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The influence of feed composition on fouling and stability of a polyethersulfone ultrafiltration membrane in a photocatalytic membrane reactor

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HIGHLIGHTS

- Permeate flux decline in the presence of HCO_3^- ions due to dense fouling cake.
- Higher permeate flux in case of SO_4^{2-} due to repulsion of TiO_2 by the membrane.
- Severe flux decline in the presence of humic acids and ions due to bridging effect.
- The highest loss of membrane separation properties in the absence of humic acids.
- Decrease of efficiency of humic acids removal in the presence of inorganic salts.

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ABSTRACT

The investigations on the influence of humic acids (HAs) being representatives of Natural Organic Matter (NOM) and inorganic salts ($NaHCO_3$, Na_2HPO_4 and Na_2SO_4) representing inorganic ions in natural waters, on fouling and stability of a polyethersulfone ultrafiltration membrane in a photocatalytic membrane reactor (PMR) are reported. The influence of inorganic ions on the permeate flux was dependent on their concentration and was more significant at higher salts content. The HCO_3^- ions contributed to the permeate flux decline to the highest extent, which was attributed to both a higher feed pH and a formation of a dense fouling layer. In the presence of SO_4^{2-} the permeate flux was higher than in case of other ions which was explained in terms of lower thickness of the fouling cake caused by repulsion of TiO_2 particles by the membrane under such conditions. The most severe decrease of the permeate flux observed in the presence of a mixture of HAs and inorganic salts was attributed to the formation of a thick fouling cake caused by bridging effect between HAs molecules and TiO_2 particles under high ionic strength conditions. The inorganic salts contributed also to a decrease of HAs decomposition rate due to the hole and hydroxyl radicals scavenging effect of the ions. It was found that the conditions prevailing in the PMR contributed to the loss of the membrane separation properties towards dextrans due to the abrasive action of TiO_2 particles. However, the extent of the observed decrease in the dextrans rejection was dependent on the feed composition.

1. Introduction

In recent years, due to the necessity of finding new, effective technologies designed for water purification, photocatalytic membrane reactors (PMRs) are gaining a significant attention [1–23]. PMRs are hybrid systems which combine the advantages of two techniques: photocatalysis and membrane separation. Photocatalysis is used for the decomposition of organic pollutants, while the membrane separates the photocatalyst and optionally, products or by-products of photocatalytic decomposition [1].

In PMRs the most commonly used membrane techniques are pressure-driven ones, such as: microfiltration (MF) [2–5], ultrafiltration (UF) [6–10,5] or nanofiltration (NF) [11]. Based on a configuration, two main types of PMRs can be distinguished: (i) with a photocatalyst in suspension and (ii) with a photocatalyst immobilized on/in the membrane (i.e. with photocatalytic membranes) [12]. The most often described PMRs with a photocatalyst in suspension are the systems utilizing membranes made of

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polymers. However, polymeric membranes have some disadvantages which need to be considered before their potential application in PMRs. The most serious one is their low resistance to the UV irradiation and the action of oxidative species, such as hydroxyl radicals. The polymeric membrane damage under the action of UV light and H_2O_2 was confirmed by Chin et al. [13] and Molinari et al. [14]. However, these experiments were realized in PMRs where the membrane was directly irradiated by UV light. Taking this into account, the system with the photoreactor separated from the membrane unit seems to be more perspective. In such a system the photocatalyst could be either immobilized on a carrier material other than a membrane or can be applied in a form of suspension. A majority of literature reports describes the systems with the suspended photocatalyst. However, when the suspension is used, the membrane can suffer from a mechanical damage caused by the flowing TiO_2 particles which could contribute to the shortening of the lifespan of the membranes. Our previous work [15] confirmed this statement. The deterioration of the membrane separation properties was observed in case of all examined polyethersulfone membranes, but the severity of that phenomenon was dependent on the membrane type. The membrane with the finest pores and the most delicate skin layer exhibited the lowest resistance to the conditions prevailing in the PMR. It was also found that the shape and size of the TiO_2 particles had an effect on the membrane stability. The small and sharp-edged photocatalyst particles were the most harmful. The deterioration of the separation properties was caused mainly by the abrasion of the membrane surface, however, as two membrane samples suffered also a loss of separation properties after soaking in H_2O_2 solution, the damage by the reactive oxygen species cannot be excluded [15].

In PMRs with TiO_2 in suspension the permeate flux decline due to the deposition of TiO_2 as well as organic compounds (e.g. humic acids, polysaccharides, proteins) and other substances present in the feed stream on a membrane surface can also take place [16]. The severity of the membrane fouling in PMRs depends on the process parameters such as the concentration of the photocatalyst [4,17], transmembrane pressure [18] and feed cross-flow velocity [19]. The composition of the feed is also important in this matter. Xue et al. [20] during their investigations on the feed composition and pH on the membrane fouling found that the presence of Cl^- and SO_4^{2-} ions had a detrimental effect on the permeate flux. They also reported that the permeate flux was the highest when pH close to neutral was used.

In the present research we have made an attempt to evaluate the influence of the feed composition, mainly the presence and concentration of inorganic anions such as SO_4^{2-}, HPO_4^{2-} and HCO_3^-, the solution pH as well as the presence of humic acids (HAs) on fouling and stability of a commercial polyethersulfone (PES) ultrafiltration membrane in a photocatalytic membrane reactor. The effect of feed composition on the filtration cake structure was examined based on SEM analysis. Moreover, the changes of the membrane separation characteristics after its operation in the PMR were determined. The treatment efficiency in terms of humic acids removal was also investigated.

2. Experimental

2.1. Materials

A flat sheet polyethersulfone (PES) membrane (UE10, Trisep Corp., USA) with the molecular weight cut-off (MWCO) of 10 kDa (according to the manufacturer) was used. The effective (working) membrane area was 0.0025 m^2. The physico-chemical characteristics of the examined membrane is presented elsewhere [21]. In brief, the pure water flux (PWF) of the UE10 membrane was in the range of 150 dm^3/m^2h for the transmembrane pressure (TMP) of 1 bar to 350 dm^3/m^2h for TMP = 3 bar. The membrane exhibited a 79% rejection of 40 kDa dextran and a 95% rejection of 70 kDa dextran.

A commercially available TiO_2 Aeroxide® P25 (Evonik, Germany) at a concentration of 0.5 g/dm^3 was used as a photocatalyst. A detailed physico-chemical characteristics of the photocatalyst was described elsewhere [15]. The point of zero charge (pH_{pzc}) of TiO_2 P25 was 6.3. The dependence of the zeta potential on pH is shown in Fig. 1.

Various aqueous solutions were applied as the feed: (1) ultrapure water (Elix 3, Millipore) (F1); (2) ultrapure water with pH adjusted to pH 3 using HCl (F2) and to pH 9 using NaOH (F3); (3) solutions of hydrogen carbonate, sulphate and hydrogen phosphate sodium salts in water (F4-F8) or (4) humic acids (HAs) solution with (F10) or without (F9) the addition of the inorganic salts. Humic acids (Sigma Aldrich) were applied as a representative of Natural Organic Matter (NOM), whereas hydrogen carbonates, sulphates and hydrogen phosphates represented typical inorganic anions present in natural waters. The basis for the selection of the inorganic salts concentrations was to represent both low and high amounts of these compounds found in natural waters [24,25]. The compositions of the feed solutions applied in the experiments are summarized in Table 1.

Aqueous solutions of dextrans having molecular weight of 40 kDa and 70 kDa (Polfa Kutno, Poland) at the concentration of 1 g/dm^3 were used for the determination of separation properties of the examined membrane before and after its operation in the PMR.

2.2. Experimental setup

A schematic diagram of the photocatalytic membrane reactor (PMR) applied in the experiments is presented in Fig. 2. The main elements of the PMR were a stainless steel membrane module and a flow-through photoreactor with a submerged UV-C lamp (Philips TUV 16 W, λ_{max} = 254 nm; UV light intensity: 1.54 W/m^2). The photoreactor (0.84 dm^3) was incorporated between the feed tank and the membrane module. The feed was pumped using a plunger pump equipped with a pressure dampener, a needle valve and a manometer. The transmembrane pressure (TMP) was set at 3 bar and the feed cross-flow velocity (v) was 0.8 m/s. During the experiments a 1.194 mm feed spacer was used. The temperature was maintained at 20 ± 1 °C. The inves-

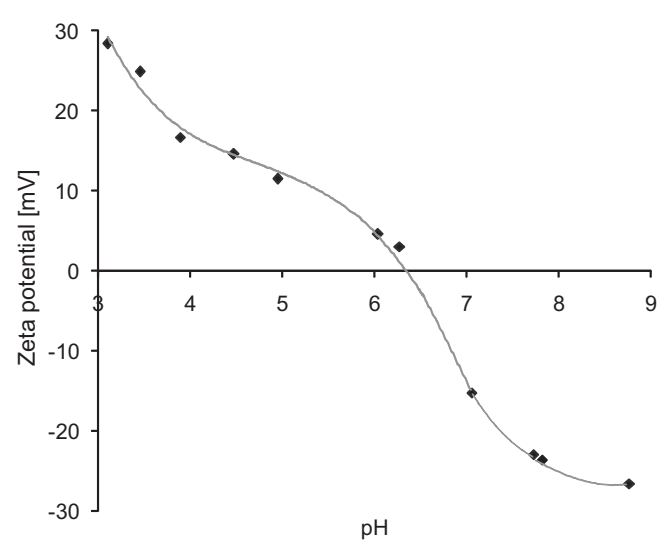

Fig. 1. The zeta potential of TiO_2 Aeroxide® P25 used in the experiments.