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ScienceDirect
Journal of Hazardous Materials 140 (2007) 369–375
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Application of carbon-coated TiO_2 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 TiO_2 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 TiO_2 catalysts containing different amount of carbon and commercially available TiO_2 (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.

Keywords: Carbon-coated TiO_2; 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. TiO_2 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 TiO_2 photocatalytic properties have been widely investigated. One of methods to obtain such a photocatalyst is preparation of TiO_2–carbon composites, including mounting of TiO_2 on activated carbon [1–5] or coating of anatase with carbon layer [6–10].

In our previous studies [6–8], TiO_2 powders having anatase phase coated with carbon layer were synthesized. It was found that carbon coating of TiO_2 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 TiO_2 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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doi:10.1016/j.jhazmat.2006.10.016

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 TiO_2 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 TiO_2 without MD was also examined.

2. Experimental

The carbon-coated TiO_2 was prepared by mixing of TiO_2 (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 N_2 flowing at a rate of 2.9 $cm^3 s^{-1}$. 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 m^2/g after heating to 900 °C [14].

BET surface area and pore size distribution were determined by N_2 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 Kα 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, $C_{16}H_{18}ClN_3S$) 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 m^2. 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

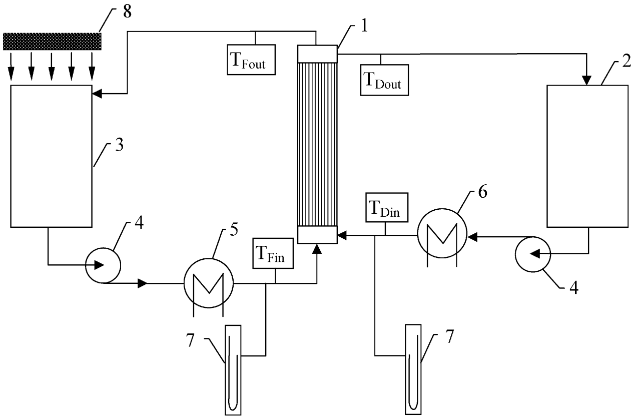

Fig. 1. Schematic diagram of the apparatus for MD: (1) membrane module; (2) distillate tank; (3) feed tank (V = 2.9 l); (4) pump; (5) and (6) heat exchangers; (7) manometers; (8) UV lamp; T_{Fin}, T_{Din}—inlet temperatures of feed and distillate; T_{Fout}, T_{Dout}—outlet temperatures of feed and distillate.