

Photodegradation of Detergent Anionic Surfactant in Wastewater Using UV/TiO₂/H₂O₂ and UV/Fe²⁺/H₂O₂ Processes

Endang Tri Wahyuni, R. Roto, M. Sabrina, V. Anggraini, N. F. Leswana, A. C. Vionita

Department of Chemistry, Faculty of Mathematic and Natural Sciences, Gadjah Mada University, Yogyakarta, Indonesia

Email address:

endtriw@yahoo.com (E. T. Wahyuni)

To cite this article:

Endang Tri Wahyuni, R. Roto, M. Sabrina, V. Anggraini, N. F. Leswana, A. C. Vionita. Photodegradation of Detergent Anionic Surfactant in Wastewater Using UV/TiO₂/H₂O₂ and UV/Fe²⁺/H₂O₂ Processes. *American Journal of Applied Chemistry*. Vol. 4, No. 5, 2016, pp. 174-180. doi: 10.11648/j.ajac.20160405.13

Received: July 13, 2016; Accepted: July 30, 2016; Published: August 31, 2016

Abstract: In order to prevent of detergent surfactant contamination to water and soil, or even in well water, decreasing surfactant in a laundry wastewater has been studied by using photodegradation under UV/TiO₂/H₂O₂ (photo-Fenton-like) and UV/Fe²⁺/H₂O₂ (photo-Fenton) processes. Photodegradation processes were performed in a batch system by exposing UV light to the laundry wastewater for a period of time. In both processes, the factors influencing the effectiveness of the photodegradation have been evaluated. The surfactant concentration left in the wastewater was determined by UV/Visible spectrophotometry using methylene blue as a coloring agent. The research results indicated that the surfactant concentration in the laundry wastewater could be decreased significantly by using both UV/TiO₂/H₂O₂ and UV/Fe²⁺/H₂O₂ processes. In both processes, it was observed the dependency of the surfactant photodegradation effectiveness on TiO₂ dose, Fe(II) and H₂O₂ concentrations, pH and time. From the influencing factors study, the optimal conditions could be obtained. To get the surfactant concentration in the wastewater that fulfills the quality standard regulated by Indonesian Government, two steps of both UV/TiO₂/H₂O₂ and UV/Fe²⁺/H₂O₂ processes were required. It also is clearly confirmed that UV/Fe²⁺/H₂O₂ (photo-Fenton) process was more effective in the surfactant photodegradation than that of UV/TiO₂/H₂O₂ (photo-Fenton-like) process.

Keywords: Surfactant, Photodegradation, UV/TiO₂/H₂O₂, UV/Fe²⁺/H₂O₂

1. Introduction

Detergent anionic surfactant is widely and intensively used in laundry activities, that can create wide contamination in rivers and soils. The surfactant polluting rivers can produce bubble that inhibit the oxygen and light penetration. Such lack of oxygen and light leads to the environmental quality decreased [1]. In addition, it has been reported that surfactant polluting river water is toxic for fishes and other water creatures [2]. Water contaminated by surfactant can cause eyes and skin irritation, and consuming such water also brings about health problems including diarrhea and kidney damaged [3]. Furthermore, soil contaminated by surfactant was reported to inhibit the plant growth [4]. Based on the facts that the surfactant is hazard for people and environment, removal of the detergent surfactant from laundry wastewater before being disposed, is urgently required.

Several methods have been assessed for removing or decreasing detergent surfactant including coagulation, adsorption, biodegradation, and photodegradation. The removal of surfactant from wastewater using coagulation-flocculation method has been carried out [5]. Surfactant treatment by adsorption method has been studied by using activated sludge flock [6], resins [7], and natural zeolite modified with CTAB [8]. These methods always produce hazardous solid waste because the contaminant is not detoxified except only to be transferred from water to the coagulant and adsorbent.

The removal of surfactant by biodegradation [9] involving a bacteria consortium isolated from the aquatic environment of Argentina, and anaerobic bacteria [10] have also been carried out. This method is only good for low level of surfactant because the high concentration of surfactant was hazard for the bacteria.

Degradation of surfactant using advanced oxidation processes (AOPs) have been assessed by ultrasonic irradiation technique [11], sonochemical technique [12], ultrasound and Fenton process [13], and by addition of several oxidizing agents [14]. The AOPs processes are also effective only for low surfactant concentration.

In addition, photodegradation involving UV light and TiO₂ photocatalyst has also been examined for surfactant removal, as reported [15-16]. Photocatalytic degradation of surfactant occurs due to the attack by OH radicals resulted from reaction between light and TiO₂ [17].

For high surfactant concentration, photocatalytic degradation process was less effective to decrease the surfactant level. Improvement of the photodegradation can be carried out by enlarging TiO₂ mass that will provide more OH radicals. The large amount of TiO₂ powder can increase the turbidity of the solution, that may inhibit the UV light penetration. The less light leads to the low photodegradation.

Increasing the number of OH radicals can be carried out by adding H₂O₂ in the degradation under TiO₂ photocatalysis and UV irradiation or UV/TiO₂/H₂O₂. The system has been assessed for degradation of blue I dyes [18], amoxicillin and its derivatives [19], and methylene blue [20], that worked successfully. So far the system of UV/TiO₂/H₂O₂ has not been explored for decreasing detergent surfactant.

In addition to UV/TiO₂/H₂O₂ system, other system that can result in OH radicals is Fenton using Fe(II) ion and H₂O₂ as reagents [21], and photo-Fenton involving UV light, Fe(II), and H₂O₂ or UV/Fe(II)/H₂O₂ [22].

Fenton process has been studied for degradation of hydrocarbon contaminating water [23], cresol [24], dimethylaniline [25], acridine orange dye [26], linier alkyl benzene sulfonate [27], surfactant [28], and dyes [29], and for organic compounds from cosmetic waste water [30], and from olive mill water [31].

Photo-Fenton method has been examined for degradation of phenol [22], organic compounds from pulp waste water [32], formic acid [33], formaldehyde [34], 4-chloroguaicol [35], organic of actual agro industrial waste water [36], and carbofuran pollutant [37]. It was concluded that photo-Fenton process was success for treatment the organic pollutants.

Moreover, from the comparison study of Fenton with photo-Fenton process, it was reported that photo-Fenton showed stronger activity in degradation of phenol [38], 4-chloroguaicol [39], and 3-aminopyridine [40]. Accordingly, in this present research, photo-Fenton (UV/Fe(II)/H₂O₂) process was chosen to be studied for degradation of detergent surfactant from laundry waste water, that was compared to UV/TiO₂/H₂O₂ process.

2. Experimental Method

2.1. Chemicals

Chemicals used were TiO₂ powder, H₂O₂, Fe(NH₄)₂(SO₄)₂, anionic surfactant dodecyl benzene sulfonate, methylene blue, chloroform, and several buffer solutions with various pH. All

chemicals purchased from Merck were in pro analysis quality and were used without any purification. As a subject of the research was laundry wastewater containing detergent anionic surfactant.

2.2. Procedures

2.2.1. Analysis of Anionic Surfactant in the Laundry Waste Water

The concentration of anionic surfactant in the laundry wastewater was determined by using UV spectrophotometry method with methylene blue as a color formation agent. The laundry wastewater as much as 5 ml in a separation tunnel was reacted with 5 ml of methylene blue solution 100mg/L, forming colorless solution. The solution was extracted with 5 ml of chloroform, and blue solution was formed. Then the blue solution in chloroform solvent was measured by using Visible spectrophotometer at 650nm of the wavelength. The concentration of surfactant in the wastewater was calculated by plotting the absorbance of the sample to a standard curve showing relationship of absorbance versus concentration of the respective standard solution.

2.2.2. Photodegradation of Anionic Surfactant

Photodegradation process by UV/TiO₂/H₂O₂ system was carried out by following procedure: The laundry wastewater as much as 100 ml was added with 40 mg of TiO₂ and 30 mM of H₂O₂ solution and was put in the photodegradation flask. Then the flask was put in the photodegradation apparatus (Fig. 1) and was exposed by UV lamp for 24 h. The photo-Fenton (UV/Fe(II)/H₂O₂) process was proceeded as follow. In the photodegradation flask was filled by 100 ml of the laundry wastewater, 5mM of Fe(II) solution and 200 m M of H₂O₂ solution, and then the final volume was made to be 100 ml. Then the flask was put in the photodegradation apparatus and was exposed by UV light for 3h.

The mixture from both photodegradation processes were centrifuged and filtered to get clear solutions. All of the clear solutions obtained were taken 5 ml, and were reacted with 5ml of 100 mg/L methylene blue solution, then were extracted by 5 ml of chloroform by shaking them for 5 min. The blue solutions obtained were analyzed by using Visible spectrophotometry.

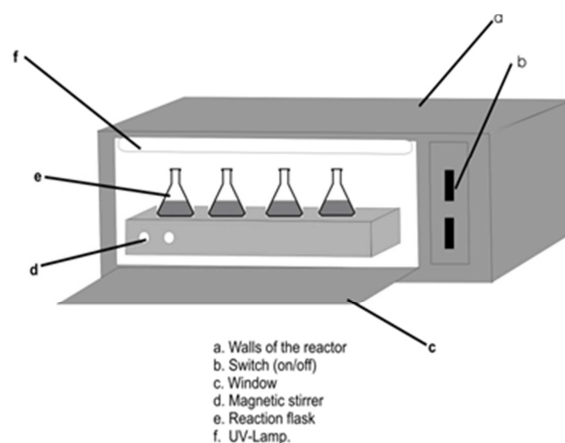


Fig. 1. A set of apparatus for photodegradation.

3. Results and Discussion

3.1. Photodegradation of Surfactant from Laundry Wastewater by Using UV/TiO₂/H₂O₂

3.1.1. Influence of TiO₂ Mass

The surfactant photodegradation by UV/TiO₂/H₂O₂ process with various TiO₂ mass is presented in Fig. 2. The figure shows that photodegradation degree of surfactant in the laundry wastewater improved drastically when the dose of TiO₂ photocatalyst was enlarged. But further increase of the mass does not influence the effectiveness of the surfactant photodegradation.

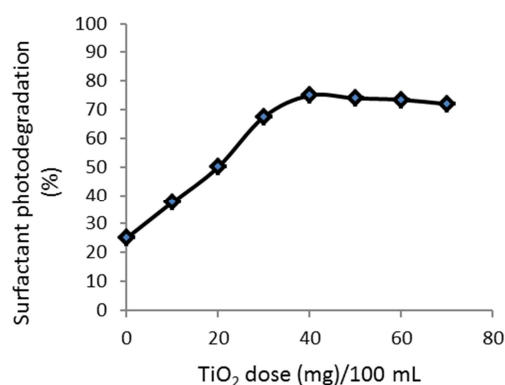
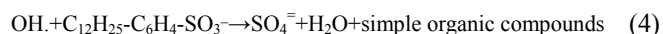
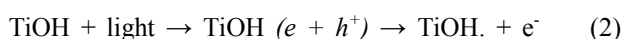
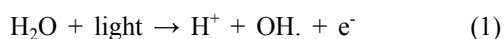


Fig. 2. The influence of TiO₂ dose.

The surfactant photodegradation is induced by the attack of OH radicals resulted from H₂O and H₂O₂ photolysis and TiO₂ photocatalysis during UV light exposure. The reactions of OH radical formation and the surfactant (C₁₂H₂₅-C₆H₄-SO₃⁻) photodegradation by OH radicals are written as reactions (1), (2), (3), and (4).



The larger mass of TiO₂ provided more OH radicals, that could induce more effective photodegradation.

With very large amount of TiO₂, the turbidity of the wastewater increased that screened the UV light penetration. The light inhibition must prevent the OH radicals formation [18], so that no more number of OH radicals for photodegradation were available.

3.1.2. The Influence of H₂O₂ Concentration

The role of H₂O₂ on UV/TiO₂/H₂O₂ system is as OH radicals supplying agent. The dependency of the surfactant photodegradation on the concentration of H₂O₂ is illustrated by Fig. 3. It is seen in the figure the sharp increase of the surfactant photodegradation as the increasing H₂O₂ concentration. The increase of H₂O₂ concentration could enhance the number of OH radicals, that promoted more effective photodegradation. The effectiveness of the surfactant

photodegradation appears to drop as the further increasing H₂O₂ concentration. H₂O₂ in excessive could react with OH radicals that were present to form water and oxygen, following reactions (5) and (6) [41]:

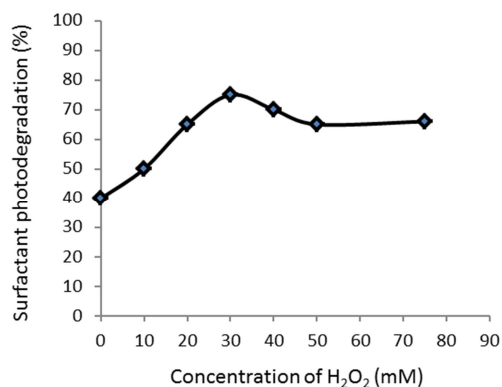
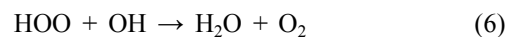
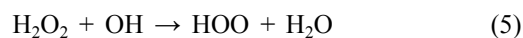


Fig. 3. The influence of H₂O₂ concentration.

The dissociation of H₂O₂ led to a decrease in the number of OH radicals and so the surfactant photodegradation.

3.1.3. Influence of the Process pH

The effect of pH on the surfactant photodegradation was represented by Fig. 4. It can be seen in the figure that increasing pH up to 5 has improved the photodegradation. At very low pH, much number of hydrogen ions was available that would react with H₂O₂ to form peroxone ion (H₃O₂⁺) following reaction (7) [39]. The peroxone ion was less reactive to release OH radicals, and so the only lesser OH radicals could be resulted.



In addition, at low pH, TiO₂ existed as TiOH that might be also protonated by the excessive hydrogen ions, written as reaction (8), that could reduce the OH radicals formation. These conditions made the photodegradation became considerably less effective.

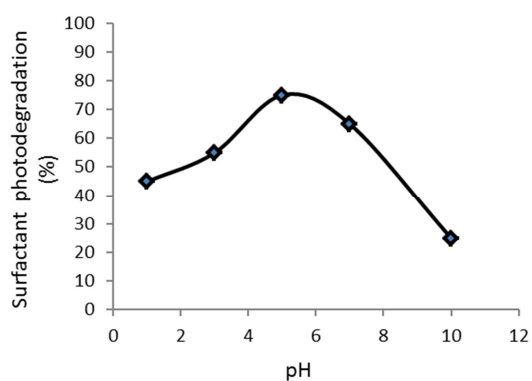
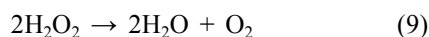


Fig. 4. The influence of the process pH.

Increasing pH up to 5, where the lesser number of hydrogen ions were available, could prevent protonation of H₂O₂ and TiO₂ that does not reduce their amount. This has promoted the faster photodegradation.

When the pH was further increased, H₂O₂ could be dissociated into water and oxygen [41], seen as reaction (9), that reduced the number of OH radical formed. In addition, TiO₂ became TiO⁻ following reaction (10) that was more difficult to form OH radicals. These explained the decrease of the photodegradation.



3.1.4. The Influence of the Process Time

Fig. 5 represents the influence of the process time on the surfactant photodegradation. It is observed the significant enhancement in the photodegradation as the process time was extended. The extension time facilitated the more effective contact between the light with TiO₂ and H₂O₂, to form more OH radicals, and between the radicals with the surfactant.

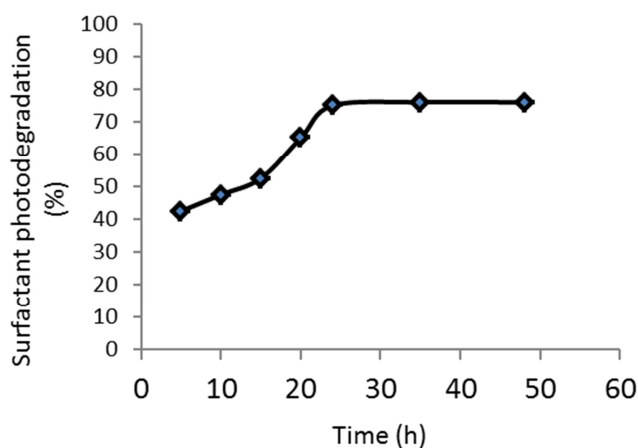


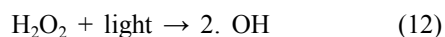
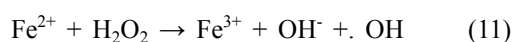
Fig. 5. The effect of the process time.

In the process running in 24h, the surface of TiO₂ and H₂O₂ have been exhausted that could not release OH radicals, so that the maximum interactions was reached. Consequently, in the process longer than 24 h, the photodegradation was independence on the time.

3.2. Photodegradation of Surfactant from Laundry Wastewater by Using UV/Fe(II)/H₂O₂

3.2.1. The Influence of Fe(II) Concentration

In the photo-Fenton (UV/Fe(II)/H₂O₂) system, there are reactions between H₂O₂ with light and Fe(II) with H₂O₂ to form OH radicals, following reactions (11) and (12) [42]. The radical was used for surfactant photodegradation.



It is clear that Fe(II) plays important role on the photodegradation of the surfactant. Accordingly, the influence

of Fe(II) concentration was evaluated and the data is displayed as Fig. 6.

It can be seen in the figure that increasing Fe(II) concentration has sharply raised of the photodegradation of the surfactant from the laundry wastewater. The effective photodegradation was induced by larger amount of OH radicals provided by higher Fe(II) concentration.

But, when the concentration of Fe(II) was further increased, the effectiveness of the surfactant photodegradation remained constant. In this condition, all of H₂O₂ have already reacted with Fe(II). Accordingly, although Fe(II) was present in excess, no more reaction between Fe(II) and H₂O₂ happened.

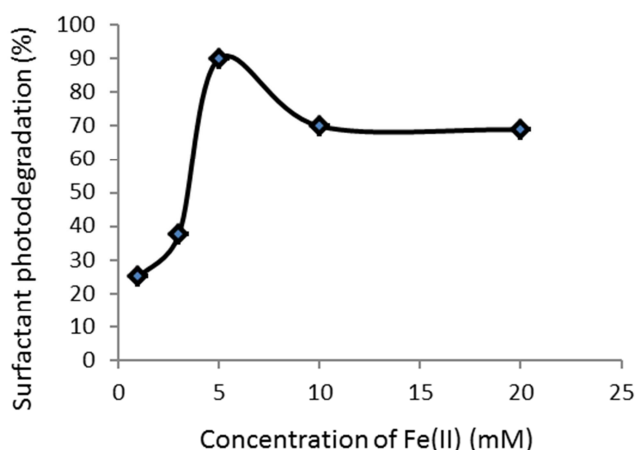


Fig. 6. The influence of Fe(II) concentration.

3.2.2. The Influence of H₂O₂ Concentration

As presented previously that H₂O₂, during UV light exposure, will form OH radicals functioned for surfactant photodegradation. It is interesting therefore to study the effect of H₂O₂ concentration on the photodegradation. Fig. 7 illustrated that increasing H₂O₂ concentration gave rise the surfactant photodegradation, that must be stimulated by more OH radicals available.

The photodegradation appeared to drastically decline when the concentration of H₂O₂ was further enlarged. The reason was same as explained previously.

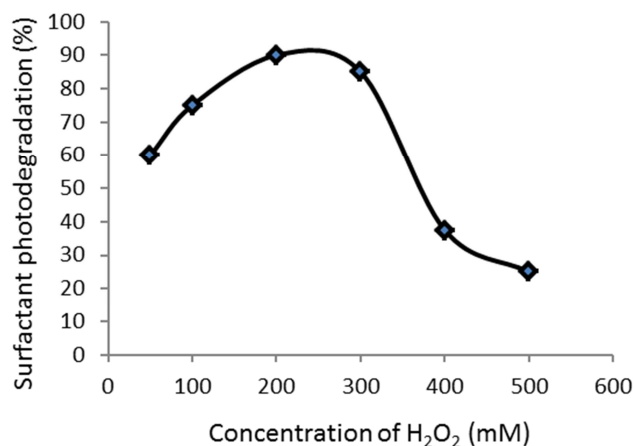


Fig. 7. The influence of H₂O₂ concentration.

3.2.3. Influence of the Process pH

Fig. 8 demonstrates the change of the surfactant photodegradation with the pH alteration during photo-Fenton process. At very low pH, Fe(II) was present as Fe^{2+} that readily reacted with H_2O_2 to form OH radicals with large amount. But because H_2O_2 was protonized by excessive hydrogen ion to form peroxone (H_3O_2^+) ions, that was less reactive to react with Fe^{2+} , only smaller amount of OH radicals could be provided. Consequently, the low effectiveness of the photodegradation proceeded.

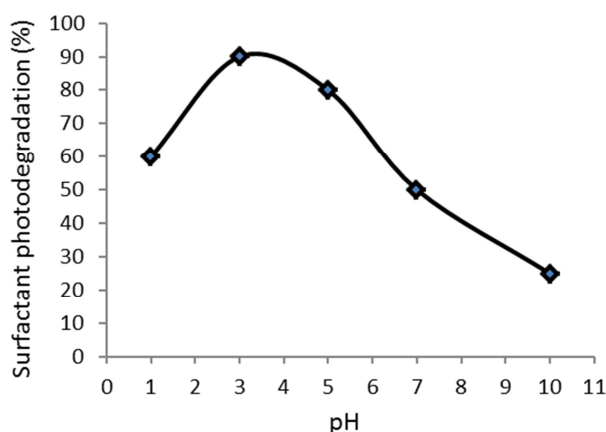


Fig. 8. The influence of the process pH.

The increase of pH up to 3, the significant raising surfactant photodegradation was observed. Increasing pH or decreasing number of hydrogen ions, can prevent the protonation of H_2O_2 . As a result a lot of H_2O_2 were should be present, that promoted more effective photodegradation.

Further increase of the pH led to the less effective surfactant photodegradation. At higher pH, as presented previously, H_2O_2 could be dissociated into water and oxygen. Meanwhile Fe^{2+} as well as Fe^{3+} resulted from reaction (11) would react with the excessive OH^- to precipitate as $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$. These cases considerably inhibited the photodegradation.

3.2.4. The Influence of the Process Time

The influence of the process time on the surfactant photodegradation is demonstrated by Fig. 9.

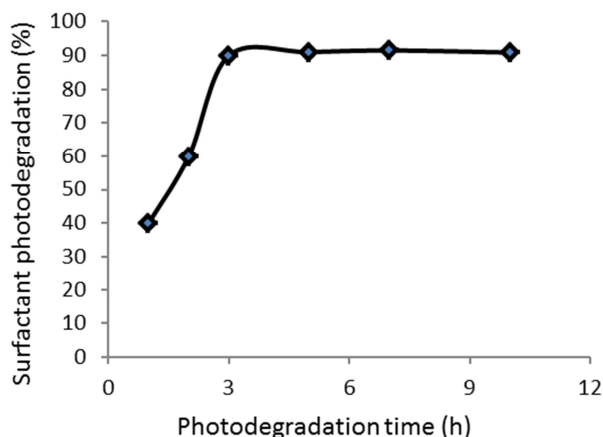


Fig. 9. The dependency of surfactant photodegradation on time.

The figure shows that the expansion of the process time has enriched the photodegradation and achieved the maximum photodegradation during 3 h of the process. After 3 h process, the formation of OH radicals has been saturated giving constant photodegradation.

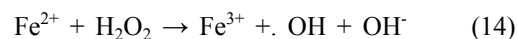
3.3. Comparison Effectiveness of the Surfactant Photodegradation by UV/ TiO_2 / H_2O_2 and UV/ $\text{Fe}(\text{II})$ / H_2O_2

From the study of factors influencing the effectiveness of the surfactant photodegradation in both UV/ TiO_2 / H_2O_2 and UV/ $\text{Fe}(\text{II})$ / H_2O_2 processes, the optimal conditions were obtained. The conditions were summarized in table 1.

Table 1. The optimal conditions in the surfactant photodegradation from 100 ml of the laundry wastewater.

Process variables	Optimal value	
	UV/ TiO_2 / H_2O_2	UV/ $\text{Fe}(\text{II})$ / H_2O_2
Mass of TiO_2 (mg)	40	-
Concentration of H_2O_2 (mM)	30	200
Concentration of $\text{Fe}(\text{II})$ (mM)	-	5
Process pH	5	3
Reaction time (h)	24	3
The degree of the photodegradation (%)	75.24	90.15
The concentration of surfactant after photodegradation (mg/L)	50.8	20.36

The table also displayed that UV/ $\text{Fe}(\text{II})$ / H_2O_2 process was more effective in surfactant photodegradation with shorter time than UV/ TiO_2 / H_2O_2 did. As presented previously, in the former process, OH radicals were originated from H_2O_2 photolysis by UV light, and reaction of Fe^{2+} with H_2O_2 forming Fe^{3+} . Then Fe^{3+} be reduced into Fe^{2+} , and then Fe^{2+} reacted again with H_2O_2 to form OH radicals. These repetition reactions providing much more number of OH radicals compared to UV/ TiO_2 / H_2O_2 . The sequent reactions were presented as reactions (13) up to (15).



The quick reaction in the photo-Fenton was produced from the homogenous system that facilitate effective contact among the reactants.

In contrast, in UV/ TiO_2 / H_2O_2 the presence of TiO_2 powder with larger dose can provide more number of OH radicals. However TiO_2 in further larger dose could create higher turbidity, that might inhibit the light penetration. This inhibition led to the low photodegradation. In addition, regarding the reaction rate, this process was in heterogeneous system that took more time for TiO_2 to release OH radicals.

Furthermore, the final concentrations of surfactant after photodegradation by both processes have not fulfilled yet the standard quality regulated by Government that is 0.50 mg/L. This may be caused by the high concentration of surfactant in the wastewater sample, that can not be fully degraded by all OH radicals present.

In order to fulfill the standard quality, second step of both photodegradation processes have been carried out and the results were presented as Fig. 10.

It can be seen in the figure that by two steps of UV/TiO₂/H₂O₂ and UV/Fe(II)/H₂O₂ processes, the surfactant concentration could decrease from 50.08 mg/L into 0.48 mg/L and from 20.36 mg/L into 0.26 mg/L respectively, that have fulfilled the standard quality.

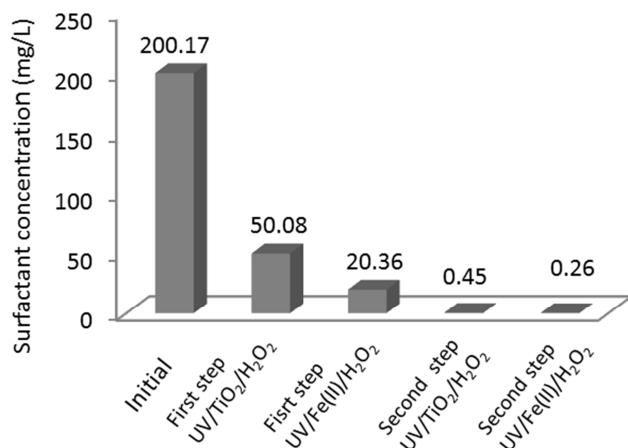


Fig. 10. Decreasing surfactant concentration in the wastewater by UV/TiO₂/H₂O₂ and UV/Fe(II)/H₂O₂ processes.

In the second step, much amount of OH radicals were available, meanwhile the concentration of surfactant left in the wastewater after first photodegradation was already low. This explained the very effective photodegradation.

4. Conclusion

It can be concluded that photodegradation of the detergent anionic surfactant in the laundry wastewater by UV/TiO₂/H₂O₂ (photo-Fenton like) and UV/Fe(II)/H₂O₂ (photo-Fenton) processes could significantly decrease the surfactant concentration. The effectiveness of the surfactant photodegradation was found to be controlled by TiO₂ dose, pH, H₂O₂ concentration, and the process time for UV/TiO₂/H₂O₂ system, and that of by Fe(II) and H₂O₂ concentrations, pH and the UV exposure time for UV/Fe(II)/H₂O₂ (photo-Fenton) process. The optimum conditions for both processes could be also formulated. It is also clearly confirmed that UV/Fe(II)/H₂O₂ (photo-Fenton) showed stronger activity in the decreasing surfactant concentration than UV/TiO₂/H₂O₂ process did. Further more it was also found that decreasing surfactant concentration in the wastewater that fulfills the Indonesia standard quality (0.5 mg/L) could be obtained by using two (2) steps of both UV/TiO₂/H₂O₂ and UV/Fe(II)/H₂O₂ processes.

Acknowledgements

Great acknowledgement is delivered to Chemistry Department, Gadjah Mada University for the financial support granted with the Project Number: 0101/J01.1.28/L.06/2015

References

- [1] Holmberg, K., Johnson, B., Kronberg, B., and Lindman, B., 2002, *Surfactant and Polymers in Aqueous Solution*, John Wiley and sons, London.
- [2] Ogundiran, M. A. Fawole, O. O, Adewoye, S. O., and Ayandiran, T. A., 2010, Toxicological Impact of Detergent Effluent on Juvenile of African Catfish, *Agr. Bio. J. N. Am.*, 1 (3), 330-342.
- [3] Bizukojc, E. L., Miksch, K., Jutsz, A. M., and Kalka, J., 2005, Acute Toxicology and Genotoxicity of Five Selected Anionic Nonionic Surfactants, *Chemosphere*, 58, 1249-1253.
- [4] Moreno-Caselles, Joaquin, Prats, Daniel, Moral, D., Perez-Murcia, M. D., Perez-Espinosa, A., Paredes, C., and Leon, V., 2006, Effects of Linear Alkylbenzene Sulfonates (LASs) in Sewage Sludge-Amended Soils on Nutrient Contents of Broccoli Plants, Poster Paper, *Communications in Soil Science and Plant Analysis*, 37: 2605-2614, ISSN 0010-36.
- [5] Aboulhassan, M. A., Souabi, S., Yaacoubi, A. and Boudou, M., 2006, Removal of Surfactant from Industrial Wastewater by Coagulation-Flocculation Process, *J. Environ. Sci. Tech.*, 3 (4), 327-332.
- [6] Conrad, A., Cadoret, A., Corteel, P., Leroy, P., and Block J. C., 2006, Adsorption/Desorption of Linear Alkylbenzenesulfonate (LAS) and Azoprotein by /from Activated Sludge Flocs, *J. Chemosphere*, 62, 53-60.
- [7] Yang, W. B., Li, A., Fan, J., Yang, L., and Zhang, Q., 2006, Adsorption of Branched Alkylbenzene Sulfonate on Styrene and Acrylic Ester resins, *J. Chemosphere*, 64, 984-990.
- [8] Taffarel, S. R., and Rubio, J., 2010, Adsorption of Sodium Dodecyl Benzene Sulfonate from Aqueous Solution Using a Modified Natural Zeolite with CTAB, *J. Min. Eng.*, 23, 771-779.
- [9] Peressutti, S. R., Olivera, N. L., Babay, P. A., Costagliola, M., and Alvarez, H. M., 2008, Degradation of Linear Alkylbenzene Sulfonate by a Bacterial Consortium Isolated from the Aquatic Environment of Argentina, *Journal of Applied Microbiology*, 105 (2008) 276-484, ISSN 1364-5072.
- [10] Marretig-Bruns and Jelen, E., 2009, Anaerobic Biodegradation of Detergent Surfactant, *Materials*, 2, 181-206.
- [11] Manousaki, E., Psillakis, E., Kalogerakis, N., and Mantzavinos, D., 2004, Degradation of sodium Dodecylbenzene Sulfonate in water by Ultrasonic Irradiation, *J. Wat. Res.*, 38, 3751-3759.
- [12] Deghani, M. H., Najafpoor, A. A., and Azam, K., 2010, Using Sonochemical Reactor for Degradation of LAS from Effluent of Wastewater Treatment, *J. Desalination*, 250, 82-86.
- [13] Naldoni, E., Schiboula, A., Bianchi, C. L., and Bremmer, D. H., 2011, Mineralization of Surfactant Using Ultrasound and advanced Fenton Process, *Water, Air, Soil Pollut.*, 215, 487-495.
- [14] Diaz, J. D. M., Sanchez-Polo, M., Rivera-Utrilla, J., and Bautista-Toledo, M. L., 2009, Effectiveness of Different Oxidizing Agents for Removing Sodium Dodecyl Benzene Sulphonate in Aqueous System, *Water. Res.*, 43, 1621-1629.
- [15] Eng, Y., Sharma, V. K., and Ray, A. K., 2010, Photocatalytic Degradation of Nonionic Surfactant Brij 35 in Aqueous TiO₂ Suspensions, *J. Chemosphere*, 79, 205-209.

- [16] Sugiharto, E., Suratman, A., Natsir, T. A., and Wahyuni, E. T., 2014, Determination of Surfactant in the river from laundry waste water disposal and the removal by photocatalytic degradation with TiO_2 , *American Chemical Science Journal*, 4 (6), 715-725.
- [17] M. R. Hoffmann, S. T. Martin, W. Choi, and D. W. Bahnemann, 1995, "Environmental Application of Semiconductor Photocatalysis", *Chem. Rev.* vol. 95, 69-96.
- [18] Saquib, M., Tariq, M. A., Haque, M. M., and Muneer, M., 2008, Photocatalytic Degradation, Disperse Blue I Using UV/ TiO_2 / H_2O_2 Process, *J. Environ. Manage*, 88, 300-306.
- [19] Elmola, E. S. and Malay, C., 2010, Photocatalytic Degradation of Amoxicillin, Amphotericin, and Cloxacillin Antibiotics in Aqueous Solution Using UV/ TiO_2 and UV/ H_2O_2 / TiO_2 Photocatalysis, *J. Desalination*, 252, 46-52.
- [20] Sanchez, E., Taxt-Lamolle, S. F. M., Hole, E. O., Krivokapic, A., Sagstuen, E., and Haugen, H. J., 2013, TiO_2 Suspension Exposed to H_2O_2 in Ambient Light of Darkness: Degradation of Methylene Blue and EPR Evidence for Radical Oxygen Species, *Appl. Catal. B.*, 142-142, 662-667.
- [21] Kang, Y. W., and Hwang, K. Y., 2000, Effect of Reaction Conditions on The Oxidation Efficiency In The Fenton Process. *Water Res.*, 34, 10, 2786– 2790.
- [22] Kusic, H., Koprivanac, N., Bozic, A. L., and Selanec, I., 2009, Photo-assisted Fenton Type Process for The Deradation of Phenol: A Kinetic Study. *Journal of Hazardous Materials B.*, 136, 632-644.
- [23] Moraes, J. E. F., Quina, F. H., Nascimento, C. A. O., Silva, D. N., and Chiavone-Filho, O., 2004, Treatment of saline wastewater contaminated with hydrocarbons by the photo-Fenton process, *Environ. Sci. Technol.*, 38 (4), 1183-1187.
- [24] Kavitha, V. and Palanivelu, K., 2005, Destruction of Cresols by Fenton Oxidation Process, *Water Res*, 39, 3062-3072.
- [25] Masomboon, N., Chavalit, R., and Ming-chun, L., 2009, Chemical Oxidation of 2,6-Dimethylaniline in the Fenton Process, *Environ. Sci. Technol.*, 43, 8629-8634.
- [26] Chen, C. C., and Wu, R. J., 2009, Chemical Oxidation Degradation of Acridine Orange Dye in Aqueous Solution by Fenton's Reagent, *Journal of the Chinese Chemical Society*, 56, 1147-1155.
- [27] Mousavi, S. A. R., Mahvi, S., and Nasser, Sh. Ghafari, 2011, Effect of Fenton Process ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) on Removal of Linear Alkylbenzene Sulfonate Using Central Composite, *Iran. J. Environ. Health. Sci. Eng.*, Vol. 8, No. 2, pp. 129-138.
- [28] Nideesh, P. V., Gadhimathi, R., and Ramesh, S. T., 2013, Degradation of Dyes from Aqueous solution of Fenton Process: a Review, *Environ. Sci. Pollut. Res.*, 20, 2099-2132.
- [29] Bautista, P. Mohedano, M. A., Gillaranz, J. A., Casas, J. A., and Rodriguez, J. J., 2007, Application of Fenton Oxidation to Cosmetics Wastewater Treatment, *J. Hazard Mater*, 143, 128-134.
- [30] Lucas, M. S., and Peres, J. A., 2009, Removal COD from Olive Mill Wastewater by Fenton's Reagent: Kinetic Study. *J. Hazard Mater.*, 168, 1253-1259, ISSN 0304-3894.
- [31] Aris, A. and Sharraf, P. N., 2007, Evaluation of Photo-Fenton Degradation of Reactive Black 5 Using Resonance Surface Method, *Malays. J. Civ. Eng*, 19 (1), 26-41.
- [32] Xiu, M., Wan, Q., and Hao, Y., 2007, Removal of Carbon From Wastewater Pulp Effluent by Lab Scale Solar-Photo-Fenton Process. *J. Hazard Mater*, 148, 1003-1009.
- [33] Farias, J., Germa, H., Rossetti, E. D. A. and Orlando, M. A., 2007, Solar Degradation of Formic Acid: Temperature Effects on the Photo-Fenton Reaction, *Ind. Eng. Chem. Res.*, 46, 7580-7586.
- [34] Kajitvichyanukul, P., Lu, Ming-Chun, and Jamroensan, A., 2008, Formaldehyde Degradation in The Presence of Methanol by Photo-Fenton Process, *Journal of Environmental Management*, 86, 545-553.
- [35] Samet, Y., Hmani, E. and Abdelhedi, R., 2012, Fenton and Solar Photo-Fenton Processes for Removal of Chlorpyrifos Insecticide in Wastewater, *Water Res.*, 38, 4.
- [36] Ahmed, B., Limem, E., Wahab, A., and Nasr, B., 2011, Photo-Fenton Treatment of Actual Agro-industrial Wastewater, *Indian J. Eng. Chem. Res.*, 50, 6673-6680.
- [37] Hernandez, M. A., Marin, C. M., and Castaneda, H. T., 2012, Solar photo-Fenton Optimisation in Treating Carbofuran-Contaminated Water, *Ing. E. Investigation*, 32, 1, 71-76.
- [38] Kavitha, V., and Palanivelu, K., 2004, The Role of Ferrous Ion in Fenton and Photo-Fenton Processes for the Degradation of Phenol, *Chemosphere*, 55, 1235-1243.
- [39] Karale, R. S., Manu, B., and Shirari, S., 2013, Fenton and Photo-Fenton Oxidation Processes for Degradation of 3-Aminopyridine from Water, *Procedia APCBEE*, 9, 25-29.
- [40] Hu, Q., Zhang, C., Wang, Z., Chen, Y., Mao, K., Zhang, X., Xiong, Y., and Zhu, M., 2008, Photodegradation of Methyl tert-Butyl Ether (MTBE) by UV/ H_2O_2 and UV/ TiO_2 , *J. Hazard Mater*, 154, 795-803.
- [41] Tabrizi, G. B. and Mehrvar, M., 2006, Pilot-Plant Study for The Photochemical Treatment of Aqueous Linear Alkylbenzene sulfonate, *Sep. Purif. Technol.*, 49, 115-121.
- [42] Dincer, A. R., Karakaya, N., Gunes, E. and Gunes, Y., 2008, Removal of COD from oil recovery Industry Wastewater by Advanced Oxidation Processes (AOP) based on H_2O_2 , *J. Global Nest*, 10, 1, 31-38.