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Photocatalytic membrane reactor (PMR) coupling photocatalysis and membrane distillation—Effectiveness of removal of three azo dyes from water

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Abstract

The results of the investigation on the possibility of coupling photocatalysis and direct contact membrane distillation (DCMD, MD) for degradation of azo dyes (Acid Red 18, Acid Yellow 36 and Direct Green 99) in aqueous solution are described. TiO_2 Aeroxide® P25 (Degussa, Germany) was applied as a photocatalyst. It was found that the addition of TiO_2 P25 to the feed did not affect the distillate flux, regardless of the catalyst concentration applied. The MD process is very effective in separation of photocatalyst particles. After 5 h of the experiment, the turbidity of distillate was similar to that measured for ultrapure water, regardless of the TiO_2 loading used. The highest effectiveness of photodecomposition was obtained in case of Acid Red 18, and the most difficult degraded was Acid Yellow 36, having the lowest molecular weight from all the dyes used. The composition of the feed solution slightly influenced the quality of distillate. Among the volatile compounds that passed through the membrane some organic compounds were present as was indicated by the measurements of TOC concentration. After 5 h of the process the TOC concentration, conductivity and TDS content in distillate did not exceed the value of 1.2 mg C/dm^3, 2.2 μS/cm and 1.4 mg/dm^3, respectively, being the highest in case of Direct Green 99.

Keywords: Photocatalytic membrane reactors (PMRs); Photocatalyst separation; Titanium dioxide; Membrane distillation; Dye decomposition

1. Introduction

Recently, coupling photocatalysis and different membrane techniques have been widely investigated by many researchers [1–12]. This is mainly due to the possibility of solving the problem concerning separation of photocatalyst particles from the treated solution as well as, at least partially, products and by-products of photodegradation of pollutants. Moreover, application of photocatalytic membrane reactors (PMRs) instead of a conventional photoreactor allows avoiding some additional operations, such as coagulation–flocculation–sedimentation, that are necessary to remove particles from the treated solution when a suspension of a photocatalyst is applied. One benefit from this is energy saving and reducing the size of installation. Another one is possibility of reusing of the photocatalyst in further runs, what is practically impossible when coagulation is applied.

The PMRs 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 case (II) the light source is positioned above the membrane module, whereas in case (I) there are two possible configurations: irradiation of the feed tank or membrane module. The PMRs described in literature combine photocatalysis with pressure-driven membrane techniques, such as nanofiltration (NF) [2,5,9], ultrafiltration (UF) [3–5,7] and microfiltration (MF) [1,6]. However, when a catalyst in suspension is applied, the membrane fouling is observed, especially in case of MF and UF membranes. Moreover, the quality of permeate is not very high, as small molecules can pass easily through the membranes used, even in case of NF.

In our previously published paper [13] we described a new type of PMR, where direct contact membrane distillation

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(DCMD, MD) was applied instead of pressure driven membrane techniques. MD is a process of evaporation of feed volatile components through a porous hydrophobic membrane. During the process, the gas phase is maintained inside the pores of the membrane. The driving force of the mass transfer through the membrane pores is a vapor pressure difference on both sides of membrane, which depends on the temperature and the solutions composition in the layers adjacent to the membrane. The MD process might be utilized for the preparation of ultrapure water as well as separation and concentration of organic matter, acids and salt solutions [14,15]. The quality of MD permeate is very high as only water vapour and volatile components can pass through the membrane.

The presented paper describes the results obtained during photocatalysis performed in the PMR utilizing DCMD. The presence of TiO_2 in a feed on the process performance was investigated. Moreover, the effectiveness of the decomposition of three model azo dyes as well as the rejection of MD process towards TiO_2 and photodegradation products was determined.

2. Materials and methods

The DCMD process was conducted in a laboratory-scale installation presented in Fig. 1. A detailed description can be found in our previous paper [13]. The main element of the system was a capillary module equipped with 9 polypropylene (PP) membranes Accurel PP S6/2 (Membrana GmbH, Wuppertal, Germany), with outer/inner diameter $d_{out}/d_{in} = 2.6/1.8$ mm. The effective area of PP membranes was equal to 0.014 m^2. In all the experiments the warm feed and cold distillate streams flowed in the module in a co-current mode. The feed flowed inside the capillaries with a flow rate of 0.31 m/s, whereas the distillate flowed outside the capillaries with a flow rate of 0.09 m/s. The temperature of the reaction mixture in the feed tank amounted to 333 K. The inlet temperature of distillate was equal to 293 K. The permeate flux was determined using the weight balance.

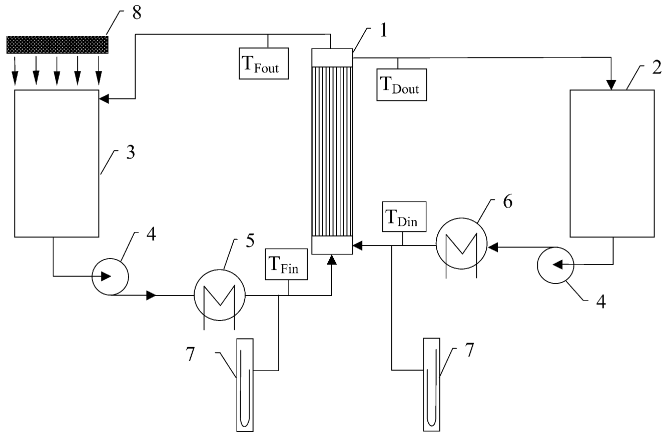

Fig. 1. Schematic diagram of the apparatus for MD; (1) membrane module; (2) distillate tank; (3) feed tank ($V = 2.9$ dm^3); (4) pump; (5) and (6) heat exchangers; (7) manometers; (8) UV lamp; T_{Fin}, T_{Din} – inlet temperatures of feed and distillate, T_{Fout}, T_{Dout} – outlet temperatures of feed and distillate.

Acid Red 18 ($C_{20}H_{11}N_2Na_3O_{10}S_3$), Direct Green 99 ($C_{44}H_{28}N_{12}Na_4O_{14}S_4$) and Acid Yellow 36 ($C_{18}H_{14}N_3NaO_3S$) obtained from Chemical Factory Boruta—Kolor Sp.z.o.o (Poland) were applied as model azo dyes. Chemical structures of the model compounds are presented in Fig. 2.

The concentration of a dye was equal to 30 mg/dm^3 and the catalyst (Aeroxide® P25, Degussa, Germany) loading amounted to 0.1, 0.3 and 0.5 g TiO_2/dm^3. Before photodecomposition the solution containing a fixed amount of the photocatalyst was stirred for 15 min in the dark in order to allow adsorption of the dye molecules on the TiO_2 surface. The hybrid process photocatalysis-MD was conducted for 5 h. The volume of distillate (ultrapure water, Simplicity™, Millipore) at the beginning of the process was equal to 1.3 dm^3 and the volume of feed was 2.9 dm^3. The reaction solution was illuminated with a mercury lamp Philips Cleo, emitting UV-A light ($\lambda_{max} = 355$ nm). The UV illumination intensity at the irradiation plate (feed tank) was 146 W/m^2. After a defined time of irradiation the samples of feed solution were filtered through a 0.45 μm membrane filter and analyzed. The effectiveness of TiO_2 separation by the MD membrane was determined on the basis of turbidity removal. Turbidity was measured using HACH 2100N IS turbidimeter. The decomposition rate of model azo dyes was estimated on the basis of changes in UV–vis spectra (Jasco V530 spectrometer, Japan), total organic carbon (TOC) concentration (“Multi N/C 2000” analyzer, Analytik Jena, Germany), total dissolved substances (TDS) content and conductivity (Ultrameter™ 6P, MYRON L COMPANY USA). Moreover, pH of the feed solution and distillate was measured.

In order to determine the photostability of the dyes under the conditions applied (i.e. temperature equal to 333 K and the intensity of UV light equal to 146 W/m^2), an additional experiment without TiO_2 addition was performed. The solution was placed in the same batch reactor that was applied in the photocatalysis experiments. To limit the evaporation of water the upper side of the reactor was covered with a plate from PMMA that was transparent to UV radiation. The parameters monitored were: dye concentration, TOC content, conductivity and TDS value. It was found that after 5 h of illumination of dye solution the measured parameters were practically constant, what means that no degradation of model compounds took place. A negligible change of reaction volume was observed due to evaporation of water during heating. Therefore, it can be stated that in the presence of TiO_2 a true heterogenous catalytic regime takes place.

3. Results and discussion

During the first step of the research the effect of the presence of TiO_2 in a feed on the permeate flux was investigated. It was found that the addition of Aeroxide® TiO_2 P25 to the feed solution did not affect the permeate flux, regardless of TiO_2 concentration and dye applied. In all the experiments the permeate flux was about 0.34 m^3/m^2 d, similarly as during the process, in which ultrapure water was applied as a feed. This is an important advantage of application of MD in a PMR. It is

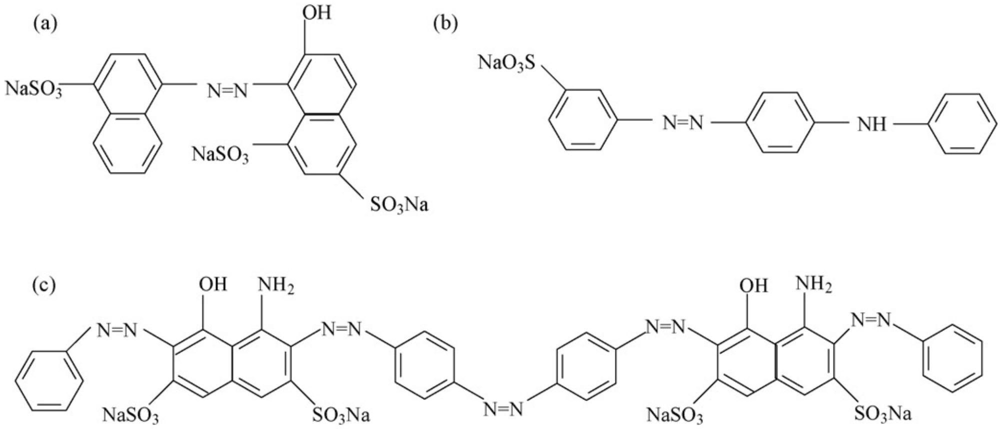

Fig. 2. Chemical structures of (a) Acid Red 18, (b) Acid Yellow 36, and (c) Direct Green 99.

known from literature that in case of the reactors utilizing pressure driven membrane processes a significant deterioration of process capacity is observed, especially in case of MF and UF [1,3,5].

In order to determine the effectiveness of TiO_2 separation by the MD membrane the turbidity of distillate was measured. It was found that the MD process is very effective in separation of photocatalyst particles. After 5 h of the process, regardless of the TiO_2 loading used, the turbidity of distillate was in the range of 0.10–0.20 NTU, which value is similar to the value measured for water used for preparation of the model solutions (0.15 NTU). Turbidity of suspension of Degussa P25 in water with concentration of 0.1, 0.3 and 0.5 mg TiO_2/dm^3 was equal to 369, 984 and 1680 NTU, respectively.

The effectiveness of removal of the model compounds in the PMR was determined on the basis of concentration of dye and TOC, as well as TDS and conductivity measured in feed and distillate. Moreover, pH of the solutions was monitored. Table 1 presents changes of concentration of the model dyes and TOC in a feed as a function of irradiation time.

Table 1
Photodecomposition of Acid Red 18, Acid Yellow 36 and Direct Green 99 in the PMR (changes of dye and TOC concentration in the feed vs. time for different TiO_2 loadings. Time $t = 0$ h means time after adsorption in the dark)

Time (h)	0.1 g TiO_2/dm^3		0.3 g TiO_2/dm^3		0.5 g TiO_2/dm^3	
	Concentration (mg/dm^3)					
	Dye	TOC	Dye	TOC	Dye	TOC
Acid Red 18						
0	30.0	11.9	29.8	11.7	29.6	11.7
2.5	10.7	11.6	5.2	9.7	0.9	7.6
5	8.5	10.2	0	6.2	0	4.4
Acid Yellow 36						
0	30.0	18.4	30.0	18.3	29.9	18.3
2.5	29.9	23.6	27.9	21.5	25.1	21.2
5	20.2	30.4	20.2	26.6	17.5	26.2
Direct Green 99						
0	29.2	13.5	27.6	13.0	25.7	12.2
2.5	26.1	16.0	14.6	13.2	9.3	11.9
5	24.9	20.1	9.6	15.1	5.0	12.9

It can be observed that the highest effectiveness of decomposition was obtained in case of Acid Red 18 (Table 1). After 5 h of irradiation with TiO_2 loadings of 0.3 and 0.5 g/dm^3 a complete decolorization of the solution was obtained; when 0.1 g TiO_2/dm^3 was applied, the dye concentration decreased for ca. 72%. In case of Acid Yellow 36 the concentration of the dye at the end of the process was lower, compared to the initial concentration, for ca. 40% in case of 0.5 g TiO_2/dm^3 and ca. 33% in case of 0.1 and 0.3 g TiO_2/dm^3, respectively. Direct Green 99 was decomposed during 5 h of the process with photocatalyst loadings of 0.1, 0.3 and 0.5 g TiO_2/dm^3 for ca. 15, 65 and 81%, respectively. The fading of the solutions was associated with cleavage of azo linkage in the molecules. Azo dyes are characterized by nitrogen to nitrogen double bonds (–N=N–) that are usually attached to two radicals of which at least one but usually both are aromatic groups (benzene or naphtalene rings—what can be observed in Fig. 2). The color of azo dyes is determined by the azo bonds and their associated chromophores and auxochromes. Azo bonds are the most active bonds in azo dye molecules and can be oxidized by positive hole or hydroxyl radical or reduced by electron in the conduction band [16]. The cleavage of –N=N– bonds leads to the decoloration of dyes, what was observed in the discussed experiment. From the obtained results it was found that the most easily decomposed was Acid Red 18, having the molecular weight of 640.4 g/mol. The effectiveness of photodecomposition of Acid Yellow 36, exhibiting the lowest molecular weight from all the dyes used (i.e. 375.4 g/mol) was significantly lower not only than that of Acid Red 18, but also than that of Direct Green 99, having the highest molecular weight (i.e. 1169 g/mol). With the photocatalyst loading of 0.1 g/dm^3 only, the observed order was different, i.e. Direct Green 99 was less easily decomposed than Acid Yellow 36. Higher effectiveness of decomposition of Direct Green 99 than Acid Yellow 36 at 0.3 and 0.5 g TiO_2/dm^3 might be associated with the adsorption ability of the dye to the photocatalyst surface. It can be seen in Table 1 that concentration of Direct Green 99 after the period of adsorption in the dark ($t = 0$ h) was lower than 30 mg/dm^3. For 0.1 g TiO_2/dm^3 the dye concentration amounted to 29.2 mg/dm^3, for 0.3 g TiO_2/dm^3 – 27.6 mg/dm^3 and for 0.5 g TiO_2/dm^3 – 25.7 mg/dm^3. In case of Acid Red

18 (Table 1) the difference between the concentration of dye before and after adsorption in the dark at the highest catalyst loading was lower than 0.5 mg/dm^3 and in case of Acid Yellow 36 no noticeable difference in the concentration was observed. The molecules of Direct Green 99, more difficult to be degraded due to higher molecular weight but better adsorbed on photocatalyst support than Acid Yellow 36, could be oxidized by more active sites. This conclusion might be supported by the results obtained at the lowest catalyst loading applied. At 0.1 g TiO_2/dm^3 degradation of Direct Green 99 was lower than Acid Yellow 36 probably due to the fact that the number of active sites at this amount of catalyst was too low to assure effective dye decomposition. On the other hand, the most easily decomposed Acid Red 18 molecules, even if they are oxidized by less active sites (due to lower adsorption ability than that of Direct Green 99), could be degraded more effectively than Direct Green 99 due to lower molecular weight of this dye, and consequently release active surface in favour of other molecules more quickly. The most resistant to UV irradiation Acid Yellow 36, despite the lowest molecular weight from all the dyes used, is poorly adsorbed, what might be one of the reasons of its low decomposition rate. The resistance of Acid Yellow 36 to UV light might be also associated with the presence of electron donating –NH– group in *para*-position to azo bond and electron withdrawing $-SO_3Na$ group in *meta*-position to –N=N– bond, what probably stabilizes the dye molecule. Another explanation of the difference in the photodegradability of the three dyes could be the effect of some by-products of their decomposition which might block active sites on the photocatalyst surface. However, in order to state unequivocally what intermediates could affect the photodegradation rate of the model azo dyes, further extensive investigations are necessary.

Table 1 presents also changes of TOC concentration in the feed versus time of irradiation. The concentration of organic carbon could be an indicator of mineralization of organic compounds present in the solution. It was found that only during photodecomposition of Acid Red 18 the concentration of organic carbon decreased in time. The TOC content after 5 h of the process was lower for ca. 14, 47 and 62% with TiO_2 loadings of 0.1, 0.3 and 0.5 g/dm^3, respectively. In case of Acid Yellow 36 and Direct Green 99 (Table 1) an increase of TOC concentration in time was observed, regardless of the TiO_2 loading applied. At the end of the process the TOC content with photocatalyst loadings of 0.1, 0.3 and 0.5 g/dm^3 was higher for ca. 40, 31 and 30% when Acid Yellow 36 was used as a model dye and for ca. 33, 14 and 5% when Direct Green 99 was applied, respectively. Mechanism of photocatalytic degradation of different azo dyes has been widely discussed in the literature [16–19]. In general, it is often reported that amongst the organic by-products of the photodegradation of azo dyes both, aromatic and aliphatic compounds are present. The aromatic intermediates include either aromatic amines or phenolic compounds. The main aliphatic species are formic and acetic acids. Other organic acids detected were oxalic, glycolic, glyoxylic and malonic acids. The formation of these acids could correspond to the cleavage of benzene and naphthalene rings followed by a sequence of oxidation steps which leads to progressively lower molecular weight acids and the evolution of CO_2 [17]. From Table 1 it can be observed that concentration of all the dyes used decreased in time; therefore, the observed increase in TOC value during decomposition of Acid Yellow 36 and Direct Green 99 is associated mainly with the presence of the by-products of degradation of these compounds. It could be supposed that the photoproducts formed are more resistant to UV irradiation than the original dyes. In case of Acid Red 18 the degradation was faster than concentration of the feed, therefore no increase of TOC concentration was observed. However, during the experiments with the two other dyes (Table 1) the reaction rate became slower than the transport of water vapour and volatile compounds present in the feed through the membrane pores, and as a result an increase of TOC concentration in the feed was observed. In the MD process water and volatile compounds present in warm feed are transported through the pores of the MD membrane and then condensed/dissolved directly in cold distillate. Therefore, the volume of feed solution is continuously decreasing and the concentration of non-volatile compounds (both, organic and inorganic) present in the solution is increasing, which eventually affects the decomposition rate.

Another parameters indicating the rate of decomposition of the dyes could be conductivity and TDS content. It was observed that elongation of the reaction time resulted in an increase of the values of these parameters in the feed. Moreover, the higher the photocatalyst loading was applied, the higher conductivity and TDS concentration were determined, regardless of the azo dye used. For example, initial conductivity of the feed when Acid Red 18 was applied as model dye was equal to 44.5 μS/cm, whereas after 5 h of photodecomposition the value of this parameter was about 3.2–3.4 times higher, for TiO_2 loadings of 0.1–0.5 g/dm^3. For Acid Yellow 36 and Direct Green 99, conductivity at the end of the process, in comparison with the initial value, was ca. 1.95–2.1 times higher. Similar dependence was found for TDS content. The two discussed parameters show that during photocatalytic degradation of azo dyes a large number of other species is formed. As a result a higher conductivity, that is associated with the number of ions present in the solution, and also higher TDS concentration, that is an indicator of the quantity of different substances dissolved in the solution, were determined. The observed increase of the values of the discussed parameters was also associated with concentration of feed solution resulting from transport of water vapour through membrane pores.

The product of the hybrid process photocatalysis—MD; however, is not the feed solution, but distillate. Therefore, the quality of distillate was monitored during the process performance. The parameters measured were pH, conductivity, TDS content as well as dye and TOC concentration. It was found that, regardless of the model compound applied, the total amount of a dye remained on the feed side and its concentration in distillate amounted to 0 mg/dm^3. These results from the fact that MD membrane is permeable for volatile compounds and water vapour only. Azo dyes are non-volatile compounds, therefore are not transported through the membrane pores. It is a significant advantage of the PMR presented in this study, because in other PMRs, that are described in the literature, utilizing pressure-driven membrane techniques, a complete separation of dyes was not achieved [4,20]. Among the volatile compounds that passed through the membrane some organic compounds were present. This conclusion is supported by the measurements of TOC concentration in distillate (Fig. 3).

It was found that the quality of distillate depended on both, the dye applied and the photocatalyst loading used. It can be observed that the highest TOC concentration was measured for Direct Green 99. After 5 h of the process the value of this parameter ranged from 1.2 to 1.0 mg C/dm^3, for catalyst loadings of 0.1–0.5 g TiO$_2$/dm^3, respectively. The lowest concentration of organic carbon was determined in case of Acid Yellow 36 (0.2–0.5 mg C/dm^3 for TiO$_2$ loadings of 0.1–0.5 g/dm^3). For Direct Green 99 and Acid Red 18 it was observed that with increasing of TiO$_2$ loading the TOC concentration in distillate decreased, whereas in case of Acid Yellow 36 increased. The observed results are associated with the degradation rate of the azo dyes in the feed solution. As was mentioned earlier, the formation of by-products, such as organic acids could correspond to the cleavage of benzene and naphthalene rings followed by a sequence of oxidation steps which leads to progressively lower molecular weight acids and the evolution of CO$_2$. Direct Green 99 has two naphthalene and four benzene rings in the molecule (Fig. 2), therefore, it can be supposed that the highest amount of organic intermediates is formed in case of this dye. Acid Red 18, although the most effectively degraded, contains only two naphthalene rings, whereas Acid Yellow 36—three benzene rings (Fig. 2). From the molecular weight it can be found; however, that the highest carbon concentration in the 30 mg/dm^3 solution of the dye is in case of Acid Yellow 36, i.e. 17.3 mg C/dm^3 (versus 11.9 mg C/dm^3 and 13.6 mg C/dm^3 for Acid Red 18 and Direct Green 99, respectively). However, the decomposition rate of Acid Yellow 36 was the lowest from all the dyes applied, therefore the TOC concentration determined in distillate was in case of this dye the lowest. On the other hand, Acid Red 18 was degraded with the highest efficiency, the organic intermediates formed were mineralized into CO$_2$, water and inorganic species more effectively than in case of Direct Green 99, thus the amount of volatile organic compounds that passed through the membrane was significantly lower than that measured for the latter dye.

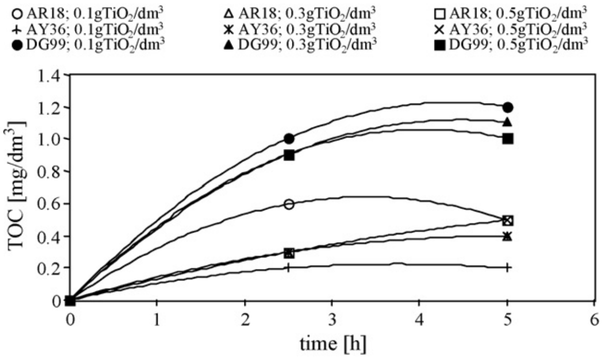

Fig. 3. Photodecomposition of Acid Red 18 (AR18), Acid Yellow 36 (AY36) and Direct Green 99 (DG99) in the PMR. Changes of TOC concentration in distillate vs. time.

Other parameters measured in distillate were conductivity, TDS content and pH (data not shown). After 5 h of the process the conductivity and TDS did not exceed the value of 2.2 μS/cm and 1.4 mg/dm^3, respectively, being the highest in case of Direct Green 99. For comparison, these values measured in ultrapure water applied as distillate at the beginning of the process amounted to 1.3 μS/cm and 0.8 mg/dm^3, respectively. The pH of distillate slightly decreased, especially in case of the decomposition of Acid Red 18, from pH 5.6 at the beginning to pH 5 at the end of the process conducted with TiO$_2$ loading of 0.5 g/dm^3. The observed decrease of pH might suggest that some acidic compounds formed during photodecomposition of azo dyes passed through the membrane. However, in order to determine what compounds are responsible for this decrease, further investigations are needed. Moreover, it should be noticed that the amount of these substances transported through the membrane was rather low. This conclusion arises from the fact that the difference between initial and final pH of distillate was not significant (pH 5.6 versus pH 5).

From the obtained results it could be concluded that the product (distillate) is high quality water, containing only a small amount of volatile compounds that passed through the membrane. Moreover, the MD membrane effectively separates the photocatalyst particles, what was proved on the basis of turbidity measurements. It should be stressed that it is not possible to get a product of so high quality in a classical batch reactor.

4. Conclusions

The presented results reveal that the hybrid photocatalysis—MD system has many advantages over a typical photocatalytic batch reactor. Moreover, it is an interesting alternative for other PMRs combining photocatalysis with pressure-driven membrane processes. Degradation and separation could be performed at the same time and in the same place what minimizes the size of the installation. MD process can be successfully applied for separation of photocatalysts from the solution. It was also found that the addition of Aeroxide® TiO$_2$ P25 to a feed did not affect the permeate flux, regardless of the catalyst concentration applied. Thus, from this point of view, the application of DCMD is much more advantageous in comparison with pressure-driven membrane processes, where a significant fouling was observed. It should be mentioned; however, that MD is still the process under development and, therefore, the pressure driven membrane processes such as MF, UF or NF, have more potential full scale applications than MD.

The chemical structure of azo dye affected the effectiveness of its photodecomposition. After 5 h of the process performance the dye concentration decreased for ca. 40% in case of Acid Yellow 36, ca. 81% in case of Direct Green 99 and in case of Acid Red 18 the solution was completely decolorized. The composition of the feed solution slightly influenced the quality of distillate. Among the volatile compounds that passed through the membrane some organic compounds were present as was indicated by the measurements of TOC concentration in distillate. However, the amount of these substances was very low, therefore it can be concluded, that the product (distillate) is high quality water.

The hybrid process coupling the photocatalysis and DCMD is very promising method of removal of organic compounds, such as azo dyes from water. The MD membrane is a very effective barrier for the catalysts particles as well as the non-volatile compounds present in the feed solution.

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