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Research Article

Methyl Violet Degradation Using Photocatalytic and Photoelectrocatalytic Processes Over Graphite/$PbTiO_3$ Composite

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Abstract

Photocatalytic and photoelectrocatalytic degradation of methyl violet dye using Graphite/$PbTiO_3$ composites has been conducted. The purposes of this research were to examine photocatalytic and photoelectrocatalytic degradation of methyl violet using Graphite/$PbTiO_3$ composite. Synthesis of Graphite/$PbTiO_3$ composite was successfully performed via sol-gel method by mixing graphite powder, titanium tetra isopropoxide precursor solution (TTIP) and $Pb(NO_3)_2$. The Graphite/$PbTiO_3$ composites were characterized using X-Ray Diffraction (XRD), Fourier Transform-Infra Red (FT-IR), and Scanning Electron Microscopy (SEM). The XRD diffractogram and IR spectrum of Graphite/$PbTiO_3$ composite revealed all characteristic peak of graphite and $PbTiO_3$. Photocatalytic degradation process showed that Graphite/$PbTiO_3$ composite with ratio 1/1 decreased concentrations of methyl violet up to 92.20 %. While photoelectrocatalytic degradation processed for 30 minutes at neutral pH and 10 V voltage degraded the methyl violet until 94 %. However, the photoelectrocatalysis is still not significance to improve methyl violet degradation compared with photocatalysis.

Keywords: Graphite/$PbTiO_3$; Photocatalytic; Photoelectrocatalytic degradation; Methyl violet

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1. Introduction

Textile industrial wastewater containing synthetic dyes, having chromophore groups, is extremely harmful to the environment, especially the river ecosystem in Indonesia. Methyl violet dye, a class of triphenilmethane, is one of commonly dyes intensively used in nylon, wool, silk, and cotton dying process. Due to its complex structure, methyl violet is stable and difficult to degrade. Based on literature review, it was found that aniline contained in this compound is toxic, mutagenic and carcinogenic [1]. These chemicals trigger tumors in several species of fish [2]. Thus, it is necessary to handle this harmful substances accumulated in wastewater for sustainability.

Photocatalysts semiconductor have been utilized by some researchers on wastewater treatment to degrade the dye through photocatalytic

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degradation, electrocatalytic degradation and photo-electrocatalytic degradation. Senthilkumaar *et al.* [3] has successfully performed photocatalytic degradation of methyl violet using nanocrystalline TiO_2 with 125 W mercury lamp for 60 minutes. Another experiment was also performed by Gholami *et al.* [4] utilizing TiO_2 composed with SiO_2 as photocatalyst in dye removal with outstanding result compared to TiO_2 or SiO_2 single materials. The photocatalytic process, unfortunately was less effective in treating a high concentration of wastewater since their low adsorption of the photocatalyst resulted low reaction rate and required a long time [5]. Therefore, to enhance the TiO_2 effectiveness, it needs some modifications such as formation of new compounds derived TiO_2, adsorbent addition or electrical energy addition.

Formation of material derived from TiO_2, so called $PbTiO_3$, is one of modification conducted on preparation of TiO_2 photocatalyst materials. $PbTiO_3$, also known as perovskite oxide, is recently received great attention since its efficiency in photocatalytic activities with high quantum yields [6]. Moreover, Pb^{2+} was able to adsorb visible light because of its smaller band gap. Thus, this metal oxide, having E_g of 3.0 eV lower than TiO_2 (3.2 eV), can be utilized as an efficient visible-light photocatalyst for various purposes [7,8].

Addition of Adsorbent like graphite will increase the effectiveness of photocatalyst semiconductor and photocatalytic or photo-electrocatalytic degradation processes. Economically, graphite is abundant and cheap and readily available in waste batteries. However, utilizing of graphite extracted from batteries as photocatalyst composed with $PbTiO_3$ is still not yet studied. In this study, we combined a graphite from batteries as adsorbent and $PbTiO_3$ catalyst carrier to enhance photocatalytic or photo-electrocatalytic degradation of dye. Moreover, graphite from batteries was reported having similar physical properties to graphite electrode [5].

With the assistance of electrical energy, the transfer of electrons from valence band to conduction band flowing in the electrode rod was easier to achieve and produce a hole (h^+) in the valence band belonging to photocatalyst material. Separation of electrons and holes was better, so electrons recombination reaction on the photocatalyst can be minimized. The flow of electrons in the electrode will also oxidize the dye solution without activating photocatalyst. Consequently, the dye's oxidation-reduction (redox) reactions will go faster. Therefore, the electric current is expected to improve effectiveness of degradation. Thus, the study of methyl violet degradation methods using composite electrode Graphite/$PbTiO_3$ as modification of existing research is needed and has not been studied. Therefore this research focused on photocatalytic and photoelectrocatalytic degradation of methyl violet using Graphite/$PbTiO_3$ composite.

2. Materials and Methods

2.1 Materials

Materials used in this study were titanium tetra isopropoxide (TTIP, 97 % Sigma-Aldrich), graphite powder from dry cell batteries, $Pb(NO_3)_2$ (Merck), HNO_3 (Merck), HCl (Merck), KCl (Merck), acetic acid glacial 98 % (Merck), NaOH (Merck), silica glue (Autosil Black Gasket RTV Silicone), distilled water. Methyl violet dye was commercially available from Surakarta, Indonesia.

2.2 Synthesis of $PbTiO_3$

The $PbTiO_3$ compound was synthesized via sol-gel method with mole ratio 1:1 of $Pb(NO_3)_2$ powder and TTIP precursors. A total of 3 mL TTIP was hydrolyzed with 30 mL of acetic acid in the water bath (±14 °C). After obtaining a white viscous solution, then it was continuously stirred and heated at 90 °C to form a white gel. Then, 1.19 g of $Pb(NO_3)_2$ powders was added into the solution while stirring. After cooled at room temperature, the obtained gel was dried at 150 °C for ±24 hours. The formed composite was then annealed by varying calcination temperature at 300, 400, 500 and 600 °C with heating rate 10 °C/min to optimize the $PbTiO_3$ crystalline phase.

2.3 Synthesis and characterization of graphite/$PbTiO_3$ electrode composites

Graphite/$PbTiO_3$ composite was prepared through sol-gel method using purified graphite powder, $Pb(NO_3)_2$ powder, and TTIP. The graphite used in this research was purified from batteries pasta. The purification was carried out by soaking 10 g of graphite powder in 100 mL of 0.1 M HNO_3 for 24 hours. The powder was then filtered and neutralized using distilled water and dried at room temperature. The purified graphite powder was then sieved with 100 mesh size. Synthesis procedure of graphite/$PbTiO_3$ composites was same as the $PbTiO_3$ synthesis procedure. After obtaining a white gel, a result of TTIP hydrolysis, 1.19 g $Pb(NO_3)_2$ powders and 1.6 g of graphite powder was introduced into the gel solution. The formed gel was then dried at 150 °C for ±24 hours and then annealed at optimum calcination temperature of $PbTiO_3$ crystalline phase formation. In this study was also varied the graphite/$PbTiO_3$ ratio by 1/3, 1/2, 1/1, 2/1, and 3/1 (w/w).

Fabrication of electrode was carried by mixing the Graphite/$PbTiO_3$ composite and silica glue with 4:1 ratio (w/w). It was fabricated in electrode mold with 0.5 cm of diameter and 2.5 cm of length and pressed with 1000 psi. Then, the electrode rod was dried at 120 °C for 6 hours. Graphite/$PbTiO_3$ composite was characterized using FT-IR spectrometer, XRD and SEM-EDX. FTIR characterization was recorded at wavenumber range 500-4000 cm^{-1}, whereas the XRD was noted at 2θ range 20-80°.

2.4 Photocatalytic degradation procedure of methyl violet dye

Photocatalytic degradation process of methyl violet dye was conducted by adding 0.3 g composite powder into 30 ml of methyl violet dye solution 5 ppm. The 9 watt UV lamp was positioned 12 cm above the sample. The solution was stirred for 30 minutes. The photocatalysts employed in this study were graphite, $PbTiO_3$ and Graphite/$PbTiO_3$ composites at ratio 1/3, 1/2, 1/1, 2/1, and 3/1 (w/w).

2.5 Photo-electrocatalytic degradation procedures of methyl violet dye

A photo-electrocatalytic degradation was performed in 20 mL solution of methyl violet 5 ppm. Then the work scheme as presented in Figure 1 was assembled by placing graphite electrodes as the cathode and Graphite/$PbTiO_3$ composite as the anode with 2 cm for distance. The 9 watt UV lamp was located 12 cm above the samples. The solution was stirred while flowed with each variation of the power supply voltage by 7.5; 10, and 12.5 V for 30 minutes. Then, the absorbance of the solution was measured using UV-Vis spectrophotometer both before and after the photo-electrocatalytic degradation process. The pH was also varied in this study by conditioning the methyl violet solution at pH = 3 (acid), pH = 7 (neutral), and pH = 10 (alkaline).

3. Results and Discussion

3.1 Synthesis of $PbTiO_3$

Synthesis of $PbTiO_3$ was performed by combining sol-gel method on the TiO_2 synthesis according to previous research [9, 10] and directly added with $Pb(NO_3)_2$ after achieving TiO_2 sol-gel phase. The produced $PbTiO_3$ compounds was in the form of yellow powder. Approximately, there were five steps on $PbTiO_3$ synthesis. The first stage was the forming TiO_2 suspension by the presence of acetic acid. When the environment system reached 90 °C, TiO_2 sol-gel was formed. In the same time, $Pb(NO_3)_2$ was introduced into the system to produce $PbTiO_3$ sol-gel. The $PbTiO_3$ powder was obtained after annealed $PbTiO_3$ xerogel at temperature 300-600 °C generated by drying $PbTiO_3$ sol-gel.

The final products, $PbTiO_3$ powder, were then characterized by XRD which its diffractogram pattern is shown in Figure 2. It was clearly observed the $PbTiO_3$ diffractogram differences between the product annealed at 300, 400, 500, and 600 °C. The 2θ at 19.4195°,

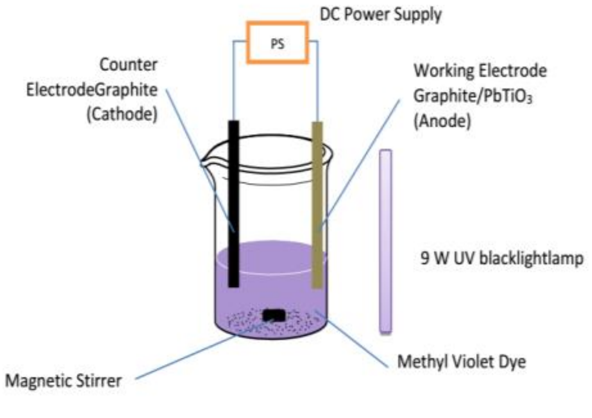

Figure 1. Photo-electrocatalytic degradation scheme process

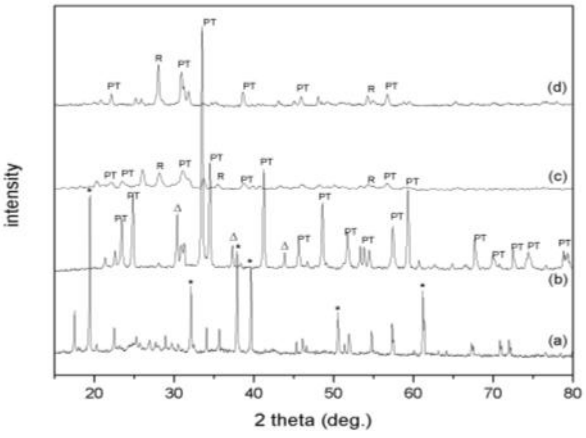

Figure 2. Diffractogram of $PbTiO_3$ annealed at (a) 300 °C, (b) 400 °C, (c) 500 °C, and (d) 600 °C. (* = $Pb(NO_3)_2$, Δ = PbO, PT = $PbTiO_3$, R = TiO_2 Rutile)

37.8565° and 39.6192° dominated with high intensity at $PbTiO_3$ XRD diffractogram annealed at 300 °C. These peaks indicated the typical peaks belong to $Pb(NO_3)_2$ according to JCPDS No. 36-1462. In this stage, there are no observed the peaks of TiO_2, PbO, or even $PbTiO_3$ crystals indicating the crystal was not yet formed. However, by annealing the sample at 400 °C, the $PbTiO_3$ compound was successfully formed which it was proofed by the presence of high intensity at 2θ of 31.4805°, 32.4616°, and 39.2179° corresponding to JCPDS No. 74-2495. The synthesized $PbTiO_3$ annealed at 400 °C has high degree of crystallinity with the crystal size 39.98 and yield by 90.16% compared to samples annealed at 300, 500 and 600 °C. The rutile phase of TiO_2 oxide formed at the synthesized product at 500 °C and 600 °C indicated by the presence of 2θ of 28.1395°, 36.6100°, 39.8133°, 41.400°, 54.2616° (Figure 2c), and 54.2155° (Figure 2d) according to JCPDS No. 87-0710. This confirmed that annealing at 500 °C and 600 °C caused the decreasing of $PbTiO_3$ crystallinity if compared to the product annealed at 400 °C. The high annealing temperature triggered fast of the formation reaction rate. Unfortunately, by this condition, the structuring and crystal formation become lower.

3.2 Characterization of graphite/$PbTiO_3$ composites

Synthesis of Graphite/$PbTiO_3$ was carried out in the same way as $PbTiO_3$ synthesis pathway. The introducing of graphite together with $Pb(NO_3)_2$ was performed after achieving TiO_2 sol-gel form. XRD diffractogram of Graphite/$PbTiO_3$ composite shows peaks at 2θ = 26.5076° which is the characteristic peaks of graphite and peaks at 2θ = 31.8382°; 2θ = 39.2949°; 2θ = 46.3154°; 2θ = 57.1402° correspond to $PbTiO_3$ (Figure 3). It can be pointed that the addition of graphite into $PbTiO_3$ system affecting of the $PbTiO_3$ crystallinity. The broad and low intensity of Graphite/$PbTiO_3$ peaks compared to $PbTiO_3$ outlined that the crystallinity decreased influenced by amorphous phase of graphite.

Ratio of graphite/$PbTiO_3$ influenced the crystallinity of the resulted product. Based on our previous report [10], the graphite/$PbTiO_3$ diffractograms outlined in Figure 4 showed that the composites constructed with graphite/$PbTiO_3$ ratio 1/1 having highest crystallinity than other composition. The addition of graphite with high concentration decreased the composites crystallinity due to the amorphous phase of graphite dominating in the system.

Infrared spectrum of the precursor materials and each graphite/$PbTiO_3$ composition are presented in Figure 5 and 6. In the TiO_2 IR spectrum (Figure 5) appears absorbance bands around 3409.33, 1630.88, and 609.5-420.5 cm^{-1} which they are TiO_2 characteristic absorption. A peak at 3409.33 cm^{-1} is the O–H stretching vibration while a peak at 1630.88 cm^{-1} is the O–H bending vibration binding to Ti. A broad adsorption band around 609.5-420.5 cm^{-1} is the characteristic vibration band belonging to O–Ti–O. In the Figure 5a and 5b revealed the peaks differences at around 600-1000 cm^{-1} between TiO_2 and $PbTiO_3$ indicating the entering of Pb into the TiO_2 structure. In the Figure 6 was observed the vibration around 3439.23 cm^{-1} indicating O–H stretching vibration of

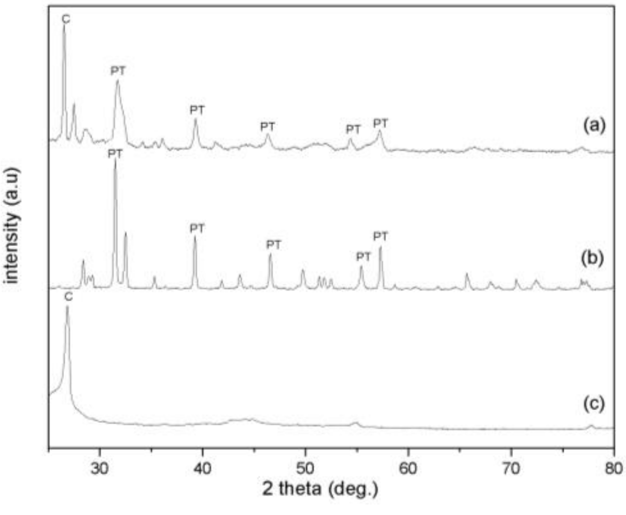

Figure 3. Diffractogram (a) Graphite/$PbTiO_3$ (b) $PbTiO_3$, and (c) Graphite

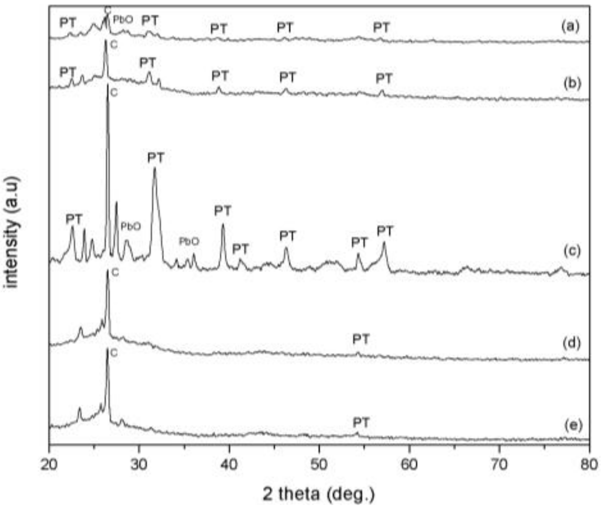

Figure 4. Diffractogram of Graphite/$PbTiO_3$ (a) 1/3; (b) 1/2; (c) 1/1; (d) 2/1; (e) 3/1 [10]

graphite. Moreover, it was also found a peak at 1323.22 cm^{-1} typically Pb–O vibrations. The Pb–O peak intensity increased by increasing of $PbTiO_3$ ratio to graphite.

Scanning Electron Microscopy (SEM) was utilized to evaluate material surface morphological structure, so that the differences of morphological structure between graphite and graphite/$PbTiO_3$ can be microscopically observed. Growing of $PbTiO_3$ in the graphite surfaces was detected by comparing morphological structure of graphite (Figure 7a) with graphite/$PbTiO_3$ (Figure 7b). The growth of $PbTiO_3$ in the graphite surfaces was shown by the presence of white layers attaching on the graphite surfaces thus the graphite pores was covered and the resulted composites to be denser than the origin graphite.

3.3 Photocatalytic degradation

Photocatalytic degradation (photodegradation) is one of methods to decrease the methyl violet dye concentration aided by photons (light). The applied light source was 9 Watt UV lamps and performed for 30 minutes in a black box reactor. The Photodegradation of methyl violet dye by various Graphite/$PbTiO_3$ ratio was aimed to determine the optimal mass ratio based on its ability to degrade the methyl violet dye observed from the decline in the

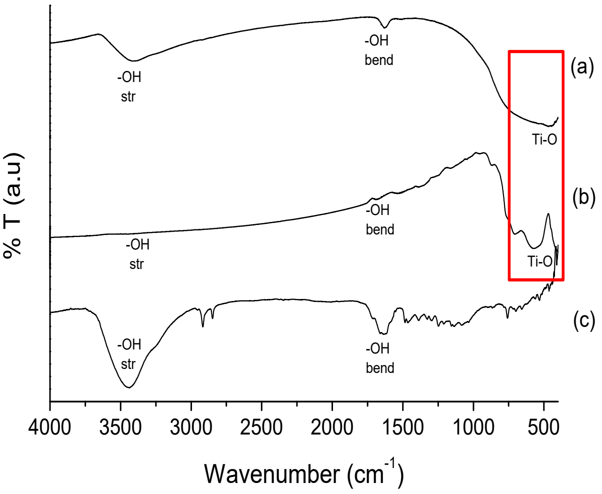

Figure 5. Infrared spectra of (a) TiO_2, (b) $PbTiO_3$ and (c) Graphite

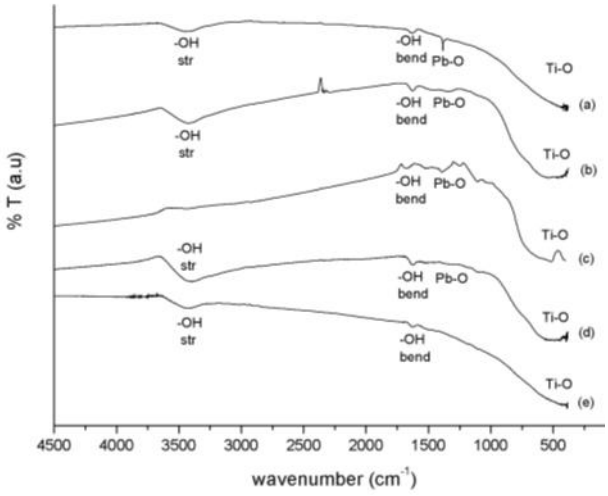

Figure 6. Infrared spectra of (a) Graphite/$PbTiO_3$ = 1/3, (b) Graphite/$PbTiO_3$= 1/2, (c) Graphite/$PbTiO_3$ = 1/1, (d) Graphite/$PbTiO_3$ = 2/1, dan (e) Graphite/$PbTiO_3$ = 3/1

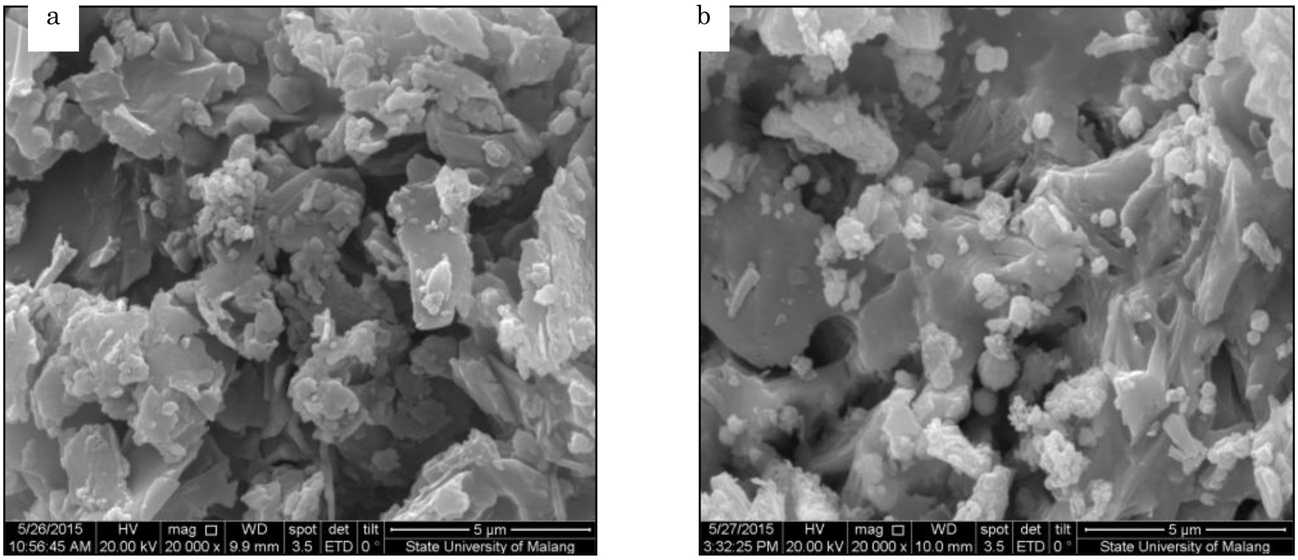

Figure 7. Morphological structure of (a) Graphite and (b) Graphite/$PbTiO_3$ composites (20.000X)

value of the absorbance at a wavelength of 586 nm.

In Figure 8 can be observed percentage of methyl violet dye degradation with initial concentration of 5 ppm processed for 30 minutes. Based on the experimental results, the optimum photodegradation was achieved at Graphite/$PbTiO_3$ ratio 1/1. This is consistent with results revealed by XRD data with best crystallinity at Graphite/$PbTiO_3$ ratio 1:1. In addition, this ratio balanced the process between the $PbTiO_3$ photocatalytic activity and dye adsorption by graphite.

Chemically, photocatalytic degradation process is initiated by reduction-oxidation reaction mechanism where the hole^{+} at valence band reacts with adsorbed water in the material surfaces to form a hydroxyl radical. Additionally, electrons of conduction band could reduce the adsorbed oxygen to generate a hydroxyl radical [11], as presented in equation 1-5.

$$TiO_2 + hv \rightarrow hole^{+} + e^{-} \tag{1}$$

$$hole^{+} + H_2O \rightarrow OH^{\cdot} + H^{+} \tag{2}$$

$$H_2O \leftrightarrow H^{+} + OH^{-} \tag{3}$$

$$hole^{+} + OH^{-} \rightarrow OH^{\cdot} \tag{4}$$

$$OH^{\cdot} + \text{substrat } (dye) \rightarrow \text{product} \tag{5}$$

However, if there are an electron (e^{-}_{cb}) involved to react with oxygen, then the reaction follows the Equation 6-10. The TiO_2 irradiated with energy that more than its bandgap energy (> 3.2 eV) will created an electron in conduction band and hole at valence band. The created electron will reacted with O_2 adsorbed in Ti(III) sites and reduced it to be superoxide radical anion ($O_2^{\cdot -}$). The formed hole oxidized either organic molecules or OH^{-} ions, and the H_2O molecules adsorbed in TiO_2 surfaces become radical $OH^{\cdot}$. Together, both hydroxyl radical anion and $O_2^{\cdot -}$ known as oxidizing agent on photocatalytic process [12].

$$e^{-}_{cb} + O_2 \rightarrow O_2^{\cdot -} \tag{6}$$

$$2O_2^{\cdot -} + 2H_2O \rightarrow H_2O_2 + 2OH^{-} + O_2 \tag{7}$$

$$H_2O_2 + e^{-} \rightarrow OH^{\cdot} + OH^{-} \tag{8}$$

$$OH^{-} + hole^{+} \rightarrow OH^{\cdot} \tag{9}$$

$$OH^{\cdot} + \text{substrat } (dye) \rightarrow \text{product} \tag{10}$$

Based on this result, the optimum photodegradation of methyl violet was achieved at Graphite/$PbTiO_3$ ratio 1/1 up to 92.20 %.

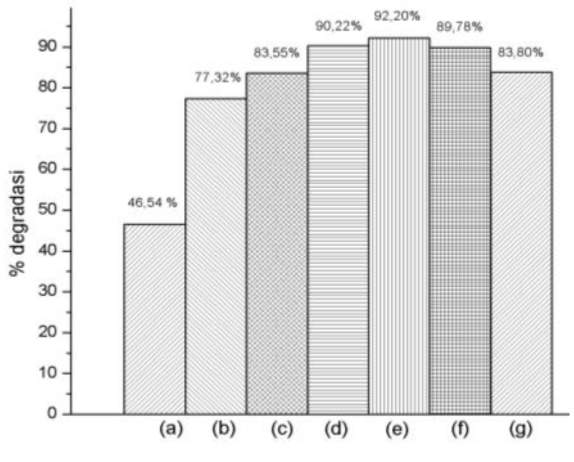

Figure 8. Degradation percentage using materials (a) Graphite, (b) TiO_2, (c) Graphite/$PbTiO_3$= 1/3, (d) Graphite/$PbTiO_3$ = 1/2, (e) Graphite/$PbTiO_3$= 1/1, (f) Graphite/$PbTiO_3$ = 2/1, and (g) Graphite/$PbTiO_3$ = 3/1

3.4 Photo-electrocatalytic degradation

Photo-electrocatalytic degradation combined the photodegradation and electrodegradation methods. With the assistance of light energy and electricity are expected more effective process to degrade the dye. Graphite/$PbTiO_3$ composite act as electrodes on the positive pole (anode). Using the KCl in photo-electrodegradation system serves as a medium taking place quickly to degrade the dye.

Degradation of methyl violet performed because of the electrocatalytic and photocatalytic processes. By placing graphite electrode in catode and the graphite/$PbTiO_3$ composite in anode, the possible reaction probably occurred at each electrodes following equation 11-21. The outside potential given to the system is not only can separating electrons on conductive band from oxidation process, but also reducing the electron-hole recombination and separating the oxidation and reduction sides [13]. TiO_2 is also electrochemically oxidized forming electron (e^{-}_{cb}) and hole (h^{+}_{vb}). The hole (h^{+}_{vb}) could initiated the oxidation reaction and in other side the e^{-}_{cb} initiated reduction reaction in the semiconductor surfaces [14]. The occurring reduction-oxidation reaction mechanism is that h^{+}_{vb} oxidized water or hydroxyl group of methyl violet adsorbed in the material surfaces to form a hydroxyl radical ($OH^{\cdot}$). However, in the same times, e^{-}_{cb} reduced the adsorbed oxygen to form superoxide and hydroperoxide radical anions [11].

Catode

$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-} \tag{11}$$

Anode

Electrocatalytic process

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (12)$$

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \quad (13)$$

Photocatalytic Process

$$PbTiO_3 + hu \rightarrow h^+_{vb} + e^-_{cb} \quad (14)$$

$$e^-_{cb} + O_2 \rightarrow O_2^\cdot \quad (15)$$

$$2O_2^\cdot + 2H_2O \rightarrow H_2O_2 + 2OH^- + O_2 \quad (16)$$

$$H_2O_2 + e^-_{cb} \rightarrow OH^\cdot + OH^- \quad (17)$$

$$h^+_{vb} + OH^- \rightarrow OH^\cdot \quad (18)$$

$$h^+_{vb} + H_2O \rightarrow H^+ + OH^\cdot \quad (19)$$

$$OH^\cdot + \text{methyl violet} \rightarrow \text{simple compound} \quad (20)$$

$$O_2^\cdot + \text{methyl violet} \rightarrow \text{simple compound} \quad (21)$$

Photo-electrodegradation was performed by irradiating 9 watt UV lamp at voltage variation by 7.5, 10, and 12.5 V. Providing positive potential on photo-electrodegradation process, it resulted electrons generated by the excitation of TiO_2 with a faster flow rate thus the photodegradation of methyl violet occurred. The percentage degradation of methyl violet dye concentration in the 30 minutes can be seen in Figure 9.

Generally, the addition of electrical charge enhanced the dye degradation to form a simple compound. However, based on this experiments, the best applied electrical charge was achieved at 10 V with degradation value up to 94%. Since, the addition of 12.5 V could be attributed the electron flow in electrode becoming faster thus the ion moving from anode to catode also faster. Consequently, the anode ability to adsorb the dyes molecules was limited due to it cannot balancing the ion flow rate in the solution. Moreover, the result of applied high electrical charge produced more gasses just like Cl_2 and H_2 in bulky solution which in turn the surrounding electrode prevents degradation process of dyes by Graphite/$PbTiO_3$ composites. Therefore, the photoelectron-degradation is still not significant to improve methyl violet degradation. But the photoelectrocatalytic may important and significantly improve the degradation when the dyes concentration is higher.

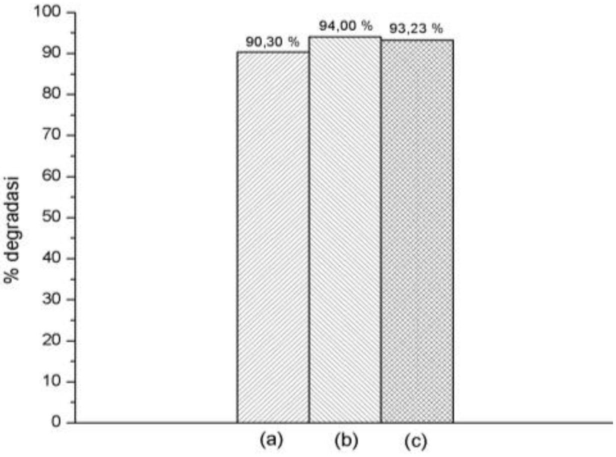

Figure 9. Percentage of photocatalytic degradation of methyl violet in the 30 minutes with a variation of the potential by (a) 7.5 V, (b) 10 V, and (c) 12.5 V

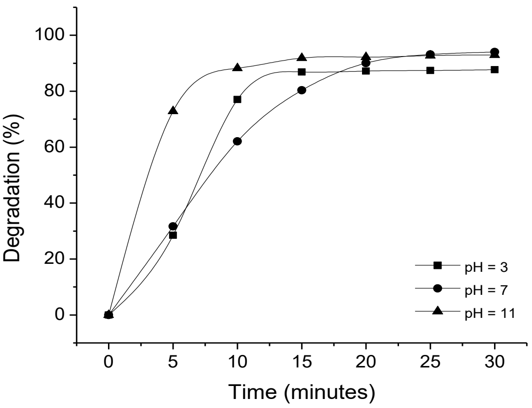

Figure 10. Degradation percentages trend of methyl violet on different pH condition at 10 V

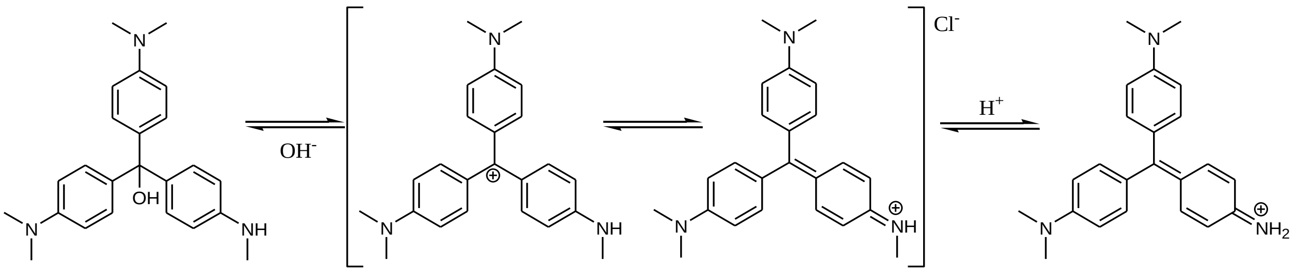

Figure 11. Methyl violet chemical structure at acid and basic condition

3.5 Effect of pH on photoelectrocatalytic degradation of methyl violet

On of condition should be noticed influencing the photoelectron-degradation of methyl violet, is pH condition. In this study, we carried out photoelectron-degradation process at three pH condition, i.e. 3 (acid), 7 (neutral), and 11 (base). The testing was conducted at variation of times with electrical charge by 10 V. The degradation trend of methyl violet toward pH condition was showed in Figure 10. In the initial stage, methyl violet showed higher degradation achieved at basic condition (pH = 11). However, at the equilibrium state, the best condition is in the neutral condition (pH =7) with degradation percentage by 94.00 %. At the neutral condition, the dyes will be degraded into anion and cationic substances. However, by decreasing the pH (acid condition), the presence of H^+ undergoes chemically reaction with nitrogen atom in methyl violet chemical structure by substituting methyl group [15], as illustrated in Figure 11. In this stage, by the formation of new structure of methyl violet containing N atom bounded with two hydrogen atom to form $-NH_2$, made the methyl violet harder to interact with anodes since it tend to be more partial positive (δ^+) than before causing the chromophore group to further away from the anode due to the charge interpolation. Consequently, degradation of methyl violet at acid condition was lower compared to others. Another reason also came from the presence of Cl_2 gas generated from HCl. The presence of the Cl_2 gas will coated the electrode surfaces preventing the degradation process.

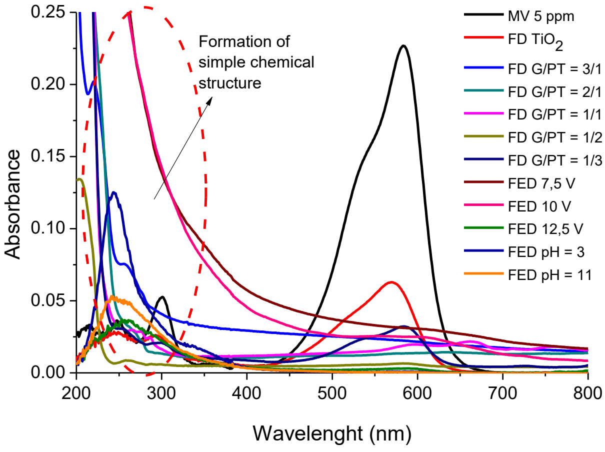

Figure 12. UV-Vis absorbance spectra of methyl violet before and after degradation

At the basic condition, since the methyl violet contain aromatic rings having resonance effect, the OH^- substances (represented as basic condition), chemically interacted with cationic site at chromophore group. The oxygen atom on $-OH$ group is electronegative and it has pair of free electrons which able to fill the electron void at the anode. Therefore, the ability to degrade the methyl violet at basic condition was higher than at the acid. Moreover, the basic condition also predisposed the interaction between dyes molecules and graphite electrode surfaces. By increasing of anionic group number in the electrode surfaces, the cation from chromophore group will be easily to attach in the graphite electrode surfaces. Subsequently, the degradation ability of electrodes was also enhanced.

Qualitative analysis of methyl violet degradation using UV-Vis spectrophotometer was carried out to proofing the degradation of methyl violet structure into simple chemical substances. Figure 12 reveals the UV-Vis spectra of methyl violet before and after degradation recorded from 200-800 nm. The maximum wavelength of methyl violet at 586 nm after degradation decreased indicating the decreasing of methyl violet concentration in solution. Moreover, it was also observed that after degradation process at all pH condition appeared new absorbance peak around 200-350 nm. It indicated that the methyl violet structure degraded or transformed into simple chemical structure.

4. Conclusion

The composition of the mass ratio between graphite and $PbTiO_3$ of Graphite/$PbTiO_3$ composite electrode influenced the formed crystals structure and its ability to degrade the dye. By using photodegradation method, the effectiveness of Graphite/$PbTiO_3$ composite performance was achieved at a ratio of 1/1 degrading methyl violet until 92.20 %. Meanwhile, effectiveness of photoelectrocatalyst of Graphite/$PbTiO_3$ composite electrode was accomplished at 10 V and neutral pH (pH = 7) with degradation percentages reaches up to 94.00 %. However, the photoelectrodegradation is still not significant to improve methyl violet degradation.

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