



# Integration of photocatalysis and membrane distillation for removal of mono- and poly-azo dyes from water<sup>☆</sup>

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## ABSTRACT

The paper reports investigations on the application of anatase-phase TiO<sub>2</sub> for the removal of azo dyes in a hybrid system coupling photocatalysis with direct contact membrane distillation (DCMD, MD). The process was conducted in a laboratory-scale installation equipped with a PP capillary module. The influence of reaction temperature and initial concentration of azo dyes on the effectiveness of their photodegradation was especially investigated. Two mono-azo dyes: Acid Red 18 (AR18) and Acid Yellow 36 (AY36) and one poly-azo dye, Direct Green 99 (DG99) were applied as model compounds. The increase of the reaction temperature from 313 to 333 K resulted in an improvement of the efficiency of photodecomposition of the dyes, as was found on the basis of changes of their masses in the feed solution. The comparison of the results obtained during photocatalysis alone and hybrid photocatalysis–MD process revealed that the reduction of feed volume in MD did not affect the photodegradation rate of the azo dyes. An improvement of the effectiveness of the degradation of dyes was obtained by an application of solutions with lower initial concentration (10 instead of 30 mg/dm<sup>3</sup>). Regardless of the process parameters applied, the product (distillate) was almost pure water with conductivity lower than 0.3 mS/m and pH above 5.2.

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## 1. Introduction

Over the last decade an increasing attention has been focused on the so-called photocatalytic membrane reactors (PMRs) which take advantage of photodegradation of pollutants in water and membrane technology. These reactors seem to be a very promising method of solving problems concerning separation of photocatalysts as well as products and by-products of photodegradation from reaction mixture. Photocatalytic membrane reactors can be divided generally into two main groups: (I) reactors with catalyst suspended in a feed solution and (II) reactors with catalyst supported in/on the membrane. In both configurations, the membrane might act as a barrier for the molecules that are degraded and products and by-products of their degradation. However, this role strongly depends on the separation characteristics of the membrane used and the membrane process applied.

Most of the PMRs described in the literature combine photocatalysis using photocatalyst in suspension with pressure-driven membrane processes such as microfiltration (MF) [1–8], ultrafiltration (UF) [9–12] and nanofiltration (NF) [9,13,14]. However, when a catalyst in suspension is applied, membrane fouling is observed, especially in case of MF and UF membranes. Moreover, the quality of

permeate is not very high, because small molecules can easily pass through the membranes used, even in case of NF.

Recently new types of photocatalytic membrane reactors combining photocatalysis with catalyst in suspension and dialysis [15] or pervaporation [16] have been described. In our previous publications [17,18] we have also presented another type of PMR in which photocatalysis was coupled with direct contact membrane distillation (DCMD, MD). The main advantage of the PMRs utilizing membrane processes other than the pressure-driven ones is that the membrane fouling has not been observed.

Membrane distillation is a process of evaporation of feed volatile components through a porous hydrophobic membrane. During the process operation, the gas phase is maintained inside the pores of the membrane. The driving force of the mass transfer through the membrane pores is a vapour pressure difference on both sides of membrane, which depends on the temperature and the solution composition in the layers adjacent to the membrane.

MD was found to be very effective in concentration of dyes solutions [19–21]. This is mainly due to the fact that MD membranes are permeable for volatile compounds only. Dyes are non-volatile substances, therefore are completely separated by MD membranes. Nevertheless, concentration of dyes solutions by MD is reasonable only in case when a reuse of these solutions is planned. However, the wastewaters from textile industry usually contain a mixture of different dyes, not a single dye. Therefore, application of membrane processes for treatment of these wastewaters is focused mainly on

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water recovery rather than recovery of dyes. In such a case, despite from product (water), a concentrated dyebath, which needs to be further treated, is obtained. In view of this an application of a process which allows complete mineralization of organic substances seems to be more reasonable than a membrane process alone. Such a process might be hybrid photocatalysis–MD system.

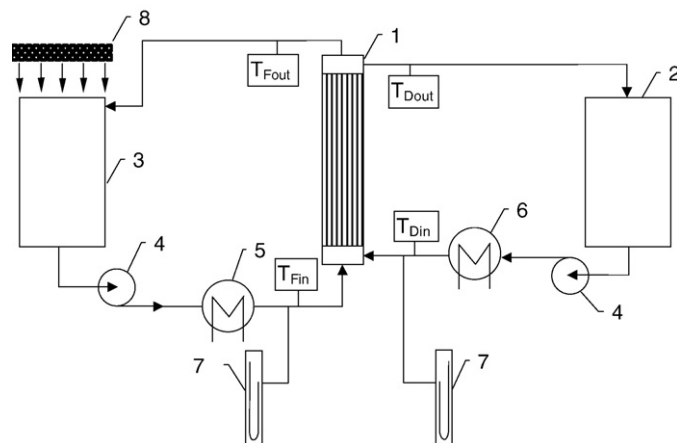
The present studies have focused on the application of a new anatase-phase  $\text{TiO}_2$  for degradation of mono- and poly-azo dyes in a photocatalytic membrane reactor (PMR) coupling photocatalysis with DCMD. The effect of different process parameters such as concentration of the pollutants in the solution and the temperature of the photocatalytic reaction on photodegradation of model compounds in the PMR was especially investigated.

## 2. Materials and methods

The catalyst used in this study (denoted as A-700-1 h) was prepared from a crude  $\text{TiO}_2$  obtained directly from the production line (sulfate technology) at the Chemical Factory “Police” (Poland) by calcination for 1 h at 700 °C in air. The A-700-1 h contained primarily anatase phase (97%). The crystallite size of anatase was 27 nm and the BET surface area was equal to 33.4  $\text{m}^2/\text{g}$ . The photocatalyst loading amounted to 0.5  $\text{g TiO}_2/\text{dm}^3$ .

Acid Red 18 (AR18,  $\text{C}_{20}\text{H}_{11}\text{N}_2\text{Na}_3\text{O}_{10}\text{S}_3$ ), Acid Yellow 36 (AY36,  $\text{C}_{18}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$ ) and Direct Green 99 (DG99,  $\text{C}_{44}\text{H}_{28}\text{N}_{12}\text{Na}_4\text{O}_{14}\text{S}_4$ ) were applied as model azo dyes. The molecular weights (MW) of the dyes were equal to 375.4, 640.4 and 1169  $\text{g/mol}$  for AY36, AR18 and DG99, respectively. Chemical structures of the model compounds are presented in Fig. 1. The initial concentration ( $c_0$ ) of the dyes was 10 or 30  $\text{mg}/\text{dm}^3$ .

The hybrid photocatalysis–MD process was conducted in a laboratory-scale installation presented in Fig. 2. The main element of the system was a capillary module equipped with 9 polypropylene (PP) membranes (Accurel PP S6/2,  $d_{\text{out}}/d_{\text{in}} = 2.6/1.8$  mm, Membrana GmbH, Wuppertal, Germany), with the effective (internal) area of 0.0127  $\text{m}^2$ . The nominal pore size of the PP membranes was 0.2  $\mu\text{m}$  and the maximum pore size was  $\leq 0.65$   $\mu\text{m}$  (according to the manufacturer). The feed flowed inside the capillaries with a flow rate of 0.5 m/s, whereas the distillate flowed outside the capillaries with a flow rate of 0.18 m/s, respectively. The inlet temperatures of the feed amounted to 313, 324 or 335 K for the reaction temperatures (in the feed tank) of 313, 323 or 333 K, respectively, whereas the inlet temperature of distillate was constant and equal to 293 K. The



**Fig. 2.** Schematic diagram of the PMR coupling photocatalysis and MD: 1) membrane module; 2) distillate tank; 3) feed tank ( $V = 2.9 \text{ dm}^3$ ); 4) pump; 5) and 6) heat exchangers; 7) manometers; 8) UV lamp;  $T_{\text{Fin}}$ ,  $T_{\text{Din}}$ ,  $T_{\text{Fout}}$ ,  $T_{\text{Dout}}$ —inlet and outlet temperatures of feed and distillate, respectively.

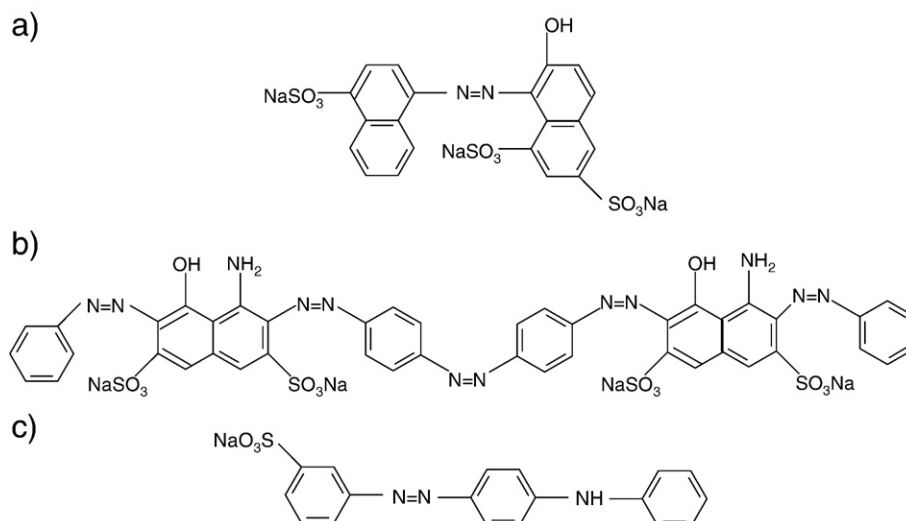
reaction solution was irradiated with UV-A light ( $\lambda_{\text{max}} = 365 \text{ nm}$ ; UV light intensity at the irradiation plate: 80  $\text{W}/\text{m}^2$ ).

Before photodegradation the solution containing a fixed amount of the photocatalyst was stirred for 30 min. in the dark in order to allow adsorption of the dye molecules on the  $\text{TiO}_2$  surface. The photocatalytic process was conducted for 5 h. After a defined time of irradiation the samples of feed solution were filtered through a 0.45  $\mu\text{m}$  membrane filter and analyzed. The degradation rate of the dyes was estimated on the basis of (I) changes in UV/VIS spectra ( $\lambda_{\text{max}} = 431 \text{ nm}$ , 507  $\text{nm}$  or 626  $\text{nm}$  for AY36, AR18 and DG99, respectively), (II) conductivity and (III) concentration of selected organic acids being photoproducts of dye degradation (HPLC ELITE LaChrom, Hitachi, Japan; Unison UK-C8 column; analysis conditions: eluent—20 mM  $\text{H}_3\text{PO}_4$ , flow rate of eluent: 0.6  $\text{cm}^3/\text{min}$ , temperature: 37 °C; UV detector wavelength: 210 nm). Moreover, pH of the feed solution and distillate was measured.

## 3. Results and discussion

### 3.1. Effect of $\text{TiO}_2$ presence in a feed on permeate flux

We have found during our previous studies [17,18] that an addition of pure  $\text{TiO}_2$  such as commercially available Aeroxide® P25



**Fig. 1.** Chemical structures of (a) Acid Red 18, (b) Direct Green 99 and (c) Acid Yellow 36.

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