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Photo-Processes as Effective and Low-Cost Methods for Laundry Wastewater Treatment

Endang Tri Wahyuni

Abstract

In this chapter, surfactants as cleansing agent in detergent used in laundry, are described. The negative effects of the laundry wastewater on the environment and human health are highlighted. Several methods examined for laundry wastewater treatment are also illustrated. Among the treatment methods, photo-process in the presence of TiO_2 photocatalyst and Fenton reagents are described in more detail. Furthermore, the factors influencing the effectiveness of photo-process including reagent dose, reaction time, and pH are discussed. Additionally, modifications of the photo-process to improve its performance that is associated with effectiveness and operational cost are also demonstrated. The photo-methods discussed in this chapter offered low-cost due to simplicity and effective technique for treating the laundry wastewater.

Keywords: laundry, wastewater, treatment, photo-process, TiO_2 , photo-Fenton

1. Introduction

Laundry activity is intensively and routinely conducted in domestic activities including homes, hotels, hospitals, as well as public laundry services. In the laundry activity, large amount of detergent as cleansing agent must be used. Further, in general, washing machines can typically produce from 50 to 200 L of effluent per wash [1], implying that laundry activity always disposes large volume of wastewater. The active component with high content in the detergent is anionic surfactant prior to linear alkyl benzene sulfonate (LAS) [1–21]. It is reasonable therefore that high concentration of LAS is contained in the laundry wastewater, as reported [2], that was around 200 mg/L from the first rinse. The presence of LAS in water can cause damage to the ecosystem thereby affecting the environment, and consumption of LAS above 0.5 mg/L can be harmful to health [1]. Considering the negative effects, treatment of LAS from laundry wastewater before reaching the environment is urgent.

Various methods have been dedicated to remove LAS surfactant in water and wastewater, such as adsorption [3–4], coagulation [2, 5–6], and filtration [7–8]. By adsorption, coagulation, and filtration techniques, the surfactant of LAS is only replaced from water to the adsorbents, coagulants and membranes with the same toxicity [1], then they are collected as hazardous solid wastes. Further the hazardous solid wastes must create new environmental problems.

In recent years, various destructive methods including biological, chemical and combination of physical–chemical techniques have been employed for removal of the LAS surfactants from waters. The destructive techniques that have been developed for removal LAS are biodegradation [9–10], ozonation [1], photocatalytic degradation over TiO_2 [11–16], and Fenton and photo-Fenton [16–21]. Biodegradation of LAS in water was found to be less effective for high concentration of LAS, since the LAS is harmful for the bacteria [1]. Ozonation method for treatment of wastewater is believed to be uneconomical due to the use of the high dose of the ozone and pressurized and complicated equipment [22]. On the other hand, photo-degradation of LAS over TiO_2 photocatalyst under UV irradiation and by photo-Fenton process are intensively used as the effective methods to destroy the hazard LAS into smaller and safer molecules [11]. In addition, the methods only need light, and low cost and harmless chemicals, allowing them to be applied in large scale.

2. Surfactant in laundry waste water

Laundry activity always uses detergent that contains surfactant as the cleansing agent. The word surfactant is short for “Surface Active Agent.” In general surfactants are constructed by hydrophobic long alkyl chain as tail, and a hydrophilic group as a head, as illustrated by **Figure 1**. In general, they are chemicals that, when dissolved in water or organic solvent, orient themselves at the interface (boundary) between the liquid and a solid (i.e. the dirt or grease that want to be removed), and modify the properties of the interface [23]. The cleansing dirt or grease occurs when the hydrophobic long chain is attracted to dirt, while the hydrophilic part of the molecule is attracted to water. When dirt or grease is present, the surfactants surround it then it is dislodged from the boundary. The dirt/grease removed from the fabric will come into water [23].

The hydrophobic long alkyls in the surfactants can refer as branched and linear chains. One of the branched long alkyl used in the detergent surfactant was dodecyl having molecular formula $\text{C}_{18}\text{H}_{30}$ or $(\text{CH}_3)_3(\text{CH}_2)_{10}\text{CH}_2$ [23]. The branched alkyl offered superior tolerance to hard water and better foaming. Unfortunately,

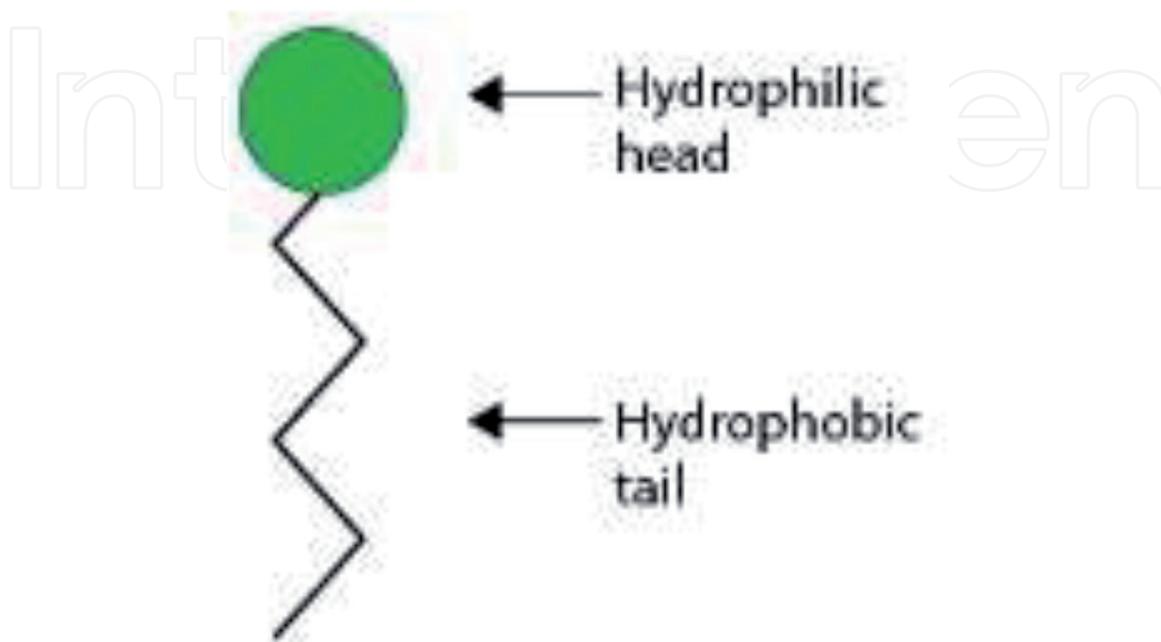


Figure 1.
The schema of surfactant structure [23].

highly branched tail made it difficult to biodegrade, that was widely blamed for the persistent foam in sewage treatment plants, streams, and rivers, and created environmental problems. Hence, the branched surfactants have been replaced by linear alkyl long chain, that is environmentally friendly and easily biodegrades to simpler substances [23]. For the linear alkyl long chain usually used are C10–15, such as hexadecyl ($C_{16}H_{33}$).

The hydrophilic part of the surfactant is found as non-ionic, cationic, and anionic forms as shown by **Figure 2**. These different groups refer to the names of the surfactants as non-ionic, cationic, and anionic surfactants. Structurally, non-ionic surfactants combine uncharged hydrophilic and hydrophobic groups that make them effective in wetting and spreading and as emulsifiers and foaming agents [23]. One of the major types of nonionic surfactants includes alkyl phenol ethoxylate as seen as **Figure 2a** [23]. Nonionic surfactants represent a major component material for applications ranging from personal care to a wide range of industrial uses [23]. Concurrently, such surfactants have minimal skin and eye irritation effects and exhibit a wide range of critical secondary performance properties [23]. Cationic surfactants are positively charged in the hydrophilic part, as an example is hexadecyl trimethyl ammonium bromide or cetyl trimethyl ammonium bromide (CTAB) as seen in **Figure 2c** [23]. The cationic surfactants are much less used in laundry detergents, due to their tendency to rapidly adsorb to – and not desorb from – the fabric having negatively charged surfaces under normal conditions [23]. The surfactant is bounded strongly by the fabric, inhibiting in the removal of the dirt from the fabric [23].

One of the major groups of anionic surfactants are linear alkyl benzene sulfonates (LAS), that are characterized by an anion hydrophilic of sulfonate [1–21]. The commercially produced LAS comprises alkyl chains of 10–14 carbon atoms, such as dodecyl benzene sulfonate (DBS) as seen in **Figure 3** [11–12]. LAS type surfactants pose a lot of usage because of its high cleaning power and efficiency [1–21]. The superior property originates from the fact that the anionic sulfonate group is repulsed to attach strongly with fabric of cloths, that results in the maximal cleansing the dirt [12].

LAS surfactants are the most commonly used detergents, that is more than 1.8×10^6 tons/year) in the past 40 years [12]. In terms of quantity, LAS is the most prominent group of anionic surfactants which is mainly used in heavy-duty laundry powders, light-duty liquid dish detergents, heavy-duty laundry liquids, and specialty cleansers [12]. Consequently, a significant amount of LAS exists in municipal

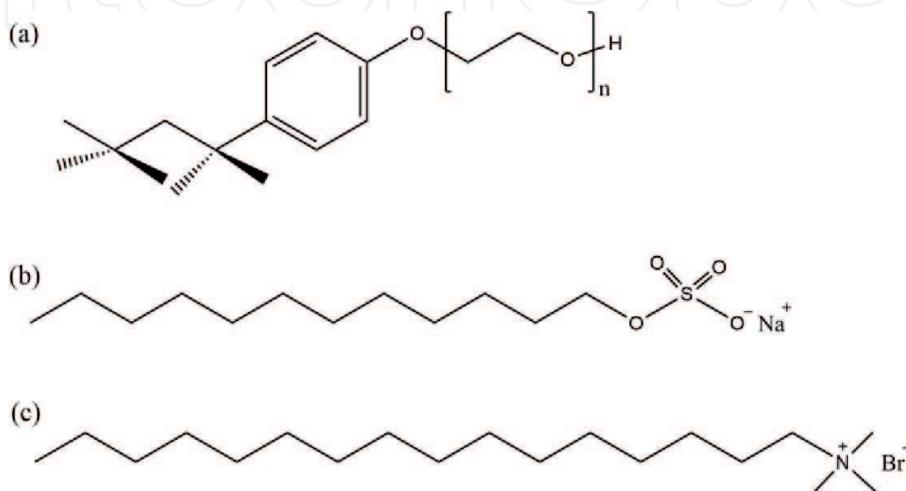


Figure 2.
The structures of (a) non-ionic, (b) anionic and (c) cationic surfactants [23].

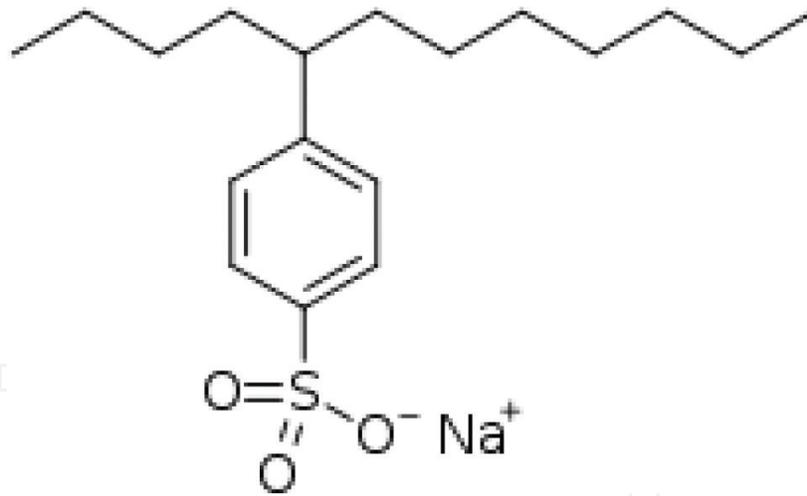


Figure 3.
The structure of LAS type [1].

disposed from homes, hotels, hospitals, and public laundry services, and industrial wastewater such as textile, leather, food, paint, cosmetics, polymer, oil recovery, mining and paper industries [12].

There was evident that less effective biodegradation of LAS in the water environment can occur [1]. Accordingly, LAS concentration of 3.5 mg/L has been measured in untreated sewage [12]. The values for concentrations of LAS in domestic effluents ranged from 3 to 21 mg/L [1] was also reported. From the laundry public services, 137 to 200 mg/L of the concentration of anionic surfactant in sewage was detected by other researchers, [2, 16].

Determination of the concentration of LAS in the solution or wastewater can be conducted by using visible spectrophotometry method. It is important hence to describe the analysis method. The method is based on the reaction between LAS with methylene blue to form a pair of methylene blue- linear alkyl sulfonate (MB-LAS), as shown by **Figure 4**, to form blue solution. The MB-LAS is insoluble in water, that has to be extracted into organic solvent such as chloroform. Then the MB-LAS as blue chloroform solution is measured by using spectrophotometer instrument at 650 nm of the wavelength, to obtain its absorbance [2, 12].

To calculate the LAS concentration in the solution or in the wastewater, the absorbance is plotted in the respective standard curve. The standard curve of LAS is displayed in **Figure 5**, showing that the straight linear line are obtained at 2–10 mg/L of the standard solution concentrations [14].

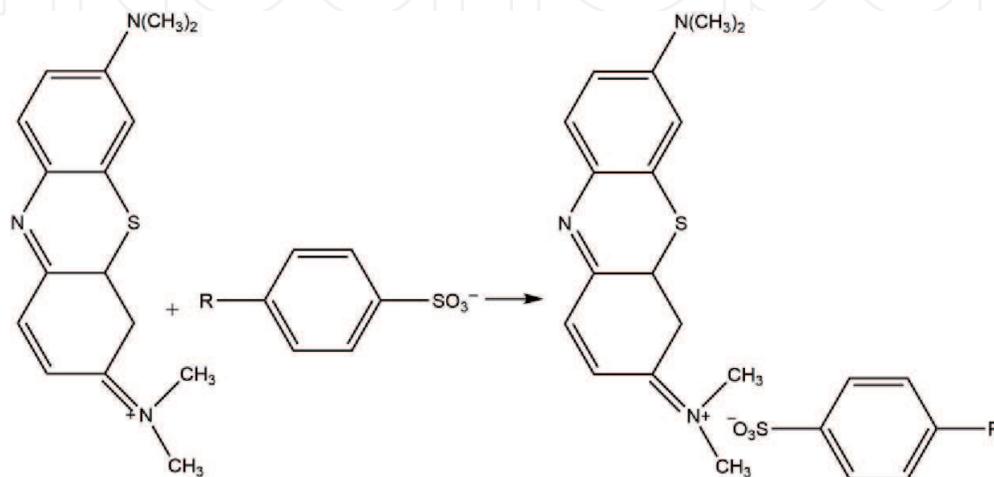


Figure 4.
The formation of MB-LAS pair giving blue color in chloroform solution [12].

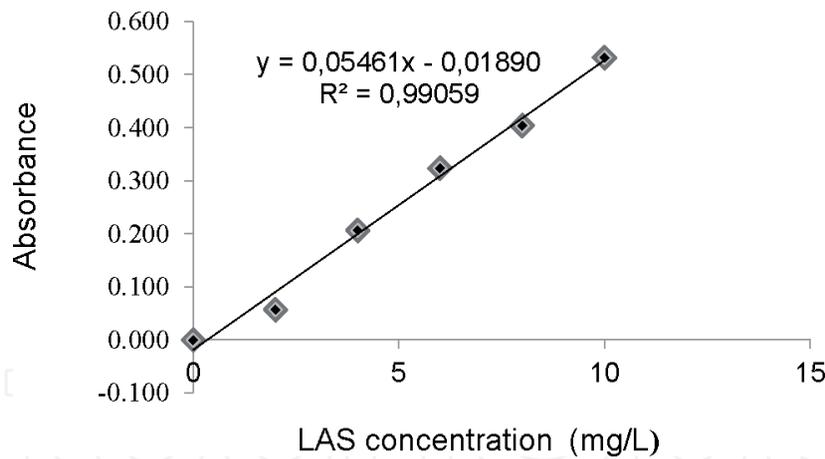


Figure 5.
The standard curve of LAS used for concentration determination [14].

LAS is reported to be toxic for aquatic organisms in higher than 0.1 mg/L [11]. Moreover, it can be accumulated in fish and consequently spread in the whole ecosystem. As a result it alters the natural balance of water which changes water into a harmful source for the aquatic organisms and human [11]. It also has some pathological, physiological, biological and other effects on aquatic animals [11]. For specific aquatic plants, LAS damages their chlorophyll protein and membrane leading to delay in growth and metabolism of cells [1]. With the same mechanism, LAS can also decrease the soil fertility [14]. Moreover, consumption of LAS above 0.5 mg/L can be harmful to people health [1].

Due to negative effects of anionic surfactant on organisms and environment, many environmental and public health regulatory authorities have considered restrictions. As an example, Indonesian Government regulates that anionic surfactants in laundry wastewater has to be lower than 1.0 mg/L, as MBAS (Methylene Blue-Active-Substance), allowed to be discharged to the environment [2].

3. The laundry wastewater treatment methods

Various methods have been developed to remove LAS surfactant in water and wastewater, such as adsorption [3–4], coagulation [2, 5–6], and filtration [7–8]. By adsorption, coagulation, and filtration techniques, the surfactant of LAS is only replaced from water to the adsorbents, coagulants and membranes with the same toxicity [1], then they are collected as hazardous solid wastes. Further the hazardous solid wastes must create new environmental problems.

The methods presented in this chapter are focused on photo-degradation process by photocatalysis over TiO_2 , and by photo-Fenton.

3.1 TiO_2 photocatalyst and the photocatalysis process

TiO_2 is a semiconductor with electronic structure that is characterized by valence band filled with electrons and empty conduction band, separated by gap as much as 3.0–3.2 eV [24], as illustrated by **Figure 6**. The gap is known as band gap energy (E_g), that is equal to the light with wavelength lower than 387 nm emerging the UV light. This fact allows TiO_2 to absorb the UV light, resulting in the excitation of electron in the valence band (e_{CB}^-) into conduction band while leaving a hole in the valence band (h_{VB}^+), as presented in Eq.1 [24–28]. The releasing electron and hole formation processes are demonstrated by **Figure 6**.

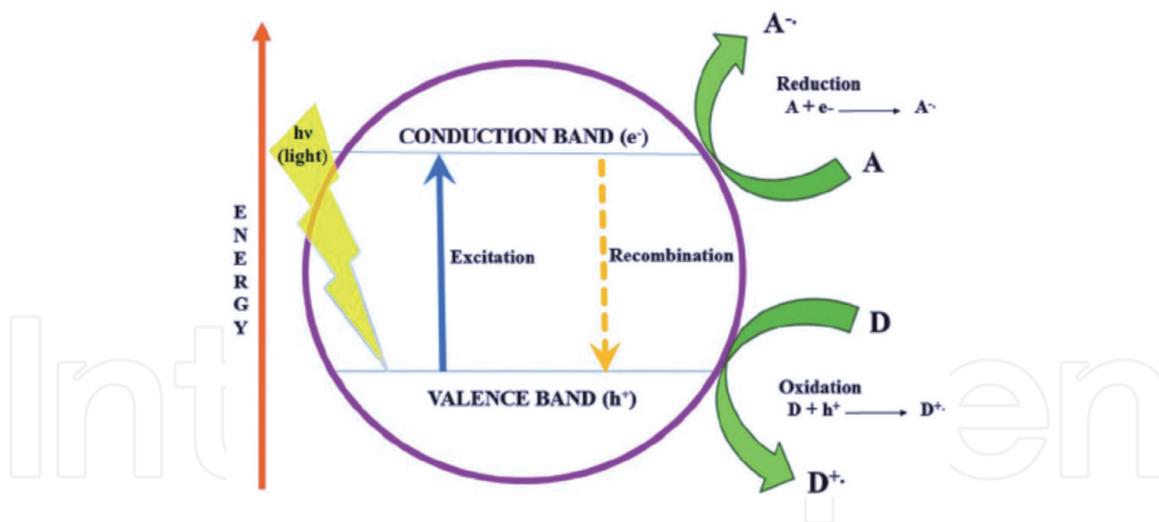
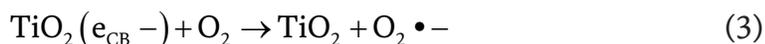
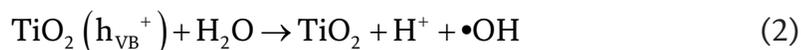
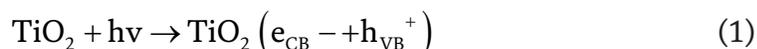


Figure 6.

The schema of semiconductor structure, and the electron excitation and hole formation [1].

In water medium, the holes formed can react with water and also with the surface of TiO_2 , to form OH radicals, while the electrons released can react with O_2 dissolved in water to form superoxide radical anions ($\text{O}_2^{\bullet-}$), and further the anionic radicals will react with hydrogen ions from water to form hydroperoxy radicals (HO_2^{\bullet}). The reactions of various radical formations are shown by Eq. 2 up to Eq. 4. Hydroxyl radical ($\bullet\text{OH}$) is a strong oxidizing agent with oxidation potential (E) as much 2.80 V, that is stronger than H_2O_2 with E as 1.23 V [24] and ozone with E of 2.07 V [24–25]. The two other radicals are also oxidizing agent, but the activity is weaker than the OH radicals strength [25].



The strong OH radical from TiO_2 has been proven to be able to degrade various organic pollutants such as amoxicillin [22, 27], dyes [24], and phenols [26] effectively. This process is called as photocatalysis degradation, that has also been intensively examined to remove LAS in water media as well as to treat laundry wastewater in the lab scale [11–16]. The reaction of the LAS degradation takes place by hydroxyl radicals ($\bullet\text{OH}$), superoxide radical anions ($\text{O}_2^{\bullet-}$), and hydroperoxy radicals (HO_2^{\bullet}). Under the photocatalysis degradation, the long chain hydrocarbons of LAS are primarily degraded into smaller organic compound then to form CO_2 and H_2O , and then the sulfonate group is oxidized into sulfate ions SO_4^{2-} [11]. The possible degradation pathway of alkyl-benzene sulfonate in photocatalytic oxidation as shown in **Figure 7** [11]. From the reaction, it is clear that the effective degradation of LAS yields smaller and harmless molecules.

The effectiveness of the degradation of LAS surfactant, whether in water and in the laundry wastewater under photocatalysis process is controlled by several factors, that are photocatalyst dose, irradiation time, pH of the water, and initial LAS concentration in the wastewater. The influence of these factors are describe below.

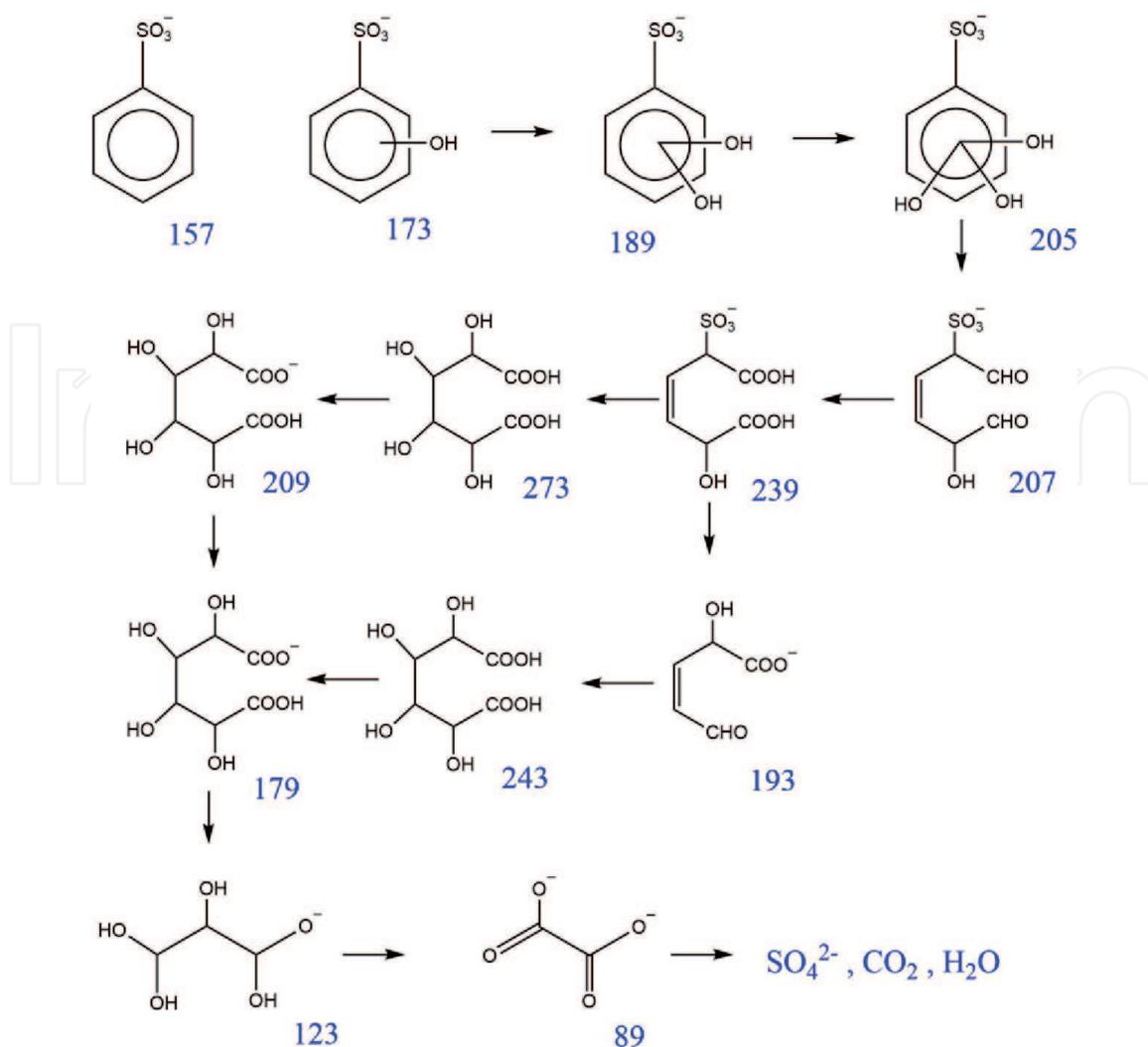


Figure 7.
 The reaction mechanism of LAS degradation by OH radicals [11].

3.1.1 The influence of photocatalyst mass

The mass or dose of TiO₂ photocatalyst deals with the active surface in providing OH radicals, where the number of OH radicals provided will be enriched as the photocatalyst mass is enlarged. The correlation of the photocatalyst dose with the LAS degradation has been reported by some studies [11–16], and as an example is displayed in Figure 8 [16].

It is observable that increasing the photocatalyst dose gives rise to the degradation, but for the further enlargement of the dose, the degradation effectiveness is found to decrease [2, 12–15]. Extending photocatalyst dose provides more OH radicals and so promotes more effective degradation. In contrast, higher dose than the optimal level, leads to an increase in the turbidity, causing a filter effect of the light entering. As a consequence, the interaction of the light with TiO₂ is inhibited, resulting in the less of OH radicals, decreasing the degradation. The optimum level of the photocatalyst mass obtained was varied from one to other authors [11–16], ranges from 50 mg/L to 750 mg/L depending on the initial LAS concentration and the reaction time.

3.1.2 The influence of the irradiation time under UV light

For the industrial removal process of LAS, reaction time is a key factor. The irradiation time is associated to the time of contact between light with TiO₂ and

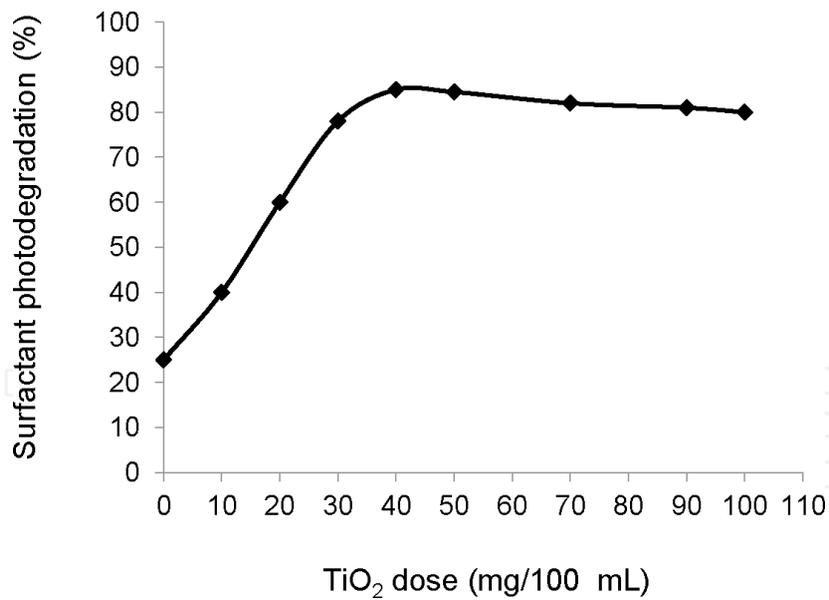


Figure 8.
The influence of the photocatalyst mass on the degradation of LAS in the wastewater [16].

between OH radicals with LAS molecules. Some studies [2, 11, 13, 15–16] have observed the effect of the UV irradiation time on the LAS degradation and they have similar trend, as seen in **Figure 9** [16]. The improvement of the LAS degradation appears with the expanding irradiation time but longer than the optimum time, the degradation effectiveness is independence on the time. In the beginning of the reaction, effective contact between light and TiO₂ and between OH radical with LAS proceed effectively. Prolong the irradiation time allows more effective contact and further results in higher effectiveness of the degradation up to reach the saturated condition. The optimum time reported were varied, one study found 60 min [11], while others reported of 50 min [12] and 100 min [15]. Very long irradiation optimum time was also possible, that was 24 h, due to high LAS initial concentration and photoreactor construction [2, 16].

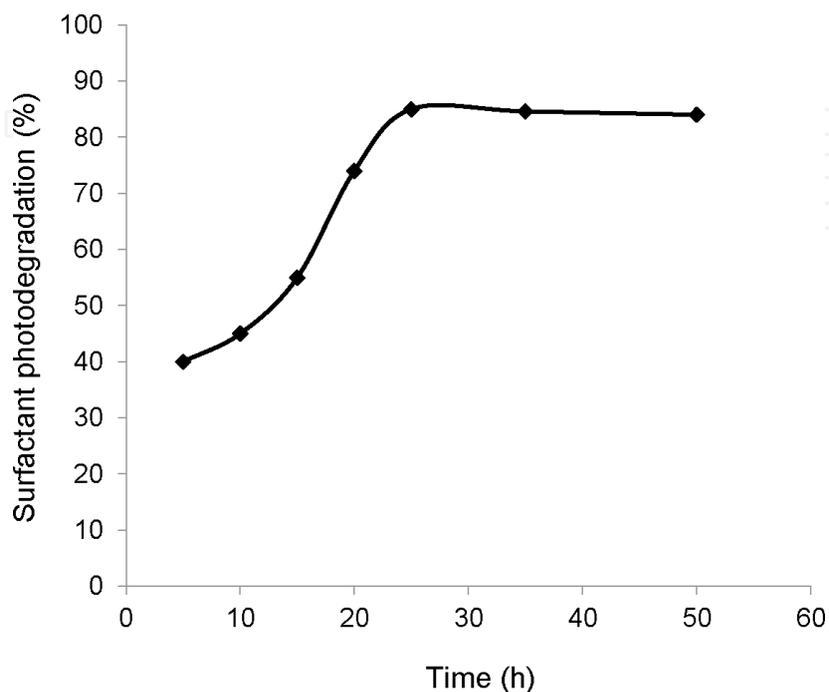


Figure 9.
The influence of the irradiation time on the degradation of LAS in the laundry wastewater [16].

3.1.3 The influence of the solution pH

The influence of the pH on the LAS degradation is one of the important factor, since pH determines the species of TiO_2 surface as well as LAS structure. **Figure 10** assigns [16] a trend of the degradation as function of the solution pH. It is observable an increase of the LAS degradation as the pH elevation up to 7, but further increase of pH causes a decline in the degradation. The trend can be explained based on the speciation of TiO_2 and LAS due the pH alteration.

At low pH, the surface of TiO_2 is protonated to form TiOH_2^+ that is difficult to provide OH radicals. With respect to LAS, at low pH, the LAS structure is also protonated that changes from negative to neutral surface. This condition can prevent the LAS to be adsorbed on the TiO_2 surface. Consequently, only little amount of LAS can interact with OH radicals, and further low degradation can occur. Increasing pH up to 7, most TiO_2 is found in neutral charge as TiOH [11, 13, 15]. It is important to takes a note that the zero point charge of TiO_2 is at pH 6.5 [11], referring uncharged TiO_2 surface, that can provide OH radicals maximally. At the same pH, LAS structure may form as anionic species, that allow them to be adsorbed on TiO_2 surface effectively. This high LAS adsorption can promote more effective LAS degradation.

At higher pH than the zero point charge, that is higher than 7, both TiO_2 and LAS are existed as negative species, that creates electrostatic repulsion. Hence, the LAS adsorption on the TiO_2 surface determents and further declines the LAS degradation. It is clear that pH strongly influences on the adsorption of the LAS on the TiO_2 surface, that effects the degradation effectiveness. The interactions at low and high pH are described as Eq. (5) and (6) [11, 13, 15].



From the lab study for LAS in the artificial wastewater [11–15], it is demonstrated that the effective degradation is reached at low pH, that was 4 [11], while other study for real laundry wastewater obtained the most effective degradation at pH 5 [16]. However, in the application for real laundry wastewater having pH 5–6, adjusting pH is not required.

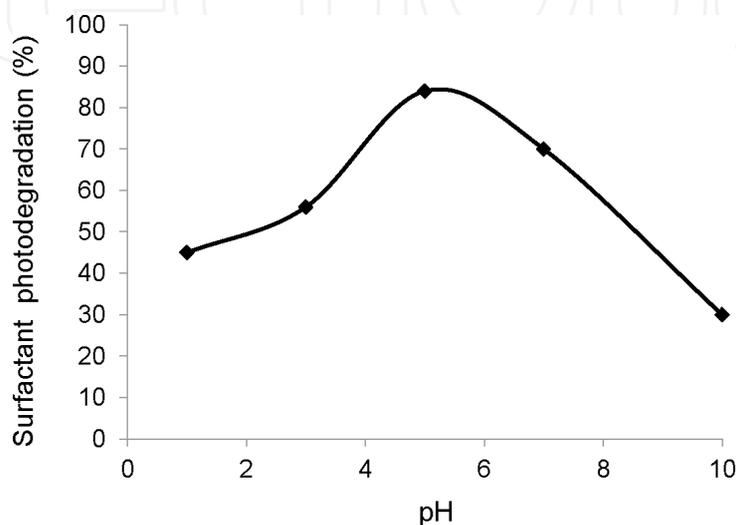


Figure 10.
Influence of pH on the degradation of LAS in the laundry wastewater [16].

3.1.4 The influence of the initial LAS concentration and the kinetic

The influence of the initial concentration of LAS in the real laundry wastewater is investigated by diluting the wastewater into the various desired concentrations. It was reported [11, 13] that increasing the initial LAS concentration leads to a decrease in the degradation. It can be explained that when the initial concentration of LAS is increased, more LAS adsorbed on the TiO_2 surface inhibiting the formation of OH radicals. Therefore less OH radicals are available, that decreases the LAS degradation [11, 13].

A kinetic study of the LAS photodegradation is desirable as it describes information about the rate of the degradation, which is important for efficiency of the process. The rate of a reaction is represented by rate constant (k), that depends on the concentrations. The relation between k and the concentration depends on the order of the reaction. The formulas of the first and second orders are given as Eq. 7 and Eq. 8, respectively. C_t represent the substrate concentration left in the media after t time of the reaction. C_o is the initial substrate concentration.

$$\ln C_t = -kt + \ln C_o \quad (7)$$

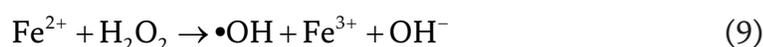
$$\frac{1}{C_t} = kt + \frac{1}{C_o} \quad (8)$$

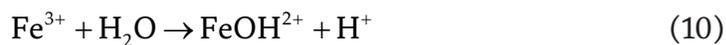
For determination of the reaction order, a curve is constructed generally by plotting time versus concentration. When a curve of $\ln C_t$ versus time gives a straight line, it is confirmed that the reaction agrees with first order reaction. Further, in order to confirm the second order reaction, a curve of $1/C_t$ versus time should be created, that results in the straight line.

In the LAS photodegradation by OH radicals, the rate of the LAS degradation reaction is determined by concentrations of LAS and OH radicals. When the reaction depends on both the concentrations of LAS and OH radicals, the LAS degradation should follow the second order model. The second order has been reported [11] with k value as much as 0.0031 L/mg. min. When the degradation is only controlled by the LAS concentration, the first order reaction must be followed, as obtained by Ghanbarian et al. [13], with k as much 0.020 1/min. The other possible condition is found as follow [15]. The reaction is dictated by both LAS and OH radical concentrations, but because the OH radicals are in the excessive amount that are assumed to be constant during the reaction. Accordingly the reaction rate is only influenced by the LAS concentration. Such condition allows the reaction rate to agree with the pseudo first-order. From the curve k as much 0.01–0.014 1/min is obtained [15].

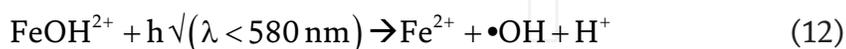
3.2 Photo-Fenton process

Fenton is a process by using ferrous ion (Fe^{2+}) and hydrogen peroxide (H_2O_2), called as Fenton's reagent. In this process, hydrogen peroxide is decomposed catalytically by ferrous ions at acidic pH value, yielding hydroxyl radicals ($\bullet\text{OH}$) and hydroxide anionic (OH^-), while ferrous ions are transformed to ferric ions. In general the accepted mechanism of Fenton reaction to form hydroxyl radicals is presented as Eq.(9) and Eq. (10) [16–21, 29–34]:





Further, photo-Fenton is a process involving a combination of Fenton reagents (H_2O_2 and Fe^{2+}) with UV radiation ($\lambda < 310 \text{ nm}$) that gives rise to extra OH radicals [18–19, 21, 30–31]. The major reactions in the photo-Fenton process for the formation of $\bullet\text{OH}$ radical include Fenton reaction, photolysis of H_2O_2 and photoreduction of Fe^{3+} , as shown in Eq. (11) and (12) [30–31].



The addition of UV or artificial light to Fenton's process is detected to accelerate LAS degradation as it influences the direct formation of $\bullet\text{OH}$ radicals [18–19]. Consequently, the organic degradation rate of photo-Fenton is accelerated compared to Fenton process. The improvement is due to the continuous reduction of ferric ions (Fe^{3+}) to ferrous ions (Fe^{2+}) under illumination, and then the Fe^{2+} reacts back with H_2O_2 to result in Fe^{3+} and OH radicals. The Fenton reaction can be terminated when H_2O_2 is exhausted. The OH radicals from Fenton and photo-Fenton processes, as produced from photocatalysis of TiO_2 , also own strong ability as an oxidizing agent, that can destroy various organic pollutants in acid condition [29–31].

The primary benefits of Fenton type process are their ability to convert a broad range of pollutants to harmless or biodegradable products and the fact that their relatively cheap reagents are safe to handle and are environmentally acceptable. Fenton process because of high oxidation power, rapid oxidation kinetics, being relatively cheap with easy operation and maintenance is used for treating various industrial wastewaters, including phenol [29], dyes [30], and various organic pollutant in the wastewater [31].

Considering the reagent involved in the Fenton and photo-Fenton processes, the effectiveness of LAS degradation is controlled by H_2O_2 and Fe^{2+} (Fenton's reagent) concentrations. In addition, reaction time, solution pH, and initial concentration of the substrate also contribute in the degradation effectiveness. Following are discussion of the effect of the factors on the LAS photodegradation by Fenton and photo-Fenton processes.

3.2.1 Effect of H_2O_2 concentration

The concentration of H_2O_2 is a critical variable in the degradation through Fenton and photo-Fenton processes. Many researchers have observed the influence of H_2O_2 concentration on the LAS degradation by Fenton and photo-Fenton methods. One example data is taken and exhibited in **Figure 11** [16]. It is seen that the low concentration of H_2O_2 did not generate enough $\bullet\text{OH}$ in solution, giving less effective degradation. Increasing H_2O_2 concentration improved the LAS degradation due to more $\bullet\text{OH}$ available. Addition of H_2O_2 above the optimum level lead to a decrease in the LAS degradation, that is caused by the depletion of the $\bullet\text{OH}$ amount due to free radical scavenging by the excess H_2O_2 to produce hydroperoxy radicals ($\bullet\text{O}_2\text{H}$). Then the hydroperoxy radical will further react with OH radical to form water and O_2 [17–20]. The reactions are exhibited by Eq. (13) and Eq. (14) below:

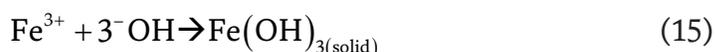


It is obvious that there is an optimum H_2O_2 concentration to achieve the maximum percentage of LAS removal, although the values of the concentration range varies for different conditions. In a study the optimum photo-Fenton condition was mediated by a $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$ ratio = 40 [16]. The effect of mode of reagent addition was also studied giving ratio of 10 [17]. Similar results were obtained in other studies, that were 1.4 [18], 7.6 [20], and 11 [21].

3.2.2 Effect of Fe^{2+} concentration

The amount of ferrous ions is one of the primary parameters that influences the Fenton and photo-Fenton processes. In a study [16], it was observed that the extent of degradation increases with increasing initial Fe^{2+} concentration, promoted by more OH radicals, as presented by **Figure 12** [16].

Contrary, the excessive Fe^{2+} ion produced larger amount of Fe^{3+} ions (reaction in Eq. 7) that further allowed them to react with hydroxide ions to form $\text{Fe}(\text{OH})_3$ precipitate, as also seen in Eq. (13) [17–21]. The precipitate formation created turbid solution that could inhibit the light entering into the solution. This situation depleted the number of OH radical formed, that further declined the degradation. This finding was in a good agreement with the other observations elsewhere [17–20]. However, the optimal values of Fe^{2+} concentration was varied among the reports, that were 5 mg/L [16], 56 mg/L [17], 40 mg/L [18], 130 mg/L [20], and 120 mg/L [21].



3.2.3 Effect of initial pH

The solution pH plays an important role in the efficiency of the photo-Fenton reaction, since it greatly influences the speciation of Fe, H_2O_2 and LAS. The relationship between pH alteration and the effectiveness of LAS degradation as

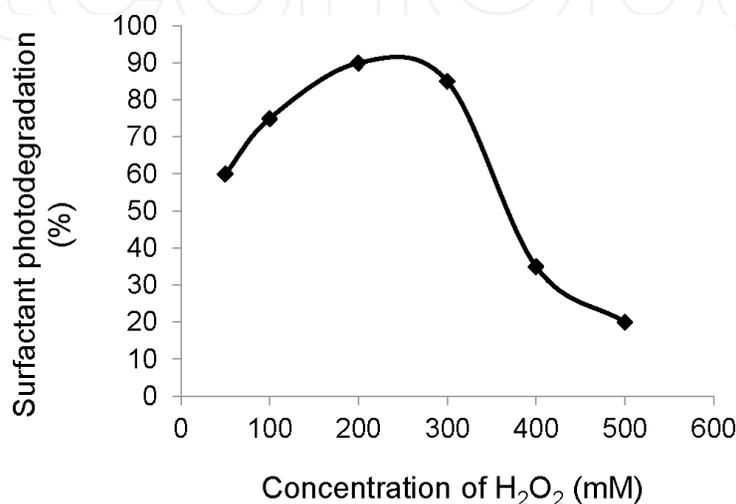


Figure 11. Effect of H_2O_2 concentration on the LAS degradation effectiveness through photo-Fenton process [16].

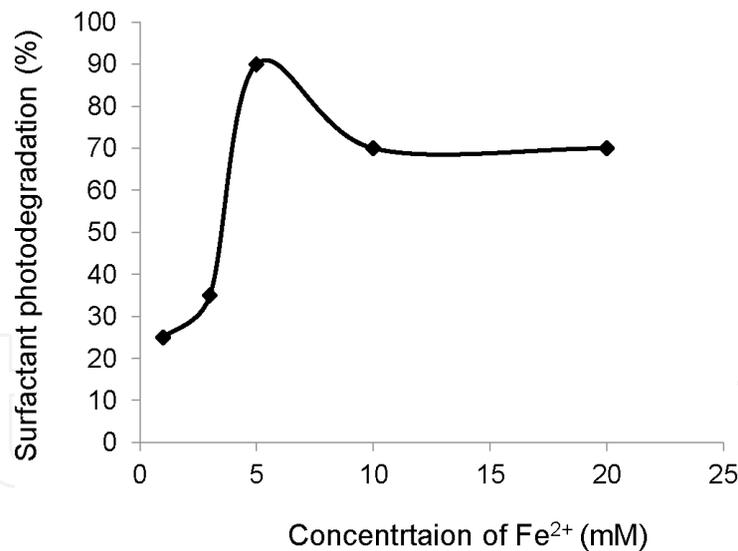


Figure 12.
Effect of Fe²⁺ concentration on the LAS degradation effectiveness [16].

reported by a study [16], is displayed as **Figure 13**. It can be observed a trend, that the LAS degradation is less efficient at very low pH, and the efficiency of the degradation improves considerably when the pH is increased up to 3. The higher pH than 3 causes a sharp decrease in the degradation.

At very low level of pH, hydrogen ions (H⁺) were present in large amount, that could protonate H₂O₂ to form protonated hydrogen peroxide or H₃O₂⁺ [17–20], as shown by Eq. (16).



The protonated hydrogen peroxide can inhibit the hydroxyl radical generation, resulting in small number of OH radicals, that further led to the lower photodegradation. An other reason proposed is that Fe²⁺, found in abundant, may form a stable complex with H₂O₂, which neutralized the Fe²⁺ catalyst [16]. The neutral catalyst

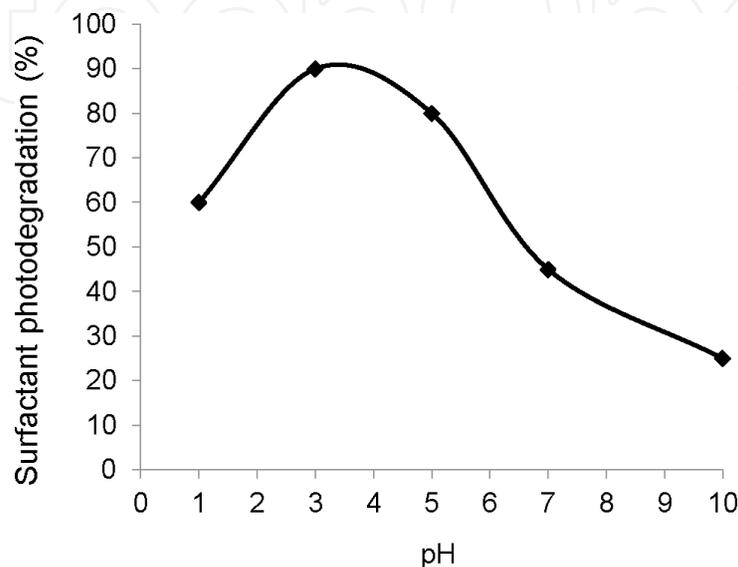


Figure 13.
Effect of pH on the LAS degradation effectiveness [16].

could only generate few amount of OH, that significantly declined of the photo-degradation. Further, increasing pH up to 3, provided smaller amount of H⁺ than at pH 1, so that the protonation of H₂O₂ could be prevented, and further enhances the number of the OH radicals formed. In addition, at pH 3, the complex of Fe²⁺ with H₂O₂ should be decomposed allowing Fe²⁺ to catalyze H₂O₂ maximally, and much OH radicals could be provided [17–21]. These explained clearly the highest photo-degradation occurred at pH 3.

When the pH was increased up to 7, the number of hydroxide ion (OH⁻) were enriched, allowing Fe³⁺ ions to deposit as Fe(OH)₃ (Eq. 15). As an effect, the sufficient Fe²⁺ catalyst did not remain in the solution. This caused lower decomposition of H₂O₂ and reduced the efficiency of the Fenton's process. Also, studies have shown that at higher pH, the oxidative potential of OH radical decreased and H₂O₂ was believed to be less stable [16, 18–19]. All the mentioned conditions obviously reduced the produced of OH radicals, and hence the amoxicillin degradation. The finding optimum pH (= 3) agreed with several other studies [17–21].

4. Modifications of photocatalysis and photo-Fenton processes

4.1 Photocatalysis method

Photocatalytic degradation using TiO₂ has recently received considerable attention for removal of the persistent organic pollutants (POPs) due to its cost-effective technology, non-toxicity, fast oxidation rate, and chemical stability [24–28]. However, the wide band gap of TiO₂, that is 3.2 eV for anatase, allows it only to be excited by photons with wavelengths shorter than 385 nm or UV region that limits its application under visible light [14, 22]. Therefore, an effort has been focused to overcome this deficiency, such as by doping TiO₂ structure with either non-metal, and metals elements.

Doping Ag metal on TiO₂ to increase the activity on the degradation of LAS in the laundry wastewater under visible light has been studied [14]. The results are seen as **Figure 14**. The increase of the TiO₂-Ag activity is promoted by the smaller E_g allowing TiO₂-Ag to be activated by visible light to provide OH radicals in adequate number. In contrast, TiO₂ with higher E_g (3.0–3.2 eV) is difficult to be excited by the visible light, that can only form fewer number of OH radicals. Moreover, the process with TiO₂-Ag under visible light takes place faster than TiO₂-Ag under UV

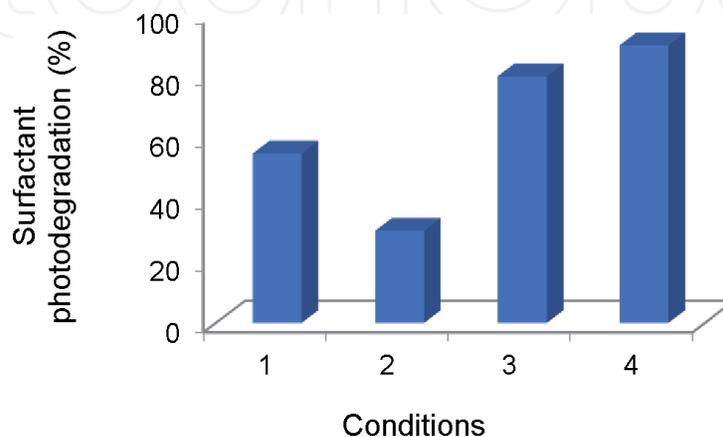


Figure 14.

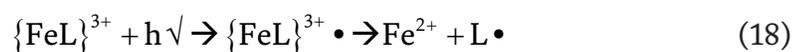
The effectiveness of the LAS degradation with conditions of: (1) TiO₂/UV light, (2) TiO₂/visible light, (3) TiO₂-Ag/UV light, and (4) TiO₂-Ag/visible light [14].

light. In this case, the metal dopant can act as a separation center, where electron transfer from the TiO₂ conduction band to Ag particles at the interface is thermodynamically possible because the Fermi level of TiO₂ is higher than that of Ag metal [14, 22]. This doping resulted in the formation of a Schottky barrier at metal semiconductor contact region and improved the photocatalytic activity of TiO₂. Hence doping Ag atoms essentially reduced the band gap of TiO₂ for the photo-excitation or red shift, and simultaneously reduced the recombination rate of photogenerated electron-hole pairs [14, 22].

4.2 Photo-Fenton modification

The photo-Fenton process appears as an attractive alternative for removing emerging contaminants. Photo-Fenton processes are reported to be effective in removing several classes of contaminants, such as phenols [29], amoxicillin [30], and dyes [31]. On the other hand, the use of photo-Fenton process is restricted to acidic pH values, with associate high operating costs for industrial scale applications. To overcome these drawbacks, photo-Fenton processes modified by adding selected chelating agents such as polycarboxylates and amino polycarboxylates compounds, can be successfully performed at neutral pH. The chelating agent acting as a ligand is able to form strong complexes with Fe³⁺ that can prevent the precipitation of Fe(OH)₃ [32–33].

As pointed out in Eq. (17) and (18), such ligand (L) should be able to form stable complexes with Fe³⁺ which significantly absorb UV-vis light and then undergo photochemical reductions leading to Fe²⁺ ions [33].



A study [32] reported that by addition of ethylenediamine-N,N'-disuccinic acid (EDDS), photo-Fenton process was more effective at neutral pH compared to the process at acidic condition. Other study as referred by Clarizia, *et al.* [33] also examined the effect of the adding humic acid to an aqueous solution containing benzene compound in the pH range of 5.0–7.0. The result exhibited that the rate for the oxidation of benzene were as high as those measured at pH 3.0 in absence of humic acid. However, so far, the use of chelating agents in the photo-Fenton for degradation of LAS in wastewater has not been explored. Therefore, there is a great challenge to realize experimentally the use of chelating compounds in the photo-Fenton for laundry wastewater treatment through LAS degradation.

In addition, the other drawback appearing in photo-Fenton is the use of UV light, that is more expensive and hazard for people health and ecosystem [14]. This limits in the large scale application of the photo-Fenton process [14, 21, 34]. Finding solutions of such weakness is obviously essential. An example solution of the weakness is by exploring synthetic or real solar light. The synthetic solar light is represented by wolfram or tungsten lamp [14] emitting visible light, that is low price and environmentally benign.

The results of the nitro-phenols degradation under solar light photo-Fenton, as well as under UV photo-Fenton [33] exhibit that the use of solar light can result in the degradation as high as resulted by UV photo-Fenton process. It is implied that the amount of OH radicals produced by decomposition of H₂O₂ induced by visible

light is equal to that of by UV light. In fact, the power of UV light ($\lambda < 350$ nm) is higher than the visible one ($\lambda > 350$ nm), that should give more OH radicals, as seen in Eq. 8. This fact suggests that OH radicals provided by Fenton's reagent is much more prominent compared to that of by light. With the promising results, the possibility of employing solar energy in photo-Fenton processes helps improving their economic and environmental sustainability.

5. Closing marks

Laundry wastewater containing high linear alkyl benzene sulfonate (LAS) surfactant is disposed into the environment with large volume, that can create serious environmentally and health problems. Removal of LAS in water and laundry wastewater can be successfully conducted through photodegradation mechanism by photocatalysis over TiO_2 and by photo-Fenton process. In order to reach maximal degradation, the process has to be performed by employing the optimal TiO_2 mass, or $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ mole ratio, irradiation time, and pH at a certain LAS concentration. Under the optimal condition, the LAS photodegradation effectively yields smaller and harmless molecules. Moreover, modifications of both methods allow them to be more effective and wider used methods for laundry wastewater treatment. In addition to the simplicity and effectiveness, the processes also suggest the low cost treatment method. It is obvious hence that the photodegradation methods have large potential to be applied in the field and large scale.

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