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Effect of process parameters on photodegradation of Acid Yellow 36 in a hybrid photocatalysis–membrane distillation system

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ABSTRACT

Photocatalytic membrane reactors (PMRs) seem to be a very promising method of solving problems concerning separation of photocatalyst as well as products and by-products of photodegradation from the reaction mixture. In the presented studies an anatase-phase TiO_2 was applied for degradation of Acid Yellow 36 (AY36) in the PMR coupling photocatalysis and direct contact membrane distillation (DCMD). The effect of different process parameters such as dye concentration, reaction temperature and photocatalyst loading on the effectiveness of degradation of AY36 was investigated. Moreover, in order to compare the effectiveness of AY36 photodegradation during photocatalysis alone and the hybrid process, additional experiments without application of MD were conducted. The addition of TiO_2 to a feed did not affect the permeate flux, regardless of the process conditions applied. The flux remained constant and equal to the maximum permeate flux during about 400 h of experiments. The highest decolorization of AY36 solution during hybrid process was observed at the highest photocatalyst loading applied (0.5 g TiO_2/dm^3). The increase of the reaction temperature from 313 to 333 K resulted in an increase of the photodegradation rate of AY36. After 5 h of the hybrid process the effectiveness of dye degradation calculated on a basis of AY36 mass in a feed solution amounted to 31, 36 and 42% for the reaction temperatures of 313–333 K. Similar results were obtained when photocatalysis was conducted in the MD installation but with disconnected MD module. It was found that an improvement of AY36 photodegradation could be achieved by a decrease of initial dye concentration. Comparing the results obtained in a conventional slurry photoreactor and in the PMR and taking into account both, the rate of azo dye degradation and the quality of the product, it could be concluded that more beneficial configuration seems to be the PMR.

1. Introduction

The photocatalytic reactors described in literature can be divided in the two main groups: (a) reactors with TiO_2 suspended in the reaction mixture and (b) reactors with TiO_2 fixed on a carrier material (e.g. glass, quartz, stainless steel). In the former case the catalyst particles have to be separated from the treated water after the process. A very promising method for solving problems concerning separation of photocatalyst as well as products and by-products of photodegradation from the reaction mixture might be application of hybrid photocatalysis–membrane processes. Utilization of the hybrid system instead of a conventional photoreactor allows avoiding some additional operations, such as coagulation–flocculation–sedimentation that are necessary in order to remove catalyst from the treated solution. One benefit from this might be energy saving and reducing the size of installation. Another one is possibility of reusing of the photocatalyst in further runs.

Hybrid photocatalysis–membrane systems are usually called “photocatalytic membrane reactors” (PMRs). The literature [1,2] presents a few possible configurations of PMRs. They include: (A) irradiation of the membrane cell (module) and (B) irradiation of a feed tank containing catalyst in suspension. In configuration (A) two sub-cases can be distinguished: (A1) catalyst deposited in/on the membrane, (A2) catalyst in suspension. In the PMRs utilizing immobilized TiO_2 the membrane acts as a support for the photocatalyst and might act as a barrier for the molecules present in the solution (initial compounds and products or by-products of their decomposition). In the PMRs with catalyst in suspension the membrane would play both the role of a simple barrier for the photocatalyst particles and of a selective barrier for the molecules to be degraded and the photodegradation intermediates. The latter role depends on the separation characteristics of the membrane used and the membrane process applied.

When a photocatalytic membrane is applied (A1), the photodegradation of the pollutants takes place on a surface of a

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membrane or within its pores. Photocatalytic membranes for the PMRs can be prepared from different materials and in different ways. They include TiO_2/Al_2O_3 composite membranes [3–7], TiO_2 supported on polymer or metallic membranes [8–10] or doted polymer membranes containing TiO_2 particles entrapped within a membrane structure during membrane formation step [11–13]. The effectiveness of photodegradation of contaminants in case of PMRs utilizing a photocatalytic membrane with immobilized TiO_2 was found to be lower than in case of PMRs with suspended catalyst [12]. Moreover, when polymer membranes are used, there is a danger of destruction of the membrane structure by UV light or hydroxyl radicals [14]. In view of this, a promising configuration seems to be hybridization of membrane process and photocatalysis in suspension.

The PMRs utilizing catalyst in suspension that are described in literature have been applied to liquid phase photodegradation of humic [15–18] and fulvic [19] acids, bisphenol A [20,21], phenol [1], 4-nitrophenol [2], 4-chlorophenol [18], pharmaceutical and diagnostic residues [22–24], grey water from domestic washing operations [25], para-chlorobenzoate [26], river water [27], dyes [1,12,18,28–30] and many other pollutants. Most of these PMRs combine photocatalysis with pressure driven membrane processes such as microfiltration (MF) [15,18–22,25–28], ultrafiltration (UF) [1,16,17,29,30] and nanofiltration (NF) [1,2,12,23,24]. 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, because small molecules can pass easily through the membranes used, even in case of NF.

Recently new types of photocatalytic membrane reactors combining photocatalysis with dialysis [31] and pervaporation [32] have been described. In our previous publications [33–35] we have also presented a new type of the PMR utilizing photocatalysis using TiO_2 P25 (Degussa) and direct contact membrane distillation (DCMD, MD) for removal of azo dyes from water. 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 vapour pressure difference on both sides of membrane, which depends on the temperature and the solutions composition in the layers adjacent to the membrane [36,37]. Feed temperatures in MD usually range from 333 to 363 K, although temperatures as low as 303 K have been used. 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 main obstacles for the full scale application of MD are rather high energy demand and low permeate flux. However, some attempts to apply a low-grade, waste and/or alternative energy sources such as solar and geothermal energy have been recently made in order to design a cost efficient, energy efficient liquid separation system [38]. It can be found in literature [38,39] that MD systems powered by solar energy could be cost competitive with reverse osmosis (RO) installations.

In our previous papers [33–35] we have shown, that one of the main advantages of utilization of MD in a photocatalytic membrane reactor was high quality of the product (distillate). Moreover, no membrane fouling due to the presence of TiO_2 was observed.

The presented studies have focused on application of an anatase-phase TiO_2 for degradation of azo dye Acid Yellow 36 (AY36) in a PMR combining photocatalysis and DCMD. The effect of different process parameters such as initial dye concentration, reaction temperature and photocatalyst loading on the effectiveness of photodegradation of AY36 was investigated. Moreover, in order to compare the photodegradation efficiency during photocatalysis alone and hybrid process photocatalysis–MD, additional experiments without application of MD were conducted. The effect of the presence of TiO_2 in a feed on DCMD process performance was also determined.

2. Experimental

The catalyst used in this study (denoted as A-700-1 h) was prepared from crude 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 was characterized by N_2 adsorption measurement at 77 K (Autosorb 3, Quantachrome, USA) and XRD analysis (Rigaku RINT-2000 diffractometer with Cu Kα radiation (λ = 1.54056 Å) from an 18 kV source). The A-700-1 h contained primarily anatase-phase (97%). A trace amount of rutile was not due to the heat treatment, because it was also detected in the as-received sample of the crude TiO_2. The crystallite size of anatase in A-700-1 h was 27 nm. BET surface area of the A-700-1 h amounted to 33.4 m^2/g. The photocatalyst loadings amounted to 0.1, 0.3 or 0.5 g TiO_2/dm^3.

Acid Yellow 36 obtained from the Chemical Factory Boruta–Kolor Sp.z.o.o (Poland) was used as a model azo dye. AY36 is widely applied for dyeing of wool, nylon, silk, paper, ink, wood, fur and cosmetics. The initial concentration of AY36 ($C_{18}H_{14}N_3NaO_3S$) was equal to 10 or 30 mg/dm^3. Chemical structure of the model compound is presented in Fig. 1.

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_{out}/d_{in} = 2.6/1.8 mm, Membrana GmbH, Wuppertal, Germany), having the effective (internal) area of 0.0127 m^2. The nominal pore size of the PP membranes applied was 0.2 μm and the maximum pore size was $\leq$0.65 μm (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. Feed solution and photocatalyst were

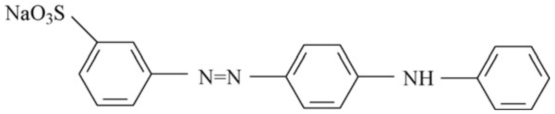

Fig. 1. Chemical structure of Acid Yellow 36.

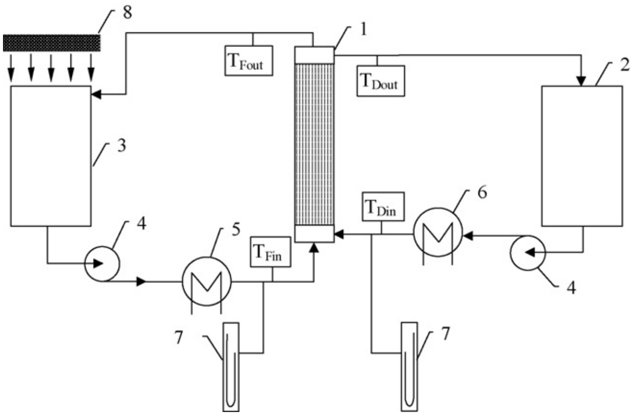

Fig. 2. Schematic diagram of the apparatus for hybrid photocatalysis–MD process: (1) membrane module; (2) distillate tank; (3) feed tank (V = 2.9 dm^3); (4) pump; (5) and (6) heat exchangers; (7) manometers; (8) UV lamp; T_{Fin}, T_{Din}, T_{Fout}, T_{Dout} – inlet and outlet temperatures of feed and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

introduced to the feed tank (Fig. 2) at the beginning of the experiment. The retentate was recirculated to the feed tank whereas permeate was collected in the distillate tank. The reaction solution was irradiated with UV-A light (λ_{max} = 365 nm; UV light intensity at the irradiation plate: 80 W/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 TiO_2 surface. The process was conducted for 5 h. After a defined time of irradiation the samples of feed solution were filtered through a 0.45 μm membrane filter and analyzed. The photodegradation rate of AY36 was estimated on the basis of (I) changes in UV/VIS spectra (λ_{max} = 431 nm), (II) conductivity and (III) concentration of selected organic acids being photoproducts of dye decomposition (HPLC ELITE LaChrom, Hitachi, Japan; Unison UK-C8 column; analysis conditions: eluent – 20 mM H_3PO_4, flow rate of eluent: 0.6 cm^3/min, temperature: 37 °C; UV detector wavelength: 210 nm). Moreover, pH of the feed solution and distillate was measured.

In order to compare the effectiveness of AY36 removal during photocatalysis alone, MD alone and hybrid process photocatalysis–MD, additional experiments were conducted: (1) photocatalysis in the MD installation but with disconnected membrane module (case 1), (2) photocatalysis in a batch slurry photoreactor (case 2) and (3) MD without photocatalyst addition (case 3). In the case 1 the MD membrane module was disconnected and a tube having the same length as the module was connected instead. The process parameters were as follows: solution flow rate: 0.5 m/s, photocatalyst loading: 0.5 g/dm^3, reaction temperature: 313, 323 or 333 K, respectively. In the case 2 the photocatalysis was conducted in a batch slurry reactor having the same geometry as the reactor in the hybrid process. The solution in the reactor was continuously stirred with a magnetic stirrer. The TiO_2 loading amounted to 0.5 g/dm^3 and the reaction temperature was 298 K. The MD alone (case 3) was conducted at the solution flow rate of 0.5 m/s. The feed temperature in the feed tank amounted to 333 K. Other parameters were the same as previously described.

3. Results and discussion

3.1. Effect of TiO_2 presence in a feed on permeate flux

During our previous investigations [33–35,40] we have found that addition of pure TiO_2 such as commercially available Aeroxide® P25 (Degussa, Germany) or ST-01 (Ishihara-Sangyo Co. Ltd., Japan) did not affect the permeate flux through the MD membrane, regardless of the catalyst loading applied. Similar results were obtained with application of A-700-1 h as a photocatalyst. The permeate flux remained constant during the experiments and was not affected by the presence of the A-700-1 h, regardless of the process conditions (i.e. temperature and catalyst loading). In other words, the value of the permeate fluxes measured during the hybrid photocatalysis–MD process and during MD in which pure water was applied as a feed were the same, i.e. about 302 dm^3/m^{2}d at the inlet feed temperature (T_{Fin}) of 335 K; 164 dm^3/m^{2}d at T_{Fin} = 324 K and 86 dm^3/m^{2}d at T_{Fin} = 313 K, respectively.

It should be mentioned here that the membrane module which was applied in the presented experiments has been working in the hybrid photocatalysis–MD system for about 400 h. During this time different TiO_2 photocatalyst loadings, reaction temperatures and feed flow rates were applied. At the end of each experiment, usually after 5 or 8 h of the process, the MD module was washed with distilled water for about 30 min. At the end of the research we have found that the permeate flux was stable and equal to the maximum flux measured for distilled water. From this point of view, the application of DCMD is much more advantageous in comparison with pressure-driven membrane processes, such as MF and UF, where a significant deterioration of the flux was observed.

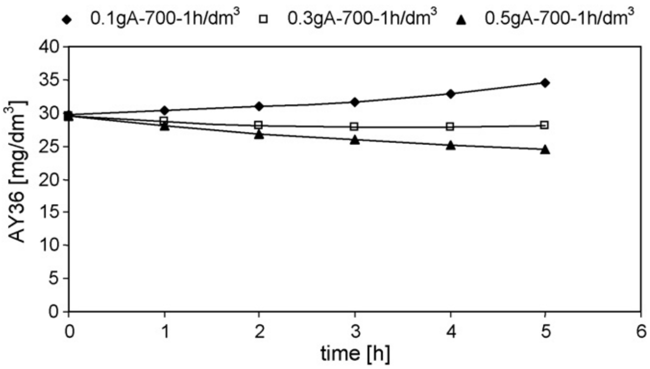

Fig. 3. Changes of dye concentration in a feed during photocatalytic decomposition of Acid Yellow 36 in the PMR; c_0 = 30 mg/dm^3, TiO_2 loadings: 0.1–0.5 g/dm^3, T = 333 K.

3.2. Effect of photocatalyst loading on photodegradation rate of AY36 in the hybrid photocatalysis–MD system

The photocatalytic degradation of AY36 in the PMR was conducted for 5 h at the temperature of 333 K. The photocatalyst loadings ranged from 0.1 to 0.5 g/dm^3 and the initial concentration of the dye was 30 mg/dm^3. Changes of the dye concentration in feed solution vs. time of the hybrid process performance are presented in Fig. 3.

It can be observed that the photocatalyst concentration had a significant effect on the AY36 degradation. At the lowest A-700-1 h loading (0.1 g/dm^3) the concentration of the dye was continuously increasing in time, from c_0 = 30 mg/dm^3 at the beginning of the process to c_5 = 34.6 mg/dm^3 at the end. When the catalyst loading of 0.3 g/dm^3 was applied, the AY36 concentration was slightly decreasing; however, there was no significant difference between c_0 (30 mg/dm^3) and c_5 (28 mg/dm^3). In case of the highest A-700-1 h loading (0.5 g/dm^3) the azo dye concentration decreased more, reaching at the end of the process the value of 24.6 mg/dm^3.

The data presented in Fig. 3 might be confusing, especially in case of the catalyst loading of 0.1 g TiO_2/dm^3, at which an increase of AY36 concentration in time can be observed. The reason for such results is the reduction of feed volume due to the transport of water vapour through the membrane pores. In the MD process the volatile compounds present in warm feed are transported through the pores of the membrane and then condensed/dissolved directly in cold distillate. As a result, the volume of feed solution is continuously decreasing and the concentration of non-volatile compounds (such as AY36) present in the solution is increasing.

In our earlier investigations on the hybrid photocatalysis–MD process [41] we have already observed a phenomenon similar to the one presented in Fig. 3 in case of catalyst loading of 0.1 g TiO_2/dm^3. During photodegradation of methylene blue (MB) on different photocatalysts the concentration of the dye was decreasing during first few hours of the process and then started increasing. When we express the amount of the dye in the feed solution not in terms of concentration but in the unit of mass we may found that during the final hours of the process the mass of MB remained almost constant. These results led us to a conclusion that the degradation of MB was probably inhibited by the by-products of its decomposition [41].

If we present the data shown in Fig. 3 in terms of mass units instead of concentrations we will obtain the relationship as demonstrated in Fig. 4. Now, it can be clearly seen that AY36 was continuously degraded in time of irradiation, regardless of TiO_2 loading applied. In view of the above, in order to avoid confusion concerning the interpretation of the results, all the data associated

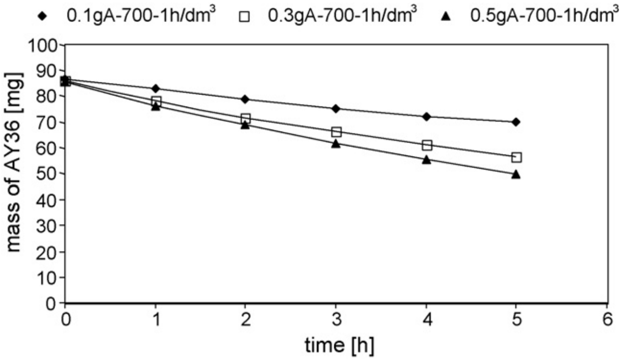

Fig. 4. Changes of mass of the dye in a feed solution during photocatalytic decomposition of Acid Yellow 36 in the PMR; $c_0 = 30\,mg/dm^3$, TiO_2 loadings: 0.1–0.5 g/dm^3, $T = 333$ K.

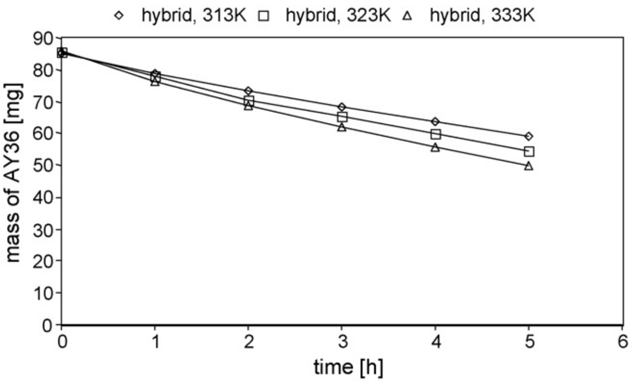

Fig. 5. Changes of mass of AY36 in a feed during hybrid photocatalysis–MD process conducted under different reaction temperatures; $c_0 = 30\,mg/dm^3$, TiO_2 loading: 0.5 g/dm^3.

with concentrations of the dye and products of its degradation that have been discussed in this paper were presented in the mass units [mg].

In Fig. 4 it can be observed that the effectiveness of photodegradation of AY36 increased with increasing the catalyst concentration. However, the difference between the photodegradation rate at 0.3 and 0.5 g TiO_2/dm^3 was less substantial than between the rate at 0.1 and 0.3 g TiO_2/dm^3, what was especially observable during initial 2 h of the process. It is generally known that when the catalyst loading is increased, there is an increase in the surface area of the catalyst available for adsorption and degradation. On the other hand, an increase in the catalyst loading increases the solution opacity leading to a decrease in the penetration of the photon flux in the reactor and thereby decreasing the photocatalytic degradation rate [42]. Moreover, the loss in surface area by agglomeration (particle–particle interactions) at high solid concentration is observed [43]. A smaller effect of an increase of catalyst concentration from 0.3 to 0.5 g TiO_2/dm^3 than from 0.1 to 0.3 g TiO_2/dm^3 on the effectiveness of decolorization of AY36 is in agreement with these statements. Light scattering and reduction of light penetration through the solution probably affected the photodegradation rate of the dye in case of photocatalyst concentration of 0.5 g/dm^3. However, the catalyst loading of 0.5 g/dm^3 was probably not a limiting concentration in the discussed system, because the photodegradation rate was still increasing with increasing the amount of TiO_2. On the other hand, from the presented data it could be also supposed that further increase of photocatalyst loading would not significantly improve the photodegradation efficiency of the dye. Therefore, a loading of 0.5 g TiO_2/dm^3 was applied in further investigations.

3.3. Effect of reaction temperature on the effectiveness of photodegradation of AY36 in the hybrid photocatalysis–MD system

During the next stage of the investigations the effect of the reaction temperature on the process performance was examined. The photocatalyst loading was 0.5 g/dm^3 and the concentration of the dye was 30 mg/dm^3.

The temperature is especially important when the PMR is being considered in terms of direct contact membrane distillation. As was mentioned earlier, the driving force of the mass transfer through the MD membrane pores is a vapour pressure difference on both sides of the membrane, which depends on the temperature and the solutions composition in the layers adjacent to the membrane. Roughly, at constant distillate temperature, an increase of the feed temperature results in an increase of the DCMD permeate flux.

The reaction temperature is also important when the photodegradation rate is being considered. During our earlier investigations on photodegradation of another azo dye, Acid Red 18 [44], we have found that a linear correlation between the rate constant of photodegradation of the dye and the reaction temperature exists in the range of 293–333 K. This means that although the O_2 solubility in water decreases with increasing reaction temperature, the effectiveness of photodegradation increases.

Fig. 5 presents a comparison of the effectiveness of AY36 photodegradation during hybrid photocatalysis–MD process conducted at different temperatures. After 5 h of irradiation the efficiency of decolorization of the solution calculated on a basis of AY36 mass present in the feed amounted to ca. 31, 36 and 42% for the reaction temperatures of 313–333 K, what corresponds to about 59, 54.5 and 50 mg of the dye in the feed solution, respectively. The obtained results clearly show that an increase of the reaction temperature increases the effectiveness of AY36 photodegradation. Chen and Ray [45] attributed the increase of the photodegradation rate with rising the temperature from 283 to 323 K to the increasing collision frequency of molecules in solution. The effect of the temperature on the photocatalytic reaction has been explained in details by Hermann [46]. The decrease of the temperature favors adsorption of the reactant which is a spontaneous exothermic phenomenon. In addition, the lowering of the temperature also favors the adsorption of the final reaction products, whose desorption tends to inhibit the reaction. On the opposite, when temperature increases above 353 K and tends to the boiling point of water, the exothermic adsorption of reactant becomes disfavored and tends to limit the reaction. Therefore, the optimum temperature is generally comprised between 293 and 353 K [47].

As was mentioned earlier, during the MD process a continuous decrease of the feed volume takes place. As a result the solution opacity associated with the catalyst and dye concentrations is increasing. The increase of the solution opacity might lead to light scattering and reduction of light penetration. Moreover, at higher TiO_2 concentrations the loss in catalyst surface area by particles agglomeration might take place. It could be supposed that these phenomena might result in a decrease of the photocatalytic degradation rate of the dye. Therefore, in order to determine the effect of the reduction of feed volume due to the transport of water vapour through the membrane on the photodegradation efficiency of AY36 at different temperatures, the photocatalysis in the MD installation with disconnected membrane module (case 1, see Section 2) was performed. The results are presented in Fig. 6. It can be clearly seen that when MD was not applied the efficiency of AY36 photodegradation increased with increasing solution temperature. After 5 h of irradiation the concentration of the azo dye

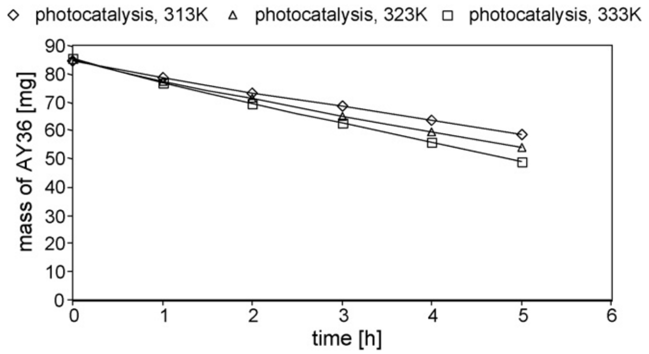

Fig. 6. Comparison of the effectiveness of AY36 photodegradation during photocatalysis (case 1) conducted at different reaction temperatures; TiO_2 loading: 0.5 g/dm^3, c_0 = 30 mg/dm^3.

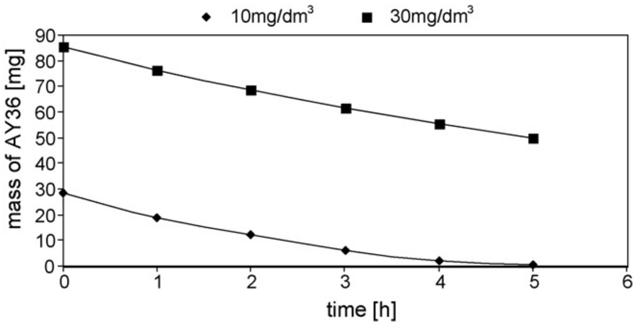

Fig. 7. Changes of mass of the dye in a feed during photocatalytic degradation of Acid Yellow 36 in the hybrid photocatalysis–MD system; c_0 = 10 and 30 mg/dm^3, TiO_2 loading: 0.5 g/dm^3, T = 333 K.

decreased for 31, 37 and 43% for the temperatures of 313–333 K, respectively, what corresponds to about 59, 54 and 49 mg of the dye in the feed solution. From the data presented in Figs. 5 and 6 it can be concluded that the reduction of feed volume during MD did not affect the photodegradation rate of AY36 under the conditions applied. The masses of the dye in the reaction solutions (but not the concentrations) at the end of both processes (i.e. photocatalysis and hybrid photocatalysis–MD) were practically the same. However, when the concentrations of the dye were considered instead of masses, the results suggested that photodegradation of AY36 during the hybrid photocatalysis–MD process was less effective than during photocatalysis alone conducted under the same conditions. The AY36 concentration in a feed solution after 5 h of the hybrid process decreased for ca. 25, 24 and 17%, whereas during photocatalysis alone for ca. 31, 37 and 43%, for the reaction temperatures of 313–333 K, respectively. It was also observed, that the decrease of AY36 concentration in the feed solution was lower at 333 K than at 313 K, what is inconsistent with the previous statements concerning the influence of the reaction temperature on the effectiveness of the dye degradation. These results might lead to a conclusion that in case of hybrid processes coupling photocatalysis and membrane techniques the masses of the pollutants instead of their concentrations should be considered when determining the effectiveness of a system. This seems to be especially important in case of these membrane processes during which a high rejection of the pollutants is obtained, such as membrane distillation, pervaporation, reverse osmosis, nanofiltration, etc. In some cases, it might be also useful to show the data on a feed volume reduction during the membrane process applied what might be helpful in an interpretation of the results.

Summing up, it can be concluded that in the PMR coupling photocatalysis and MD an increase of the reaction temperature is beneficial from both, photocatalysis and membrane process point of view. At higher temperatures not only higher degradation rates but also higher permeate fluxes were obtained. The permeate fluxes measured at the reaction temperatures of 313, 323 and 333 K (inlet feed temperatures of 313, 324 and 335 K) amounted to about 86, 164 and 302 dm^3/m^{2}d, respectively. It can be clearly seen that an increase of the temperature for 10 K resulted in about twice higher permeate flux and about 6% increase of the AY36 photodegradation efficiency.

3.4. Effect of AY36 initial concentration on its degradation rate in the hybrid photocatalysis–MD system

The concentration of a dye is a very important parameter which affects the effectiveness of its photodegradation. It is often reported that an increase of a dye concentration initially increases the rate of its degradation. However, further increase above a certain value leads to a decrease of its degradation rate. One reason for that is covering of the catalyst surface with dye ions what suppresses the generation of hydroxyl radicals. Another possible explanation might be the UV-screening effect of the dye itself. At high dye concentrations, a significant portion of UV light might be absorbed by the dye molecules rather than the TiO_2 particles. This phenomenon reduces the efficiency of the catalytic reaction because the concentrations of $^{\bullet}OH$ and $O_2^{\bullet -}$ decrease [48].

In order to determine to what extent the initial dye concentration affects the rate of its degradation an additional experiment with application of solution containing 10 mg/dm^3 AY36 was performed. The photocatalytic degradation of AY36 in the PMR was conducted for 5 h at the temperature of 333 K and feed flow rate of 0.5 m/s. TiO_2 loading amounted to 0.5 g/dm^3. Fig. 7 presents a comparison of changes of the mass of the dye in the feed solution vs. time for initial AY36 concentrations of 10 and 30 mg/dm^3. It can be clearly seen that a decrease of the initial azo dye concentration led to a significant improvement of the effectiveness of its degradation. For c_0 = 10 mg/dm^3 the mass of AY36 in the feed after 5 h of irradiation was only 0.3 mg, whereas for c_0 = 30 mg/dm^3 the mass of the dye at the end of the process was still very high and amounted to about 50 mg. It can be seen that when the initial dye concentration decreased three times, the effectiveness of its degradation, calculated after 5 h of irradiation, increased more than twice, from 42 to 99% for c_0 = 30 and 10 mg/dm^3, respectively. If the amount of the dye present in the solution after 1 h of irradiation is considered, the difference is more significant (11 vs. 33%, respectively).

The fading of the azo dye solution is associated with cleavage of azo bonds (–N=N–) which are the most active bonds in the dye molecules. During the subsequent stages of photodegradation the cleavage of benzene and naphthalene rings followed by a series of oxidation steps takes place what further leads to progressively lower molecular weight aliphatic acids and eventually to a complete mineralization to water, CO_2 and mineral salts (sulphates, nitrates, etc.) [48]. The overall reaction equation can be presented as follows:

$$\begin{aligned}&C_{18}H_{14}N_3NaO_3S \rightarrow \text{aromatic intermediates} \rightarrow \text{carboxylic acids}\\&\quad + \text{inorganic anions}\,(SO_4{}^{2-},\ NO_3{}^{-},\ NO_2{}^{-},\ NH_4{}^{+}) + Na^{+}\\&\quad \rightarrow \text{final products}\,(CO_2,\ H_2O,\ SO_4{}^{2-},\ NO_3{}^{-},\ Na^{+})\end{aligned}$$

Fig. 8a and b shows generation of selected aliphatic acids during photodegradation of AY36 for initial dye concentrations of 10 and 30 mg/dm^3. It was found that the kinetics of formation of organic acids was dependent on the initial concentration of the dye. In case of c_0 = 30 mg/dm^3 the amount of oxalic acid (HOOCCOOH) in the feed continuously increased with the time of illumination, reaching at the end of the process the value of 1.36 mg. For c_0 = 10 mg/dm^3 the course of changes of HOOCCOOH amount was quite different.

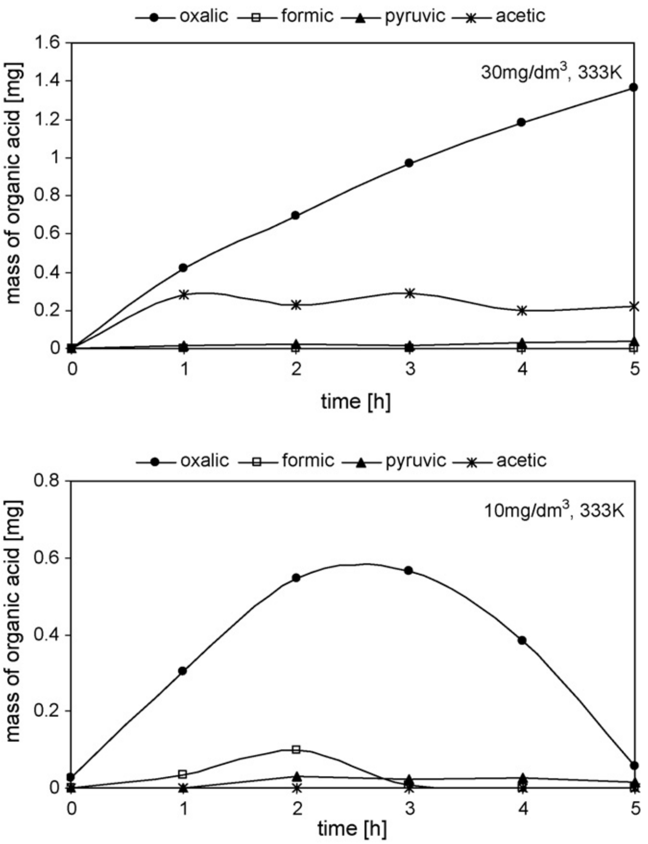

Fig. 8. Kinetics of the formation of selected aliphatic acids during photodegradation of AY36 in the hybrid photocatalysis–MD system; c_0 = 10 and 30 mg/dm^3, TiO_2 loading: 0.5 g/dm^3, T = 333 K.

The highest mass of oxalic acid was determined after 3 h of irradiation (0.57 mg) and then it started to decrease. Formation of formic acid (HCOOH) was observed only in case of c_0 = 10 mg/dm^3. The amount of this by-product increased for the first 2 h of the experiment up to ca. 0.10 mg and then decreased. When the kinetics of formation of acetic acid (CH_3COOH) was taken into consideration, it was observed that this compound was present only in case of higher AY36 initial concentration. The amount of acetic acid was almost constant during the whole process and at the end of irradiation reached a value of 0.22 mg. The mass of pyruvic acid (CH_3COCO_2H) in case of c_0 = 30 mg/dm^3 increased during the whole process, whereas in case of c_0 = 10 mg/dm^3—increased during the initial 4 h and then started to decrease. The observed decrease of the amount of aliphatic acids during the final hours of the process in case of c_0 = 10 mg/dm^3 might suggest that the mineralization of the organic species present in the solution took place much faster than in case of higher initial dye concentration.

3.5. Comparison of the effectiveness of AY36 removal during single operations (photocatalysis or MD) and hybrid photocatalysis–MD process

Taking into consideration that photocatalysis is usually conducted under ambient conditions, without solution heating, the effectiveness of AY36 photodegradation in a batch slurry reactor at a temperature of 298 K was also investigated (case 2, see Section 2). The rate of the degradation of the model dye during photocatalysis conducted in the batch photoreactor was compared with the effectiveness of AY36 removal during hybrid photocatalysis–MD process as well as MD alone. Fig. 9 presents changes of AY36 mass in the reaction solution (feed solution in case of MD and hybrid photocatalysis–MD) vs. time. It can be observed that when photocatalysis was conducted alone the amount of the dye after 5 h of irradiation was for about 28% higher than during the hybrid process (i.e. ca. 69 mg vs. 50 mg, respectively). These results are consistent with the previous conclusions that the effectiveness of AY36 photodegradation was increasing with increasing the reaction temperature. On the other hand, when MD was conducted alone, the mass of the dye in the feed remained constant what resulted from the fact that no degradation of the dye but only reduction of feed volume due to the transport of water vapour through the membrane took place in this case. During 5 h of the MD process the volume of the feed decreased for about 30% what corresponded to an increase of AY36 concentration to ca. 46 mg/dm^3. This means that the concentration of the dye after 5 h of the MD was almost twice higher than in case of the other two processes (ca. 24 mg/dm^3).

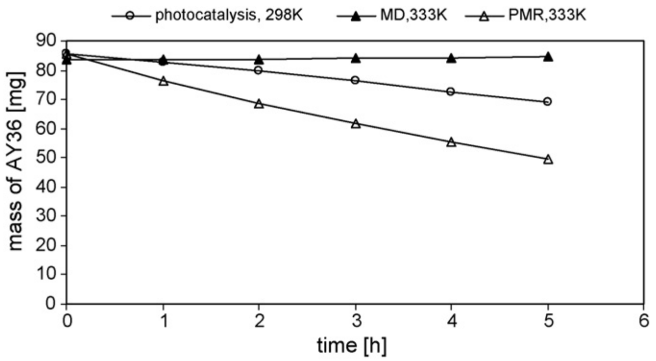

Fig. 9. Changes of mass of AY36 in the reaction solution (feed solution in case of MD and PMR) during (a) photocatalysis alone (298 K, 0.5 g TiO_2/dm^3), (b) MD alone (333 K) and (c) hybrid photocatalysis–MD (333 K, 0.5 g TiO_2/dm^3); initial dye concentration: 30 mg/dm^3.

It should be noticed here that the three discussed processes give different product and waste streams (Fig. 10). The product when photocatalysis is conducted without MD is a suspension of the photocatalyst in the reaction solution. After 5 h of the process performance the composition of the reaction solution was as follows: dye concentration: 23.8 mg/dm^3, conductivity: 44.6 μS/cm, pH 4.5. From these results it is clear that the product of the photocatalysis conducted alone is still wastewater. When the hybrid process combining photocatalysis and MD is applied, the product is distillate, being high quality water. For the same TiO_2 loading, as in case of photocatalysis alone, the conductivity of distillate amounted to 1.8 μS/cm (vs. 0.9 μS/cm measured in water used for preparation of solutions) and pH was 5.3 (vs. pH 5.6). Moreover, a complete retention of the model dye (Fig. 10) and photocatalyst was observed.

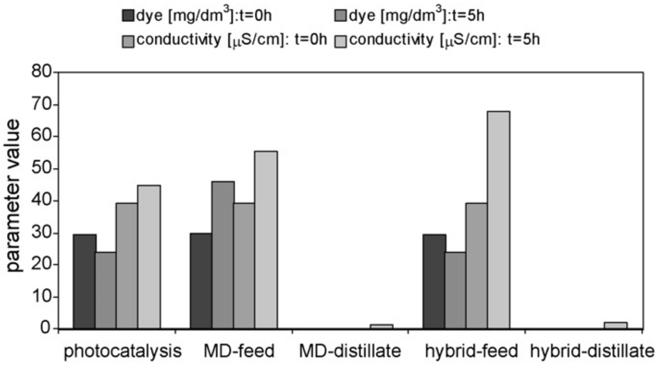

Fig. 10. Comparison of product quality in different processes: (a) photocatalysis alone (298 K, 0.5 g TiO_2/dm^3), (b) MD alone (333 K) and (c) hybrid photocatalysis–MD (333 K, 0.5 g TiO_2/dm^3); initial dye concentration: 30 mg/dm^3; initial conductivity: 39 μS/cm.

Similar quality of the product (distillate) was observed in case of MD conducted alone: conductivity was equal to 1.2 μS/cm and pH was 5.5. However, as was mentioned earlier, in case of MD alone the waste still exists, because only reduction of feed volume due to evaporation takes place. In the hybrid photocatalysis–MD system it is possible to mineralize the wastes. Therefore, the feed solution at the end of the process during which a complete mineralization was achieved, contains only water, photocatalyst and, depending on the initial composition of the wastewaters, mineral salts. The literature data [49] show that TiO_2 can be reused without loss of photoactivity for many cycles. Taking this into consideration, a fresh wastewater could be added to the feed tank and the process could be conducted again with the same photocatalyst, what might reduce the cost of application of a catalyst. However, the photocatalytic activity of TiO_2 might be reduced in the presence of high concentrations of inorganic salts [49]. An MD membrane separates (theoretically) 100% of non-volatile compounds, such as salts. Therefore, loss of photocatalytic activity due to the discussed phenomenon must be taken into consideration. In some cases it might occur that another membrane process should be additionally used in order to separate a catalyst from the treated water stream containing high concentrations of the salts. After that it might be possible to reuse the photocatalyst in the hybrid photocatalysis–MD process. However, in order to state unequivocally how the salts concentrations affect the photocatalytic activity of TiO_2 in the PMR utilizing MD further investigations are necessary. In case of irreversible loss of photocatalytic activity the catalyst should be disposed. Taking into consideration that a recovery factor in membrane distillation could be as high as 77% [50], the feed that should be disposed would be a highly concentrated suspension of a photocatalyst and mineral salts.

As was mentioned earlier, in the hybrid photocatalysis–MD system it is possible to mineralize the wastes. Mineralization can be also achieved during photocatalysis alone; however, the time required to obtain a product, which in this case means the time necessary to complete the degradation of organics present in the solution, is much longer than in a PMR. When photodegradation is conducted in the hybrid system, the product (distillate) can be collected from the very beginning of the process. Moreover, even when a complete mineralization is achieved, the solution after photocatalysis still contains inorganic ions such as NO_3^- or SO_4^{2-}, depending on the composition of the treated wastes. Application of MD together with photocatalysis allows separation of these ions, because they are non-volatile species. This means that the quality of the product in case of the PMR will be much higher than in a classical batch photoreactor. Besides, when photocatalysis in suspension is conducted alone, it is necessary to separate the catalyst from the reaction solution, either by conventional methods (i.e. coagulation–flocculation–sedimentation and/or filtration) or by using a membrane.

In view of all above, it could be concluded that application of the hybrid photocatalysis–MD system is more beneficial method of removal of azo dyes, such as AY36, than photocatalysis alone or MD alone.

4. Conclusions

The rate of photodegradation of AY36 in the PMR was dependent on all the parameters investigated: initial dye concentration, photocatalyst loading and reaction temperature. When the effectiveness of the process was estimated on a basis of a mass of the dye present in the feed solution, it was found that AY36 was the most effectively degraded when the highest TiO_2 loading (i.e. 0.5 g/dm^3) and the highest reaction temperature (333 K) were applied. However, when AY36 concentration in a feed was taken into consideration, the results suggested that the degradation of AY36 at the highest reaction temperature used was less effective than that observed at 313 K. This was associated with a feed volume reduction due to evaporation of water through the MD membrane. Therefore, in order to avoid confusion concerning the interpretation of the results, it was proposed to use masses [mg] instead of concentrations [mg/dm^3] of the dye. Such way of presentation of experimental data seems to be especially important in case of these membrane processes during which a high rejection of the pollutants is obtained, such as membrane distillation, pervaporation, reverse osmosis or nanofiltration.

The data obtained during photocatalysis conducted in the MD installation but with disconnected membrane module also showed that the model dye was the most effectively degraded at 333 K. Moreover, it was found that the masses of the dye in the reaction solutions (but not the concentrations) at the end of photocatalysis and hybrid photocatalysis–MD were practically the same. This suggests that the reduction of feed volume did not affect the photodegradation rate of AY36 in the PMR.

Effectiveness of AY36 photodegradation during process conducted in the batch slurry photoreactor under ambient conditions was lower than during the process conducted in the PMR. Taking into account both, the degradation rate and the quality of the product, the most beneficial configuration seems to be the PMR.

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. Another obstacle in application of MD in PMRs might be permeate flux which is in case of MD lower than in the above mentioned pressure driven membrane processes. On the other hand, the addition of TiO_2 to a feed did not affect the MD 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. Moreover, application of PMR utilizing MD allows obtaining high quality water that could be possibly applied in different processes requiring deionized water, including cosmetics, food processing, plating or electronics industries. For applications in which degradation of organics is desired but the presence of different salts is also required (for example in case of drinking water), the purified during photocatalysis–MD water could be remineralized before supply to the consumer.

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