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Kinetics of photocatalytic decolourization of cationic dye using porous TiO_2 film

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Abstract

In this work, the kinetics of the photocatalytic decolourization of methylene blue (MB) is investigated using different surface morphologies of multilayer TiO_2 coating onto a glass plate under irradiation from a 55-W household florescent lamp. A simple direct dip-coating technique was used, and the coating properties of TiO_2 powder were improved by adding epoxidized natural rubber (ENR) as an organic binder in the coating formulation. The effects of the fundamental parameters that govern the kinetics of the photocatalytic decolourization of MB, such as the mass of TiO_2 coated onto the glass plate, the pH and the TiO_2 surface morphology, were also studied. The kinetics of the MB decolourization in all cases was found to be pseudo-first-order kinetics and was fitted to the Langmuir–Hinshelwood model. The degraded part of the ENR binder led to generating pores within the surface of the TiO_2/ENR film and converting it into porous form, as confirmed by SEM analysis. Furthermore, TGA, FTIR and leachability analyses were conducted to further confirm the depletion of the ENR from the TiO_2/ENR film. The kinetics of the MB decolourization and the efficiency of the MB colour removal indicated that the porous TiO_2/ENR film becomes approximately twice as fast as the non-porous TiO_2/ENR film.

Keywords: Kinetics; Decolourization; Methylene blue; Immobilization; TiO_2

1. Introduction

Among all of the semiconductor photocatalysts, titanium dioxide (Anatase) currently stands as an ideal benchmark photocatalyst in environmental photocatalysis applications because of its many desirable properties, such as being inexpensive and readily available, biologically and chemically inert, and having good photoactivity compared to other semiconductors [1,2]. However, there are two major technical challenges that have remarkably limited its potential field applications. First is the relatively wide band gap of TiO_2, which absorbs only 3–4% of the energy of the solar spectrum

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and has restricted its applications to UV excitation sources [3]. Second, the effective slurry or suspension mode application of TiO_2 needs a post-treatment catalyst-recovering step, which is normally difficult, energy consumptive and not cost-effective [4]. Moreover, TiO_2 powder has a strong tendency to aggregate, especially at high concentrations, which provides a real limitation to applications to continuous flow systems and suffers from the scattering of incident UV light by the suspended particles [5]. Another important factor that must be considered in photocatalysis applications is the pH of the solution; the pH of the aqueous solution significantly affects TiO_2, including the charge on the particles, the size of the aggregates it forms, and the positions of the conductance and valence bands [6,7].

Immobilization of TiO_2 powder on solid supports is an alternative convenient method for solving the problem of the post-treatment catalyst powder recovery and for facilitating the photocatalyst usage for long-term applications [8]. However, the photocatalytic efficiency of the immobilized TiO_2 system could be less than that of the slurry system due to having less surface area that is accessible for photocatalytic reactions as well as low porosity of the supported catalyst layer [9,10]. In addition, cracking and peeling off of the catalyst layer can also be expected because of the poor adherence of the photocatalyst/support. Thus, it was proven that adding an organic binder, such as epoxidized natural rubber (ENR) combined with phenol-formaldehyde resin (PF) in an immobilizing solution can produce a good quality coating formulation of TiO_2 powder onto a solid support [11]. However, mixing more than one organic binder for TiO_2 powder immobilization is responsible for generating different types of transformation products and undesirable intermediates during the photocatalytic reaction [12].

In recent years, a large amount of attention has been paid to using a compact household fluorescent lamp as an alternative light source to replace a conventional UV light source. It was found that a very low UV content in a compact fluorescent lamp is sufficient to induce TiO_2 particles for a wide range of applications, such as photocatalytic oxidation of biopolymers [13], crosslinked biopolymers [14,15], colourless organic water pollutants [11,12] and cationic dye [16]. Therefore, the aim of this work is to study the decolourization kinetics of methylene blue on the surface of an immobilized TiO_2 layer under most significant experimental parameters, such as the mass of TiO_2 coated onto a glass plate, pH and surface morphology of the immobilized TiO_2 film. Among various types of cationic dyes, MB was chosen as a probe in this study due to its complicated chemical structure and because it is not easy to be removed from wastewater by conventionally used techniques such as biological treatments and chemical precipitation.

2. Materials and methods

2.1. Materials

Titanium (IV) oxide (99% anatase) powder with a particle size of $\leq 150\,\mu m$ was obtained from Sigma–Aldrich. Epoxidized natural rubber (ENR50) was obtained from Kumpulan Guthrie Sdn. Bhd., Malaysia. Toluene and acetone were purchased from BDH Analar. Hydrochloric acid (HCl) obtained from R & M Chemicals and sodium hydroxide (NaOH) pellets purchased from Mallinkoot were used to adjust the pH. Methylene Blue dye (c.a. 98%, Colour Index Number: 52015) was purchased from R & M, and Table 1 summarizes the chemical structure, molecular weight and λ_{max} for MB. All of the materials were used as received without further purification. Ultra-pure water ($18.2\,M\Omega\,cm^{-1}$) was used to prepare all solutions in this study. The chemicals used in this experiment were all of the analytical grade and were used without further purification.

2.2. Instruments and methods

A Daihan Ultrasonic cleaner model WUC-D06H (50–60 KHz) from Scientific Co., Inc. Company was used to homogenize TiO_2 dip-coating solutions. A spectrophotometer, model DR 2800 from HACH, was used to determine the concentration of MB. The chemical oxygen demand (COD) was determined by using a high-range digestion solution according to an analytical procedure [17]. In this analysis, the samples were placed in vials that contained a high range of COD digestion solution and a small amount of mercury sulfate. The vials were inverted many times to ensure complete mixing before being placed in a COD reactor (HACH 2000), which was preheated to 150 °C. The samples were kept in the COD reactor for 2 h. The samples were then withdrawn from the reactor and cooled down to room temperature, followed by COD measurement at 620 nm by a DR 2800 HACH spectrophotometer. Digested ultrapure water was used as the blank reference solution, and the difference between the absorbance of the digested blank sample and the digested sample was the COD measurement of the sample. The peel-off rate of the immobilized TiO_2/ENR film was observed using sonication according to a published procedure [12]. The leaching ratio (LR) of TiO_2/ENR film was calculated according to a published procedure [13]. A