Photocatalytic and Photoelectrocatalytic Degradation of Methyl Orange Using Graphite/$PbTiO_3$ Composite

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ABSTRACT

Synthesis of graphite/$PbTiO_3$ composite as a catalyst in photodegradation and photoelectrodegradation process of methyl orange have been conducted. The purposes of this research are to study the effect of radiation time, composition of composite, voltage and pH of solution for methyl orange degradation. Photodegradation process of methyl orange was carried out for 5; 10; 15; 20; 25 and 30 min. Ratio of graphite : $PbTiO_3$ (w/w) were varied at 1:3; 1:2; 1:1; 2:1 and 3:1. Meanwhile, the applied voltages were 7.5; 10 and 12.5 V and the photoelectrodegradation was conducted under pH condition of 3; 7; and 11, respectively. The result showed that optimum composition of graphite/$PbTiO_3$ in the methyl orange photodegradation was obtained at 1:1 ratio for 30 min with degradation up to 90.43% ± 0.062. The degradation reaction follows first order reaction with a rate constant of 0.0688 min^{-1}. The optimum voltage is 10 V, in which it reduced the methyl orange concentration up to 92.65% ± 0 with a rate constant 0.0941 min^{-1} for first order reaction. The optimum pH is pH = 11, that provide methyl orange reduction up to 95.28% ± 0.082.

***Keywords**: graphite/$PbTiO_3$; methyl orange (MO); photodegradation; photoelectrodegradation*

ABSTRAK

Penelitian tentang sintesis komposit grafit/$PbTiO_3$ sebagai katalis fotodegradasi dan fotoelektrodegradasi metil oranye telah dilaksanakan. Penelitian ini bertujuan untuk mengetahui pengaruh waktu radiasi, komposisi komposit grafit/$PbTiO_3$, beda potensial, dan pH larutan terhadap degradasi metil oranye. Fotodegradasi metil oranye dilakukan dengan waktu radiasi selama 5, 10, 15, 20, 25, dan 30 menit dengan rasio komposisi grafit/$PbTiO_3$ 1:3, 1:2, 1:1, 2:1, 3:1. Sedangkan fotoelektrodegrasi metil oranye dilaksanakan dengan beda potesial 7,5; 10,0; dan 12,5 V dengan kondisi pH larutan sebesar 3, 7, dan 11. Hasil penelitian menunjukkan komposisi optimum grafit/$PbTiO_3$ dalam degradasi metil oranye adalah 1:1 selama 30 menit hingga 90,43% ± 0,062. Fotodegradasi metil oranye mengikuti orde reaksi 1 dengan konstanta laju reaksi 0,0688 $menit^{-1}$. Beda potensial optimum fotoelektrodegradasi metil oranye diperoleh pada 10 V hingga 92,65% dan mengikuti orde reaksi 1 dengan konstanta laju reaksi sebesar 0,0941 $menit^{-1}$. Sedangkan pH optimum adalah pH = 11 dengan degradasi hingga 95,28% ± 0,082.

***Kata Kunci**: grafit/ $PbTiO_3$; metil oranye (MO); fotodegradasi; fotoelektrodegradasi*

INTRODUCTION

Titanium dioxide (TiO_2) has been widely used in various application in recent years, such as for purification of water and air, destruction of microorganism such as bacteria and viruses, the manufacture of hydrogen gas from water [1], as well as the photocatalyst on the degradation process an organic pollutant [2-7]. TiO_2 widely applied as a photocatalyst because it has a high photoactivity, inert, inexpensive and non-toxic [8-9]. However, TiO_2 still has disadvantages about bandgap (E_g), which is TiO_2 has wide bandgap (E_g) (3.2 eV) and its ability to experience recombination of electron-hole so that decreasing of catalytic activity [10]. To improve the catalytic ability, then the modification to perform the synthesis of TiO_2 compounds derivative such as $PbTiO_3$ in order to obtained material that has a better catalytic ability. $PbTiO_3$ has a band gap energy smaller than TiO_2 i.e. 2.75 eV. Therefore, the excitation of electron from valence band to conduction band might occur easier [15].

Pb oxide is a semiconductor material from transition metal ion Pb^{2+} is known to absorb visible light because it has small band gap energy [12]. In addition, Pb oxide has a high conductivity, therefore it also widely used as an electrode for the degradation of organic pollutants [13-14]. To optimize of degradation ability of $PbTiO_3$, then addition of graphite to form graphite/$PbTiO_3$ composite. This study, use graphite

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waste from a dry cell battery. Graphite is an electrode with high resistant at high temperature [15]. Moreover, graphite is widely used as an adsorbent for organic pollutants and also as an electrode for photoelectrocatalytic process due to its high electrical conductivity [16-20].

In this research, graphite/$PbTiO_3$ composite powder was prepared by sol-gel method. The powder then to be used in photocatalytic process. In addition, this research also prepared an electrode from the composite which was used for photoelectrocatalytic process. The crystalline structure and surface morphology of graphite/$PbTiO_3$ composite were analyzed with XRD and SEM. The effect of the ratio of graphite:$PbTiO_3$ was studied. The photocatalytic oxidation of Methyl Orange (MO) (Fig. 1) using grafit/$PbTiO_3$ composite powder with various ratio graphite and $PbTiO_3$ were investigated. The photoelecrocatalytic ability of this composite and the effect of potential and pH on this photoelectrocatalytic process were discussed.

EXPERIMENTAL SECTION

Materials

Titanium tetraisopropoxide (TTIP) (Aldrich), acetic acid glacial (Merck), $Pb(NO_3)_2$ (Merck), silica glue (Autosil Black Gasket RTV Silicone), graphite from dry cell, nitric acid (Merck), potassium chloride (Merck), hydrochloric acid (Merck), sodium hydroxide (Merck) and methyl orange (Merck).

Instrumentation

Glassware, oven, furnace (Thermolyne 48000), centrifuge (Profuge 6K). X-ray data were collected by using a Shimadzu XRD-6000 based on CuKα radiation. Surface morphology was obtained by a FEI Inspect-S50, EDAX Ametex). Absorbance of dye solution was obtained by a UV-Vis Spectrophotometer (Perkin Elmer Lambda 25). Electrochemical experiments were performed with a DC Power Supply (ATTEN TPR6005S). The two electrode system consisted of a graphite/$PbTiO_3$ electrode as the working electrode and a graphite electrode as the counter electrode, as shown in Fig. 2. The radiation source was a UV lamp (9 W).

Procedure

Pretreatment of graphite

Graphite rods of dry cell batteries was pulverized into fine powder and then soaked with a solution of HNO_3 0.1 M for 24 h. Then, it was filtered, washed with distilled water until continued with filtration and drying at room temperature. The prepared graphite powder then was sieved into 100 mesh size.

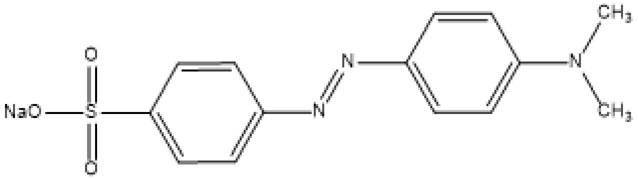

Fig 1. Structure of Methyl Orange

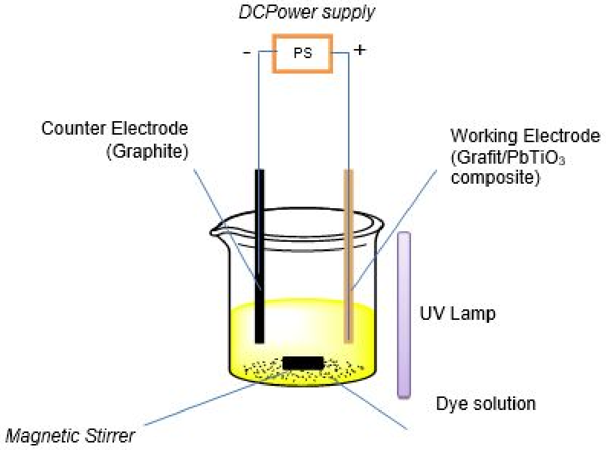

Fig 2. Photoelectrocatalytic degradation reactor

TiO_2 preparation

A 10 mL solution of TTIP was hydrolyzed in the 100 mL acetic acid glacial solution and mixed under vigorous stirring in a waterbath (14 °C) until a solution of TiO_2 nanocrystals was formed. The solution was heated at 90 °C to became a gel. The gel formed, then was heated in the oven at 150 °C for 24 h to undergo an aging process. Next, the TiO_2 xerogel was ground and pulverized into a fine powder and calcined in a furnace at 400 °C for 2 h to obtain nanocrystalline anatase phase.

Preparation of $PbTiO_3$

A 10 mL solution of TTIP was hydrolyzed in the 100 mL acetid acid glacial solution and mixed under vigorous stirring in a waterbath (14 °C) until a solution TiO_2 nanocrystals was formed. The solution was heated at 90 °C until became a gel, $Pb(NO_3)_2$ was added and stirred until became sol. The sol was placed in an oven at 150 °C for 24 h to undergo an aging process. Next, the $PbTiO_3$ xerogel was ground and pulverized into a fine powder and calcined in a furnace at 400 °C for 2 h.

Preparation of graphite/$PbTiO_3$ composite

A 10 mL solution of TTIP was hydrolyzed in the 100 mL acetid acid glacial solution and mixed under vigorous stirring in a waterbath (14 °C) until a solution TiO_2 nanocrystals was formed. The solution was heated at 90 °C until became a gel, $Pb(NO_3)_2$ was added and stirred until became sol. Then, the graphite powder was added to the mixture. The sol was placed in an oven at 150 °C for 24 h to undergo an aging process. Next, the xerogel was ground and pulverized into a fine powder and calcined in a furnace at 400 °C for 2 h.

This method carried out with various of ratio graphite : $PbTiO_3$ (w/w) were 1:3, 1:2, 1:1, 2:1 and 3:1.

Preparation of graphite/$PbTiO_3$ composite electrode

Graphite/$PbTiO_3$ composite powder was mixed with silica glue at a ratio (w/w) 4:1 and it was given the pressure of 1000 psi until an electrode rod was formed. Furthermore, the electrode rod was placed in an oven at 120 °C for 6 h in order to obtain electrode which was ready for use.

Photodegradation of methyl orange

In order to investigate the photocatalytic (PC) activity of the graphite/$PbTiO_3$ composite powder, a series of degradation experiments of methyl orange in aqueous solutions were performed. The initial concentration of methyl orange was 5 mg L^{-1}. The total volume of solution was 20 mL. The front of the reactor was irradiated with a 9 W UV lamp and the progress of the photocatalytic degradation was recorded by UV-VIS spectroscopy. The PC degradation of MO was performed at radiation time of 5 to 30 min and at various ratio graphite and $PbTiO_3$.

Photoelectrodegradation of methyl orange

In order to investigate the photoelectrocatalytic (PEC) activity of the graphite/$PbTiO_3$ composite, a series of degradation experiments of methyl orange in aqueous solutions were performed. The initial concentration of methyl orange was 5 mg L^{-1}, with KCl 0.1 M used as the supporting electrolyte. The total volume of solution was 20 mL. Experiments were carried out with two electrode system. A graphite electrode was used as the counter electrode and a graphite/$PbTiO_3$ composite electrode as the working electrode. The front of the working electrode was irradiated with a 9 W UV lamp and the progress of the photoelectrocatalytic degradation was recorded by UV-VIS spectroscopy. The PEC degradation of MO was performed at voltages of 7.5 V to 12.5 V and at various pH.

RESULT AND DISCUSSION

The Characteristics of TiO_2

The TiO_2 powder prepared by sol-gel method from Titanium tetra isopropoxide precursor was characterized by XRD, as shown in Fig. 3. In this method, TiO_2 synthesis was carried out under acidic condition with acetic acid glacial as solvent.

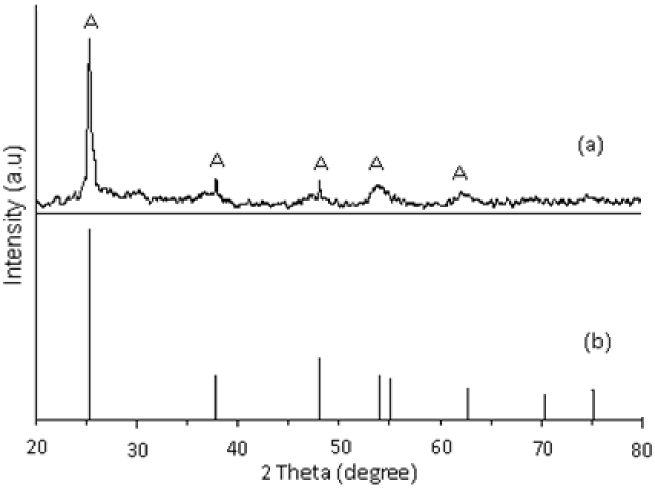

Fig 3. XRD pattern of TiO_2 (a) as compared with JCPDS Standard 86-1157 (b), A = TiO_2 anatase

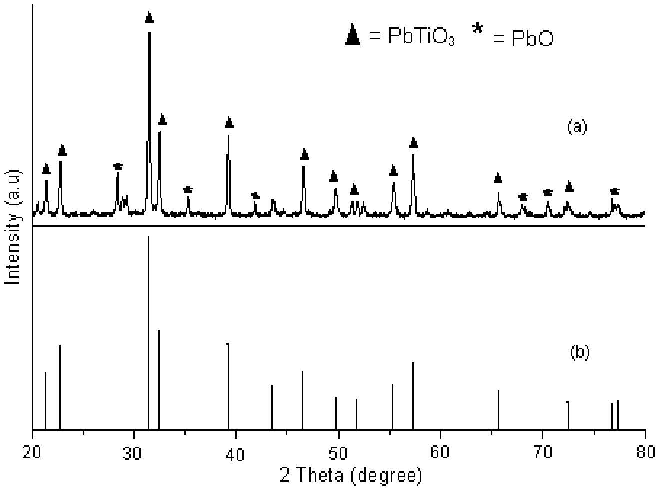

Fig 4. XRD pattern of $PbTiO_3$ (a) as compared with JCPDS Standard 74-2495 (b)

The use of acetic acid glacial as solvent, as well as activating the formation of Ti complexes and via hydrolysis and condensation steps, nano-TiO_2 will be formed. Heating at 90 °C aims to evaporate the solvent thus forming a TiO_2 sol-gel. Whereas, to remove organic impurities and residue of solvents, the sample was heated at 150 °C to form a TiO_2 xerogel. Annealing process at 400 °C is to form anatase phase of TiO_2. Fig. 3 shows that the XRD pattern of TiO_2 exhibits strong diffraction peaks at $2\theta = 25.320°$; $2\theta = 37.860°$ and $2\theta = 48.060°$ indicating that TiO_2 is formed by the anatase phase. All peaks are in a good agreement with the standard spectrum (JCPDS No. 86-1157).

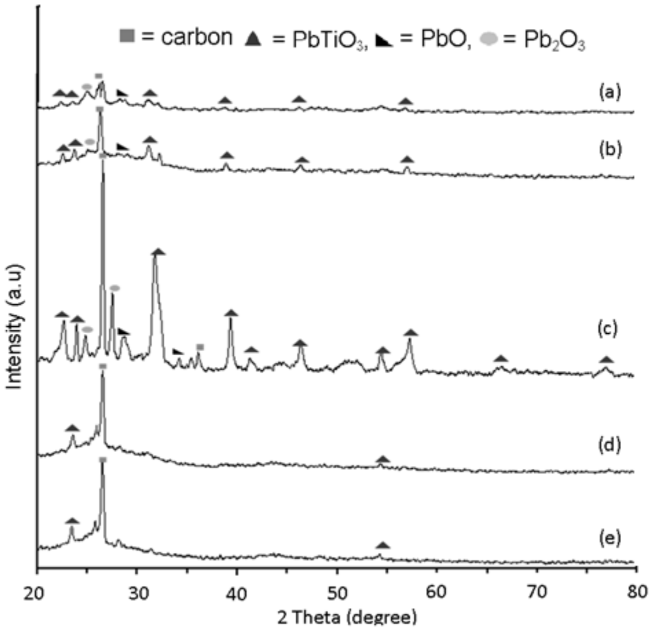

Fig 5. XRD pattern of Graphite/$PbTiO_3$ composite (a) 1:3 (b) 1:2 (c) 1:1 (d) 2:1 (e) 3:1

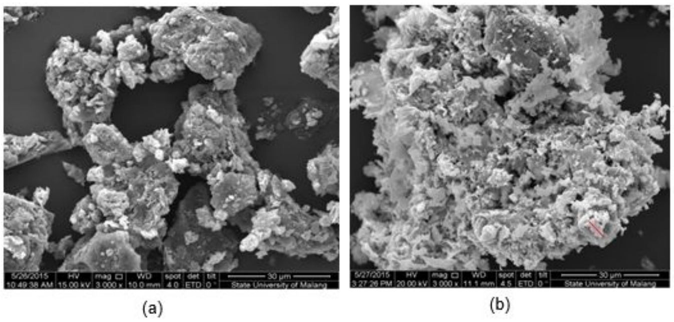

Fig 6. Surface morphology of (a) Graphite (b) Graphite/$PbTiO_3$ composite ratio 1:1

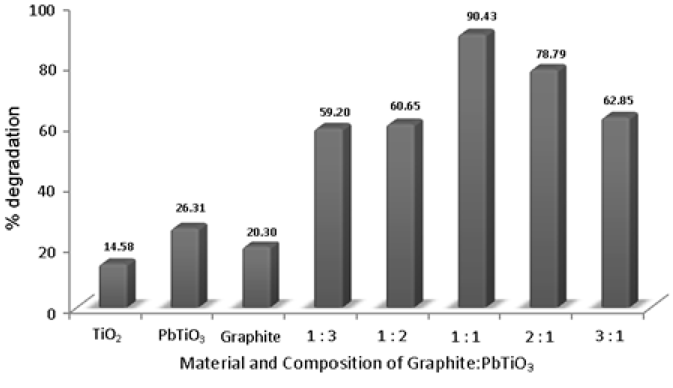

Fig 7. Degradation of MO after PC for 30 minutes with variation composition of Graphite/$PbTiO_3$ composite

The Characteristics of $PbTiO_3$

$PbTiO_3$ compound was obtained after an annealing process at 400 °C for 2 h. Fig. 4 shows that the XRD pattern of $PbTiO_3$ exhibits strong diffraction peaks at $2θ = 21.419°$; $2θ = 22.810°$; $2θ = 31.480°$; $2θ = 32.461°$; $2θ = 39.217°$; $2θ = 43.589°$; $2θ = 46.564°$; $2θ = 49.717°$; $2θ = 51.778°$; $2θ = 55.387°$; $2θ = 57.283°$; $2θ = 65.676°$ and $2θ = 72.420°$. All peaks are in a good agreement with the standard spectrum JCPDS No. 74-2495 for $PbTiO_3$ and No. 85-0711 for PbO. Based on that diffractogram, the abundance of $PbTiO_3$ was 90.16%. Diffractogram of $PbTiO_3$ is completely different with diffractogram of TiO_2 anatase that have strong diffraction peaks at $2θ = 25.320°$; $2θ = 37.860°$ and $2θ = 48.060°$.

The Characteristics of Graphite/$PbTiO_3$ Composite

The graphite/$PbTiO_3$ Composite prepared by sol-gel method and was obtained after an annealing at 400 °C for 2 h was characterized by XRD, as shown in Fig. 5.

Fig. 5 shows a composite material ratio of 1:1 has the most excellent crystallinity than other composites with highest peak of graphite at $2θ = 26.50°$ and highest peak of $PbTiO_3$ at $2θ = 31.48°$. Diffractogram of graphite:$PbTiO_3$ is completely different with diffractogram of TiO_2 anatase that have strong diffraction peaks at $2θ = 25.320°$; $2θ = 37.860°$ and $2θ = 48.060°$. In addition to the composite ratio graphite : $PbTiO_3$ 1:1, crystallinity of Graphite and $PbTiO_3$ becomes lower. The presence of Graphite resulted $PbTiO_3$ crystal regularity becomes lower even amorphous. In the composite ratio of 2:1 and 3:1, with the amount of Graphite more than $PbTiO_3$, resulting in growth of $PbTiO_3$ on Graphite becomes irregular so $PbTiO_3$ crystal regularity becomes very low and were amorphous.

Fig. 6 is the SEM images of Graphite/$PbTiO_3$ composite. The images shows there were growth $PbTiO_3$ on Graphite surface in the form of white fibers so the Graphite pores be closed and Graphite/$PbTiO_3$ composite was looked more solid than Graphite. In addition, the structure of Graphite/$PbTiO_3$ composite was irregular and has average particle grain size of 5.21µm.

Photocatalytic Process of Methyl Orange (MO)

The degradation percentage of MO after photocatalytic (PC) shown in Fig. 7. The curve show that the highest degradation percentage was produced

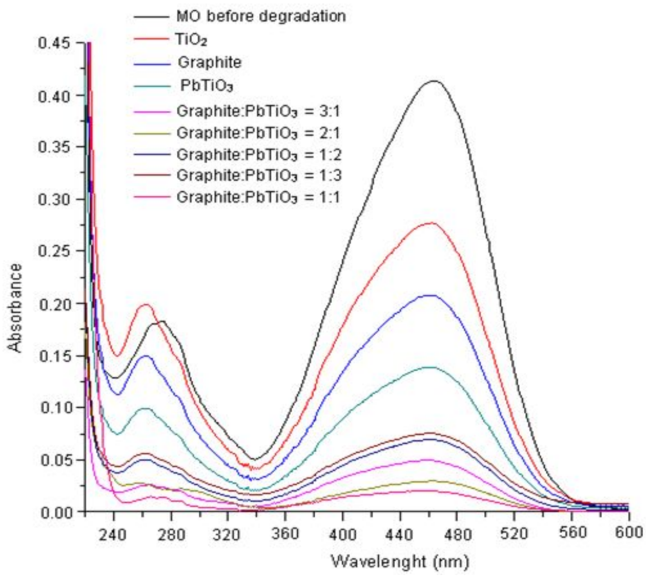

Fig 8. Absorbance of MO before and after degradation using composite

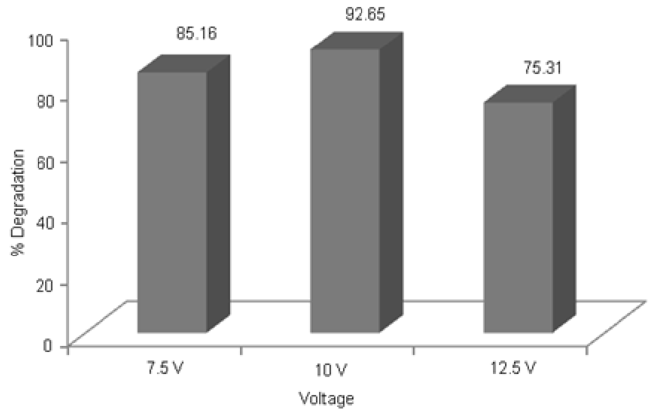

Fig 9. Degradation of MO after PEC for 30 min using Graphite/$PbTiO_3$ composite electrode with ratio of 1:1, and variation of voltage

by PC process with the composite ratio of Graphite/$PbTiO_3$ 1:1 in the amount of 90.43% ± 0.062. Overall, the degradation percentage of MO is higher when the degradation process was conducted with the composite, other than with the single material of TiO_2, $PbTiO_3$ and Graphite. This suggested that addition of Graphite and Pb can increase photocatalytic activity of TiO_2 in degradation of MO.

Increasing the concentration of Graphite in the composite, it also increases the photocatalytic activity. However, after reaching the optimum condition (1:1), the activity was decreases. This is due to the Graphite/$PbTiO_3$ composite ratio of 1:1, spread of $PbTiO_3$ on Graphite evenly which will lead to synergy between the adsorption activity of Graphite and the photocatalytic activity of $PbTiO_3$ and led to a high catalytic activity. In addition, the crystallinity of the composite Graphite/$PbTiO_3$ 1:1 is highest so that the excitation of electron and hole formation becomes easier and lead to the degradation of MO to be more effective.

When amount of Graphite in composite was too much, photocatalytic activity also decreased. The greater amount of Graphite in the composite, the amount of free Graphite will be higher. The presence of free Graphite was likely to cause the interaction between photons and $PbTiO_3$ be hampered so photons were not able to reach the surface of $PbTiO_3$ and catalytic activity was decreases. Based on the calculations, the photodegradation kinetic of MO using Graphite/$PbTiO_3$ composite ratio of 1:1 was likely followed first order kinetics with a reaction rate constant of 0.0688 min^{-1} (R = 0.979).

Qualitatively, decreasing the concentration of methyl orange is supported by decreasing in absorbance of the solution of MO that has been degraded by Graphite/$PbTiO_3$ shown in Fig. 8.

Influence of Voltage on Photoelectrodegradation Process of MO

Variation of voltage had affected photoelectrodegradation of MO. The highest degradation percentage of MO was produced by 10 volt of applied voltage, i.e. 92.65%. Fig. 9 also shows that the larger voltage applied, the degradation percentage of MO was also getting bigger until the optimal point (voltage = 10 V). This was caused by the larger voltage applied, the current following from cathode to anode were also faster so that the rate of flow of electrons from valence band to conduction band were also getting faster and the catalytic activity of composite material at the anode were increases. However on a voltage 12.5 V, the degradation percentage of MO was decreased in the amount of 75.31% ± 0.041 due to the greater currents following in the electrode so that collisions between electrons accelerated were resulting gases which produce from photoelectrodegradation process cover the surface of anode so that interaction between the UV light and anode was disturbed and decreased photocatalytic activity. In addition, decreasing of photocatalytic activity by giving a voltage of 12.5 V was caused by a decrease in the photocatalytic activity with a voltage of 12.5 V caused by ion dyes are attracted to the anode is very much and not balanced with the ability of the anode to degrade the dye so that the degradation of MO is decreased. Reaction rate constant (*k*) of photoelectrodegradation process was greater than photodegradation process with value k = 0.0941 min^{-1} (R = 0.9867) which shows that addition of electric current from outside can increase the rate of degradation

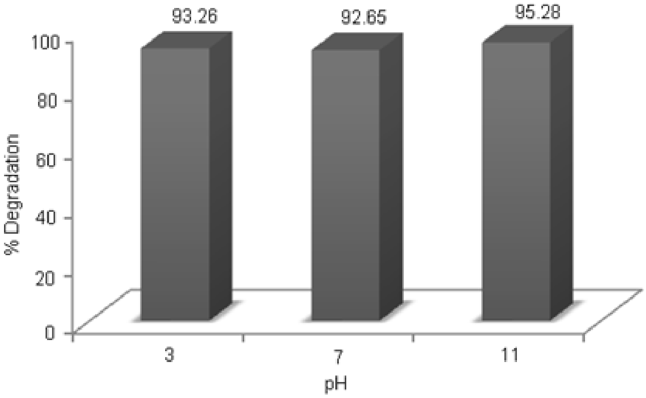

Fig 10. Degradation of MO after PEC for 30 min using Graphite/$PbTiO_3$ composite electrode with ratio 1:1, voltage = 10 V, and variation of pH

MO so that catalyst activity was also increasing.

Influence of pH

Fig. 10 shows that the optimal condition of photoelectrodegradation process of MO at pH 11. The pH was giving influence on degradation of MO because pH affects the structure of MO. At low pH (pH = 3) MO was a cation (positively charged at N), at higher pH (pH = 7), MO were as *zwitterion* and at high pH (pH = 11) MO were as anion. Because of the anionic form, MO will be attached to the anode (Graphite/$PbTiO_3$ composite electrode) were positively charged so that causing decrease in the concentration of MO. Formation of OH radicals on the anode. These OH radicals react with the dye so that the concentration of MO was decreased in the amount of 95.28% ± 0.082.

CONCLUSION

The optimum composition of Graphite/$PbTiO_3$ composite in the methyl orange photodegradation was obtained at 1:1 ratio for 30 min. The methyl orange concentration decreased up to 90.43% ± 0.062. The degradation reaction follows first order reaction with a rate constant of 0.0688 min^{-1}. The optimum voltage is 10 V, in which it reduced the methyl orange concentration up to 92.65% ± 0 with a rate constant 0.0941 min^{-1} for first order reaction. The optimum pH is pH = 11, that provide methyl orange reduction up to 95.28% ± 0.082.

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