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PHOTOCATALYTIC ACTIVITY OF TiO₂ IMMOBILIZED ON GLASS BEADS

This paper reports the study of the photocatalytic activity of immobilized pure and boron-modified TiO_2 on glass beads. In situ formation and a dip-coating technique fixing catalyst onto the support surface was used. The photoreactor consists of a cylindrical quartz tube (i.d. 40 mm, length 100 mm) and was packed with the immobilized catalyst. The photocatalytic activity was determined by the degradation of phenol in water (0.21 mmol/dm^3). The pure TiO_2 catalyst could be reused for at least 3 cycles.

1. INTRODUCTION

Heterogeneous photocatalysis in the presence of semiconductors is a promising technology, which decomposes and mineralizes organic contaminants in water by the generation of radicals ($^{\bullet}OH$, $O_2^{\bullet-}$) under irradiation (Fujishima et al., 2000). TiO_2 is the most widely used photocatalyst because of its high photocatalytic activity, non-toxicity and durability (Han et al., 2009). It exhibits a band gap of 3.2 eV and thus radicals are

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formed under UV irradiation. In our previous investigation, we presented a boron-modified photocatalyst (B-TiO$_2$), which is active in the presence of visible light (Zaleska et al., 2009). The photocatalytic activity was investigated in a slurry type reactor.

Slurry type reactors are commonly used whereupon the photocatalyst particles have to be separated by filtration, coagulation, flocculation or centrifugation achieving a catalyst free solution and recycling the catalyst. These downstream processes are costly, which is a reasonable limitation of using a slurry reactor on an industrial scale. To avoid the separation step the photocatalyst has to be attached onto a support. Immobilization and the support material influence the photocatalyst activity. The surface area of the catalyst is minimized since the coating layer has a lower porosity (Balasubramanian et al., 2004). It was reported that also the type of support material influences the adsorption characteristics and consequently the decomposition rate of pollutants (Sakthivel et al., 2002). Furthermore, immobilized catalyst showed flow rate dependence of the reaction (Bideau et al., 1995; Kobayakawa et al., 1998). Thus, the support should have the following characteristics (Pozzo et al., 1997): (a) transparent to irradiation; (b) strong surface bonding with the TiO$_2$ catalyst without negatively affecting the reactivity; (c) high specific surface area; (d) good absorption capability for organic compounds; (e) separability; (f) facilitating mass transfer processes and (g) chemical inert.

In view of technical application, the reactor has to be designed in the way so that optimal irradiation of the immobilized catalyst is guaranteed and that it is operated continuously. Several designs were proposed, like fixed bed, fluidized bed, floating bed, coated reactor tube wall, falling film and a kind of membrane "sandwich" reactor (Balasubramanian et al., 2004; Pozzo et al., 1997; O'regan et al., 1990).

In the present paper, both pure and doped TiO$_2$ deposited at the surface of glass beads were used to study the efficiency of model wastewater treatment. Pure TiO$_2$ and boron modified TiO$_2$ were immobilized at the support by in-situ formation and dip-coating technique and the photocatalytic activity was tested in a fixed-bed photoreactor equipped with a parabolic mirror.

2. MATERIALS AND METHODS

The following chemicals were used without further purification: titanium (IV) isopropoxide (97%, Aldrich Chem. Co.), ethanol (POCh, 96%), boric acid triethyl ester (99%), phenol (POCh, pure p.a.), hydrochloric acid (2M) and diluted hydrofluoric acid (5 wt.%). The glass beads used as a support material were obtained from Metal-Chem Sp. Z o.o. (ø 5 mm, ρ = 2.5 g/cm^3 for pure TiO$_2$, ø 4 mm, ρ = 2.5 g/cm^3 for B-TiO$_2$). ST-01 from Ishihara Sangyo, Japan (anatase, surface area 300 m^2/g, particle size 7 nm)

was used as TiO$_2$ source for boron doped photocatalyst preparation. Before coating, the beads were etched for 24 h in diluted hydrofluoric acid, washed thoroughly with deionized water and dried at 105 °C for 2 h. The immobilization of pure TiO$_2$ was carried out by in situ formation of TiO$_2$ procedure similar to the method reported by Kobayakawa et al. (1998). 30 cm^3 titanium (IV) isopropoxide and 200 cm^3 ethanol were mixed with 5.4 cm^3 HCl. A hydroxide sol was obtained by hydrolysis of titanium (IV) isopropoxide. The surface modified glass beads were immersed for 10 min in the hydroxide sol. Subsequently, they were filtrated and dried at 105 °C in an oven and calcinated at 450 °C for 2 h. The procedure was repeated until the beads were coated with 5 layers. Boron modified catalyst was prepared, according to the method reported in our previous investigation (Zaleska et al., 2009). ST-01 powder was grinded with boric acid triethyl ester in an agate mortar achieving boron content of 2 wt.%. The obtained powder was dried at 80 °C and calcinated at 400 °C for 1 h. The resulting powder was dispersed in deionized water achieving coating suspension with 30 g/l catalyst. Glass beads were dipped into suspension for 10 min. After coating, they were dried at 110 °C and calcinated at 400 °C for 1 h.

Fig. 1 shows the experimental setup used for photocatalytic measurements. The photoreactor, made of a cylindrical quartz tube (i.d. 40 mm, length 100 mm), was filled with TiO$_2$-coated glass beads and positioned over an aluminum parabolic mirror. Two liters of phenol solution (0.21 mmol/dm^3) were pumped in a loop with a flow rate of 1.2 cm^3/s. The TiO$_2$ immobilized photocatalyst was reused 3 times with a new stock solution. The immobilized B-TiO$_2$ catalyst was used for a single cycle. The fixed bed was irradiated by UV-Vis light using a 1000 W Xenon lamp (Oriel). Phenol concentration was determined by a colorimetric method measuring the UV-Vis absorbance with spectrophotometer (DU-7, Beckman). UV-flux was measured by UV-power meter (Hamamatsu Photonics, measurements range: 310 nm to 380 nm).
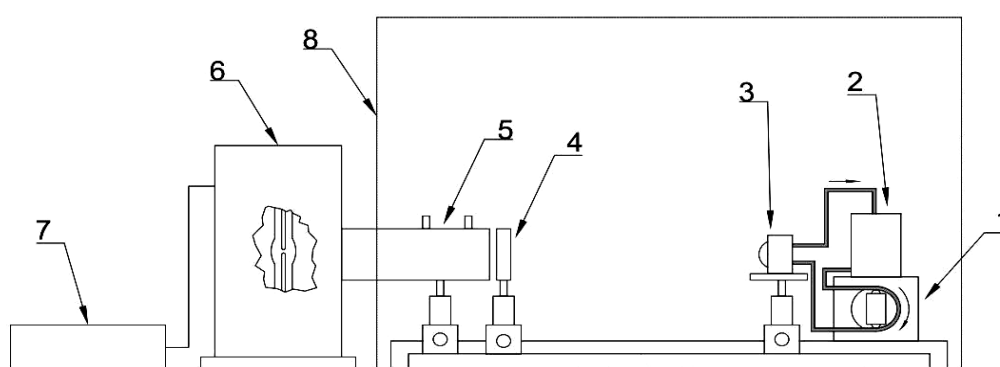

Fig. 1. Experimental setup: 1) peristaltic pump, 2) storage tank, 3) photoreactor with parabolic mirror, 4) filter, 5) IR filter, 6) Xenon lamp, 7) power supply, 8) darkroom

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3. RESULT AND DISCUSSION

Table 1 and Fig. 2 show the change in phenol concentration vs. time profile observed during the photocatalytic degradation in the presence of glass beads coated with pure and boron-doped TiO_2. It has been observed that the temperature of phenol solution increased during irradiation and converged against 40 °C. The glass beads coated with pure TiO_2, prepared by sol-gel method, were used for 3 cycles. Considering the phenol solution flow rate (1.2 cm^3/s) it can be estimated that the whole volume of wastewater solution (2 dm^3) was circulated through the photoreactor almost 11 times during one cycle of irradiation (300 min). Under the experimental conditions, the efficiency of phenol removal in the presence of glass beads coated with pure TiO_2 was 30, 28 and 23% for the first, second and third cycle, respectively. Thus, the obtained result suggests that photocatalyst obtained by deposition of TiO_2 at the glass beads surface could be reused at least three times with negligible loss in photoactivity. The mass of the coated beads was measured before the first cycle and after the third one and the mass loss, due to TiO_2 removal, was 0.75 g. Thus, the decrease of phenol degradation rate is contributed to depletion of photocatalyst.

Table 1. Reaction conditions and photocatalytic activity of immobilized pure TiO_2 for three reactor runs with the same catalyst beads and immobilized B-TiO_2 under UV-Vis irradiation

Reaction time (min)	1st cycle			2nd cycle			3rd cycle			B-TiO_2		
	T (°C)	UV flux (mW/cm2)	Efficiency of phenol degradation C/C_0	T (°C)	UV flux (mW/cm2)	Efficiency of phenol degradation C/C_0	T (°C)	UV flux (mW/cm2)	Efficiency of phenol degradation C/C_0	T (°C)	UV flux (mW/cm2)	Efficiency of phenol degradation C/C_0
0	21	14.8	1	26	16.1	1	30	19	1	30	10.8	1
60	31	14.9	0.86	33	17.5	0.97	32	19.5	0.96	32	13.2	0.73
120	35	14.9	0.82	35	18.1	0.94	35	19.8	0.97	34	13	0.7
180	37	16.2	0.73	39	18.2	0.87	38	20.7	0.89	36	13.9	0.69
240	38	16.1	0.71	40	18.3	0.79	38	20.8	0.83	38	14.1	0.68
300	39	16.2	0.7	41	18.3	0.72	39	21.1	0.77	38	13.8	0.67

Slightly higher efficiency of phenol degradation was determined for the photocatalyst in the form of glass beads coated with boron-doped TiO_2. 300 min irradiation resulted in 33% of phenol degradation. After one cycle, the immobilized B-TiO_2 had changed its color from brownish to white and 0.23 g catalyst mass was removed. Thus, the B-TiO_2 catalyst was not reused for an additional cycle. We believe that the high loss of the catalyst is subjected to the high flow rate (72 cm^2/min). In comparison, the maximum flow rate of Kobayakawa et al. (1998) was 15 cm^2/min.
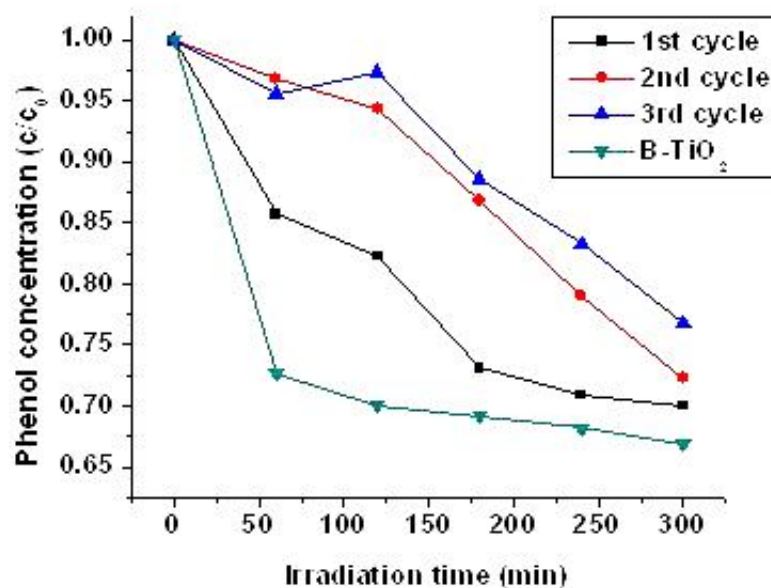

Fig. 2. Efficiency of phenol degradation in the presence of pure and B-TiO_2
under UV-Vis irradiation

Table 2 shows that the phenol degradation efficiency in the fixed-bed photoreactor was much lower than the efficiency, obtained for the system with suspended TiO_2 in the laboratory photoreactor, as reported in our previous investigation. However, it is worth mentioning that these results were achieved for a 10 times greater volume of an irradiated solution. Moreover, the ratio of TiO_2 amount to phenol solution amount was much lower than for the fixed-bed photoreactor system. In this regard, it was confirmed that the fixed-bed photoreactor system with pure or doped TiO_2 immobilized at the glass beads surface proved efficient for a photocatalytic reaction. The observed phenol degradation rate per gram of immobilized B-TiO_2 photocatalyst was higher than for pure TiO_2 supported on glass beads. The degradation rate per gram was 0.42 and 0.15 μmol dm^{-3} h^{-1} g^{-1} for B-TiO_2 and pure TiO_2, respectively.

Table 2. Comparison of fixed-bed photoreactor system and laboratory setup for phenol oxidation
(initial phenol concentration: 0.21 mmol/dm^3, UV-Vis irradiation)

Processing Conditions		Fixed-bed photoreactor	Laboratory setup with suspended TiO$_2$
Volume of oxidized solution [dm^3]		2	0.025
Volume of photoreactor [dm$_3$]		0.125	0.025
Volume of irradiated solution [dm^3]		0.074*	0.025
Irradiation time [min]		300	60
Reaction conditions		polytropic temperature profile	isothermal
Temperature [ºC]		28 – 40	10
Power of radiation source [W]		1000	1000
Mass of the photocatalyst per loading [g]		~1.23 (pure TiO$_2$) 0.6 (B-TiO$_2$)	0.125
Irradiation power per reactor volume [W/dm^3]		8000	40000
Introducing gas		-	air
Gas flow rate [dm^3/h]		-	5
Rate of phenol degradation [μmol·dm^{-3}·min^{-1}]	Pure TiO$_2$	0.18	2.8
	B-TiO$_2$	0.25	2.9
Rate of phenol degradation per gram of catalyst [μmol·dm^{-3}·min^{-1}·g^{-1}]	Pure TiO$_2$	0.15	22.4
	B-TiO$_2$	0.42	23.2

*Calculated according to: $V_{ir} = V_r – V_{gb}$, where V_{ir} – volume of irradiated solution, V_r – volume of photoreactor, V_{gb} – volume of glass beads

The lifetime and regeneration of supported TiO$_2$ for the degradation of phenol under UV-C light in a batch reactor was investigated by Tasbihi at al. (2007). Three type of TiO$_2$ material using sol-gel technique were obtained: TiO$_2$ supported on glass beads, silica gel and quartz sand. The reaction time of 6 h, an initial phenol concentration varied from 25 to 115 mg/dm^3 and 0.25 g of each photocatalyst (supported on 30 g of different support) were chosen for each cycle. After each cycle the photocatalyst was re-calcinated at 600ºC for TiO$_2$/quartz sand and TiO$_2$/silica gel, while it was 700ºC for TiO$_2$/glass beads. TiO$_2$ supported on quartz sand gave the highest efficiency with 90% degradation of 50 mg/dm^3 phenol solution in 6h, followed by TiO$_2$ supported on silica gel and glass beads with 86% and 74%, respectively. The supported TiO$_2$ was found to be stable for repeated use. Their results suggested that TiO$_2$/quartz sand and TiO$_2$/glass

beads gave very good performances in the phenol degradation reaction. However, with TiO$_2$/silica gel, the percentage of degradation decreased to about 11% when used for the second time. Unfortunately, they did not report if depletion of photocatalyst took place, which might be the reason of the degradation decrease after reusing.

4. CONCLUSION

TiO$_2$ and B-TiO$_2$ photocatalyst supported on glass beads were synthesized using in-situ formation (sol-gel method) and dip-coating technique for pure and doped-TiO$_2$, respectively. The boron-doped TiO$_2$ supported on glass beads was used for the first time in this research. Photocatalytic degradation of phenol was observed for both immobilized catalysts. The adherence of photocatalyst has to be improved for both, TiO$_2$ and B-TiO$_2$, since depletion was observed.

ACKNOWLEDGMENTS

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