Photodegradation of Detergent Anionic Surfactant in Wastewater Using UV/TiO$_2$/H$_2$O$_2$ and UV/Fe$^{2+}$/H$_2$O$_2$ Processes

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

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

Email address: endtriw@yahoo.com (E. T. Wahyuni)


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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/TiO$_2$/H$_2$O$_2$ (photo-Fenton-like) and UV/Fe$^{2+}$/H$_2$O$_2$ (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/TiO$_2$/H$_2$O$_2$ and UV/Fe$^{2+}$/H$_2$O$_2$ processes. In both processes, it was observed the dependency of the surfactant photodegradation effectiveness on TiO$_2$ dose, Fe(II) and H$_2$O$_2$ 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/TiO$_2$/H$_2$O$_2$ and UV/Fe$^{2+}$/H$_2$O$_2$ processes were required. It also is clearly confirmed that UV/Fe$^{2+}$/H$_2$O$_2$ (photo-Fenton) process was more effective in the surfactant photodegradation than that of UV/TiO$_2$/H$_2$O$_2$ (photo-Fenton-like) process.

Keywords: Surfactant, Photodegradation, UV/TiO$_2$/H$_2$O$_2$, UV/Fe$^{2+}$/H$_2$O$_2$

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 plan 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 floc [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 TiO$_2$ 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 TiO$_2$ [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 TiO$_2$ mass that will provide more OH radicals. The large amount of TiO$_2$ 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 H$_2$O$_2$ in the degradation under TiO$_2$ photocatalysis and UV irradiation or UV/TiO$_2$/H$_2$O$_2$. 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/TiO$_2$/H$_2$O$_2$ has not been explored for decreasing detergent surfactant.

In addition to UV/TiO$_2$/H$_2$O$_2$ system, other system that can result in OH radicals is Fenton using Fe(II) ion and H$_2$O$_2$ as reagents [21], and photo-Fenton involving UV light, Fe(II), and H$_2$O$_2$ or UV/Fe(II)/H$_2$O$_2$ [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-chloroguacil [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-chloroguacil [39], and 3-aminopyridine [40]. Accordingly, in this present research, photo-Fenton (UV/Fe(II)/H$_2$O$_2$) process was chosen to be studied for degradation of detergent surfactant from laundry waste water, that was compared to UV/TiO$_2$/H$_2$O$_2$ process.

2. Experimental Method

2.1. Chemicals

Chemicals used were TiO$_2$ powder, H$_2$O$_2$, Fe(NH$_4$)$_2$(SO$_4$)$_2$, 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 funnel 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/TiO$_2$/H$_2$O$_2$ system was carried out by following procedure: The laundry wastewater as much as 100 ml was added with 40 mg of TiO$_2$ and 30 mM of H$_2$O$_2$ 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)/H$_2$O$_2$) 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 H$_2$O$_2$ 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 \( \text{UV/TiO}_2/\text{H}_2\text{O}_2 \)

3.1.1. Influence of \( \text{TiO}_2 \) Mass

The surfactant photodegradation by \( \text{UV/TiO}_2/\text{H}_2\text{O}_2 \) process with various \( \text{TiO}_2 \) mass is presented in Fig. 2. The figure shows that photodegradation degree of surfactant in the laundry wastewater improved drastically when the dose of \( \text{TiO}_2 \) photocatalyst was enlarged. But further increase of the mass does not influence the effectiveness of the surfactant photodegradation.

\[ \text{H}_2\text{O} + \text{light} \rightarrow \text{H}^+ + \text{OH}^- + e^- \]  
\[ \text{TiOH} + \text{light} \rightarrow \text{TiOH}^- (e^{-} + \text{h}^+) \rightarrow \text{TiOH}^- + e^- \]  
\[ \text{H}_2\text{O}_2 + \text{light} \rightarrow 2 \text{OH}^- \]  
\[ \text{OH}^- + \text{C}_{12}\text{H}_25\text{C}_6\text{H}_4\text{SO}_3^- \rightarrow \text{SO}_4^{2-} + \text{H}_2\text{O} + \text{simple organic compounds} \]

The larger mass of \( \text{TiO}_2 \) provided more \( \text{OH}^- \) radicals, that could induce more effective photodegradation.

With very large amount of \( \text{TiO}_2 \), the turbidity of the wastewater increased that screened the UV light penetration. The light inhibition must prevent the \( \text{OH}^- \) radicals formation [18], so that no more number of \( \text{OH}^- \) radicals for photodegradation were available.

3.1.2. The Influence of \( \text{H}_2\text{O}_2 \) Concentration

The role of \( \text{H}_2\text{O}_2 \) on \( \text{UV/TiO}_2/\text{H}_2\text{O}_2 \) system is as \( \text{OH}^- \) radicals supplying agent. The dependency of the surfactant photodegradation on the concentration of \( \text{H}_2\text{O}_2 \) is illustrated by Fig. 3. It is seen in the figure the sharp increase of the surfactant photodegradation as the increasing \( \text{H}_2\text{O}_2 \) concentration. The increase of \( \text{H}_2\text{O}_2 \) concentration could enhance the number of \( \text{OH}^- \) radicals, that promoted more effective photodegradation. The effectiveness of the surfactant photodegradation appears to drop as the further increasing \( \text{H}_2\text{O}_2 \) concentration. \( \text{H}_2\text{O}_2 \) in excessive could react with \( \text{OH}^- \) radicals that were present to form water and oxygen, following reactions (5) and (6) [41]:

\[ \text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \]  
\[ \text{HO}_2^- + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}_2 \]  

The dissociation of \( \text{H}_2\text{O}_2 \) led to a decrease in the number of \( \text{OH}^- \) 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 \( \text{H}_2\text{O}_2 \) to form peroxygen ion (\( \text{H}_3\text{O}_2^+ \)) following reaction (7) [39]. The peroxygen ion was less reactive to release \( \text{OH}^- \) radicals, and so the only lesser \( \text{OH}^- \) radicals could be resulted.

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow \text{H}_3\text{O}_2^+ \]  

In addition, at low pH, \( \text{TiO}_2 \) existed as \( \text{TiOH} \) that might be also protonated by the excessive hydrogen ions, written as reaction (8), that could reduce the \( \text{OH}^- \) radicals formation. These conditions made the photodegradation became considerably less effective.

\[ \text{TiOH} + \text{H}^+ \rightarrow \text{TiOH}_2^+ \]
Increasing pH up to 5, where the lesser number of hydrogen ions were available, could prevent protonation of H\textsubscript{2}O\textsubscript{2} and TiO\textsubscript{2} that does not reduce their amount. This has promoted the faster photodegradation.

When the pH was further increased, H\textsubscript{2}O\textsubscript{2} could be dissociated into water and oxygen [41], seen as reaction (9), that reduced the number of OH radical formed. In addition, TiO\textsubscript{2} became TiO\textsuperscript{−} following reaction (10) that was more difficult to form OH radicals. These explained the decrease of the photodegradation.

\[ 2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \]  
\[ \text{TiOH} + \text{OH}^- \rightarrow \text{TiO}^- + \text{H}_2\text{O} \]  

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 TiO\textsubscript{2} and H\textsubscript{2}O\textsubscript{2}, to form more OH radicals, and between the radicals with the surfactant.

![Fig. 5. The effect of the process time.](image)

In the process running in 24h, the surface of TiO\textsubscript{2} and H\textsubscript{2}O\textsubscript{2} 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)/H\textsubscript{2}O\textsubscript{2}

3.2.1. The Influence of Fe(II) Concentration

In the photo-Fenton (UV/Fe(II)/H\textsubscript{2}O\textsubscript{2}) system, there are reactions between H\textsubscript{2}O\textsubscript{2} with light and Fe(II) with H\textsubscript{2}O\textsubscript{2} to form OH radicals, following reactions (11) and (12) [42]. The radical was used for surfactant photodegradation.

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH} \]  
\[ \text{H}_2\text{O}_2 + \text{light} \rightarrow 2 \text{OH} \]

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 H\textsubscript{2}O\textsubscript{2} have already reacted with Fe(II). Accordingly, although Fe(II) was present in excess, no more reaction between Fe(II) and H\textsubscript{2}O\textsubscript{2} happened.

![Fig. 6. The influence of Fe(II) concentration.](image)

3.2.2. The Influence of H\textsubscript{2}O\textsubscript{2} Concentration

As presented previously that H\textsubscript{2}O\textsubscript{2}, during UV light exposure, will form OH radicals functioned for surfactant photodegradation. It is interesting therefore to study the effect of H\textsubscript{2}O\textsubscript{2} concentration on the photodegradation. Fig. 7 illustrated that increasing H\textsubscript{2}O\textsubscript{2} 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 H\textsubscript{2}O\textsubscript{2} was further enlarged. The reason was same as explained previously.

![Fig. 7. The influence of H\textsubscript{2}O\textsubscript{2} concentration.](image)
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_{2}O_{2} to form OH radicals with large amount. But because H_{2}O_{2} was protonized by excessive hydrogen ion to form peroxy (H_{2}O_{2}{^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.

Further increase of the pH led to the less effective surfactant photodegradation. At higher pH, as presented previously, photodegradation was observed. Increasing pH or decreasing amount. But because H_{2}O_{2} was protonized by excessive hydrogen ion to form peroxy (H_{2}O_{2}{^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.

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_{2}O_{2}. As a result a lot of H_{2}O_{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_{2}O_{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 Fe(OH)_{2} and Fe(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.

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_{2}O_{2} and UV/Fe(II)/H_{2}O_{2}

From the study of factors influencing the effectiveness of the surfactant photodegradation in both UV/TiO_{2}/H_{2}O_{2} and UV/Fe(II)/H_{2}O_{2} processes, the optimal conditions were obtained. The conditions were summarized in table 1.

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

\[
\text{H}_{2}\text{O}_{2} + \text{light} \rightarrow \text{OH}^{-} + \text{H}^{+} + \text{e} \quad (13)
\]

\[
\text{Fe}^{2+} + \text{H}_{2}\text{O}_{2} \rightarrow \text{Fe}^{3+} + \text{OH}^{-} + \text{OH}^{-} \quad (14)
\]

\[
\text{Fe}^{3+} + \text{e} \rightarrow \text{Fe}^{2+} \quad (15)
\]

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_{2}O_{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/TiO$_2$/H$_2$O$_2$ and UV/Fe(II)/H$_2$O$_2$ 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/TiO$_2$/H$_2$O$_2$ and UV/Fe(II)/H$_2$O$_2$ processes.](image)

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/TiO$_2$/H$_2$O$_2$ (photo-Fenton like) and UV/Fe(II)/H$_2$O$_2$ (photo-Fenton) processes could significantly decrease the surfactant concentration. The effectiveness of the surfactant photodegradation was found to be controlled by TiO$_2$ dose, pH, H$_2$O$_2$ concentration, and the process time for UV/TiO$_2$/H$_2$O$_2$ system, and that of by Fe(II) and H$_2$O$_2$ concentrations, pH and the UV exposure time for UV/Fe(II)/H$_2$O$_2$ (photo-Fenton) process. The optimum conditions for both processes could be also formulated. It is also clearly confirmed that UV/Fe(II)/H$_2$O$_2$ (photo-Fenton) showed stronger activity in the decreasing surfactant concentration than UV/TiO$_2$/H$_2$O$_2$ 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/TiO$_2$/H$_2$O$_2$ and UV/Fe(II)/H$_2$O$_2$ processes.

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