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

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 it role in plant 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 TiO$_2$. When photocatalytic semiconductors, such as TiO$_2$, 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 TiO$_2$ 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 TiO$_2$ 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 TiO$_2$ 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 TiO$_2$ thus obtained composite nano TiO$_2$. Materials which has a structure similar to the resin and can be used to make TiO$_2$ in nano size is lignin. Lignin has an active side and pores that could restrict the growth of TiO$_2$ 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 TiO$_2$ 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 TiO$_2$ and decrease of particle size. The research TiO$_2$-Lignin has never been studied for Cr(VI) photoreduction. Therefore, in this study Cr(VI) photoreduction was conducted using TiO$_2$-lignin as catalyst.

**MATERIALS AND METHODS**

**Materials**

Chemicals used in this study are TiO$_2$ powder, K$_2$Cr$_2$O$_7$ crystal, H$_2$SO$_4$, 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 TiO$_2$-lignin**

Preparation of TiO$_2$ -lignin photocatalyst with various concentration of TiO$_2$ was conducted using following steps; TiO$_2$ 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 TiO$_2$-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 TiO$_2$-lignin**

A 500 ppm stock solution of Cr(VI) was prepared by dissolving K$_2$Cr$_2$O$_7$ in distilled water. All the batch studies were carried out using this chromate stock solution. The calibration curve of Cr(VI) was obtained at $\lambda_{max} = 540$ 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 TiO$_2$-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 TiO$_2$-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 TiO$_2$-lignin

X-ray diffraction. The presence of TiO$_2$ in the TiO$_2$-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 TiO$_2$ standard show sharp peaks at 2θ: 24.8°, 37.2°, and 47.7° which are characteristic for TiO$_2$-anatase (Fig 1.f) Fig. 1(b), (c), (d) and (e) are diffraction pattern of TiO$_2$-lignin which has different TiO$_2$ contents. Peaks that appear in the image is similar to peak of the standard types of TiO$_2$-anatase. This image confirms that dispersing TiO$_2$ powder in water-ethanol did not change the structure of TiO$_2$ in the TiO$_2$-lignin.

FT-IR. The possible TiO$_2$ 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 CH$_2$ and CH$_3$ 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 TiO$_2$-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 TiO$_2$ 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 TiO$_2$ (Riyani et al., 2012).

Absorption band of TiO$_2$-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 TiO$_2$. 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\(_2\)O 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 –OCH\(_3\), - CO and –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 occured 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\(_2\)-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 3. Photoreduction of Cr(VI) in TiO\(_2\) (a) without and (b) with irradiation, TiO\(_2\)-lignin (c) without and (d) with irradiation.](image)

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 war 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.](image)

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.

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The optimum iradiation 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 TiO$_2$ photocatalyst has been maximized so that despite the extended time photoreduction do not increased in a significant way.

Effect of the photocatalyst mass

Study on effect of the mass of the photocatalyst is conducted by the addition of TiO$_2$-lignin 2:1 (optimum condition) into a 50 ml solution of Cr(VI) 5 ppm with variations of weight TiO$_2$-lignin i.e. 10, 25, 50, 75, 100, 125, 150 mg, irradiated for 40 h and stirred in a closed reactor. Fig. 6 shows TiO$_2$-lignin mass influence the reduction of Cr(VI) proportionally. It occurs because the more TiO$_2$-lignin weight added the more electrons generated in it surfaces, thus increased photoreduction, but data also shown that even larger TiO$_2$ 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.

Conclustion

Photoreduction of Cr(VI) is more effective using TiO$_2$-lignin photocatalyst compare to TiO$_2$ powder. The higher mass of TiO$_2$ in the TiO$_2$-lignin provides higher photoreduction effectiveness of Cr(VI) in the solution and reached a maximum at the mass ratio of TiO$_2$-lignin 2:1. Mass of photocatalyst TiO$_2$-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 TiO$_2$-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%.

REFERENCES


