Hybrid membrane processes for the treatment of surface water and mitigation of membrane fouling

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ABSTRACT

Membrane-based processes are well recognized treatment methods for waters and wastewaters of different origin. However, the biggest drawback connected with membranes' filtration is their severe fouling, which deteriorates the process effectiveness. Combining membrane filtration with another water/wastewater treatment method in a hybrid process is a promising way of improving the overall membrane operation. In this study an approach of combining ceramic membrane filtration with chemical oxidation processes, i.e. ozonation and ozonation combined with hydrogen peroxide, is presented. A flat sheet ceramic microfiltration membrane of a submerged type has been used in the experimental unit. Ozone–oxygen gas mixture was introduced to the system by appropriate ceramic gas spargers and two flow rates of the gas mixture were tested: 0.1 L/min and 0.2 L/min with corresponding ozone dosages of 2.5 and 5.0 mg O_3/min of ozone addition, respectively. The water treated in this experimental system was a simulated (contaminated) surface water with Total Organic Carbon (TOC) content of 8 (±0.3) mg/L and turbidity of 20 (±0.5) NTU. The collected permeates were evaluated for selected pollution parameters, such as turbidity, TOC, UV_{254} absorbance and SUVA values. HPLC analysis has been performed for the calculation of molecular weights of products in the permeates obtained during hybrid processes. The fouling of membrane was evaluated by the calculation of Fouling Index (FI) and monitoring changes in the Trans Membrane Pressure during membrane operation. The obtained results indicated that the membrane fouling was mitigated during the hybrid processes, increasing the overall efficiency of membrane microfiltration for the treatment of contaminated surface water.

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1. Introduction

Membrane systems are widely used for drinking water production and the treatment of polluted waters and wastewaters for other purposes. The main limiting factor during membrane filtration is connected with membrane fouling, which leads to the deterioration of membrane operation. A new approach for the mitigation of membrane fouling is combining the membrane process with another water treatment method in a hybrid process. Attempts have been made to combine membrane filtration with different water treatment processes, such as coagulation [1], flocculation [2], photocatalysis [3] or chemical oxidation, such as ozonation [4]. Among the various oxidation processes, ozonation and ozonation in the presence of hydrogen peroxide seem to be good selections for combining them in a hybrid process with membrane filtration, due to the high oxidative capabilities of O_3 and O_3/H_2O_2 systems and the possibility of performing both of these processes in one reactor/cell.

Ozone based oxidation is usually applied during water treatment for such purposes as disinfection and pathogens removal, while the main operational goal is the control of ozone consumption during the process, i.e. ensuring as high ozone consumption as possible in order to lower the operational cost. It is a common practice to place ozone destroyers or traps at the end of the process line in order to capture the non-reacted ozone after the oxidation of pollutants present in the contaminated water, which generally increases the cost of the overall process. However, when the concentration of applied ozone dose is carefully selected the total consumption of added ozone is possible, which makes the overall process more economical. The ozone dosage selected for specific applications should depend on such parameters as the nature of the treated water and its pollutants' content, the contact time of ozone-treated water, the contact surface of gas–liquid interface etc.

The addition of ozonation to the microfiltration of surface water seems to have the capability to mitigate the membrane fouling, as ozone is able to decompose the main fouling agents, such as humic acids, which are present in surface waters [5]. Nevertheless, as it

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was presented in a previous study [6], although the hybrid micro-filtration–ozonation process results in the efficient mitigation of membrane fouling, a significant improvement of the permeate quality in terms of Total Organic Carbon (TOC) removal could not be achieved. Although ozone is a powerful oxidant and has the ability to oxidize the unsaturated bonds in the organic substances, transforming them to saturate ones, it shows rather limited Dissolved Organic Carbon (DOC) removal [7]. The reported reductions of DOC content in the drinking water treatment plants are in the range of 10–20% only, with O_3 doses in the range 2–5 mg/L [8].

There are two major paths of possible ozone reactions with pollutants present in the treated water, i.e. the direct oxidation by molecular ozone and the indirect oxidation by the radical species formed during ozone decomposition, among which the hydroxyl radicals are believed to be the most reactive ones [9]. While the ozone molecules react selectively with the unsaturated bonds, the hydroxyl radicals are reported to be rather non-selective oxidants, reacting fast with the majority of inorganic and organic compounds, which are present in the waters to be treated [10]. The decomposition of ozone in water was investigated by Staehelin and Hoigne [11] and it was found that it takes place by a radical type chain reaction. The addition of hydrogen peroxide (H_2O_2) to the solution where ozonation is conducted, improves the production rate of hydroxyl radicals, fact which consequently improves further the oxidation of ozone-resistant compounds. The optimal molar ratios of H_2O_2/O_3 depend highly on the composition of the water to be treated, i.e. the types and the concentrations of the pollutants present [12], as well as the alkalinity of water [13], noting that these parameters have to be determined experimentally for each specific application. Generally, the molar ratios of H_2O_2/O_3 reported in the literature for the treatment of surface waters containing NOM, are in the range of 0.1–1 [7,14].

Ozone treatment is usually applied for oxidation purposes and for the disinfection of drinking water, as it is a very effective process for oxidation of organic matter. Several studies have been conducted in order to establish the effect of ozonation for the mitigation of membrane fouling and for the improvement of permeate quality. The impact of ozone dosages on the hybrid ozonation ceramic ultrafiltration system treating natural waters was previously investigated by Kim et al. [15]; in this case ozone was injected in the feed stream before the application of membrane filtration. The addition of ozone to this system resulted in reduced fouling during the process and this improvement was mainly dependent on the ozone concentrations used and the respective hydrodynamic conditions. A similar system of combined ozonation and membrane filtration has been tested by Karnik et al. [16] for the removal of natural organic matter (NOM) by oxidation and the control of disinfection by-products formation. In this case ozone gas was added to the water stream prior to membrane filtration. Ozone addition resulted in an improvement of produced water quality, although the permeate quality was mainly dependent on the molecular weight cut-off (MWCO) of the membranes used in this system. Similar studies can be found, which are also based on the introduction of a gas containing ozone to the water to be treated by means of injectors located on the feed water line, before the membrane modules [17–20].

The addition of hydrogen peroxide to the ozonation process for the treatment of water containing NOM is able to improve the removal of DOC, when comparing with the application of ozonation only [14]. However, no literature entries were detected on the issue of hybrid and simultaneous O_3/H_2O_2–membrane filtration process.

The aim of this work was the investigation of hybrid membrane filtration, combined with chemical oxidation, such as ozonation and ozonation in the presence of hydrogen peroxide. This hybrid combination is expected to improve the membrane operation by

mitigation of membrane fouling, and to improve the permeate quality, when compared with single microfiltration process. The simultaneous use of membrane filtration and AOPs has not been studied so far and it is a novel approach to address the issues connected with membrane fouling. The addition of H_2O_2 to ozone oxidation is expected to improve the efficiency of humic acid oxidation, as it improves the hydroxyl radicals' production and increases the kinetics of organic substances destruction by oxidation. The ozone–oxygen gas mixture was added directly in the reactor vessel, by means of gas spargers, producing fine bubbles, which is a significantly different configuration, when comparing with the aforementioned studies on this topic. The total ozone consumption was achieved for all the experiments performed, applying different concentrations and flow rates, and expecting to lower the cost of overall process and to eliminate the need for implementation of ozone post-destroyers. The molar ratios of hydrogen peroxide in the hybrid O_3/H_2O_2 experiments were selected, based upon relevant literature [7,14], where the molar ratio around 0.3 or less was found to give the best results, regarding the oxidation of waters containing NOM. The treated water in the presented experiments was a simulated contaminated surface water containing organic matter (humic acid) and turbidity (clay). This kind of model water is a typical artificial surface water used in studies performed for the initial evaluation of effectiveness of novel water treatment methods [3,19,21,22], which also offers a possibility of results comparison. The effectiveness of the hybrid process was evaluated by examining both the permeate quality, including the molecular weights distribution of the products of oxidation of humic acid, as well as the membrane operation and mitigation of membrane fouling.

2. Materials and methods

2.1. Experimental unit of the hybrid ozonation–microfiltration

The experimental unit for the hybrid ozonation–microfiltration simultaneous processes is presented in Fig. 1. It consists of a cylindrical reaction vessel (cell) made of Plexiglass (height 44 cm, diameter 11.75 cm) with a working volume of 16 L, and housing a flat sheet ceramic membrane of a submerged type (dimensions 21.5 cm × 11 cm). Ozone–oxygen gas mixture was produced by an ozone generator (model TOGC2A, Ozonia Triogen), equipped with a gas flow meter, where pure oxygen was used as the feed gas at the (constant) pressure of 0.2 bar. The pressure of produced ozone–oxygen gas mixture was monitored with a digital pressure meter (Wika, model DG-10, number 7 in Fig. 1), and by using 2 on-off valves it could be also used for the measurement of gas pressure inside the cell (for safety reasons). The flow rate of ozone–oxygen gas mixture was measured and adjusted by an appropriate ozone resistant flow meter equipped with a needle valve (Aalborg, model PMR-1). Ozone–oxygen gas mixture was introduced to the experimental unit by three ROBU porous diffusers (of nominal porosity No. 4, i.e. having pore size 10–16 μm and diameters 50 mm), which were located at the bottom of experimental vessel, producing fine bubbles. Needle valves were placed at the connecting lines directly before every diffuser to ensure the uniform gas bubbles distribution within the whole area of the experimental unit. In order to achieve the appropriate (low) flow rates of ozone–oxygen gas mixture, introduced to the system, a by-pass valve was placed on the outlet line after the ozonator (number 2 in Fig. 1) which divided the main ozone–oxygen gas mixture into two sub-streams: the stream entering the unit, where the gas flow was accurately measured with a flow meter (number 4 in Fig. 1) and the stream directed to the ozone traps (number 3 in Fig. 1), which was used for the measurement of ozone concentration in the initial gaseous mixture; this was performed by
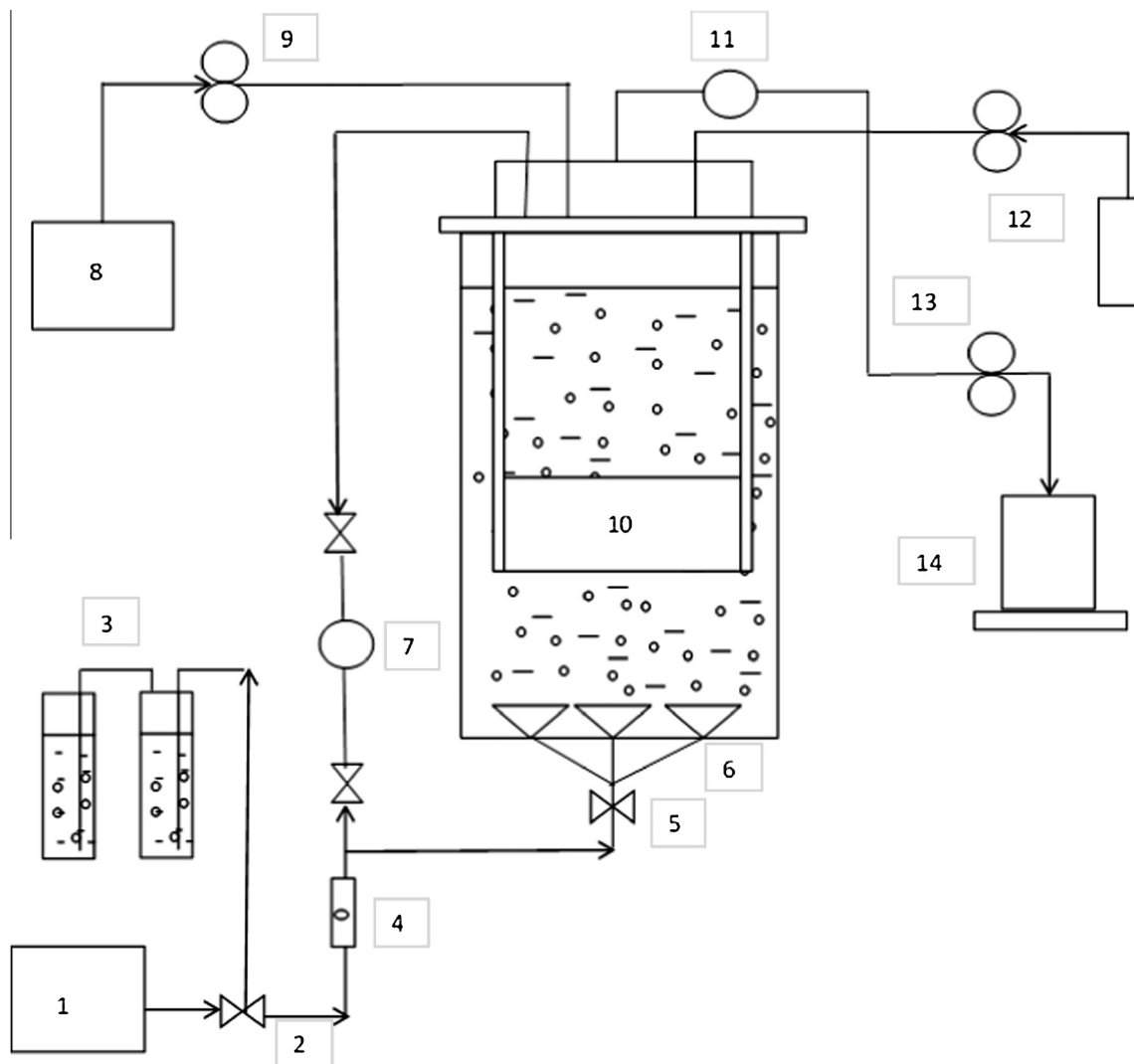
Fig. 1. Experimental unit: (1) ozone generator, (2) needle valve, (3) ozone traps, (4) ozone gas flow meter, (5) needle valve, (6) ceramic gas spargers, (7) pressure meter, (8) feed water tank, (9) peristaltic pump for the feed, (10) vessel with the flat sheet submerged membrane, (11) trans membrane pressure meter, (12) dosing pump for hydrogen peroxide addition, (13) peristaltic pump for permeate withdrawal and (14) balance.

passing the corresponding gas stream through a 2% KI trap and ozone was determined in the resulting solution, according to Standard Methods [23]. The dissolved ozone concentrations in the treated water inside the experimental unit, as well as in the permeate samples during the experiments were measured by an ozone sensor (ProMinent, type OZE).

The membrane used for the simultaneous microfiltration of ozonated water was a flat sheet submerged type ceramic membrane (ItN Nanovation), located in the middle of the reaction unit. The membrane was made of α-Al$_2$O$_3$ and had an active membrane area of 0.04 m^2 and an average pore diameter of 200 nm. Permeate was withdrawn by a peristaltic pump (Watson Marlow, model 503U), and the Trans-Membrane Pressure (TMP) was measured by a digital pressure meter (Wika, model DG-10). The water to be treated was fed to the experimental unit by a peristaltic pump (Watson Marlow, model 505U) at a flow rate similar to the permeate removal rate, in order to maintain a stable amount of treated water in the reactor vessel. The experiments were performed in continuous mode Hydrogen peroxide at required concentrations was added to the experimental unit by a dosing pump (SEKO, type PR1), when needed.

2.2. Water to be treated and analytical determination methods

The water treated in presented experiments was a simulated surface water with a medium content of organic matter [21]; it was prepared by the addition of 25 mg/L of humic acid (Sigma Aldrich) and commercially available kaolin (clay) in the form of fine particles into the tap (drinking) water of the city. Kaolin used for the preparation of the treated water had a medium particle size of 5–10 μm, as provided by the manufacturer, and after initial dissolving g in tap water was kept in suspension due to the motion of bubbles in the experimental vessel. The alkalinity of used tap water was 160 mg CaCO$_3$/L, measured with the titration method, according to Standard Methods [23]. Before every experiment a fresh surface water sample was prepared from the stock solutions of humic acid and kaolin and the pH of final solution was adjusted to ~7 with conc. HCl [19]. The initial turbidity of resulting water to be treated was 20 (±0.5) NTU, while the Total Organic Carbon (TOC) content was 8 (±0.3) mg/L.

The initial samples and the obtained permeates were analyzed for the determination of the following parameters: UV absorbance measured at 254 nm (as an indication of organic matter

concentration) by a Hitachi UV–Vis spectrophotometer; Total Organic Carbon (TOC) measured by a TOC-V_{CSH} Total Organic Carbon Analyzer (Shimadzu); turbidity measured by a Hach Ratio/XR turbidity meter and pH measured by a Jenway pH-meter (model 3540). SUVA values were calculated from the UV_{254} absorbance and TOC content of permeates, according to the equation SUVA = UV_{254}/TOC [25]. Most of the experiments were performed 2–3 times and the average values are presented in the figures, while the respective error bars are not presented in the figures as their value of 1–2% is roughly the same as the size of markers used in the figures.

2.3. HPLC analysis of the permeates

HPLC measurements of the permeate samples were performed with a High Performance Liquid Chromatography (HPLC) system (Shimadzu Liquid Chromatograph, LC-20AD prominence), equipped with Degasser (DGU-20A$_5$ prominence), Auto Sampler (SIL-20A$_{HT}$ prominence), Diode Array Detector (SPD-M20A prominence) and Column Oven (CTO-20A prominence). The column used in this study was the TSKgel G3000SW from Tosoh Bioscience (7.5 mm ID × 30.0 cm), which according to the literature [24] is the only column commercially available, able to separate effectively the different molecular size fractions of humic substances. The UV detector used a wavelength of 254 nm and as an eluent sodium acetate solution was used at a flow rate 1 mL/min and concentration 0.01 M. All the samples tested were initially filtered through 0.45 μm membrane micro-filters and their pH was adjusted to 7 with the use of a conc. phosphate buffer. The column used in the measurements have been initially calibrated by the manufacturer with protein standards for molecular weights ranging from 600 kDa to 13.7 kDa, showing a very good semi log calibration curve (r^2 = 0.94). This data has been used for the calculation of the fractions of humic acid, resulting after the application of hybrid processes; however, it has to be noticed that this data should be used only as rather approximate indicative (semi-quantitative) results, due to the complexity of the system.

3. Results and discussion

3.1. Hybrid treatment method of ceramic membrane microfiltration coupled with ozone based oxidation

Hydrogen peroxide was added to the experimental unit at various concentrations, in order to obtain ozone/hydrogen peroxide ratios of 0.2, 0.1 and 0.05 (mM O_3/mM H_2O_2). These ratios were selected based on relevant literature data [7,14]. Two flow rates of ozone–oxygen gas mixture inlet were also examined, i.e. 0.1 L/min and 0.2 L/min with corresponding ozone dosages of 2.5 and 5.0 mg O_3/min of ozone addition, respectively. These flow rates were selected based on preliminary experiments performance, as they ensure nearly 100% consumption of ozone added to the experimental unit during the whole time period of each experimental run. Ozone–oxygen gas mixture was added in the vessel in continuous mode, starting from the 10th minute of every experiment, while the duration of each experimental run was 120 min. The dosing of hydrogen peroxide was also started at the 10th minute of the respective experiment. All experiments were performed under a stable permeate flow rate of 7.2 L/h and corresponding flux of 180 L/h m^2, while the retention time was 2.2 h. An initial TMP value of −0.250 bar was selected for all the experimental runs, based on preliminary experiments, as this specific value was found to be the most suitable for the investigation of membrane fouling. However, due to the progressive membrane fouling, the TMP values were gradually increasing during the experiments. The initial 5 min of

every experiment were used for establishing the initial TMP of −0.250 bar, by adjusting the speed of peristaltic pump used for the permeate withdrawal. Permeates collected during these initial 5 min of membrane operation were discarded, while permeate samples collected from the 5th minute onwards were used for analytical determinations.

Turbidity was not detected in any of permeate samples, hence the respective results regarding turbidity removal are not further presented, because for all the conditions studied, the removal of solids reached 100%. Dissolved ozone also was not detected in any of the permeates collected during all the experiments presented, as well as it was not detected in samples of treated water taken from the experimental vessel during the experiments, hence the total consumption of ozone added to this system can be assumed. In the following results the initially measured parameters, i.e. up to around 30th minute of membrane operation, differ somehow from the respective results obtained during the later stages of operation, as approximately 30 min of membrane operation was needed in order to obtain stable permeate quality. The duration of experiments (120 min) was selected based on preliminary experiments, where longer system operation did not result in any changes in the permeate quality.

3.2. Quality of permeates

The results of UV_{254} absorbance removal as a function of membrane operation time are presented in Fig. 2(a and b) for the two initial ozone flow rates examined. In the case of lower ozone flow rate used (0.1 L/min) the absorbance removal was similar for all the experiments performed. Single membrane microfiltration resulted in UV_{254} removal up to almost 79%, whereas the hybrid process of microfiltration with ozonation and H_2O_2 (at molar ratio 0.05) showed a comparable removal (around 78%). The lowest UV_{254} removal (75%) was the result of hybrid process, but without the addition of hydrogen peroxide. For the higher ozone flow rate tested (0.2 L/min) the hybrid process as applied with the addition of H_2O_2 (at molar ratio 0.2), resulted in the highest UV_{254} removal of (81%), although it was similar with the case of MF only. It is noted that the simultaneous addition of H_2O_2 in the hybrid process of O_3/MF improves generally the permeate quality, which is indicated by the increased UV_{254} removal, as well as by the TOC improved removal, when compared with hybrid processes with single ozone addition. This suggests that higher efficiency of the oxidation process, due to the presence of hydrogen peroxide, has the capability of improving the permeate quality.

Similar trend can be noticed for the removal of Total Organic Carbon (TOC) content of permeates, showed in Fig. 3(a and b), where the hybrid process using ozone flow rate of 0.1 L/min and the lower H_2O_2 molar ratio tested (0.05) resulted in similar TOC removal as the single MF. However, for the higher ozone flow rate examined (0.2 L/min) the addition of H_2O_2 resulted in better TOC removal, when compared with hybrid process with single ozonation. According to the literature [25], the UV_{254} absorbance is an indication of the presence of organic matter in water samples, especially of organic molecules containing aromatic rings and multiple bonds. The results of TOC removal indicate that the total amount of organic material in permeates after the application of hybrid processes increases, depending on the added dose of ozone, while the removal of organic compounds containing aromatic rings and multiple bonds is similar to the removal obtained during single MF. This is a result of specific reactions of oxidants with the humic acid molecules, where different Molecular Weight (MW) fractions of humic acid are expected to be produced [24], as well as the produced humic acid fractions have different properties in terms of hydrophobicity and hydrophilicity, as will be discussed later. As the UV_{254} removal is higher than the TOC content removal for

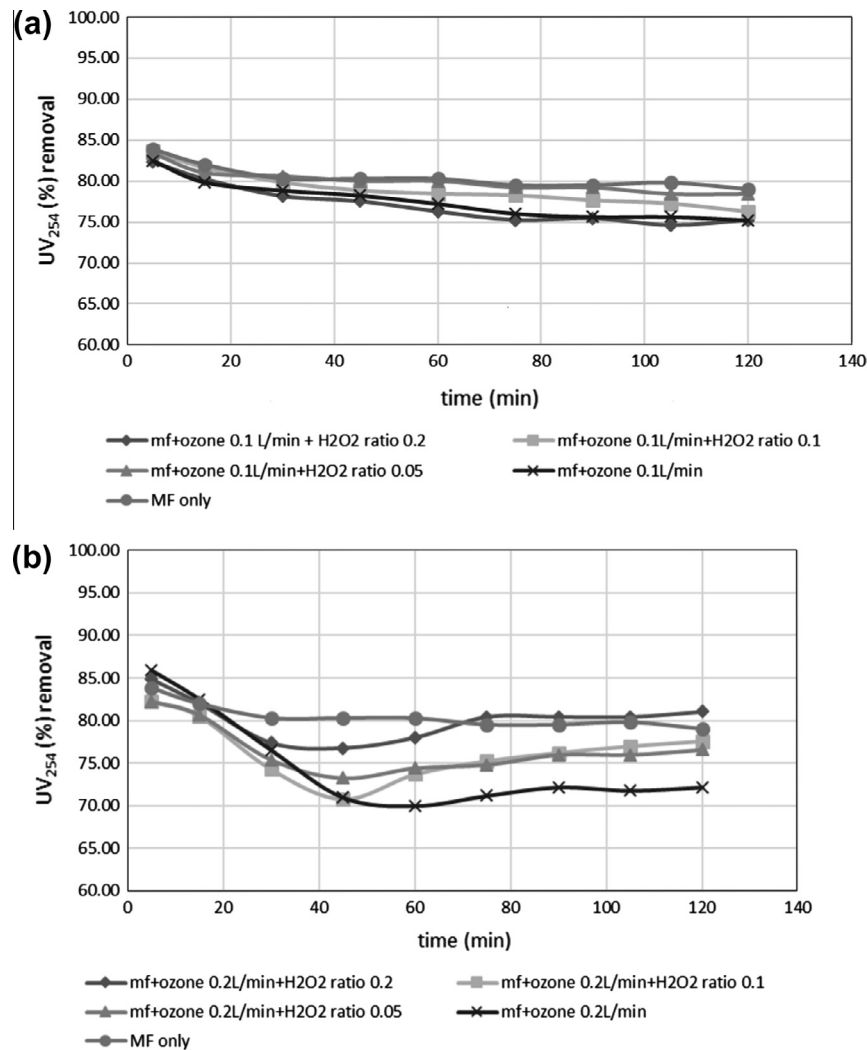**Fig. 2.** UV_{254} percentage reduction for the use of single microfiltration and for the hybrid processes, performed with the ozone–oxygen mixture flow rate of: (a) 0.1 L/min (corresponding ozone dosage 2.5 mg O_3/min of experiment) and (b) 0.2 L/min (corresponding ozone dosage 5.0 mg O_3/min of experiment).

the hybrid processes, it can be assumed that the hybrid processes despite the applied concentrations of ozone and the molar ratios (in case of adding H_2O_2), generally result in a bigger decrease of concentration of organic matter containing unsaturated bonds. From the ratios of H_2O_2 studied, the lowest one tested (0.05) gives the best results, regarding the improvement of permeate quality, although all the investigated molar ratios resulted in improvement of permeate quality when compared with hybrid process with single ozonation and their results were quite similar. The addition of hydrogen peroxide to the ozone oxidation process results not only in the oxidation of multiple bonds, as is the case when single ozone addition is used, but also in a more substantial removal of the total TOC present in the treated water.

The evaluation of impact of hybrid processes of O_3/MF and ($O_3 + H_2O_2$)/MF on the nature of humic acids, which are present in the water to be treated, was carried out with the calculation of corresponding SUVA values (Specific UV Adsorption). This ratio describes the nature of NOM in water in terms of hydrophobicity and hydrophilicity. SUVA values >4 correspond to mainly hydrophobic and especially aromatic compounds, whereas SUVA values <3 illustrate hydrophilic substances [25]. In the simulated surface water used in these experiments the DOC content was equal with the TOC content. Fig. 4(a and b) shows the SUVA values calculated for permeates, noting that the initial SUVA value of the treated

water was 6. For the experiments performed with lower ozone dosages SUVA values are presented since 60th minute onwards, as the results from first 60 min of membrane operation were scattered due to the time needed in order to obtain stable permeate quality for the hybrid processes. It can be seen that the hybrid processes performed with the lower ozone flow rate (0.1 L/min) did actually change the nature of humic acid molecules, but not enough for a definite shift from hydrophobic to hydrophilic properties. In case of the higher ozone flow rate used (0.2 L/min) the SUVA values for permeates were lower than 3, which clearly indicate a change in the nature of humic acids molecules, becoming hydrophilic. The changes in SUVA values recorded for the hybrid experiments happen due to the oxidation of multiple bonds and aromatic rings present in the humic acid structure [7]. The SUVA values were also calculated for the treated water inside the experimental vessel during the experiments, and those values were the same as values presented in Fig. 4 for the permeates. From the SUVA values, UV_{254} absorbance removal and TOC content obtained during single MF it has to be noted that the membrane filtration and semipermeable cake formed on the membrane surface during membrane operation, together result in different humic acid composition in the permeate than in the initial samples. Abovementioned results indicate that the permeate obtained during single microfiltration has highly hydrophobic properties, which suggests
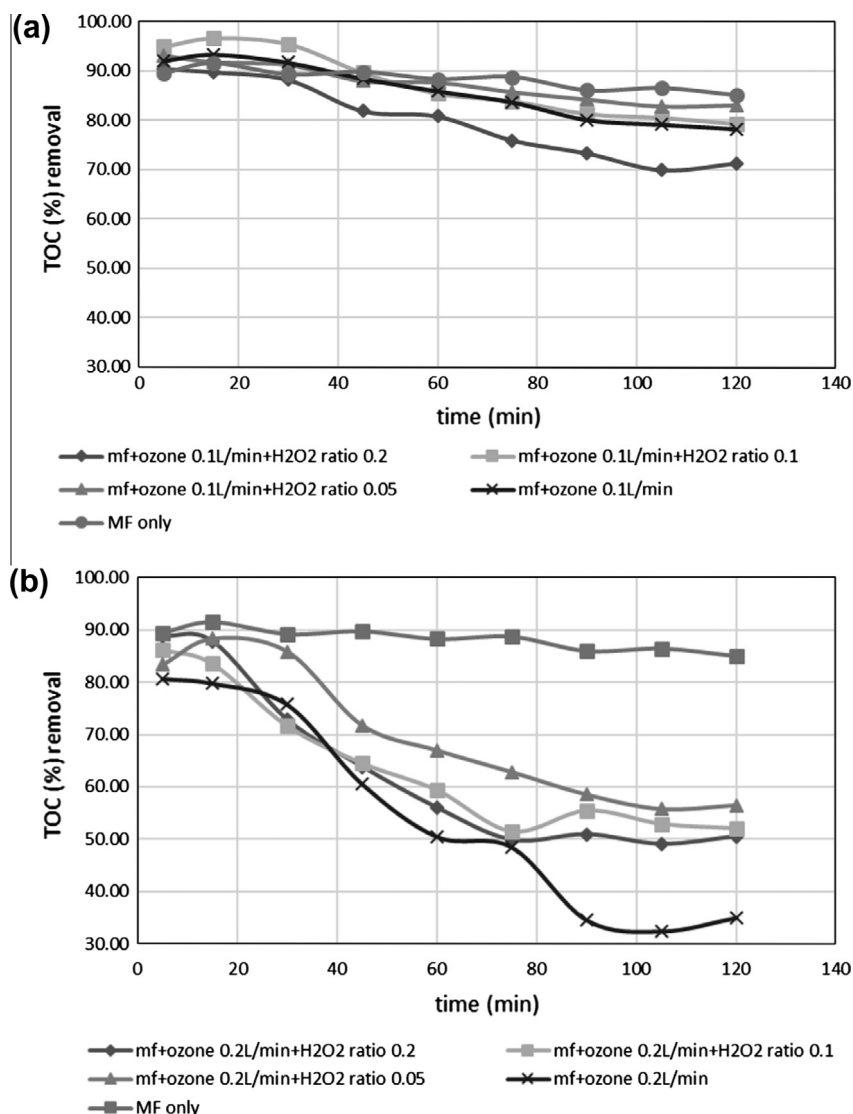
Fig. 3. Total Organic Carbon (TOC) percentage removal for the case of single microfiltration and for the hybrid processes, performed with the ozone–oxygen gas mixture flow rate of: (a) 0.1 L/min (corresponding ozone dosage 2.5 mg O_3/min of experiment) and (b) 0.2 L/min (corresponding ozone dosage 5.0 mg O_3/min of experiment).

that the high humic acid retention during single MF is based not only on the MWCO of the membrane used, but is also based on the fouling mechanisms occurring during membrane filtration. This specific result of membrane microfiltration will be discussed in detail in Section 3.4 as it is connected with the membrane fouling mechanism.

3.3. HPLC analysis of the permeates

The results of HPLC analysis regarding the products of hybrid processes, as applied for various ozone flow rates and H_2O_2/O_3 molar ratios, are presented in Tables 1 and 2, as well as for the initial humic acid samples and for the single MF process. The HPLC analysis of the initial samples of humic acid dissolved in tap water revealed 5 molecular weight fractions around 140, 105, 70, 44 and 14 kDa present in the treated water. Single microfiltration resulted in the same fractions of humic acid present in the permeate but at different relevant presence, where the presence of the two highest MW fractions (140 and 105 kDa) was higher in the permeate than in the treated water, the presence of lowest MW fraction (14 kDa) was similar and the presence of the two medium MW fractions (70 and 44 kDa) was lower in the permeate than in the initial treated

water. These results are consistent with the aforementioned change in the SUVA values for initial and permeate samples collected during single microfiltration, where the permeate exhibited higher hydrophobicity than the initial samples, a fact that can be attributed to the higher presence of the highest MW fraction in the permeate.

In the case of hybrid experiments performed with the ozone flow rate 0.1 L/min with and without the addition of hydrogen peroxide, similar to the results obtained for single microfiltration, the results showed an increased presence of higher MW fractions of humic acids oxidation products (i.e. 140 kDa). The presence of the smallest MW fraction of humic acids (14 kDa) decreased generally during the application of all hybrid processes and consequently, with the exception of the experiment performed with molar ratio of 0.05, where the presence of smaller MW fractions was higher. Consequently, the average MW of humic acids during the hybrid processes was higher, than measured for the initial humic acid samples. Generally, it seems that the ozonation of humic acids, when using the lower ozone dosage applied, resulted in a similar relevant presence of various molar fractions of humic acid molecules as in the case of single microfiltration, and the applied ozone dosage was not high
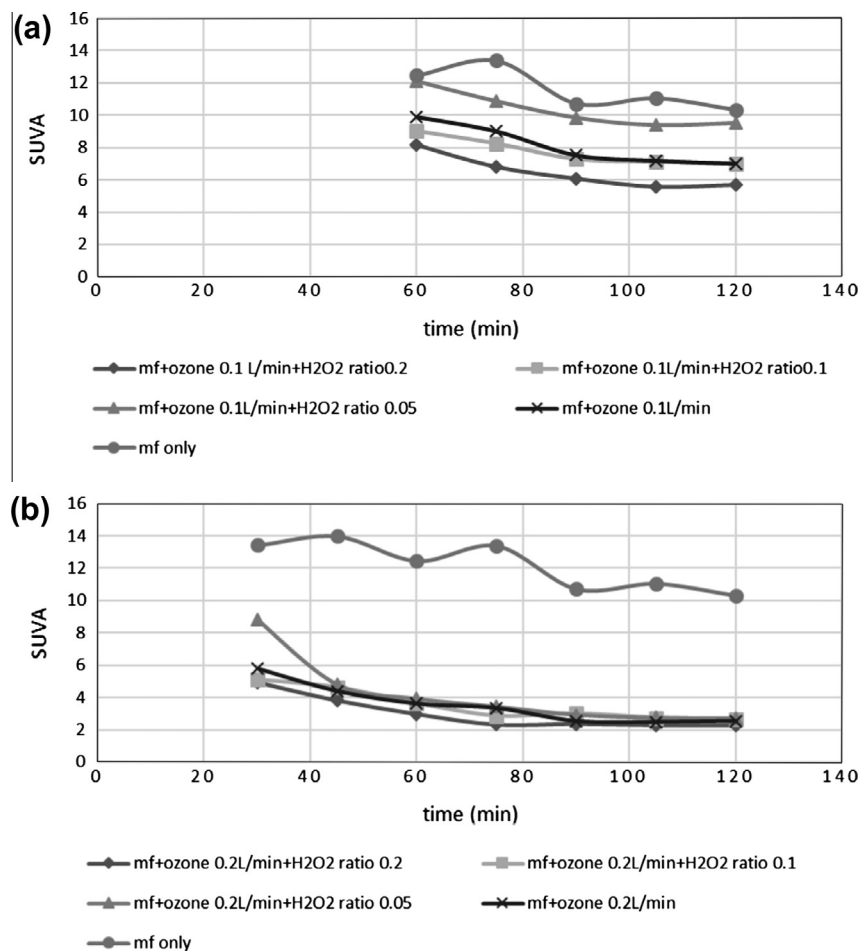
Fig. 4. SUVA values for the case of single microfiltration and for the hybrid processes, performed with the ozone–oxygen gas mixture flow rate of: (a) 0.1 L/min (corresponding ozone dosage 2.5 mg O_3/min of experiment) and (b) 0.2 L/min (corresponding ozone dosage 5.0 mg O_3/min of experiment).

enough for a significant mineralization of the humic acid MW fractions.

It has been reported in the literature [24] that despite the fact that ozone oxidation has an impact on the MW fractionation of humic substances, it may not have any effect on the TOC content of the treated samples. From the TOC content of permeates it can be noticed that the hybrid process with the lower H_2O_2/O_3 molar ratio (0.05) resulted in similar TOC reduction, i.e. at the same level, as after the application of single MF. It is possible that under these experimental conditions the amount of TOC is not changing, but the fractionation of humic acids MWs is appropriately altered [18] and therefore, the respective fouling behavior can be mitigated, as it can be seen in the following part of this study.

In the case of hybrid processes with the application of higher ozone flow rate (0.2 L/min) the differences between the hybrid processes and the single MF are more distinctive. The first peak indicating the fraction with the highest MW was shifted from 140 kDa to values around 130 kDa and the concentrations of these compounds were significantly lower for all the hybrid processes when compared with single microfiltration, with the exception of experiment using H_2O_2/O_3 ratio of 0.1, where the relevant presence of this fraction (%) was increased from 46% (for the case of single MF) to 57% for this experiment. Similarly, the results for ozone flow rate at 0.1 L/min indicate that the relevant presence (%) of species with the lowest MW (14 kDa) were lower for the hybrid processes (5–6%), when comparing with the single MF (11%), again with the exception of the experiment using H_2O_2/O_3 ratio of 0.1, where this presence was increased up to 22%.

The increase of TOC content of permeates obtained after the application of hybrid processes can be attributed to the lower (relevant) presence of the highest MW fraction, while the concentrations of the middle MW fractions (104 kDa, 75 kDa, 40 kDa) were found to increase, when comparing with the results of the single MF. Noting also that the hybrid process with H_2O_2/O_3 molar ratio of 0.1 resulted in different humic acid fractionations, than all the other hybrid processes. Not only the relevant presence of the biggest MW fraction was increased up to 57%, but also the MW sizes of the other fractions were different, for example the 2nd biggest fraction was around 87 kDa, as compared with the other processes, being 104 kDa.

When comparing the HPLC results obtained for the two ozone dosages studied, it can be noticed that the higher ozone dosage resulted in more significant changes in the humic acid fractionation than the lower ozone dosage applied. The addition of hydrogen peroxide, which improves the hydroxyl radicals oxidation pathway, resulted generally in a production of lower MW fractions than for the hybrid processes with single ozonation.

As has been mentioned before, the humic acid removal by single MF cannot only be based on the MWCO of the membrane, as the ceramic membrane used in this study has an average pore diameter of 200 nm, which theoretically should have a Molecular Weight Cut-Off (MWCO) in the range of around 2000 kDa, while the average size of humic acid fraction with the highest MW present in the initial samples was 140 kDa. Hence, the observed MWCO is much bigger than the MWs of the treated humic acid molecules, but still the removal of organic content, as indicated by the UV_{254} adsorption

Table 1
Fractionation of humic acids for the experiments using ozone–oxygen gas mixture flow rate of 0.1 L/min (corresponding ozone dosage 2.5 mg O_3/min of experiment).

Peak	Initial humic acid		MF only		MF with O_3		MF with O_3/H_2O_2 (molar ratio 0.05)		MF with O_3/H_2O_2 (molar ratio 0.10)		MF with O_3/H_2O_2 (molar ratio 0.20)	
	MW (kDa)	Relevant presence (%)	MW (kDa)	Relevant presence (%)	MW (kDa)	Relevant presence (%)	MW (kDa)	Relevant presence (%)	MW (kDa)	Relevant presence (%)	MW (kDa)	Relevant presence (%)
1	140	24.1	140	46.1	145	50.8	145	44.9	140	51.3	140	48.7
2	105	17.0	105	18.5	105	19.9	105	19.1	105	19.1	105	19.2
3	70	19.3	70	16.4	70	15.2	70	14.7	70	15.2	70	15.2
4	44	28.3	44	7.8	44	8.9	44	9.0	44	9.8	42	9.8
5	14	11.4	14	11.2	14	5.2	13	12.3	14	4.6	14	7.2
Average MW (kDa)	79		100		100		110		108		104	

Table 2
Fractionation of HA for the experiments using ozone flow rate 0.2 L/min (corresponding ozone dosage 5.0 mg O_3/min of experiment).

Peak	Initial humic acid		MF only		MF with O_3		MF with O_3/H_2O_2 (molar ratio 0.05)		MF with O_3/H_2O_2 (molar ratio 0.10)		MF with O_3/H_2O_2 (molar ratio 0.20)	
	MW (kDa)	Relevant presence (%)	MW (kDa)	Relevant presence (%)	MW (kDa)	Relevant presence (%)	MW (kDa)	Relevant presence (%)	MW (kDa)	Relevant presence (%)	MW (kDa)	Relevant presence (%)
1	140	24.1	140	46.1	133	41.0	133	38.5	127	57.0	127	36.5
2	105	17.0	105	18.5	104	25.2	104	25.9	87	11.1	104	25.2
3	70	19.3	70	16.4	75	17.8	75	18.1	56	5.5	73	19.9
4	44	28.3	44	7.8	45	11.0	45	11.5	35	4.1	41	11.7
5	14	11.4	14	11.2	14	5.0	14	6.0	17	22.2	14	6.0
Average MW (kDa)	165		100		118		111		91		93	

and TOC values, for the case of single MF is quite high. Given these facts, it seems that the retention of humic acid molecules does not happen only by size exclusion, but that the removal process is also based on the adsorption of humic acid molecules onto the membrane surface. It has been reported in the literature that during the ceramic membrane ultrafiltration of synthetic humic acids solution the membrane fouling happens probably by pore constriction, or formation of a semipermeable cake layer on the membrane surface, which exhibits additional mass transfer resistance [26]. This type of membrane fouling could explain the high humic acid retention, noticed during the application of single MF. According to the literature, the pore sizes of MF membranes are much larger than the sizes of NOM, so they should not be effective in the removal of NOM [27]. As the presence of the highest MW fractions (140 and 105 kDa) in the permeates obtained during single MF is higher than in the water to be treated, it seems that in fact the smaller MW fractions of humic acid are responsible for the pore constriction and semi-permeable cake build up on the membrane surface during membrane operation rather than the higher MW fractions of humic acid.

3.4. Membrane fouling

The TMP was monitored during all the experimental runs, as an indication of membrane fouling during the membrane operation. The TMP increase during experiments is presented in Fig. 5 as a ratio of TMP_t recorded at specific time intervals to the initial TMP_0 (−0.250 bar). The highest increase of TMP values were obtained during single MF experiments. The addition of ozonation or of ozonation in the presence of H_2O_2 resulted in the mitigation of membrane fouling, as shown in Fig. 5(a and b), where it can be noticed that the increase of TMP in the case of single MF is stable during the whole period of membrane operation. However, in the case of hybrid processes with the higher ozone dosage used, after approximately 45 min of membrane operation there were no

further changes in the TMP; it seems that the membrane fouling achieved a steady state and as it did not proceed considerably anymore, as there were no further changes in the TMPs, especially for the case of higher ozone–oxygen gas mixture flow rate. It can be concluded that the oxidation of organic matter, which was present in the experimental unit after 35 min of continuous ozonation was oxidized up to the point, where the produced fragments of humic acids, having certain MWs, could not be foul the membrane further and the cake formation was limited.

This observation can also be connected with the change in the treated humic acid properties, as is indicated by the SUVA values presented before, where for the hybrid processes performed at the higher ozone dosage after 45 min of experiments there was a definite change in the humic acid properties from hydrophobic to hydrophilic.

It is interesting to notice that there is also a decline in the quality of permeates, obtained from the hybrid processes after 45 min of membrane operation. This could indicate that the extent to which the membrane is fouled during these experiments has an impact on the quality of permeates obtained. As the extent of membrane fouling and the retention of humic acids seem to be correlated, this finding could explain why the quality of permeates during the hybrid processes can be even lower, than during the single MF. As the membrane during the application of a hybrid process does not get significantly fouled, the retention (separation) of humic acids cannot be improved by the process of formation of semipermeable cake on the membrane surface as is the case during single microfiltration.

In order to further evaluate the membrane fouling, Fouling Indexes (FI) were calculated for every experiment and are presented in Table 3. FI were calculated as the ratio of deionized water flux through the clean membrane before each experiment to the corresponding deionized water flux through the fouled membrane after each experimental run [28]. Values of FI close to 1 indicate very small extent of membrane fouling, whereas values close to
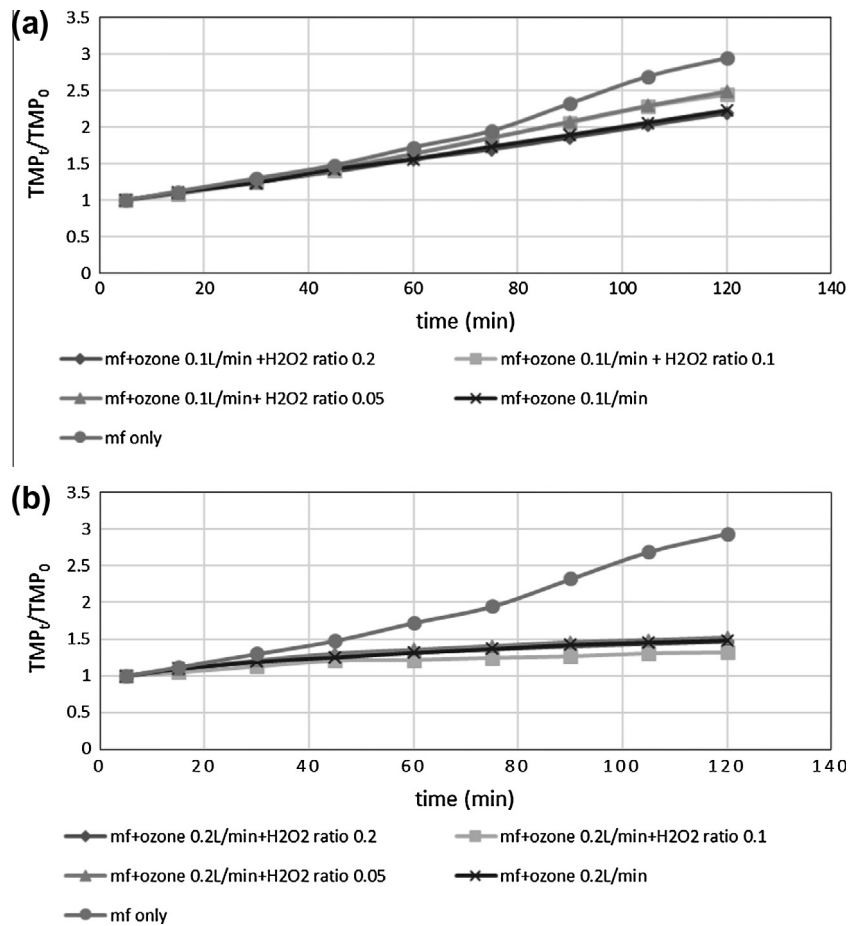
Fig. 5. Trans Membrane Pressure (TMP) changes during the experiments applying single microfiltration or hybrid processes, performed with the ozone–oxygen mixture flow rate: (a) 0.1 L/min (corresponding ozone dosage 2.5 mg O_3/min of experiment) and (b) 0.2 L/min (corresponding ozone dosage 5.0 mg O_3/min of experiment).

Table 3
Fouling indexes calculated for the experiments with either single microfiltration or hybrid processes, performed with the ozone–oxygen mixture flow rate: (a) 0.1 L/min (corresponding ozone dosage 2.5 mg O_3/min of experiment) and (b) 0.2 L/min (corresponding ozone dosage 5.0 mg O_3/min of experiment).

Process	FI	Process	FI
MF only	0.40	MF only	0.40
MF + ozone 0.1 L/min	0.49	MF + ozone 0.2 L/min	0.66
MF + ozone 0.1 L/min + H_2O_2 ratio 0.05	0.46	MF + ozone 0.2 L/min + H_2O_2 ratio 0.05	0.63
MF + ozone 0.1 L/min + H_2O_2 ratio 0.1	0.48	MF + ozone 0.2 L/min + H_2O_2 ratio 0.1	0.73
MF + ozone 0.1 L/min + H_2O_2 ratio 0.2	0.51	MF + ozone 0.2 L/min + H_2O_2 ratio 0.2	0.64

0 indicates that the membrane is almost completely fouled. The lowest FI values were calculated for the single MF experiments, whereas the hybrid processes resulted in the mitigation of membrane fouling, as indicated by the higher FI values.

When comparing the results of TOC and UV_{254} removals for the hybrid processes, it can be noticed that there is a significant decline in permeates quality, starting approximately from the 30th–45th min of membrane operation onwards. Also, from the 30th–45th min of membrane operation, the fouling achieves a rather steady state and is not increasing significantly anymore for the application of hybrid processes. As aforementioned, the process of membrane fouling during the MF of humic acid takes place mainly by the pore constriction mechanism and semi-permeable cake formation, which affects the humic acid retention in a positive way. When fouling is being decreased during the application of hybrid (MF/ O_3, or MF/(O_3 + H_2O_2) processes the quality of permeates is slightly deteriorated, due to the absence of the positive impact of fouling. However, the oxidation of humic acid molecules during ozonation in the presence of H_2O_2 is beneficial enough to maintain the higher quality of permeates, while reducing the membrane fouling at the same time.

4. Conclusions

The hybrid process of ceramic membrane filtration combined with ozonation in the presence of H_2O_2 has proved to be effective for the mitigation of membrane fouling, without the significant deterioration of permeate quality, at least for the membrane configuration and water to be treated studied. The extent of mitigation of membrane fouling was dependent on the concentration of ozone added to the system; when a higher ozone–oxygen gas mixture flow rate was applied (0.2 L/min), it resulted in a better reduction of membrane fouling, while a total consumption of ozone dosages added to the system was achieved. Coupling of ozone based oxidation with ceramic membrane microfiltration affected the

composition and properties of humic acid treated by this system, with a result of mitigation of membrane fouling due to the less hydrophobic properties of humic acid. The supplementary addition of H_2O_2 resulted in better quality of permeate, as compared with the hybrid process of membrane MF with ozonation only, which is correlated with the improvement of hydroxyl radicals production during the O_3/H_2O_2 oxidation. The oxidation of humic acids resulted in a different fragmentation of humic acids MWs, when comparing with the application of MF process only. The quality of permeates and the extent of membrane fouling seem to be correlated. As fouling during the MF of humic acid is considered to take place mainly by the pore constriction mechanism and semi-permeable cake formation, it is expected to increase the retention of humic acids, while also causing severe membrane fouling.

Acknowledgments

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