



Dye decolorization test for the activity assessment of visible light photocatalysts: Realities and limitations



Sugyeong Bae^a, Sujeong Kim^a, Seockheon Lee^b, Wonyong Choi^{a,*}

^a School of Environmental Science and Engineering/Dept. of Chemical Engineering, Pohang University of Science and Technology (POSTECH), Pohang 790-784, Republic of Korea

^b Center for Water Resource Cycle Research, Korea Institute of Science and Technology (KIST), Seoul 136-791, Republic of Korea

ARTICLE INFO

Article history:

Received 24 September 2013

Received in revised form

29 November 2013

Accepted 9 December 2013

Available online 10 January 2014

Keywords:

Photocatalytic activity test

Visible light photocatalyst

Dye degradation

Environmental photocatalyst

Dye sensitization

ABSTRACT

The development of photocatalysts with visible light activity has been extensively investigated. Their activities are usually tested by measuring the degradation rate of different organic compounds. Among these organic substrates, dyes are the most widely employed due to their rapid decolorization and simple kinetic analysis using a spectrophotometric method. However, the dye test has much uncertainty in the evaluation of photocatalytic activity. To assess the validity of the dye test, six visible-light photocatalysts (N-TiO₂, C-TiO₂, C₆₀(OH)_x/TiO₂, Pt/WO₃, BaBiO₃, and Bi₂WO₃) were tested and compared for the degradation of five organic dyes (anionic: acid orange 7, indigo carmine, and new cocine; cationic: methylene blue and rhodamine B) in this study. This study aimed to assess how the measured activities depend on the kind of test dyes and how reliable the dye test is as an activity evaluation method. The activities determined by the dye test were highly specific to the kind of dye and photocatalyst. For example, N-TiO₂ is the most active photocatalyst for the degradation of acid orange 7 at pH 3 but is one of the least active at pH 9; Pt/WO₃ is the best photocatalyst for the degradation of methylene blue but not much active for the degradation of acid orange 7. This is ascribed to the fact that the dye test is significantly influenced by various factors such as the dye sensitization of catalyst particles, the absorption spectral overlap between dyes and photocatalysts in the visible region, the electrostatic interaction (attractive or repulsive), and the properties of dye degradation intermediates. In general, the dye decolorization efficiency was poorly correlated with the dye mineralization efficiency, which limits the practical value of the dye test. Therefore, the practice of dye test for the activity assessment of visible light photocatalysts should not be recommended and the activity results obtained for a specific combination of a dye and a photocatalyst should not be generalized.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Photocatalysts have been widely investigated for various energy and environmental applications including hydrogen production [1], degradation of organic pollutants [2], bacterial disinfection [3,4], and CO₂ reduction [5]. In particular, the photocatalytic remediation of contaminated water and air has been extensively investigated to demonstrate its viability as a useful cleanup process. Various contaminants such as chlorinated aromatics [6], chlorinated hydrocarbons [7], heavy metal ions [8,9], and volatile organic compounds [10,11] can be degraded or transformed by photocatalysis. Among numerous kinds of organic compounds, dyes are the most tested substrates in photocatalytic studies because not only they are common industrial pollutants [12], but also their

degradation can be simply monitored by a colorimetric method. Dye discoloration test is now widely used as a *de facto* standard method of photocatalytic activity assessment although the concerns about the dye test problems have been repeatedly raised [13,14]. The research publications on photocatalysis that used the dye decolorization as a test method have rapidly increased for the last decade (see Fig. 1). In particular, the dye test is being widely used as an activity test method for visible-light active photocatalysts. Table 1 shows some recent examples that used the dye test in the studies of visible light photocatalysis: the dye test studies are classified according to the kind of photocatalytic materials such as doped TiO₂ [15–27], composite semiconductor [28–31], and binary metal oxide [32–39].

The dye decolorization as an activity test method for visible-light active photocatalysts suffers from many problems such as: (1) Dye itself absorbs visible light and its degradation can be initiated from the excited dye (e.g., direct photolysis [40], dye sensitization [41,42]), not the excited photocatalyst. The decolorization result

* Corresponding author. Tel.: +82 54 279 2283; fax: +82 54 279 8299.
E-mail address: wchoi@postech.edu (W. Choi).

Table 1
Literature study examples of photocatalyst activity test using dye decolorization under visible light.

Photocatalyst type		Type of dye	Ref.
Doped semiconductor	N-TiO ₂	Acid orange 7 (Azo)	15
		Methylene blue (xanthene)	16–18
	C-TiO ₂	Acid orange 7 (Azo)	19–21
		Methylene blue (xanthene)	22–24
	S-TiO ₂	Rhodamine B (phenothiazine)	25
		Methylene blue (xanthene)	26
Composite semiconductor	CdS/TiO ₂	Indigo carmine (indigo)	27
		Methylene blue (xanthene)	28, 29
	WO ₃ /TiO ₂	Acid orange 7 (Azo)	30
		Methylene blue (xanthene)	31
Binary metal oxide semiconductor	Bi ₂ WO ₆	Acid orange 7 (Azo)	32
		Methylene blue (xanthene)	33
	Bi ₂ VO ₄	Rhodamine B (phenothiazine)	34–36
		Methylene blue (xanthene)	37
		Rhodamine B (phenothiazine)	38, 39

obtained via the excited dye does not represent the intrinsic photocatalytic activity of the tested materials. In addition, the visible light absorption by the dyes themselves attenuates the incident light flux available to the photocatalyst (i.e., dyes shield the photocatalyst from irradiation), which may underestimate the intrinsic visible light activity of the catalyst material. (2) The decolorization of dye reflects the selective transformation of chromophoric groups only, and not necessarily the full degradation (or mineralization). It has been frequently demonstrated that there is poor correlation between the color removal and TOC (total organic carbon) removal [43,44]. Therefore, the selective degradation of a specific functional group in a dye molecule should lead to the rapid decolorization, but the overall degradation can be inefficient. (3) The decolorization monitored by absorbance measurement at a single wavelength can be inaccurate because the generation of intermediate products is usually accompanied by the spectral change. Therefore, the Beer's law that relates the absorbance to the dye concentration cannot be applied to such system. (4) Most commercially available dyes are impure (typically 70–90%). They contain many unknown components that may interfere with the photocatalytic degradation of the parent dye, which makes dyes unsuitable as a test substrate.

Keeping the above general problems in mind, this study aims to evaluate the validity and limitation of the dye test in a systematic way. We measured the activities for various combinations of five dyes and six visible-light photocatalysts and assessed how the measured activities depend on the kind of test dyes and how

reliable the dye test is as an objective evaluation method. Despite the wide popularity of dye tests in the field of environmental photocatalysis, this is the first comprehensive study that compared and assessed the validity of various dye tests.

2. Experimental

2.1. Reagents and materials

Six visible light active photocatalysts were selected for this study and pure TiO₂ (P25) was compared as a control sample (listed in Table 2). The following visible-light photocatalysts were synthesized according to the literature method: nitrogen-doped TiO₂ (N-TiO₂) [45], carbon-doped TiO₂ (C-TiO₂) [46], fullerol-anchored TiO₂ (C₆₀(OH)_x/TiO₂) [47] and Pt/WO₃[43], BaBiO₃[48], and Bi₂WO₆[49]. Five dyes that were selected as the substrate for the activity test are acid orange (AO7, Aldrich), new cocine (NC, Aldrich), indigo carmine (IC, Aldrich), methylene blue (MB, Aldrich), and rhodamine B (RhB, Aldrich). Their structures and properties are listed in Table 3. Methyl orange (MO, Aldrich) was also used as a substrate in a separate activity test.

2.2. Photocatalysts characterization

All photocatalysts were characterized, and their properties are listed in Table 2. X-ray powder diffraction analysis using Cu K α radiation (Marc Science Co. M18XHF) was carried out to measure the crystalline phase. The BET surface area of powder samples was measured using nitrogen as an adsorptive gas. The zeta potentials of the photocatalyst particles suspended in water were measured using an electrophoretic light scattering spectrophotometer (ELS 8000, Otsuka) equipped with a He-Ne laser and a thermostated flat board cell. Diffuse reflectance UV/visible absorption spectra (DRUVS) were recorded using a spectrophotometer (Shimadzu UV-2600) with an integrating sphere attachment and BaSO₄ was used as the reference.

2.3. Photocatalytic activity measurement

Photocatalyst powder was dispersed in distilled water at the concentration of 0.5 g/L. An aliquot of the dye substrate stock solution was subsequently added to the suspension to make a desired substrate concentration (100 μ M). The pH of the suspension was adjusted to 3 or 9 with HClO₄ or NaOH solution, and then the suspension was stirred for 30 min in the dark to reach the adsorption equilibrium of dyes on the photocatalyst surface. A 300 W Xe arc lamp (Oriel) was used as a light source. The light beam was passed through a 10 cm IR water filter and a cutoff filter ($\lambda > 420$ nm

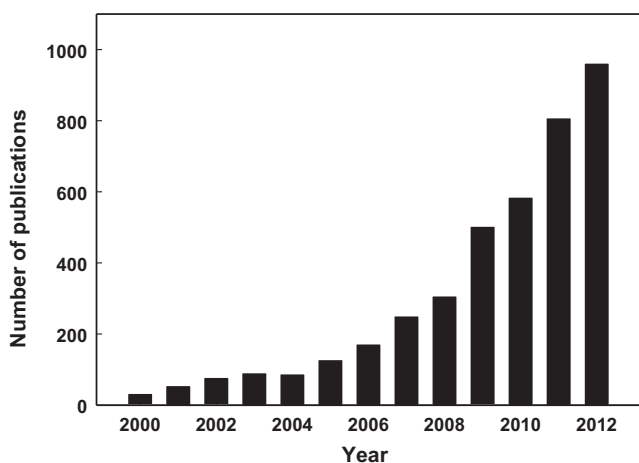


Fig. 1. Annual number of papers published in the subject area of "photocatalytic dye degradation". The literature search was carried out at the Scopus website (www.scopus.com) using the key words "photocatal*" and "dye degradation, removal, decolorization, or decoloration".

Download English Version:

<https://daneshyari.com/en/article/6505362>

Download Persian Version:

<https://daneshyari.com/article/6505362>

[Daneshyari.com](https://daneshyari.com)