Asian Journal of Chemistry; Vol. 29, No. 11 (2017), 2504-2508

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2017.20836

Plasmon Enhanced by Ag-Doped S-TiO_2/Ti Electrode as Highly Effective Photoelectrocatalyst for Degradation of Methylene Blue

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Received: 1 June 2017; *Accepted*: 25 July 2017; *Published online*: 29 September 2017; AJC-18582

The degradation of methylene blue dye has been conducted by Ag@S-TiO_2/Ti electrode to increase the plasmon effect on visible light. The addition of silver metal was applied using electrodeposition method. While the S-TiO_2 was prepared by sol-gel and immobilization on TiO_2/Ti electrode. The results showed that the X-ray diffraction pattern of TiO_2/Ti electrode was anatase crystal. Fourier transform infrared analysis in the wavenumber of 1120 and 413 cm^{-1} indicated the existence of S-O and Ti-O bonds. Supporting by scanning electron microscope and energy dispersive X-ray (SEM-EDX) on Ag@S-TiO_2/Ti electrode, the existence of Ag, Ti and S were 2.9, 4.5 and 2.3 KeV, respectively. The plasmon effect identity was active on visible light irradiation confirmed by the photoelectrocatalyst system using linear sweep voltammetry (LSV). Based on the UV-visible spectrophotometer measurement the efficiency of methylene blue degradation was 81.15 % on 0.5 ppm.

Keywords: TiO_2, Silver, Sulfur, Photoelectrocatalysis, Plasmon, Methylene blue.

INTRODUCTION

The colouring was an important factor in the fashion, garment, equipment, paper and printing industries [1]. Dye is a compound that gives colour to a material and usually used in colouring process [2]. In every year, the dye was used reaches about 280,000 tons per capita [3], the high demand of textile industries in the world as an effect of human population on clothing needs so this industry keeps development [4].

Methylene blue (MB) is a dye with the characteristic of blue colour. The colourful waste produced by the industries of dye and textile can cause the aquatic ecosystem damage because of the high concentration of organic compounds containing the waste [5,6]. The waste has gotten the most attention because of it is spreading anywhere, strong effects to the environment, ability in forming the poisonous aromatic smell and low rate of decomposition [7]. This waste is through out during the process of production and consumption.

The process of removing the dyeing wastewater produced by the textile industries has become an issue of discussion and regulation all over the world [8]. The photocatalyst based on semiconductor has offered one of the best solutions for the problem [9]. IUPAC Commission defined the photocatalyst as a catalytic that involved the absorption of light by the catalyst. The catalyst is a substance that increases the speed of reaction [10]. The photocatalysis was activated by the ultra violet (UV) light to decompose the organic compounds [11].

Titanium dioxide (TiO_2) is one of the semiconductor oxides that has been studied extensively as a photocatalyst since the effect of light sensitization was found by Fujishima and Honda in 1972 [12]. TiO_2 is mostly used as photocatalyst because it has the characteristics of optic and electronic, very photoreactive, non-poisonous, having long-term chemical stability and relatively low-cost [13,14].

Some efforts had been done by the researchers to increase the activities of TiO_2, such as combining the process of photocatalysis and electrochemical, which is popular as a photoelectrocatalysis method [15,16]. Photoelectrocatalysis proved as a method that is very effective to degrade the organic pollutants in the water [17,18]. The principal of the photocatalysis is the oxidation efficiency that can be increased by the application of potential bias to flow the electrons through the external circuit so that it can prevent the recombination of the positive holes and electrons.

The TiO_2 photoelectrocatalysis activities can be increased by adding the dopant to obtain the optimum result [19]. The dopant added to the catalyst system is divided into two types, which are metal and non-metal [20,21]. The addition of dopant on S-TiO_2/Ti as the new catalyst could active on the smaller energy gap value for absorbing the visible energy. The dopant

of metal ions has the role in reductor absorbing and giving the oxidizer space, then slowing the electron recombination, whereas the non-metal dopant was used to move into TiO_2 surface to be active in visible light.

The decoration of S-TiO_2/Ti electrode using Ag metal, giving the plasma effect on the S-TiO_2/Ti surface to be able active under visible light [22]. It has advantages in spectral absorption in the visible region that converted by electron separation in the photoelectrochemical process. In this study, the sulfur is used as the non-metal and silver as the metal sources to give the plasmon effect on the S-TiO_2 surface to enhance in the visible light area. The development of this research to sunlight utilization will be applied to solar energy.

EXPERIMENTAL

Preparation of TiO_2/Ti electrode: The preparation of TiO_2/Ti was done by cutting the Ti plate with the size of 4 cm × 0.5 cm, then it was cleaned by using sandpaper with the size of 1200CC so that the surface became clean and shiny. After that, it was washed by using detergent and distilled water solution. Then, the Ti plate was soaked (etching) by using the mixed HF: HNO_3: distilled water in the ratio of 1:3:6 for 2 min. The last step in this preparation was rinsing the Ti plate with distilled water to remove the residues of etching solution on the surface of Ti plate, then it was dried in the air.

Fabrication of TiO_2 thin film by anodizing method: The Titanium plate prepared was put into a probe filled with 0.27 M NH_4F electrolyte solutions and 98 % glycerol. The anodizing process was done by placing the Ti plate as an anode and the Cu plate as a cathode by giving 25 volts bias potential. This anodizing process was done in 4 h. The last step done was heating the Ti plate for 1.5 h at 500 °C.

TiO_2/Ti electrode doped sulfur (S): To obtain the S source, the solution was made by using 9.8 mL titanium(IV) isopropoxide (TTIP 97 %) added to 15 mL of 99 % ethanol in a beaker and it was stirred for 2 h at the temperature of 30 °C. Then, it was continued by adding 4 mL of 1 M acetic acid and dropwise of 4 mL H_2SO_4 1 M, it was stirred for 0.5 h at 30 °C. The formed sol was evaporated at the room temperature for 24 h and then it was heated at 80 °C for 20 min. The formed sol-gel was put into a beaker. The coating process was done by covering TiO_2. The dyeing technique was applied for 10 min and then it was lifted slowly. In last step, it was calcined at 500 °C for 0.5 h.

S-TiO_2/Ti electrode doped Ag metal: The electrodeposition process of S-TiO_2/Ti electrode was done by using $AgNO_3$ solution with a 0.04 g of electrolyte solution dissolved in 100 mL distilled water, with the addition of 0.5 g EDTA in 100 mL, then both solutions were mixed. The electrodeposition was done in 5 sec, with 1.0 volt bias potential. The formed Ag@S-TiO_2/Ti electrode was kept in a desiccator for 24 h.

Degradation test by photoelectrocatalysis system: Methylene blue was made by the concentration of 0.5, 1.0, 2.0 and 3.0 ppm (+0.1 M $NaNO_3$). The degradation test was done by multi-pulse amperometry (MPA) method with the duration of 10 min and 0.5 volt bias potential in the condition. Then, the absorbance measurement was done by using UV-visible spectrometer to observe the concentration decreasing of dye. The measurement was done to the Ag@S-TiO_2/Ti electrode.

RESULTS AND DISCUSSION

Characterization of TiO_2/Ti electrode by XRD: The electrode has been prepared by the anodizing method in the process of oxidation-reduction. This method was to grow the metal oxide on Ti surface were placed in the anode, whereas Cu was placed on the cathode. The anodizing method was mostly done by the researchers because of its simple use, a good stability and it also produced the TiO_2 nanotube structure. The anodization process got the uniformity of the nanotube surface and then it was ended by the calcination process at 500 °C to obtain the anatase TiO_2 crystals.

The characterization result of TiO_2/Ti electrode by using XRD (Fig. 1) showed that the TiO_2 thin film was formed by the anodizing method. The diffraction pattern compared with the Joint Committee on Powder Diffraction Standards (JCPDS) No. 21-1272 were confirmed the TiO_2 crystal structure formed in the fields of 101, 004, 200, 105, 211, 204, 116 [23].

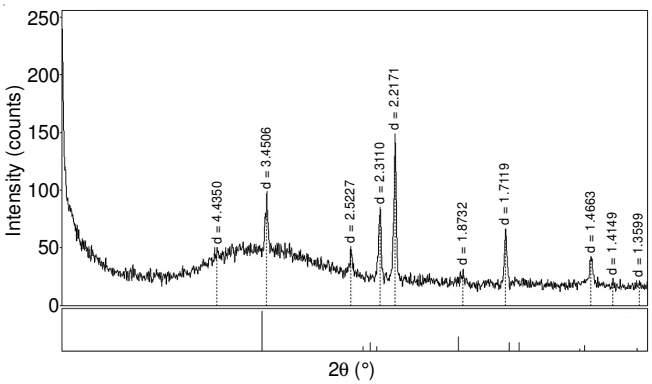

Fig. 1. XRD spectrum of TiO_2 on the surface of TiO_2 plate

Characterization of Ag@S-TiO_2/Ti electrode by FTIR: Qualitative determination of existence the non-metal elements in the TiO_2 lattice was detected by using FT-IR analysis. The bonding of non-metal element (S) was identified the functional group of S-bonded to other metal or non-metal. Fig. 2 indicated the Ti-O bond and S-bonded by O (S-O).

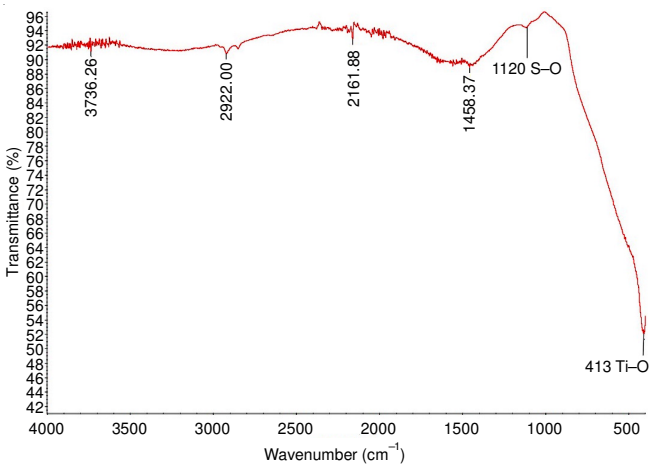

Fig. 2. FTIR spectrum of S-TiO_2/Ti

The wavenumber of 1250-400 cm^{-1} indicated the Ti-O stretching bond with the absorption area of 413 cm^{-1} [24]. The wavenumber of 1200-1000 cm^{-1} was observed the bond of S-O from sulfur bonded to one of the oxygen atoms of TiO_2 with the asymmetric stretching at 1120 cm^{-1} [25,26]. The existence of S indicated the occurrence of interstitial bonds in the anionic TiO_2 anatase crystal lattice by replacing some O atoms from the TiO_6 octagonal. According to Umebayashi *et al.* [27], the low intensity of S-O bonds on the FTIR spectrum was relatively easy to obtain in the experiment with the calculation of *ab initio* analysis of 3p mixing S and the decreasing of band gap happened. The success of S doping had been done by Liu *et al.* [28] that could decrease the band gap value of 2.68 eV.

Characterization of Ag@S-TiO_2/Ti electrode by SEM-EDX: The SEM-EDX was performed by analyzing the existence of Ag and S elements on the TiO_2/Ti electrode. The high energy giving the electrons and protons in the sample gave the electromagnetic emission difference with the specific peak of each element of Ti, O, S and Ag.

The surface morphology (Fig. 3A) showed the occurrence of nano-particle sol-gel coating of S and Ag on TiO_2/Ti surface. The sol-gel method had various advantages in term of purity, homogeneity, flexibility, stoichiometry [29]. The morphological analysis of Ag@S-TiO_2/Ti electrode, the spread of silver evenly was done by electrodeposition method. The use of electric current in the same direction with silver doping that placed the nano-sized metal deposit was distributed more evenly on the surface of Ag@S-TiO_2/Ti electrode [30]. Supported by the EDX spectra (Fig. 3C), the peaks showing each existence of Ti, O, S and Ag elements were reached in the area of 4.5, 0.52, 2.3 and 2.9 keV with the percentages of existence 68.72, 30.79, 0.13 and 0.36 %, respectively.

Activity test of TiO_2/Ti and Ag@S-TiO_2/Ti electrodes: The activity test of photocurrent response on each electrode of TiO_2/Ti and Ag@S-TiO_2/Ti showed the current produced by each electrode measured during the irradiation process of UV and visible light. The response was measured by using LSV method started from -1 to +1. The LSV data showed the oxidation process on the working electrode occurred in the system as a photocurrent signal that induced by the electron transfer process [11]. The electrons flow could be observed as photocurrent and proportional with the electrolyte in solution.

Fig. 4A showed the activity test of TiO_2/Ti electrode. The electrode was active when irradiated by UV light, compared

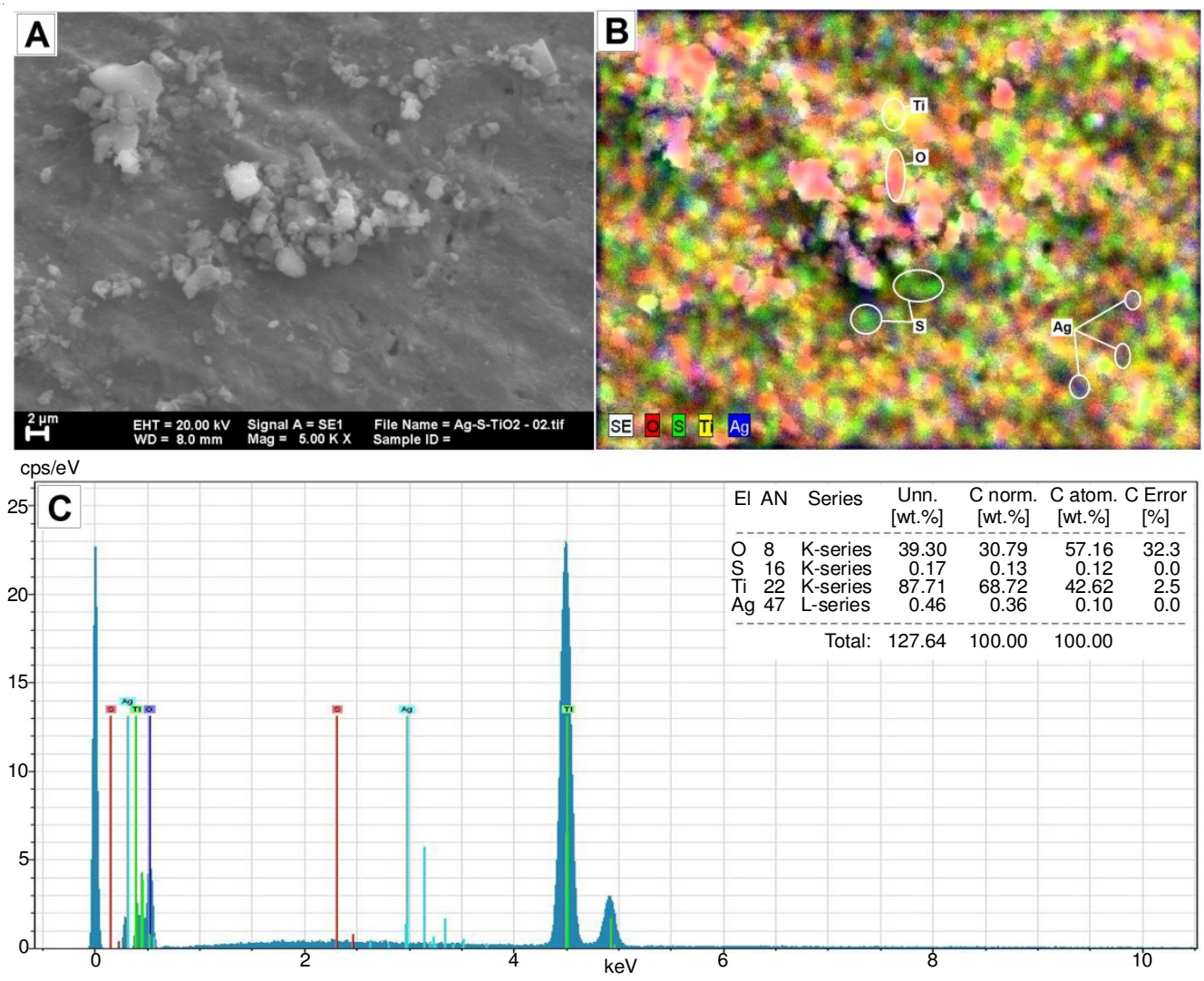

Fig. 3. Result of Ag@S-TiO_2/Ti electrode characterization using SEM-EDX electrode; (A) The morphology of the surface; (B) The morphology of the surface element; (C) The EDX Spectra and the percentage of the element amount

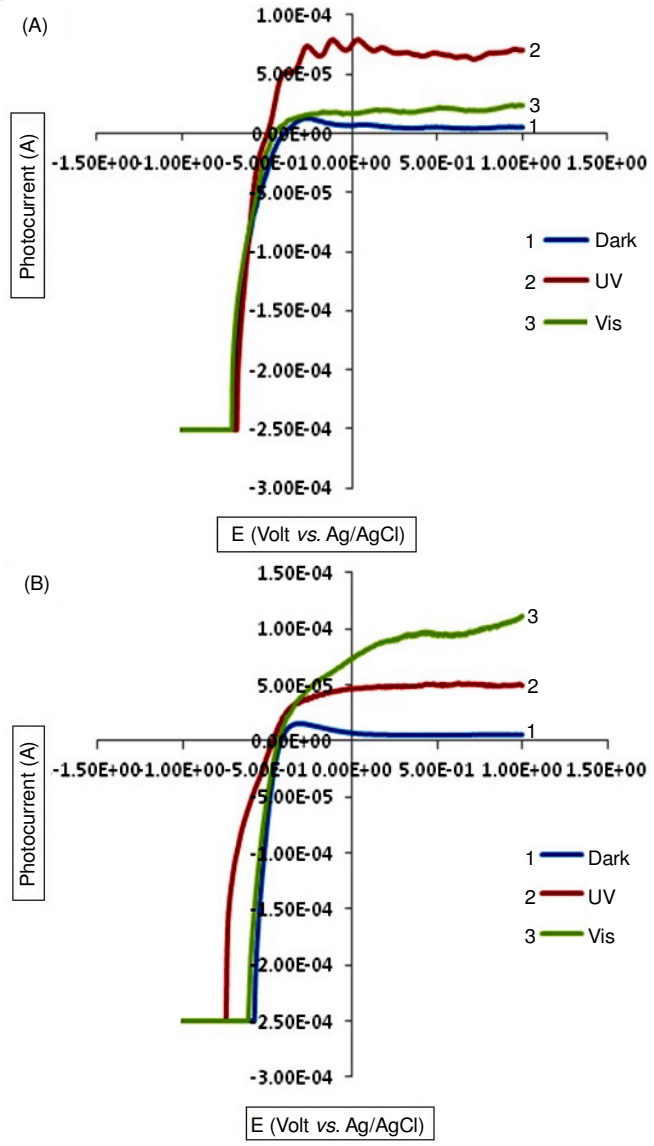

Fig. 4. Test of electrode activities by LSV method (A) TiO_2/Ti and (B) Ag@S-TiO_2/Ti electrodes

to irradiate with visible light. The energy needed to activate the performance of TiO_2/Ti oxidation was more because TiO_2 was more responsive to the UV rather than visible light. Whereas the electrode doped by Ag@S-TiO_2/Ti gave the better activities when it was irradiated by visible light, compared to when it was irradiated by UV light or in the darkness. This showed the activate of Ag@S-TiO_2/Ti electrode by giving low energy in the visible light.

Degradation of methylene blue by photoelectrocatalysis: The degradation test of methylene blue compound was performed by photoelectrocatalysis with the variation of concentration 0.5; 1.0 ; 2.0 ; and 3.0 ppm using the potential current and the radiation variation of UV and visible light. In the potentiostat system, the bias energy of +0.5 volt, the electrons were moved to the back contact on the working electrode that was then transferred to the counter electrons (Pt). Thus, the reaction on the working electrode initiated the oxidation reaction (h^+) entirely, whereas on the electrode, counter electrons initiated the reduction reaction (e-) so that the photoelectrocatalysis became more efficient and faster because counter electrons suppressed the recombination of electrons and holes [2]. Therefore, it could accelerate the process degradation of methylene blue.

Fig. 5A showed the methylene blue degradation using TiO_2/Ti electrode by photoelectrocatalysis for 1 h with the variation of UV and visible light showing the decreasing in the UV irradiation. Degradation percentage (%) (Fig. 5B) of methylene blue at the concentration of 0.5 ppm was 73.91 %. The TiO_2 was active on the UV light so it can work well compared to when it was irradiated by visible light.

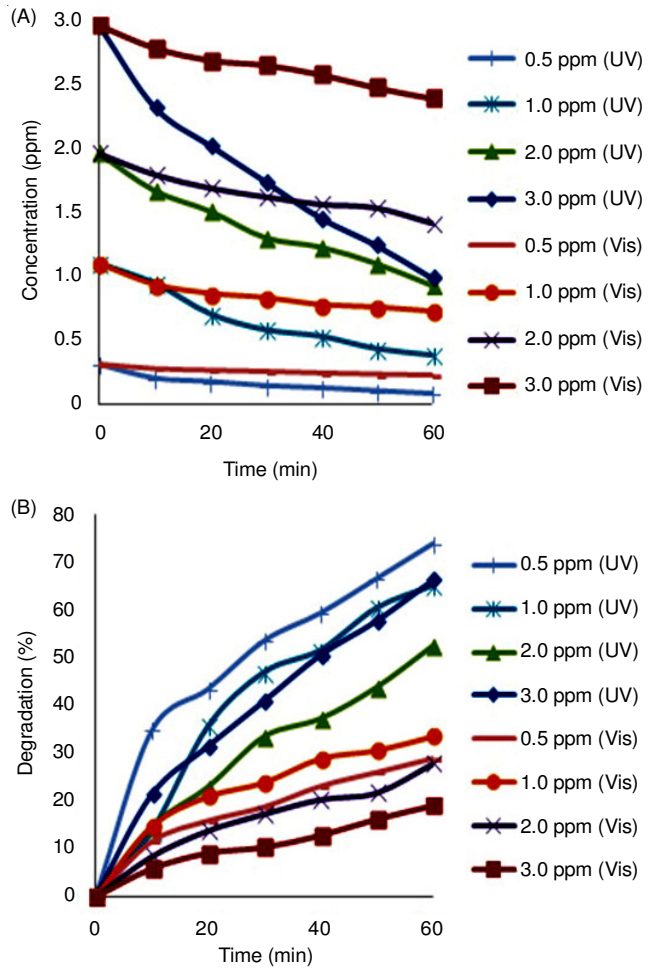

Fig. 5. Graphic of methylene blue degradation by using TiO_2/Ti electrode: (A) the curve of concentration decreasing, (b) of degradation

Fig. 6A shows the methylene blue degradation by photoelectrocatalysis using Ag@S-TiO_2/Ti electrode showed the decreasing concentration of methylene blue on the UV-visible light irradiations. Ag@S-TiO_2/Ti electrode could work well on the irradiation by either UV or visible light. The percentage of degradation (Fig. 6B) could be seen that the comparison of electrodes performances in degrading of methylene blue showed the highest result when it was irradiated by the visible light at the concentration of 0.5 ppm with the value of 81.15. This result proved that performance of the TiO_2/Ti working electrode could be improved from the UV area in the visible area after being doped by using Ag and S.

Conclusion

The TiO_2/Ti electrode gave the better activities when it was irradiated by the UV light, whereas Ag@S-TiO_2/Ti gave the

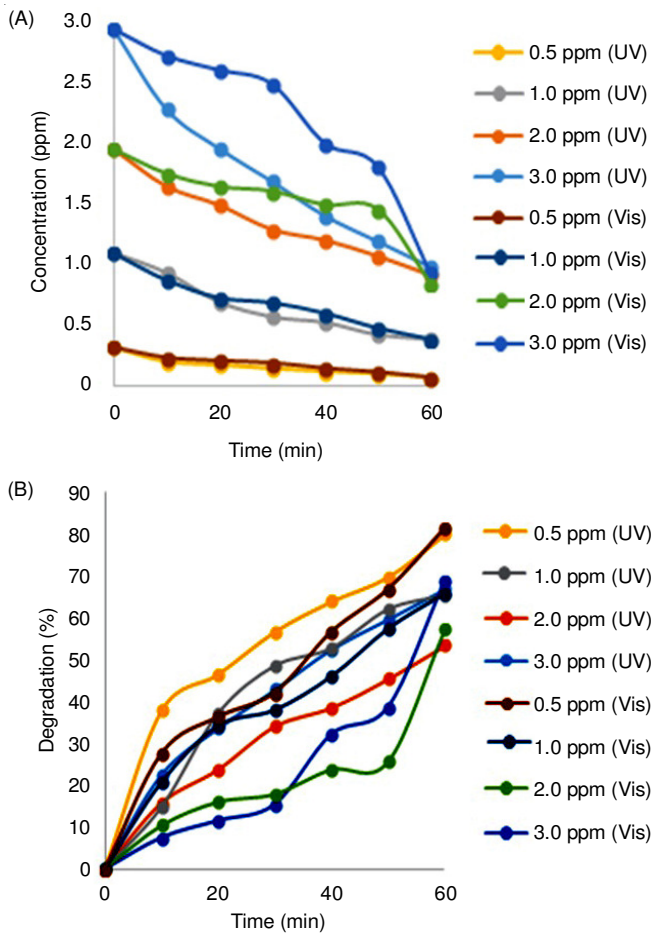

Fig. 6. Graphic of methylene blue degradation by using Ag@S-TiO_2/Ti electrode: (A) the curve of concentration decreasing (B) of degradation

better activities when it was irradiated by visible light. The result of methylene blue degradation for each of TiO_2/Ti and Ag@S-TiO_2/Ti electrodes showed the optimum value to degrade methylene blue at the concentration of 0.5 ppm with the percentage of degradation were 73.91 and 81.15 %, respectively.

ACKNOWLEDGEMENTS

The authors acknowledge for the financial support from DRPM-Ministry of Research, Technology and Higher Education, Republic of Indonesia.

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