Photocatalytic Degradation of Yellow-GCN dye using C-N-codoped TiO$_2$ Thin Film in Degradation Reactor Using Visible-Light Irradiation

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ABSTRACT

Yellow-GCN ($C_{28}H_{14}N_2O_2S_2$) textile dye was successfully degraded by photolysis process under solar and visible light irradiation using C-N-codoped TiO$_2$ thin film photocatalyst. Yellow-GCN [120 mg/L] was irradiated by using 2 visible lamps (philips LED 7 watts 600 lumen and 14 watts 1400 lumen) and solar intensity around 25,000 lux with concentration and time variation. Degradation efficiency was measured by spectrophotometer UV-Vis ($\lambda$=300-800 nm). The optimum C-N-codoped TiO$_2$ thin film used under solar irradiation was 5 coatings. From both different light sources can be concluded that degradation under solar irradiation was better than visible light irradiation due to its degradation percentage during 120 minutes was 30.25%.

Key words: yellow-GCN, solar light, visible light, C-N-codoped TiO$_2$, thin film, photocatalyst.

INTRODUCTION

Yellow-GCN can be found in industrial wastewater which has carcinogenic effect. It is synthetic organic dye, stable with aromatic heterocyclic chains. Its stable structure can produce cotton with a longer lifetime dye, unfortunately, effluent consumption contribute negative impact to water ecosystem. The dye influences water characteristic just by impede solar, penetration and decrease photosynthesis cycle process [1]. Thus, it is very important to degrade the dyes into environmentally friendly simple compounds.

Technologies have been developed to reduce or even removal synthetic dyes from wastewater, such as membrane filtration [2], absorption technique [3], coagulation-floucculation [4], biology technique by using microba or pure enzyme [5,6]. As promising alternative, heterogeneous photocatalysis using semiconductor which one of AOPs (Advanced Oxidation Processes) method could be used for dyes wastewater treatment.

Titania (TiO$_2$) is one of semiconductor catalyst which has great potential in organic wastewater treatment [7,8] due to its high catalytic activity and high biological and chemical stability [9]. However, the main deficiency of TiO$_2$ that active only under UV light irradiation because of its large band gap (anatase \(\approx 3.2\) eV) [10]. To increase photocatalytic performance of TiO$_2$, doping TiO$_2$ with other elements is the best way.

TiO$_2$ doping with non metal elements (C, N and S) is the most important method to raise utilization of visible light irradiation in dye wastewater degradation [11]. TiO$_2$ doped carbon and nitrogen show amazing photocatalytic activity than using another TiO$_2$ modification (N-doped TiO$_2$, La-doped TiO$_2$, Fe-doped TiO$_2$, Bi$_2$WO$_6$/TiO$_2$) [12-15]. Mostly, application of photocatalytic processes are widely carried out in slurry system operating using TiO$_2$ or TiO$_2$ modification powder. The major problem in these systems is needed much time and difficult process to
separate and recycle the catalyst powder\[16\]. Thus, to solve this problem semiconductor catalyst powder are coated on supporting substrate to form thin film. Supporting substrate, including glass (2011, Fang Li), glass sphere (2015, V.Vaiano), hollow glass microsphere (2014, Lei Sun), and stainless steel (2003)

C-N-codoped TiO\(_2\) was synthesized by using peroxo sol-gel method. The advantage of this method are using water as solvent and lack of chemical which beneficially low cost, environmental friendly, and simple steps \[17\]. Meanwhile, immobilization of C-N-codoped into glass substrate is formed by dip-coating method.

In previous research, powder of C-N-codoped TiO\(_2\) photocatalyst was used to degrade dyes in aqueous medium and irradiated by solar light without degradator\[18,19\]. Based on its great photocatalytic activity under solar-light irradiation, in this research C-N-codoped TiO\(_2\) in two dimensional system as thin film which is mobilized into glass substrate. With the result that, it could be applied to larger wastewater volume using degradation reactor which was planned. This application became effective, efficient, simple and low cost technology to solve environmental problems.

**MATERIALS AND METHODS**

**Equipments**

Spectrophotometer UV-Vis (S.1000 Secomam Sarcelles, French), Degradator reactor (SFN-Deg 001), Visible light (Phillips LED, 21 watt), analytical balance, and glasses equipments.

**Materials**

Yellow-GCN dyes (C\(_{29}\)H\(_{14}\)N\(_2\)O\(_2\)S\(_2\), Mr = 474.56 g/mol from Silungkang Industry, distilled water, C-N-codoped TiO\(_2\) thin film.

![Figure 1. Structure of Yellow-GCN dyes](image)

**Photocatalytic Activity of C-N-codoped TiO\(_2\) Thin Film**

The photocatalytic activity was evaluated by the degradation of 120 mg/L yellow-GCN aqueous solution. The solution (40 mL) were put into beaker glass which is the container of the degradation reactor. Then, thin film catalyst is inserted into the solution and set spinning at constant speed by the reactor system. The reactor was enclosed in a cabinet during visible irradiation to avoid interference from natural light. While, irradiation under solar light the reactor was open widely. The experiment was carried out under visible light using 2 visible lamps (philips LED 7 watts 600 lumen and 14 watts 1400 lumen) and solar intensity around 25,000 lux. Degradated dyes solution was analyzed at \(\lambda_{\text{max}} = 419\) nm by spectrophotometer UV-Vis (S.1000 Secomam Sarcelles, French).

The degradation percentage of dye from solution at different time interval and condition is shown as :

\[
\% \text{deg} = \frac{A_o - A_t}{A_o} \times 100\%
\]

Where \(A_o\) is the initial absorbance of yellow-GCN and \(A_t\) is absorbance of yellow-GCN at different condition. The effect of C-N-codoped TiO\(_2\) amount on glass substrate and irradiation time on photodegradation of yellow-GCN was tested.

**RESULTS AND DISCUSSION**

**Effect of C-N-codoped TiO\(_2\) amount on glass substrate**

In order to define the best C-N-codoped TiO\(_2\) amount deposited on glass substrate, number of coating was varied into 1, 3, and 5 coating and each was irradiated under solar light for an hour. Figure 2 shown the effect of C-N-codoped TiO\(_2\) amount on glass substrate. The percentage removal of dyes with 1, 3, and 5 coatings about 8.42; 7.55; 11.24\%, respectively. From 3 coatings into 5 coatings evidenced that up number of coating increased the amount of
C-N-codoped TiO$_2$ deposited on glass substrate. Thus, photocatalytic activity increased and the dyes in aqueous solution will be more degraded[19].

![Figure 2. Effect of C-N-codoped TiO$_2$ amount on glass substrate](image)

**Effect of irradiation time under visible and solar light**

![Figure 3. Effect of irradiation time under (a) solar light (b) visible light](image)

Figure 3 shown the effect of irradiation time under both of solar light and visible light irradiation. The percentage removal of dyes increasing by increment of irradiation time. During the photocatalytic reaction, C-N-codoped TiO$_2$ absorbs light to produce electron-hole pair which migrates to the catalyst surface to react with absorbed O$_2$ and H$_2$O, to produce strong oxidizing agents in the form of O$_2^-$ and HO• radicals, respectively, which are the main species responsible for the degradation of organic pollutants[20]. By increasing the irradiation time, C-N-codoped thin film photocatalyst will more produce strong oxidizing agents. Thus, the photocatalytic degradation will increase. From figure 3, we can see that glass substrate has no photocatalytic activity due to its low degradation percentage. The structure compound of yellow-GCN dyes is also very difficult to be degraded naturally. It is shown in figure 3 that degradation percentage without catalyst is only 4.07% and 11.15% under visible light and solar light irradiation, respectively. Highest degradation percentage of yellow-GCN is achieved about 30.25% under solar light irradiation for 120 minutes.
Recyclability of C-N-codeped TiO$_2$ thin film coating

![Graph showing recyclability of C-N-codeped TiO$_2$ thin film coating](image)

Figure 4. Recyclability of C-N-codeped TiO$_2$ thin film after 4 recycling experiments

![Graph showing analysis of Yellow GCN before and after degradation](image)

Figure 5. Analysis of Yellow GCN before and after degradation
Recyclability is one of the most important factors in catalysis research. To confirm the recyclability of C-N-codoped TiO$_2$ thin film with 5 coatings, the photocatalytic decolorization reaction was repeated up to four cycles in different irradiation time under visible light. The results are shown in figure 4. The results demonstrated that there was about 2% reduction of degradation percentage in 30, and 60 minutes of irradiation and about 4% in 90 and 120 minutes of irradiation after four cycles. These results confirm that there is no leaching of C-N-codoped TiO$_2$ from immobilized on glass substrate.

**Analysis using High Performance Liquid Chromatography**

Figure 5 describes that peak high and peak areas of Yellow-GCN decrease after degradation using C-N-codoped TiO$_2$ thin film in degradation reactor under solar-light irradiation, without other peaks appeared.

**CONCLUSION**

Yellow-GCN dyes in aqueous solution was successfully degraded by C-N-codoped TiO$_2$ immobilized on glass substrate. The degradation percentage of 120 mg/L yellow-GCN (40mL) is 4.07% and 11.15% without catalyst under visible and solar light irradiation for 120 minutes, respectively. By the addition of C-N-codoped TiO$_2$ thin film with 5 coatings and set constant spinning speed, the degradation percentage increase to 16.7% and 30.25% under visible and solar light irradiation, respectively. The C-N-codoped TiO$_2$ thin film photocatalyst confirm that there is no leaching while mineralization of dyes occurred. Photocatalytic degradation of yellow-GCN dyes in aqueous solution is more effective under solar light irradiation.

**Acknowledgement**

We would like to express our gratitude to PUPT Grand No.38/UN.16/UPT/LPPM/2016 DP2M DIKTI, Research Centre Andalas University for all the support provided.

**REFERENCES**


