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Landfill Leachate Degradation by TiO_2-Immobilized White Cement

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ABSTRACT

This report presented the characterization of white cement and TiO_2-immobilized white cement prior and after photodegradation treatment. The study was aimed at measuring the effectiveness of catalyst during the photodegradation at various different reaction times. The characteristic of the white cement was evaluated by XRD, whereas the effectiveness of the catalyst was evaluated by monitoring the COD values. The results showed that the white cement formed crystals with highest peak at 2θ 29.7990° and crystal size of 36.15 nm. In addition, the highest peak of the TiO_2-immobilized white cement before and after photodegradation was 2θ 29.4634° (crystal size 36.52 nm) and 29.4735° (crystal size 45.37 nm) respectively. Moreover, dissolved organic matter in landfill leachate decreased during the seven-hour photodegradation as indicated by the decrement of 71.43% of the COD values.

Key word : landfill leachate, photodegradation, TiO_2 immobilized, white cement.

INTRODUCTION

Landfill leachates consist of dissolved organic matters, heavy metals, and xenobiotic organic compound such as fulvic acid and humic acid, which have the potential to pollute the environment such as soil, surface water and ground water. The pollution can happen when there is not any pretreatment before drawn away. The advanced oxidation process is one of wastewater treatment methods for contaminant which is not easily biodegraded like xenobiotic organic substances. This method uses O_3, O_3/UV, O_3/H_2O_2, UV/H_2O_2, photo Fenton reaction, and UV/TiO_2 (Deng and Zhao, 2015). The usage of TiO_2 catalyst for landfill leachate degradation had been reported by Yuningrat, Gunamantha, and Wiratini (2012). She claimed that it could reduce the COD value of Bengkala landfill leachate in Singaraja Bali. There was a problem in TiO_2 powder reused after photodegradation process because of its very small particle size.

Several researchers have tried to solve this problem by immobilizing TiO_2 on solid support, like carbon materials from earth (Colmenares, Varma, and Lisowski, 2016), glass (Yuningrat and Oviantari, 2013), pumice stone (Yuningrat, Retug, and Gunamantha, 2016), cement (Hafizah, Jamal, Karim and Sopyan, 2009) and white cement (Sopyan, Hafizah, and Jamal, 2011).

There are several advantages of white cement such as high aesthetic value, available and cheap which can cause the white cement to be used as a solid support for TiO_2 photocatalyst (Sopyan et al., 2011), in addition to pumice stone-cement (Yuningrat et al., 2016) and fossiliferous limestone (Pinho and Mosquera, 2011). The white cement as a solid support also can utilize to overcome much turbidity in the system, whereas the TiO_2 powder causes the light was difficult to penetrate the solution in the system. Sopyan et al.(2011) reported that TiO_2 immobilized on white cement could degrade phenol up to 45% under UV lamp irradiation with the intensity of 2.6 mW/m^2 for 400 minutes.

The phenol content in the landfill leachate of Bengkala municipal solid waste was 35.28 mg/L as reported by Yuningrat and Oviantari (2013) which exceeded the maximum allowable for drinking and clean water (0.0002 mg/L) according to the Regulation of Environmental Ministry 2010. The negative effect of phenol can irritate eyes, skin, brain, lung, kidney and death (Wong, Tan, and Mohamed, 2011). Yuningrat et al.(2012) and Yuningrat, Oviantari, and Gunamantha (2015) reported that landfill leachate of Bengkala municipal solid waste treatment with oxidation process using TiO_2/H_2O_2/UV and TiO_2 immobilized on glass had not reduced the organic substances efficiently. The TiO_2 powders usage inhibited the light and the landfill leachate contact so that the photodegradation process was not effective. The solid support of glass plate for TiO_2 immobilization could increase the effectiveness of COD landfill leachate until 71.38%. The transparant properties of glass plate might contribute to the effectiveness of landfill leachate photodegradation process, but the plate glass usage was easy to be broken. To solve the problems, this study used the white cement as an alternative of natural solid support for TiO_2 to reduce organic substances in landfill leachate of Bengkala municipal solid waste. The organic substances in landfill leachate were measured by COD value which have not been reported by another researcher. Characterization of TiO_2 immobilized on white cement synthesized before and after photodegradation process were analyzed by X Ray Diffractometer (XRD) to reveal out the crystal structures. The TiO_2 immobilized on white cement synthesized was applied on landfill leachate photodegradation process for 1, 2, 3, 4, 5, 6, 7, 8, and 9 hours to know its effectiveness for reducing the organic substances.

EXPERIMENTAL SECTION

Materials and Methods

Glassware, stainless steel mould 8×5×2 cm, reservoir (sample container), COD reactor HI 839800 merk Hanna, furnace carbolite type ELF 11/6B and UV lamp (Sankyo Denky, FT10T8BLB, 10 W, 325 nm) were available in Chemical Analysis Laboratory of Universitas Pendidikan Ganesha. Meanwhile X Ray Diffractometer (XRD) with specification XRD-7000S Shimadzu (3kW) with X Ray Tube Target Cu LLF scan range 5-70° scan speed deg/min sampling pitch 0.02 deg was ready at Integrated Laboratory of Universitas Diponegoro Semarang.

Precursor like titanium tetraisopropokside (TTIP) 95% was purchased from Sigma Aldrich, HCl 37%, NaOH, HNO_3 65%, $K_2Cr_2O_7$, Ag_2SO_4, $HgSO_4$, and H_2SO_4 were pro analysis from PT Merck. Milliqueaquades was ready in Chemical Analysis Laboratory of Universitas Pendidikan Ganesha. White cement powders (SP) were purchased at Bumi Pertiwi building store Buleleng.

Landfill leachate samples were collected from landfill municipal solid waste of Bengkala Buleleng Bali. Synthesized TiO_2 immobilized on white cement was done using Sopyan et al. (2011) methods. The TiO_2 sol produced were mixed with white cement and then dried at room temperature for 30 days. The process was followed by drying it in an oven at temperature 60 °C and calcined at temperature 400 °C for 2 hours. Photodegradation of landfill leachate was carried out for 1, 2, 3, 4, 5, 6, 7, 8, and 9 hours with constant stirring and irradiated by UV lamp.

Crystal structure of TiO_2 (T), white cement (SP) and TiO_2 immobilized on white cement synthesized before (SPTS) and after photodegradation (SPTT) were analyzed by X Ray Diffractometer (XRD). COD value of landfill leachate sample was analyzed after certain time reaction of photodegradation. The decreased landfill leachate COD values were shown by the time graphic versus the percentage of reduced COD. The figure described any organic substances in landfill leachate which were degraded in batch reactor for certain time photodegradation process.

RESULTS AND DISCUSSIONS

The diffractogram of T, SP, SPTS and SPTT were shown on **Figure 1**. From **Figure 1,** it can be seen that TiO_2 has anatase phase crystal with the highest peak at 2θ 25.6881°. The crystal of TiO_2 has 9.02 nm size was calculated by Scherrer equation. The SP usage as solid support has crystal phase at 2θ 29.799° with the particle size of 36.15 nm.

The photocatalyst of SPTS and SPTT have crystal shape with their highest peak at 2θ 29.4634° with 36.52 nm and 2θ 29.4735° with 45.37 nm, respectively. The diffractogram of SPTS and SPTT have similar peak with T and SP diffractograms. The highest peak of XRD on TiO_2–white cement was dominated by the peak of SP as a solid support. The new peak at 2θ 18.1591° that appeared on diffractogram of SPTS was different from the diffractogram of T or SP. It might be caused by a new contaminant produced after synthesis of TiO_2–white cement. The TiO_2 sol was mixed with the white cement and then dried for 2 months at room temperature. Drying process was continued in an oven at temperature of 80 °C for 2 hours, followed by the calcination at temperature of 400 °C for 2 hours.

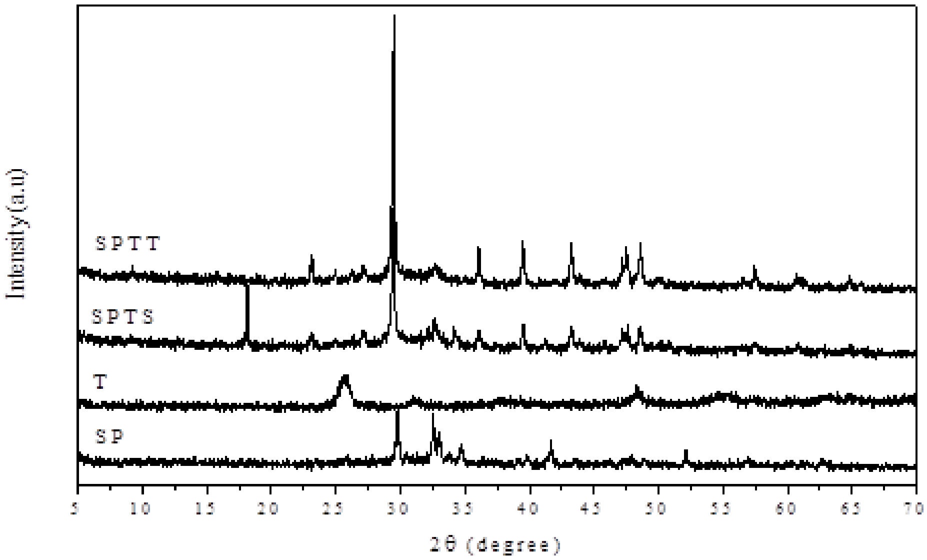

Figure 1. Diffractogram of white cement (SP), TiO_2 (T), TiO_2-white cement before photodegradation (SPTS), TiO_2-white cement after photodegradation (SPTT).

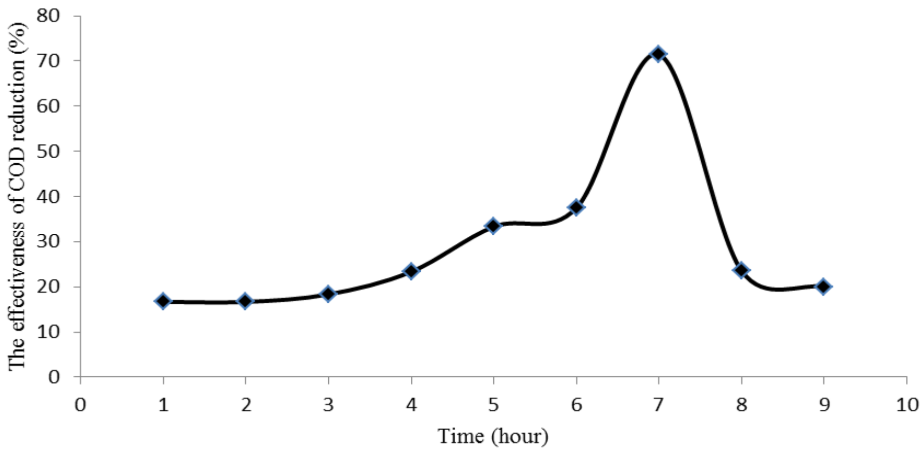

Figure 2. The effectiveness of COD reduction after photodegradation process at pH 8

The diffractogram of SPTS and SPTT were almost similar, but they have different intensity. The new peak at 2θ 18.1591° on SPTS was not appeared on SPTT. The dissappearance of the new peak might be caused by the reduction of contaminant along landfill leachate photodegradation process.

The colour of SPTT was changed to be brown. The colour changes might be caused by the adsorption process with the dark brown landfill leachate. This phenomenon did not happen to the mass of TiO_2–white cement photocatalyst. After photodegradation process, the mass of synthesized TiO_2–white cement was not changed significantly, compared to the TiO_2–white cement before using for landfill leachate photodegradation.

The synthesized TiO_2–white cement was evaluated to degrade organic substances of landfill leachate in a batch reactor which was irradiated by UV lamp for 1, 2, 3, 4, 5, 6, 7, 8, and 9 hours. Organic substances in landfill leachate were monitored through COD value that were shown in **Figure 2**.

From **Figure 2**, the effectiveness of COD reduction increases along the photodegradation process from 1 until 7 hours. Decreasing the COD value of landfill leachate occurred after 7 hours of photodegradation process. The percentage of COD reduction from 1 until 9 hours of photodegradation process were 16.67%, 16.67%, 18.33%, 23.33%, 33.33%, 37.50%, 71.43%, 23.53%, and 20.00%. The optimum effectiveness of COD reduction using TiO_2 immobilized on white cement for 7 hours irradiation was 71.43%.

The crystal structure of synthesized TiO_2 is anatase phase that indicated by the highest peak at 2θ 25.6881°. This might contribute to the photodegradation product. Therefore, the COD value of landfill leachate decreased significantly. In titania with the anatase phase, the electron from valence band could be excited into conduction band after absorbing the light which is higher energy than the band gap of titania anatase phase Eg = 3.2 eV (Hassan, Zhao, and Xie, 2016). Irradiation source in this research was UV lamp with λ=325 nm. According to Planck equation, energy calculated from the UV lamp was 3.81 eV which was higher than band gap of titania anatase phase. Photons yielded from UV lamp were absorbed by TiO_2-white cement to produce electron and hole on the surface of catalyst. So that the electron (negative charge) from valence band of TiO_2 could be excited to conduction band. The electron reacted with the oxygen and hydrogen ion to produce the hydroxyl radical. The hole (positive charge) produced on the surface of TiO_2 immobilized on white cement, reacted with hydroxide ion to produce hydroxyl radical. The hydroxyl radicals in the system oxydized the organic substance yielding simple substances like carbon dioxide and water (Pinho and Mosquera, 2011).

The diffractogram of TiO_2 immobilized on white cement have narrow peak and the highest peak at 2θ 29.4634°. The highest peak of SPTS is near 2θ 29.799° belong to the peak of SP. It means that the synthesis of TiO_2-white cement is dominated by white cement. The high intensity of peak indicated high crystalline degree. High crystallinity degree reduced recombination between electron and hole that enhance the photocatalytic activity (Kominami, Murrakami, Kato and Ohtani, 2002). Hafizah et al. (2009) reported that higher crystalline contribute to enhanced phenol degradation process, although the crystal size was bigger. High crystalline could produce more charge carrier on the surface of the catalyst to increase phenol degradation.

The photocatalyst of TiO_2 immobilized on white cement has 36.52 nm, which was bigger than TiO_2 crystal size (9.02 nm). If the crystal size was small then the surface area was bigger. Therefore, more pollutant in landfill leachate was adsorbed on the surface of catalyst and converted to CO_2 and H_2O. The degree of catalyst crystallinity contributed to the higher decrease of COD value than the crystal size of TiO_2–white cement photocatalyst.

The effectiveness of COD value reduction obtained in this research was almost similar to the landfill leachate treatment using TiO_2 immobilized on glass plate for 6 hours irradiation time reported by Yuningrat et al. (2015) which was 71.38%. Whereas Rojviroon, Rojviroon, and Sirivithayapakorn (2015) reported that landfill leachate treatment using TiO_2 immobilized on activated carbon from coconut shell reached the maximum at 48.5% for 30 minutes irradiation with the intensity of 32 $\mu W/m^2$. The effectiveness of COD value reduction increase little significant as reported by Zhang, Yang, Song, Xu, Xu, Huang, Li, and Zhou. (2016), in which, the organic substances in landfill leachate decreased up to 55% using TiO_2 immobilized on organobentonite modified cetyltrimethylammonium chloride at solution pH 5 for 3 hours irradiation.

CONCLUSIONS

The anatase crystal phase was identified in the TiO_2-white cement before photodegradation (SPTS) with the highest peak at 2θ = 29.4634° in diffractogram of XRD. The organic substances degradation in landfill leachate increases from 1 hour to 7 hours photodegradation and decreases after 7 hours of photodegradation. The optimum effectiveness of landfill leachate COD reduction is 71.43%, obtained after 7 hours of irradiation time. The diffractogram of XRD in SPTT is similar to the diffractogram of XRD in SPTS with the highest peak at 2θ 29.4735°.

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