



## Immobilized bilayer TiO<sub>2</sub>/chitosan system for the removal of phenol under irradiation by a 45 watt compact fluorescent lamp

M.A. Nawi\*, Ali H. Jawad, S. Sabar, W.S. Wan Ngah

School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

### ARTICLE INFO

#### Article history:

Received 25 March 2011

Received in revised form 23 June 2011

Accepted 9 July 2011

Available online 10 August 2011

#### Keywords:

TiO<sub>2</sub>  
Chitosan  
Bilayer  
Photodegradation  
Phenol

### ABSTRACT

A simple bilayer system consisting of TiO<sub>2</sub> and chitosan (CS) biopolymer has been fabricated and immobilized onto a glass plate. The deposition properties of TiO<sub>2</sub> powder were improved by adding epoxidized natural rubber (ENR<sub>50</sub>) and phenol-formaldehyde resin (PF) in the coating formulation. SEM analysis indicated that the degraded ENR<sub>50</sub> acted as macro-pores forming agent to generate macro-pores within the surface of TiO<sub>2</sub> layer and was quantitatively determined by TGA and EDX analyses as well. The highly porous structure of immobilized TiO<sub>2</sub> layer allows better diffusion of pollutants, increases the light penetration and improves the optical property as indicated by photoluminescence spectroscopy (PLS) analysis. Consequently, the photocatalytic activity and mineralization rate of the immobilized bilayer TiO<sub>2</sub>/CS system becomes approximately twice as fast as an immobilized TiO<sub>2</sub> single layer system and as good as TiO<sub>2</sub> powder in a slurry system. Moreover, the adsorption effect was extremely negligible and the photodegradation of phenol was mainly due to the photocatalytic process.

© 2011 Elsevier B.V. All rights reserved.

### 1. Introduction

Among all of the semiconductors photocatalysts, titanium dioxide TiO<sub>2</sub> is close to be an ideal bench mark photocatalyst in the environmental photocatalysis applications because of its many desirable properties such as inexpensive and readily available, biologically and chemically inert, and good photoactivity [1]. In fact, there are two main technical challenges that really restricted the large-scale applications of TiO<sub>2</sub>, firstly is the relatively wide band gap of TiO<sub>2</sub> which absorbs only 3–4% energy of the solar spectrum and restricts its applications to UV excitation source [2] and secondly, the effective slurry or suspension mode application of TiO<sub>2</sub> requires post-treatment catalyst recovering step which is normally difficult, energy-consuming and not cost-effective. Moreover, the TiO<sub>2</sub> powder has a great tendency to aggregate especially at high concentrations provides a real limitation to apply to continuous flow system and suffers from scattering of incident UV light by the suspended particles [3,4].

Thus, several methods have been made in order to extend the spectral sensitivity of TiO<sub>2</sub> towards visible light region as adequately reviewed by Chatterjee and Dasgupta [5] which generally involved sensitization by dyes, doping with metallic and non-metallic species, heterojunction systems and utilizing thin film. Moreover, immobilization of TiO<sub>2</sub> powder on solid supports is an alternative convenient method to solve the problem of the post-treatment catalyst powder

recovery and facilitate the photocatalyst usage for long-term applications [6]. However, the photocatalytic efficiency of the immobilized TiO<sub>2</sub> system may be less than that of the slurry system due to less surface area that is accessible for photocatalytic reaction as well as low porosity of the supported catalyst layer [7]. In addition, cracking and peeling off of the catalyst layer can be also expected because of the poor adherence of the photocatalyst/support [8].

In recent years, chitosan biopolymer (CS) has exhibited multi-functional performance with TiO<sub>2</sub> in heterogeneous photocatalysis technology, including its use as a stabilizer [9], a recovery agent [10], as an auxiliary coagulant [11], for increasing the adsorption capacity of CS-TiO<sub>2</sub> adsorbent in the removal of metal ions [12,13] and for enhancing the adsorption-photocatalytic process of the dye species [13–18]. This is due to the presence of pendant hydroxyl and amino groups on the backbone of CS. Thus, the advantages of the bioadhesiveness, binder-free and excellent film forming ability of CS biopolymer inspired us to fabricate a simple bilayer system, consisting of TiO<sub>2</sub> layer stacked on a CS sub-layer immobilized onto a glass substrate. This immobilized bilayer TiO<sub>2</sub>/CS system would be introduced as a convenient pathway for green chemistry applications because of its many desirable properties, such as free of initiators and super oxidizing agents, long-term reusability, elimination of the need for catalyst powder recovery, easy storage and applicable under ambient conditions.

Additionally, it was proven in our previous work [18] that the CS sub-layer also allows us to fix photosensitizer such as reactive red 4 dye (RR4) for further improvement of the adjacently immobilized TiO<sub>2</sub> photocatalyst. We also found that adding of the organic binder

\* Corresponding author. Tel.: +60 4 6534031; fax: 60 4 6574854.  
E-mail address: [masri@usm.my](mailto:masri@usm.my) (M.A. Nawi).

like epoxidized natural rubber (ENR<sub>50</sub>) into immobilizing solution had also improved the adhesiveness, robustness and significantly speed up the immobilization process of TiO<sub>2</sub> [19]. In this regard, Amar [20] reported that combining of phenol-formaldehyde resin (PF) with ENR<sub>50</sub> produced a good quality coating formulation of TiO<sub>2</sub> powder for direct immobilization of TiO<sub>2</sub> on various solid supports.

The objectives of this work were firstly to produce a porous structure of immobilized TiO<sub>2</sub> as a single layer supported on glass plate or on immobilized CS sub-layer to form a bilayer TiO<sub>2</sub>/CS system, thus, containing highly-ordered macro-pores for efficient diffusion of pollutants and hydroxyl radicals through the TiO<sub>2</sub> layer into the CS sub-layer. Secondly, to investigate the role of the photocatalytically-oxidized CS sub-layer on the photocatalytic performance of the adjacent TiO<sub>2</sub> layer for the removal of phenol. In fact, in our recent work [21], we have proven that such an assemblage of the bilayer TiO<sub>2</sub>/CS system led to the transformation of CS sub-layer into a chemically stable form of oxidized CS. Thirdly, following to this success, we moved forward to apply the same bilayer TiO<sub>2</sub>/CS system for the environmental remediation purposes. Phenol was chosen as the model pollutant in order to evaluate the photocatalytic activity of TiO<sub>2</sub> in the bilayer TiO<sub>2</sub>/CS system because it was found that phenol as a colorless and neutral organic pollutant within the pH range studied did not show adsorptive properties on the immobilized CS layer. This characteristic allows us to avoid any possible complication of the adsorptive synergistic effect as normally observed by other works.

## 2. Materials and methods

### 2.1. Materials

Chitosan (CS) flakes of medium molecular weight (322 g mol<sup>-1</sup>) with a 68.20% degree of deacetylation as determined by infrared spectroscopy method [22] were purchased from Sigma-Aldrich. Titanium (IV) oxide (99% anatase) was obtained from Sigma-Aldrich. Phenol (99.5%) was obtained from Scharlau. Phenol-formaldehyde resin (PF) Novolac type was bought from Borden Chemical Sdn. Bhd. Epoxidized natural rubber (ENR<sub>50</sub>) was obtained from Kumpulan Guthrie Sdn. Bhd. Reactive Red 4 (RR4) with 50% dye content was provided by Aldrich Chemical. All the materials were used as received without further purification. Ultra-pure water (18.2 MΩ cm<sup>-1</sup>) was used throughout this work.

### 2.2. Preparation and immobilization of the bilayer TiO<sub>2</sub>/CS system

CS solution was prepared by adding 6.0 g of CS flakes in 400 mL of 5% (v/v) acetic acid solution and was homogenized by grinding for 30 h using a ball mill grinder. The bubbles-free white viscous CS solution was then casted onto glass plates, each of dimension 4.7 cm × 6.5 cm. It was then heated in an oven for 4 h at 100 °C to remove the acetic acid. The final form of immobilized CS on the glass plate appeared light-yellow in color and is hereafter called CS/glass system. The average of the optimum thickness of CS layer was determined by SEM analysis to be 6.35 ± 0.61 μm. This was obtained by casting 0.65 ± 0.08 mg cm<sup>-2</sup> of CS solution onto glass plate. Moreover, the average of the optimum thickness of TiO<sub>2</sub> top layer was determined previously by SEM analysis also to be 40.94 ± 1.16 μm. This was obtained by depositing 1.30 ± 0.08 mg cm<sup>-2</sup> of TiO<sub>2</sub> formulation onto the glass plate. In fact, the procedure for the preparation of TiO<sub>2</sub> formulation, immobilization and the irradiation set-up was described adequately in our previous work [18].

### 2.3. Generation of macro-pores on the TiO<sub>2</sub> layer

The bilayer TiO<sub>2</sub>/CS system was irradiated in 20 mL ultra-pure water with 45-W compact fluorescent lamp of UV leakage 4.4 W m<sup>-2</sup> and aeration of 25 mL min<sup>-1</sup> for one cycle and five cycles of

irradiation to generate macro-pores on the TiO<sub>2</sub> top layer (Each cycle was equivalent to 2 h of irradiation). According to our hypothesis, the generation of macro-pores will allow better diffusion of the pollutant molecules and also increase the penetration of light irradiation into the inner layer of immobilized materials. In order to verify our hypothesis, two separate experiments were conducted as follow.

#### 2.3.1. Diffusion of pollutants molecules

Fresh and irradiated bilayer TiO<sub>2</sub>/CS systems for one cycle and five cycles of irradiation in ultra-pure water were used for the adsorption study of RR4 dye which can be considered as a function of the diffusion of RR4 dye from the aqueous solution towards the CS sub-layer via the open macro-pores of the TiO<sub>2</sub> top layer. Thus, each of the photocatalyst plates stated above was respectively placed uprightly inside a glass cell containing 30 mL of 30 mg L<sup>-1</sup> anionic RR4 dye solution. Each system was conducted in the dark and aerated with air at 200 mL min<sup>-1</sup> throughout the adsorption process. The concentrations of RR4 were monitored at a different time interval using a HACH DR/2000 Direct Reading Spectrophotometer at a wavelength of 517 nm.

#### 2.3.2. Diffusion of hydroxyl radicals to the interface of TiO<sub>2</sub>/CS layers

The study on the diffusion of hydroxyl radicals through the TiO<sub>2</sub> layer towards the interface of the TiO<sub>2</sub> and CS sub-layer was performed by the degradation of the adsorbed anionic RR4 dye on the CS sub-layer after generation of macro-pores on the immobilized form of TiO<sub>2</sub>. A fixed amount of RR4 dye of 30 mg g<sup>-1</sup> was adsorbed on the fresh and previously irradiated bilayer TiO<sub>2</sub>/CS system for one cycle and five cycles. These three systems were then subjected to the irradiation process in 20 mL ultra-pure water using a 45-W compact fluorescent lamp with a UV leakage of 4.4 W m<sup>-2</sup> and aeration flow rate of 25 mL min<sup>-1</sup> for 4 h for each system. The degradation of the adsorbed RR4 dye on the immobilized CS sub-layer was monitored by UV-vis DRS spectrophotometer, after removing the TiO<sub>2</sub> top layer intensively with acetone. The CS/glass plate with adsorbed RR4 dye was used as the control system.

### 2.4. Evaluation of the photocatalytic performance

The photocatalytic performance of the bilayer TiO<sub>2</sub>/CS system for the removal of phenol was evaluated in comparison with TiO<sub>2</sub> single layer system as well as the slurry TiO<sub>2</sub> system. The slurry TiO<sub>2</sub> system was carried out by suspending similar weight of TiO<sub>2</sub> powder as that of the immobilized TiO<sub>2</sub> layer in phenol solution. All systems were subjected to the 45-W compact fluorescent lamp with UV leakage of 4.4 W m<sup>-2</sup> and aeration flow rate of 25 mL min<sup>-1</sup>.

### 2.5. Measurements

Scanning electron microscopy (SEM-EDX, Model Leica Cambridge S360) was used to observe the surface morphology of the TiO<sub>2</sub> layer during the photocatalytic process. EDX and Thermogravimetric analyses (TGA) (Perkin Elmer thermogravimetric analyzer TGA7) were carried out to monitor quantitatively the depletion of organic binders from TiO<sub>2</sub> formulation during the photocatalytic process. The concentrations of RR4 were monitored at a different time interval using a HACH DR/2000 Direct Reading Spectrophotometer at a wavelength of 517 nm. UV-vis diffuse reflectance spectroscopy (DRS) was carried out by using a Perkin-Elmer, Lambda 35 UV-vis spectrometer to monitor the photodegradation of adsorbed RR4 dye on the CS sub-layer in the bilayer TiO<sub>2</sub>/CS system. The concentration of degraded phenol was followed by using Shimadzu LC-10 ATPV high performance liquid chromatography (HPLC) with a stationary phase LC-18 column (Supelcosil, 25 cm × 4.6 mm, 5 μm) at room temperature. The ingredients of applied mobile phase were methanol

متن کامل مقاله

دریافت فوری ←

**ISI**Articles

مرجع مقالات تخصصی ایران

- ✓ امکان دانلود نسخه تمام متن مقالات انگلیسی
- ✓ امکان دانلود نسخه ترجمه شده مقالات
- ✓ پذیرش سفارش ترجمه تخصصی
- ✓ امکان جستجو در آرشیو جامعی از صدها موضوع و هزاران مقاله
- ✓ امکان دانلود رایگان ۲ صفحه اول هر مقاله
- ✓ امکان پرداخت اینترنتی با کلیه کارت های عضو شتاب
- ✓ دانلود فوری مقاله پس از پرداخت آنلاین
- ✓ پشتیبانی کامل خرید با بهره مندی از سیستم هوشمند رهگیری سفارشات