HYBRID OZONATION-MICROFILTRATION SYSTEM FOR THE TREATMENT OF SURFACE WATER

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EXTENDED ABSTRACT

The aim of this work was the investigation of the performance efficiency of a hybrid treatment system integrating two processes, i.e. membrane filtration and ozone oxidation, as a potential method for contaminated surface water quality improvement and mitigation of the membrane fouling during the process. Ozone treatment is a well-known method applied for the effective oxidation and disinfection of water; however, coupling of this process with membrane filtration requires the utilization of ozone resistant membranes. Therefore, a bench scale unit was designed and constructed, where ceramic microfiltration membrane was used in a submerged configuration; ozone-oxygen gas mixture was added to the reactor by gas spargers located at the bottom of the experimental tank producing fine bubbles at various gas flow rates and ozone concentrations. Ozone – oxygen gas flow rates ranged from 0.3 L/min to less than 0.05 L/min, while ozone concentrations in the gas mixture varied from 6.6 mg O₃/min to less than 1.1 mg O₃/min. The treatment of simulated surface water was studied in this unit, prepared by the addition of 25 mg/L humic acid and 25 mg/L kaolin in tap water, corresponding to TOC content of 7.5 mg/L, turbidity 25 NTU and pH 7.5, aiming to the identification of optimum performance conditions. Treated water samples were collected and analysed for the determination of the quality of the permeate, including the measurement of turbidity, pH, UV₂₅₄ absorbance and Total Organic Carbon (TOC) content. Nevertheless, the operation of the membrane modules and the estimation of the membrane fouling rate were evaluated by monitoring the Trans Membrane Pressure (TMP), and by the calculation of the corresponding Fouling Indices. The addition of ozone resulted mainly in mitigation of the membrane fouling; for the single process of microfiltration, the TMP increased 0.86 times of the initial TMP during the 2 hours of membrane operation, while for the hybrid process using ozonation at a gas flow rate of 0.3 L/min and ozone concentration of 6.6 mg O₃/min, the TMP increased only 0.17 times after the same period of membrane operation. The hybrid process of membrane microfiltration – ozonation resulted in a substantial reduction of the membrane fouling rate for all the concentrations and flow rates of ozone, while the quality of the permeate varied depending on the ozone concentration used.

KEYWORDS: ceramic membranes, ozonation, hybrid process, surface water;

1. INTRODUCTION
Implementation of membrane processes is a well-established method for the treatment of various waters and wastewaters. However, the most important drawback associated to membrane operation is the membrane fouling, which results to the deterioration of the process effectiveness. For surface and groundwater treatment, membrane fouling is mainly attributed to the abundance of Natural Organic Matter (NOM). In order to minimize
membrane fouling, filtration can be combined with another water treatment method, such as coagulation (Park et al, 2010), flocculation (Peleka et al, 2009) or Advanced Oxidation Processes (Song et al, 2010) in a hybrid process. Ozone treatment is usually applied for oxidation and disinfection of water. However, coupling ozone treatment with membrane filtration requires the utilization of ozone resistant membranes, such as ceramic ones, as ozone being a very strong oxidant destroys polymeric membranes. In addition, ozonation usually takes place using ozone diffusers requiring high amounts of ozone for effective reaction; excess ozone is then removed by ozone destroyers. Therefore, ozonation is often a high cost process; a benefit of using ceramic membranes for ozone addition is related to the low cost of ozone which is added to the reactor at the exact required doses. Hybrid process of membrane filtration with ozonation has been investigated by a few researchers, although most of those studies are focused on using ozonation as a pre-treatment step prior to membrane filtration (Song et al, 2010; Benitez et al, 2008; Schlichterb et al, 2003).

The aim of this work was the investigation of the hybrid membrane microfiltration – ozonation process by the utilization of as low as possible ozone doses and examination of the following membrane filtration. A bench scale unit was designed and constructed, with a submerged ceramic microfiltration membrane. Ozone – oxygen gas mixture was added to the experimental tank by means of ceramic gas spargers producing fine bubbles. This study focused on the optimization of the hybrid process for the mitigation of membrane fouling during microfiltration of surface water. Various flow rates and concentrations of ozone have been used in a continuous mode simultaneously to membrane microfiltration.

2. EXPERIMENTAL:

2.1 Experimental unit:

The experimental unit used in this work is shown in Figure 1. The cylindrical reaction tank with a working volume of 16 L was made of Plexiglass (15X50 cm). Ozone-oxygen gas mixture was introduced to the reactor with three Schott porous diffusers producing fine bubbles (nominal porosity 4, pore size 10-16 μm), located at the bottom of the reaction tank. The reactor was covered with a Plexiglass lid to ensure air-tight conditions within the reactor. Ozone-oxygen gas mixture was produced by an ozone generator (model TOGC2A, Ozonia-Triogen), where pure oxygen was used as a feed gas. The pressure of ozone-oxygen gas mixture produced by the ozonator was measured by a digital pressure meter (Wika, model DG-10), whereas the flow rate of the ozone-oxygen gas mixture was measured and adjusted by a flow meter equipped with a needle valve (Aalborg, model PMR-1). Estimation of ozone in the influent gas mixture, and of the non reacted ozone at the outlet of the reactor, took place by passing the corresponding gas stream through a 2% KI trap and determination of ozone in the solution according to Standard Methods (Benitez et al, 2008). The dissolved ozone in the reactor tank was measured by an ozone sensor (ProMinent, type OZE). A flat sheet submerged ceramic membrane (ItN Nanovation) was located at the middle of the reaction tank; the membrane had an average pore diameter of 200 nm and active membrane area of 0.04 m². Permeate was withdrawn by a peristaltic pump (Watson Marlow, model 503U), and the Trans Membrane Pressures (TMPs) were measured by a digital pressure meter (Wika, model DG-10). Influent water was fed to the reaction tank by a peristaltic pump (Watson Marlow, model 505U) at a flow rate similar to permeate removal rate.
Figure 1. Hybrid experimental unit: (1) ozone generator, (2) needle valve, (3) ozone traps, (4) ozone gas flow meter, (5) valve, (6) ceramic gas spargers, (7) pressure meter, (8) feed water tank, (9) peristaltic pump, (10) reactor with the submerged membrane, (11) trans membrane pressure meter, (12) peristaltic pump, (13) peristaltic pump for permeate withdrawal, (14) balance.

2.2 Materials and Methods

Artificial water was used as influent simulating contaminated surface water; it was prepared by the addition of 25 mg/L humic acid (Sigma-Aldrich) and kaolin in tap water. A fresh sample of water was prepared from stock solutions of humic acid and kaolin before every experiment and the pH of final solution was adjusted to 7.5 with concentrated hydrochloric acid. The TOC content of the initial samples was 7.5 mg/L, while the turbidity was 25 NTU.

Samples collected from the effluent were analyzed for the determination of the following parameters: UV absorbance measured at 254 nm by a Hitachi UV-Vis spectrophotometer as an indication of organic molecules concentrations; Total Organic Carbon (TOC) by a TOC-VCSH Total Organic Carbon Analyzer (Shimadzu); turbidity by a Hach Ratio/XR turbidity meter and pH by a Jenway, model 3540 pH-meter. Ozone concentrations in the gas phase were determined by the potassium iodide method of Standard Methods (APHA, 1989).
3. RESULTS AND DISCUSSION

3.1 Microfiltration with a continuous use of ozonation

Experiments were performed in a continuous mode, and influent water was added to the reaction tank by a peristaltic pump at the same flowrate as the permeate was withdrawn from the tank in order to maintain a constant water volume in the tank. Ozone-oxygen gas mixture was added to the reaction tank in a continuous mode, starting from the 10th minute of every experiment, while each experiment lasted for 120 minutes. Flow rates of the ozone-oxygen gas mixture were 0.3, 0.2, 0.1 and 0.05 L/min with ozone concentrations of 6.6, 4.8, 2.22 and 1.00 mg/min. During each experiment water samples were collected from the reactor aiming to investigate the effect of ozonation on the treated water before it was filtered through the membrane. All the experiments were performed under a stable permeate flow rate, achieved by the adjustment of Trans Membrane Pressure (TMP). An initial TMP value of -0.250 bar was selected for each experiment; however, due to the fouling of the membrane, TMP gradually increased during the experiments.

3.2 Ozone consumption during the experiments

The dissolved ozone concentrations during each experiment were measured in the permeate and in the reactor, whereas ozone in off gases was measured by an ozone trap in order to estimate the corresponding ozone mass balance aiming to the determination of ozone consumption rate. Negligible dissolved ozone was measured in the permeates, while dissolved ozone in the reactor water and in the off gas were measured only for the experiment with the highest ozone flow rate (0.3 L/min). For the experiments with an ozone-oxygen mixture gas flow rate of 0.2 L/min or less, the concentration of dissolved ozone in the treated water was lower than the detection limit of the ozone sensor (0.01 ppm), while ozone was not measured in the reactor gases. It can be assumed that ozone consumption was almost 100 % for almost all the tests. The corresponding ozone mass balance for the experiment performed using an ozone flow rate of 0.3 L/min is shown in Figure 2.

![Figure 2. Ozone mass balance for the experiment performed with an ozone-oxygen mixture gas flow rate of 0.3 L/min.](image-url)
3.3 Quality of the permeates

The results of UV$_{254}$ absorbance as a function of reaction time for the single filtration experiments and for the hybrid processes are shown on Figure 3. Hybrid process with ozonation at the highest flow rate (0.3 L/min) resulted in deterioration of permeate quality. However, when ozone was applied at lower flow rates (0.2 L/min or less), the rate of humic acid removal was similar to the one obtained during single microfiltration.

![Figure 3. UV$_{254}$ percentage reduction for single microfiltration and hybrid process with various flow rates of ozone – oxygen gas mixture.](image)

Similar trend can be observed for the TOC content of the permeates. For the highest flow rate of ozone the removal of TOC is the lowest one, about 20%. In general, the lower the flow rate of ozone, the higher the removal of TOC. The low TOC removal capacity at high ozone contents could be attributed to the high oxidation rate of humic acids resulting therefore to the production of secondary by-products of lower molecular weight, that could pass through the membrane during the subsequent filtration (Miao and Tao, 2008),

![Figure 4. Total Organic Carbon (TOC) percentage removal for single microfiltration and hybrid process with various flow rates of ozone – oxygen gas mixture.](image)
The evaluation of the effect of ozonation on humic acid removal was carried out by the calculation of the corresponding SUVA values: SUVA (UV adsorption at 254 nm/ (mg C/L)) is defined as the UV absorbance of a given sample at 254 nm divided by the DOC (Dissolved Organic Carbon) concentration of the sample. This ratio describes the nature of NOM in the water in terms of hydrophobicity and hydrophilicity. SUVA values >4 correspond mainly to hydrophobic and especially to aromatic compounds while SUVA<3 illustrates hydrophilic substances (Matilainen et al, 2011). SUVA values calculated for the permeates produced under various treatment conditions are shown in Figure 5. As shown, ozonation at flow rates higher than 0.2 L/min results in changing the nature of humic acid molecules in the treated water from hydrophobic and aromatic towards more hydrophilic.

![Figure 5. SUVA values in the permeates as a function of reaction time at various treatment conditions. The initial SUVA value of the treated water is 7.41.](image)

3.4 Membrane fouling

Membrane fouling during the experiments was evaluated by the measurement of the Trans Membrane Pressure and the calculation of the corresponding Fouling Index. As shown in Figure 6, the TMP during single microfiltration increased 0.86 times of the initial TMP value (from -0.250 bar to -0.464 bar) after 120 minutes of membrane operation. When the highest ozone flow rate of 0.3 L/min was used the TMP increased only 0.17 times (from -0.250 bar to -0.271 bar). The mitigation of membrane fouling depended on the flow rate and the concentrations of ozone – the higher the ozone flow rate, the lower the membrane fouling rate. The Fouling Index was calculated as the ratio of the deionized water flux through the clean membrane before each experiment to the corresponding flux through the fouled membrane after the experiment and the corresponding results are shown in Figure 7. As shown in Figures 6 and 7, TMP and Fouling Index values showed similar behavior in the various runs: low values of Fouling Index were calculated for single microfiltration or low ozone flow rate experiments, while values as high as 0.8 were obtained at the highest ozone flow rate, indicating a small fouling rate of the membrane.
4. CONCLUSIONS

The hybrid process of ceramic membrane microfiltration - ozonation has proved to be very effective in mitigation of membrane fouling. However, the quality of permeates could not be improved when using ozonation at higher doses. It seems that an optimum ozone dose may minimize the membrane fouling without deteriorating the permeate quality.
ACKNOWLEDGMENTS

We gratefully acknowledge the financial support of the State Scholarship Foundation (IKY) and the financial support through the co-financed by the European Union and the Greek State programme EPAN –II / ESPA: ‘SYNERGASIA’ Project NanoMemWater (09SYN-42-440).

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