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## Utilization of floating materials coated with TiO<sub>2</sub> film for photodegradation of organic compounds

K. Hayakawa<sup>1,\*</sup>, C. Yokobaba<sup>1</sup>, N. Ichiki<sup>1</sup>, Muh. Z. Muzakkar<sup>2</sup>, T. Shinmura<sup>3</sup>, S. Nagaoka<sup>4</sup>

1. Department of Chemistry & BioScience, Kagoshima University, Korimoto 1-21-35, Kagoshima 890-0065, Japan

2. Department of Chemistry, Haluoleo University, Kendari-Southeast Sulawesi 93231, Indonesia

3. Department of Planning and Information, Kagoshima Prefecture Center of Industrial Technology

4. Titan Kogyo K. K., R&D Department, Kogushi, Ube-shi, Yamaguchi 755-8567, Japan

\*Corresponding author e-mail address: hayak@sci.kagoshima-u.ac.jp; phone:

+81-99-285-8101; fax: +81-99-285-8117

### Abstract

*The floating photocatalysts were synthesized by coating inorganic balloon (PC-S1) and pumice with TiO<sub>2</sub> film, which was prepared by the painting of TiO<sub>2</sub> fine powder and the sol-gel technique from titanium tetraisopropoxide, respectively, and the photocatalytic degradation was examined for some organic compounds and dyestuffs. The effective photodegradation of some organic compounds and dyestuffs was observed in the presence of the floating photocatalysts PC-S1 and Pumice under the UV and outdoor irradiations. The floating photocatalysts were effective for the highly concentrated dye solutions of absorbance 5.0 at 1 cm light-path length. The rate of photodegradation was not high for the floating photocatalysts and it took many days for the complete decomposition of some organic compounds under the outdoor irradiation. These results suggest a potential use of the floating photocatalysts for waste processing of water combined with a slow degradation technique like biodegradation.*

**Keywords:** Floating photocatalysis; TiO<sub>2</sub>, Photodegradation, Dyes, Aromatic compounds

### Introduction :

Degradation of pollutants is the increasing important subject in order to keep our environment clean and comfortable. Since amounts of industrial production and the waste from general houses in developed countries exceed the ability of natural biodegradation, techniques for more effective degradation and for minimizing waste by improved recycle system are waited for developing. Titanium

dioxide is well known to be useful for the photocatalytic decomposition of many organic compounds and attracts an increasing interest as a cleaning material of our environment. It is already applied for some construction items to decompose air pollutants<sup>1-3</sup>. The TiO<sub>2</sub> photocatalyst powders have been examined for photodegradation of many organic compounds in aqueous solution and proved the effectiveness for dilute pollutant solutions due to the inevitable light irradiation<sup>4-16</sup>. Because the TiO<sub>2</sub> has larger density than water, the powder tends to sink and interfere the light irradiation. Heller and coworkers developed the floating photocatalysts, in which TiO<sub>2</sub> film was coated on the hollow aluminosilicate microspheres of 100 μm size, and proved the effectiveness for the photodegradation of crude oil spilled out on the sea under the irradiation of sunlight<sup>17</sup>.

In this paper, floating materials coated with TiO<sub>2</sub> photocatalyst film on the surface were examined for the photodegradation of some organic compounds and the heavy color dye solutions. The effective photodegradation of some organic compounds and dyestuffs was observed under the UV and outdoor irradiations. The rate of photodegradation was not high under the outdoor irradiation.

### Experimental :

**Materials :** Two floating photocatalysts were prepared. The one was the pumice coated with TiO<sub>2</sub> film by sol-gel technique (Pumice). The other was PC-S1 (Titan Kogyo) that was coated with TiO<sub>2</sub> paint on assembling particles of inorganic fine balloons made from "Shirasu,"

pyroclastic deposit of ancient times. The synthesis of the former photocatalyst is given in Scheme 1. The pumices were collected in Kagoshima Bay, cut into the small block of  $1\text{ cm}^3$  and wash thoroughly with water. They were soaked in a silica sol (HAS-10, Korukoto) for 10 minutes and kept at  $80\text{ }^\circ\text{C}$  for a day before the procession of  $\text{TiO}_2$  coating, because the sodium ion in the pumice interfere the formation of the photoactive anatase type  $\text{TiO}_2$  crystal at the calcination<sup>18</sup>. The silica-coated pumices were dipped in an ethanol solution of titanium tetraisopropoxide and acetylacetone, kept one night at room temperature for condensation. After drying the pumices were calcined at  $400\text{ }^\circ\text{C}$  for 2 hours. The organic compounds examined were rhodamine B (RB), acridine orange (AO), methylorange (MO), methylene blue (MB), crystal violet (CV), benzoic acid, phenol, pyridine, hexadecylpyridinium chloride (HPyC), sodium dodecylbenzenesulfonate (DBS), some acid dyestuffs, and direct dyestuffs. The molecular structures of some dyes are given in Figure 1. The molecular structures of some dyestuffs were unknown.

**Measurements of photodegradation :** Photodegradation of aqueous solutions of organic compounds was examined in the absence and presence of few floating photocatalyst blocks under the irradiation with natural daylight or UV light (black light, the maximum intensity at  $360\text{ nm}$ ). The absorbance at the characteristic wavelength of the organic compounds was monitored by using Shimadzu Spectrophotometer UV-1200. The wavelength used for the measurements of photodegradation was listed in Table 1. The absorption spectra were also monitored for some organic compounds by the use of Jasco Spectrophotometer V560. The cuvette of  $2\text{ mm}$  light-path length was used for the dye solutions of high concentration. The sample bottles were placed under the irradiation as shown in Figure 2. The irradiation intensity by the UV light was  $0.32\text{ mW cm}^{-2}$  at the sample place. The UV intensity was measured by the UV irradiation meter UVA-365 (N. T. Corporation). The photodegradation was so slow that the

increase in absorbance of open samples made it difficult to measure the photodegradation rate, because of the evaporation of water. Therefore, the capped Pyrex bottles were used as the sample container. The real irradiation intensity for the sample solutions was less than  $0.32\text{ mW cm}^{-2}$  due to the absorption of UV light by the Pyrex glass. The samples irradiated by the natural sunlight were just kept outdoors for a week without shaking and the absorbance was measured day by day.

### Results and Discussion :

**Photodegradation of some organic compounds in thinner solution :** Figure 3 shows the time dependence of the absorbance at  $553\text{ nm}$  of RB under the both UV and outdoor irradiations. The starting absorbance of the sample solutions was around unity at the monitoring wavelength, which means that the light intensity decreases 90% at the  $1\text{ cm}$  depth. The UV irradiation in the presence of the photocatalysts, Pumice or PC-S1, indicates quick degradation of RB (A), whereas the UV irradiation in the absence of the photocatalysts indicates no degradation (Reference). The complete decomposition of RB after 24 h was confirmed from the absorption spectrum: no detectable spectrum in the range of  $200 - 700\text{ nm}$ . The outdoor irradiation requires 5 to 7 days for the complete decomposition of RB (B), but the both photocatalysts indicate the effectiveness for the degradation of RB compared with Reference<sup>19</sup>. This slow degradation may be compared with the environmental cleaning cycle of nature or the natural biodegradation.

AO indicated a quick degradation under the both irradiation. The outdoor irradiation induced the 95% absorbance decrease at  $492\text{ nm}$  after 24 hours. Reference data of AO also indicated the considerable degradation of AO under the outdoor irradiation even in the absence of photocatalyst, indicating the inferior photoresistance. MB also indicated the weak photodegradation under the outdoor irradiation in the absence of photocatalyst. The absorbance decreases 90% of the initial value after two weeks. MO indicated the strong photoresistance under the both irradiations

even in the presence of photocatalysts. The photocatalysts were also effective for benzoic acid, phenol and pyridine. Pyridine was also decomposed after 24 hours by the UV irradiation in the absence of photocatalyst. The degradation of the anionic and cationic surfactants was tested in the presence of the photocatalysts. The TiO<sub>2</sub> photocatalysts have been proved to decompose the anionic, cationic and nonionic surfactants and the rate and efficiency depends on the surfactant molecular structure<sup>8, 10, 20-26</sup>. The floating photocatalysts were expected to be effective for the surfactant photodegradation because of the property of surface accumulation of surfactant. The cationic surfactant HPyC indicates a rapid absorption decrease in the first stage, followed with the slow decrease in the presence of the photocatalysts, suggesting the rapid adsorption on the photocatalyst surface. The anionic surfactant DBS did not show such quick decrease in the absorbance. The floating photocatalysts show a similar photocatalytic effect for the surfactants as for the other organic compounds.

The time dependence of the absorbance was analyzed by the first-order rate equation 1.

$$\ln A = \ln A_0 - k t \quad (1)$$

In this analysis, we used the data obtained for the first 8 hours for the system of UV irradiation and for the first 7 days for the system of outdoor irradiation. Many data fitted to Equation 1 and the correlation coefficient was larger than 0.9. But some data indicated a poor fitting. The results are listed in Tables 2 and 3 for the UV and outdoor irradiations, respectively. The tables include also the residual absorbance after 24 hours for the UV irradiation data and after a week for the outdoor irradiation data.

Under the UV irradiation, both the photocatalysts indicate effective photodegradation for the every dye except MO: the every dye decomposed nearly completely one day later (Table 2). The photocatalysts indicates the effective photodegradation for benzoic acid. Pyridine was also decomposed in the presence of the photocatalysts, but the similar decomposition was observed under the UV irradiation in Reference, too. Phenol

indicated the induction period for photodegradation and the calculation resulted in zero for k in Pumice and 0.02 for k in PC-S1 because the first 8 data were used. The residual absorbance at 24 h was much less for the photocatalytic systems than for Reference. The surfactant tends to adsorb on water surface and the effective decomposition was expected by the floating photocatalysts. Table 4 indicates the poor photodegradation for the surfactants, in particular, for DBS.

Under the outdoor irradiation, the slow but effective photodegradation by the photocatalysts was observed for the dyes except MO, benzoic acid and HPyC. These organic compounds indicated no photodegradation in the absence of the photocatalysts. The photocatalysts indicated a poor photodegradation for MO, phenol and DBS, but the photocatalytic effect was observed compared to Reference where no photodegradation was observed for these compounds. It is very difficult to compare the efficiency quantitatively because of the uncontrolled quantity, size and surface area of the photocatalysts. A rough evaluation of the data in Tables 2 and 4 indicates a little better efficiency for PC-S1. Table 4 indicates the qualitative efficiency of the two photocatalysts for the organic compounds.

### Photodegradation of dyestuffs in concentrated solution :

Dyestuffs developed for textile dyeing have strong photoresistance. The floating photocatalysts were examined for the photodegradation of the concentrated solution of direct dyes and acid dyes. Some studies have revealed the photocatalytic effect of TiO<sub>2</sub> powder for the photodegradation of dyestuffs<sup>12, 16, 19, 27-30</sup>. In the present study, the concentrated dye solutions were examined. The initial absorbance was 5.0 at the wavelength of maximum absorption for 1-cm light path length, which means that the irradiation intensity decreases to 1/10<sup>5</sup> for each 1-cm depth.

Figure 4 indicates the spectrum change of acid dyes under the UV irradiation as a function of irradiation time. The color fading is clearly observed at 650 nm for C. I. Acid Green 16 and at 450 nm for C. I. Acid Brown 16. However,

the absorbance at ultraviolet region does not decrease but somewhat increases partly due to the decomposed intermediates of the dye and partly due to the light scattering by colloidal fine particles.

The residual absorbance at the monitoring wavelength is shown in Figure 5 after 7 days under the UV irradiation and in Figure 6 after 10 days under the outdoor irradiation. Because of the very high concentration of dye, the dye solutions indicated the considerable residual absorbance even after the UV irradiation of 7 d. The both photocatalysts indicate an excellent photodegradation for the dyes, C. I. Acid Red 97 and Green 16 under the UV irradiation. PC-S1 shows the effective photodegradation for C. I. Acid Blue 220 and 127, too, but Pumice shows poor photodegradation effect for them. The dyes, C. I. Acid Brown 51 and C. I. Direct Green, indicated the high photoresistance for the UV irradiations even in the presence of PC-S1. Under the outdoor irradiation, the photodegradation by PC-S1 is less effective for C. I. Acid Blues 220 and 127 than those under the UV irradiation. PC-S1 always indicated the better effect for the photodegradation of these dyes than Pumice.

The apparent first-order rate constants are given in Table 5. The constant was estimated from the first few points. As seen in the residual absorbance, the rate constant roughly corresponds to the residual absorbance; the larger the rate constant is, the smaller the residual absorbance is after a few days irradiation. Though the residual absorbance is very small for C. I. Acid Blue 127 under the UV irradiation in the presence of PC-S1, the rate constant is less for C. I. Acid Blue 127 than for C. I. Direct Green. The latter dye indicated the quick fading for the first few days, but the absorbance decrease became very slow after 5 days.

Figure 7 indicates the photodegradation for the natural dyestuff Wanteks used in Indonesia under the outdoor irradiation in Indonesia. The initial absorbance at 1-cm light-path length was 1.0. The photodegradation by PC-S1 is compared to those by TiO<sub>2</sub> powder (PC-101, Titan Kogyo) and by irradiation without photocatalyst (Reference). The finding that

no photodegradation was observed for Reference indicates the high photoresistance of Wanteks. The both photocatalysts indicate the effective photodegradation for Wanteks. The TiO<sub>2</sub> powder shows more effective than PC-S1. The TiO<sub>2</sub> powder of 2.5 mg was suspended in 100 mL water and the surface area was much higher than that of PC-S1. The adsorption of the dye on TiO<sub>2</sub> powder may be responsible to the initial quick decrease in the absorbance. The separation of the TiO<sub>2</sub> powder was difficult and the considerable loss of the TiO<sub>2</sub> powder for repeated use was observed. From these results, PC-S1 proves the effectiveness for the photodecomposition of Wanteks by outdoor irradiation and can be utilized as an environmental cleaner without any energy cost.

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**Table 1**  
**Photodecomposition of organic compounds in thinner solution by UV irradiation :**  
**The first-order rate constant and the absorbance after 24 hours.**

Organic Compounds	Wavelength monitored (nm)	Rate Constant	Residual Absorbance	Rate Constant	Residual Absorbance
		$k / h^{-1}$	after 24 h	$k / h^{-1}$	after 24 h
		(Pumice)		(PC-S1)	
<Dyes>					
AO	492	$0.17 \pm 0.03$	1% ( $\pm 1$ )	$0.18 \pm 0.03$	2% ( $\pm 1$ )
MB	660	$0.14 \pm 0.02$	2% ( $\pm 1$ )	$0.15 \pm 0.00$	1% ( $\pm 0$ )
RB	553	$0.11 \pm 0.02$	3% ( $\pm 2$ )	$0.11 \pm 0.02$	1% ( $\pm 1$ )
CV	588	$0.11 \pm 0.02$	4% ( $\pm 1$ )	$0.14 \pm 0.01$	1% ( $\pm 1$ )
MO	470	$0.02 \pm 0.01$	41% ( $\pm 19$ )	$0.03 \pm 0.01$	16% ( $\pm 10$ )
<Aromatic compounds>					
Benzoic Acid	228	$0.06 \pm 0.01$	10% ( $\pm 3$ )	$0.06 \pm 0.01$	7% ( $\pm 1$ )
Phenol	210	$0.00 \pm 0.01$	50% ( $\pm 8$ )	$0.02 \pm 0.01$	21% ( $\pm 1$ )
Pyridine	254	$0.07 \pm 0.05$	10% ( $\pm 3$ )	$0.15 \pm 0.07$	5% ( $\pm 2$ )
<Surfactants>					
HPyC	260	$0.06 \pm 0.01$	40% ( $\pm 7$ )	$0.08 \pm 0.01$	28% ( $\pm 1$ )
DBS	220	$0.02 \pm 0.01$	47% ( $\pm 30$ )	$0.02 \pm 0.01$	35% ( $\pm 10$ )

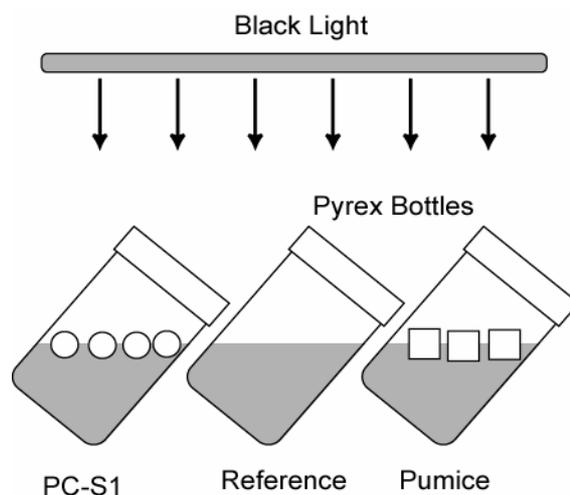
**Table 2.**  
**Photodecomposition of organic compounds by natural irradiation : The first-order rate constant and the absorbance after 1 week.**

Organic Compounds	Rate Constant	Residual Absorbance	Rate Constant	Residual Absorbance
	$k / d^{-1}$	After 1 week	$k / d^{-1}$	After 1 week
	Pumice		PC-S1	
<Dyes>				
AO	$0.13 \pm 0.01$	4% ( $\pm 1$ )	$0.12 \pm 0.01$	4% ( $\pm 2$ )
MB	$0.73 \pm 0.05$	5% ( $\pm 2$ )	$0.75 \pm 0.03$	5% ( $\pm 3$ )
RB	$0.37 \pm 0.05$	2% ( $\pm 1$ )	$0.43 \pm 0.00$	1% ( $\pm 0$ )
CV	$0.41 \pm 0.02$	17% ( $\pm 10$ )	$0.82 \pm 0.02$	5% ( $\pm 1$ )
MO	$0.02 \pm 0.01$	81% ( $\pm 5$ )	$0.04 \pm 0.00$	67% ( $\pm 1$ )
<Aromatic compounds>				
Benzoic Acid	$0.26 \pm 0.12$	3% ( $\pm 1$ )	$0.12 \pm 0.02$	12% ( $\pm 9$ )
Phenol	$0.12 \pm 0.03$	31% ( $\pm 16$ )	$0.13 \pm 0.05$	22% ( $\pm 5$ )
Pyridine	$0.10 \pm 0.00$	24% ( $\pm 5$ )	$0.16 \pm 0.06$	20% ( $\pm 1$ )
<Surfactants>				
HPyC	$0.14 \pm 0.01$	11% ( $\pm 5$ )	$0.14 \pm 0.02$	10% ( $\pm 3$ )
DBS	$0.10 \pm 0.06$	38% ( $\pm 28$ )	$0.07 \pm 0.03$	41% ( $\pm 26$ )

**Pumice**

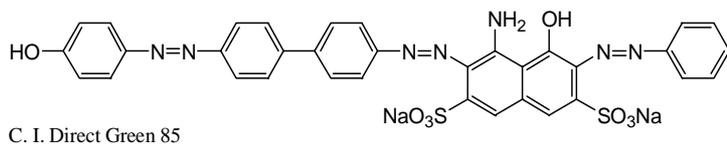
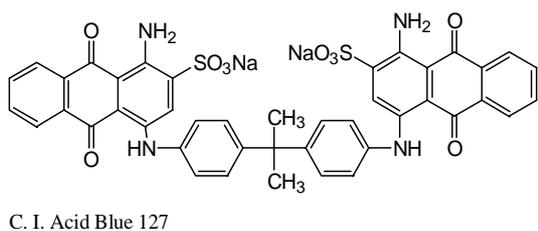
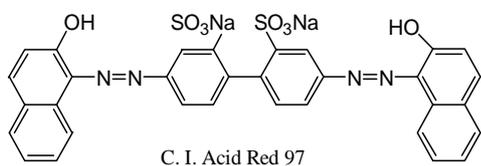
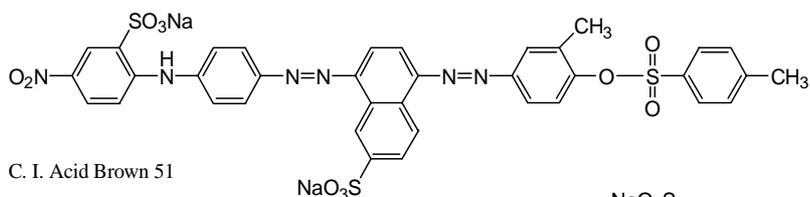
Double Coating with Silica  
Dip into Tetraethyl Orthosilicate  
Dry at 80 oC one night

Double Coating with TiO<sub>2</sub>  
Dip in the EtOH Solution of  
(Ti(IV) propoxide and 2,4-Pentanedione)  
Dry overnight under 30% humidity  
Calcination at 400 oC for 2 h

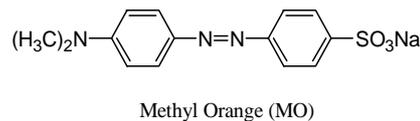
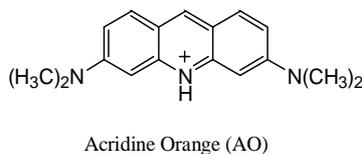
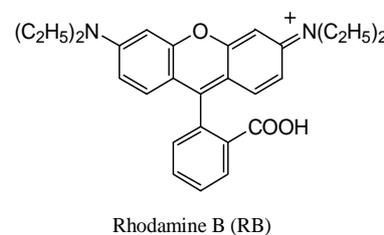
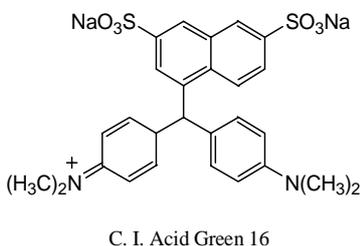
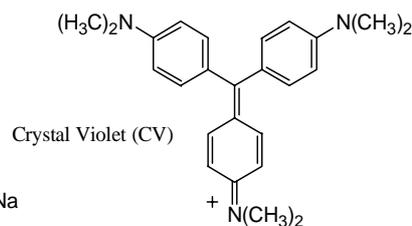


**Pumice coated with TiO<sub>2</sub>**

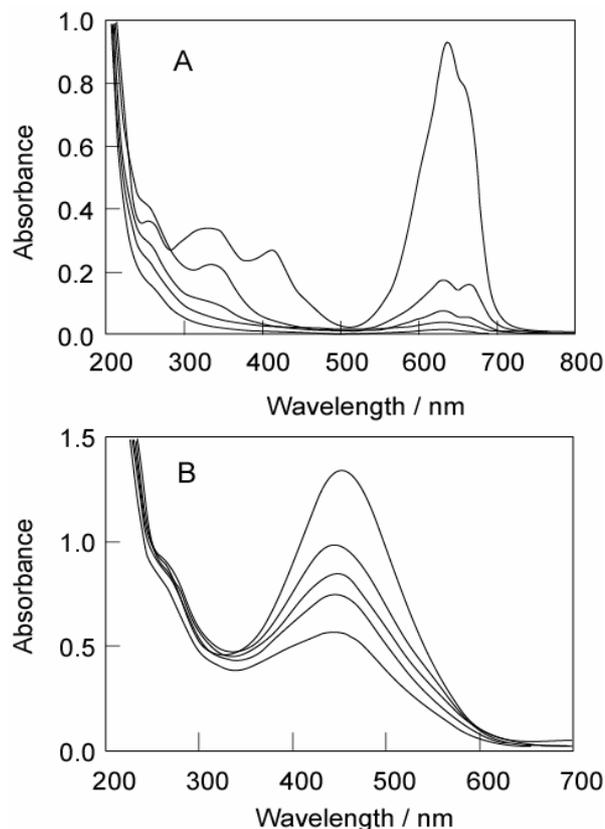
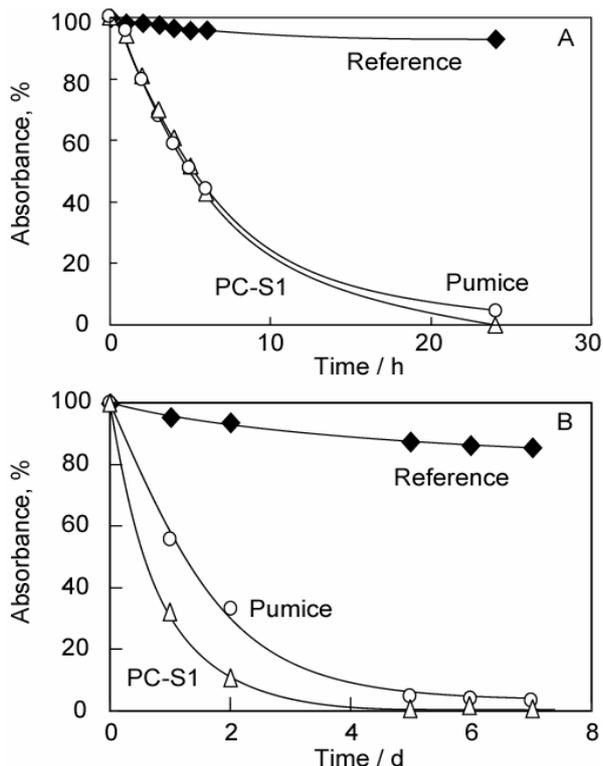
**Scheme 1 : The preparation scheme of the pumice photocatalyst**



**Figure 2 : Irradiation outline for testing the photodegradation in the presence of photocatalysts**

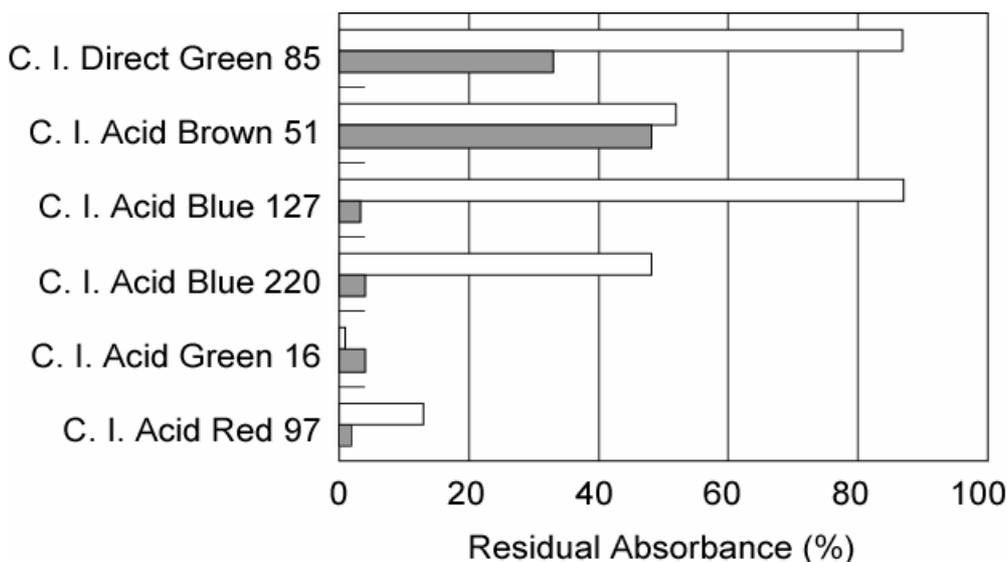


**Figure 1 : Molecular structure of dyes**



**Figure 3 : Photodegradation of rhodamine B in the presence of photocatalysts. A: UV irradiation, B: natural irradiation. Open circle: Pumice, Open triangle: PC-S1, Solid diamond: Reference (No photocatalyst)**

**Figure 4 : Spectrum change of C. I. Acid Green 16 (A) and C. I. Acid Brown 51 (B) by UV irradiation in the presence of PC-S1. From top to bottom: (A) 0, 9, 18, 24, 35, and (B) 0, 3, 12, 18, 29 days under UV irradiation. The absorbance is represented with a 2-mm light path**



**Figure 5 : Residual absorbance under UV irradiation for 7 days. The absorbance is represented by the percent of the initial absorbance. Shaded rod: PC-S1, White rod: Pumice**

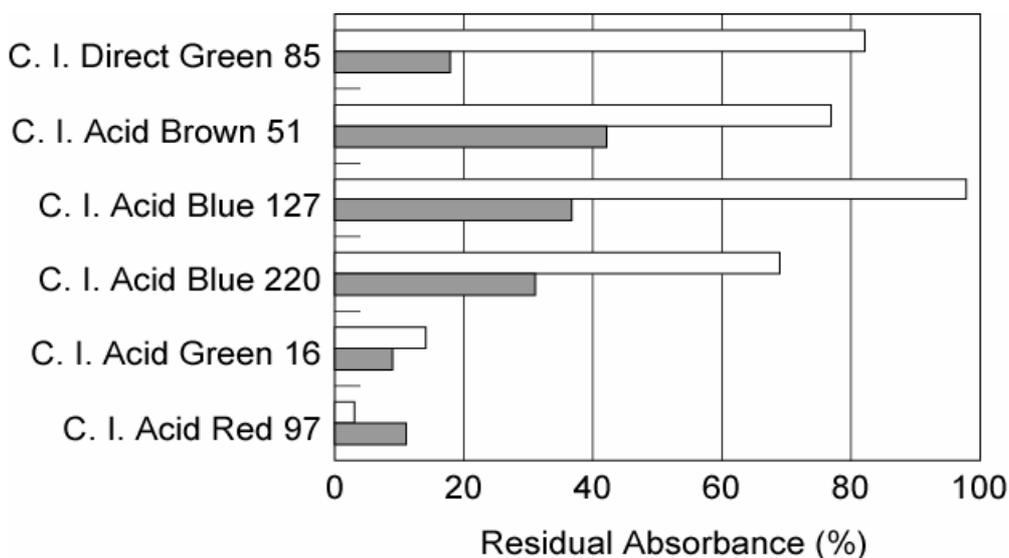


Figure 6 : Residual absorbance under natural irradiation for 10 days. The absorbance is represented by the percent of the initial absorbance. Shaded rod: PC-S1, White rod: Pumice

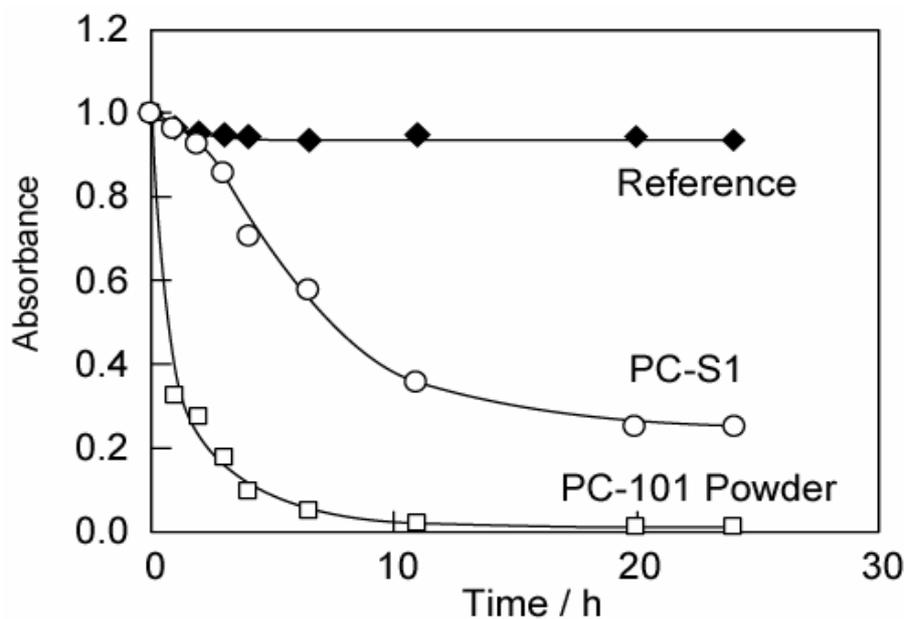


Figure 7 : Photodegradation of Wanteks under natural irradiation