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Tailoring amount of TiO₂ doped onto fibrous silica ZSM-5 for enhanced photodegradation of paracetamol

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Abstract. Photocatalytic degradation of paracetamol has received much attention due to its low energy consumption, high efficiency and safety to environment. A simple electrolysis system was used to synthesis a series of titania (1-5 wt%) supported on fibrous silica ZSM-5 (TiO₂/FZ). The FESEM images showed the cockscomb-like surface of FZ was preserved even after the addition of TiO₂. FTIR results confirmed that TiO₂ is successfully incorporated with FZ through the Si-O-Ti bonds. The adsorption edge of TiO₂ shifted to the higher wavelength after supported on FZ and lowering the band gap of TiO₂. The photodegradation of paracetamol was resulted in the following order: 3 wt% TiO₂/FZ (90%) > 5 wt% TiO₂/FZ (71%) > 1 wt% TiO₂/FZ (65%). 3 wt% TiO₂/FZ exhibits excellent photodegradation of paracetamol owing to the highest number of Si-O-Ti bonds and lowest band gap. The result obtained give new insight for other wastewater treatment processes over photodegradation of various pollutants.

1. Introduction

Nowadays, the accumulation of paracetamol in wastewaters represent a pollution problem that must be solved urgently due to their potential toxic effects to aquatic organisms [1]. Thus, many efforts have been used to develop suitable methods that can remove the paracetamol from water due to its inappropriate conditions for biodegradation [2,3]. Advanced Oxidation Process (AOP) has been broadly used as one of practical way in wastewater treatment technology [4]. The technique uses the light that plays an effective role in producing highly free radical species such as hydroxyl radicals and superoxide radicals by using heterogeneous photocatalyst semiconductors [5]. The semiconductors that commonly used are TiO₂ (titanium dioxide), ZnO (zinc oxide) and CdS (cadmium sulfate) [6-8]. Titanium dioxide (TiO₂) has been established as the most active photocatalyst and semiconductors for environmental remediation [9]. However, unsupported TiO₂ has some limitations in its practical use, such as the difficulties in recycling, low adsorption capacity and high aggregation tendency [10]. Those drawbacks have driven the production of silica zeolite as supported photocatalysts [11].

Zeolite, has been marked as a promising supported material to improve the properties of TiO₂ due to their unique porous network, large surface area and excellent adsorption of reactants [12,13]. However, conventional zeolite has low accessibility of active site due to its morphology. Recently, fibrous silica ZSM-5 (FZ) has been introduced to increase the accessibility of active site that allowed good achievement in catalytic reaction including benzene methylation and cumene hydrocracking [14,15]. Previously, we studied the good potential of in situ electrochemical method for producing



various metal nanoparticles such as NiO₂, TiO₂ and ZnO doped onto MSN [16-18]. All of the catalysts showed exceptional performances for excellent CO₂ methanation and photodegradation of various organic contaminants. Considering the advantages of fibrous materials, thus we extend the studies on synthesization of TiO₂ catalysts supported on FZ (TiO₂/FZ) by electrolysis [9], where the effect of TiO₂ amount doped on FZ for degradation of paracetamol has not been reported. All of the samples were characterized by FESEM, FTIR and UV-Vis DRS. Kinetics studies of the photodegradation of paracetamol are also reported. The modified catalyst, would be useful as a new catalyst especially for applications in wastewater treatment.

2. Methods

2.1 Materials

ZSM-5 zeolite (98% purity) with Si/Al=23 was obtained from Zeolyst International. Paracetamol (4-acetamidophenol) with 97% purity, was purchased from Fisher Scientific (M) Sdn. Bhd., Malaysia. Cetyltributylammonium bromide (98%, CTAB), urea (99%), butanol (99.5%), toluene (95.5%) and tetraethyl orthosilicate (98%, TEOS), tetraethylammonium bromide (>99%, TEAB) and hydrogen perchloric acid (97%, HP) from Merck Sdn. Bhd., Malaysia were used. The titanium plates were acquired from Nilaco Metal, Japan (99% purity). Tetraethylammonium perchlorate (TEAP) was used as supporting electrolyte and the synthesis method will be explained in the synthesis.

2.2 Synthesis of catalysts

FZ was prepared by microemulsion method [15]. Toluene and butanol were added in the mixture of water (250 mL), CTAB (20 g) and urea (5 g). After 30 min, ZSM-5 seed (1 g) and TEOS (3 mL) was added and stirred for another 2 h. Then, the mixture was exposed to microwave radiation at 393 K (2 h). The sample was dried at 383 K (24 h) and calcined at 823 K (6 h) with heating rate 273 K min⁻¹. The TiO₂/FZ catalysts were prepared according to the literature and the weight percentage (wt%) of Ti doped was varied between 1% to 5% by electrolysis method [19]. Firstly, TEAP was synthesized by adding TEAB and HP into 600 mL of distilled water. Then the solution was retained overnight for crystallization. Next, the solution was filtered and the crystal was collected before being added with 150 mL distilled water. After that, the solution was heated at 353 K to form homogeneous solution and retained for the recrystallization. The TEAP formed as a white needle in 90% yield [20]. TiO₂/FZ was prepared by electrolysis method. the FZ was added in a cell fitted with a Pt plate (2 cm x 2 cm) cathode and a Ti plate (2 cm x 2 cm) anode which containing distilled water (20 mL) and TEAP. The electrolysis was conducted at a constant current 120 mA cm⁻² and at 273 K under atmospheric pressure and Ti ions were produced to undergo titanation. After electrolysis, the sample was dried overnight at 383 K and calcined at 823 K for 6 h.

2.3 Characterization

Surface morphology of the prepared catalysts were observed by field emission scanning electronmicroscopy (FESEM) (Zeiss supra VP35). The samples' functional group was utilized by PerkinElmer Spectrum GX FTIR Spectrometer (400-4000 cm⁻¹). UV-Vis diffuse reflectance spectra were collected by using PIKE Technologies DiffusIR between (200- 800 nm). The band gap of each samples was determined based on the Eq. 1,

$$E_g (eV) = \frac{1240}{\lambda} \quad (1)$$

where E_g is the band gap (eV) and λ is the wavelength of the absorption edges (nm).

2.4 Photodegradation of paracetamol

The photocatalytic performances of all samples toward the photodegradation of paracetamol were carried out in a batch reactor, in which 36 W metal halide lamp (400 nm) for visible light source is served with a cooling system. 0.375 g L⁻¹ of sample was added in 10 mg L⁻¹ of paracetamol solution (100 mL). The mixture was magnetically stirred for 1 h in the dark to get the equilibrium of paracetamol adsorption-desorption on the photocatalysts surfaces. The samples were withdrawn for every 30 mins and the concentration of paracetamol was estimated according to the adsorption band wavelength at 274 nm by UV-Vis spectrophotometry.

3. Results and Discussion

3.1. Structural investigation

The morphological properties of the catalysts were analyzed using FESEM and shown in Fig. 1. The effect of titanium on the FZ structure can be verified from FESEM analysis. It can be seen from Fig. 1a the cockscomb-like surface of FZ with uniform size of 400-500nm was successfully synthesized. After addition of TiO₂ the morphology of FZ was preserved (Fig 1b-d). However, denser dendrimeric fibre was observed after 5 wt% of TiO₂ doped on FZ.

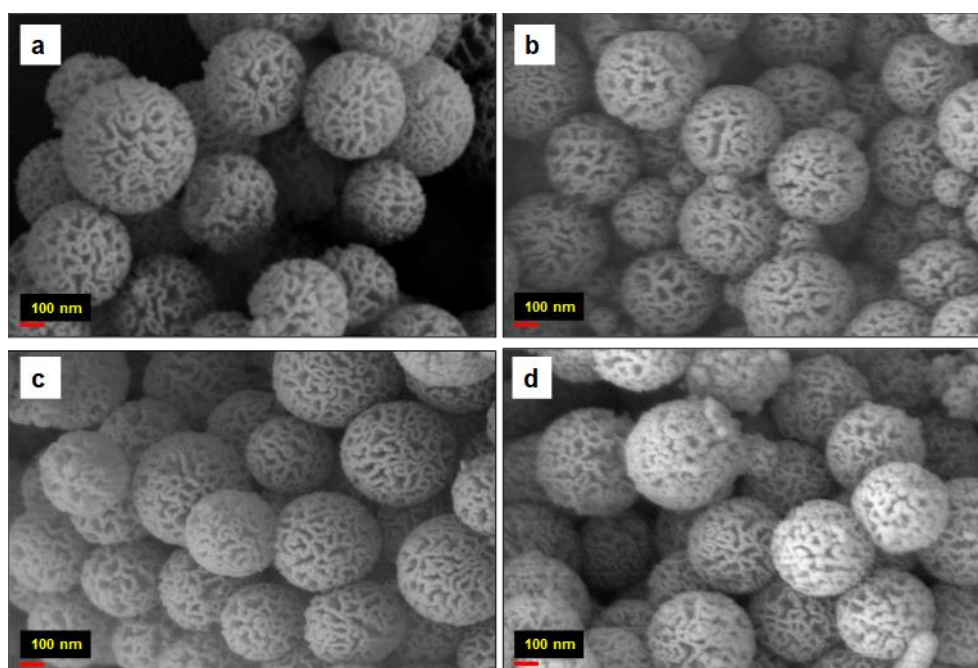


Figure 1. FESEM images of (a) FZ (b) 1 wt% TiO₂/FZ (c) 3 wt% TiO₂/FZ (d) 5 wt% TiO₂/FZ.

The FTIR spectra of the catalysts were conducted in the region of 4000 to 400 cm⁻¹ in Fig 2A and the intensities of the bands were presented in Fig 2B. The band at 3460 cm⁻¹ represents the hydroxyl group caused by incorporated humidity of KBr during the preparation of samples [17]. The peaks at 1090, 966, 800 and 465 cm⁻¹ can be assigned to Si-O-T (T=Si or Al) assymmetric vibration, external Si-OH group, symmetric vibration and Si-O-T bending, respectively [21]. Comparing with FZ spectra, it can be seen that all the peaks for TiO₂/FZ become shorter in intensity with increasing TiO₂ amount. This suggested that the interaction between FZ framework and TiO₂ due to dealumination, desilication and titanation during the preparation of sample by electrolysis. The weak peak of five-membered ring vibration of ZSM-5 can be seen at 550 cm⁻¹ [22]. It was also observed that the peak of FZ at 966 cm⁻¹ due to Si-O-H stretching decreased by the introduction of TiO₂, ascribed that relatively rearranged of

the framework during the electrolysis. Similar trend was stated previously when TiO₂ was doped onto mesoporous silica nanoparticles (MSN) [23]. This band seems decreased with the increasing TiO₂, proving the probable restructuring of the hydroxyl groups and forming Si-O-Ti bonds [24]. The metal ion could be simply substituted with the H atom from the silanol groups of FZ during the electrolysis. This was approved by the presence of a weak band shoulder which is characteristic peak of Si-O-Ti vibration at 960 cm⁻¹, and it was increased with the increasing TiO₂ loading up to 3wt % [25]. The band then decreased due to the some Ti ions might not inserted into the system and it is proved by the agglomeration that happened in 5 wt% TiO₂/FZ [26]

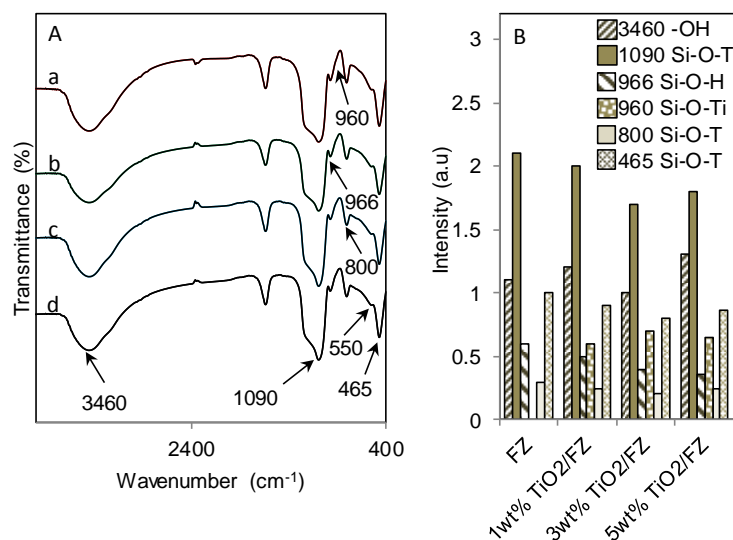


Figure 2. (A) FTIR spectra of (a) FZ (b) 1wt% TiO₂/FZ (c) 3wt% TiO₂/FZ (d) 5wt% TiO₂/FZ (B) Intensity.

The UV-Vis DRS analysis for FZ and TiO₂/FZ are shown in Fig. 3A. It shows that the absorption edge of all sample in the range between 300 to 400 nm. Compared with FZ, the absorption bands of all TiO₂/FZ catalysts acquired higher absorption band area assisted to the large number of photons being absorbed by the catalysts to produce higher amounts of electron-hole pairs to enhance the photocatalytic activity [27]. 3wt% TiO₂/FZ shows the highest absorption, which responsible in photocatalytic activity of catalyst. In addition, the TiO₂/FZ spectra shows that a blue shift in comparing with FZ, referring to the lower band gap energy. The red shift happened when increasing TiO₂ doping from 3 to 5% as higher loading TiO₂ may agglomerated on the surface of FZ and cover the active site which in turn causing to low penetration of light [28]. The band gap energies of all the catalysts were obtained from Kubelka-Munk theory (Fig. 3B) the calculated band-gap energies of FZ, 1 wt% TiO₂/FZ, 3 wt% TiO₂/FZ and 5 wt% TiO₂/FZ are 3.4, 3.1, 2.7 and 2.9 eV, respectively. This improvement offers great potential for photocatalytic reactions to be conducted under visible light irradiation [29].

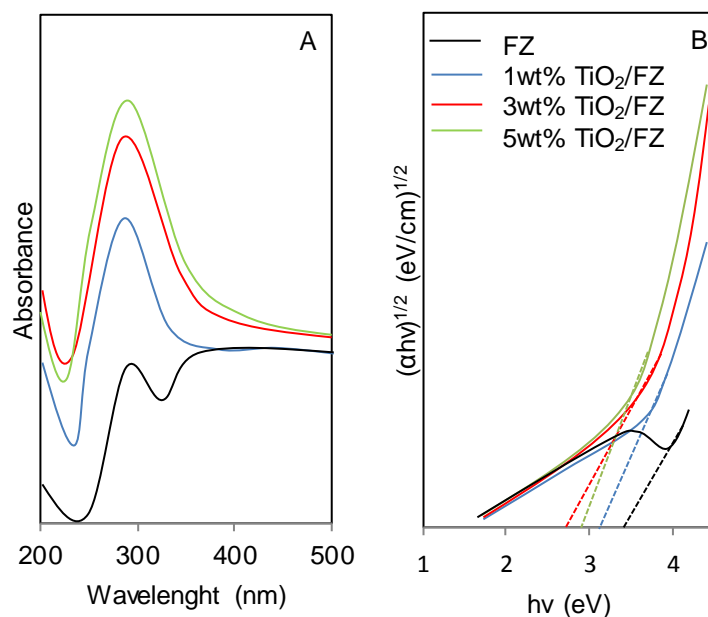


Figure 3. (A) Absorbance spectra (B) Kubelka-Munk spectra.

3.2 Photocatalytic activity

The pH shows a major role in the photodegradation of paracetamol since the charge of the photocatalyst surface influence the interaction with paracetamol. It can be seen that the photocatalytic performance enhanced along with increased in pH to achieve the maximum of 90% at pH 5 and then decreased for pH values in between 7 to 11 (Fig. 4A). The catalytic performances are influenced by the electrostatic interaction between the negatively charge paracetamol with the positively charge catalyst surface [30]. Since the zero point charge of the photocatalyst was at pH 6.1 (Fig. 4B), 3 wt% TiO₂/FZ carried positive charge and attracted to the negative charge of paracetamol. The large number of hydroxyl group in high alkaline solutions competed with the paracetamol ions and thus decreasing the photocatalytic efficiency.

Fig. 4C illustrated the photocatalytic trend of FZ, TiO₂, 1 wt% TiO₂/FZ, 3 wt% TiO₂/FZ and 5 wt% TiO₂/FZ on the photodegradation of paracetamol. The degradation of paracetamol for FZ is less than 10%, indicating that it had a small degradation effect of paracetamol. The degradation of paracetamol was lower for 1 and 5 wt% of TiO₂ doped due to the limitation of available reactive site and agglomeration of TiO₂ on the catalyst surface which reduce the light penetration for an efficient photocatalytic activity, respectively [31]. The result clearly showed that the photodegradation of paracetamol under visible light using 3 wt% TiO₂/FZ performed better, which may be due to its smaller band gap and the existence of the highest Si-O-Ti bonds. The 3 wt% TiO₂/FZ achieved the maximum degradation of paracetamol (90%), followed by 5 wt% TiO₂/FZ (71%), 1 wt% TiO₂/FZ (65%), TiO₂ (63%) and FZ (9%). This result suggested that FZ and Ti acted as a significant part in the photocatalytic degradation of paracetamol.

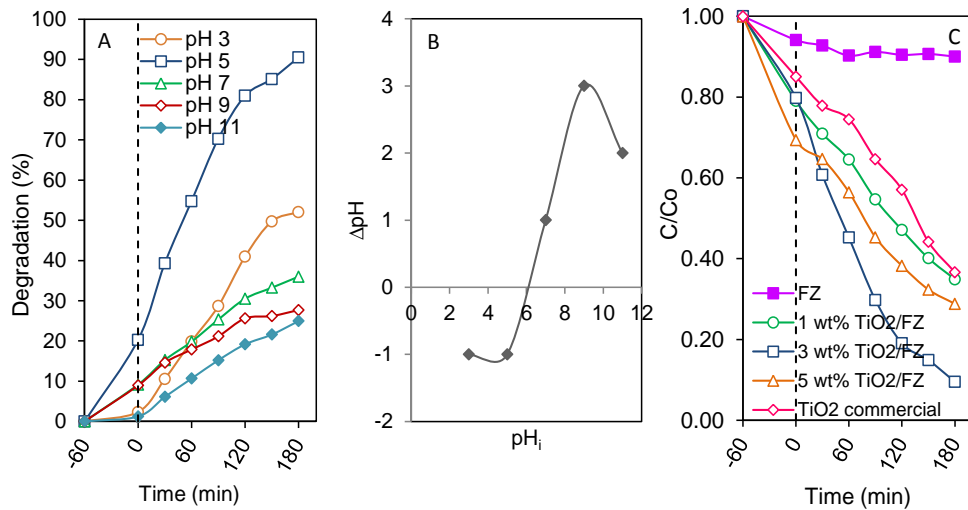


Figure 4. (A) Effect of pH for photodegradation of paracetamol under visible light irradiation [$C_{\text{paracetamol}} = 10 \text{ mg L}^{-1}$; $W = 0.375 \text{ g L}^{-1}$; 3wt% TiO_2/FZ] (B) pH_{pzc} of 3wt% TiO_2/FZ (C) Effect of TiO_2 percentage.

The kinetics of the degradation of paracetamol over the 3 wt% TiO_2/FZ was also studied. A series of reactions, with initial concentration of paracetamol in the scale of 10 and 100 mg L^{-1} were presented (Fig. 5A) to get the photodegradation rate for paracetamol (Fig. 5B). Generally, the pseudo-first order reaction kinetics be represented as equation (2):

$$\ln\left(\frac{C_0}{C}\right) = k_{\text{app}}t \quad (2)$$

where t is the time of the reaction, k_{app} is the reaction rate constant, C_0 is the initial concentration of paracetamol and C is the final concentration of paracetamol, respectively. The degradation rate constants were calculated as 0.0103, 0.0061, 0.0046, 0.0026 and 0.0011 min^{-1} , for solutions contained 10, 30, 50, 70 and 100 mg L^{-1} . The system was favourable at low concentration due to low rate constants for higher initial concentration [32,33]. In addition, large amounts of active sites are needed to occupied the larger amount of paracetamol compounds to improve photodegradation. Next, the Langmuir-Hinshelwood kinetics model was constructed based on the Eq. 3:

$$\frac{1}{k_{\text{app}}} = \left(\frac{1}{k_r K_{\text{LH}}}\right) + \frac{C_0}{k_r} \quad (3)$$

where C_0 is assigned as its concentration before the reaction (mg L^{-1}), the adsorption coefficient of the paracetamol presented as K_{LH} (L mg^{-1}) and the reaction rate constant is presented as k_r ($\text{mg L}^{-1} \text{ min}^{-1}$). The values of k_r and K_{LH} were 0.115 $\text{mg L}^{-1} \text{ min}^{-1}$ and 0.089 L mg^{-1} , respectively. It is proved that the reaction would take place at the surface of the 3 wt% TiO_2/FZ catalyst due to the k_r value was higher than K_{LH} . Comparable trend has also been stated previously for photodegradation of ibuprofen [34].

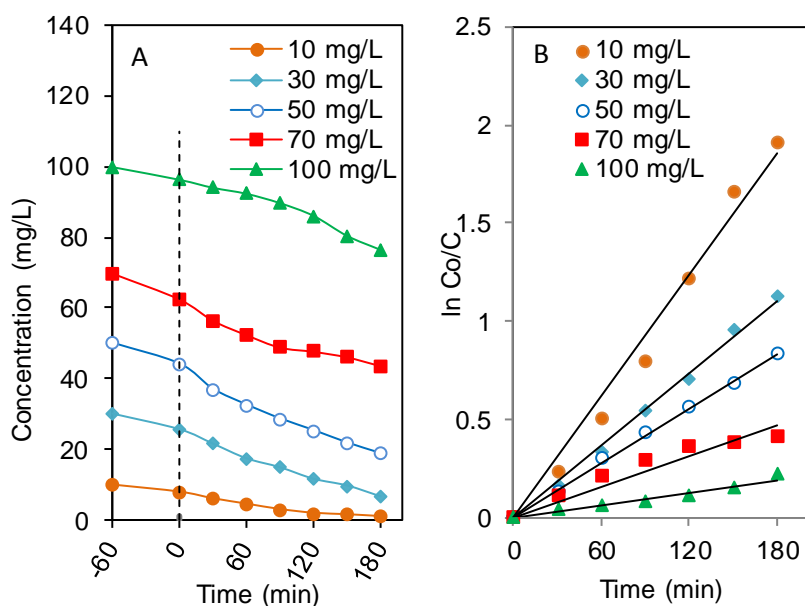


Figure 5. (A) Effect of initial concentration for photodegradation of paracetamol under visible light irradiation [pH= 5; W = 0.375g L⁻¹; 3wt% TiO₂/FZ] (B) kinetics degradation of paracetamol

4. Conclusions

In conclusion, a microemulsion technique and a simple electrolysis method were used to prepare TiO₂/FZ with different amounts of Ti to produce 1 wt% TiO₂/FZ, 3 wt% TiO₂/FZ and 5 wt% TiO₂/FZ catalysts. The results show, the wt% of TiO₂ gave a significant role in controlling the creation of Si-O-Ti bonds that confirmed by FTIR analysis. The higher the number of Si-O-Ti introduced in the framework, the smaller the band gap leading to great photodegradation activity of paracetamol. Thus, 3 wt% TiO₂/FZ showed the most efficient catalyst with the highest Si-O-Ti bonds and the lowest band gap energy. Furthermore, the kinetic study for photodegradation of paracetamol obeyed first-order kinetics that determine by Langmuir-Hinshelwood model. Finally, it could be concluded TiO₂/FZ synthesized using electrolysis method could be employed as promising way to treat other pollutants in waste water treatment.

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