Therefore, there exist an optimum H_2O_2 to O_3 ratio, which is generally lower than one [31]. However, there is no optimal dosage of H_2O_2 detected in these experiments.

Table 1
Influence of pH on the decomposition of Fluka humic acids (same reaction conditions as in Fig. 1, no $NaHCO_3$ added for solutions at pH $\sim$ 2)

pH	1.8	8.0	11.1	2.5	6.9	11.0	2.2	6.8	11.2
Gas phase O_3 concentration (mg/L)	24	18	18	58	60	59	92	90	86
Residual organic matter									
COD (%)	66	58	67	51	39	59	51	38	49
Hydrophobic COD (%)	47	45	51	28	30	36	31	14	24
Residual UVA (%)	52	42	46	35	14	28	35	12	22
UVA (cm^{-1})	1.468	1.409	1.310	1.004	0.442	0.800	1.010	0.392	0.631
UVA > 20 kg/mol (cm^{-1})	0.689	0.886	0.721	0.353	0.240	0.232	0.328	0.212	0.220

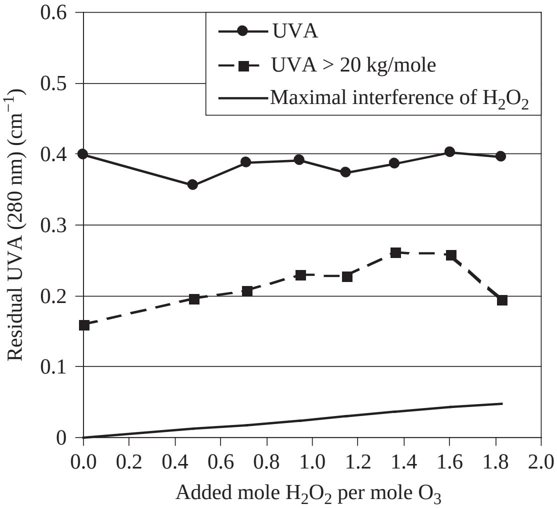

Fig. 3. Influence of the H_2O_2 dosage on total UVA and UVA after filtration through an UP020 membrane (MWCO: 20 kg/mol) (O_3 concentration in the gas phase: 38–40 mg/L (STP), same reaction conditions as in Fig. 1). The maximal interference of H_2O_2, which is calculated from the applied dosage, is subtracted from the UVA data shown.

Conclusions

Concentrated humic acid solutions, which occur in NF modules and are severe membrane foulants, are treated with ozone and hydrogen peroxide. The fouling of the membranes is mainly caused by hydrophobic organic matter with a high molecular mass. COD decreases fast with increasing ozone concentrations and reaches an asymptotic value of 40% of the initial COD. There is a selective removal of hydrophobic COD and the hydrophobic COD decreases gradually with increasing ozone concentrations. Ozonation is also very effective in the decomposition of high molecular mass chains into smaller fragments. It is known that advanced oxidation can be applied to mineralize the reaction products of ozone. However, if H_2O_2 is added to the ozonated solution, the degree of mineralization did not improve in these experiments. Further research is needed to find the process parameters (ozone concentration, reaction time, hydrogen peroxide dosage and dosage time) in order to improve the mineralization degree and to confirm these results with fouling tests.

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