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ScienceDirect

Catalysis Today 118 (2006) 181–188

CATALYSIS TODAY

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Hybridization of photocatalysis and membrane distillation for purification of wastewater

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Abstract

The presented paper describes the results of the investigation on the possibility of coupling photocatalysis and membrane distillation (MD) for the degradation of organic pollutants in aqueous solution. Acid Red 18 was applied as a model dye and titanium dioxide Aeroxide® P25 (Degussa, Germany) was used as a photocatalyst. It was found that the addition of TiO_2 P25 did not affect the permeate flux through the MD membrane, regardless of the catalyst concentration applied. The model dye was removed completely. Moreover, after 5 h of the hybrid process performance almost complete retention of TOC, TDS and inorganic ions ($N–NO_3^-$, $N–NO_2^-$, $N–NH_4^+$, SO_4^{2-}) was obtained.

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

1. Introduction

Over the last few decades, a great deal of interest has been focused on the photodegradation of organic compounds present in wastewater with the application of TiO_2 as a photocatalyst. The photocatalyst reactors described in literature can be divided in the two main groups: (i) reactors with TiO_2 suspended in the reaction mixture and (ii) reactors with TiO_2 fixed on a carrier material (e.g. glass, quartz, stainless steel or fixed by polymer glue [1]). When the photocatalyst is immobilized on a support the active surface accessible to components of the solution is significantly reduced which results in a loss of photoactivity. In the case of catalyst suspension the active surface is much greater; however, the catalyst particles have to be separated from the treated water after detoxification. A very promising method for solving problems concerning separation of the photocatalyst as well as products and by-products of photodecomposition from the reaction mixture is the application of photocatalytic membrane reactors (PMRs). The membrane would play both the role of a simple barrier for the photocatalyst and of a selective barrier for the molecules to be degraded [2]. Photocatalytic membrane reactors have some advantages with respect to conventional photoreactors, such as [3]: (I) confining of the photocatalyst in the reaction environment by means of the membrane; (II) control of a residence time of molecules in the reactor; (III) realization of a continuous process with simultaneous catalyst and products separation from the reaction environment. Moreover, the application of PMR instead of a conventional photoreactor allows avoiding some additional operations, such as coagulation–flocculation–sedimentation that are necessary in order to remove the catalyst from the treated solution. One benefit of this is energy saving and reducing the size of the installation. Another one is the possibility of reusing of the photocatalyst in further runs, which is practically impossible when coagulation is applied.

The PMRs described in the literature combine photocatalysis with pressure-driven membrane techniques, such as nanofiltration (NF) [2–6], ultrafiltration (UF) [3,7–9] and microfiltration (MF) [10]. However, it was found [2,6,7] that coupling photocatalysis and pressure-driven membrane processes resulted in a decrease of the permeate flux. A significant deterioration of process capacity was especially observed with microfiltration and ultrafiltration. The least effect of TiO_2 presence in the feed on the permeate flux was observed in the case of nanofiltration. Moreover, the membranes used in UF and MF do not have the capacity to remove low-molecular

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doi:10.1016/j.cattod.2005.12.003

organic compounds present in wastewaters as well as the products and by-products of their photodegradation.

The aim of the presented work was the investigation on the possibility of the application of a new hybrid process combining photocatalysis and direct contact membrane distillation (DCMD) for the degradation of azo-dye in aqueous solution. Membrane distillation (MD) 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 vapor pressure difference on both sides of the membrane, which depends on the temperature and the solution composition in the layers adjacent to the membrane [11,12]. Feed temperatures in MD usually range from 60 to 90 °C, although temperatures as low as 30 °C have been used. Therefore, low-grade, waste and/or alternative energy sources such as solar and geothermal energy can be coupled with MD systems for a cost efficient, energy efficient liquid separation system [13]. It can be found in the literature [13,14] that MD systems powered by solar energy could be cost competitive with reverse osmosis (RO) installations.

Comparing MD and pressure-driven processes such as RO, UF and MF it can be noticed that MD is a safer, more efficient process than RO for removing ionic components and non-volatile organic compounds from water. Since MD operates on the principles of vapor–liquid equilibrium, 100% (theoretical) of ions, macromolecules, colloids, cells, and other non-volatile constituents are rejected; pressure-driven processes such as RO, UF, and MF have not been shown to achieve such high levels of rejection. When applied to desalination, a well-designed MD system typically achieves water fluxes as high as 75 kg/m^2 h (i.e. ca. 1800 dm^3/m^2 day), which is comparable to RO [13].

In the present work the effect of the presence of TiO_2 in a feed on DCMD process performance, especially on permeate flux was investigated. Moreover, the rejection of the membrane distillation (MD) process regarding TiO_2 and photodegradation products was tested.

2. Experimental

The DCMD process was conducted in a laboratory-scale installation presented in Fig. 1. The main element of the system was a capillary module equipped with nine hydrophobic polypropylene (PP) membranes Accurel PP S6/2 (Membrana GmbH, Wuppertal, Germany), $d_{out}/d_{in} = 2.6/1.8$ mm. The effective area of the PP membranes used was equal to 0.014 m^2. The nominal pore size of the PP membranes applied amounts to 0.2 μm and the maximum pore size is ≤0.65 μm (according to the manufacturer). The bubble point value versus isopropyl alcohol (IPA) is ≥0.95 bar and the transmembrane flow (TMP) determined for IPA at 25 °C is ≥2.5 ml/min cm^2 bar [15].

In all the experiments the warm feed and cold distillate streams flowed in the module in a co-current mode. The volatile compounds present in a warm feed were transferred through the pores of the MD membrane and then condensed/dissolved directly in cold distillate (ultrapure water), whereas the non-volatile compounds were retained on the feed side. 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. In order to obtain this value the inlet feed temperature was set up at a level of 340 K. The inlet temperature of distillate was equal to 293 K.

Acid Red 18 ($C_{20}H_{11}N_2Na_3O_{10}S_3$) was applied as a model monoazo-dye. A chemical structure of the model compound is presented in Fig. 2. The concentration of model dye was equal to 10 or 30 mg/dm^3. Titanium dioxide Aeroxide® P25, Degussa, Germany was used as a photocatalyst. The catalyst loading

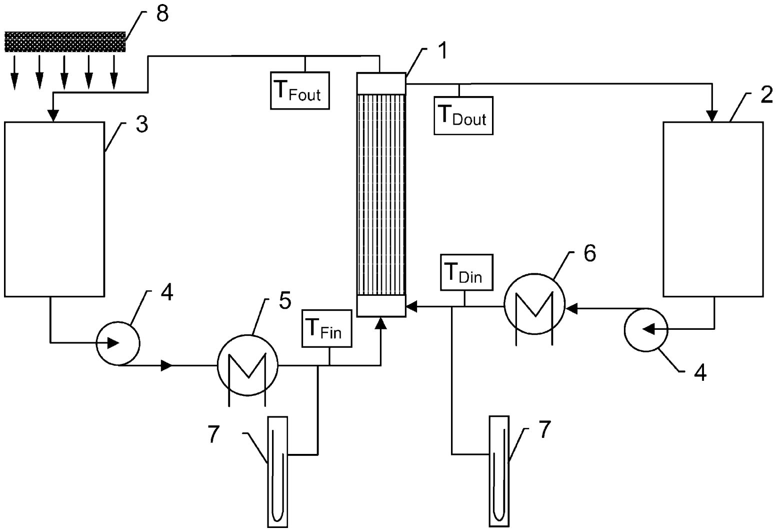

Fig. 1. Schematic diagram of the apparatus for MD: (1) membrane module; (2) distillate tank; (3) feed tank ($V = 2.9$ dm^3); (4) pump; (5) and (6) heat exchangers; (7) manometers; (8) UV lamp.

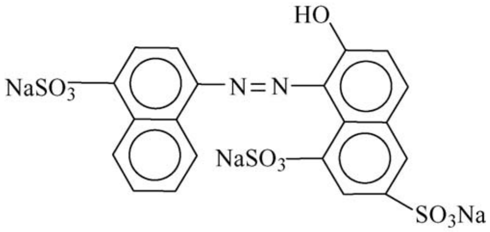

Fig. 2. Chemical structure of Acid Red 18.

ranged from 0.1 to 0.5 g TiO_2/dm^3. The basic properties of TiO_2 applied are presented in Table 1.

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 1305 cm^3. During the time of the experiment the water recovery (calculated on the basis of initial feed volume and final volume of distillate) amounted to ca. 36%. The reaction solution was illuminated with a mercury lamp Philips Cleo, emitting UV-A light ($\lambda_{max} = 355$ nm). The illumination intensity at the irradiation plate (feed tank, Fig. 1) was 146 W/m^2 for UV and 117 W/m^2 for vis range. The illumination intensities were measured with an LB 901 illumination meter equipped with the PD204AB (Macam Photometrics Ltd.) and CM3 (Kipp & Zonen) external sensors.

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 Acid Red 18 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), concentrations of ions (SO_4^{2-}, N–NO_3^-, N–NO_2^-, N–NH_4^+), total dissolved substances (TDS) content and conductivity (Ultrameter™ 6P, MYRON L COMPANY, USA). The SO_4^{2-} concentration was determined using the barium sulfate turbidimetric method. The N–NO_3^-, N–NO_2^-, N–NH_4^+ concentrations were determined colorimetrically using sodium salicylate method, Saltzman method and Nessler method, respectively. Moreover, the pH of the solutions was measured.

Table 1
Physico-chemical properties of Aeroxide® P25, Degussa, Germany (data provided by the manufacturer)

Properties	Value
Specific surface area (BET) (m^2/g)	50 ± 15
Average primary particle size (nm)	21
pH-value in 4% dispersion	3.5–4.5
TiO_2 content (wt.%)	>99.50
Fe_2O_3 content (wt.%)	<0.010
HCl content (wt.%)	<0.300
Sieve residue (by Mocker, 45 μm), acc. to DIN EN ISO 787/18, Apr. 1984 (wt.%)	<0.050

3. Results and discussion

3.1. Effect of TiO_2 concentration in a feed on MD process performance

The experimental results indicated that the addition of Aeroxide® TiO_2 P25 to the feed solution did not affect the permeate flux, regardless of the TiO_2 dosage applied. Fig. 3 presents the results obtained during the MD of ultrapure water and model dye solutions with the addition of different loadings of TiO_2. It can be seen that during the whole process the permeate flux was maintained at a level of about 335 dm^3/m^2 day, regardless of the catalyst dosage applied. It is known from the literature [3,8,10] that coupling photocatalysis and pressure-driven membrane processes resulted in a decrease of the permeate flux. A significant deterioration of the process capacity was especially observed with microfiltration and ultrafiltration. The least effect of the TiO_2 presence in the feed on permeate flux was noticed in the case of nanofiltration [4]. Sopajaree et al. [8] found a linear relationship between the permeate flux during UF and the concentration of TiO_2 in a feed. They observed a systematic decrease of permeability for the catalyst loading in the range from 0.5 to 3.0 g/dm^3. Xi and Geissen [10] investigated the effect of the presence of TiO_2 in a feed on permeate flux during MF. They reported that in the range of photocatalysts loadings of 0.5–2.0 g/dm^3 a decline of the permeate flux was observed, whereas for TiO_2 concentrations ranging from 2.0 to 5 g/dm^3 the flux increased with feed concentration; however, it still remained lower than the pure water flux. They attributed the phenomenon to the polylayer behavior of TiO_2 particles with a wide size (and shape) distribution. The authors concluded that the boundary layer near the membrane surface contains exclusively the larger particles and has a higher porosity, while the upper layer formed later consists of the finer particles with a lower porosity. At a relatively low TiO_2 concentration, the boundary layer near the membrane surface is so thin that the finer particles in the upper layer can enter into the pores of the porous lower one, resulting in a higher cake layer resistance and a lower permeate flux [10].

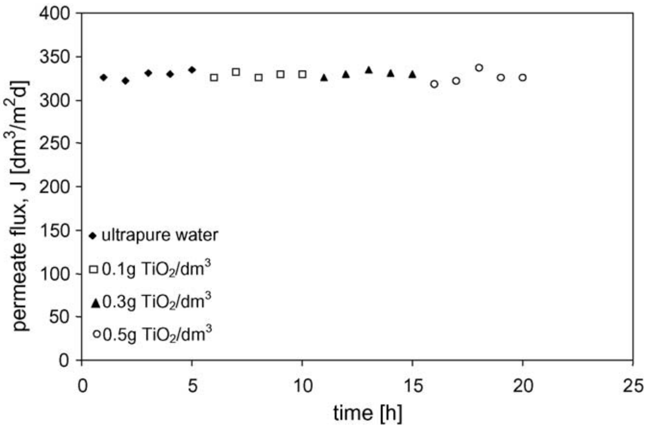

Fig. 3. Changes of permeate flux during MD; feed: distilled water and model dye solutions with different TiO_2 dosages; feed temperature: 343 K; distillate temperature: 293 K.

As was mentioned earlier, the addition of Aeroxide® TiO_2 P25 to the feed solution did not affect the permeate flux through the MD membrane, regardless of the TiO_2 dosage applied. The possible reason for the obtained results might be the different mechanism of mass transfer in the discussed pressure-driven processes and MD. The driving force in the case of UF, MF or NF is a pressure difference, whereas during MD transport through the membrane is due to vapor pressure difference on both sides of the membrane. Higher pressure applied during pressure-driven processes enhances cake formation on the membrane surface.

Taking into account the obtained results it can be concluded that MD could be a promising method of separation of TiO_2 from water streams. However, it should be also mentioned, that in general, the permeate fluxes in the hybrid processes photocatalysis–UF (MF), similarly as during UF or MF alone, are higher than during the investigated process utilizing MD. For example, the results described by Xi and Geissen [10] show, that MF of suspension of 0.135 vol.% of TiO_2 produces limiting fluxes of about 9840, 18,000 and 30,720 dm^3/m^2 day at a transmembrane pressure of 0.125 MPa and cross-flow velocities of 1–3 m/s, respectively. During nanofiltration [4] of TiO_2 suspension (1 g/dm^3) conducted at a pressure of 0.35 MPa, the permeate flux amounted to 240 dm^3/m^2 day, being lower than the flux obtained in the presented new PMR (i.e. 335 dm^3/m^2 h). On the other hand, a very important factor is also the quality of the permeate, which is significantly higher in case of the proposed hybrid system photocatalysis–MD, than in the systems combining photocatalysis and pressure-driven membrane processes, what will be discussed later in the paper.

On the basis of turbidity measurements it was found that the MD process is very effective in the separation of TiO_2. For catalyst dosage of 0.1 g/dm^3 the turbidity of the feed was equal to 369 NTU, whereas after 5 h of the process performance the turbidity of the distillate amounted to 0.13 NTU. In the case of TiO_2 dosages equal to 0.3 and 0.5 g/dm^3 these values amounted to 984 versus 0.13 NTU and 1680 versus 0.19 NTU, respectively.

3.2. Effectiveness of the removal of model azo-dye Acid Red 18 during hybrid process photocatalysis–DCMD

The photocatalytic decomposition of Acid Red 18 was conducted for 5 h at a temperature of 333 K. In order to obtain this value the inlet feed temperature was set up at a level of 340 K. The reaction temperature was selected on the basis of our earlier investigations [16]. It was found that a linear correlation between the apparent rate constant of photodecomposition of Acid Red 18 and the reaction temperature exists in the range of 293–333 K. From that it can be observed that although the O_2 solubility in water decreases with increasing reaction temperature, the effectiveness of photodegradation increases.

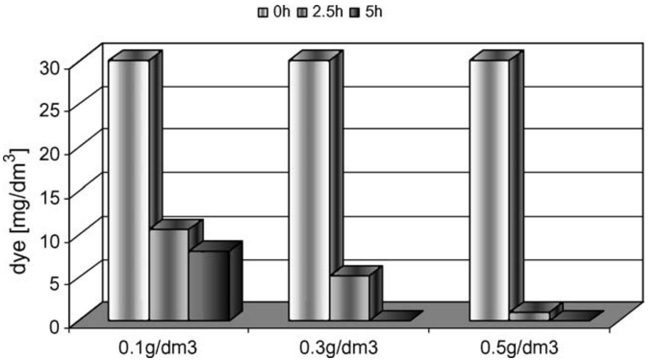

Fig. 4. Changes of Acid Red 18 concentration in the feed during photocatalytic decomposition in the PMR; $c_0 = 30$ mg/dm^3; catalyst loading: 0.1–0.5 g/dm^3.

The obtained results showed that hybrid process photocatalysis–MD is a very effective method of removal of organic compounds such as azo-dye from water. For an initial dye concentration equal to 10 mg/dm^3 the solution was decolorized during the first hour of illumination with all of the catalyst concentrations used. In the case of initial Acid Red 18 concentration equal to 30 mg/dm^3 it was found that the catalyst dosage of 0.1 g/dm^3 was too low to obtain complete dye decomposition. After 5 h of irradiation the dye concentration in the feed was equal to ca. 8 mg/dm^3 (Fig. 4). With higher catalyst concentrations the solution was faded after 5 h of illumination. The fading of the solution was associated with the cleavage of azo linkage in the dye molecule. 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 naphthalene rings). 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 [17]. The cleavage of –N=N– bonds leads to the decolorization of the dyes, which was observed in the discussed experiment.

Fig. 5 presents the UV–vis spectra of Acid Red 18 recorded for the initial solution ($c_0 = 30$ mg/dm^3) and for the solution after 2.5 h of photodegradation in the PMR. The catalyst loading amounted to 0.3 g/dm^3. The spectrum of dye before photodegradation ($t = 0$ h) exhibits three main peaks at a

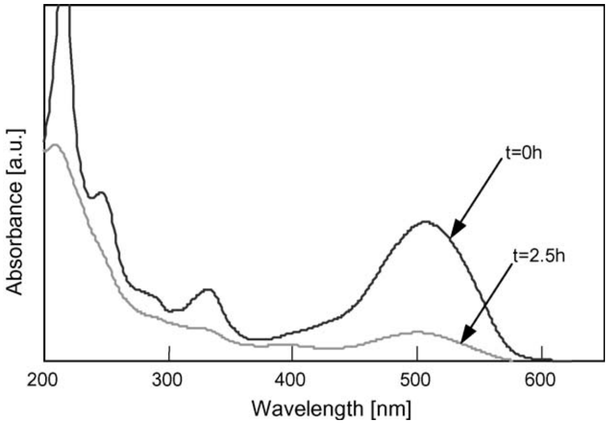

Fig. 5. Changes in the UV–vis spectra of Acid Red 18 during photodegradation; initial dye concentration: 30 mg/dm^3; catalyst loading: 0.3 g TiO_2/dm^3.

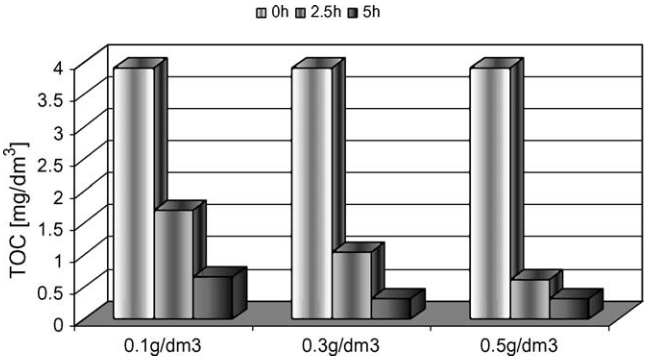

Fig. 6. Changes of TOC concentration in time for different photocatalyst loadings; initial dye concentration: 10 mg/dm^3.

wavelengths of 507, 330 and 215 nm. The absorption in the visible region can be attributed to chromophore containing azo linkage, whereas the bands observed in the UV region can be assigned to aromatic (naphtalene) rings present in the Acid Red 18 molecule (Fig. 2). It can be observed that during irradiation not only a rapid decolorization of the dye, but also significant degradation of the aromatic structure proceeds.

Decolorization of the solution does not provide a complete data on the azo-dye degradation. Therefore, monitoring of other parameters such as TOC is very important. Fig. 6 shows changes of TOC concentration in the feed during the decomposition of the Acid Red 18 for an initial solution concentration of 10 mg/dm^3 and different catalyst loadings. It can be seen that the highest rate of organic photodegradation was obtained at the beginning of illumination. After 2.5 h of the process the TOC content was lowered by ca. 56% for a TiO_2 concentration of 0.1 g/dm^3, by ca. 73% in the case of 0.3 g TiO_2/dm^3 and by ca. 84% when 0.5 g TiO_2/dm^3 was applied. After 5 h of irradiation the concentration of TOC ranged from 0.3 to 0.6 mg/dm^3 (Fig. 6).

In the case of an initial Acid Red 18 concentration equal to 30 mg/dm^3 a high TOC concentration (Fig. 7) indicated that a significant amount of by-products of photodegradation of azo-dye were still present in the feed and the decomposition was not complete. For TiO_2 loading of 0.1 g/dm^3 the TOC content after 5 h of irradiation was equal to 10.2 mg/dm^3, whereas for 0.5 g TiO_2/dm^3 the concentration of organic carbon in the feed amounted to 4.4 mg/dm^3 (Fig. 7).

The mechanism of photocatalytic degradation of different azo-dyes has been widely discussed in the literature [17–20]. In general, it is often reported that amongst the 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 [18].

Taking into account the composition of the permeate it was found that only a small amount of by-products of Acid Red 18 photodegradation was transported through the MD membrane. Moreover, a complete retention of the model dye was observed. This results from the fact that the MD membrane is permeable for volatile compounds and water vapour only. Acid Red 18 is a non-volatile compound, therefore the total amount of the dye remained on the feed side. Among the volatile compounds that passed through the membrane some organic compounds were present. This conclusion is supported by the measurements of the TOC concentration in the distillate. The value of this parameter after 5 h of the process performance was in the range of 0.4–1.0 mg/dm^3 (Fig. 8). According to the literature data [18] it can be supposed that the organic compounds passing through the membrane were volatile organic acids, such as formic and acetic acid.

It can be observed (Fig. 8) that changes of the TOC value in the distillate for a low (i.e. 10 mg/dm^3) and high (i.e. 30 mg/dm^3) initial dye concentration as a function of catalyst loading have a slightly different course. Taking into account the accuracy of the TOC measurement technique it can be concluded that for a low dye concentration the TOC content was practically independent of the catalyst loading. The measured values amounted to 0.4 mg C/dm^3 when 0.1 and 0.3 g TiO_2/dm^3 was applied and 0.5 mg C/dm^3 in the case of 0.5 g TiO_2/dm^3. When a higher initial dye concentration was used, the TOC content in the distillate was equal to 1.0, 0.9 and 0.6 mg C/dm^3 for TiO_2 concentrations of 0.1, 0.3 and 0.5 g/dm^3, respectively. Similar to what has been discussed above, it can be assumed that for catalyst loadings of 0.1 and 0.3 g

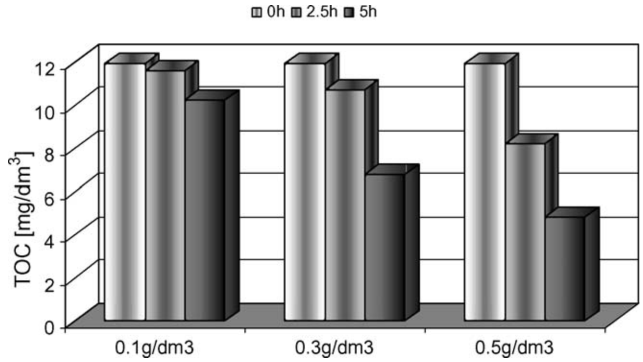

Fig. 7. Changes of TOC concentration in time for different photocatalyst loadings; initial dye concentration: 30 mg/dm^3.

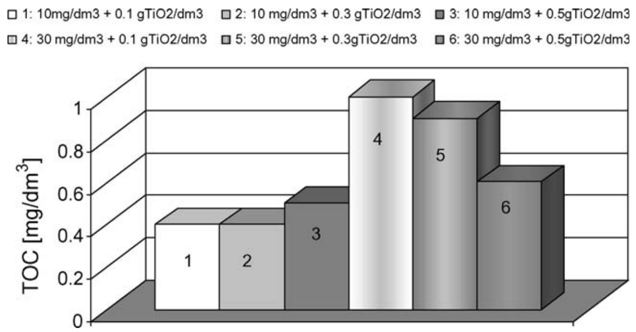

Fig. 8. TOC concentration in distillate for different initial dye concentrations and catalyst loadings.

TiO_2/dm^3 the TOC concentration was constant and independent of the catalyst concentration and only in the case of the highest TiO_2 loading the TOC value was lower. The latter result might be explained by a more efficient decomposition of the Acid Red 18 with a highest catalyst loading. In Fig. 8 it can be also seen that for the initial dye concentration of 10 mg/dm^3 TOC content in distillate was almost twice lower than in case of the higher Acid Red 18 concentration. This can suggest that the initial dye concentration has a significant effect on the composition of the distillate. With lower dye concentration the photodecomposition of organic compounds in the feed was almost complete (Fig. 6), moreover, the quantity of volatile organic acids formed was much smaller. In the case of an initial Acid Red 18 concentration of 30 mg/dm^3 the amount of organic compounds that were decomposed giving CO_2 was not so high. Additionally, the concentration of organic products of degradation was much higher than in the previous case, thus, the TOC concentration in the distillate was also higher.

Although a complete rejection of organic compounds was not achieved, it should be noticed that the TOC concentration in the distillate was very low. Moreover, the product quality was significantly higher than in case of other PMR combining photocatalysis with pressure-driven membrane processes. Comparing the discussed results with the literature data on PMRs it can be found that the presented hybrid process is one of the most effective methods of treatment of colored waters. Molinari et al. [21] performed photocatalytic decomposition of Congo Red and Patent Blue in PMR utilizing nanofiltration. They found that the application of the NF membrane was beneficial because in addition to its role as a barrier for the catalyst, the product (permeate) contained a very low concentration of dye with respect to the feed. In our experiments, when a solution of Acid Red 18 was treated using DCMD, a complete rejection of the model dye was obtained. Sopajaree et al. [8] investigated the effectiveness of the photodecomposition of methylene blue (MB) in an integrated photoreactor–UF unit operation. The process was carried out in a separate mode, i.e. the solution of model dye was irradiated separately and then incorporated in the UF process. The removal of MB and TOC was high (85.6–97.7 and 41.9–73.8%, respectively) although dependent on the agglomeration of TiO_2 particles. The authors found that agglomerates of photocatalyst that are formed during the course of the process negatively affect the effectiveness of dye photodegradation.

Other parameters monitored were conductivity and total dissolved solids (TDS) concentration. The TDS parameter includes all the dissolved species present in water, i.e. inorganic ions (e.g. sulfates, nitrates, etc.) and all manner of organic compounds. It was observed (data not shown) that elongation of the reaction time resulted in an increase of conductivity as well as concentration of TDS in the feed. In the case of the initial dye concentration of 10 mg/dm^3 the initial conductivity of the feed amounted to ca. 17 μS/cm, whereas after 5 h of photodecomposition the value of this parameter was about three times higher, regardless of the catalyst loading applied. Similarly, the initial concentration of TDS in the feed amounted to ca. 11 ppm and after 5 h of the process performance it reached the value of ca. 35 ppm. In the case of the initial concentration of Acid Red equal to 30 mg/dm^3 some differences between feed composition for different catalyst loadings were observed. The highest TDS and conductivity values were found for catalyst concentration of 0.3 g TiO_2/dm^3. After 5 h of illumination the TDS content amounted to ca. 104 ppm and the conductivity was equal to 160 μS/cm. Lower values of these parameters in the case of 0.5 g TiO_2/dm^3 might suggest that the decomposition rate of the dye was higher than in the case of 0.3 g TiO_2/dm^3, which is in agreement with the TOC concentration in this solution. During decomposition of the organic compounds water and CO_2 were formed—thus, the amount of species present in the solution decreased. On the other hand, for a catalyst concentration of 0.1 g TiO_2/dm^3 the effectiveness of photodegradation was lower, thus the TDS content and conductivity were also lower than in the previous case.

The two discussed parameters show that during photocatalytic degradation of Acid Red 18 a large number of other species is formed, which results in higher conductivity that is associated with the number of ions present in the solution and also a higher TDS concentration, which is an indicator of the quantity of different substances dissolved in the solution. The observed increase of the values of the discussed parameters was also associated with decreasing of the volume of the feed solution resulting from the transport of water vapour through the membrane pores.

Taking into account the composition of the distillate it was found that at the beginning of the process the conductivity and TDS concentration increased significantly, e.g. for an initial dye concentration $c_0 = 10$ mg/dm^3 and 0.1 g TiO_2/dm^3 conductivity increased from 1.5 to 2.7 μS/cm and TDS from 0.9 to 6.1 ppm, respectively. During the next hours of the process performance the values of these parameters in the distillate became lower—for the discussed example they amounted to 2.3 μS/cm and 3 ppm after 5 h of the hybrid process operation. Similar changes were observed for other dye concentrations and catalyst loadings. It can be supposed that at the beginning of the process a significant amount of by-products of photodegradation is produced. Then, the species transported through the MD membrane during the first hours of the process performance are diluted in an increasing volume of pure water obtained on the distillate side. Moreover, it can be supposed that during the next hours of the process performance the amount of volatile compounds transferred through the membrane was significantly lower. A simultaneous effect of these two factors resulted in a decrease of the values of the discussed parameters in time.

From the molecular formula of Acid Red 18 (Fig. 2) it can be found that amongst the final products of its photodegradation some inorganic species such as NH_4^+, NO_2^-, NO_3^-, and SO_4^{2-} should be found. Therefore, other parameters investigated were changes of concentration of these ions in the feed and distillate. Fig. 9 presents a concentration of inorganic N in the feed and distillate after 5 h of photodecomposition of the model dye for an initial concentration of 10 mg/dm^3 with different photocatalyst loadings. The inorganic N shown is a sum of

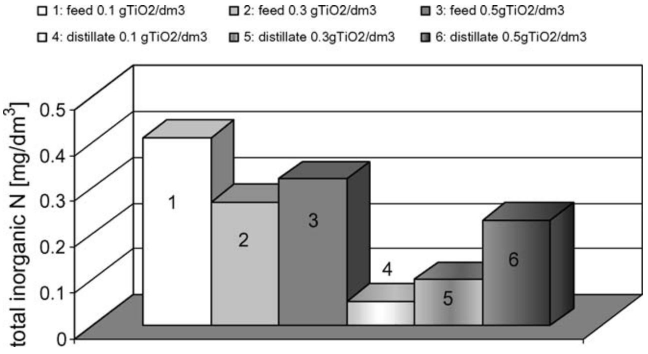

Fig. 9. Concentration of inorganic nitrogen (sum of N–NO_3^-, N–NO_2^- and N–NH_4^+) in feed and distillate after 5 h of photodecomposition for different catalyst loadings; initial dye concentration: 10 mg/dm^3.

N–NO_3^-, N–NO_2^- and N–NH_4^+. It can be observed that inorganic N was present not only in the feed, but also in the distillate. This inorganic nitrogen was mainly in the form of ammonia, as gaseous NH_3 can be transported through the pores of the MD membrane. In the feed solution also N–NH_4^+ was found to be the main form of nitrogen. In the performed experiments, the concentration of N–$NH_4^+$was almost twice higher than the concentration of N–NO_3^-. This might be associated with the process parameters applied. The feed temperature was high (333 K) which restricts the solubility of oxygen in the solution. Thus, the O_2 concentration was probably too low to assure the complete oxidation of NH_4^+ to NO_3^-.

It can be also observed (Fig. 9) that the trend of changes of inorganic N concentration in the feed and distillate was inversed, i.e. the nitrogen concentration in the feed decreased with increasing catalyst loading; whereas, in the case of the distillate, higher catalyst loading resulted in higher N content. One reason for the obtained results can be that with the catalyst loading of 0.5 g TiO_2/dm^3 the decomposition rate was higher than in the case of lower photocatalyst concentrations. Thus, at the beginning of the process significant amount of inorganic N could be produced. Some amount of these ions was immediately transported through the membrane and condensed in the distillate. As a result the concentration of inorganic N in the feed was lower and in the distillate higher, in comparison with the results obtained for 0.1 and 0.3 g TiO_2/dm^3.

As was mentioned earlier, another parameter monitored was SO_4^{2-} content. It was found (data not shown) that the concentration of sulphates in the distillate did not exceed the value of 0.3 mg/dm^3. The concentration of SO_4^{2-} in the feed varied from ca. 11 to 18 mg/dm^3, for different dye concentration and catalyst loading. The obtained results show that the MD process is very effective in the removal of inorganic ions.

4. Conclusions

The presented results reveal that hybrid photocatalysis–MD system has many advantages over a typical photocatalytic batch reactor as well as other PMRs combining photocatalysis with pressure-driven membrane processes. Degradation and separation could be performed at the same time and in the same place, which minimizes the size of the installation.

Another advantage of the PMR presented is the complete separation of the dye and other non-volatile compounds, thus the product (permeate) is practically pure water. After 5 h of the hybrid process performance almost complete rejection of TOC, TDS and inorganic ions (N–NO_3^-, N–NO_2^-, N–NH_4^+, SO_4^{2-}) was obtained. Among the volatile compounds that passed through the membrane some organic compounds were present as was indicated by the measurements of the TOC concentration in the distillate. The value of this parameter after 5 h of the process performance was in the range of 0.4–1.0 mg/dm^3. For the initial dye concentration of 10 mg/dm^3 the TOC content in the distillate was almost twice lower than in the case of a higher Acid Red 18 concentration, which suggests that the initial dye concentration has a significant effect on the composition of the distillate. Conductivity of the distillate was lower than 2.5 μS/cm and the TDS concentration did not exceed the value of 3 ppm. The inorganic nitrogen detected in the distillate was mainly in the form of ammonia, as gaseous NH_3 can be transported through the pores of the MD membrane. The concentration of total N in the distillate was not higher than 0.23 mg/dm^3.

It should be mentioned also, that hybridization of photocatalysis and MD allows avoiding an increase of the feed concentration. During MD alone, since the obtained permeate is practically pure water, the feed concentration gradually increases. When the process is combined with photocatalysis, a continuous degradation of the compounds present in the feed solution proceeds and thus, the above mentioned increase of concentration does not exist.

The process can be performed at a feed temperature considerably lower than its boiling point. This permits the utilisation of waste heat existing at various industrial sites and thus the cost of heating of the solution can be significantly reduced. Moreover, no cooling of the UV source must be applied and the heat emitted by this source can also be utilized for heating of the feed. Since it was found that the photodecomposition rate of Acid Red 18 was higher when the process was conducted at 333 K than at a room temperature, application of MD instead of pressure-driven membrane processes in a PMR seems to be more beneficial.

Another advantage is that the MD process can be successfully applied to the 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, the application of DCMD is much more advantageous in comparison with pressure-driven membrane processes, where a significant fouling was observed.

In view of this, the application of MD in photocatalytic membrane photoreactors seems to be a very promising method of water and wastewater treatment.

Acknowledgement

In the years 2004–2007 this work has been supported by a grant from The Polish State Committee for Scientific Research, No. 3 T09B 136 27.

References

[1] J. Grzechulska, A.W. Morawski, Appl. Catal. B Environ. 46 (2003) 415.
[2] R. Molinari, M. Borgese, E. Drioli, L. Palmisano, M. Schiavello, Catal. Today 75 (2002) 77.
[3] R. Molinari, L. Palmisano, E. Drioli, M. Schiavello, J. Membr. Sci. 206 (2002) 399.
[4] R. Molinari, C. Grande, E. Drioli, L. Palmisano, M. Schiavello, Catal. Today 67 (2001) 273.
[5] M.A. Artale, V. Augugliaro, E. Drioli, G. Golemme, C. Grande, V. Loddo, R. Molinari, L. Palmisano, M. Schiavello, Ann. Chim. 91 (2001) 127.
[6] R. Molinari, M. Borgese, E. Drioli, L. Palmisano, M. Schiavello, Ann. Chim. 91 (2001) 197.
[7] K. Sopajaree, S.A. Qasim, S. Basak, K. Rajeshwar, J. Appl. Electrochem. 29 (1999) 533.
[8] K. Sopajaree, S.A. Qasim, S. Basak, K. Rajeshwar, J. Appl. Electrochem. 29 (1999) 1111.
[9] R. Molinari, M. Mungari, E. Drioli, A. Di Paola, V. Loddo, L. Palmisano, M. Schiavello, Catal. Today 55 (2000) 71.
[10] W. Xi, S.-U. Geissen, Water Res. 35 (2001) 1256.
[11] M. Tomaszewska, M. Gryta, A.W. Morawski, Sep. Purif. Technol. 14 (1998) 183.
[12] M. Gryta, M. Tomaszewska, J. Grzechulska, A.W. Morawski, J. Membr. Sci. 181 (2001) 279.
[13] K.W. Lawson, D.R. Lloyd, J. Membr. Sci. 124 (1997) 1.
[14] S. Bouguechaa, B. Hamrounib, M. Dhahbia, Desalination 183 (2005) 151.
[15] R.K. O'Leary, P.J. LaRocca, Growth environment assembly and method of use thereof, United States Patent 5,482,854 (1996).
[16] S. Mozia, M. Tomaszewska, A.W. Morawski, Desalination 185 (2005) 1873.
[17] Ch. Zhu, L. Wang, L. Kong, X. Yang, L. Wang, S. Zheng, F. Chen, F. MaiZhi, H. Zong, Chemosphere 41 (2000) 303.
[18] I.K. Konstantinou, T.A. Albanis, Appl. Catal. B Environ. 49 (2004) 1.
[19] C. Galindo, P. Jacques, A. Kalt, J. Photochem. Photobiol. A Chem. 130 (2000) 35.
[20] N. Daneshvar, D. Salari, A.R. Khataee, J. Photochem. Photobiol. A Chem. 157 (2003) 111.
[21] R. Molinari, F. Pirillo, M. Falco, V. Loddo, L. Palmisano, Chem. Eng. Process. 43 (2004) 1103.