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Photocatalysis of Phenolic Compounds with Synthesized Nanoparticles TiO₂/Sn₂

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Abstract: This study was aimed to determine the photocatalytic degradation of phenolic compounds contaminated in the pulp and paper wastewater with the synthesized nanoparticle TiO₂/Sn₂ and the commercial TiO₂ (Sigma Aldrich). The studied phenolic compounds included 2-methoxy phenol (guaiacol), 2,6-dimethoxy phenol (syringol) and phenol. The synthesized TiO₂/Sn₂ was prepared by sol-gel technique, mixture of titanium solution and ethanol/polymer with 2% of tin. The characterization of the synthesized TiO₂/Sn₂ and the commercial TiO₂ were performed by XRD, BET and SEM. The synthesized TiO₂/Sn₂ were: mixed phase of anatase:rutile of 85: 15, 14 nm crystalline size of anatase (101) and 47 nm rutile (110) and 65.7 m² g⁻¹ surface area by BET. On the other hand the commercial TiO₂ (Sigma aldrich) only showed the anatase phase with particle size of 41 nm and 10.9 m² g⁻¹ surface area by BET. The photocatalytic degradation were tested on the individual and mixed phenolic compounds. The phenolic compound solution suspended with the catalyst was irradiated with UV light. The photocatalytic degradation of phenolic compounds by such two types was significantly different. TiO₂/Sn₂ presented the sequential degradation as syringol > guaiacol > phenol for both individual and mixed phenolic compounds. While the commercial TiO₂ indicated the degradation as phenol>guaiacol>syringol for the individual phenolic compound and the reverse order of degradation as syringol>guaiacol>phenol for the mixed compounds.

Key words: Guaiacol, syringol, phenol, photocatalysis, titanium dioxide

INTRODUCTION

The main organic matter of pulp and paper wastewater are phenolic compounds, which are 2-methoxy phenol (guaiacol) and 2,6-dimethoxy phenol (syringol) and phenol. Guaiacol and syringol are non-toxic substance while phenol is toxic substance. However, degradation of phenolic compounds is the prime concern for pulp and paper wastewater treatment. One of the most popular technique to accelerate degrading of organics compound is photocatalysis (Hoffman *et al.*, 1995; Mills and Hunte, 1997; Bhatkhande *et al.*, 2002). Photocatalytic technique is based on the interaction between a catalyst and the UV radiation. Irradiated catalyst promotes an electron (e⁻) from the valence band to the conduction band, creating a positive hole (h⁺) in the valence band.

The electron-hole (e⁻h⁺) pairs are able to initiate oxidation and reduction reaction to break down the organic compound (Fujishima *et al.*, 2000). The most common catalyst in photocatalysis is TiO₂. Many researches have been developed to synthesize nanoparticles TiO₂ (Li *et al.*, 2002; Bessekhoud *et al.*, 2003; Boujday *et al.*, 2004). Recently, there are a number of studies related to the photocatalytic activity of metal oxide-TiO₂ catalysts for the purpose of improving TiO₂ photocatalytic activity, this metal was including CDS, SnO₂, WO₃, SiO₂, ZrO₂, V₂O₅. The metal oxide-TiO₂ catalysts may increase the efficiency of photocatalytic process by increasing the charge separation and extending the energy range of photoexcitation (Li *et al.*, 2001). Therefore, the purpose of this study was to determine the photocatalytic degradation of guaiacol, syringol and phenol which are the

contaminants of pulp and paper wastewater. The catalysts used were synthesized nanoparticle TiO₂/Sn₂ and the commercial TiO₂ (Sigma Aldrich). In addition, the characterization of the synthesized and commercial catalysts was performed in order to identify the phase components that have the role on degradation.

MATERIALS AND METHODS

Materials: The chemicals were purchased from different companies as follows: Titanium (diisopropoxide) bis (2, 4-pentanedionate) 75 wt% in 2-propanol (TIAA), 99% purity (Acros Organics), Polyvinyl pyrrolidone (PVP) (M_n = 1 300 000) and Titanium dioxide (anatase) powder, 99.8% purity, Tin (IV) chloride, guaiacol, syringol (Sigma aldrich.) Acetic acid, methanol and ethanol, 100% purity (BDH). Phenol (Merck). Water used to make up solutions was Milli-Q water.

Sample preparation: The synthesized nanoparticles titanium dioxide (TiO₂/Sn₂) was used as catalyst. To obtain the TiO₂/Sn₂ the mainly precursor were divided in two sources which are polymer source and metal source. Polymer source was prepared by using a ratio of 4.5 g PVP to 75 mL ethanol. To obtain a solution of metal source, 14.85 g of TIAA was dissolved in the solution of 30 mL acetic acid and 30 mL ethanol and 2% Tin by mole of Titanium was added in the metal source. The solution was then dissolved in the prepared PVP/ethanol solution. The mixture was vigorously stirred at room temperature to get the homogeneous polymer solution and air dry until the dense gel was obtained and oven for 24 h. The dry gel was calcined at 550°C for 3 h in the Muffle Furnace (Fisher Scientific, USA). The calcined nanoparticles were ground and passed through the sieve mesh No. 230.

Materials characterization: The TiO₂/Sn₂ and commercial TiO₂ were characterized by using X-Ray Diffraction (XRD) on a Bruker AXS (D8 ADVANCE) diffractometer at 40 kV, 40 mA (Cu Kα = 0.15406 nm). The step size was 0.02 degree/step and step time was 0.2 sec/step. The working range was 2θ = 20-80. The strongest peaks of TiO₂ corresponding to anatase (101) and rutile (110) were selected to evaluate the crystallite size according to Equation (1) is commonly known as the Scherer's equation (Suryanarayana and Norton, 1998).

$$L = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where L is the length of the crystal in the direction of the d spacing, k is a constant of 0.9, λ is the wavelength of

the x-ray, β is the full width at half-maximum (FWHM) of the selected peak and θ is the Bragg's angle of diffraction for the peak. The mass fraction of content phase anatase and rutile in the samples was calculated from intensities of XRD spectra according to the Spurr's equation as showed in the Eq. 2 (Spurr and Myers, 1957).

$$F_r = \frac{1}{1 + 1.26 [I_A(101)/I_R(110)]} \quad (2)$$

where F_r is the percentage content of rutile, I_A(101) and I_R(110) are the integral intensities (101) of anatase and (110) of rutile, respectively. The morphology of the nanoparticles, after being coated with gold, was characterized by SEM (LEO SEM 1450VP, U.K.). Specific surface areas of the TiO₂ were obtained by using the standard BET method on a Micromeritics ASAP 2010 sorption analyzer with common adsorbate, N₂, at -196°C. Before measurement, samples were pretreated with heat at 105°C overnight to remove moisture.

Photocatalytic degradation experiments: Photocatalytic testing was performed in a Pyrex vessel. For each experiment, 200 mL of 10 mg L⁻¹ phenolic compounds solution suspended with 0.4 g of TiO₂/Sn₂ or commercial TiO₂. The mixture was maintained as a suspension by magnetic stirring. The ambient air was circulated by an electric fan to control at the room temperature. Aeration was provided through an aquarium aerator. Prior to irradiation, the suspension was left for 1 h in the dark in order to achieve the maximum adsorption of the phenol onto the catalysts surface (Bekkouche *et al.*, 2004). The suspended solution was then illuminated by two Philips TLD 15 W/05 lamps, emitting ultraviolet radiation with a maximum radiation peak at 375 nm. The distance between the liquid surface and light source was about 15 cm. Sample of 2 mL was withdrawn at the regular intervals of time and filtered to separate the solid phase from liquid by nylon filter pore size 0.45 μm. The liquid phase was analyzed according to the procedure described below. Blank testing also was performed with phenol solution of 10 mg L⁻¹ both of irradiation without catalyst and with commercial TiO₂ (Sigma Aldrich) as catalyst without irradiation.

Phenolic compounds analysis: The phenolic compounds concentrations were determined by the high performance liquid chromatography (HPLC). The HPLC separations were carried out at room temperature on a system consisting of a LC-10AD pump (Shimadzu, Japan) equipped with a SPD-10A UV/VIS spectrophotometer detector (Shimadzu, Japan). Samples were injected in a

sample loop of 20 μL and detection wavelength was 270 nm. Phenolic compounds were chromatographed on a Shimp-pack CLC-ODS (150 \times 6.0 mm i.d., 5 μm) and eluted by methanol/water (3:7, v/v), flow rate 1 mL min^{-1} .

RESULTS AND DISCUSSION

Material characterization: XRD pattern of commercial TiO_2 was sharper than TiO_2/Sn_2 (Fig. 1). The commercial TiO_2 revealed the predominant phase of anatase while TiO_2/Sn_2 existed with the mixed phase of anatase: rutile in the ratio of 85: 15. The crystallite sizes of TiO_2/Sn_2 were 14 and 47 nm calculated from the strongest peaks corresponding to anatase (101) and rutile (110), respectively. The commercial TiO_2 only presented the crystallite size of anatase (101) of 41 nm. According to the result of SEM. Morphology of nanoparticles, TiO_2/Sn_2 was observed in the scale of nanoparticles (Fig. 2a) and also clearly observed the agglomeration in the SEM micrographs. The commercial TiO_2 presented the nanoparticles having spherical particles and less agglomeration (Fig. 2b). Not only SEM results confirmed the nanosize catalysts but also surface areas (BET) revealed the high surface area of TiO_2/Sn_2 . The surface area of TiO_2/Sn_2 of 65.7 $\text{m}^2 \text{g}^{-1}$ whereas the commercial TiO_2 's surface area of 10.9 $\text{m}^2 \text{g}^{-1}$ (Table 1). The role of phase components, combination of anatase and rutile and only anatase phases would affect the degradation of phenolic compounds are going to discuss further.

Table 1: Grain size of anatase/rutile phase and surface area (BET)

Semiconductors	Crystallite size (nm)		BET ($\text{m}^2 \text{g}^{-1}$)
	Anatase(101)	Rutile (110)	
TiO_2/Sn_2	14	47	65.7
Sigma Aldrich	41	-	10.9

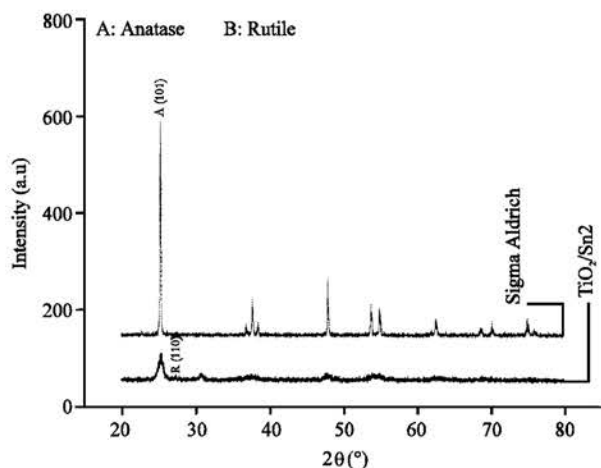


Fig. 1: X-ray diffraction patterns of TiO_2/Sn_2 and Sigma Aldrich

Photocatalytic degradation of phenolic compounds:

Photocatalytic degradation is shown by the percentage remaining of phenolic compounds (C/C_0 , %) with irradiated time. Figure 3a and b present the photocatalytic degradation with the synthesized TiO_2/Sn_2 and commercial TiO_2 for the individual guaiacol, syringol and phenol. Phenolic compounds, respectively. For degradation with the synthesized TiO_2/Sn_2 , the sequence of higher degradation were syringol>guaiacol>phenol, respectively. Outstandingly, the highest decomposition of syringol was performed after 2 h of irradiation. After 6 h irradiation, guaiacol and phenol were still remained as 1 and 32%, respectively. While the commercial TiO_2 presented the degradation in the reverse order with TiO_2/Sn_2 . The commercial TiO_2 showed the sequence of higher degradation as phenol>guaiacol>syringol. Phenol and guaiacol were almost decomposed but the syringol was still remained about 13% after 6 h irradiation. TiO_2/Sn_2 completely degraded syringol within 3 h of irradiation (Fig. 4a and b). After 6 h degradation, guaiacol and phenol were remained of about 9 and 75%, respectively. Notably, the commercial TiO_2 resulted a slower degradation for these three mixed compounds. The amount of remaining of syringol, guaiacol and phenol

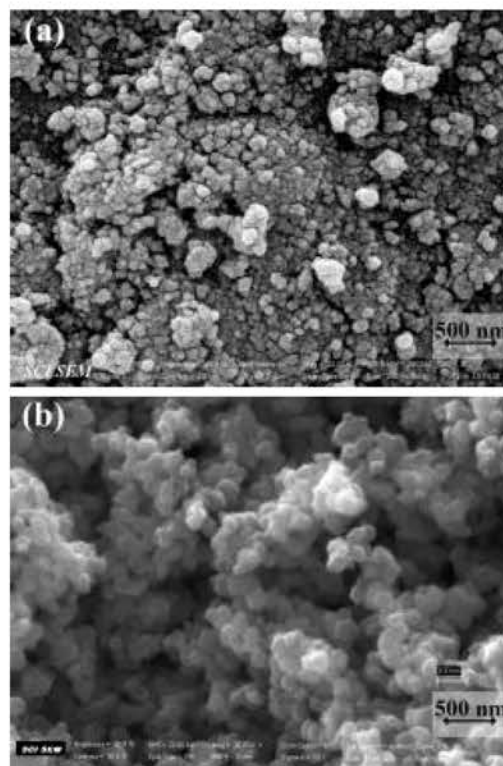


Fig. 2: SEM images of (a) TiO_2/Sn_2 (b) Sigma Aldrich TiO_2 (Magnification: X 20 000)

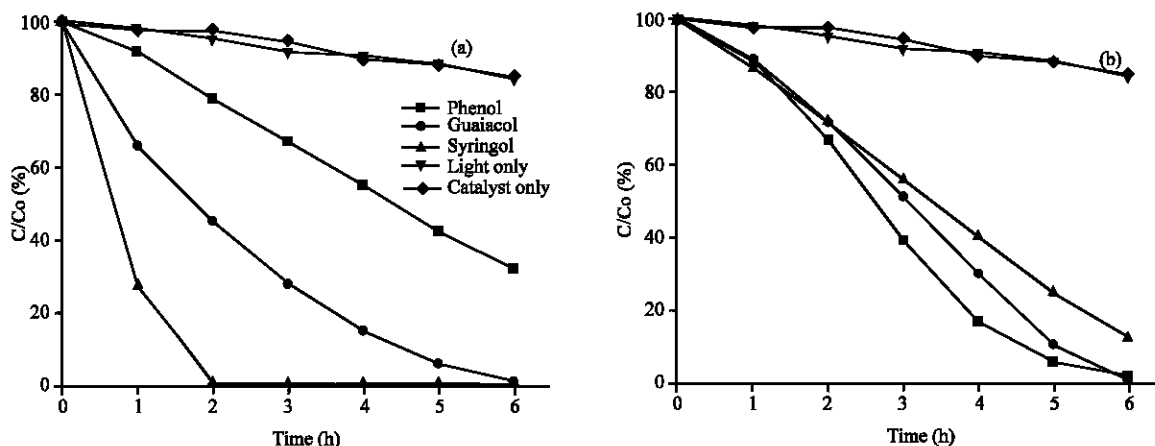


Fig. 3: The relative concentration of phenolic compounds during its irradiation with (a) TiO₂/Sn₂ (b) Sigma Aldrich

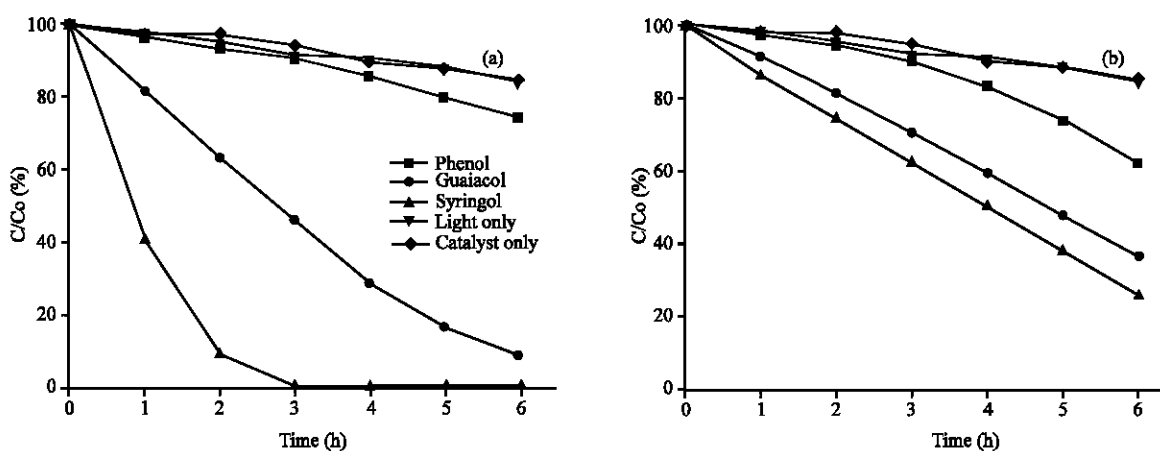


Fig. 4: The relative concentration of mixed phenolic compounds during its irradiation with (a) TiO₂/Sn₂ (b) Sigma Aldrich

were about 26, 37 and 62%, respectively. In addition, with the observation by chromatogram of HPLC, the degradation of phenolic compounds by the commercial TiO₂ showed the higher amount of the intermediates than TiO₂/Sn₂. The intermediates during degradation of syringol and/or guaiacol probably effected to the degradation of phenol. These intermediates significantly effected to the mixed compounds degradation by the commercial TiO₂. In accordance with the characteristics of the catalysts, the characteristics of catalysts, combination of anatase and rutile phases of the synthesized TiO₂/Sn₂ and only the anatase phase of the commercial TiO₂ would generate different intermediates. It was observed that the intermediates generated by the synthesized one were less than the commercial one. Therefore, the inhibition of degradation of phenol in the mixed solution was accordingly lower. This inhibition of intermediates could also be seen by the degradation of individual solution of phenol compound and the mixed phenolic compound solution with the commercial TiO₂ which have only anatase phase, the degradation of phenol compound of

the individual solution was significantly higher than the mixed one and the sequence of degradation was reversed as stated above. While TiO₂/Sn₂ presented the same order of degradation both of individual compound and mixed compounds solution. It is important to study the role of intermediates as well as the mechanism on the degradation of these phenolic compounds.

CONCLUSIONS

Photocatalytic degradation of the individual and mixed phenolic compounds by the synthesized TiO₂/Sn₂ and the commercial TiO₂ were significantly different. The TiO₂/Sn₂ showed the consistency of photocatalytic degradation of both individual and mixed phenolic compound solution. It also showed the highest degradation efficiency of methoxy phenol. While the commercial TiO₂ showed the inconsistency of the degradation between the mixed and individual compounds. The commercial one presented the higher degradation for a single solution of phenol. The phenol

degradation efficiency was substantially decreased for the mixed solution. It was observed that the phase components of the catalysts existed with combination of anatase and rutile of the synthesized one or only anatase phase of the commercial one influenced on intermediates generation which then further to the photocatalytic degradation.

In addition, as the wastewater contain the mixed phenolic compounds, the synthesized one yielded the higher degradation of phenolic compounds. Therefore, the synthesized TiO_2/Sn_2 has potential for using as catalyst on degradation of phenolic contaminated wastewater

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