International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.9, No.11 pp 113-120, 2016

Photoelectrocatalysis Performance of La_2O_3 Doped TiO_2/Ti Electrode in Degradation of Rhodamine B Organic Compound

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Abstract : Photoelectrocatalytic degradation towards rhodamin B (RhB) organic compound has been conducted by using Lanthanum Oxide (La_2O_3) doped TiO_2/Ti as the working electrode compared to the TiO_2/Ti electrode. The preparation of the La_2O_3 doped TiO_2/Ti working electrode was conducted by using electrodeposition method and TiO_2/Ti was prepared using anodizing method to compare the data related to the activity of the electrodes. The result shows that during fabrication process of La_2O_3 doped TiO_2/Ti electrode the concentration of 0.05 mol/L ion La^{3+} with 10 minutes of doping period caused fine RhB degradation activity from each methods of photodegradation (PD), electrochemistry (EC), photocatalytic (PC), and photoelectrocatalytic (PEC). The optimum condition shows the La_2O_3 doped TiO_2/Ti electrode provided efficient degradation activity of RhB under PEC method by 98.04% compared to the others, while TiO_2/Ti electrode reaches 45.42%.
Key words: photoelectrocatalytic degradation, rhodamin B, La_2O_3, TiO_2/Ti.

Introduction

Pigment pollution has become an environmental issue for years. The emergence of pigment or stain in aquatic environment is triggered by textile industry which always uses and produces stain[1-3]. Textile industry is considered as the main source of environmental pollution because more than 100,000 kinds of pigments are commercially available and more than 800,000 tons of pigments are produced globally[4,5]. If they are accumulated in particular aquatic environment, they will become the industrial wastewater which is hazardous for other beings[6-8]. Various methods have been developed to overcome the problem of textile industry's wastewater, one of them is utilizing oxidation process which is effective in degrading organic pigments in aquatic environment[9-11]. The top priority in developing oxidation method is by using semiconductor as the material of photocatalyst[12,13]. Titanium dioxide (TiO_2) is a semi-conductor material which has been widely studied and applied to solve environmental pollution caused by textile industry's waste because TiO_2 is photocatalyst material which has many potencies, i.e. it is environmentally safe, economical, and harmless; it also possesses high rate of PC activity[14-17].

Many kinds of developments of TiO_2 powder as photocatalyst material have been reported to have some flaws such as the difficulty of photocatalyst recovery which causes new pollutions and the rapid pace of recombination of electron-hole pair which happens to make the process of degradation less-optimum[18,19]. On the

other hand, the application of TiO_2 is obstructed by many obstacles which are materialized since TiO_2 are activated only by UV light ($\lambda \leq 388$) which composition is only around 4-6% of the sunray[20,21].

As one of the solutions for TiO_2 compound, doping method either in the form of metal or non-metal in the surface of Titanium plate is reported increase degradation activity and broaden the performance area of TiO_2 photocatalyst to the visible light[22-25]. Besides, the PEC oxidation process is believed decrease the recombination pace of electron-hole pair and it has better degradation efficiency rather than PC method[26,27].

Some researches show that rare earth doping can increase PC activity TiO_2 [28]. Lanthanum ion (La^{3+}) is reported increase the PC activity of TiO_2[29-31]. There is few researches concerning ion La^{3+} doping for TiO_2 powder and the utilization of La_2O_3 doped TiO_2 to degrade stain. Therefore, it is suggested that researchers conduct studies on the development of La^{3+} doped TiO_2/Ti nanotube-based textile industry waste degradation which is activated by visible light.

In this study, RhB was used as the stain to examine the PEC degradation capacity of La_2O_3 doped TiO_2/Ti electrode. RhB was selected as the analyte due to its broad utilization in textile industry and its finest stability on earth. To examine the performance of La_2O_3 doped TiO_2/Ti electrode, TiO_2/Ti electrode was used as the comparison and it was applied to observe the activity of PEC degradation in RhB organic compound.

Research Methods

1. The fabrication of electrode TiO_2/Ti using anodizing method

Titanium foils 4 cm x 0.70 cm, (1 mm thickness, purity 99.98%, was purchased from Shanxi Yuanlian Rare Metals Limited, China). It was washed by acetone and methanol solutions for 10 minutes. Electrolyte solution was contain 87% glycerol, 0.27 mol/L NH_4F and destilation water. Ti foil was placed as anode and Cu foil as cathode. Anodizing process was carried out for 4 hours at potential 25 V with the distance between the two electrodes was kept at 2.5 cm [32]. TiO_2/Ti electrode was rinsed with distillation water and dried in the air.

2. The fabrication of La^{3+} doped TiO_2/Ti electrode

From anodizing process, the step proceeds to doped La_2O_3 on the surface of TiO_2/Ti using electrodeposition method. The development of operational La_2O_3 doped TiO_2/Ti electrode used several concentration of electrolyte solution that are 0.005 M, 0.01 M, and 0.05 M, then the doping period used in the process of electrodeposition are 5, 10, 15, and 20 minutes.

3. The activity of photoelectrocatalytic degradation

The PEC degradation was applied in UV reactor using two electrode systems, La_2O_3 doped TiO_2/Ti and TiO_2/Ti were used as working electrodes (photo-anode) and Pt wire was used as the countered electrode (cathode). Operational and countered electrodes were connected to DC power supply (GW Instek GPS 30300) and given potential bias as much as 1.5 V. Himawari YZ10RR26 UV Rays 10 Watt was used as the source of ray. The degradation process of RhB was performed by using mixture of 1.2 mg/L pH 4. The UV-Vis Spectrophotometer Agilent 8453 was used to determine the concentration of solution tested.

4. Determining the period and supporting electrolyte in photoelectrocatalytic degradation

The period and supporting electrolyte for PEC degradation were determined by using TiO_2/Ti electrode. TiO_2/Ti was positioned as photo-anode and situated in the solution of RhB 1.2 mg/L containing supporting electrolyte. UV radiation was exposured for 140 minutes to find the effect of degrading period towards the activity of PEC degradation. For the supporting electrolytes, NaCl, Buffer Phosphate Solution (BPS), KNO_3, and Na_2SO_4 which concentration are 0.1 M per each were selected and examined to find their effects towards the activity of PEC degradation. The measurements during the process of determining the period and supporting electrolytes were conducted for 20 minutes.

5. The effect of concentration and doping period of La^{3+} ion

In the PEC cell containing 1.2 mg/L of RhB, La_2O_3 doped TiO_2/Ti electrode was positioned as the anode and Pt wire was places as the cathode. The effect of concentration and doping period of La^{3+} ion for PEC degradation was investigated for 100 minutes. Measurements were conducted every 20 minutes to observe the change of RhB concentration.

Results and Discussions

1. Conceptual process of fabricating TiO_2/Ti and La_2O_3 doped TiO_2/Ti electrodes

The addition of potential bias during anodizing process happened to make Ti^{4+} migrate from Ti metal to the body of the solution and unite to F^- ion forming complex titanium hexafluoride $[TiF_6]^{2-}$. The emergent anions such as O^{2-} and OH^- of water breakdown will migrate along with F^- ion towards the anode. Ti^{4+} ion will unite to either O^{2-} or OH^- and cause oxide production in the surface of Ti metal. F^- ion will break oxide layer formed so it can form pores. The EC reactions occurring during anodizing process are [33]:

Anode: $Ti + 2H_2O \rightarrow TiO_2 + 4H^+ + 4e^-$ (1)

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

Cathode: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (3)

$4H^+ + 4e^- \rightarrow 2H_2$ (4)

Other reaction during anodizing process:

$Ti^{4+} + 6F^- \rightarrow TiF_6^{2-}$ (5)

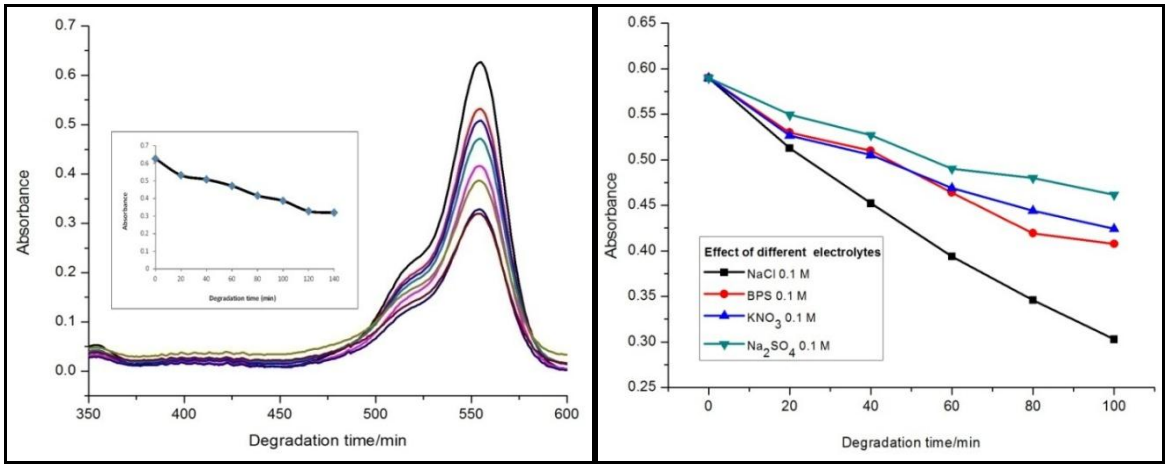
The EC cell containing $La(NO)_3.6H_2O$ electrolyte solution will produce OH^- ion through hydrolysis process of H_2O. OH^- ion will migrate and attach to the surface of TiO_2/Ti electrode and unite to La^{3+} ion forming the sediment of $La(OH)_3$. $La(OH)_3$ doped TiO_2/Ti which will be calcinated to form La_2O_3 doped TiO_2/Ti electrode. The forming reactions of $La(OH)_3$ in TiO_2/Ti electrode are:

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (6)

$La^{3+} + 3OH^- \rightarrow La(OH)_3$ (7)

2. The effect of time and supporting electrolyte in photoelectrocatalytic degradation

The peak of absorption decreases by the increase of degradation time, it clarifies the linear relationship between the decrease of concentration and degradation period. Within the absorption spectrum (Figure 1A), it can be seen that RhB degradation at the 140 minutes showed the smallest peak of degradation and it indicated that the performance of TiO_2/Ti as photocatalyst decreases at the 140 minutes; the occurrence of recombination of electron-hole pair is one of the causes of the decrease, thus the period of degradation was set up by 100 minutes only. Figure 1B shows the effect of supporting electrolyte in degrading RhB by using PEC and it indicates the increase of conductivity property of the solution. The solution containing 0.1M NaCl provided better degradation result than the solution containing 0.1M BPS, KNO_3, and Na_2SO_4. This kind of result has been also proven by Zanoni [27], Carneiro [32], and Fang [19].

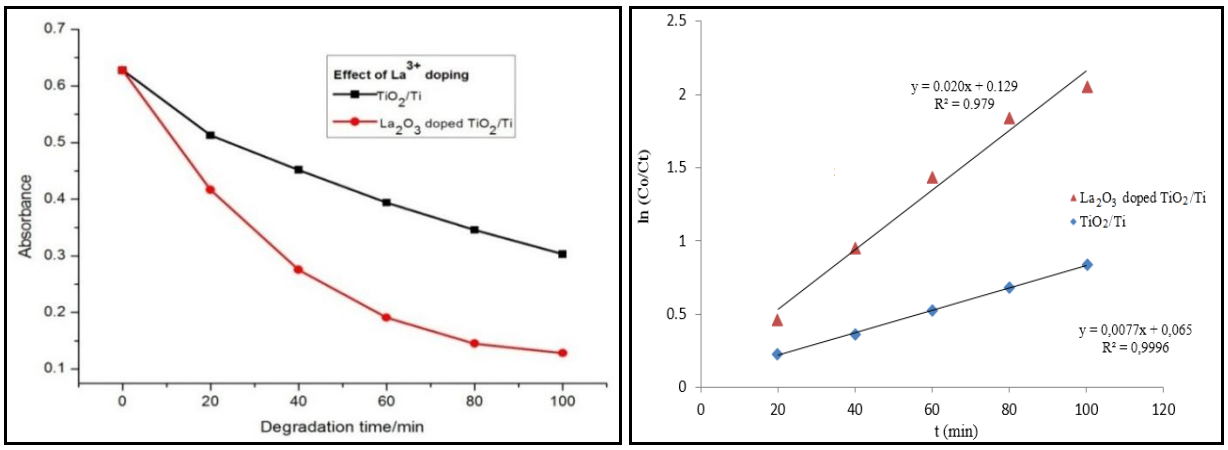


(A) **(B)**

Figure 1. (A) The effect of RhB degradation period by using operational TiO_2/Ti electrode, (B) The effect of supporting electrolyte in RhB degradation

3. The effect of La^{3+} doping towards degradation activity

The presence of La_2O_3 on the surface of TiO_2/Ti increased the degradation activity (Figure 2A), the result shows the rapid decrease of the concentration of RhB over operational La_2O_3 doped TiO_2/Ti electrode. The forming bond of Ti-O-La over the surface of TiO_2 could decrease the recombination of electron-hole pair so the increase of degradation activity of RhB could take place[17]. The kinetics of PEC activity either for La_2O_3 doped TiO_2/Ti or TiO_2/Ti which occurred due to the linear relationship between the concentration and the period shows that the PEC degradation kinetics of both electrodes chased the model of pseudo order 1 represented in Figure 2B[5,34].



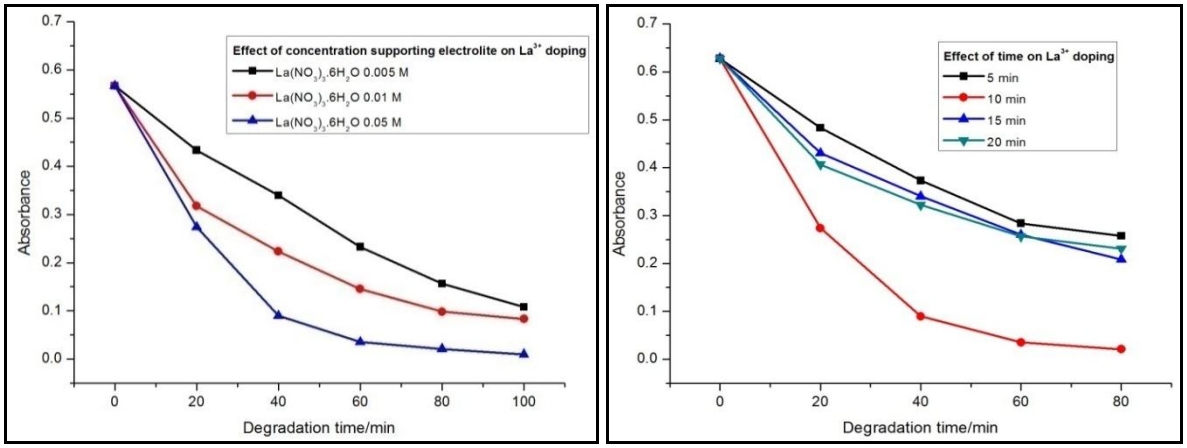
(A) **(B)**

Figure 2. (A) The effect of lanthanum oxide towards RhB degradation, (B) PEC degradation kinetics of La_2O_3 doped TiO_2/Ti and TiO_2/Ti electrodes

4. The effect of concentration and doping period of La^{3+} ion

Figure 3A exhibits the effect of concentration of $La(NO_3)_3.6H_2O$ as the supporting electrolyte used as the source of La^{3+}. The slightest or the vast amount of La^{3+} ion can obstruct the degradation process[17,31,35]. $La(NO_3)_3$ 0.05M provides better activity than those of 0.005M and 0.01M. Figure 3B presents the effect of La^{3+} doping period; doping period which occurred rapidly decreased the efficiency of degradation, while longer period of doping could increase the amount of La^{3+} ion on the surface of TiO_2 and it happened to make the

degradation become less-optimum. Doping period of 10 minutes that provides better degradation activity than those of 5, 15, and 20 minutes of doping periods.

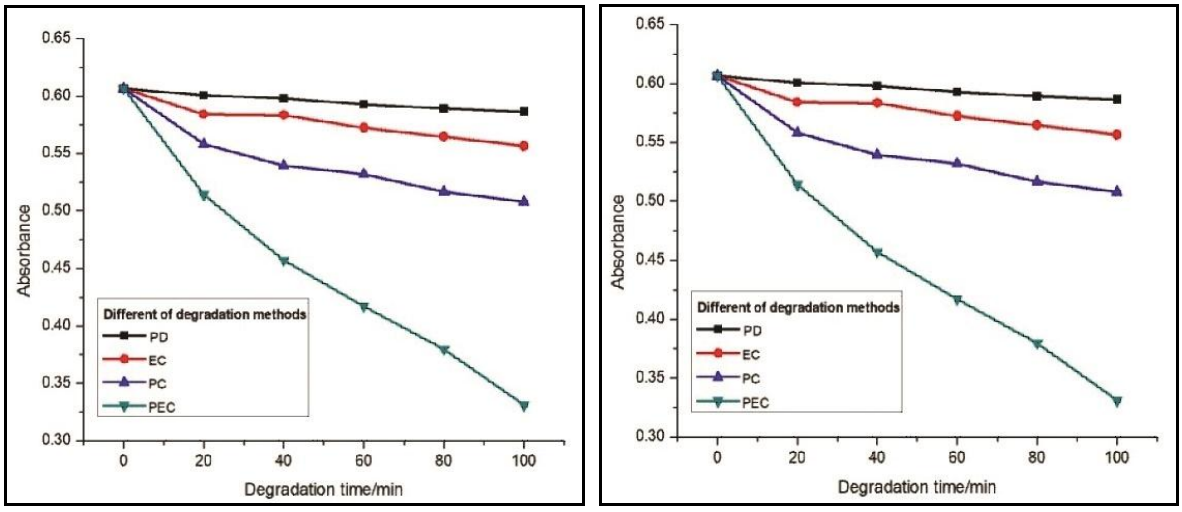


(A) **(B)**

Figure 3. (A) The effect of concentration of $La(NO_3)_3.6H_2O$ as the supporting electrolyte during PEC degradation, (B) The effect of La^{3+} ion doping period during PEC degradation

5. The effect of differences of degradation methods

Four methods of degradation were selected in this study; they are PD, EC, PC, and PEC. Figure 4A shows the effect of degradation method towards TiO_2/Ti electrode. The result shows that PEC method served better result than the methods of PD, EC, and PC, which is as much as 45.42%. Figure 4B shows the effect of degradation methods towards electrode La_2O_3 doped TiO_2/Ti. La_2O_3 doped TiO_2/Ti with the concentration of 0.05 M and 10 minutes doping period was used as the operational electrode. The highest rate of degradation activity is provided by PEC method with the percentage (%) of degradation reaches 98.04%. The rates of degradation activity for PD, PC, and EC methods using La_2O_3 doped TiO_2/Ti electrode are 20.19%, 7.58%, and 2.72%, respectively. The presence of La_2O_3 can increase the adsorption rate of RhB and decrease the recombination rate of electron-hole pair. The high rate of decrease of RhB concentration at the 20 minutes indicated the effect of La_2O_3 for PEC.



(A) **(B)**

Figure 4. Effect of RhB degradation different methods using (A) working of TiO_2/Ti electrode, (B) working of La_2O_3 doped TiO_2/Ti electrode

6. Reproducibility and Stability Test of La_2O_3 doped TiO_2/Ti electrode

Figure 5 shows the result of the reproducibility and stability test of La_2O_3 doped TiO_2/Ti electrode. Reproducibility test was managed by drawing 5 operational electrodes randomly, while for stability test, one electrode was selected and examined repeatedly to identify its degradation activity. Five operational electrodes served the rate of degradation efficiency as much as ≥ 91%. For the stability of the electrode, it can be noticed that there is significant decrease of efficiency of RhB degradation in the fifth measurement.

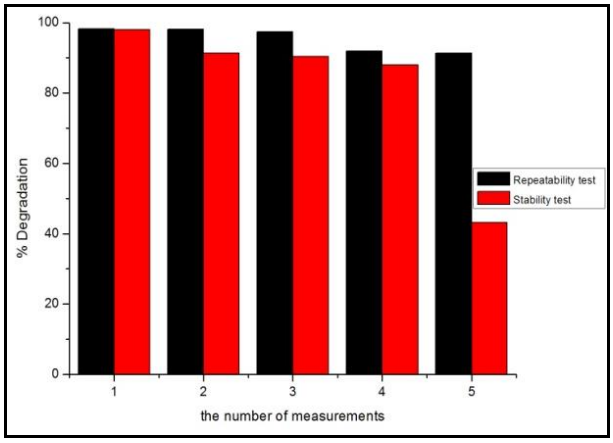


Figure 5. The histogram of reproducibility and stability test of operational La_2O_3 doped TiO_2/Ti electrode

Conclusion

Based on the result of the investigation managed to identify the performance of La_2O_3 doped TiO_2/Ti electrode in degrading stains, it can be concluded that doping method using lanthanum as the dopan can increase stain degrading activity. The combinations of doping and PEC methods are proven effective in increase the rate of stain degradation. La_2O_3 doped TiO_2/Ti Electrode has better degradation activity than TiO_2/Ti electrode does. Furthermore, the addition of potential bias during the process of PEC degradation based on the oxidation potential scores of stains is becoming an interesting issue to be studied in advance.

Acknoledgement

The researcher would like to thank The Ministry of Research, Technology, and Higher Education for the financial support.

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