

Application of carbon-coated TiO₂ for decomposition of methylene blue in a photocatalytic membrane reactor

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Received 17 June 2006; received in revised form 2 October 2006; accepted 7 October 2006

Available online 12 October 2006

Abstract

An application of carbon-coated TiO₂ for decomposition of methylene blue (MB) in a photocatalytic membrane reactor (PMR), coupling photocatalysis and direct contact membrane distillation (DCMD) was investigated. Moreover, photodegradation of a model pollutant in a batch reactor without membrane distillation (MD) was also examined. Carbon-modified TiO₂ catalysts containing different amount of carbon and commercially available TiO₂ (ST-01) were used in this study. The carbon-coated catalyst prepared from a mixture of ST-01 and polyvinyl alcohol in the mass ratio of 70/30 was the most effective in degradation of MB from all of the photocatalysts applied. Photodecomposition of MB on the recovered photocatalysts was lower than on the fresh ones. The photodegradation of MB in the PMR was slower than in the batch reactor, what probably resulted from shorter time of exposure of the catalyst particles to UV irradiation. The MD process could be successfully applied for separation of photocatalyst and by-products from the feed solution.

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Keywords: Carbon-coated TiO₂; Methylene blue; Photocatalytic membrane reactor (PMR); Photodecomposition; Direct contact membrane distillation

1. Introduction

Increasingly stringent regulations concerning the quality of water make a need to develop new methods of treatment of wastewater streams before they are introduced into the environment. One alternative to the conventional water and wastewater treatment methods are advanced oxidation processes (AOP) from which photocatalysis has become very popular during last decades. TiO₂ having anatase phase has attracted attention of the scientists because of its photocatalytic activity, due to the semiconductor characteristics, for the decomposition of various environmental pollutants. Recently, different ideas of the improvement of the TiO₂ photocatalytic properties have been widely investigated. One of methods to obtain such a photocatalyst is preparation of TiO₂–carbon composites, including

mounting of TiO₂ on activated carbon [1–5] or coating of anatase with carbon layer [6–10].

In our previous studies [6–8], TiO₂ powders having anatase phase coated with carbon layer were synthesized. It was found that carbon coating of TiO₂ fine particles was very effective to suppress the phase transformation from anatase to rutile, to result in a high crystallinity and consequently to give high photoactivity, even better than the one without carbon coating. Another advantages are relatively high adsorptivity due to porous carbon layers coated and ability to prevent the reaction of organic binders with TiO₂ particles.

However, the catalyst particles have to be separated from the treated water after the decomposition of organic pollutants. One of promising methods for solving the above mentioned problem is the coupling of the photocatalysis with membrane techniques. The membrane would play both the role of a simple barrier for the photocatalyst and a selective barrier for the molecules to be degraded. Photocatalytic membrane reactors (PMRs) have some advantages with respect to conventional photoreactors, such as

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Table 1
Selected properties of the photocatalysts applied

Sample code	TiO ₂ /PVA ratio (mass%)	Heat treatment conditions	Amount of carbon coating (mass%)	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ /g)			Crystalline phase of catalyst
					Total	Meso 2–50 nm	Macro 50–150 nm	
ST-01	100/0	As-received	0	300	0.851	0.708	0.101	Anatase
SP-50-900	50/50	900 °C, 1 h	10	170	0.973	0.413	0.558	Anatase
SP-70-900	70/30	900 °C, 1 h	8	130	0.416	0.376	0.032	Anatase

[13]: (I) confining of the photocatalyst in the reaction solution by means of the membrane; (II) control of a residence time of molecules in the reactor; (III) realization of a continuous process with simultaneous separation of products from the reaction solution.

A new type of photocatalytic membrane reactor (PMR) combining photocatalysis with direct contact membrane distillation (DCMD) was investigated in the presented study. The driving force of the mass transfer through the DCMD membrane pores is a vapour pressure difference on both sides of membrane, which depends on the temperature and the composition of solutions in the layers adjacent to the membrane. Membrane distillation (MD) is a process of evaporation of feed volatile components through a porous hydrophobic membrane. During this process, the gas phase is maintained inside the pores of the membrane [11,12]. In the proposed configuration, the photocatalyst is separated by the MD membrane. Moreover, high quality water containing only a small amount of volatile compounds is obtained as a product.

The investigation on the possibility of application of carbon-coated TiO₂ in the PMR combining photocatalysis and DCMD was discussed. The effectiveness of photodegradation of methylene blue (MB) as a model dye on fresh and regenerated photocatalysts in this proposed system was especially determined. Moreover, photodegradation of MB on the carbon-coated TiO₂ without MD was also examined.

2. Experimental

The carbon-coated TiO₂ was prepared by mixing of TiO₂ (ST-01, Ishihara-Sangyo Co. Ltd.) and polyvinyl alcohol (PVA, Nippon Synthetic Chem. Ind. Co. Ltd.), in different mass ratios: 50/50 (SP-50-900) and 70/30 (SP-70-900), respectively. After mixing the powders were heated at 1173 K for 1 h in N₂ flowing at a rate of 2.9 cm³ s⁻¹. Carbon-coated anatase powders were found to keep almost the same morphological features as pristine (i.e. ST-01 as received, non-coated) anatase. Without carbon coating, the pristine anatase particles were sintered to grow much larger, consequently BET surface area decreased to 2 m²/g after heating to 900 °C [14].

BET surface area and pore size distribution were determined by N₂ adsorption at 77 K (Autosorb 3, Quantachrome, USA). Pore size distribution was calculated according to the BJH equation from the desorption branch. Carbon content was measured through the combustion of carbon in air at 1000 °C using TG apparatus. XRD patterns of samples were recorded with scanning speed of 2° min⁻¹ using Cu K α radiation from a 18 kV

source (Rigaku, RINT-2000). Basic properties of photocatalysts are presented in Table 1. A detailed discussion concerning preparation and properties of the catalysts used in the present study can be found in the papers previously published by the co-authors [6–8,14–18].

Methylene blue (MB, C₁₆H₁₈ClN₃S) was applied as a model pollutant. The concentration of MB in the solution at the start of photodecomposition was 3.2 × 10⁻⁵ mol dm⁻³. The photocatalyst loading amounted to 0.5 g dm⁻³. The carbon-coated photocatalysts were saturated with MB before the photodecomposition by stirring the catalyst suspension in the dye solution for 24 h.

The DCMD process was conducted in a laboratory-scale installation presented in Fig. 1. The main element of this system was a capillary module equipped with nine polypropylene (PP) membranes Accurel PP S6/2 (Membrana GmbH, Wuppertal, Germany), having outer/inner diameters $d_{out}/d_{in} = 2.6/1.8$ mm. The effective area of PP membranes was 0.014 m². During the experiments the warm feed and cold distillate streams flowed in the module in a co-current mode. The volatile compounds present in 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⁻¹, whereas the distillate flowed outside the capillaries with a flow rate of 0.09 m s⁻¹. The temperature of the reaction mixture in the feed tank amounted to 333 K. In order to obtain such a value the inlet feed temperature was

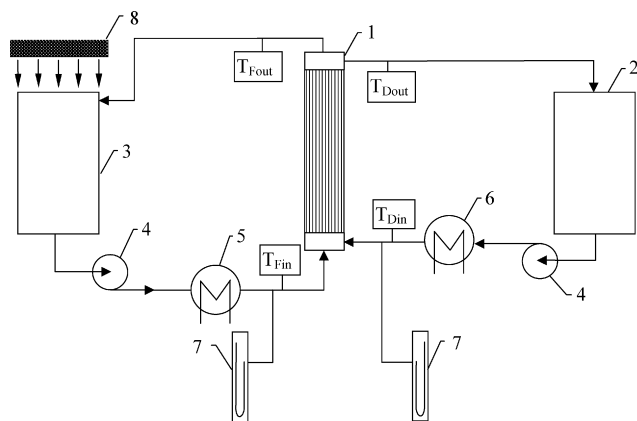


Fig. 1. Schematic diagram of the apparatus for MD: (1) membrane module; (2) distillate tank; (3) feed tank ($V = 2.9$ l); (4) pump; (5) and (6) heat exchangers; (7) manometers; (8) UV lamp; T_{Fin} , T_{Din} —inlet temperatures of feed and distillate; T_{Fout} , T_{Dout} —outlet temperatures of feed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

set up at a level of 340 K. The inlet temperature of distillate was 293 K. The volume of distillate (ultrapure water, Simplicity™, Millipore) at the beginning of the process was equal to 1.3 dm³. The initial volume of the feed amounted to 2.9 dm³. The reaction solution was illuminated with a mercury lamp Philips Cleo, emitting UV-A light ($\lambda_{\max} = 355$ nm), positioned above the reactor. The UV intensity at the irradiation plate was 146.1 W m⁻². The illumination intensity was measured with an LB 901 radiometer equipped with the PD204AB (Macam Photometrics Ltd.) and CM3 (Kipp & Zonen) external sensors.

In the second step of the investigation photodegradation of MB in a batch reactor without application of DCMD was performed. The photodegradation reaction was carried out in glass reactors containing 0.7 dm³ of a model solution of MB and 0.5 g dm⁻³ of a respective photocatalyst. The solutions in the reactors were continuously stirred during the experiment at a room temperature. The UV intensity at the irradiation plate was 137.8 W m⁻².

After a defined time of irradiation the samples were filtered through a 0.45 μ m membrane filter and analyzed. The effectiveness of TiO₂ 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 MB was estimated on the basis of changes in UV/vis spectra (Jasco V530 spectrometer, Japan). The quality of distillate was determined on a basis of 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 investigate the possibility of reusing of the catalysts, the cyclic performance of the photocatalytic decomposition of MB in two runs was carried out. After the 1st run of photocatalysis or photocatalysis–MD the all catalyst was collected from the installation, filtered through a 0.45 μ m membrane filter and transferred carefully into the fresh dye solution in order to saturate with MB. That catalyst sample was taken again to the fresh MB solution (3.2×10^{-5} mol dm⁻³) and the respective process was started (2nd run).

In order to compare the effectiveness of MB decomposition on different photocatalysts during the 1st and 2nd run, the rate constants k were calculated. The Langmuir–Hinshelwood model (Eq. (1)) has been widely applied by researchers [19,20] for the description of the photocatalytic oxidation of organic pollutants:

$$-\frac{dc}{dt} = \frac{k_1 Kc}{1 + Kc}, \quad (1)$$

and after integration:

$$\ln\left(\frac{c_0}{c}\right) + K(c_0 - c) = k_1 Kt, \quad (2)$$

where c_0 is the initial concentration of dye, c the concentration of dye after time t of the photocatalytic decomposition, K the constant of adsorption equilibrium and k_1 is a true rate constant, which takes into account several parameters such as catalyst's mass, efficient photon flow, O₂ layer, etc. [20].

Eq. (1) will be of zero order when the concentration c (mol dm⁻³) is relatively high, $>5 \times 10^{-3}$, $Kc \gg 1$, in which case the reaction rate will be maximal. When the solution is highly diluted, c (mol dm⁻³) $< 10^{-3}$, the term Kc becomes $\ll 1$, the denominator of Eq. (1) is neglected and the reaction is essentially an apparent first order reaction [20]:

$$-\frac{dc}{dt} = Kk_1c = kc, \quad (3)$$

and after integration:

$$c = c_0 \exp(-kt), \quad (4)$$

where k is the apparent rate constant of a pseudo first order reaction [19,20]. The rate constants k were calculated from the linear regressions by plotting $\ln(c/c_0)$ versus time.

In order to determine the photostability of MB under the conditions applied (i.e. temperature equal to 298 or 333 K and the intensity of UV light of ca. 140 W/m²), an additional experiment without TiO₂ 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. It was found that during 10 h of illumination of dye solution the concentration of MB decreased for less than 3%, regardless of the temperature applied. The change of concentration was so insignificant that could be neglected with respect to the decrease of dye concentration during photocatalysis. A negligible change of reaction volume was observed due to evaporation of water during heating. In view of the obtained results it can be stated that in the presence of TiO₂ a true heterogeneous catalytic regime takes place.

3. Results and discussion

3.1. Photocatalysis conducted without DCMD

The photocatalytic decomposition of MB without MD was conducted for 20 h at a room temperature. Fig. 2 presents the results obtained during the 1st and 2nd runs, respectively.

It was found that the highest MB decomposition was obtained with the SP-70-900 photocatalyst. For the 1st run (Fig. 2), during the first hour of irradiation concentration of the model dye decreased for ca. 80%. After the same time of the process per-

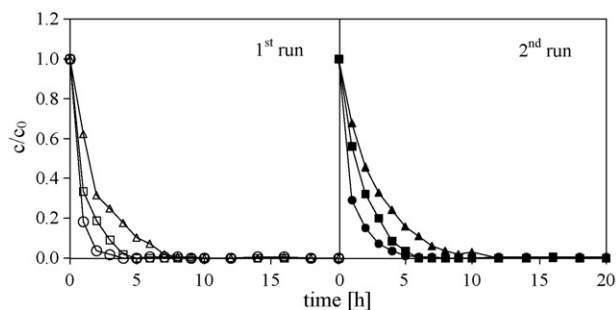


Fig. 2. Photocatalytic decomposition of MB; photocatalysis conducted without membrane distillation (MD); open symbols—1st run; closed symbols—2nd run; (□, ■) ST-01; (△, ▲) SP-50-900; (○, ●) SP-70-900.

formed with the other two photocatalysts, color fading of the solution was less effective, i.e. with the ST-01 catalyst the MB was decomposed for ca. 70% and with SP-50-900 for ca. 40%. During the 2nd run (Fig. 2) color fading after the first hour of decomposition amounted to ca. 70% for SP-70-900 and ca. 40% for SP-50-900 and ST-01.

The photodegradation rate of MB was well described by the first order kinetics Eq. (4). However, the time of a complete or almost complete fading of the solution was different for different catalysts and dependent on their photoactivity, i.e. for ST-01 $t_1 = 5$ h during the 1st run and $t_2 = 7$ h during the 2nd run, for SP-50-900 $t_1 = 8$ h and $t_2 = 12$ h, for SP-70-900 $t_1 = 4$ h and $t_2 = 6$ h, respectively. After that time the concentration of the dye in the solution was close to the zero; moreover was varying in time (what will be discussed later in this chapter). Therefore, to make it easy to compare the photoactivity of the catalysts, for calculation of the rate constants the results obtained during the initial 5 h of the experiment were only taken into account. During this time the relation between $\ln(c/c_0)$ and the irradiation time can be approximated to be linear. The rate constants k are presented in Table 2.

From the rate constants (Table 2) it was found that the SP-70-900 catalyst was the most effective for the photodecomposition of MB, regardless of the run. However, the effectiveness of MB removal was higher during the 1st run in comparison with the 2nd one. It might be suggested that a complete degradation of the organic compounds was not achieved. One possible explanation could be that some amount of MB adsorbed on the catalysts was not decomposed. Another, more probable reason for lower effectiveness of MB degradation during the 2nd run could be adsorption of by-products of MB photodecomposition. These substances probably blocked the catalyst surface, thus lowering its activity towards MB decomposition. This explanation is consistent with the adsorption capacity of fresh and recovered photocatalysts determined on the basis of the difference in the concentration of the dye in the solution before and after saturation (that was performed before photodecomposition). The amount of MB adsorbed on the fresh catalysts was equal to 2.40, 40.5 and 34.1 mg g^{-1} for ST-01, SP-50-900 and SP-70-900, respectively. In case of the recovered photocatalysts, these values amounted to 2.03, 24.2 and 24.3 mg g^{-1} , respectively. Thus, the adsorption capacity was lowered for ca. 15% in case of ST-01, ca. 40% of SP-50-900 and ca. 29% of SP-70-900. The observed decrease in the adsorption capacity might be associated with adsorption of by-products of MB decomposition or the dye itself, as was mentioned earlier. It can be supposed that further extension of irradiation time could result in a complete recovery of the photoactivity of the catalysts. This hypothesis can be supported by the previously performed experiments [6],

Table 2
Rate constants k (h^{-1}) of photocatalytic decomposition of MB

ST-01		SP-50-900		SP-70-900	
1st run	2nd run	1st run	2nd run	1st run	2nd run
0.93	0.63	0.45	0.37	1.50	0.89

which proved that cyclic usage of carbon-coated anatase-type TiO_2 was possible and no detectable reduction in photocatalytic activity was observed.

It was found from the obtained results that the presence of carbon in the catalyst particles might lead to improvement of MB decomposition; however, the effect depends on the amount of the carbon coated on TiO_2 . From the two carbon-coated photocatalysts the SP-70-900 exhibited much higher activity towards MB. This catalyst contained smaller amount of carbon than SP-50-900. Therefore, it can be concluded that there is an optimum ratio of carbon to TiO_2 that assures high activity of the catalyst. The decrease in k with increasing carbon content is reasonably supposed to be due to the decrease in the amount of UV rays reaching the surface of the anatase particles through the coated carbon layer. Another important factor is the crystallinity of anatase, what we pointed out in one of our previous papers [18]. For a high rate of MB decomposition in the solution, a relatively high crystallinity, i.e. relatively small full width at half maximum intensity (FWHM) of the 101 diffraction line of anatase, was required. A detailed discussion on the role of carbon layer on photocatalytic activity of anatase can be found in [15].

On the basis of the obtained results, it was found that MB adsorbed into carbon layer was also decomposed by UV irradiation on TiO_2 particles. Moreover, it was observed that MB concentration in the solution varied in time, what was especially noticeable during the final hours of the experiment. For example, during the 1st run of photodegradation performed using SP-70-900 the MB concentration after 9 h of irradiation was equal to 0 mg dm^{-3} , and then increased up to 0.01 mg dm^{-3} after 10 h, 0.04 mg dm^{-3} after 14 h, 0.08 mg dm^{-3} after 16 h and finally decreased up to 0.02 mg dm^{-3} at the end of the process. During the 2nd run the MB concentration amounted to 0 mg dm^{-3} after 12 h of irradiation, and then increased up to $0.3\text{--}0.4 \text{ mg dm}^{-3}$. After 20 h the dye concentration again decreased reaching the value of 0.01 mg dm^{-3} . Such changes of MB concentration might suggest that during the photodegradation the dye molecules adsorbed into carbon layer were desorbed and adsorbed continuously, what was probably associated with approaching of adsorption equilibrium in the investigated system. Fig. 3 presents, as an example, changes in the UV-vis

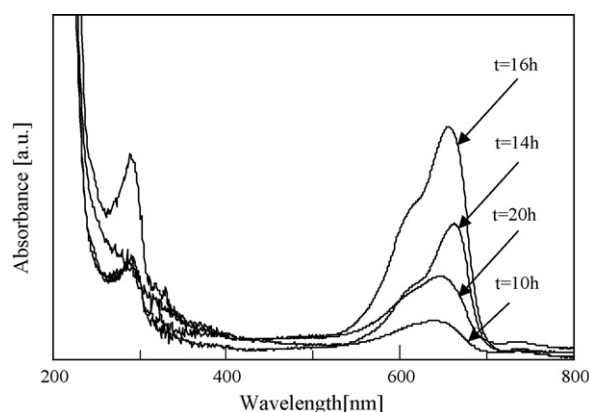


Fig. 3. Changes in the UV-vis spectra during photodegradation of MB on SP-70-900; 1st run.

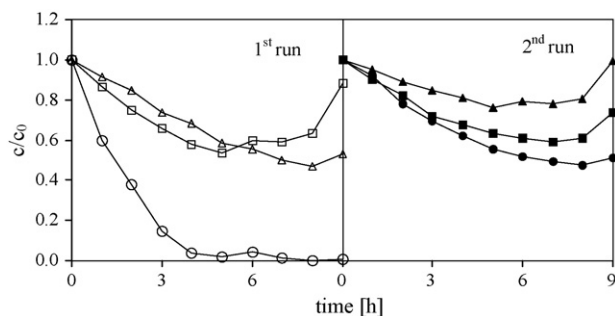


Fig. 4. Changes of MB concentration in the feed during photocatalysis–MD process performance; reaction temperature: 333 K; open symbols—1st run; closed symbols—2nd run; (□, ■) ST-01; (△, ▲) SP-50-900; (○, ●) SP-70-900.

spectra during photodegradation of MB using SP-70-900 (1st run).

3.2. Photocatalysis–MD hybrid system

The photocatalytic decomposition of MB in the PMR was conducted for 9 h at the temperature of 333 K (inlet feed temperature was set up at a level of 343 K). Fig. 4 presents changes in MB concentration in the feed with irradiation time.

It can be observed that the highest rate of MB photodecomposition was obtained for the SP-70-900 catalyst, similarly as in the suspended system without DCMD. Moreover, it was found that the solution was completely faded during the 1st run only in case of SP-70-900, whereas for the other two catalysts the feed solution remained colored during the time of the experiment. Fig. 4 presents also changes in MB concentration with irradiation time during the 2nd run. In this case the SP-70-900 photocatalyst was also the most effective from all of the catalyst applied. However, similarly like in the process conducted without MD, the effectiveness of photodecomposition of MB during the 2nd run was lower than in the 1st run.

During hybrid process photocatalysis–MD the effect of feed concentration due to transport of water and volatile compounds through the membrane affects the photodegradation rate constant k . In this case the first order kinetics Eq. (4) described well the first 8 h of the photocatalytic reaction when SP-70-900 was used, regardless of the run. For SP-50-900 Eq. (4) can be applied for the initial 8 h during the 1st run and only 5 h during the 2nd run. After that time the feed concentration significantly influenced the results. In case of ST-01, for both runs, the first order kinetics equation could be applied only for the initial 5 h of photodegradation. Therefore, for all the photocatalysts used, the rate constants were calculated for the first 5 h of the process in order to facilitate comparison of the results.

The rate constants k calculated for the initial 5 h of irradiation during the 1st run amounted to 0.10 h^{-1} for SP-50-900, 0.13 h^{-1} for ST-01 and 0.74 h^{-1} in case of SP-70-900, respectively. The values of k in the 2nd run were equal to 0.05, 0.10 and 0.12 h^{-1} for SP-50-900, ST-01 and SP-70-900, respectively. It can be observed, that the rate constants decreased for 50% in case of SP-50-900, ca. 84% in SP-70-900 and for ca. 23% in ST-01, respectively. As was mentioned earlier, during the 1st

run only in case of SP-70-900 the color of MB solution was completely faded. This could suggest that the largest amount of final products (i.e. CO_2 , H_2O and inorganic compounds) and by-products of MB degradation is formed especially in case of this photocatalyst. These substances could be adsorbed on the catalyst surface and decrease its activity.

In case of the ST-01 and SP-50-900 photocatalysts the decomposition of MB was not complete, therefore much smaller amount of the degradation by-products, in comparison with SP-70-900, was formed and the catalyst surface was occupied mainly by MB, which was further degraded in the 2nd run. For the SP-70-900 it can be supposed that during the 2nd run the by-products of MB photodecomposition adsorbed on catalyst surface were primarily degraded, what led to lower rate of MB decomposition. However, in order to state unequivocally, what compounds could remain adsorbed on the photocatalyst particles and affect the photodecomposition of MB, further extensive investigations are needed.

It was found that concentration of the feed solution was faster than the photodegradation of MB (Fig. 4) at the end of the photocatalysis–MD process. The increase of MB concentration in the feed was especially significant in case of the pristine ST-01 catalyst. Changes in MB concentration reached a constant value after ca. 6 h of irradiation and then significantly increased (Fig. 4), especially during the 1st run. In case of SP-50-900 MB concentration decreased in the 1st run up to 6 h, during the next 2 h changes in concentration were insignificant, and after 8 h the concentration slightly increased. During the 2nd run MB concentration increased after 6 h (Fig. 4). Effect of feed concentration was recognised with the SP-70-900 photocatalyst at least. In the 1st run solution was faded after 8 h with UV irradiation and kept transparent until the end of the process. The MB concentration slightly increased after 8 h in the 2nd run. The rate of the photodegradation was significantly higher at the beginning of the decomposition. When the reaction proceeds the by-products formed can block the photocatalyst surface and the rate of photodecomposition could decrease. Higher rate of MB decomposition on SP-70-900 might suggest that the number of reaction active sites (i.e. at which the redox reactions are induced), on this photocatalyst surface is significantly higher than in case of the other two catalysts. SP-70-900 exhibits similar carbon content to SP-50-900 (8% versus 10%, respectively; Table 1), but contains much higher amount of TiO_2 (70% versus 50%, respectively; Table 1). This can enhance the formation of hydroxyl radicals on the SP-70-900 surface what might result in an increase of its activity. From the values of the rate constants it can be supposed that when the reaction rate is similar to that for SP-70-900 (for which k was equal to 0.74 h^{-1}) or higher the degradation is faster than concentration of the feed. However, during the experiments with ST-01 and SP-50-900 the reaction rate became slower than the transport of water vapour and volatile compounds present in the feed, therefore an increase of MD concentration in the feed was observed. This conclusion can be supported by the results obtained during photocatalysis performed without MD. In that process the volume of the solution was not decreased due to evaporation of water and volatile compounds through the membrane and, therefore, no increase of MB concentration was observed.

Comparing the results obtained in the experiments performed with and without application of MD it can be observed that the rate of color fading of the solution in the hybrid process was lower than during the photocatalysis alone. Lower effectiveness of MB degradation in this hybrid system could be related to the concentration of the feed solution. In the MD process the 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 (such as MB) present in the solution is increasing, which finally affects the decomposition rate. It was also considered that UV irradiation of the feed solution was shorter than in case of photocatalysis, because only the feed tank was irradiated.

Application of the membrane process, such as MD, makes an opportunity to separate the catalyst from the treated solution. On the basis of turbidity measurement it was found that the MD process is very effective in retention of the photocatalyst particles. For SP-50-900 the turbidity of the feed was equal to 24.6 NTU (normalized turbidity units), whereas the turbidity of distillate amounted to 0.15 NTU. In case of SP-70-900 these values amounted to 50.6 NTU versus 0.13 NTU, respectively. For comparison, the turbidity of distilled water used to prepare the model solution amounted to 0.14 NTU. The obtained results indicate also that separation of catalyst by MD makes an opportunity to reuse the catalyst in further runs.

It should be also mentioned, that the product (distillate) is high quality water, containing only a small amount of volatile compounds that passed through the membrane. After 9 h of the process performance the conductivity of distillate was in the range of 1.5–2 $\mu\text{S}/\text{cm}$, TDS content ranged from 0.9 to 1.2 ppm, pH from 5.2 to 5.4 and TOC concentration did not exceed the value of 0.5 mgC/dm^3 , regardless of the catalyst applied. For comparison, the quality of ultrapure water applied as distillate at the beginning of the process was as follows: conductivity, 1 $\mu\text{S}/\text{cm}$; TDS, 0.5 ppm; pH 5.7; TOC, 0 mgC/dm^3 . It should be also noticed that the concentration of MB in the permeate was equal to 0 what means that the model dye was separated completely by the MD membrane. These results from the fact that the MD membrane is permeable for volatile compounds and water vapour only, as was mentioned earlier. MB is a non-volatile compound, therefore the total amount of the dye remained on the feed side. A slight increase of conductivity, TDS and TOC values and simultaneous decrease of pH might suggest that during the photodecomposition of MB some acidic compounds are formed. Moreover, some of these compounds are volatile and could be transported through the MD membrane what might result in an insignificant acidification of distillate. However, in order to determine what exactly are these compounds, further investigations are needed.

It was revealed that hybrid photocatalysis–MD system has a lot of advantages over a typical photocatalytic batch reactor. Degradation and separation could be performed at the same time and in the same place what minimizes the size of the installation. Moreover, the product (permeate) is high quality water because only water vapour and volatile compounds are passing through the MD membrane. It should be stressed that it is not possible

to get a product of so high quality in a classical batch reactor. However, a disadvantage of the hybrid system proposed is lower degradation rate than in case of classical batch reactor. Therefore, further investigations are necessary to improve the process performance.

4. Conclusions

The highest activity towards MB decomposition exhibited SP-70-900 photocatalyst. The MB solution was decolorized in two ways—adsorption into carbon layer on TiO_2 particles and photodecomposition during UV irradiation. The photodecomposition of MB during the 2nd run was lower than in the 1st one. Possible reason might be occupation of the catalyst surface by the by-products of photodegradation. Moreover, the time of the reaction during the 1st run was probably not long enough to obtain a complete photodegradation of MB and to recover the initial activity of catalysts. The photodegradation of MB in the PMR was slower than in the batch reactor, which might be due to shorter time of exposition of the solution into UV irradiation. The MD process can be successfully applied for separation of photocatalysts from the solution. A very important advantage of the PMR is complete separation of dye and other non-volatile compounds. Thus, the product (permeate) has higher quality than in case of photocatalysis conducted without MD.

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