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## Research Article

# Use of Visible Light for Photo Degradation of Linear Alkyl-benzene Sulfonate in Laundry Wastewater over Ag-doped TiO<sub>2</sub>

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### Abstract

**Background and Objective:** Laundry wastewater containing high concentration of Linear Alkyl-benzene Sulfonate (LAS) can create environmental and health problems. This research aimed the elimination of LAS in the laundry wastewater by visible-light driven degradation over Ag-doped TiO<sub>2</sub> photocatalyst. **Materials and Methods:** Doping TiO<sub>2</sub> with Ag was performed by photodeposition of AgNO<sub>3</sub> under UV-light irradiation for 24 h. The doped photocatalysts were characterized by XRD, FTIR, DRUV and TEM methods. The photodegradation of LAS in the laundry wastewater was conducted by batch technique, over TiO<sub>2</sub>-Ag under visible light for different Ag content, time and photocatalyst dose. **Results:** The characterization data assigned that Ag has been successfully doped in TiO<sub>2</sub> with various amount proportional to the AgNO<sub>3</sub> concentrations. The Ag-doping has decreased the Energy gap (E<sub>g</sub>) that shifted the absorption into visible region. The E<sub>g</sub> decrease was influenced by the amount of Ag-doped and the highest decrease was shown by TiO<sub>2</sub>-Ag prepared from 150 × 10<sup>-2</sup> M of AgNO<sub>3</sub> giving Ag-doped as 131 mg g<sup>-1</sup>. The concentration of LAS as much 110.05 mg L<sup>-1</sup> in the laundry wastewater could be reduced through photo degradation over TiO<sub>2</sub>-Ag driven by visible light. The TiO<sub>2</sub>-Ag demonstrated stronger photo activity compared to un-doped one. The photodegradation efficiency was controlled by the amount of Ag-doped, the irradiation time and the photocatalyst dose. **Conclusion:** Ag particles have been successfully doped in TiO<sub>2</sub> and the doped photocatalyst showed higher activity in the LAS removal under visible and UV lights, compared to the un-doped one. The highest LAS photodegradation (78%) could be obtained by using TiO<sub>2</sub>-Ag containing 131 mg Ag/g, 24 h and 50 mg/100 mL of the photocatalyst dose.

**Key words:** Alkyl-benzene sulfonate, laundry wastewater, Ag dopant, doped photocatalyst, visible light

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**Competing Interest:** The authors have declared that no competing interest exists.

**Data Availability:** All relevant data are within the paper and its supporting information files.

## INTRODUCTION

Increasing detergent use, both in homes and public laundry services has produced greater volume of wastewater containing Linear Alkyl-benzene Sulfonate (LAS) in high concentration<sup>1-3</sup> and some time the LAS concentration is found to exceed the permissible level<sup>1</sup>. Accordingly, disposal of laundry wastewater directly to the environment can create several problems. At low concentrations of LAS were toxic to certain fish, aquatic animals and aquatic plants including bacteria and algae<sup>4</sup>. It is also reported that consumption drinking water or food contaminated by LAS higher than  $0.5 \text{ mg L}^{-1}$  can be harmful to health<sup>5</sup>. The chemical structure of LAS represented by dodecyl benzene sulfonate is displayed as Fig. 1, that is usually resistant to biodegradation<sup>1,3</sup> and thus, the toxicity and environmental persistence of these surfactants are emerging concerns. Justifying the negative effect, removal of LAS in laundry wastewater is essential.

Several treatment methods have been considered for LAS removal from water, especially the methods that can degrade the LAS effectively. The degradation methods were operated by involving OH radicals that can be created through photo-Fenton<sup>1</sup>, photo-Fenton like<sup>2</sup>, photocatalysis over  $\text{TiO}_2$ <sup>3,4</sup> and ozonisation<sup>5</sup>. Photocatalytic degradation using  $\text{TiO}_2$  has recently received considerable attention for Persistent Organic Pollutants (POPs) removal due to its cost-effective technology, non-toxicity, fast oxidation rate and chemical stability<sup>4,6-7</sup>. However, the wide band gap of  $\text{TiO}_2$ , 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<sup>8-15</sup>. Therefore, an effort has been focused to overcome this deficiency by doping  $\text{TiO}_2$  crystal structure with either non-metal elements<sup>8,9</sup> and metals<sup>10-15</sup> elements.

From the metals, silver as a dopant has received intensively attention since, it can significantly decrease the band gap of  $\text{TiO}_2$ <sup>13-15</sup>, allowing it to be more active under visible light. In addition, Ag dopant can also effectively trap electrons that delay the recombination and it turns to improve the photocatalysis process both under UV and visible light<sup>14,15</sup>.

Ag-doped  $\text{TiO}_2$  has been frequently reported for water splitting<sup>12</sup>, degradation of organic pollutants<sup>13,15</sup> and bacterial abatement<sup>14,16</sup>. However, no reports of  $\text{TiO}_2$  doped with Ag used for LAS degradation were found in the previous papers. Under the circumstance, in this present study, Ag-doped  $\text{TiO}_2$  prepared by photodeposition method is examined for elimination of LAS in the real laundry wastewater under

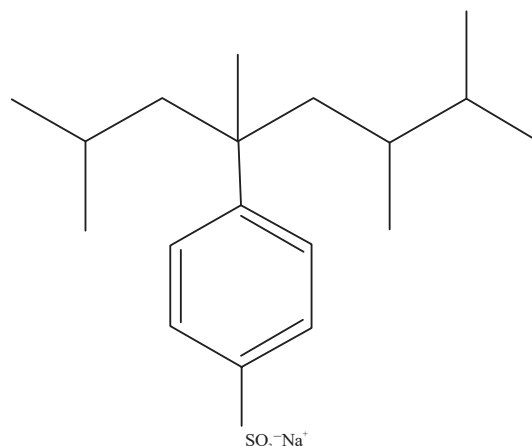


Fig. 1: Chemical structure of dodecylbenzene sulfonate  
Source: Wahyuni *et al.*<sup>1</sup>

visible light exposure at the laboratory scale. To evaluate the efficiency of the visible photodegradation, several process parameters including the content of Ag-doped in  $\text{TiO}_2$ , photocatalyst dosage and irradiation time were optimized in this study.

## MATERIALS AND METHODS

**Study area:** The research was conducted in April-October, 2019, at Laboratory of Analytical and Environmental Chemistry, Department of Chemistry, Universitas Gadjah Mada, Yogyakarta, Indonesia.

**Materials:**  $\text{TiO}_2$ ,  $\text{AgNO}_3$ , dodecyl-benzene sulfonate and methylene blue were purchased from E. Merck and used without any purification. Laundry wastewater taken from a laundry service in Yogyakarta, Indonesia, was used as a photodegradation subject.

**Method:** The research method consists of doping process, characterization of the doped photocatalyst and photoactivity of the doped photocatalyst for degradation of LAS in the laundry wastewater sample.

**Doping process:** Doping was performed by photodeposition of Ag(I) from  $\text{AgNO}_3$  solution over  $\text{TiO}_2$  powder under UV irradiation by following procedure: 100 mL  $\text{AgNO}_3$  solution in the beaker glass was added with 50 mg  $\text{TiO}_2$  powder to form suspense and the pH was set at 4, where the photoreduction proceeded maximally. Next, the suspense was placed in the apparatus as illustrated by Fig. 2 and it was irradiated by UV light accompanied by magnetically stirring for 24 h. The amount of Ag-doped on  $\text{TiO}_2$  was measured by Atomic

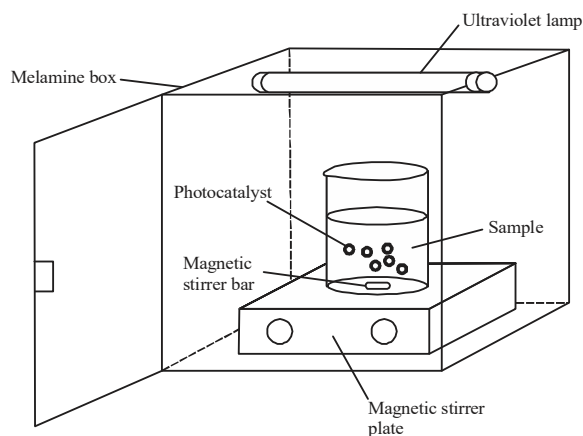


Fig. 2: A set of apparatus used for doping and LAS photodegradation processes

Source: Wahyuni *et al.*<sup>16</sup>

Absorption Spectrophotometry (AAS) method. In this step, the concentrations of Ag(I) in the solution were varied as  $50 \times 10^{-2}$ ,  $100 \times 10^{-2}$ ,  $150 \times 10^{-2}$ ,  $200 \times 10^{-2}$  and  $2.0 \times 10^{-2}$  mole  $L^{-1}$ .

**Characterization:** The doped photocatalysts obtained were characterized by using Shimadzu 6000X-XRD, Bruker-2000 FTIR, Variant-DRUV and TEM machines. In the FTIR analysis, the samples were pelleted with KBr and the spectra were recorded from  $4000-400 \text{ cm}^{-1}$ . The XRD patterns were recorded on XRD machine with Cu-K $\alpha$  from  $5-80^\circ$  of diffraction angles. By using DRUV machine, the spectra were scanned at 200-800 nm of the wavelength. The samples were coated with gold for taking TEM images.

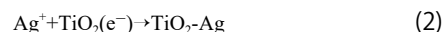
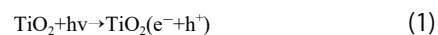
**Photocatalytic degradation of LAS in the laundry wastewater:** The photodegradation was conducted by batch technique in the apparatus seen in Fig. 2. The wastewater 100 mL in Erlenmeyer flask was mixed with 50 mg of  $TiO_2-Ag$ , then the flask was put in the photodegradation apparatus. Next, the Erlenmeyer in the apparatus flask was irradiated with the visible lamp accompanied by magnetic stirring for a period of time. The LAS left in the wastewater was analyzed by visible spectrophotometer at the wavelength of 650 nm based on the reaction with methylene blue. The concentration of the LAS was determined by plotting its absorbance on the corresponding standard curve. The same procedure was repeated for processes with  $TiO_2-Ag$  having different Ag content and various irradiation time and photocatalyst dosage.

## RESULTS AND DISCUSSION

The results of the research consists of influence of the initial concentration Ag into  $TiO_2$  structure, characterization of the Ag-doped  $TiO_2$  photocatalyst by using XRD, FTIR, DRUV/Vis. and TEM methods and the photoactivity evaluation for photodegradation of LAS in the laundry wastewater with various amount of Ag-doped, irradiation time and photocatalyst dose.

### Influence of Ag(I) initial concentration on the amount of Ag-doped in $TiO_2$ :

The amount of Ag-doped on  $TiO_2$  prepared from various concentration of  $AgNO_3$  solution is presented as Fig. 3. The reaction of Ag-doped on  $TiO_2$  structure via photodeposition was initiated by the formation of electron (e) and hole ( $h^+$ ) pair (Eq. 1) during UV-light (or  $h\nu$ ) exposure, then the electron was captured by  $Ag^+$  ion to induce reduction to form  $Ag^0$  (Eq. 2)<sup>5</sup>:



It is seen in Fig. 3, a sharp increasing amount of Ag-doped when the initial  $AgNO_3$  concentration was increased, but only slight increase was observed for the initial concentration higher than  $150 \times 10^{-3} \text{ M}$ . For very high concentration, large amount of Ag has been doped on  $TiO_2$  structure that might cover the surface of  $TiO_2$ , that inhibited the contact between  $TiO_2$  with the light. Consequently, the less electrons was released from  $TiO_2-Ag$  that resulted in slower reduction of Ag(I) in the solution. Similar results were also found by previous study<sup>12,13,15,16</sup>. Based on the amount of Ag-doped, the photocatalyst prepared were coded as  $TiO_2-Ag(46)$ ,  $TiO_2-Ag(90)$ ,  $TiO_2-Ag(131)$ ,  $TiO_2-Ag(150)$  and  $TiO_2-Ag(165)$ .

**XRD data:** The XRD patterns of  $TiO_2$  doped with Ag is displayed as Fig. 4. Several  $2\theta$  values of  $25.25^\circ$ ,  $37.52^\circ$ ,  $48.02^\circ$ ,  $53.58^\circ$ ,  $54.88^\circ$ ,  $62.61^\circ$ ,  $68.78^\circ$ ,  $70.33^\circ$ ,  $75.07^\circ$  and  $82.68^\circ$  are observed, which were assigned to anatase  $TiO_2$ <sup>13,15,16</sup>. It is also observable that doping Ag caused a decrease in the XRD intensities and the decrease was larger with the increase of the amount of Ag-doped<sup>13-16</sup>. The decrease of the intensities represented the partial crystallinity destroyed, due the insertion of Ag dopant in the  $TiO_2$  lattice<sup>14,15</sup>. In addition, new peaks of Ag were not appeared, implying that Ag particles were inserted in the lattice of  $TiO_2$  and /or the small amount

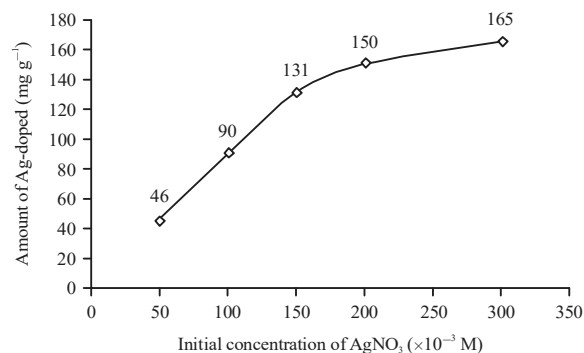


Fig. 3: Influence of AgNO<sub>3</sub> initial concentration on the amount of Ag-doped in TiO<sub>2</sub>

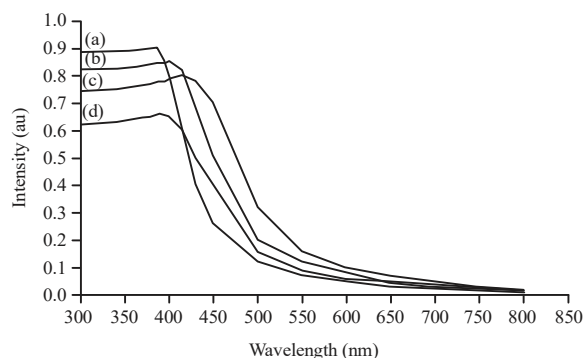


Fig. 6: DRUV spectra of (a) TiO<sub>2</sub>, (b) TiO<sub>2</sub>-Ag (46), (c) TiO<sub>2</sub>-Ag (131) and (d) TiO<sub>2</sub>-Ag (165)

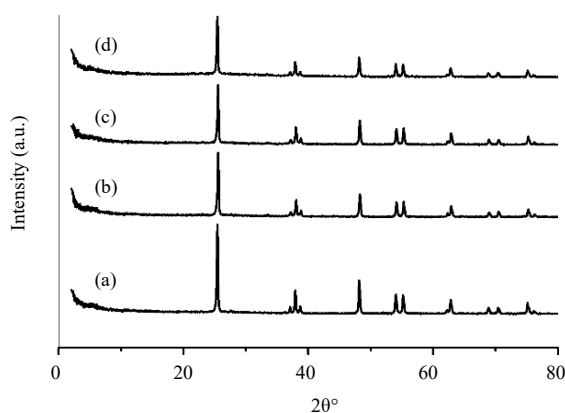


Fig. 4: XRD patterns of (a) TiO<sub>2</sub>, (b) TiO<sub>2</sub>-Ag (46), (c) TiO<sub>2</sub>-Ag (131) and (d) TiO<sub>2</sub>-Ag (165)

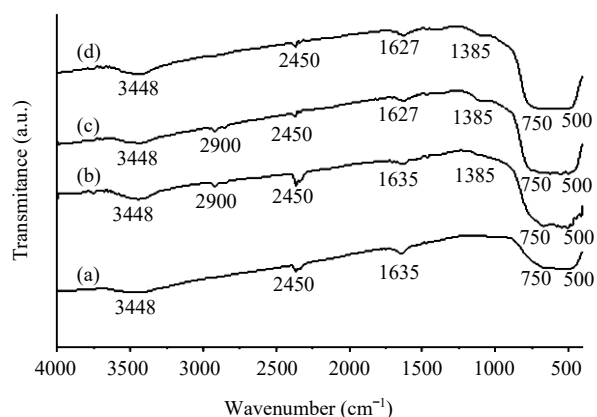


Fig. 5: IR spectra of (a) TiO<sub>2</sub>, (b) TiO<sub>2</sub>-Ag (46), (c) TiO<sub>2</sub>-Ag (131), and (d) TiO<sub>2</sub>-Ag (165)

of Ag were formed in TiO<sub>2</sub>-Ag that were un-detectable by XRD<sup>13-16</sup>. It could be confirmed that Ag particles have been doped in the structure of TiO<sub>2</sub>.

Table 1: Band gap energy changed resulted by Ag doping

Photocatalyst	λ(nm)	Eg (eV)
TiO <sub>2</sub>	387	3.20
TiO <sub>2</sub> -Ag (46)	400	3.11
TiO <sub>2</sub> -Ag (131)	415	3.05
TiO <sub>2</sub> -Ag (165)	390	3.14

**FTIR data:** In the Fig. 5, it was seen that the IR spectra of all TiO<sub>2</sub>-Ag samples are similar to that of un-doped TiO<sub>2</sub> where several peaks are observed at around 3400, 2450, 1630 and 700-500 cm<sup>-1</sup> of the wavenumbers. Some studied also reported the same IR spectra<sup>13,15,16</sup>. The peaks appearing at around 3400 and 2450 cm<sup>-1</sup> were attributed to the Ti-OH bond. In addition, the spectra also showed as harp band at ~1630 cm<sup>-1</sup> due to the OH bending vibration of chemisorbed and/or physisorbed water molecule on the surface of the catalysts<sup>14</sup>. The strong band in the range of 700-500 cm<sup>-1</sup> appearing was attributed to stretching vibrations of Ti-O-Ti bond. The FTIR spectra of all Ag-TiO<sub>2</sub> samples revealed a weak peak at about 1385 cm<sup>-1</sup>, which was not observed for the un-doped TiO<sub>2</sub>. The intensity of this peak was seemed to increase with the increase of Ag amount doped in TiO<sub>2</sub>. The peak at 1385 cm<sup>-1</sup> was assigned tentatively to the interaction between Ag and TiO<sub>2</sub> particles<sup>13,15,16</sup> implying that Ag particles have been inserted in the TiO<sub>2</sub> structure.

**DRUV data:** The DRUV spectra was exhibited by Fig. 6. Attributing that Ag doping into TiO<sub>2</sub> has shifted the absorption into longer wavelength emerging the visible area. The shift was resulted by narrowing the gap or reducing the band gap energy (Eg) as presented in Table 1. A study has also found the same finding<sup>14,15</sup>. It was implied that the narrowing was created by the insertion of Ag particles into the gap between conduction and valence bands. Further, increasing amount of Ag-doped in TiO<sub>2</sub> gave higher effect in the declining the Eg values, but very large Ag amount caused the



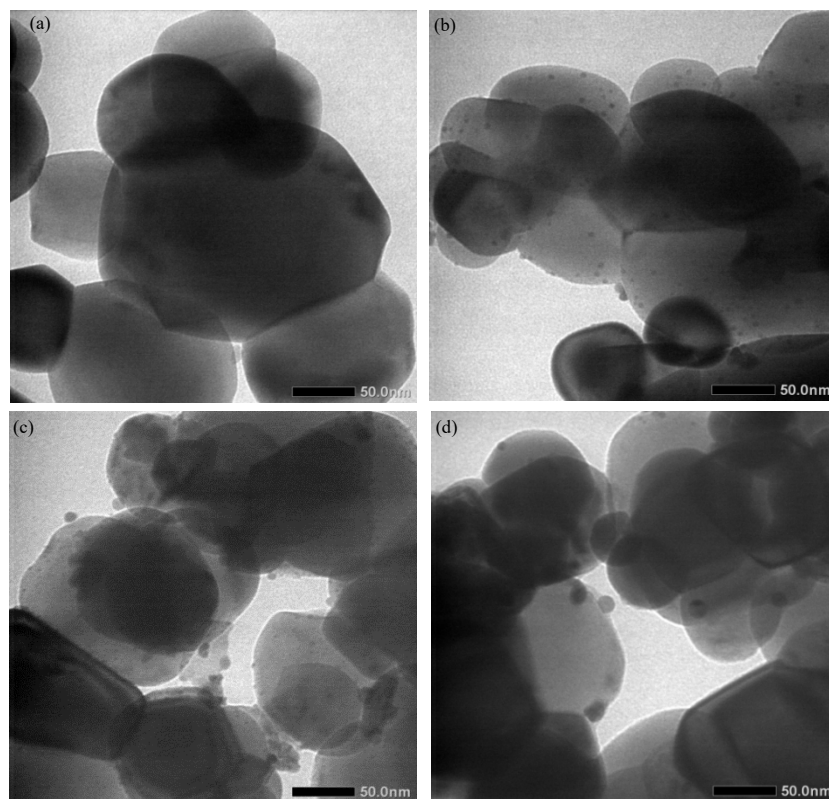


Fig. 7(a-d): TEM images of (a)  $\text{TiO}_2$ , (b)  $\text{TiO}_2\text{-Ag}$  (46), (c)  $\text{TiO}_2\text{-Ag}$  (131) and (d)  $\text{TiO}_2\text{-Ag}$  (165)

narrowing decreased. With very large Ag amount that might form larger aggregate, some Ag particles were inhibited to insert into the gap causing smaller amount of Ag could be doped.

The enhancement of light absorption in the visible region provided a possibility for improving the photocatalytic performance of  $\text{TiO}_2$  under visible light irradiation as also previously reported<sup>13-16</sup>.

**TEM data:** In order to investigate the surface morphology of the synthesized Ag-doped  $\text{TiO}_2$  nanoparticles, SEM studies were performed. The SEM images of  $\text{TiO}_2$  and Ag/ $\text{TiO}_2$  samples are shown in Fig. 7a-d. As can be seen, most of the  $\text{TiO}_2$  particles are spherical or square shaped with a particle size of 15-35 nm (Fig. 7a). The dark spots with diameter of 1-5 nm were seen uniformly deposited in the  $\text{TiO}_2$  structure prepared from lower Ag(I) concentration. The Ag formed in the  $\text{TiO}_2$  crystal clearly confirmed that Ag particles were inserted in the lattices. The larger dark spots and more spots on the  $\text{TiO}_2$  surface are observable with the further increasing amount of Ag-doped. Some studies reported the similar findings<sup>15,16</sup>. These data well agreed with the data from XRD and FTIR analysis was.

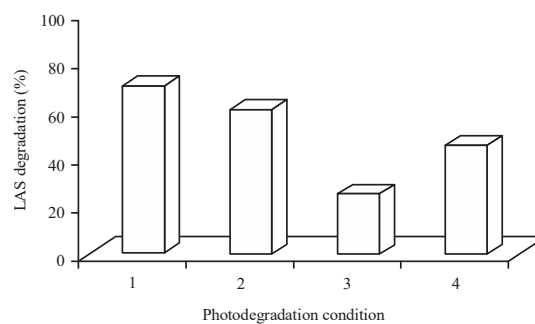


Fig. 8: Effectiveness of the degradation with the condition of (1)  $\text{TiO}_2\text{-Ag}$  under visible light, (2)  $\text{TiO}_2\text{-Ag}$  under UV light, (3)  $\text{TiO}_2$  under visible light and (4)  $\text{TiO}_2$  under UV light

**Concentration of LAS in the laundry wastewater:** The concentration of LAS in the laundry wastewater was measured as  $110.05 \text{ mg L}^{-1}$ , which was beyond the permissible level in the corresponding wastewater that was  $2 \text{ mg L}^{-1}$  as regulated by Indonesian Government<sup>1</sup>.

**Influence of Ag-doping on the activity of  $\text{TiO}_2$ :** The results of the LAS photodegradation under visible and UV light, whether over un-doped and doped  $\text{TiO}_2$  are illustrated in Fig. 8.

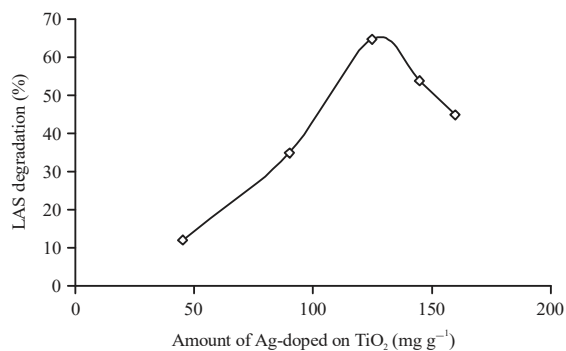


Fig. 9: Influence of the amount of Ag-doped in TiO<sub>2</sub>

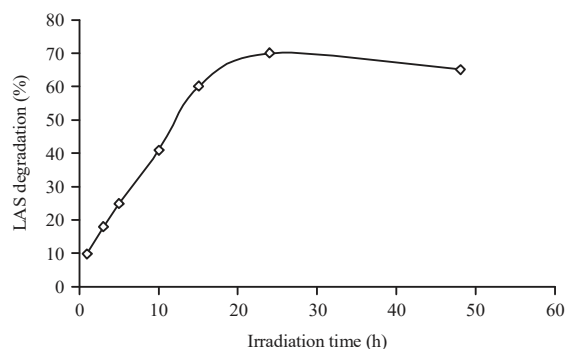


Fig. 10: Influence of the irradiation time

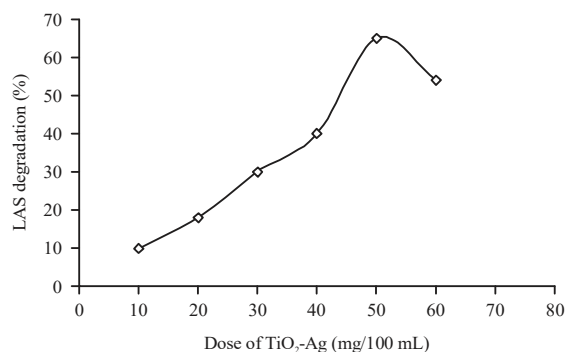


Fig. 11: Influence of the photocatalyst dosage on the LAS degradation

Figure 8 assigned that the activity of the doped TiO<sub>2</sub> or TiO<sub>2</sub>-Ag in the LAS photodegradation under visible was higher compared to that of the un-doped TiO<sub>2</sub> photocatalyst. The improvement of the activity of the doped photocatalyst under visible light exposure was promoted by decreasing gap energy (E<sub>g</sub>) that allowed the photocatalyst to absorb visible light, which could not occur in the un-doped TiO<sub>2</sub>. Additionally, the doped of TiO<sub>2</sub>-Ag also showed higher activity in the UV light than the un-doped one did. In the doped photocatalyst of TiO<sub>2</sub>-Ag, the Ag dopant was found as electron-hole separation center, where electron transfer from the TiO<sub>2</sub> conduction band

to Ag particles at the interface was thermodynamically possible, because the fermi level of TiO<sub>2</sub> was higher than that of Ag metal<sup>11,13,16</sup>. This doping resulted in the formation of a Schottky barrier at metal semiconductor contact region and improved the photocatalytic activity<sup>11,13</sup> of TiO<sub>2</sub>. Hence, doping of Ag atoms essentially reduced the band gap of TiO<sub>2</sub> for the photo-excitation or red shift and simultaneously reduced the recombination rate of photogenerated electron-hole pairs.

Moreover, photodegradation over un-doped TiO<sub>2</sub> under UV light was more effective than that of under visible light. The E<sub>g</sub> of TiO<sub>2</sub> was 3.2 eV that was equal to UV light allowing TiO<sub>2</sub> to be activated by UV irradiation and so more OH radicals could be provided. In contrast, the energy of visible light was lower than the E<sub>g</sub> of TiO<sub>2</sub> that could not promote TiO<sub>2</sub> in releasing electrons.

**Influence of Ag amount doped in TiO<sub>2</sub>:** Figure 9 illustrated that increasing amount of Ag-doped gave raise in the photodegradation efficiency and reached maximum at 131 mg g<sup>-1</sup> of Ag amount in the photocatalyst. More amount of Ag dopant should elevate the retardation of the recombination, that further enhanced the photodegradation of LAS in the wastewater. On the contrary, at the Ag content beyond its optimum value, the degradation efficiency of LAS seems to be detrimental. With further more Ag content, the Ag particles may also act as recombination centers of e and h<sup>+</sup> that should reduce the number OH radicals available. The excess doping of metal ions might also cover the active sites on the TiO<sub>2</sub> surface, thereby inhibiting the OH radical formation<sup>13,15,16</sup>. These conditions explained the decrease in the photodegradation. Same finding was also found by some studies<sup>12-16</sup>.

**Influence of irradiation time:** As seen in Fig. 10, prolong irradiation time up to 24 h could improve of the degradation, but further expansion of the irradiation time longer than 24 h, no influence on the degradation could be observed. Photodegradation than 24 h led to the photocatalyst exhausted in the OH radical formation, that was un-abled to improve the degradation<sup>15</sup>.

**Influence of photocatalyst dose:** Increasing dosages of the photocatalyst gives different effect on the LAS photodegradation as demonstrated by Fig. 11. The increase of the photocatalyst dosage provided more OH radicals, that could enhance the photodegradation. The larger dosage that exceeded the optimum level caused a detrimental in the photodegradation. The excessive photocatalyst made the turbidity of the mixture elevated that could inhibit the penetration light. As a consequent, the OH radical formation

was prevented and the photodegradation efficiency was reduced. Other studies also found similar results<sup>13,15,16</sup>.

### CONCLUSION

From this study it was concluded that, the Ag dopant was confirmed to be inserted in the TiO<sub>2</sub> lattice that narrowed the band gap energy, allowing it to absorb visible light. It was found that doping Ag on TiO<sub>2</sub> structure could improve its activity in the photodegradation of LAS in the laundry wastewater driven by visible light irradiation. The highest degradation (~78%) of LAS as much as 110.05 mg L<sup>-1</sup> contained in the laundry wastewater could be achieved by using TiO<sub>2</sub>-Ag with 131 mg g<sup>-1</sup> of Ag-doped during 24 h of the irradiation time and with 50 mg/100 mL of TiO<sub>2</sub>-Ag dose.

### SIGNIFICANCE STATEMENT

This study discovered the doping TiO<sub>2</sub> with Ag, conducted by simpler and cheaper method that could successfully enhance TiO<sub>2</sub> photocatalytic activity under visible light illumination for effectively removal of Linear Alkylbenzene Sulfonate (LAS) in laundry wastewater. It can be beneficial for the developing photocatalyst material as well as a treatment method of the hazardous LAS residue in the laundry wastewater. This study will help the researchers to uncover the critical areas of wastewater treatment method that many researchers were not able to explore. Thus, a new theory on linear alkylbenzene sulfonate photocatalytic degradation under visible light irradiation may be arrived at.

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