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NOVEL PHOTOCATALYST IMMOBILIZED ON SPRINGS AND PACKED PHOTOREACTOR

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Abstract. TiO_2 photocatalysts immobilized on novel supports of Pyrex glass springs using the dip-coating technique were prepared. A packed photoreactor was developed with advantages such as uniform-distributed light throughout the reactor, high ratio of illuminated surface areas to the reactor volume, low pressure drop, and no mass transfer limitation. This photoreactor provides a promising candidate to scale-up for the commercial application.

1. INTRODUCTION

For the prospect of complete mineralization of almost all toxic organic pollutants, it has been proven that heterogeneous photocatalysis is an advanced water treatment process with great application potential. In order to be used commercially, however, photocatalysts have to be immobilized to avoid the complicated separation of ultrafine photocatalyst particles from the treated water. Since reactions take place only on the surface of the photocatalysts illuminated by UV light, the effective sites in a photocatalytic reactor are those places where photocatalysts, UV light and reactants exist at the same time. Thus, a uniform distribution of UV light, a high ratio of catalyst surface area to volume and very little mass transfer limitation of reactants are required in the development of highly effective immobilized photocatalyst and photoreactor [1,2].

Ray suggested a novel photocatalytic reactor using extremely narrow artificial fluorescent lamps by immobilization of P25 TiO_2 on their outer side surface, and a large κ, the illuminated catalyst surface area per unit volume of liquid treated in the reactor, was reported [3]. However, only if the lamps are arranged closely can the influence of external mass transfer be avoided. Both the resistance to the flow of fluid and the penetration depth of UV radiation were discussed by Kobayakawa in the fixed photoreactor packed with catalysts immobilized on silica gel beads. A tube reactor with an inner diameter of only 8 mm was used, presumably because of the limitation of penetration depth of the UV light [4].

Here we report a fixed photoreactor packed with TiO_2 catalyst immobilized on a novel support of Pyrex glass springs. The results show that this photoreactor has a number of advantages, such as a large κ value, a uniform distribution of light, no limitation of mass transfer and low resistance to fluid, etc. Thus, it provides a promising candidate to scale-up for commercial applications.

2. EXPERIMENTAL

The dimensions of the packing support of Pyrex glass shaped in a spring are: free height L = 20 mm, span l = 0.7 mm, outer diameter D = 4.6 mm and wire diameter d = 0.75 mm, respectively (Fig. 1). Spring packed beds are a highly effective packing material, and it is well known that there is little limitation of the mass transfer of reactants and the resistance to fluid flow is very low. Furthermore, there are many uniformly-distributed gaps in the photoreactor packed with the springs and incident

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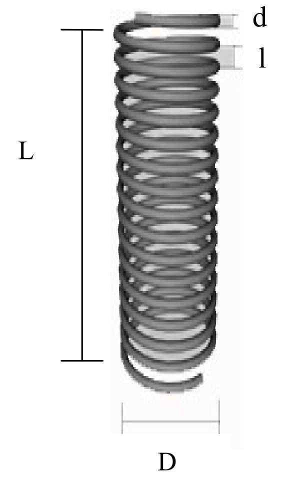

Fig. 1. The structure and dimensions of spring supports. *L* is the free height, *l* span, *D* outer diameter, and *d* wire diameter.

photo flux can pass through these gaps and penetrate deeply into the packed bed, giving a uniform distribution of radiation energy throughout the photoreactor. The Pyrex glass bead (mean bead diameter of 1.5 mm) was used as a reference for packing supports.

Degussa P25 TiO_2 was immobilized onto the Pyrex glass springs and beads by dip-coating technique, similar to that by Ray [3].

The apparatus designed to measure the light distribution in a fixed bed packed with immobilized catalysts or filled with slurry is shown in Fig. 2. The transmission of parallel UV light passing through the packed bed immersed in de-ionized or distilled water or 0.5% P25 slurry was measured. The distribution of light intensity along the packed bed was obtained by changing the packed depth of the catalyst in the Pyrex glass vessel.

To evaluate the photocatalytic efficiency, two sets of annular photoreactor were used, with annulus width of 10 mm and 30 mm, respectively. Methylene blue dye was used as a model pollutant. An 8W fluorescent black light was placed inside the inner tube with an outer diameter of 45 mm. The immobilized photocatalysts were packed in the annulus through which the reaction liquid flowed. An annular reactor with the outer tube coated with P25 TiO_2 catalyst was used as a reference of an annular film reactor.

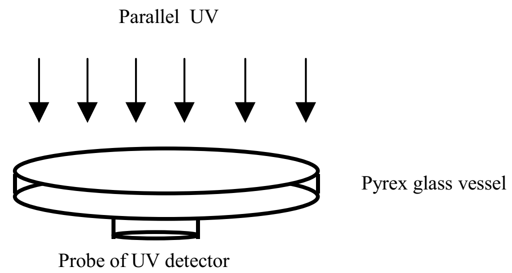

Fig. 2. Schematic diagram of experimental setup for light distribution measurements.

3. RESULTS AND DISCUSSION

3.1. Distribution of light intensity

Fig. 3 shows the distribution of light intensity across the Pyrex test vessel containing slurry, packed beads and packed springs. The UV light can only pass through a 2 mm depth in 0.5% P25 slurry. Using the fixed bed packed with catalyst immobilized on beads (TiO_2/B), light can pass up to 5 mm deep. In a bed packed with catalysts immobilized on the novel spring support (TiO_2/WS), however, UV light can penetrate more than 30 mm. The light penetration depth is a critical factor in determining the possibility of the scale-up of a photoreactor. Because of the low penetration depth of UV light, we believe that the Pyrex glass tube reactor with an inner diameter of only 8 mm used by Kobaykawa is difficult to scale up [4].

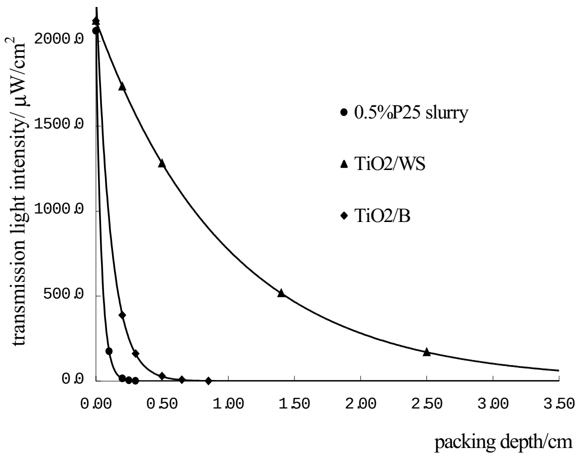

Fig. 3. The distribution of light along the different packed beds.

Table 1. The ratio of surface area to the volume of treated liquid (κ).C_c is the catalyst concentration. d_p is the average diameter of P25 TiO_2 particles. ρ_c is the density of TiO_2 . d_i is diameter of reactor's inner tube. $d_{0,10}$ and $d_{0,30}$ are the diameters of reactor's outer tube of 10 mm and 30 mm annulus width respectively. The ρ_d is the pile density of the catalyst. S is the specific surface area. κ_{10} and κ_{30} are the effective κ values in the reactors of 10 mm and 30 mm annulus width respectively.

Reactor	*Slurry*	*Annular Film*	*TiO_2/B*	*TiO_2/ WS*
Formulae κ (m^2/m^3)	$6C_c/(\rho_c d_p)$	$4d_0/(d_0^2 - d_i^2)$	$\rho_d S$	$\rho_d S$
Parameter values	d_p=0.3 μm C_c=0.5 kg/m^3	$d_{0,10}$=0.065 $d_{0,30}$=0.105 d_i=0.045m	ρ_d=1818 kg/m^3 S=2.0 m^2/kg	ρ_d=236 kg/m^3 S= 3.8m^2/kg
κ (m^{-1})	2631	118	3636	897
κ_{10}(m^{-1})	526	118	1818	897
κ_{30}(m^{-1})	175	47	303	897

3.2. Illuminated Specific Surface Area

Ray proposed a parameter κ, the illuminated specific surface area, representing the total illuminated surface area of catalyst within the reactor that is in contact with the reaction liquid. The κ values of different photoreactor systems in our experiments were calculated and shown in Table 1. κ is the ratio of catalyst surface area to the volume of liquid regardless of the illumination. κ_{10} and κ_{30} are the calculated values using the light distribution results in Fig. 3. Because the pile density of TiO_2/B is very large, the volume of liquid held inside the reactor is very small, and therefore the reactor packed with TiO_2/B has the largest κ value. For the reactors packed with 0.5%P25 slurry and TiO_2/B, the κ values decreased greatly when the depth increased. In comparison, the k of the reactor packed with the novel (spring) catalyst TiO_2/WS remained unchanged as long as the annulus width was less than 30 mm. The result indicates that the reactor packed with the novel TiO_2/WS catalyst is promising to scale up for the commercial application.

3.3. Photocatalytic efficiency

The photocatalytic efficiency is defined as the amount of methylene blue reacted within 15 minutes per unit volume of reactor, i.e. R (see Table 2). When an annular reactor of 10 mm annulus width was used, the TiO_2/WS system has a much higher catalytic efficiency than that of the TiO_2/B system. Although the efficiency of the 0.5% P25 slurry system was also high, it decreased significantly when the annulus increased to 30 mm due to the light penetration depth limitation. The ratio R_{10}/R_{30} was used to evaluate the degree of efficiency drop when the annulus became wider. For the three systems studied, the efficiency of the TiO_2/WS reactor is the least dependent on the annulus width. In Table 2, the R/κ can be taken as a parameter of specific activity of illuminated catalyst. Because of the great difference of the penetration depth between 0.5%

Table 2. Comparison of photocatalytic efficiency of different packed beds. The photocatalytic efficiency (i.e. bleach rate R) was defined as the ratio of conversion amount of methylene blue to packed volume of the photocatalyst within 15 minutes (mg/L). R_{10} and R_{30} were the bleach rates with the packed bed thickness of 10 mm and 30 mm respectively, i.e. the annulus of the annular reactors being 10 mm and 30 mm respectively. The R/κ values in the table are multiplied by 10^3.

System	TiO_2/B bed	TiO_2/WS bed	0.5%P25 slurry
R_{10}(mg/L)	0.996	3.189	3.370
R_{30}(mg/L)	0.203	1.566	0.440
R_{10}/R_{30}	4.906	2.036	7.659
R_{10}/κ_{10} (mg·m/L)·10^3	1.267	3.556	15.320
R_{30}/κ_{30} (mg·m/L)·10^3	1.036	1.746	8.148

P25 slurry and TiO_2/WS packed bed, the R_{30} value of the 0.5% P25 slurry is much smaller than that of the TiO_2/WS packed bed. However, when the effective catalysts illuminated by UV light (κ_{30}) is also considered in the evaluation of the photocatalytic effeciency, one finds that the R_{30}/κ_{30} value of 0.5% P25 slurry is much larger than that of TiO_2/WS packed bed. This means that the activity of P25 TiO_2 is severely blocked by the immobilization treatment.

4. CONCLUSIONS

Springs are a well-known packing material. In the fixed bed packed with the novel (spring) immobilized photocatalyst, there was no mass transfer limitation, the pressure drop was very low, the distribution of light was uniform throughout the bed, and the κ value remained large even when the packed depth increased. The photoreactor packed with the novel TiO_2 / WS catalyst provides a promising candidate to scale-up for commercial applications.

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