

Treatment of surface water contaminated with ketoprofen: submerged photocatalytic membrane reactor vs. membrane distillation unit

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ABSTRACT

The investigations on a long-term continuous operation of two membrane systems: direct contact membrane distillation (DCMD) unit and a submerged photocatalytic membrane reactor utilizing direct contact membrane distillation (SPMR-DCMD) are presented. The efficiency of treatment of simulated surface water contaminated with ketoprofen as well as the polypropylene membrane performance were analyzed. Moreover, the toxicity of the retentate and distillate was evaluated. No significant membrane scaling was observed, however, a noticeable humic acid deposit in the case of DCMD, and TiO_2 deposit in the case of SPMR-DCMD was found. Despite that the permeate flux was stable in both systems during 200 h of operation. Moreover, for the SPMR-DCMD the flux enhancement compared to pure water flux was observed due to the presence of TiO_2 . The concentration of total organic carbon in SPMR-DCMD distillate was lower compared to DCMD, while conductivity and total inorganic carbon content were visibly higher indicating passage of CO_2 originating from the photodegraded contaminants through the membrane. In DCMD a continuous concentration of the treated water resulted in an increased toxicity of retentate, while in the SPMR-DCMD the retentate was non-toxic. Moreover, a protective effect of humic acids against the toxic effects of ketoprofen towards *Aliivibrio fischeri* was proved.

Keywords: Submerged photocatalytic membrane reactor; Membrane distillation; Ketoprofen; Humic acid; Toxicity

1. Introduction

Pharmaceuticals and micropollutants in the environment are attracting more and more attention due their persistent biological activity, frequent release, and potential health concerns to humans and aquatic life [1]. There are currently about 3,000 distinct pharmaceutically active compounds in use worldwide, and the number is reportedly growing due to population expansion and aging [2]. These contaminants are only partially removed by conventional wastewater treatment processes [3], which contributes to their increasing presence in lakes, rivers, groundwater, sea

water, or even in drinking water in many places around the world [4]. Non-steroidal anti-inflammatory drugs (NSAIDs) are among the most commonly reported pharmaceutical contaminants [4,5]. An example of NSAIDs is ketoprofen – a drug typically applied for treatment of rheumatic diseases, inflammatory and musculoskeletal conditions, or traumatic and postoperative pain, as well as other pain syndromes [6,7]. Ketoprofen was one of the most commonly detected drugs in water systems in the years 2019–2021 [5]. It poses a high risk of gastrointestinal complications and potential cytotoxicity and genotoxicity at high exposure concentrations [8,9]. Its toxicity to vultures was also proved [10,11].

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The concentration of ketoprofen in environmental samples is typically in ng/L– μ g/L level [4]. Its removal efficiency in a municipal wastewater treatment plant (WWTP) utilizing primary physico-chemical treatment, a secondary biological treatment (nitrification and denitrification), and disinfection using UV radiation was found in the range of 0%–89% with an average value of 45% [12]. Other sources report removal of ketoprofen in WWTPs in the range of 38% to nearly 100% [4].

Taking into account that the conventional water and wastewater treatment methods are not effective enough in removal of pharmaceutical contaminants, it is necessary to develop new effective technologies. A promising solution is the application of membrane processes, amongst which membrane distillation (MD) has attracted special attention. MD has demonstrated significant promise in treating surface water containing complex contaminants, including pharmaceuticals [13–15], personal care products [16,17], phenolic compounds [18,19], pesticides [20,21] or heavy metals [22–24]. In recent years, MD is considered as perspective method of producing small quantities of drinking water for households (decentralized water supply systems) [25]. This technique exhibits significant advantages such as possibility of treatment of high saline solutions, less membrane fouling than in pressure driven processes, as well as high water recovery and production of high purity water. MD does not need high heat to generate quality water, and it also has the potential to become a sustainable water treatment method when combined with solar energy, thermal collectors, or industrial waste heat sources [26,27].

Direct contact membrane distillation (DCMD) is the most established and used MD arrangement. The mass transfer in DCMD occurs when two liquid phases (hot feed and cold distillate) are in direct contact with both sides of a hydrophobic porous membrane [28]. Theoretical rejection of non-volatile contaminants in MD is 100%, thus, the product (distillate) is characterized by a high quality. However, due to the high rejection of non-volatile species and high-water recovery (even up to 98% [29]) the MD retentate contains a concentrated load of the rejected contaminants. Therefore, its further post-treatment is required. An alternative to that can be a hybridization of MD with photocatalysis. The systems coupling both technologies are called photocatalytic membrane reactors (PMRs). The use of PMR ensures the simultaneous recovery and reuse of the photocatalyst and the separation of various contaminants (including photo-degradation intermediates) from the treated solution.

Recently, we have proposed a novel configuration of a PMR utilizing DCMD, based on a submerged membrane module [30]. This submerged photocatalytic membrane reactor (SPMR) was applied for removal of ketoprofen from various aqueous matrices. To further study this process, the preliminary investigations on a long-term performance of the submerged photocatalytic membrane reactor utilizing direct contact membrane distillation (SPMR-DCMD) applied to treat simulated surface water contaminated with ketoprofen were realized [13]. It was found that during 200 h of process operation a stable permeate flux was maintained, which is a significant advantage of the proposed system over the PMRs utilizing pressure driven membrane techniques. Moreover, a high ketoprofen and total organic carbon (TOC)

degradation rate was obtained (98% and 69%, respectively). Furthermore, no ketoprofen was detected in distillate, its conductivity was lower than 3 μ S/cm, while TOC concentration did not exceed 0.7 mg/L.

The aim of present study was to compare a long-term performance of the SPMR-DCMD with the operation of a single DCMD unit, considering the composition and toxicity of retentate and distillate as well as stability of permeate flux. The investigations included the analysis of changes of concentration of ketoprofen, TOC, total inorganic carbon (TIC), as well as conductivity in retentate and distillate. Moreover, the toxicity of the process solutions using the bioluminescence inhibition bioassay was examined to evaluate the effect of both treatment approaches on the environment. Furthermore, the permeate flux was monitored and the fouling and scaling phenomena were analyzed using scanning electron microscopy (SEM), X-ray diffraction (XRD) and attenuated total reflectance-Fourier-transform infrared (ATR-FTIR) spectroscopy.

2. Experimental set-up

In the experiments a simulated surface water (SuW) contaminated with ketoprofen was used as a feed. To prepare the feed, various salts (12.2 mg $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 8.7 mg CaCl_2 , 18.7 mg CaCO_3 , 3.5 mg $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 16.3 mg Na_2SO_4 , 1.7 mg NaHCO_3 and 2.5 mg KHCO_3) were dissolved in deionized water, and subsequently humic acids (HA, 8 mg/L of TOC) and ketoprofen (10 mg/L) were added. The concentration of ketoprofen was higher than reported in the environmental samples to better track the kinetics of degradation. The inorganic salts were provided by Avantor Performance Materials Poland S.A., Poland, while ketoprofen and humic acids were supplied by Sigma-Aldrich, USA. Moreover, AEROXIDE® TiO_2 P25 (Evonik, Germany) at a concentration of 1 g/L was used as a photocatalyst. The TiO_2 loading was selected based on the previous study [13].

The investigations were conducted in two membrane installations, that is, DCMD and SPMR-DCMD, presented in Fig. 1.

In each system two membrane modules containing capillary hydrophobic polypropylene (PP) membranes (Accurel PP S6/2, Membrana GmbH, Wuppertal, Germany) were operated simultaneously. The nominal pore size of the membranes was 0.2 μ m (according to the manufacturer), and the outer/inner diameter was $d_{\text{out}}/d_{\text{in}} = 2.6/1.8$ mm. The effective outer membrane area of each module was 0.008 m².

The experiments were conducted for 200 h in a continuous mode, that is, fresh feed was continuously supplied to the system at the amount corresponding to the amount of collected permeate. The initial volume of feed was 5 L, while the initial volume of distillate (deionized water) was 0.7 L. The temperature of feed in the feed tank was 60°C, and the temperature of distillate was 20°C. In the SPMR-DCMD system the feed circulated between a feed tank, a photoreactor and a heater, whereas in the DCMD unit the feed circulated between a feed tank and a heater. The photoreactor was built of 7 quartz tubes (30 cm long and 1.6 cm in diameter) connected to each other with U-shaped glass tubes and irradiated with UV-A lamps (Philips CLEO iSOLde, $\lambda_{\text{max}} = 355$ nm, UV radiation intensity of

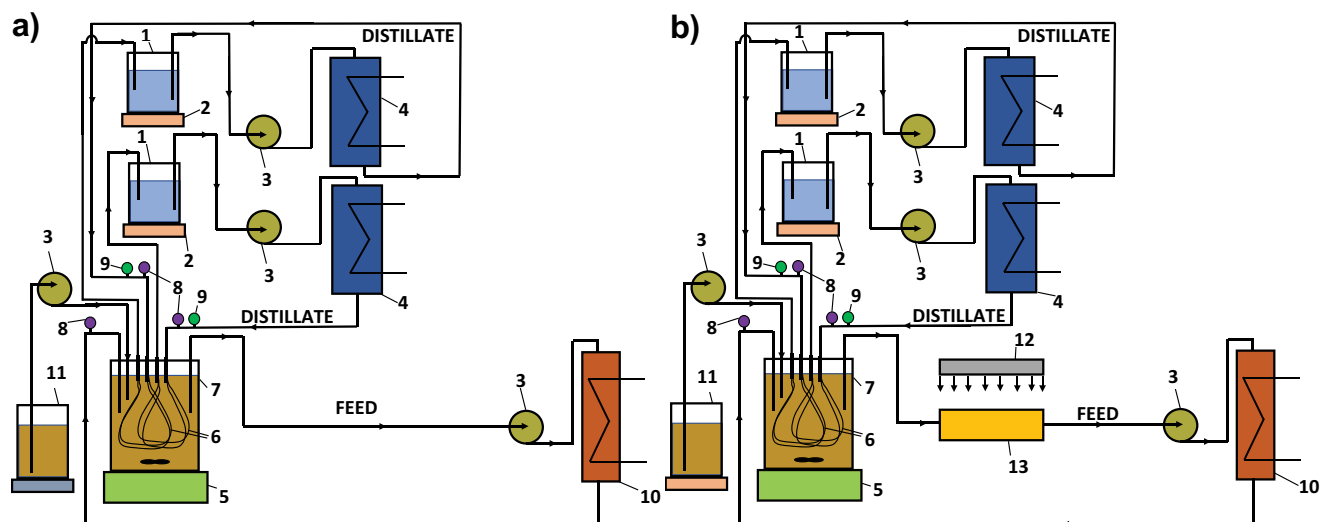


Fig. 1. Scheme of the (a) DCMD and b) SPMR-DCMD installation set-ups (1-distillate tank, 2-balance, 3-peristaltic pump, 4-cooler, 5-magnetic stirrer, 6-membrane, 7-feed tank, 8-thermometer, 9-manometer, 10-heater, 11-feed supply tank, 12-UV-A lamp, 13-labyrinth flow photoreactor).

54 W/m²). Before switching on the UV-A source, adsorption was carried out in the dark with circulation of the feed in the system for 1 h. Each experiment was repeated twice to confirm the reproducibility of the results.

After a defined time of the DCMD and SPMR-DCMD systems operation, samples of feed, retentate and distillate were collected and analyzed. The concentration of ketoprofen was determined using the high-performance liquid chromatograph (HPLC, Shimadzu, Japan) equipped with a photo-diode array detector SPD-M40. LiChroCART® 250–4 Purospher® STAR RP-18 endcapped (5 µm) column (Merck Millipore, USA) was applied. A mobile phase consisted of 60% of 20 mmol/L NaH₂PO₄ (pH = 2.6 adjusted with H₃PO₄) and 40% of acetonitrile. The limit of detection (LOD) was 8 µg/L and the limit of quantification (LOQ) was 25 µg/L. The TOC and TIC content was determined using multi-N/C 3100 analyzer (Analytik Jena, Germany). Conductivity was measured using Ultrameter™ 6P (MYRON L COMPANY, USA).

Toxicity of feed, retentate and distillate, as well as model 10 mg/L solution of ketoprofen in deionized water was evaluated using Microtox® LX system (Modern Water, USA) with application of marine bacteria *Aliivibrio fischeri* as model microorganisms. The measurement is based on the evaluation of a decrease in bacterial bioluminescence after exposure of *A. fischeri* to toxic substances [30]. During the investigations the 81.9% screening test procedure for low toxicity samples was applied. The luminescence of the samples was recorded after 5 and 15 min of incubation. The results are presented as a change (in %) in luminescence intensity of the analyzed sample compared to the luminescence measured for the control sample.

Samples of membranes collected from the DCMD and SPMR-DCMD systems were examined using Hitachi SU8020 ultra-high resolution field emission scanning electron microscope (UHR FE-SEM) equipped with energy-dispersive X-ray spectroscopy system (EDS NSS 312, Thermo Scientific). Before analysis the samples were sputter coated with

chromium using Q150T ES coater (Quorum Technologies Ltd., Lewes, UK). Moreover, the membranes were analyzed using X-ray diffraction (PANalytical Empyrean diffractometer, CuKα radiation $\lambda = 1.54056 \text{ \AA}$) and ATR-FTIR spectroscopy (Nicolet 380 FTIR spectrophotometer with Smart Orbit diamond ATR accessory (Thermo Electron Corp., USA)).

3. Results and discussion

3.1. Changes of retentate and distillate composition in DCMD and SPMR-DCMD

Membrane distillation is a process based on evaporation of feed volatile components through a porous hydrophobic membrane. As a result, the concentration of non-volatile species on the feed side of the membrane continuously increases. During treatment of aqueous solutions, mainly water vapor and dissolved gases are transported. Taking this into account, in the case of SuW the rejection of inorganic salts, HA and ketoprofen, all being non-volatile compounds, can be expected. Fig. 2 presents a comparison of retentate composition during single DCMD and hybrid SPMR-DCMD operation.

It can be seen that in the case of DCMD the concentration of ketoprofen and TOC (Fig. 2a) was continuously increasing in time and after 200 h of operation reached the value of ~63 and 84.5 mg/L, respectively. This means that the concentration of ketoprofen increased to a higher extent (~5.7 times) than the concentration of TOC (~5 times). Such results can be explained by adsorption of HA on the membrane, which after the experiment was found to be covered by a dark brown deposit (Fig. 3).

In the case of the SPMR-DCMD the concentration of ketoprofen and TOC was continuously decreasing in time up to 24 h of operation (Fig. 2a). After that the process got stabilized and the values of both parameters remained almost unchanged (reaching ~0.3 and ~4 mg/L, respectively).

In this case the deposit of HA was not visible on the membrane, instead, a thin white layer of TiO_2 photocatalyst was observed (Fig. 3).

No significant difference between the course of changes of conductivity in both analyzed systems was found (Fig. 2b). In single DCMD the feed conductivity increased ~5.3 times, while in the hybrid SPMR-DCMD system: ~5.1 times. A noticeable difference was, however, observed for TIC concentration. After 200 h of operation it increased ~5.4 times in the case of DCMD and ~6.9 times in the case of SPMR-DCMD. In other words, the TIC concentration was higher in the hybrid system, which can be attributed to the formation of CO_2 upon mineralization of ketoprofen and HA due to the photocatalytic treatment. The changes of feed composition in time affected the composition of distillate (Fig. 4).

In both systems the presence of TOC in distillate was confirmed (Fig. 4a). However, its concentration was higher in the case of DCMD alone compared to the hybrid system, which was an unexpected result. In SPMR-DCMD various intermediate products of photodegradation of HA and ketoprofen are formed. Some of the products are volatile, thus they can pass through the membrane, contributing to an increase in TOC content in distillate. However, in the

current study the amount of TOC in distillate originating from these degradation products was lower than the amount of TOC passing the membrane in the case of single DCMD. In both systems the most significant increase in TOC concentration was observed during the initial 24 h. Subsequently, in the case of SPMR-DCMD the TOC content was almost constant, while for DCMD a slight increase in its value was observed. That corresponds to changes of

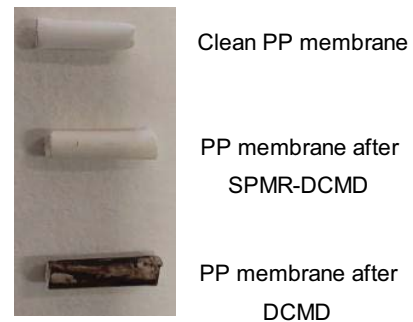


Fig. 3. Photographs of clean PP membrane, PP membrane after 200 h of operation in SPMR-DCMD and PP membrane after 200 h of operation in single DCMD unit.

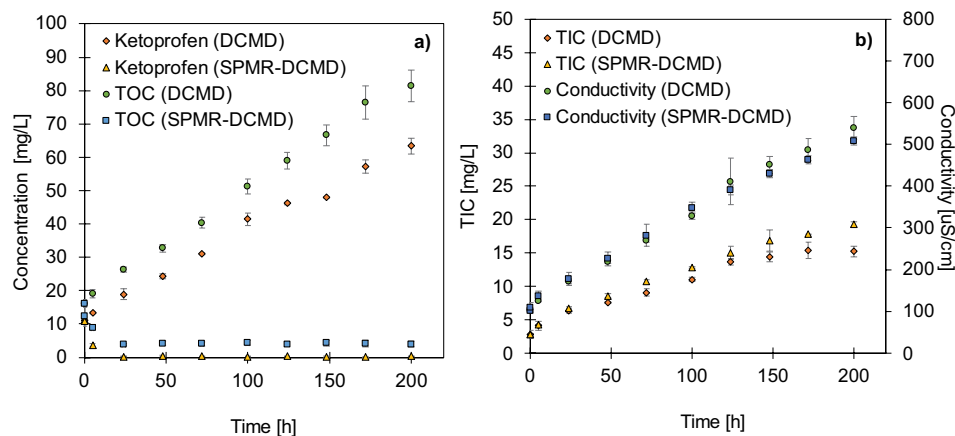


Fig. 2. Changes of retentate composition during single DCMD (a) and hybrid SPMR-DCMD (b) processes.

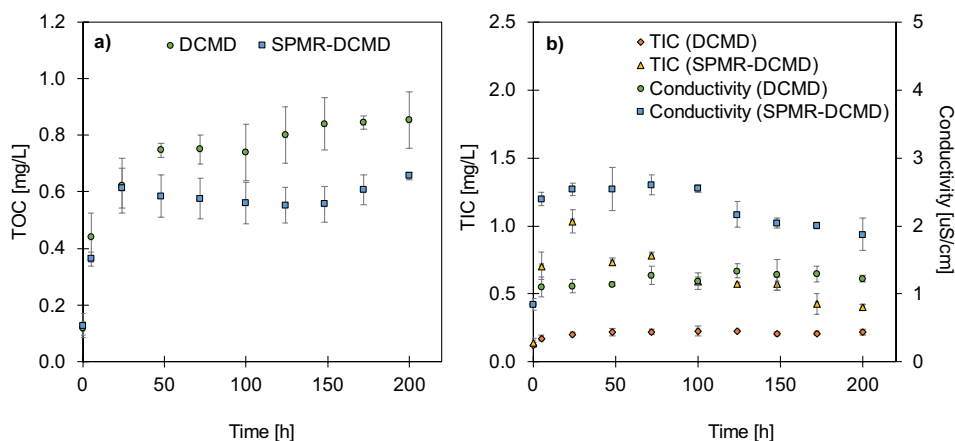


Fig. 4. Changes of distillate composition during single DCMD (a) and hybrid SPMR-DCMD (b) processes.

TOC concentration in retentate (Fig. 2a). The presence of an increased TOC content in DCMD distillate was previously attributed to diffusion of HA through the membrane due to hydrophobic interactions between the HA molecules and the membrane [31]. Simultaneously the transport based on evaporation was excluded [31]. The diffusion can be enhanced by a thermal disaggregation of HA to low molecular weight HA (LMW-HA), which can penetrate the membrane more easily than the high molecular weight species [32,33].

Fig. 4b presents changes of conductivity and TIC concentration in distillate. The TIC content was lower when DCMD was realized alone compared to the SPMR-DCMD. This corresponds well with the changes of TIC concentration in retentate (Fig. 2b). The main final products of mineralization of organic contaminants are water and CO_2 , thus during SPMR-DCMD, except from water vapor, also CO_2 gas molecules, being volatile species, are transported through the membrane. As a result, an increase in TIC concentration and conductivity of distillate is observed. Changes in conductivity followed a similar pattern to changes in TIC, indicating that the main specie responsible for the increase in conductivity was CO_2 .

3.2. Toxicity of retentate and distillate in DCMD and SPMR-DCMD

Analysis of TOC in retentate and distillate gives a general idea of the content of organic species in the treated streams. However, to evaluate whether the product is safe for the environment, the analysis of toxicity is also an important issue. Although HA are generally considered as non-toxic, the role of humic substances in the aquatic environment is very complex and not fully understood [34,35]. During photodegradation of organic contaminants various intermediate products are formed and some of them can be toxic. It was found [36] that decomposition of HA via ozonation leads to formation of toxic intermediates such as phenolic or long-chain hydrocarbon compounds. Moreover, toxicity of ketoprofen and its degradation products towards various species was previously confirmed [37–39]. For example, it was observed that ketoprofen (1–100 $\mu\text{g/L}$) revealed a more significant oxidative stress response than the by-products of its photolysis when zebrafish (*Danio rerio*) was used as a model organism [37]. Similarly, a decrease in toxicity in the case of human umbilical vein endothelial cell (HUVEC) was observed when ketoprofen (~10 mg/L) was degraded using ultrasonic treatment [39]. Moreover, it must be taken into consideration that toxic effects depend on the concentration of the contaminants, which cannot be neglected especially in the case of DCMD alone. Taking the above into account, in the present study the acute toxicity test using bioluminescent bacteria *A. fischeri* was used to determine the effect of the applied treatment on toxicity of retentate and distillate. The toxicity was measured after 5 and 15 min of incubation of the bacteria in the samples. The results are summarized in Fig. 5.

Regardless of the system the product (distillate) was non-toxic. Toxicity of retentate was visibly higher compared to that of distillate, which indicated an efficient rejection of substances possessing a toxic effect on *A. fischeri* in

the MD process. Moreover, it can be observed that toxicity of retentate decreased significantly in the case of SPMR-DCMD just after 24 h of treatment and remained stable till end of the process. This can be explained by the degradation of organic contaminants (ketoprofen and HA) in the system (Fig. 2). On the opposite, an increase in toxicity in time was found for DCMD alone. The reason is a continuous concentration of non-volatile feed components upon evaporation through the membrane during the process (Fig. 2). Taking into account that the conductivity of the feed was rather low, it can be assumed that the presence of inorganic salts had no significant effect on the retentate toxicity in the case of DCMD. Therefore, the other two feed components, that is, HA and ketoprofen should be considered as the factors responsible for the toxic effect. As was already explained, HA are in general considered as non-toxic [35], while a significant toxicity of ketoprofen was previously reported [37–39]. In order to evaluate the influence of ketoprofen on SuW toxicity a series of model solutions of the drug in deionized water was analyzed using the *A. fischeri* bioluminescence bioassay test. Fig. 6 presents a comparison of the influence of ketoprofen concentration on the toxicity of the model solutions and SuW retentate collected during DCMD operation.

It was found that for ketoprofen concentrations below 25 mg/L the toxicity of SuW was higher than that of model solution, while for the concentrations above this value it was significantly lower. This phenomenon can be attributed to the increasing concentration of HA in the DCMD system in time of the process. It was previously reported that HA can play a protective role against the lethal effects of gemfibrozil towards zebrafish due to complexation of the pharmaceutical with humic substances, leading to a reduced bioavailability and bioconcentration [40]. Alleviation of toxicity of roxithromycin and gatifloxacin to the cyanobacterium *Synechocystis* sp. [41], as well as carbamazepine towards diatom *Navicula* sp. [42] in the presence of HA was also reported. Furthermore, the Microtox® analysis applied to evaluation of the influence of HA on toxicity of chlorpyrifos revealed a reduction of toxicity due to pesticide-HA interactions [43]. The obtained results (Fig. 6) additionally prove the positive effect of HA on mitigation of toxicity of ketoprofen. Nevertheless, further research is needed to explain these results in more details.

3.3. Permeate flux in DCMD and SPMR-DCMD

One of the advantages of DCMD over pressure-driven membrane processes is its low propensity to membrane fouling by organic contaminants. This results from the mechanism of mass transfer, which in the case of DCMD is based on vapor pressure difference on both sides of a membrane and does not require application of a transmembrane pressure as a driving force. Considering the composition of SuW, the presence of HA as a membrane foulant cannot be neglected. The literature reports on HA fouling during DCMD are not consistent. Srisurichan et al. [44] observed negligible changes in the permeate flux even when HA concentration in distilled water was as high as 100 mg/L, while in the presence of CaCl_2 at a concentration of 2.265 mmol/L or higher a significant decrease in the flux took place. That was attributed

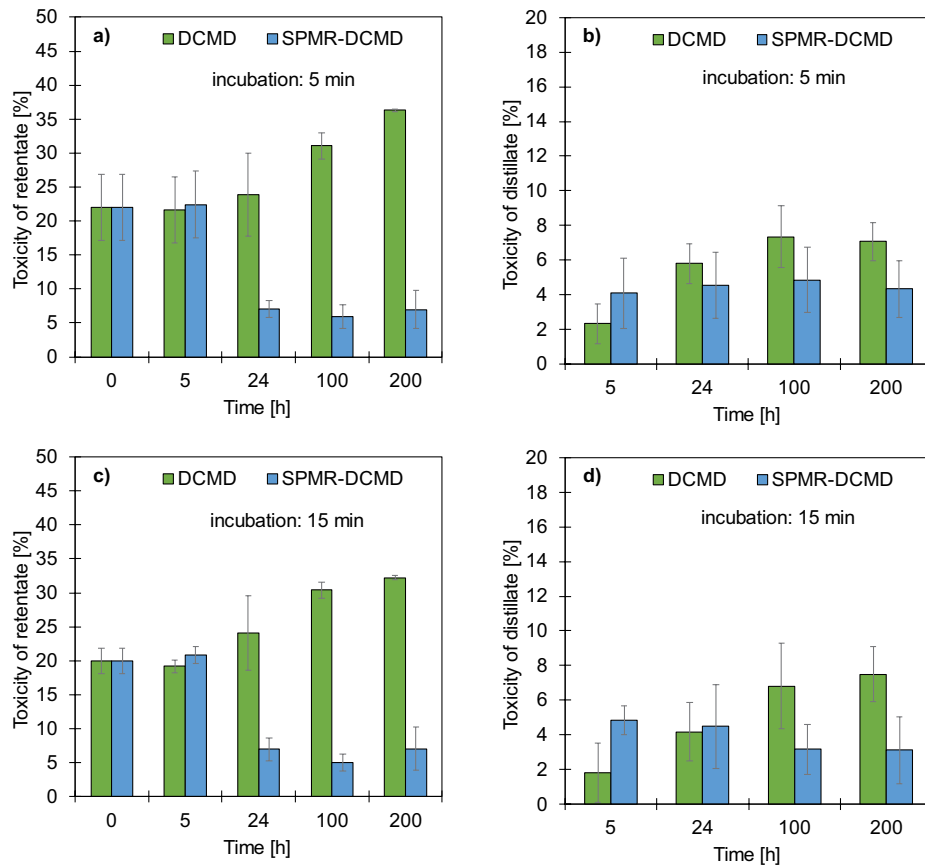


Fig. 5. Comparison of toxicity of retentate and distillate during treatment of SuW in SPMR-DCMD and DCMD systems after 5 min (a,b) and 15 min of incubation (c,d) of bioluminescent bacteria *Aliivibrio fischeri* in samples.

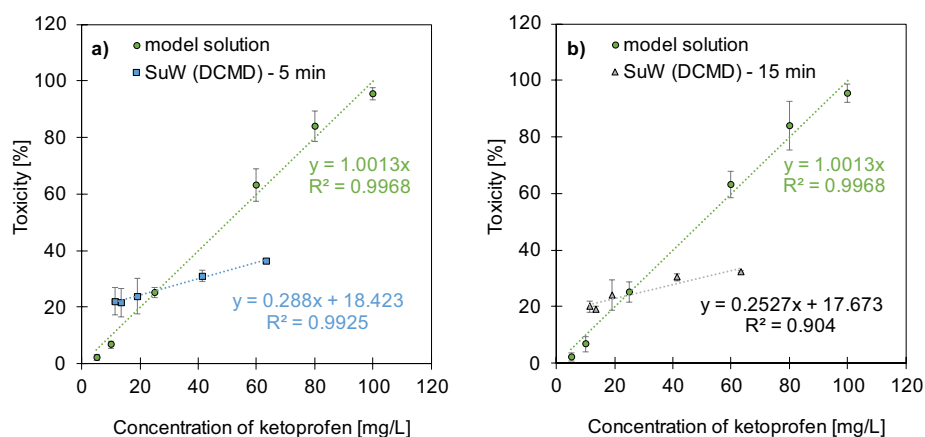


Fig. 6. Influence of solution composition on toxicity of ketoprofen towards *Aliivibrio fischeri*. Model solution corresponds to a solution of ketoprofen in deionized water. Various concentrations of ketoprofen in SuW represent feed and retentate samples collected after different time (0–200 h) of SPMR-DCMD operation.

to coagulation of HA under so high content of Ca^{2+} ions, which act as binding agents for carboxyl groups [44]. No noticeable fouling during concentration of 10 and 50 mg/L HA solutions up to volume concentration factor $\text{VCF} = 4$ was found by Hou et al. [45]. On the opposite, Naidu et al. [32] reported the deterioration of the permeate flux when $\text{VCF} > 2$. The observed fouling was attributed to a thermal

disaggregation of HA to LMW-HA, which were the only species forming the fouling layer on the membrane. It was also concluded that these species penetrated through the membrane, which could result in membrane wetting [32].

In the present study no permeate flux decline was observed during 200 h of operation of DCMD unit (Fig. 7), despite a deposition of HA on the membrane (Fig. 3). The

flux measured during SPMR-DCMD was noticeably higher compared to that in DCMD alone. That can be attributed to the effect of TiO_2 layer deposited on the membrane, as was explained previously [30]. The higher thermal conductivity of the TiO_2 deposit compared to the PP membrane itself results in an easier heat transfer via conduction, leading to improved energy efficiency of the process.

SEM analysis of the membranes collected from both installations revealed different morphology of the deposits formed on their surface and within pores (Fig. 8). The membrane applied in DCMD was uniformly covered with a thin

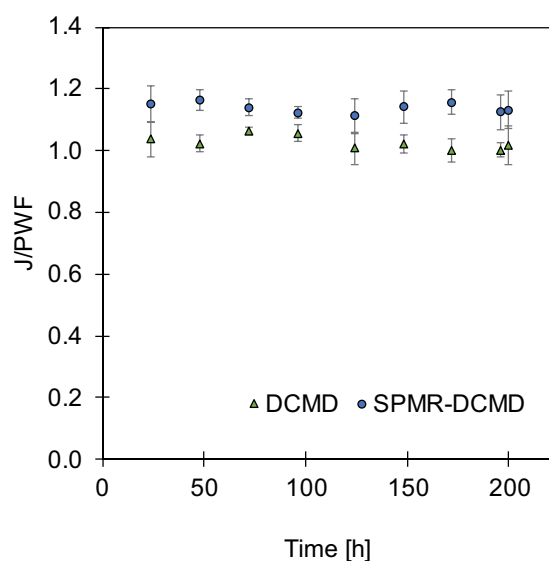


Fig. 7. Changes of permeate flux in time during treatment of SuW in DCMD and SPMR-DCMD systems.

layer of HA, while in the case of the membrane used in the SPMR-DCMD the presence of TiO_2 aggregates was found. It is worth noting that no significant membrane scaling due to precipitation of inorganic salts from feed was observed, regardless of the system. However, a more detailed SEM analysis revealed a presence of some single crystals or clusters of them scattered non-uniformly on the membrane surface (Figs. 9 and 10). The dimensions of the crystals ranged from less than a micrometer to several micrometers. Nonetheless, they were very few in number and very difficult to find, especially in the case of the membrane collected from the SPMR-DCMD. The above indicates that salt precipitation was not intense. The scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDS) analysis of the membrane collected from the SPMR-DCMD system revealed the presence of crystals built of Ca, Na, S and Cl. In the case of Ca salts, both CaCO_3 (Fig. 10d and f) and CaSO_4 (Fig. 10h) were identified, while in the case of Na salts – NaCl was detected (Fig. 10e). Since the SEM-EDS analysis of the membrane collected from the DCMD unit did not confirm the presence of sulfur, it was concluded that the crystals observed in Fig. 9 were built of CaCO_3 . However, although CaSO_4 and NaCl precipitates were not noticed on this membrane, their presence cannot be unequivocally excluded because, as was already explained, the salts crystals were non-uniformly scattered and very hard to find. It is also worth noting that in the case of the membrane collected from the SPMR-DCMD the crystals were mainly deposited on the TiO_2 covering the membrane, rather than on the membrane itself. This is an advantage of the hybrid system compared to the single DCMD since the photocatalyst layer played a role of a protective coating preventing the membrane from a damage by the developing scale deposit.

The limited precipitation of salts was confirmed by the XRD analysis. For both DCMD and SPMR-DCMD only

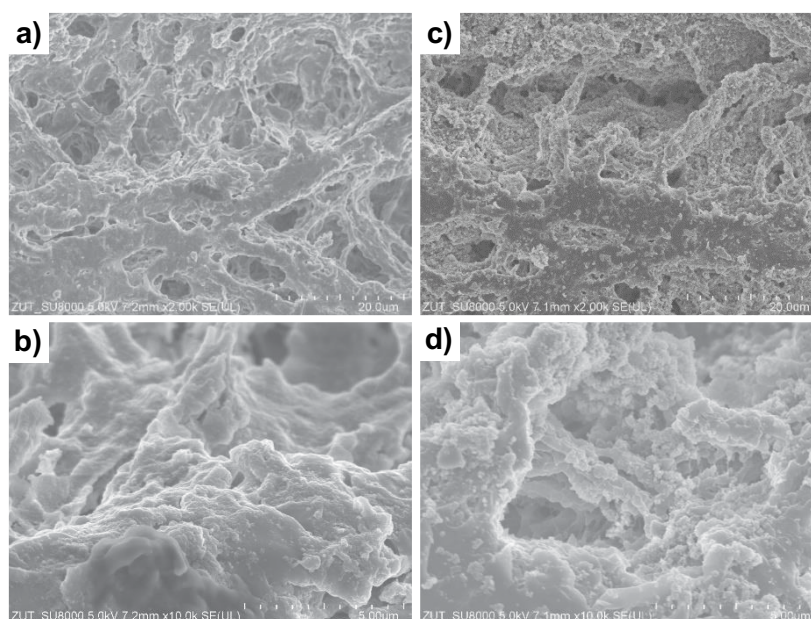


Fig. 8. Scanning electron microscopy images of the surface of PP membrane after 200 h of operation in DCMD (a,b) and SPMR-DCMD (c,d) systems.

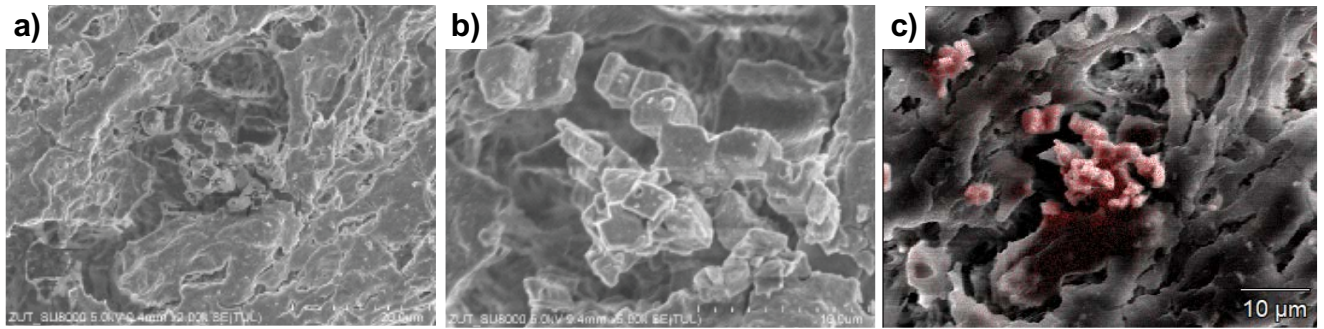


Fig. 9. Scanning electron microscopy (a,b) and SEM-EDS (c) images of salt crystals on the surface of the PP membrane after 200 h of operation in DCMD. Red color in SEM-EDS image represents Ca.

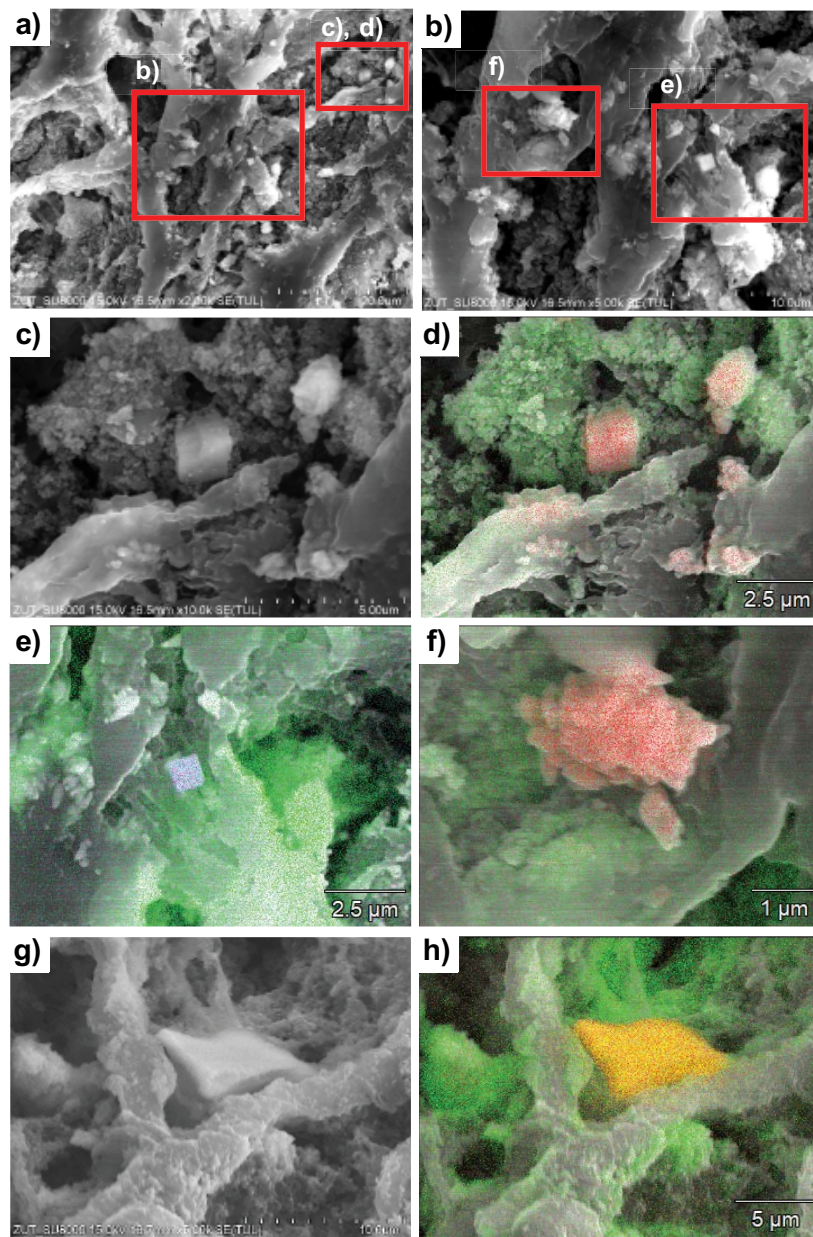


Fig. 10. Scanning electron microscopy (a,b,c,g) and SEM-EDS (d,e,f,h) images of salts deposit on the surface of PP membrane after 200 h of operation in SPMR-DCMD. Color legend in SEM-EDS images: red – Ca, green – Ti, yellow – S, pink – Cl, blue – Na.

the reflections originating from PP were found in the diffractograms of the membranes (Fig. 11a). The lack of the XRD reflections originating from the salts identified in the

SEM-EDS images (CaCO_3 , CaSO_4 and NaCl) was due to their very low content, being below the detection limit of this technique.

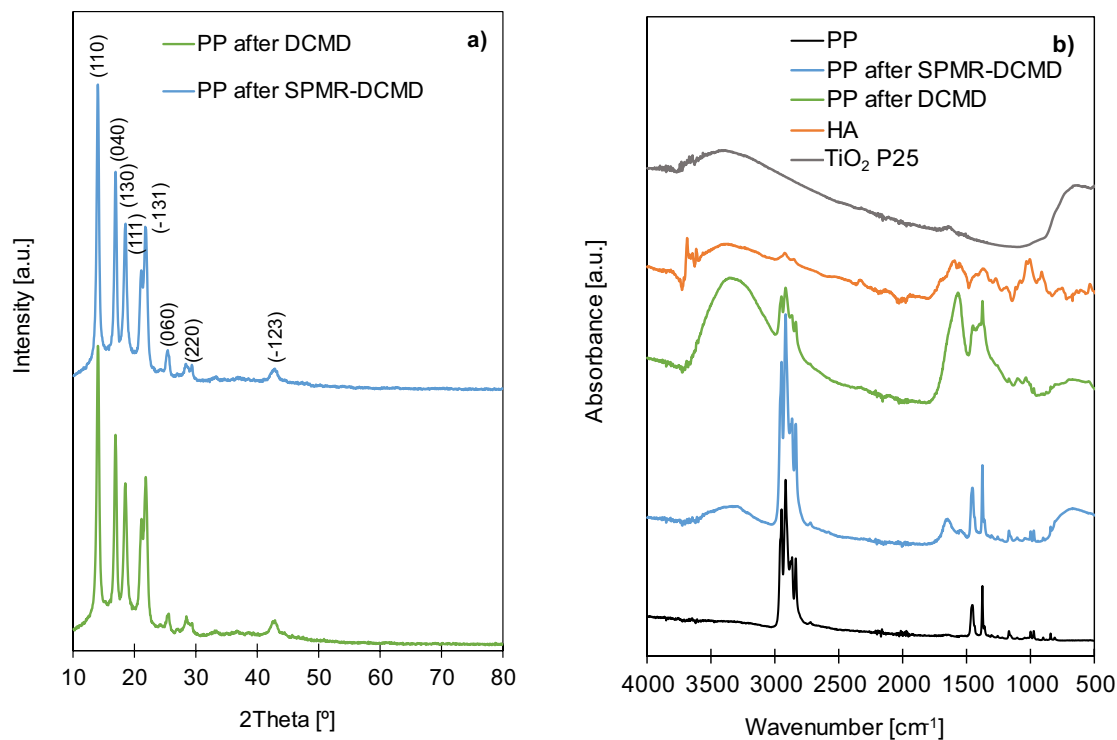


Fig. 11. X-ray diffraction patterns (a) and ATR-FTIR spectra (b) of the PP membranes after 200 h of operation in DCMD and SPMR-DCMD systems. For comparison purpose the ATR-FTIR spectra of clean PP membrane, HA and TiO_2 P25 are also shown.

Table 1
Band assignments for ATR-FTIR spectra of clean PP membrane, HA and TiO_2 P25

Sample	Wavenumber (cm^{-1})	Vibration	References
PP membrane	2,950	CH_3 asymmetric stretching	[46,47]
	2,916	CH_2 asymmetric stretching	
	2,866	CH_3 symmetric stretching	
	2,837	CH_2 asymmetric stretching	
	1,449	CH_3 symmetric bending	
	1,375	CH_3 symmetric bending	
	HA	3,600–3,000	
2,920, 2,854		Aliphatic C–H stretching in CH_2 and CH_3	[51]
1,594, 1,557		C=C aromatic group stretching, COO– asymmetric stretching	[48,52,53]
1,373		CH_3 symmetric bending; COO– symmetric stretching, CH deformation, CO stretching of phenolic OH	[46,53,54]
1,270		C–O stretching of COOH	[55,56]
1,030		C–O stretching of polysaccharide, alcohol and ether groups	[57,58]
910–750		Out-of-plane bending of aromatic C–H, vibrations of aliphatic – CH_2 – chains	[59–61]
533		Aromatic ring bending, symmetric and asymmetric C–H vibrations	[56,59,62]
TiO_2 P25	3,700–3,000	O–H stretching from adsorbed water and –OH groups	[63,64]
	1,647	Bending mode of water molecules	[64]
	632	Ti–O stretching	[63]

To further analyze the deposits formed on the membranes the ATR-FTIR spectroscopy was applied. A comparison of the spectra of clean PP membrane and the membranes collected after DCMD and SPMR-DCMD is shown in Fig. 11b), while Table 1 presents the band assignments.

The ATR-FTIR spectrum of the membrane collected from the DCMD unit confirmed the presence of a significant amount of a deposit layer (Fig. 11b). A wide band at 3,600–3,000 cm^{-1} originating from HA can be observed. This band can be attributed to O–H stretching vibrations of hydroxyl groups and adsorbed water (Table 1) [50,51]. The presence of HA on the membrane surface is also well reflected by the band at 1,567 cm^{-1} (C=C aromatic group stretching) [48]. Moreover, a wide band below 900 cm^{-1} due to C–H vibrations of aliphatic and aromatic groups in HA [56,59–62] can be seen. On the other hand, in the case of the membrane applied in the SPMR-DCMD system the intensity of the band at 1,567 cm^{-1} corresponding to HA was low. The wide band at 3,600–3,000 cm^{-1} in this case can be attributed to O–H stretching vibrations, originating from both HA and TiO_2 photocatalyst. The visibly more intensive broad band below 900 cm^{-1} in the case of the membrane from the SPMR-DCMD compared to the DCMD system reflects the presence of TiO_2 particles deposited on the former membrane, as was also observed in the SEM images (Fig. 8). The obtained results show that in the hybrid SPMR-DCMD system the membrane was covered mainly with TiO_2 layer with a small amount of undecomposed HA, while in the DCMD unit a significant amount of HA was deposited on the membrane.

4. Conclusions

The study was focused on a comparison of a long term continuous performance of two membrane systems: DCMD unit and a hybrid SPMR-DCMD system. The efficiency of treatment of simulated surface water contaminated with ketoprofen, the toxicity of the process streams as well as the PP membrane performance were analyzed. The operation of DCMD system was accompanied by a continuous increase in the concentration of organic and inorganic contaminants in retentate. After 200 h of the process the concentration of ketoprofen increased by ~5.7 times, while the concentration of TOC by ~5 times. The lower increase in TOC content was attributed to adsorption of HA on the membrane. In the hybrid system the concentration of both parameters decreased during the initial 24 h of operation and subsequently reached almost constant value. The various concentrations of organic contaminants in the DCMD and SPMR-DCMD retentate resulted in its various toxicity. The DCMD concentrate after 200 h of operation was characterized by a low toxicity, while the SPMR retentate was non-toxic. A more detailed toxicity analysis revealed that despite the increasing toxicity of the DCMD retentate in time of operation, the toxic effect of ketoprofen was mitigated by the presence of HA.

The changes of feed composition in time affected the quality of distillate. The concentration of TOC in the SPMR-DCMD distillate was lower compared to DCMD, which was explained in terms of a higher diffusion of low molecular weight fraction of HA through the polymer at higher HA concentration in retentate. On the opposite, conductivity and

TIC content were visibly higher in SPMR-DCMD distillate compared to the DCMD product, indicating passage of CO_2 originating from the photodegraded organic compounds through the membrane. The distillate collected in both investigated systems was found to be non-toxic.

The applied PP membrane exhibited excellent stability during long-term operation in both DCMD and SPMR-DCMD systems. No significant membrane scaling was observed, although the detailed SEM and SEM-EDS analyses revealed the presence of some single crystals or their clusters built of CaSO_4 , CaCO_3 or NaCl, scattered non-uniformly on the membrane surface. Nonetheless, their content was very low, which was confirmed by the lack of the reflections originating from the salts in the XRD diffractograms. The fouling layer in the case of the membrane from the DCMD unit consisted mainly of HA, while the deposit covering the SPMR-DCMD membrane was mostly built of TiO_2 with a low addition of undecomposed HA. The presence of TiO_2 on the membrane surface played a dual beneficial role in the process: (i) it enhanced the permeate flux due to the higher thermal conductivity compared to the PP membrane which resulted in an easier heat transfer via conduction, and (ii) it protected the membrane from the damage by the growing crystals which deposited on the photocatalyst layer rather than directly on the membrane.

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