

The Use of TiO₂-SiO₂ in Photocatalytic Process to Degrade Toxic and Dangerous Waste

Lia Destiarti^{1*}, Roekmiati Tjokronegoro², Diana Rakhmawaty², and Rudiyanasyah¹

1. Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Tanjungpura, Pontianak 78114, Indonesia

2 Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Padjajaran, Sumedang 45643, Indonesia

*E-mail: lia_destiarti@mipa.untan.ac.id

Abstract

This study was conducted to investigate the use of TiO₂ immobilized on SiO₂ (TiO₂-SiO₂) in a photocatalytic process to degrade toxic industrial waste, phenol, linear alkylbenzene sulfonate (LAS), and Cr(VI), which is dangerous for humans and the environment. Titanium dioxide (TiO₂), as a photocatalyst, can make the solution become turbid. Thus, TiO₂-SiO₂ was used to increase the possibility of ultraviolet (UV) transmission. The phenol and LAS levels were measured with the Indonesian National Standard (INS) while the Cr(VI) level was determined with the colorimetric method. The activity test for the catalyst in suspension and immobilization against phenol showed that TiO₂-SiO₂ was more active than TiO₂. By using the photocatalytic process with the TiO₂-SiO₂ photocatalyst for 8 h, degradation of phenol and LAS reached 50% as a single compound and 12% as a mixture. However, TiO₂-SiO₂ did not decrease Cr(VI).

Abstrak

Penggunaan TiO₂-SiO₂ dalam Proses Fotokatalisis untuk Mendegradasi Limbah Beracun dan Berbahaya. Penelitian dilakukan untuk mengamati penggunaan TiO₂-SiO₂ dalam proses fotokatalitik guna mendegradasi fenol, *linear alkylbenzene sulfonate* (LAS), dan Cr(VI), dimana ketiganya merupakan limbah industri yang beracun dan berbahaya bagi manusia dan makhluk hidup. Titanium dioksida (TiO₂), merupakan suatu fotokatalis yang dapat membuat larutan menjadi keruh. TiO₂-SiO₂ digunakan untuk meningkatkan peluang transmisi ultraviolet (UV). Kadar fenol dan LAS diukur berdasarkan Standar Nasional Indonesia, sedangkan pengukuran kadar Cr(VI) dengan metode kolorimetri. Uji aktivitas untuk katalis bentuk suspensi dan imobilisasi terhadap fenol menunjukkan bahwa TiO₂-SiO₂ lebih aktif dibandingkan TiO₂ murni. Degradasi fenol dan LAS secara tunggal dengan fotokatalisis selama 8 jam dapat mencapai 50%, degradasi fenol dan LAS dapat mencapai 12% untuk pengolahan secara campuran. Namun demikian, katalis TiO₂-SiO₂ tidak mendegradasi Cr(VI).

Keywords: Cr(VI), LAS, phenol, photocatalyst, TiO₂-SiO₂

Introduction

Photocatalysis is a technology for treating toxic and dangerous waste. Photocatalysis, an effective and inexpensive process, is a combination of a photochemical process and catalysis. The photocatalytic process treats wastewater and removes toxic and dangerous substances [1].

Tjahjanto and Gunlazuardi [2] and Kajitvichyanukul *et al.* [3] observed that catalyst immobilization in the substrate could increase photocatalytic efficiency. The photocatalytic process is inefficient if TiO₂ is used in

powder form. This form disperses homogenously in water and produces milky dispersion. Therefore, the catalyst is difficult to recover. To measure the residue from the photocatalytic process, the solution must be clear. Ultraviolet light cannot activate a catalyst in a turbid solution. Consequently, catalyst immobilization in a substrate, in granule form, should produce a clear, easy-to-handle solution.

When the light ($h\nu$) from photon light interacts with a catalyst particle, electrons and holes form according to the reaction $\text{TiO}_2 + h\nu \rightarrow e^- + h^+$. Electrons exist in the conduction band, and the hole is in the valence band.

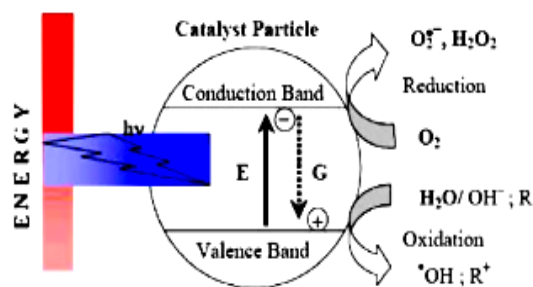


Figure 1. Simplified Mechanism for the Photocatalysis of a Semiconductor Catalyst [4]

Holes produced by TiO_2 are very active and oxidize many compounds. Electrons in the presence of oxygen can also produce an active form of oxygen that runs in the reduction process. Joshi and Shrivastava [4] stated that the charges can react directly with adsorbed pollutants, but reactions with water are more likely since the water molecules are far more numerous than contaminant molecules. Oxidation of water or OH^- by the hole produces the hydroxyl radical (OH^*), an extremely powerful oxidant (Figure 1).

In this study, a photocatalytic reactor was designed in which the type of catalyst used in the degradation process varied. Thiruvengatachari *et al.* [5] showed that the photocatalytic process was directed by the catalyst, source of light, and reactor configuration. The amount of $\text{TiO}_2\text{-SiO}_2$ used in the photocatalytic process was measured by determining each residue (model sample: phenol, linear alkylbenzene sulfonate [LAS], and Cr(VI)). Phenol and LAS were measured with the Indonesian National Standard method. Cr(VI) was measured with the colorimetric method, using an ultraviolet-visible (UV-Vis) spectrophotometer.

Materials and Methods

Materials. Commercial TiO_2 Degussa P25, silica gel 60 (SiO_2 ; 0.040-0.063 mm), aquades, phenol, potassium bromide, hydrochloric acid, potassium iodide, sodium thiosulphate, amylum, potassium bromide, ammonia, dipotassium hydrogen phosphate, amino antipyrine, potassium hexacyanoferrate (III), ethanol, chloroform, LAS, phenolphthalein, sodium hydroxide, sulfuric acid, methylene blue, sodium dihydrogen phosphate monohydrate, hydrogen peroxide, glass wool, and sodium dichromate. All materials derived from Merck.

Instrumentation. X-ray diffractometer (XRD) PANalytical, scanning electron microscope (SEM), double beam spectrophotometer UV-Vis Ultrospec 3000. The XRD and SEM measurement was done in Pusat Penelitian dan Pengembangan Geologi Kelautan, Bandung. A set of equipment to configure the photocatalytic reactor.

Construction of Photocatalytic Reactor. The photocatalytic reactor was made in the batch system. Six 10 W lamps with ultraviolet black light as the photon source were placed around the tube. The radiation process occurred in a closed system (the wall of the reservoir was made from stainless steel) and equipped with a blower. The sample tube in the center was made from quartz; the distance between the tube and the lamp was 5 cm. The tube was placed on the magnetic stirrer plate (Figure 2).

Catalyst Preparation. The catalyst was prepared by dip coating TiO_2 into SiO_2 thermally [6,7]. First, Degussa TiO_2 P25 was added by aquades, then sonicated for 20 m. Second, SiO_2 was mixed to TiO_2 solution, sonicated again for 20 m. Third, the mixture was heated in 100°C for 2 h. The last step, dried $\text{TiO}_2\text{-SiO}_2$ was furnace in 500°C for 5 h, followed by washing the $\text{TiO}_2\text{-SiO}_2$ using aquades. The ratio of $\text{TiO}_2\text{:SiO}_2$ were 1.6, 2.4, and 3.2 % (w/w), respectively.

Determination of Catalyst Activity-Preliminary Experiment. Catalyst TiO_2 (as positive control), $\text{TiO}_2\text{-SiO}_2$ (three types of composition), SiO_2 (as negative control) with 1 g/L loaded inside the designed reactor were tested to degrade 100 mg/L phenol [7]. The photocatalytic process was carried out for 3 h, and then the concentrations in the initial and final processes were measured. The data were compared, and a t-test was calculated to find the significance of the photocatalytic process for each catalyst. The most active catalyst was then applied in the following process and was characterized by using XRD and SEM.

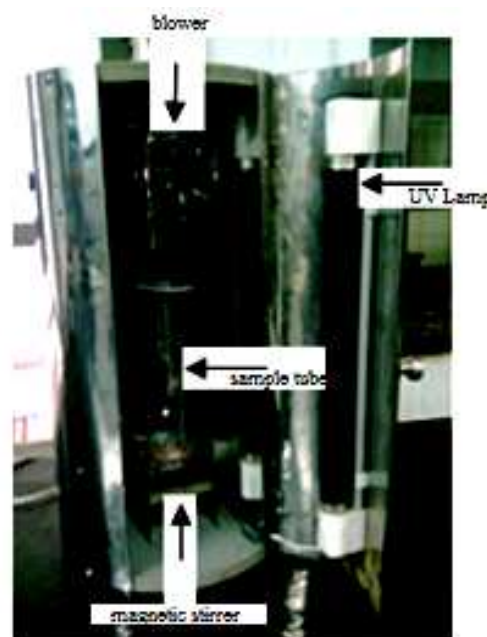


Figure 2. The Photocatalytic Reactor Measurements of the Use of $\text{TiO}_2\text{-SiO}_2$ in the Photocatalytic Process

Samples that contained phenol, LAS, Cr(VI), or a mixture of the three (phenol-LAS-Cr(VI)) were degraded and measured. The previously prepared catalyst was placed in the sample tube and stirred under UV radiation. The most active catalyst was applied in this process. The initial and final concentrations of the samples were measured each hour for 8 h.

Determination of Phenol. Phenol was measured using Indonesian National Standard No. 06-6989.21-2004 [8].

Determination of LAS. Linear alkylbenzene sulfonate was measured using Indonesian National Standard No. 06-6989.51-2005 [9].

Determination of Cr(VI). Cr(VI) was measured with the colorimetric method. The λ maximum of the potassium dichromate solution was measured using the UV-Vis spectrophotometer. Then, the absorbance of the Cr(IV) in the samples was measured in the λ [3].

Parametric Tests. The following parameters were analyzed: limit of detection, precision, accuracy, and linearity range [10].

Results and Discussion

The sample tube was made of quartz glass. Quartz glass transmits UV light. Six 10W UV-A lamps were used as the photon source and placed around the tube [11]. The wavelength of the lamps ranged from 315 to 400 nm, whereas the peak appeared at 352 or 368 nm with E_{bg} 3.37 and 3.52eV.

The irradiation process was carried out in a closed system (enclosed in containers made of stainless steel). The closed system kept the radiation inside the reactor, to make catalyst absorb the maximum UV light. Irradiation for 8 h increases the system temperature. Therefore, the reactor was equipped with a blower. The catalysts were put in a sample tube that contained the sample solution and constantly stirred to produce a homogenous catalyst system.

Immobilization of TiO₂ on SiO₂ followed the slurry precipitation method/dip coating method [5] with a specific composition. The catalyst was mixed with silica gel, and then the mixture were sonicated. After the water evaporated, calcination was carried out at 500 °C for 5 h. Based on the literature, at higher temperature, rutile is formed and decreases the catalyst's activity [2].

Figure 3 shows that the photocatalytic process decreased 2.1% of the phenol within 3 h by using silica gel (SiO₂). The decrease was due to the capacity of the silica gel-adsorbing analyte. The TiO₂ catalyst shows the highest percentage of phenol decomposition of the

catalysts. The decomposition was caused by the photocatalyst activity activated by UV light and followed by the oxidation process.

For the three types of prepared catalysts, the ability to degrade phenol was about 10-12%. Adding TiO₂ increased phenol degradation. Although the TiO₂ catalyst gave the highest result for the percentage of decomposition of phenol, TiO₂-SiO₂ also worked well. A small amount of TiO₂ on SiO₂ can reduce 10% of phenol, a fourth than 100% TiO₂ (reduce 36.6% of phenol). This study showed that 100% TiO₂ was not entirely activated by photons. This shows that turbid solution prevents photons from activating the catalyst.

In the phenol decomposition for SiO₂, 1.6% TiO₂-SiO₂, 2.4% TiO₂-SiO₂, and 3.2% TiO₂-SiO₂ differed statistically from the TiO₂ catalyst (t-test). These data indicated that 100% TiO₂ gave the best result for phenol decomposition. In addition, phenol decomposition produced by the three catalysts did not differ significantly. Thus, the ability of the catalysts was similar. Catalytic decomposition of phenol by immobilized catalysts were significantly different from that SiO₂. These results show that TiO₂, not SiO₂, has the main role in the photocatalytic process.

At the end of the procedure for preparing the catalyst, the immobilized catalyst was washed with aquadest. The filtrate that contained TiO₂ was weighed quantitatively, while the residue, TiO₂-SiO₂, was used for the degradation process. Based on the data shown in Table 1, to test the use of TiO₂-SiO₂ in the photocatalytic process in the reactor, 2.4% TiO₂-SiO₂ was used.

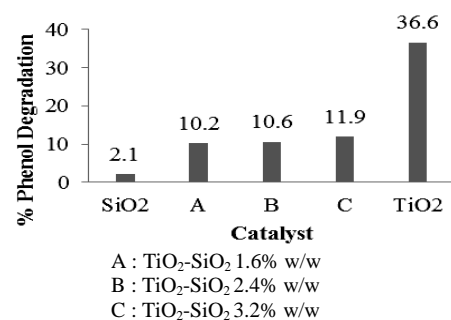


Figure 3. Effect of Various Catalysts on Degrading Phenol

Table 1. Mass of TiO₂ Released during the Washing Process

TiO ₂ -SiO ₂ (% w/w)	TiO ₂ Mass
1.6	0.093
2.4	0.076
3.2	0.087

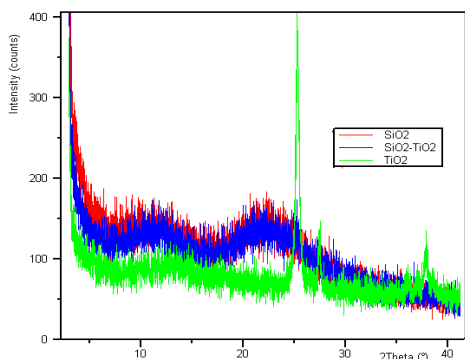


Figure 4. X-Ray diffractogram of SiO₂, 2.4% TiO₂-SiO₂, and TiO₂

Figure 4 and Table 2 show that the TiO₂.SiO₂ catalysts had a crystalline phase of the TiO₂ anatase (2θ=25.23). This is similar to the identity of the anatase phase of TiO₂ Degussa P25 as a comparison (2θ=25.29).

The rutile crystal on TiO₂ Degussa P25 disappeared in the immobilized catalyst due to the calcination process. Then a stable anatase crystalline phase appeared in these conditions. According to Tjahjanto and Gunlazuardi [2], this situation indicates that calcination techniques can change amorphous TiO₂ to become crystalline anatase, not rutile crystals [3].

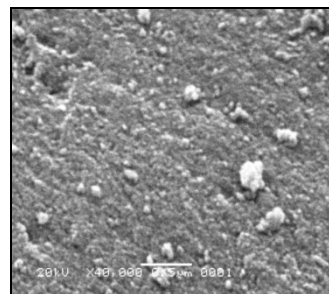
Figure 5 shows that morphology of the pure TiO₂ catalyst are nano-sized particles that have a wide surface. The size of the SiO₂ particles is not uniform in the profile obtained. The existence of immobilized TiO₂ on SiO₂ is obvious, even in small quantities.

Photocatalytic degradation of organic materials, namely, phenol and LAS, as well as inorganic materials, that is, metal ions Cr(VI) in aqueous solution as a model of industrial waste samples, was performed. Before being used to degrade the mixture samples, the photocatalytic process was used to process each type of waste (phenol, LAS, or Cr(VI) individually).

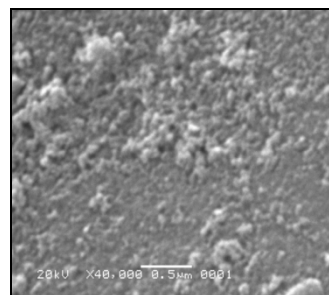
The measurement results for TiO₂-SiO₂ in 100 mg/L phenol oxidation either alone or in a mixture in the designed reactor are shown in Figure 6. In the figure, the phenol concentration tends to decrease the longer photocatalytic process lasts. The decrease in the phenol concentration for a single sample was better than that for simultaneous samples (merging with LAS and chromate), 19% and 9%, respectively.

In addition to phenol oxidation, the use of TiO₂-SiO₂ in the photocatalytic process was tested to degrade LAS. Immobilized TiO₂ on the SiO₂ catalyst was used for oxidizing 100 mg/L LAS either alone or in a mixture. The result is shown in Figure 7. In the figure, the LAS concentration continues to decline the longer

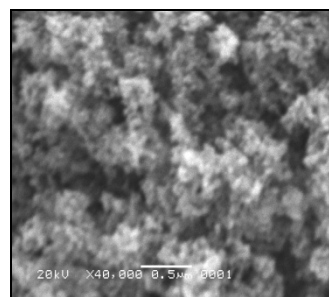
photocatalytic duration process lasts. The decrease in the LAS concentration for single samples was better than that for simultaneous processing (merging with phenol and chromate), 52% and 12.5%, respectively.



SiO₂



TiO₂-SiO₂



TiO₂

Figure 5. SEM profile of SiO₂, 2.4% TiO₂-SiO₂, and TiO₂

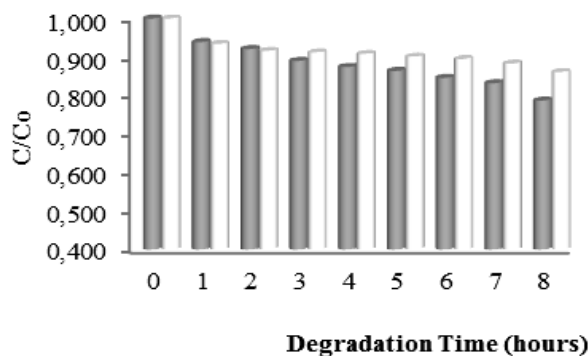


Figure 6. The Phenol Oxidation Results for Single (Grey Bar) and Mixed (White Bar) Samples

Table 2. Comparison of 2θ and Area of SiO₂, 2.4% TiO₂-SiO₂, and TiO₂

TiO ₂		SiO ₂		TiO ₂ -SiO ₂		
(2θ) (°)	Area (cts)	(2θ) (°)	Area (cts)	(2θ) (°)	Area (cts)	
		8.25	3.93			
		16.24	5.44			
		24.57	2.49			
25.29	208.60			25.23	14.80	Anatase
27.40	36.60					Rutile
31.07	2.83					
		35.45	3.76			
36.05	14.91					
37.78	30.90					
41.27	9.77					
		41.70	5.60			
		44.36	3.26			
		47.19	4.10	47.89	4.63	Silica
48.00	57.71					

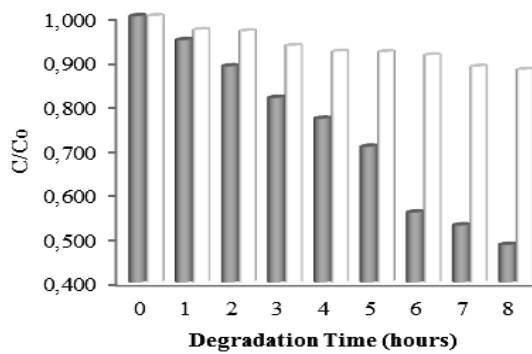


Figure 7. The LAS Oxidation Results for Single (Grey Bar) and Mixed (White Bar) Samples

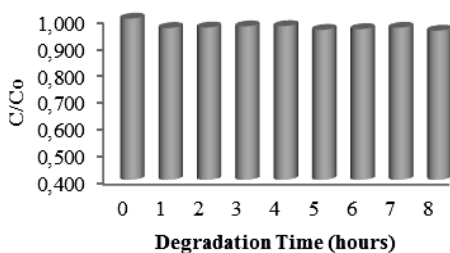


Figure 8. Chromate (VI) Reduction for TiO₂.SiO₂

Phenol and LAS are organic materials and thus have similar properties. The phenomenon of the degradation process through the oxidation reaction is initiated by a hole (h⁺) as shown in Figure 1. The results of the phenol and LAS processing (Figures 6 and 7) can be explained as the relation of the catalyst mass versus the sample concentration. The larger the sample concentration, the larger the catalyst mass needed. Therefore, C/Co of the degradation process for a mixed sample for 8 h is proportional to a single sample for 4 h.

The sample concentration affects the ability of TiO₂-SiO₂ during the photocatalytic process, as reported by Slamet *et al.* [12].

The role of reduction of TiO₂-SiO₂ was not comparable to its oxidation ability. Slamet and Daryanto [13] observed that TiO₂ catalysts reduced metals in Cr(VI) and oxidized phenolic compounds. In contrast, in this study, TiO₂-SiO₂ did not reduce Cr(VI). Figure 8 shows that by increasing the duration of the photocatalytic processes, the Cr(VI) concentrations in solution remained constant.

In addition, when TiO₂-SiO₂ could not reduce Cr(VI), Cr(VI) degradation when pure TiO₂ was used. The result shows that 40 mg/L bichromate solution was reduced up to 53.6% for 4 h. Joshi and Shrivastava [4] eliminated the toxic hexavalent form of Cr(VI) from wastewater, using TiO₂, ZnO, and CdS. They concluded that photocatalysis is a promising technique for removing heavy metals from industrial effluents. In addition, Qiu *et al.* [14] proved that Cr(VI) and phenol could be degraded simultaneously by using TiO₂ induced with visible light.

Therefore, TiO₂-SiO₂ cannot reduce Cr(VI). This result might be caused by specific properties of the catalyst in metal reduction. Additional research on TiO₂-SiO₂ in decreasing other metals is required.

The analytical parameters used to measure phenol, LAS, and K₂Cr₂O₇ at the 95% confidence level are shown in Table 2.

Table 2 shows the data for each measurement. The chosen standard concentration fulfilled the range of curve linearity. The precision and accuracy were acceptable. The limit of detection for phenol, LAS, and

Table 2. Analysis Data for Phenol, LAS, and Cr(VI)

	Phenol	LAS	Cr(VI)
Concentration (mg/L)	2.0-5.0	0.4-2.0	10.0-60.0
Linearity range (mg/L)	1.02-5.12	0.4-2.0	10.0-60.0
Precision (%)	0.17-3.47	0-0.78	0-0.25
Accuracy (%)	2.90-69.45	1.12-13.5	0.68-21.82
Limit of Detection (mg/L)	0.038	0.237	4.036

Cr(VI) determination was 0.038, 0.237, and 4.036, respectively. The sample concentration was higher than the limit of detection. To sum up, the measurement methods were verified in this research.

Titanium dioxide immobilized on silica gel can be used in a photocatalytic process to degrade toxic and dangerous waste. Titanium dioxide can reduce phenol and LAS levels using the proposed reactor. Degradation reached 50% and 12% alone and in the mixture, respectively. The catalyst cannot be used to degrade Cr(VI).

Acknowledgement

This research was funded by DIPA Universitas Padjadjaran (No:159/H6.1/Kep/HK/2009), a part of Hibah Pasca.

References

- [1] Hashimoto, K., Irie, H., Fujisima, A. 2005. TiO₂ Photocatalysis: A historical overview and future prospect, *Jpn J. Appl. Phys.* 44(12): 8269-8285. <http://dx.doi.org/10.1143/jjap.44.8269>.
- [2] Tjahjanto, R.T., Gunlazuardi, J. 2001. Preparasi lapisan tipis TiO₂ sebagai fotokatalis: Keterkaitan antara ketebalan dan aktivitas fotokatalisis, *J. Penelitian Universitas Indonesia*. 5(2): 81-91. [In Indonesia].
- [3] Kajitvichyanukul, P., Anapattarachai, J., Pongpom, S. 2005. Sol-gel preparation and properties study of TiO₂ thin film for photocatalytic reduction of Chromium (VI) in photocatalysis process. *Sci. Tech. Adv. Mat.* 6:352-358.
- [4] Joshi, K.M., Shrivastava, V.S. 2011. Photocatalytic degradation of Chromium (VI) from wastewater using nanomaterials like TiO₂, ZnO, and CdS. *Appl. Nano. Sci.* 1:147-155. <http://dx.doi.org/10.1007/s13204-011-0023-2>.
- [5] Thiruvengkatachari, R., Vigneswaran, S., Moon, S. 2008. A review on UV/TiO₂ photocatalytic process. *Korean J. Chem. Eng.* 25(1): 64-72. <http://dx.doi.org/10.1007/s11814-008-0011-8>.
- [6] Maryani, Y., Tjokronegoro, R.K., Suratno, W. Rochani, S. 2010. Photocatalytic degradation of surfactants anionic as detergent active compound using TiO₂/SiO₂ catalyst. *Proceedings of the Third International Conference on Mathematics and Natural Sciences (ICMNS)*. Bandung, Indonesia. pp. 906-910.
- [7] Doan, H.D., Saidi, M. 2008. Simultaneous removal of metal ions and linear alkylbenzene sulfonate by combined electrochemical and photocatalytic process. *J. Hazard. Mat.* 158(2-3): 557-567. <http://dx.doi.org/10.1016/j.jhazmat.2008.01.102>.
- [8] National Standardization Unit. 2004. Indonesian National Standards. No. 06-6989.21-2004. <http://www.bsn.go.id>.
- [9] National Standardization Unit. 2008. Indonesian National Standards. No. 06-6989.51-2005. <http://www.bsn.go.id>.
- [10] Miller, J.N., Miller, J.C. 2000. *Statistics and Chemometrics for Analytical Chemistry*. England: Pearson Education Limited.
- [11] Seshadri, H., Chitra, S., Paramasivan, K., Sinha, P.K., Photocatalytic degradation of liquid waste containing EDTA. *J. Desalination*. 232:139-144. <http://dx.doi.org/10.1016/j.desal.2007.12.013>.
- [12] Slamet, R., Syakur., Danumulyo, W. 2003. Pengolahan limbah logam berat chromium (VI) dengan fotokatalis TiO₂. *Makara Teknologi*. 7(1): 27-32. [In Indonesia]. <http://dx.doi.org/10.7454/mst.v7i1.132>.
- [13] Slamet, R., Arbianti, Daryanto. 2005. Pengolahan limbah organik (fenol) dan logam berat (Cr⁶⁺ atau Pt⁴⁺) secara simultan dengan fotokatalis TiO₂, ZnO-TiO₂, dan CdS-TiO₂. *Makara Teknologi*. 9(2): 66-71. [In Indonesia]. <http://dx.doi.org/10.7454/mst.v9i2.363>.
- [14] Qiu, R., Zhang, D., Diao, Z., Huang, X., He, C., Morel, J-L., Xiong, Y. 2012. Visible light induced photocatalytic reduction of Cr(VI) over polymer-sensitized TiO₂ and its synergism with phenol oxidation, *J. Water Research*. 46(7): 2299-2306. <http://dx.doi.org/10.1016/j.watres.2012.01.046>.