



## NanoMembraneWater: development of innovative hybrid processes for contaminated water treatment using nanoporous membranes

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#### ABSTRACT

This study aims at the development of a hybrid process for the efficient treatment of water and potentially of wastewater, by the combination of ozonation and membrane filtration and the investigation of the complete ozone utilization by the employment of a novel ceramic membrane reactor concept. The advantages of the process are mainly referred to the achievement of a homogeneous (down to microscale) transfer and distribution of ozone ("bubbles aeration") within the main body of bulk water stream, which results in very efficient oxidation. Ceramic membranes were prepared initially, in order to investigate the single filtration of groundwater; tubular shaped nonsymmetric ceramic membranes were developed and their efficiency was examined for the removal of As-loaded water. Microporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-17Fe (molar ratio Al and Fe: 1:1) membrane was found to adsorb the pollutant As (V) ions up to 95%. The combined process of ozonation and membrane filtration was examined in a bench scale unit, where ozone was added through a ceramic diffuser at low flow rates, under continuous and intermittent modes. Simulated ground and surface water containing  $25 \text{ mg L}^{-1}$  of kaolin and humic acid was fed to the reactor; it was found that the intermittent mode of ozone addition was beneficial over the continuous mode of operation, resulting in lower trans-membrane pressure values. However, the hybrid process of ozonation-membrane filtration resulted in a lower quality effluent with a higher Total Organic Carbon content, possibly due to the effect of ozone on organic substances: ozone resulted to the dissociation of large molecular weight compounds and the formation of smaller molecules that could easily pass through the membranes in the effluent. In addition, a new hybrid ozone-filtration unit has been constructed. In this unit, the water to be treated flows through the inner side of a tubular membrane while gaseous ozone stream flows along the outer. An appropriate pressure drop gradient causes ozone to flow towards the inner water stream through the nanopores of the ceramic membrane, causing oxidation (and decomposition) of

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the organic substances or complexes, which are present in the water stream. The retentate stream of the first step represents the influent to the second step where the removal of ions is achieved by ceramic membranes (ultrafiltration).

Keywords: Ceramic membranes; Ozonation; Water treatment; Hybrid process

### 1. Introduction

The combination of membrane filtration with other treatment processes has gained much attention in recent years for the efficient treatment of both water and wastewaters and the removal of resistant substances. Several attempts have been made aiming to couple membrane filtration with processes such as coagulation [1], flotation [2], or advanced oxidation processes (AOP's) [3]. Especially AOP's have been proved useful for the treatment of waters or wastewaters that contain nondegradable materials, as they are able to reduce the organic content and remove refractory compounds, such as humic acids that are abundant in surface water. AOPs usually combine the use of hydrogen peroxide, ozone, hypochlorite, or UV radiation. Ozone is one of the most powerful known oxidants, mainly used in water treatment for disinfection, oxidation of organic and inorganic compounds, including taste, odor, and color removal. As the main problem associated with membrane filtration is membrane fouling, which may lead to severe flux reduction, it is needed to minimize the impact of fouling particles on the membrane operation. Taking into account the high reactivity of ozone with organic substances, it is likely that combining membrane filtration with ozonation can be beneficial in foul reduction, preventing considerable flux decline during membrane operation.

Most research studies are focused on the implementation of ozone as a pretreatment step prior to the membrane filtration; ozone is usually introduced by direct mixing with the influent or by ozonation of water/wastewater in a tank before the membrane unit. Song and his coworkers investigated membrane microfiltration of a previously ozonated river water [3]; ozonation provided a degradation of macromolecular organic matter that was responsible for membrane fouling to smaller molecular organic matter, thus reducing the membrane fouling rate. The researchers estimated an optimum ozone dosage, resulting in a maximum membrane flux. Increasing the ozone concentration above this optimum dosage did not bring any additional beneficial effect on the membrane flux. Other researchers investigated the effect of ozone dosage, in ozonation-ceramic

membrane ultrafiltration system treating natural waters [4]. Ozonation significantly reduced membrane fouling and the fouling behavior was strongly dependent on ozone concentration applied and hydrodynamic conditions. Tests were also made with oxygen sparging, but, its effect on the permeate fluxes was very limited; it was concluded that the improved performance when using ozonation was due to oxidation of NOM. Combined ozonation and filtration of lake water was investigated by Karnik et al., in order to evaluate their effects on disinfection by products formation [5]. The combined treatment resulted in the improvement of the quality of permeate and in the formation of partially oxidized compounds from NOM, which were less reactive with chlorine, thus resulting in reduced concentrations of trihalomethanes and halo acetic acids. Another research made by Karnik gave insight into the effects of ozonation on the permeate flux of ceramic membranes [6]. It was found out that application of ozone gas prior to the membrane filtration decreased membrane fouling, in a significant way. There was a threshold value of ozone concentration; higher dosages did not bring additional beneficial effects on permeate flux recovery. Lee et al., investigated the mechanism of reducing fouling by means of ozone, using a sample from a wastewater treatment facility [7]. The major membrane fouling reduction was attributed to the degradation of organic compounds from high molecular weight to low molecular weight. However, no significant permeate quality improvement was observed.

It is apparent that the addition of ozone for the improvement of membrane filtration process has been investigated by certain researchers. However, as ozone is a highly reactive compound, during the combination of ozone and membrane processes, it deteriorates the surface of polymeric membranes [8] and only on chemically inert membranes, such as ceramic membranes, should it be applied. As most of the commercially available ceramic membranes are made of metal oxides like alumina, titanium or silica, they can offer a higher chemical, thermal, and mechanical stability than polymeric membranes. On the other hand, conventional methods of ozone gas addition to the water phase are taken place by using bubble columns, diffusion heads or spargers. These devices produce gas bubbles of different sizes from which ozone is transferred into the aqueous phase. However, due to the relatively low contact surface, only a part of ozone gas introduced to the system reacts with contaminants in the water while the nonreacted ozone is removed off in the process as gas and has to be further treated to avoid secondary pollution, resulting in additional increase in operation cost of the unit. An alternative approach in the addition of ozone gas might be the use of a membrane contactor, providing a high contact surface due to the formation of small gas bubbles and favoring the complete reaction and utilization of reactants [9].

The objectives of this study are the examination of the potential for the development of an innovative combined process of ozonation—membrane filtration, aiming at the complete utilization of the reactant gas, the evaluation of the hybrid process for the treatment of contaminated surface water, the investigation of the effect of experimental conditions and the membrane structure on the efficiency of the system for the removal of organic compounds aiming at the optimization of the system performance.

### 2. Experimental

### 2.1. Materials and methods

#### 2.1.1. Ultrafiltration membranes

The membrane specimens are of tubular geometry with a length  $340 \times 10^{-3}$  m, an internal diameter of  $8 \times 10^{-3}$  m, and an external diameter of  $14 \times 10^{-3}$  m; the membrane surface per specimen is therefore  $8.5 \times 10^{-3} \text{ m}^2$ . The ceramic membrane is an asymmetric 4-layer system. The first layer operates as a support, the third as a microfiltration layer (pore sizes of 100 or 200 nm depending on the firing temperature) and the fourth as an ultrafiltration layer with a pore size of 3–5 nm. The second layer (pore size of 500 nm) serves to bridge the gap between the macroporous support and the microfiltration layer. The fourth layer is prepared by a dip coating technique from colloidal nanoparticle boehmite suspension (sol) which was prepared using a sol-gel technique. In a typical synthesis, aluminum tri-sec-butylate (Merck) was added to water at 80°C; the mixture was allowed to hydrolyze slowly for 2h with constant stirring and under reflux conditions. Subsequently, the appropriate amount of iron nitrate nonahydrate (Merck) dissolved in distilled water to obtain a 1M aqueous solution was added. The sol was refluxed for 17 h at 80°C, followed by cooling to room temperature. The slip-casting procedure is followed by drying and calcination at 600 °C for the formation of the final structure of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-*x*Fe, *x* = 1, 17, 35, materials with different molar ratio Al and Fe (1:0.06, 1:1, 1:2, respectively) as described in the literature [10].

Powder XRD datas were collected on a Siemens D-500 diffractometer using Cu  $K_{\alpha}$  radiation. The diffraction patterns were collected in the 2 $\theta$  range from 5 to 80 degrees, in steps of 0.04 degrees and 1 s counting time per step. SEM images were recorded using a JEOL JSM6300 microscope operating at 20 kV. The samples were gold sputtered to avoid charging effects on the images.

The N<sub>2</sub> adsorption–desorption isotherms were measured at 77 K on a Micromeritics Tristar Porosimeter. Specific surface areas ( $S_{BET}$ ) were determined with the Brunauer—Emmett—Teller (BET) method using adsorption data points in the relative pressure P/P<sub>o</sub> range 0.01–0.30. The desorption branches of the isotherms were used for the pore size calculations according to the Kelvin equation. The samples were out gassed at 150°C for 12 h under high vacuum before the measurements.

Elemental analysis has been performed using a PerkinElmer Optima 4300DV (inductively coupled plasma) atomic emission spectrometer operating with the standard nebulizer system in the axial viewing mode. Argon flow rates of  $0.8 \,\mathrm{L\,min^{-1}}$ ,  $0.2 \,\mathrm{L\,min^{-1}}$ , and  $15 \,\mathrm{L\,min^{-1}}$  were employed for nebulizer gas, auxiliary gas, and plasma gas, respectively. The RF power was maintained at  $1.3 \,\mathrm{kW}$ . The emission wavelengths for arsenic were 197.197 nm, and 193.696 nm. A delay time of 60 s was used between each sample. Arsenic ICP standard solution (Merck CertiPUR 1.70303.0100) with initial concentration  $1,000 \,\mathrm{mg\,L^{-1}}$  As was used for calibration.

# 2.1.2. Combined ozonation—membrane ultrafiltration technology

The feed water used in the treatment experiments was a simulated contaminated surface water of medium turbidity, containing  $25 \text{ mg L}^{-1}$  of humic acid and  $25 \text{ mg L}^{-1}$  of kaolin in tap water, or a model dispersion containing the same amounts of humic acid and kaolin in deionized water. A fresh sample was prepared before each experiment from stock solutions of kaolin (1,000 mg L<sup>-1</sup>), humic acid (1,000 mg L<sup>-1</sup>) and tap water or deionized water. Solid humic acid reagent was obtained from Sigma-Aldrich, whereas the kaolin (clay) was a typical commercially available kaolin powder, giving rather stable dispersions. The rate of humic acid removal was determined by measuring the UV absorbance of the sample at 254 nm, which is used as an indication of organic molecule concentration; absorbance measurements took place on a Hitachi UV-vis spectrophotometer. pH was measured by a pH meter (Jenway, model 3540), while turbidity was measured by a Hach Ratio/XR turbidity meter. Ozone concentrations in the gas phase were determined according to the potassium iodide standard method [11]. Total Organic Carbon (TOC) measurements were performed by a TOC-V<sub>CSH</sub> total organic carbon analyzer (Shimadzu).

### 2.2. Experimental unit

### 2.2.1. Membrane ultrafiltration technology

The unit employs six specimens with a total filtration membrane area of  $51 \times 10^{-3} \text{ m}^2$  and operates under a pressure difference of  $3 \times 10^5 \text{ N m}^{-2}$ . During the filtration experiments, the high-pressure side has always been the membrane filtration layer side, while the low-pressure side has always been at atmospheric pressure. The unit is also equipped with a backflushing circuit with programable activation frequency and duration time. During most of the experiments, the retentate stream (i.e., the unprocessed fraction of the feed that did not permeate through the membrane) is guided to the stirred tank and is thus totally recycled. The efficiency of the single filtration process was examined against arsenic removal, using an As (V) influent concentration of 0.2 mg L<sup>-1</sup>.

# 2.2.2. Combined ozonation—membrane ultrafiltration technology

The experimental unit used in this study is depicted in Fig. 1. The reaction vessel consisting in a Plexiglass tank  $(50 \times 15 \text{ cm})$  had a working volume of 7 L. Ozone gas was introduced to the reactor by a Schott ceramic porous diffuser (nominal porosity 4,  $10-16\,\mu\text{m}$ ), located at the bottom of the vessel. The reactor was covered by a Plexiglass lid that ensured air-tight conditions. Ozone gas that has not reacted during the experiment was collected in an ozone trap containing 2% KI solution. A flat sheet ceramic microfiltration membrane with a multichannel geometry was placed in the vessel on a plastic rod support, 15 cm above the bottom of the vessel. The mean pore size of the membrane was 0.3 µm and the total surface area was 0.021 m<sup>2</sup>. Ozone was produced by an ozone generator (Model TOGC2A, Ozonia-Triogen), with compressed and dried air or pure oxygen as feed gases. Permeate was removed by a peristaltic pump (Watson Marlow, model 503U) and the transmembrane pressure (TMP) was recorded by a digital pressure meter (Wika, model DG-10). Influent sample



Fig. 1. Flow diagram of the combined ozone-filtration experimental unit: (1) ozone generator, (2) needle valve for the control of ozone flow rate, (3) excessive ozone gas hood directed by a three way valve, (4) ozone gas flow meter with a needle valve, (5) valve, (6) pressure meter, (7) feedwater tank, (8) peristaltic pump, (9) reaction column, (10) ceramic membrane, (11) ozone sparger, (12) TMP meter, (13) peristaltic pump, (14) volumetric cylinder, (15) KI ozone trap.

was fed to the reactor by a peristaltic pump (Watson Marlow, model 505U). The pressure of the ozone gas mixture produced by the ozonator was measured with a digital pressure meter (Wika, model DG-10) and the flow rate of the ozone gas was measured and adjusted using a flow meter equipped with a needle valve (Aalborg, model PMR-1).



Fig. 2. XRD patterns of  $\gamma\text{-}Al_2O_3$  (a),  $\gamma\text{-}Al_2O_3\text{--}1Fe$  (b),  $\gamma\text{-}Al_2O_3\text{--}17Fe$  (c),  $\gamma\text{-}Al_2O_3\text{--}35Fe$  (d).

### 3. Results and discussion

# 3.1. Ultrafiltration technology for As(V) removal from contaminated water

Fig. 2 presents the XRD patterns of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-xFe, x = 1, 17, 35, samples along with porous alumina. The positions of the diffraction lines of y-Al2O3 and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> are also indicated. As shown in this figure, the pattern of γ-Al<sub>2</sub>O<sub>3</sub>-1Fe exhibits two broad relatively intense reflections near 18° and 38° that can be attributed to the presence of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. On the other hand, the XRD patterns of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-17Fe and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-35Fe contain the characteristic reflections of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and (Fe<sub>0.86</sub>Al<sub>0.14</sub>)<sub>2</sub>O<sub>3</sub>. The surface area and the pore structure of the samples were determined from nitrogen isotherm analysis. As shown in Fig. 3, the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> displayed a type-IV isotherm, characteristic for mesoporous materials, while hysteresis was observed indicating the occurrence of capillary condensation in the pores. Using these data, the specific surface area  $S_{BET}$  was calculated to be  $267 \text{ m}^2 \text{ g}^{-1}$  and the pore size 45 Å. On the other hand, the nanocomposites



Fig. 3. Nitrogen adsorption-desorption isotherms of the samples:  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (a, **■**),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–1Fe (b,  $\bigcirc$ ),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–17Fe (c, **♦**),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–35Fe (d,  $\triangle$ ). Inset, pore size distribution calculated from the N<sub>2</sub> desorption branch.

Table 1  $S_{\text{BET}}$  and pore sizes of alumina composites

Sample	$S_{BET} (m^2 g^{-1})$	Pore diameter (Å)
γ-Al <sub>2</sub> O <sub>3</sub>	267	45
γ-Al <sub>2</sub> O <sub>3</sub> –1Fe	279	57
γ-Al <sub>2</sub> O <sub>3</sub> -17Fe	100	66
γ-Al <sub>2</sub> O <sub>3</sub> -35Fe	67	148



Fig. 4. Residual arsenic concentration of the samples:  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-1Fe ( $\bullet$ ),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-17Fe ( $\bullet$ ),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-35Fe ( $\blacktriangle$ ).

displayed similar type-IV isotherms but the curves at high P/P<sub>o</sub> values were flatter and showed greater hysteresis. Using these data, smaller effective pore radii and S<sub>BET</sub> under  $200 \text{ m}^2 \text{ g}^{-1}$  were obtained (Table 1). Among the three composites, the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-1Fe sample appeared to have the largest specific surface area. Although the reduction of S<sub>BET</sub> for all composites is predictable, since the development of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> particles inside the porous alumina or incorporation of Fe<sup>3+</sup> at  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> structure restricts the free surface of the solids [12], the reason for the observed differences in the sorption properties among them is not obvious. Probably the different amount of Fe ions, leads to different morphology for each sample, affecting their sorption properties.

According to the experimental results the fine porous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>–1Fe membrane layer was found to adsorb the As(V) ions up to 95%. The residual concentration of the arsenate in the permeate stream was 0.011 mg L<sup>-1</sup>, while the maximum available content of arsenic ions in the drinking water is 0.010 mg L<sup>-1</sup> (Fig. 4). The average operation pressure difference during the experiments was  $3 \times 10^5$  N m<sup>-2</sup>.

# 3.2. Ceramic membrane filtration with intermittent use of ozonation for the treatment of simulated surface water

In order to evaluate the effects of lower concentrations of ozone in the hybrid ceramic membrane microfiltration process on the membrane flux, additional experiments were performed using an intermittent addition of ozone. The reaction gas containing  $7.57 \text{ mg L}^{-1}$  ozone, produced by compressed and dried air as a feed gas for the ozonator, was introduced to the reactor for a period of 2 and 5 min at a flow rate of



Fig. 5. The effect of ozonation time on the permeate flux for ceramic membrane microfiltration, microfiltration combined with air sparging and microfiltration combined with ozonation under various ozone addition modes. Single membrane filtration:  $\blacklozenge$ , membrane filtration with air sparging:  $\blacksquare$ , membrane filtration with ozonation for 2 min:  $\blacktriangle$ , membrane filtration with ozonation for 5 min:  $\times$ .

 $1 \text{ Lmin}^{-1}$  (LPM), for time intervals of 15 min of the experimental time; considering that the experiment lasted for about 120 min, ozone was added seven times in the reactor. The amount of ozone gas that had not reacted was collected in an ozone trap at the bottom of the reactor, containing 200 mL of a 2% KI solution. For the experiment that was carried out by the introduction of ozone for 2 min, the ozone consumption was estimated to about  $7.1 \text{ mg L}^{-1}$ , while when ozone was added for 5 min, the corresponding consumption was  $6.7 \, \text{mg} \, \text{L}^{-1}$ . In addition, an experiment with similar conditions as an intermittent one, but using a continuous air sparging mode was performed in order to study the potential reduction of membrane fouling due to oxidation. In order to evaluate the effect of ozonation on the permeate flux properties, the experiments were performed at a constant TMP of -0.5 bar in a continuous mode, that is, water to be treated was added to the tank by a peristaltic pump at the same flow rate as the permeate flow rate.

As shown in Fig. 5, the permeate flux for the single microfiltration of the simulated surface water decreased to 75% after 2h of reaction, while for air sparging the flux was 83% of the initial flux at the same time. The



Fig. 6. Evaluation of the membrane fouling potential during: (1) microfiltration, (2) microfiltration combined with air sparging, (3) microfiltration combined with ozone added for  $2 \min$ , (4) microfiltration combined with ozone added for  $5 \min$ . Clean membrane:  $\blacktriangle$ , fouled membrane:  $\blacksquare$ .

duration of ozone addition did not significantly affect the permeate flux rate; the permeate flux remained at about 88% of the initial value when ozonation had been applied for 2 or 5 min in each cycle.

In order to determine the membrane fouling mechanism, the deionized water fluxes through the clean membrane and the membrane that had been subjected to fouling due to the filtration of humic acid and kaolin were recorded and compared. The duration of each experiment was for a few minutes, up to the time when the respective TMP and flux were stabilized. As shown in Fig. 6, severe fouling of the membrane was observed for single ceramic membrane microfiltration or for microfiltration combined with air sparging, as indicated by the change in TMP values. High differences in permeate fluxes were observed at the same pressure for clean and fouled membrane: at TMP of -0.5 bar the difference in flux was more than  $20 L h^{-1} m^{-2}$ . Air sparging improved slightly the membrane fouling rate, while the addition of ozone, even at values as low as 2 min brought a significant reduction of membrane fouling potential.

Evaluation of the results deduced by the two different modes of ozonation combined with membrane filtration, that is, continuous and intermittent mode, showed that the intermittent mode seems to be the most suitable one. Although significantly lower overall concentrations of ozone were utilized by the intermittent mode than the continuous one, a substantial reduction of membrane fouling was observed in the former case.

# 3.3. Membrane filtration with intermittent use of ozonation for the treatment of model surface water

In order to evaluate the effect of ozonation on the TOC removal during the hybrid ozonation–ceramic membrane microfiltration, experiments were performed using model surface water with constant TOC concentration. Oxygen was used as the feed gas to the ozone generator, resulting in higher ozone concentrations. The experiments were conducted for a period of 180 min: during that period ozone was added to the reactor tank three times, for a period of 1 min, corresponding to the 66th, 96th, and 126th min of the experiment. Two ozone flow rates were used, mainly 0.6 and  $1.0 \, \text{Lmin}^{-1}$ , with ozone concentrations of 15.9 and 26.5 mg L<sup>-1</sup>, respectively. Experiments were performed under a constant TMP of -0.5 bar, achieved by changing the effluent pump velocity.

As shown in Fig. 7, the permeate flux decreased to 68, 72 and 75% of the initial flux for the microfiltration, microfiltration with ozonation at a flow rate of  $0.6 \,\mathrm{L\,min^{-1}}$  and microfiltration with ozonation at a



Fig. 7. The effect of operation time on the permeate flux during treatment of model surface water using single filtration and combined filtration-ozonation at various ozone flow rates. Vertical lines represent time of addition of ozone. Single membrane filtration:  $\blacklozenge$ , membrane filtration with ozonation at 0.6 L min<sup>-1</sup>:  $\blacksquare$ , membrane filtration with ozonation at 1.0 L min<sup>-1</sup>:  $\blacktriangle$ .



Fig. 8. TOC removal rate as a function of operating time during the model water treatment by single filtration and by ozonation combined with filtration. Vertical lines represent time of addition of ozone. Single membrane filtration:  $\blacklozenge$ , membrane filtration with ozonation at  $0.6 \,\mathrm{L\,min^{-1}}$ :  $\blacksquare$ , membrane filtration with ozonation at  $1.0 \,\mathrm{L\,min^{-1}}$ :  $\blacktriangle$ .

flow rate of  $1.0 \,\mathrm{L\,min^{-1}}$ , respectively after 3 h of operating time. Low contact times of ozone with the influent and consequently low ozone concentrations added to the system are not sufficient enough to provide high effluent fluxes during a longer membrane operation.



Fig. 9. New experimental apparatus for the investigation of the combined bubble-less ozonation and filtration. (1)  $O_2$  tank; (2) ozone generator; (3) on-off valve; (4) needle valve; (5) flowmeter (0–1 L/min); (6) water tank; (7) flowmeter (2 L/h); (8) ozonation module; (9) manometer; (10) needle valve; (11) ozone trap; (12) ozone analyzer; (13) sampling valve; (14) progres. cavity pump; (15) manometer; (16) microfiltration module; (17) manometer; (18) regulator valve; (19) mass balance. A pc will be used to record pressure and weigh with time.

The UV<sub>254</sub> absorbance reduction in all cases was around 73%, while the measurement of the TOC effluent content revealed that ozonation resulted in an effluent with higher TOC values than the effluent produced by single filtration without ozonation (Fig. 8).

The lower efficiency of the combined process than the single ceramic membrane microfiltration could be attributed to the impact of ozonation on humic acid molecules: ozonation might change the molecular size distribution of the humic acid, destroying the higher molecular weight substances and resulting in the formation of several substances of lower molecular weights that could more easily pass through the membrane, and an effluent with higher organic content, as has been already reported in the literature [13].

### 3.4. New experimental unit for the hybrid ozonation-membrane microfiltration

A new bench-scale experimental apparatus was designed and constructed in order to extend the study about water and wastewater treatment by combining ozonation and microfiltration in a hybrid process. The apparatus is illustrated in Fig. 9; it consists of two ceramic membrane modules, connected in series. Tubular cross-flow  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> membranes with a nominal pore size of 0.1 µm were used for each module. The inner diameter of the membranes is 8 mm, the outer is 14 mm and their length is 340 mm. Plexiglass vessels

were constructed in order to house the membranes and the measuring devices. In the first module, which serves as the ozone-water contactor, the ozonation of contaminated water takes place. A progressive cavity pump, at bottom of the module is used to feed the polluted water in the first membrane at atmospheric pressure with a flow of  $1 L h^{-1}$ , ozone gas can be transferred to the water to be treated through the small pores of ceramic membrane with various flow rates, resulting in the formation of microbubbles, or even in a bubble-less ozonation by the application of an appropriate pressure difference, that is, by the application of an ozone pressure higher than the atmospheric pressure of influent water. An ozone flow meter, a pressure transmitter and a needle valve are used in order to adjust the flow and the pressure of ozone. After the first module, an ozone analyzer is placed in order to measure the residual concentration of dissolved ozone, which did not immediately react with the pollutants. The application of this membrane contactor for ozonation is expected to improve the ozone gas transfer, as well as the effectiveness of the process and to further reduce the fouling of the subsequent microfiltration membrane. Suspended particles and macromolecules are separated by reversing the pressure difference in the second module, housing the membrane used for microfiltration. Ozonated water is driven within the membrane by the progressive cavity pump and at a TMP of 3 bars.

The optimization of the performance of this apparatus will be investigated in ta forthcoming work, based on the results found by the current work.

#### 4. Conclusions

Different approaches for the combination of ceramic membrane microfiltration and ozonation in a hybrid process for surface water treatment have been presented. Ozonation, when used in higher concentrations, or for a longer period of time, may mitigate the impact of membrane fouling efficiently. However, it does not improve the quality of the permeate, because of the specific reactions of humic acid molecules with ozone. A new apparatus for the hybrid process was designed and presented and we expect to overcome those drawbacks.

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