

Photoreduction of Cr(VI) Catalyzed by TiO₂-Lignin

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Abstract

In order to increase the activity of TiO₂ photocatalyst, preparation and characterization of TiO₂-lignin and its activity on Cr(VI) photoreduction have been carried out. TiO₂-lignin was prepared by mixing TiO₂ powder with lignin powder in water-ethanol followed by stirring for 24 h and calcination at 400°C. The crystal structure characterizations were performed by X-ray diffraction (XRD), Lignin was identified using FT-IR whereas photoreduction of Cr(VI) was conducted in a batch reactor. The effect of TiO₂ content on TiO₂-lignin, irradiation time, weight of photocatalyst and initial concentration of Cr(VI) were studied to obtain effectiveness of photoreduction. Activity of TiO₂-lignin on the photoreduction of Cr(VI) showed higher result than TiO₂. The increased of TiO₂ content in TiO₂-lignin result in higher Cr(VI) photoreduction and gave maximum yield at mass ratio of TiO₂/lignin 2:1. The irradiation time, weight of TiO₂-lignin photocatalyst and initial concentration of Cr(VI) obtained for maximum Cr(VI) photoreduction are 40 h, 50 mg and 1 mg/L respectively which reduced Cr(VI) by 81.44%.

Keywords: TiO₂-lignin, Cr(VI) ion, photoreduction

Abstrak (Indonesian)

TiO₂ dipreparasi dan karakterisasi dalam bentuk TiO₂-Lignin untuk mendapatkan aktivitas yang lebih tinggi dalam fotoreduksi Cr(VI). Preparasi dilakukan dengan mencampur bubuk TiO₂ dan Lignin dalam air-etanol yang diaduk selama 24 jam dan dikalsinasi pada 400°C. Karakterisasi kristalin dilakukan dengan XRD sementara identifikasi Lignin dilakukan dengan teknik FTIR. Metode batch dipilih untuk menguji aktivitas fotoreduksi terhadap Cr(VI). Efektivitas fotoreduksi ditentukan dengan melakukan variasi kadar TiO₂, lama penyinaran, berat fotokatalis dan konsentrasi awal Cr(VI). Hasil analisis menunjukkan aktivitas fotoreduksi TiO₂-Lignin terhadap Cr(VI) lebih baik dari pada TiO₂ pada rasio TiO₂:Lignin sebesar 2:1. Aktivitas maksimum dimana 81,44% Cr(VI) dapat direduksi diperoleh pada lama penyinaran 40 jam, berat TiO₂-Lignin 50 mg dan konsentrasi awal Cr(VI) 1 mg/L.

Kata kunci: TiO₂-Lignin, ion Cr(VI), Fotoreduksi

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INTRODUCTION

Large amounts of chromium are introduced into the environment through various operating industries including textile, metal plating, leather tannery, paper

production, pigment paints, chemicals, petroleum refineries, etc. (Joshi and Shrivastava, 2011). These widespread chromium utilizations produced large

volume of waste water containing high levels of chromium.

Chromium exists in two oxidation states, Cr(III) and Cr(VI). Small amount of Cr(III) is an essential nutrient for metabolism of protein, insulin, glucose and fat in human bodies and mammals, whereas its role in plants is still unknown. All plants contain this element (Anonymous, 2002). Chromium compounds in high concentrations could cause irritation, ulcers, respiratory problems, kidney, and liver. Cr(VI) in particular could cause lung cancer (Anonymous, 2002).

Chromium removal treatment includes precipitation, ion exchange, photocatalysis, adsorption, and reduction. Most of these methods are high cost and recurring expenditure consequently they are not suitable for small-scale industries. Alternative method that can be used is the photocatalytic reduction using semiconductors such as TiO₂. When photocatalytic semiconductors, such as TiO₂, were illuminated with UV light, highly reductive electrons were generated and initiate the reduction of heavy metal ions in wastewaters (Ku and Jung, 2001).

Semiconductor TiO₂ photocatalyst has been studied intensively in environmental pollution degradation (Wang et al., 2008; Colon et al., 2001; Ku and Jung, 2001). This method has been developed in accordance to the principles of green chemistry which are simple process that does not require a lot of chemicals, low temperature and generated small amount of waste. Application of photocatalyst however face at least two problems arising from using fine TiO₂ powders: (1) separation of photocatalyst from the reaction media is difficult and (2) particulate suspensions are not easily applicable to continuous process. An alternative method is to immobilized TiO₂ powders onto an inert and porous supporting matrix such as silica (Ilisz et al., 2004), alumina (Ding et al., 2001), zeolite (Reddy et al., 2003), activated carbon (Yuan et al., 2005), resin (Linggarweni, 2014). In addition, the porous matrix can limit the growth of TiO₂ thus obtained composite nano TiO₂. Materials which has a structure similar to the resin and can be used to make TiO₂ in nano size is lignin. Lignin has an active side and pores that could restrict the growth of TiO₂ particles, it easily obtained from wood waste make it quite cheap and good to be used as a dispersant.

The use of lignin as a TiO₂ dispersant has been reported by Wahyuni et al, 2011 for photoreduction of Hg and Mulatsari for Ag (2012). The result gave increase of energy band gap of TiO₂ and decrease of particle size. The research TiO₂-Lignin has never been studied for Cr(VI) photoreduction. Therefore, in this

study Cr(VI) photoreduction was conducted using TiO₂-lignin as catalyst.

MATERIALS AND METHODS

Materials

Chemicals used in this study are TiO₂ powder, K₂Cr₂O₇ crystal, H₂SO₄, 1.5 -Diphenyl carbazide all provided from Merck. Alkali lignin (Aldrich), Whatman filter paper 42 and aqua destillata.

A set of closed box was used for photoreduction coated with melamine and equipped with a UV lamp type black light blue (BLB) 40 watt 220 volt with a wavelength of 340-390 nm, a magnetic stirrer spin bar 2 cm, laboratory glassware, analytical balance Mettler Toledo AB54-S, centrifuge, Oven, Spectronic 200D and X-ray diffraction type 6000X, XRD and FT-IR Shimadzu.

Preparation of TiO₂-lignin

Preparation of TiO₂ -lignin photocatalyst with various concentration of TiO₂ was conducted using following steps: TiO₂ powder was weighted (1, 2, 3, 4 g) and place in 100 ml erlenmeyer, 50 ml ethanol-water solution was added while stirred. During stirring 1 g of lignin powder was poured and continue stirring for 24 hours. Finally, the mixture was filtered to separate solids of TiO₂-lignin from ethanol water solution. The solids obtained was heated in oven at 100 °C for 1 hour, followed by calcination at 400 °C for 3 hours in a furnace. The catalyst were characterized using FT-IR and XRD.

Measurement of photocatalytic activity TiO₂-lignin

A 500 ppm stock solution of Cr(VI) was prepared by dissolving K₂Cr₂O₇ in distilled water. All the batch studies were carried out using this chromate stock solution. The calibration curve of Cr(VI) was obtained at $\lambda_{maks} = 540$ nm. Determination of Cr(VI) was conducted using SNI 0989.71: 2009 procedures.

In each experiment, solution of Cr(VI) 5 ppm was pipetted 50 ml and added to flasks containing TiO₂-Lignin (having ratio 1:1, 2:1, 3:1, 4:1) respectively. The flasks were placed in a reactor and irradiated under UV light and constant stirring for 24 hours. The photocatalyst was separated from the solution by centrifugation. The filtrate was analyzed to determine the percentage of Cr(VI) remained using spectrophotometry UV-Vis. The ratio of TiO₂-lignin which showed maximum Cr(VI) reduction was used for further photocatalytic study.

Photocatalytic study was carried out by analyzing Cr(VI) removal from solution with variation of irradiation time, photocatalyst mass and initial

concentration Cr(VI) using the same previous procedure.

RESULT AND DISCUSSION

Characterization of TiO₂-lignin

X-ray diffraction. The presence of TiO₂ in the TiO₂-lignin were identified using X-ray diffraction instrument. Fig.1 (a) shows that the standard lignin has a broad peak and showed no sharp peaks, indicates an amorphous form of lignin, same as reported by Mulatsari (2012). In the other hand TiO₂ standard show sharp peaks at 2θ : 24.8°, 37.2°, and 47.7° which are characteristic for TiO₂-anatase (Fig 1.f) Fig. 1(b), (c), (d) and (e) are diffraction pattern of TiO₂-lignin which has different TiO₂ contents. Peaks that appear in the image is similar to peak of the standard types of TiO₂-anatase. This image confirms that dispersing TiO₂ powder in water-ethanol did not change the structure of TiO₂ in the TiO₂-lignin.

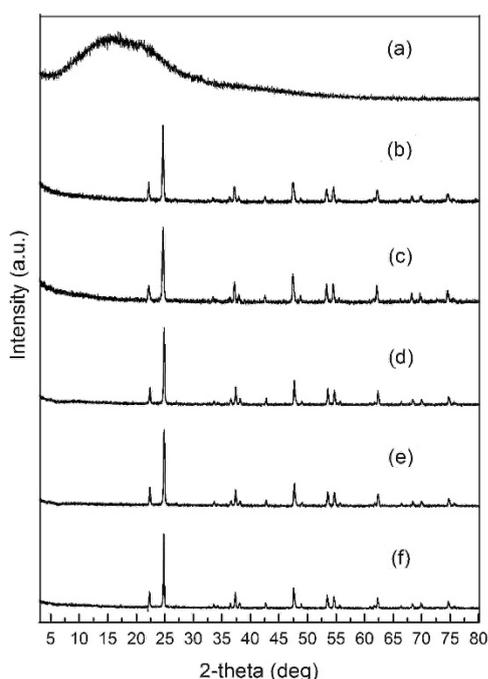


Figure 1. XRD diffractograms of (a) lignin (b) TiO₂-lignin 1: 1 (c) TiO₂-lignin 2: 1 (d) TiO₂-lignin 3: 1 (e) TiO₂-lignin 4: 1 (f) TiO₂

Fig. 1 also show that increasing content of TiO₂ into the lignin structure results in increase of intensities of their XRD pattern. The sharpness of the peaks at different TiO₂ content shown similar degree of crystallinity. Intensity of diffractogram resembles crystallinity of a solid material. The amount of sample is indicated by peak height of the XRD pattern. It can be understood that the more mass of TiO₂ introduced

into the lignin the more height of peak obtained. It is consistent with the results that had been reported by Mulatsari (2012).

FT-IR. The possible TiO₂ attachment at the lignin as depicted on fig. 2 was identified based on IR spectra. A wide absorption band at 3410 cm⁻¹ is assigned to aromatic and aliphatic OH groups while band at 2931 cm⁻¹ is vibration of CH₂ and CH₃ groups. Absorption bands at 1597, 1512, 1427 cm⁻¹ are aromatic ring vibration of phenylpropane (Tejado et al., 2007) whilst bands at 1273, 1134, 856, and 817 cm⁻¹ are typical for Guaisil. Absorption bands at 1373, 1450 cm⁻¹ are bending vibration of the phenolic -OH groups (Nair et al., 2016; Lisperguer et al., 2009 and Tejado et al., 2007) and absorption bands at 1273, 1219, 1134 and 1033 are C-O stretching vibration and ether bond or C-O-C (Xiong et al., 2015).

The specific absorption bands of TiO₂- anatase appears in region 686 cm⁻¹ and 517 cm⁻¹ are assigned as Ti-O-Ti structure. Absorption band at 3433 cm⁻¹ shows the OH stretching of Ti-OH on the surface of TiO₂ and water molecules, which is also support by absorption at 1627 cm⁻¹ assigned as OH bending of Ti-OH and water molecules adsorbed on TiO₂ (Riyani et al., 2012).

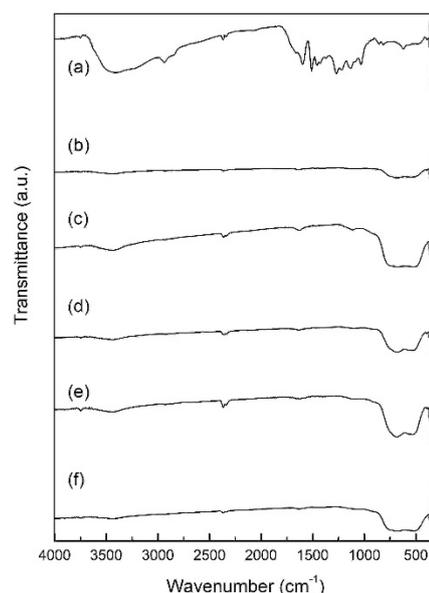


Figure 2. IR spectra (a) Lignin (b) TiO₂ lignin 1: 1 (c) TiO₂-lignin 2: 1 (d) TiO₂-lignin 3: 1 (e) TiO₂-lignin 4: 1 (f) TiO₂ powder.

Absorption band of TiO₂-lignin at 3448 cm⁻¹ is a shift of absorption of OH aromatic in lignin structure and indicates an interaction of -OH phenolic group on lignin with TiO₂. Absorption bands at 1597, 1512, 1427 cm⁻¹ which indicate the vibration of aromatic ring

phenylpropane (Tejado et al., 2007) is disappear and appears as absorption band at 1473 cm^{-1} . It shows possibility of interaction occurs on the aromatic ring of structure of lignin with TiO_2 (Nair et al., 2016). The absorption bands at 1273 , 1219 , 1134 , and 1033 cm^{-1} are stretching vibration of C-O from methoxy and ether linkage C-O-C also appears at 1111 cm^{-1} which indicates that the methoxy and ether played a role in the interaction of lignin and TiO_2 (Mulatsari, 2012). Absorption at 1627 cm^{-1} comes from the vibration of Ti-OH and H_2O indicates existence of TiO_2 that is not bound to lignin and formed double layer or trapped in the pores of lignin (Mulatsari, 2012). Characteristic bands of Ti-O-Ti at 686 cm^{-1} and 517 cm^{-1} shifted to 679 cm^{-1} and 525 cm^{-1} give forth of interaction between TiO_2 and lignin (Nair et al., 2016). It is clearly confirmed that TiO_2 interact with lignin via $-\text{OCH}_3$, $-\text{CO}$ and $-\text{OH}$ groups in the lignin structure. Ti-OH can also have trapped on the surface and entered the pores of lignin.

Effect of dispersion

Fig. 3 shows without any light, adsorption of Cr(VI) was occurred on the surface of TiO_2 but no photoreduction process undergo. In the process with no light shows that adsorption of Cr(VI) was very small when using TiO_2 bulk, but the adsorption increased with the addition of TiO_2 -lignin photocatalyst. The increase in surface area obviously is responsible for higher adsorption by TiO_2 -lignin compare to TiO_2 . Dispersing TiO_2 on lignin allows contact between the TiO_2 surface with Cr(VI) to be more effective. In addition, adsorption can also occur in the structure of lignin.

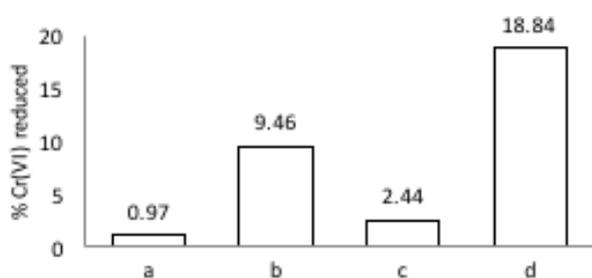


Figure 3. Photoreduction of Cr(VI) in TiO_2 (a) without and (b) with irradiation, TiO_2 -lignin (c) without and (d) with irradiation

Photoreduction process using light irradiation both on TiO_2 and TiO_2 -lignin result reduction of Cr(VI). During irradiation, TiO_2 absorbs light with appropriate energy to formed OH radicals and release electrons. The electrons are then reduced Cr(VI) into Cr(III) hence concentration of Cr(VI) decreased. Irradiation using TiO_2 -lignin catalyst showed more Cr(VI) reduce than

TiO_2 catalyst. TiO_2 -lignin particle has smaller size due to the growth of TiO_2 is limited by lignin, resulting in a surface area larger than TiO_2 . A larger surface area will increase Cr(VI) reduction. This result is supported by a previous study by Evitasari (2012) and Mulatsari (2012).

Effect of TiO_2 mass in TiO_2 -lignin

To evaluate the mass of TiO_2 influence on TiO_2 -lignin photocatalyst, photoreduction process was carried out using TiO_2 -lignin dispersed in various ratio i.e. 1:1, 2:1, 3:1 and 4:1. Experiment was conducted on 50 ml solution of Cr(VI) ions 5 ppm, weight of TiO_2 photocatalyst-lignin 50 mg and 24 hours of exposure time. The test results can be seen in Figure 4.

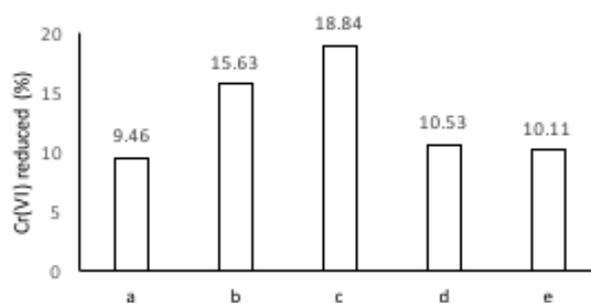


Figure 4. Effect of TiO_2 mass in the TiO_2 -lignin (a) TiO_2 (b) TiO_2 -lignin 1:1 (c) TiO_2 -lignin 2:1 (d) TiO_2 -lignin 3:1 (e) TiO_2 -lignin 4:1

Fig.4 shows that increase of TiO_2 mass in the TiO_2 -lignin can increase effectiveness of Cr(VI) reduction. The more TiO_2 content in TiO_2 -lignin increased the amount of electrons available for photoreduction hence increased its effectiveness. However, large amount of TiO_2 in photocatalyst could cause in TiO_2 aggregation make it larger in size and reduce surface area of the photocatalyst. The lower surface area of TiO_2 in the TiO_2 -lignin in turn lessen reaction contact resulting in decreased of photoreduction. This is consistent with the results of research conducted by Mulatsari (2012). From these results it can be seen that the most active photocatalyst is TiO_2 -lignin with ratio 2:1.

Effect of irradiation time

The effect of irradiation time was evaluated by illuminating 50 ml solution of Cr(VI) 5 ppm, 50 mg TiO_2 -lignin photocatalyst (2:1) for 8, 16, 24, 36, 40, 48, 62 and 70 hours. The study results are shown in Figure 5.

The optimum irradiation time was achieved after 40 hours, Increase of irradiation time after reaching the optimum time do not provide any significant improvement (relatively constant). Longer irradiation time allows contact between the light and photocatalysts more effective, electrons is more generated compare to shorter time. It also makes the effectiveness of the contact between the electrons with Cr(VI) increases. But for a time much longer than 40 hours, photoreduction is not increased. This can occur due to release of electrons on the surface of TiO₂ photocatalyst has been maximized so that despite the extended time photoreduction do not increased in a significant way.

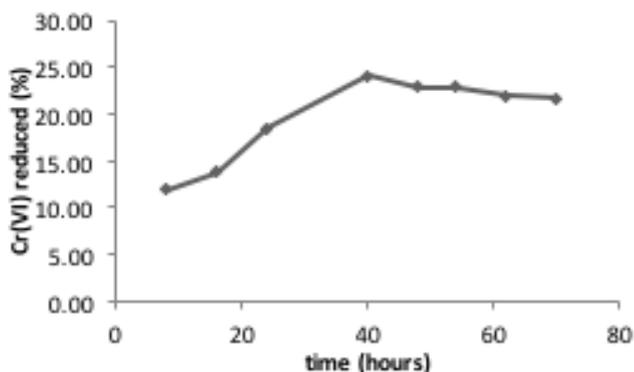


Figure 5. Effect of irradiation time to amount of Cr(VI) reduced

Effect of the photocatalyst mass

Study on effect of the mass of the photocatalyst is conducted by the addition of TiO₂-lignin 2:1 (optimum condition) into a 50 ml solution of Cr(VI) 5 ppm with variations of weight TiO₂-lignin i.e. 10, 25, 50, 75, 100, 125, 150 mg, irradiated for 40 h and stirred in a closed reactor. Fig. 6 shows TiO₂-lignin mass influence the reduction of Cr(VI) proportionally. It occurs because the more TiO₂-lignin weight added the more electrons generated in it surfaces, thus increased photoreduction, but data also shown that even larger TiO₂ mass causes photoreduction effectiveness to decrease. Mass of photocatalyst in a large number made a turbid reaction mixture hence reducing interactions between light with photocatalyst. This condition causes fewer electrons generated. The result was in accordance to research conducted by Mulatsari (2012).

Effect of initial concentration of Cr(VI)

Highly initial concentration of Cr(VI) tend to decrease photoreduction as shown on Figure 7. The higher concentration of Cr(VI) in solution creates

Cr(VI) ions increases proportionally while electrons generated by photocatalyst is constant. As a result, the electrons are no longer sufficiently enough to reduce Cr(VI) hence Cr(VI) photoreduction was decreased.

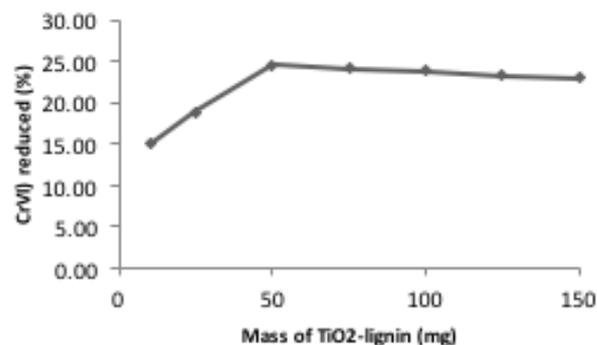


Figure 6. Effect of TiO₂ photocatalyst mass-lignin

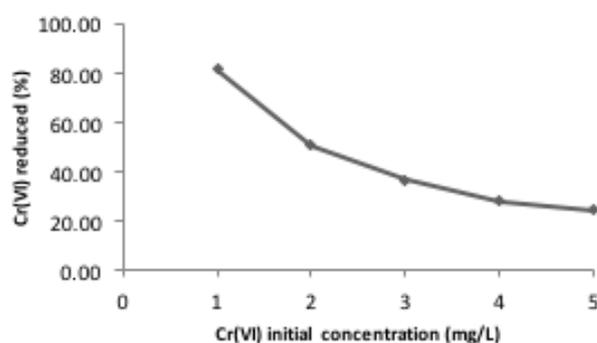


Fig. 7 Effect of initial concentration of Cr(VI)

At initial concentration of Cr(VI) 1 mg/L, the catalyst is able to reduce Cr(VI) to 81.44%, whilst concentrations higher than 1 mg/L lower reduction process. This shows that the reduction of Cr(VI) at low concentrations is more effective which is similar to result reported by Evtasari (2012) and Slamet et al. (2003).

CONCLUSION

Photoreduction of Cr(VI) is more effective using TiO₂-lignin photocatalyst compare to TiO₂ powder. The higher mass of TiO₂ in the TiO₂-lignin provides higher photoreduction effectiveness of Cr(VI) in the solution and reached a maximum at the mass ratio of TiO₂-lignin 2:1. Mass of photocatalyst TiO₂-lignin in a bigger amount provides photoreduction effectiveness of Cr(VI) in the solution is higher and reached a maximum at 50 mg. The increases of irradiation time increase the effectiveness of photoreduction of Cr(VI) and achieve maximum at 40h. Initial concentration of

Cr(VI) influenced effectiveness of photoreduction of Cr(VI) using photocatalyst TiO₂-lignin. Photoreduction was found decreases in high initial concentrations of Cr(VI). Initial concentration of Cr(VI) with maximum reduction is 1 mg/L result in percentage of Cr(VI) reduced is 81.44%.

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