Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.11408

64 (2017) 302–306
February

Surface water treatment in hybrid systems coupling advanced oxidation processes and ultrafiltration using ceramic membrane

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Received 3 April 2016; Accepted 22 July 2016

ABSTRACT

A comparison of the efficiency of treatment of surface water from Miedwie Lake (Poland) in hybrid systems coupling various advanced oxidation processes (TiO_2 photocatalysis, UVC photolysis and UV/H_2O_2) and ultrafiltration (UF) is presented. A ceramic membrane with ZrO_2 separation layer (Inside Céram, 5,000 g mol^{-1}) was used. Application of photocatalysis contributed to the improvement of the permeate flux compared with photolysis by ca. 16%–35%. Similar effect was observed in case of UV/H_2O_2 process with addition of 0.15 gH_2O_2 L^{-1}. Adsorption of organic contaminants on TiO_2 influenced significantly on the treatment efficiency in the photocatalytic membrane reactor (PMR). The highest removal rate of total organic carbon was observed in case of 1 g TiO_2 L^{-1}. Similar efficiency of mineralization was found in UV/H_2O_2–UF process with application of 0.15 gH_2O_2 L^{-1}. The UV/H_2O_2–UF system was found to be a promising alternative for the PMR during treatment of surface water.

Keywords: Photocatalytic membrane reactor; Hydrogen peroxide; Ultrafiltration; Surface water; Ceramic membrane

1. Introduction

Conventional methods of surface water treatment require very complex technological lines [1] and economical investments. Moreover, these technologies are often not enough efficient in removal of persistent organic pollutants, presence of which in natural waters is recently reported by numerous researchers [2]. A promising method of surface water treatment could be the application of hybrid systems coupling advanced oxidation processes (AOPs) and membrane separation. As a result of AOPs treatment, various organic pollutants are decomposed and mineralized due to the action of highly reactive oxidative species, such as $^{\bullet}OH$ radicals. Among numerous AOPs, photocatalysis using TiO_2, ozonation, UV irradiation and H_2O_2 oxidation, or their combinations are of a special interest, when organic contaminants removal from water is considered. Hybrid systems coupling photocatalysis and membrane separation are known as photocatalytic membrane reactors (PMRs). The main role of a membrane in such reactors is to retain photocatalyst particles in the reaction medium, which creates a possibility of its reuse [3]. Moreover, a membrane might act as a barrier for molecules present in the solution (initial compounds and products or by-products of their decomposition), what is also applied in other hybrid AOPs–membrane systems, not only in PMRs. A significant advantage of coupling of AOPs with membrane separation, beside the improvement of treatment efficiency, is also a mitigation of membrane fouling due to the decomposition of organic contaminants present in the treated water [3].

Most of the PMRs described in the literature are slurry reactors with polymeric microfiltration (MF) or ultrafiltration (UF) membranes. However, polymer membranes used in PMRs can undergo damage by UV light and hydroxyl radicals; therefore, application of ceramic membranes in these systems seems to be more perspective. Ceramic membranes are characterized by an excellent chemical stability at

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Presented at the conference on Membranes and Membrane Processes in Environmental Protection (MEMPEP 2016), Zakopane, Poland, 15–19 June 2016.

high/low pH, tolerance to high temperature and mechanical rigidity. Despite numerous advantages of ceramic membranes, the literature reports on PMRs utilizing these membranes are, however, very scanty [4,5]. A majority of papers are focused on the preparation of ceramic membranes with TiO_2 as a photocatalyst immobilized on the membrane surface and evaluation of their performance during model pollutants decomposition [4,5]. Except for our earlier works [6,7], the reports on membrane fouling by TiO_2 particles in the slurry PMRs equipped with ceramic membranes are hardly to be found. Moreover, it is difficult to find any information on the treatment of surface water in these systems. The literature data on the hybrid systems coupling H_2O_2/UV with membrane separation is also very limited [8–10]. The UV/H_2O_2 oxidation was applied as a method of mitigation of MF ceramic membrane fouling caused by soluble algal organic matter [10]. Moreover, a hybrid system coupling MF and TiO_2 photocatalysis enhanced with H_2O_2 action was proposed as a method of treatment of waste seawater from shrimp farms [11].

In the present work, the influence of the selected AOP type on the efficiency of surface water treatment in a hybrid AOP–UF system was investigated. The photocatalysis using TiO_2, UVC photolysis and UV/H_2O_2 oxidation were applied as AOPs. The effectiveness of both organic contaminants removal and membrane performance, in terms of permeate flux and membrane fouling in three examined hybrid systems, were compared and discussed.

Table 1
Typical parameters of Miedwie Lake water

Parameter	Unit	Value
TOC	mg L^{-1}	8.1–8.7
Conductivity	µS cm^{-1}	555–573
TDS	ppm	375–392
Absorbance UV_{254}	1 cm^{-1}	0.1568–0.1707
Turbidity	NTU	0.543–1.661
pH	–	6.97–7.93

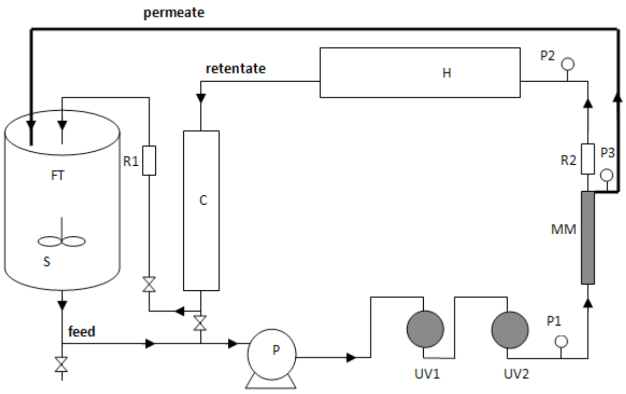

Fig. 1. Schematic diagram of the laboratory-scale photocatalytic membrane reactor used in experiments.
Note: P1, P2, P3 – manometers, R1, R2 – rotameters, FT – feed tank, S – stirrer, P – pump, UV1, UV2 – photoreactors with UV-C lamps, MM – membrane module, H – heater, and C – cooler.

2. Experimental

An asymmetric, single-channel, ceramic membrane with ZrO_2 separation layer (Inside Céram, TAMI Industries, France) was applied. The molecular weight cut-off (MWCO) of the membrane was 5,000 g mol^{-1} (according to manufacturer). The membrane length was 0.25 m, and the external and internal diameters amounted to 10 and 6 mm, respectively. The effective membrane area was 0.0047 m^2. Before experiments, the membrane was cleaned with NaOH and H_3PO_4 solutions, according to the procedure recommended by the manufacturer. The pure water flux (PWF) measured at the transmembrane pressure (TMP) of 0.1 MPa was 47 $dm^3\ m^{-2}\ h^{-1}$.

Commercially available TiO_2 Aeroxide® P25 (Evonik, Germany) was used as a photocatalyst. TiO_2 concentration amounted to 0.5, 1.0, 1.5 or 2.0 g L^{-1}.

Hydrogen peroxide (Avantor Performance Materials Poland S.A., Poland) concentration in the UV/H_2O_2 experiments was 0.03 or 0.15 g L^{-1}.

Natural surface water from Miedwie Lake was used as a feed. Miedwie Lake is a reservoir of drinking water for Szczecin, Poland. Typical parameters of the lake water are presented in Table 1.

The experiments were carried out in a laboratory-scale installation presented in Fig. 1. The system was equipped with two flow-through photoreactors containing UVC lamps (Philips TUV 16W, UVC light intensity: 1.54 W m^{-2}). Reactors were installed between the feed tank and the membrane module. At the beginning of each experiment, the feed (7 dm^3) was introduced to the feed tank. Subsequently, a defined concentration of the photocatalyst (series 1–4) or an appropriate amount of H_2O_2 (series 6 and 7) was added to the feed tank. For comparison purpose, the photolysis (i.e., a process realized at the presence of UV, but at the absence of TiO_2 or H_2O_2) was also performed (series 5). In series 1–4, before the UV lamps were switched on, a 30-min adsorption in the dark was conducted. During adsorption, the treated solution was circulated in the installation. No filtration was realized during this stage (the permeate valve was closed). After that, UV lamps were switched on, and the pump was started. The TMP was set at 0.1 MPa, and the feed cross-flow velocity (CFV) was 6 m s^{-1}. The temperature of the feed was maintained at 20°C ± 1°C. The experiments were conducted for 5 h.

Total organic carbon (TOC) and dissolved organic carbon (DOC) concentrations were measured using "multi N/C 3100" analyzer (Analytik Jena, Germany). Conductivity and total dissolved solids (TDS) were measured with the application of Ultrameter™ 6P (MYRON L COMPANY, USA). UV_{254} absorbance of feed and permeates was determined with the application of Jasco V-530 UV/VIS spectrophotometer (Japan). A thickness of the sample cell was 1 cm. Turbidity was measured using HACH 2100AN turbidimeter. pH of all solutions was also monitored.

3. Results and discussion

3.1. Treatment of Miedwie Lake water in the PMR

In the first step of the investigations, the influence of TiO_2 concentration on the permeate flux during treatment of the surface water in the PMR was determined. The results are summarized in Fig. 2.

When a suspension of TiO_2 in distilled water was applied as a feed, no membrane fouling occurred in the system, and the permeate flux was the same as PWF (data not shown). In series 1–4 (Fig. 2), the flux was, however, lower than the PWF, indicating that contaminants present in the surface water contributed to the membrane fouling. The decrease of the flux compared with PWF in the discussed experiments was ca. 15%–20%, regardless of the photocatalyst concentration. This data showed that at the investigated range of the TiO_2 doses (i.e., 0.5–2.0 g L^{-1}), the photocatalyst concentration had no significant influence on the permeate flux.

The observed results can be explained in terms of organic contaminants removal at the presence of the photocatalyst. Fig. 3 shows changes of UV_{254} absorbance of the feed during 5 h of PMR operation at various TiO_2 doses.

Changes of the discussed parameter proceeded in a similar way, indicating a comparable rate of decomposition of aromatic or unsaturated organic contaminants present in the feed, for all examined TiO_2 concentrations. These data correspond to changes of the permeate flux presented in Fig. 2, which showed no significant effect of TiO_2 amount on the flux.

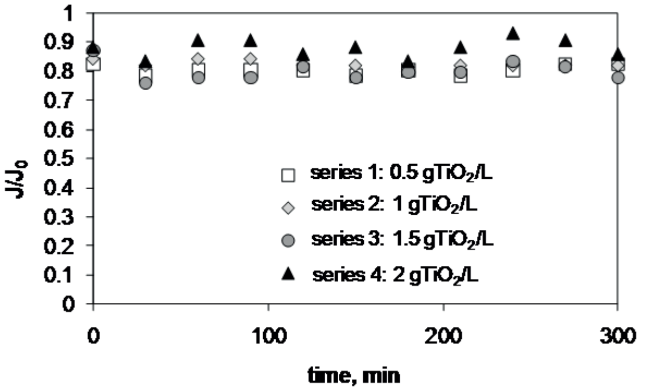

Fig. 2. The influence of photocatalyst concentration on the permeate flux during treatment of Miedwie Lake water in the PMR. Series 1–4 (t = 0 min – after 30 min of adsorption in the dark).

To evaluate the type of organic contaminants in Miedwie Lake water, the specific ultraviolet absorption (SUVA) was determined on a basis of the Eq. (1):

$$\text{SUVA} = \text{Abs UV}_{254}/\text{DOC [L/mg.m]} \tag{1}$$

where Abs UV_{254} is the absorption at λ = 254 nm [m^{-1}], and DOC is the DOC concentration (mg L^{-1}). The SUVA value for Miedwie Lake water was 2 L/mg.m, what indicates that the organic contaminants present in this water are mainly of non-humic origin.

In Fig. 4, a comparison of the efficiency of TOC removal due to adsorption on TiO_2 particles ($R_{ads} = [(F_0 - F_{ads})/F_0] \times 100\%$), the overall efficiency of TOC removal in the feed ($R_{feed} = [(F_0 - F_5)/F_0] \times 100\%$) and the total efficiency of TOC removal, regarding the composition of feed and permeate ($R_{total} = [(F_0 - P_5)/F_0] \times 100\%$) is shown. The F_0 value corresponds to the initial TOC concentration in the feed, F_5 – TOC concentration in the feed after 5 h of the experiment and P_5 – TOC concentration in permeate after 5 h of the process.

It can be observed that adsorption of organic pollutants on TiO_2 particles significantly contributed to the efficiency of TOC removal in the feed. An increase of TiO_2 concentration from 0.5 to 1.5 g L^{-1} resulted in an increase of TOC removal from ca. 18% to ca. 32%. However, further increase of photocatalyst amount did not contribute to a higher efficiency of adsorptive organic substances removal. The highest contribution of the photocatalytic treatment to TOC removal in the feed was observed in case of two lowest photocatalyst doses. At 0.5 g L^{-1}, TOC concentration decreased by additional 27% and, in case of 1.0 g L^{-1}, by ca. 29%, giving overall TOC removal rates in the feed equal to ca. 45% and 57%, respectively. An increase of photocatalyst concentration above 1 g L^{-1} led to a decrease of the R_{feed} value to ca. 48%, both in case of 1.5 and 2 g TiO_2 L^{-1}. This phenomenon can be attributed to the so-called screening effect of the photocatalyst particles. The total efficiency of TOC removal in

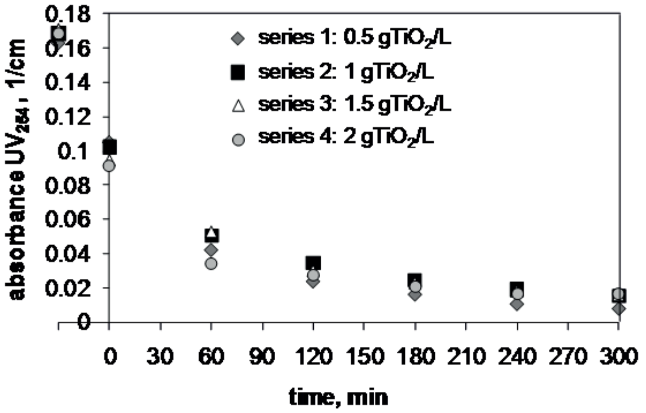

Fig. 3. The influence of photocatalyst concentration on the change of feed UV_{254} absorbance during treatment of Miedwie Lake water in the PMR. Series 1–4 (t = 0 min – after 30 min of adsorption in the dark).

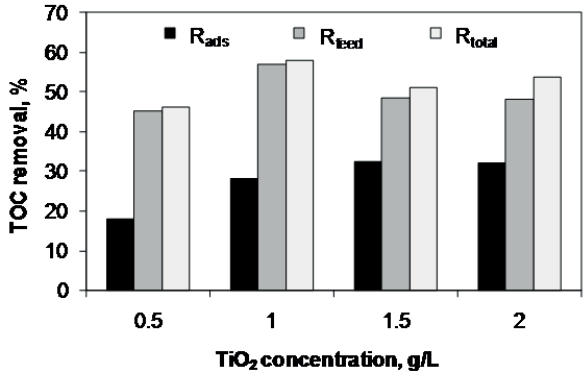

Fig. 4. The effectiveness of TOC removal via (a) adsorption (R_{ads}), (b) adsorption and mineralization (R_{feed}) and (c) adsorption, mineralization and membrane separation (R_{total}) during treatment of Miedwie Lake water in the PMR. Series 1–4.

the PMR (R_{total}) ranged from ca. 46% to ca. 58% and was the highest at 1 g TiO_2 L^{-1}. Hence, the TiO_2 dose of 1 g L^{-1} was found to be the most beneficial one among all the examined photocatalyst concentrations.

3.2. *Treatment of Miedwie Lake water during photolysis and UV/H_2O_2 processes coupled with UF.*

In the second stage of investigations, results obtained in the PMR were compared with the data collected during treatment of Miedwie Lake water in the hybrid photolysis–UF system (series 5) and the hybrid UV/H_2O_2–UF process (series 6 and 7). The concentration of H_2O_2 in series 6 and 7 amounted to 0.03 or 0.15 g L^{-1}, respectively. Fig. 5 shows the influence of the AOP type on the permeate flux.

It was found that in case of series 5 and 6 the permeate flux was significantly lower than one observed in the PMR (Fig. 2). However, when H_2O_2 concentration of 0.15 g L^{-1} was applied (series 7), the permeate flux reached the value similar to one measured at the presence of TiO_2. Comparing these results with changes of UV_{254} absorbance in feed (Fig. 6), it can be seen that the significant improvement of the permeate flux at 0.15 gH_2O_2 L^{-1} corresponded well with the decomposition of aromatic and unsaturated compounds present in the lake water. On the opposite, the decomposition rate obtained in the system with single photolysis was the lowest. As a result, the concentration of large organic molecules responsible for the membrane fouling was higher than in series 7, what led to more significant flux deterioration.

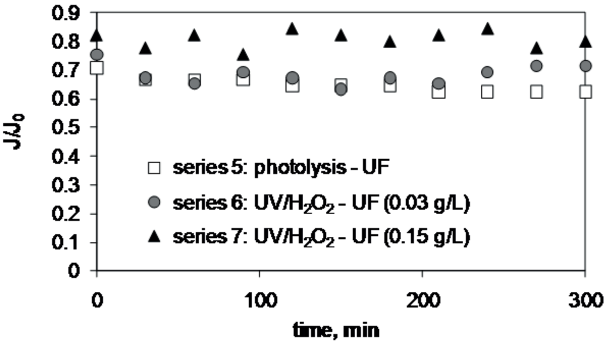

Fig. 5. Changes of the permeate flux during treatment of Miedwie Lake water via photolysis–UF (series 5) and UV/H_2O_2–UF (series 6 and 7) systems.

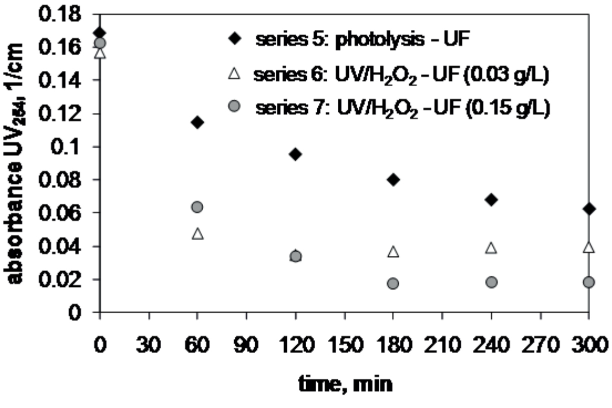

Fig. 6. Changes of UV_{254} absorbance of feed during treatment of Miedwie Lake water via photolysis–UF (series 5) and UV/H_2O_2–UF (series 6 and 7) systems.

The efficiency of mineralization in the system utilizing single photolysis was also lower than in case of processes enhanced with H_2O_2 addition. Within 5 h of the experiments, TOC removal in feed reached ca. 24% in series 5, ca. 50% in series 6 and ca. 55% in series 7. The membrane separation contributed to the improvement of TOC removal only in case of the photolysis–UF system (R_{total} = 32%). In the experiments, which were run with application of H_2O_2, R_{total} values were similar to R_{feed}, indicating more efficient decomposition of organic contaminants into low molecular weight organic compounds in this system than in photolysis–UF.

The obtained results revealed that the hybrid UV/H_2O_2–UF process could be an interesting alternative to the PMR, when treatment of surface water was considered. The former solution seems to be attractive not only with reference to the permeate flux and treatment efficiency but also in terms of retentate disposal, since the concentrate in case of the UV/H_2O_2–UF does not contain photocatalyst particles.

4. Conclusions

A comparison of three hybrid systems coupling AOPs and UF for treatment of surface water from Miedwie Lake was presented. Investigations revealed that the permeate flux in a PMR was independent of the photocatalyst dose at the investigated range of TiO_2 concentrations (i.e., 0.5–2.0 g L^{-1}). It was explained in terms of similar efficiency of removal of organic compounds present in the treated water. Nonetheless, the flux during PMR operation was lower than one measured for the photocatalyst suspension in pure water, what indicated that contaminants present in the lake water were responsible for the membrane fouling. It was confirmed by the experiment, in which the surface water was treated using UV photolysis–UF system. At the absence of TiO_2, both decomposition and mineralization of organic contaminants were less efficient comparing to ones in PMR, what resulted in a significant decrease of permeate flux. Analysis of removal of organic contaminants in the PMR revealed that adsorption on photocatalyst particles significantly contributed to the overall treatment efficiency. Based on the effectiveness of TOC removal, TiO_2 dose of 1 g L^{-1} was proposed as the most beneficial one. The hybrid UV/H_2O_2–UF system was found to be an interesting alternative for the PMR during treatment of the lake water. At H_2O_2 concentration of 0.15 g L^{-1}, both permeate flux and TOC removal were similar to ones observed in case of water treatment in PMR.

Acknowledgment

The authors would like to thank Zakład Wodociągów i Kanalizacji Sp. z o.o. in Szczecin, Zakład Produkcji Wody Miedwie for providing water samples for experiments.

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