



Photodegradation of Orange F3R Dyes: Effect of Light Sources and the Addition of CN-Codoped TiO₂ Catalyst

Safni M^{1*}, Reza Audina Putri¹, Diana Vanda Wellia², Upita Septiani²

¹Department of Chemistry, Laboratory of Applied Analytical-Chemistry, Andalas University, Padang, West Sumatra, Indonesia

²Department of Chemistry, Laboratory of Material Chemistry, Andalas University, Padang, Indonesia

ABSTRACT

The degradation of orange F3R textile dye (C.I.V at Orange 16; C₂₉H₁₂ClNO₅) has been done by UV-light, visible-light and solar-light irradiation photolysis using C-N-codoped TiO₂ catalyst. Orange F3R dyes are synthetic organic dyes which difficult degraded spontaneously in the environment. The heavy use of these dyes by industry will give negative impact to aquatic life. Degradation of orange F3R by UV-light photolysis is conducted using 10 watt UV lamp ($\lambda=365$ nm). Whereas, the intensity of visible LED light, Phillips 13 W is 2000 lux and solar-light during the degradation of orange F3R is 45.000 lux. All of photolysis method has been done without and with the addition of C-N-codoped catalyst on varied degradation times. Orange F3R dyes could be degraded by 11.82% after 180 min UV-light irradiation without catalyst, and the degradation percentage increase to 39.05% by the addition of 12 mg C-N-codoped TiO₂ catalyst. The irradiation of visible light for 180 min can degrade the orange F3R dyes by 11.83% without catalyst and increase after addition 9 mg C-N-codoped TiO₂ catalyst to 40.86%. While degradation percentage of solar irradiation photolysis is 22.81% without catalyst and increase to 64.12% by the addition of 6 mg C-N-codoped TiO₂ catalyst.

Keywords: Degradation, Photolysis, Vat orange F3R, C-N-codoped TiO₂

INTRODUCTION

Orange F3R is synthetic organic dyes which are classified to vat dyes. Orange F3R is used as dye in textile and widely applied in Sarong industry in Silungkang, Sumatera Barat. The effluent of dye wastewater form industry is mostly discharged into river water [1]. The discharge of highly effluents of synthetic dyes to water causes aesthetic pollution, eutrophication, and inhibit solar-light penetration [2,3]. So that, the dyes have to be removed from the waste water before pouring into the river water. Conventional physicochemical treatment that employs adsorption [4,5], coagulation [6], filtration [7] or ion exchange processes can lead to effective dye decolorization in wastewater. However, such treatment poses further problems such as sludge formation and the processing of the indispensable adsorbent material that needs to be regenerated [8].

Heterogeneous photocatalytic degradation offers an alternative option for decolorizing and reducing dyes wastewater loadings. Titania (TiO₂) is regarded as the most suitable photocatalytic semiconductor due to inertness, non-toxicity [9], highly photoactive, photostable [10], and relatively inexpensive. Titania has been reported successfully degraded dyes by photolysis method, such as Eriochrome Black-T [9], Remazol Yellow Gold RGB, Remazol Blue RGB, and Remazol Carbon [11]. However, all of this photolysis processes required the UV light irradiation due to a wide band gap of TiO₂ anatase (~3.2 eV).

To improve the photocatalytic activity of TiO₂ under visible light, doping non-metal atoms into substitution sites in the crystal structure of TiO₂ seems to be the simplest and promising routes [12]. Thus, the doping techniques of titania have been explored to enhance the Photocatalysis toward visible light [13,14]. The non-metal element (N, C, S, F and P) have been discovered as great potential for enhancing the visible light in TiO₂ materials [15-18].

In previous work, Safni et al. [19,20] had been successfully degraded yellow-GCN which derived to vat dyes using C-N-codoped TiO₂ photocatalyst under UV and solar light irradiation. This work present experiments which conducted to investigate effect of the addition of C-N-codoped TiO₂ catalyst on photodegradation of orange F3R under UV, visible and solar-light irradiation.

EXPERIMENTAL METHODS

Materials

Orange F3R textile dye (C.I.V at Orange 16; C₂₉H₁₂ClNO₅) (Figure 1) was obtained from Silungkang Sarong Industry, Distilled water, C-N-codoped TiO₂ powder was prepared based on Qing et al. [21].

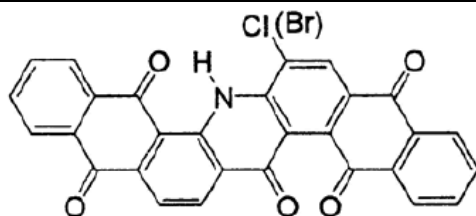


Figure 1: Structure of orange F3R dye

Equipment's

Spectrophotometer UV-Vis (S.1000 Secomam Sarcelles, French), r-HPLC Shimadzu spd 20 A, X' Pert PRO PAN atypical (Phillips Hooland), black irradiation box Visible light (Phillips LED, 13 watt), 10 watt UV lamp ($\lambda=365$ nm) analytical balance, Centrifuge (NASCO) and glasses equipment.

Degradation processes of orange F3R

Degradation of orange F3R dye started from evaluation of the dyes initial concentration. Five sets of orange F3R dye with different concentration from 10-50 mg/l were used as the model pollutant to study the effect of initial concentration. 20 ml of orange F3R solution was placed in petri dish and irradiated for 120 min under UV, visible and solar light at different location. The aliquots were taken and measured spectrophotometrically.

In order to study the effect of photocatalyst mass, a series of 20 ml of 30 mg/l orange F3R solution was degraded by respective mass of 3-15 mg C-N-codoped TiO_2 catalyst. The solution that contained each mass of catalyst was placed in petri dish separately. Then each solution was irradiated by UV, visible and solar light for 120 min. The suspension was taken and centrifuged at 2000 rpm to separate the catalyst from solution and measured spectrophotometrically.

The effect of irradiation time was also studied in this research. A series of 20 ml of 30 mg/l orange F3R solution was added catalyst and then irradiated by UV, visible and solar light. At regular interval, the suspension was taken and centrifuged at 2000 rpm to separate the catalyst from solution. The solution was then measured by spectrophotometer. The degradation percentage of dye from solution at different time interval and condition is calculated by:

$$\% \text{ Degradation} = \frac{A_0 - A_t}{A_0} \times 100\%$$

Where, A_0 is the initial absorbance of orange F3R dyes and A_t is absorbance of orange F3R dyes at different condition.

RESULTS AND DISCUSSION

Spectrophotometer UV-Vis analysis of orange F3R dyes

Orange F3R dye is a vat derivative synthetic organic dye that gives a bright orange color. Analysis of orange vat dye absorption was performed using UV-Vis spectrophotometer at a wavelength of 400-800 nm. Figure 2 shows the UV-Vis spectrum of orange vat dye solution at different concentration. The spectrum showed the maximum absorption of orange F3R dye at a 540 nm wavelength.

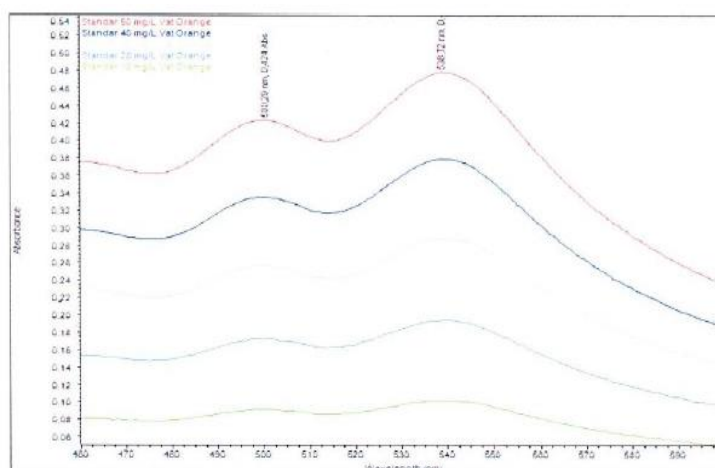


Figure 2: Absorption spectrum of orange F3R dye at different concentration

Effect of initial dyes concentration

Figure 3 shows the effect of initial concentration of orange F3R dyes solution to the degradation percentage under UV, Visible and Solar-light irradiation. The result demonstrated that the degradation percentage of orange F3R was decreased with increase in initial dye concentration from 10-50 mg/l. Since increasing the concentration of orange F3R solution will also increase the number of dyes molecules. While the different concentration solution of orange F3R was irradiated by the light at the same time. So that, there will be more undegraded dye molecules.

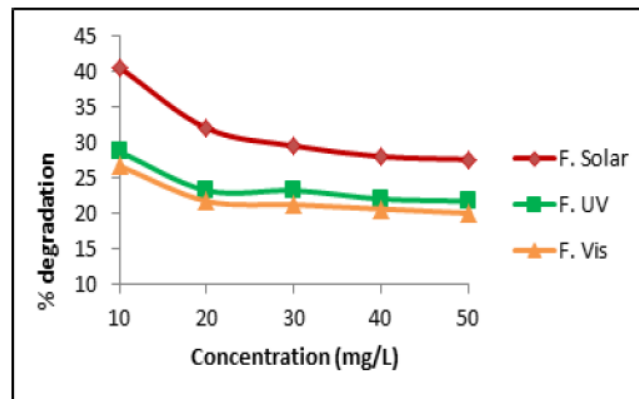


Figure 3: Effect of initial orange F3R dye concentration under different light sources

Effect of CN-codoped TiO₂ catalyst addition

Figure 4 shows the degradation percentage of 30 mg/l orange F3R dye by various amount of CN-codoped TiO₂ loading under different light sources of irradiation. The degradation percentage increased by increasing catalyst loading until 6 mg from 17.4-53.9% under solar irradiation for 120 min, 9 mg under visible light irradiation, and 12 mg under UV light irradiation. The addition of more catalyst began to be slightly decreased.

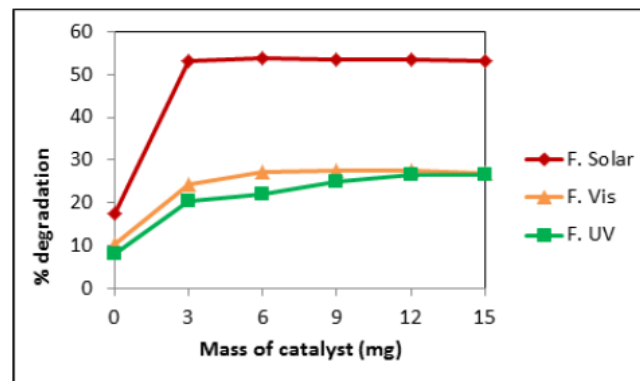


Figure 4: Effect of catalyst loading under different light sources

By increasing mass of C-N-codoped TiO₂ catalyst will produce more hydroxyl radical, •OH, as the oxidation species active which eventually caused the photocatalytic activity of CN-codoped TiO₂ increased. However, by further increasing mass of catalyst the degradation percentage decrease due to the accumulation of catalyst in a dye solution which cause scattering light and reducing light penetration into the vat dye solution during the process of photolysis [12,18,19].

Effect of irradiation time

The efficiency of photolysis methods with and without the addition of catalyst based on Advanced Oxidation Processes (AOPs) is also influenced by the length of irradiation of light sources. Efficient method means the faster dye compounds to be degraded. Figure 5 shows the effect of irradiation time (30, 60, 90, 120, 150 and 180 min) without and with the addition of CN-codoped TiO₂ photocatalyst under various light sources.

Both of photolysis without and with the addition of CN-codoped TiO₂ catalyst shows increasing irradiation time will increase the degradation percentage. Since by increasing the irradiation time, will produce more the active species, hydroxyl radical (•OH) [22]. Then the hydroxyl radical will degrade dye compound. Within 30 min irradiation time under UV, visible and solar light irradiation, the degradation percentage obtained by 23.72%, 29.75% and 36.21% respectively. Otherwise, after irradiation for 180 min the degradation percentage increases to 39.05%, 40.86% and 64.12% respectively.

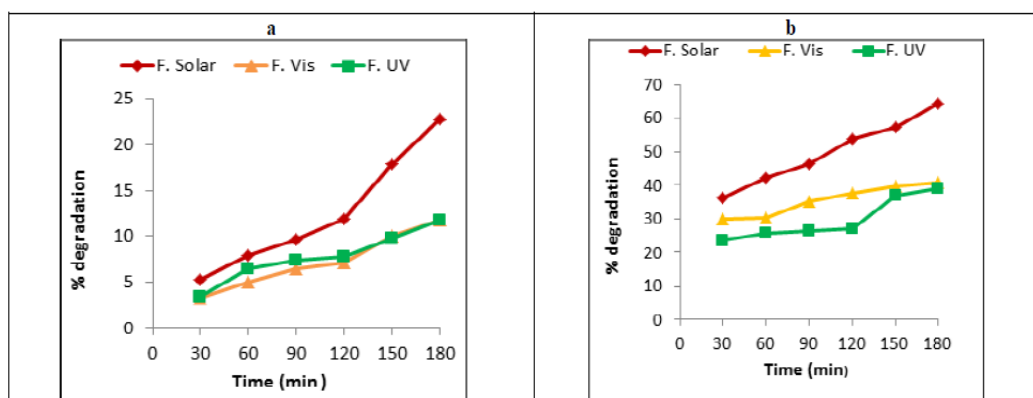


Figure 5: Effect of irradiation time (a) without the addition of catalyst (b) with the addition of catalyst under various light sources

By compared the data from Figure 5a and 5b, it is clearly seen that the addition of CN-codoped TiO₂ catalyst plays a key role in photodegradation of orange F3R. The degradation percentage increase significantly after the addition of CN-codoped TiO₂ catalyst. It can prove that hydroxyl radical ($\bullet\text{OH}$) is more produced by the addition of CN-codoped TiO₂ catalyst.

Effect of light sources

Figure 6 shows the effect of different light sources in photolysis and photocatalytic. There are three types of light used in the process of photolysis and photocatalytic substance F3R orange color, which is UV-A ($\lambda=365$ nm), visible light (2800 lux intensity) and solar light (intensity 45000-60000 lx). The largest degradation percentage of orange F3R by photolysis without and with the addition of C-N-codoped TiO₂ catalyst is used to solar-light irradiation that is 17.4% and 53.9%. Since solar-light contains both types of UV-light (about 4-5%) and visible light with a high intensity [23]. In addition, doping TiO₂ with carbon and nitrogen atoms improve photocatalytic activity of TiO₂ under visible- light irradiation.

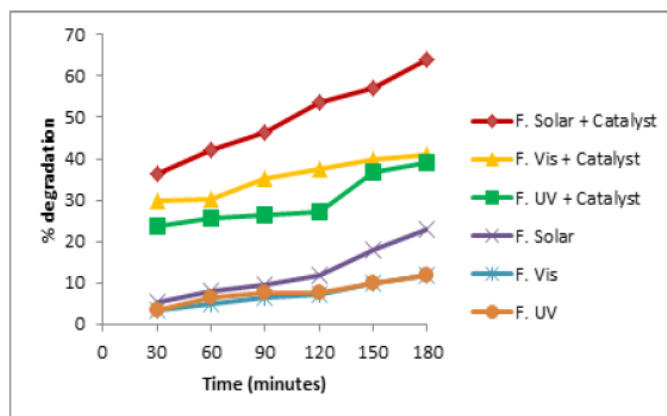


Figure 6: Effect of light sources in photolysis and photocatalytic processes of orange F3R

Analysis orange F3R by High Performance Liquid Chromatography (HPLC)

Orange F3R dyes solution was analyzed by HPLC using UV-Vis detector at 540 nm wavelength. The chromatography column C18 (250 × 4.6 mm) with mobile phases are acetonitrile and Aqua Bidest (60:40, v/v), 100 μm of volume injection and 1.0 ml/min of flow rate. Comparison of chromatogram peak between before and after degradation process of orange F3R solution under visible light irradiation by the addition of CN-codoped TiO₂ was shown in Figure 7. Before degradation, the chromatogram shows that the peak of orange F3R compound has retention time at 4.8 min. After degradation using CN-codoped TiO₂ by visible light irradiation for 180 min, the intensity of peak decrease due to the orange F3R dye compound has been degraded.

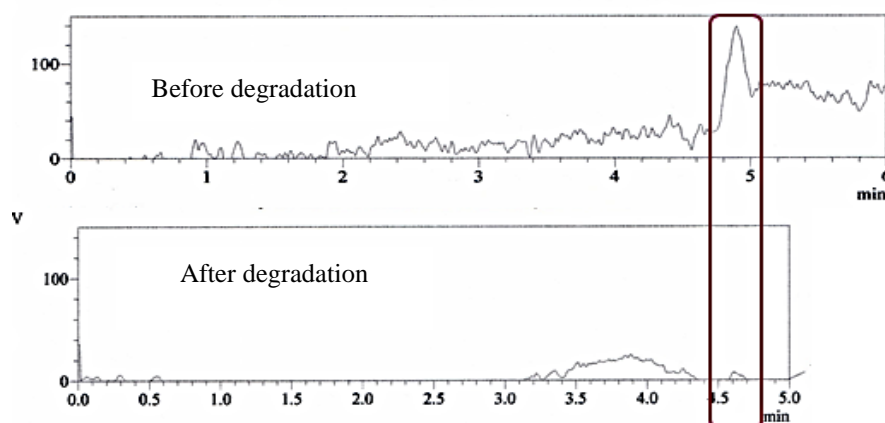


Figure 7: Chromatogram of orange F3R (above) before degradation (below) after degradation under visible-light irradiation

CONCLUSION

Orange F3R dyes had been successfully degraded by photolysis degradation with the addition of CN-codoped TiO₂ catalyst. Degradation percentage of orange F3R which was achieved under UV and visible-light by the addition of CN-codoped TiO₂ for 180 min is 39.05% and 40.86%, respectively. The highest degradation percentage is 64.12% which was achieved under solar light irradiation for 180 min with the addition of 6 mg CN-codoped TiO₂ catalyst.

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REFERENCES

- [1] K.V. Kumar, V. Ramamurthi, S. Sivanesan, *J. Colloid Interface Sci.*, **2005**, 284(1), 14-20.
- [2] Q. Guo, Z. Zhaohong, M. Xiping, J. Kui, S. Manli, Y. Ning, T. Jianhua, D.D. Dionysios, *Sep. Purif. Technol.*, **2017**, 175, 305-313.
- [3] E. Ghasemi, H. Ziyadi, A.M. Afshar, M. Sillanap, *Chem. Eng. J.*, **2015**, 264, 146-151.
- [4] A. Rahman, U. Takeo, K. Naoyuki, *Procedia Environ. Sci.*, **2013**, 17, 270.
- [5] S.K. Mousa, A. Mokhtar, G. Kamaladin, *J. Environ. Chem. Eng.*, **2013**, 1, 406
- [6] H. Li, S. Liu, J. Zhao, N. feng, *Colloids Surf. A. Physicochem. Eng. Asp.*, **2016**, 494, 222.
- [7] Y. Zhenga, G. Yaoa, Q. Chenga, S. Yua, M. Liub, C. Gaoc, *Desalination.*, **2013**, 328, 42.
- [8] A. Karci, *Chemosphere.*, **2014**, 99, 1.
- [9] K. Sushil Kumar, S. Sood, A. Umar, S.K. Mehta, *J. Alloys Compounds.*, **2013**, 581, 392-297.
- [10] J.L. Blin, M.J. Stebe, R.C. Thibault, *Colloids Surf. A. Physicochem. Eng. Asp.*, **2012**, 407, 177-185.
- [11] M.C. Gil, A. Sousa Oliveira, *Reac Kinet Mech Cat.*, **2014**.
- [12] K.T. Alex, R.W.M. Krause, B.B. Mamba, *Appl. Surf. Sci.*, **2015**, 329, 127-136.
- [13] J. Yuan, M. Chen, J. Shi, W. Shangguan, *Int. J. Hydrogen Ener.*, **2006**, 31, 13-26.
- [14] M.S. Azami, W.I. Nawawi, M.A.M. Ishak, K. Ismail, Z. Ahmad, A.H. Jawad, *Matec of Web Conferences.*, **2016**, 47, 1.
- [15] A. Jirapat, S. Seraphin, P. Kajitvichyanukul, *Environ. Sci. Pollut. Res.*, **2015**, 23, 3884.
- [16] L. Zhonghe, Y. Zhu, F. Pang, H. Liu, X. Gao, W. Ou, J. Liu, X. Wang, X. Cheng, Y. Zhang, *Ceramics Int.*, **2015**, 41, 10063.
- [17] W. Yanyan, Y. Donga, X. Xiaa, X. Liua, H. Lib, *Appl. Surf. Sci.*, **2016**, 364, 829.
- [18] S. Safni, Deliza, A. Deby, S.D. Rahmi, U. Hasnah, V.W. Diana, *Der Pharma Chemica.*, **2016**, 8(12), 30-35.
- [19] V.W. Safni Diana, S.K. Puti, A.P. Reza, *J. Chem. Pharm. Res.*, **2015**, 7, 306.
- [20] V.W. Safni Diana, S.K. Puti, A.P. Reza, Deliza, *Der Pahrma Chemica.*, **2016**, 8, 642-646.
- [21] X.C. Qing, V.W. Diana, S. Yan, D. Wei Liao, T. Mariana Lim, T.T. Yang Tan, *J. Hazard. Mater.*, **2011**, 188, 172.
- [22] S.T. Natarajan, T. Molly, N. Kalithasan, C.B. Hari, J.T. Rajesh, *Chem. Eng. J.*, **2011**, 169, 126-134.
- [23] A. Kulkarni, C. Han, D. Bhatkhande, D.D. Dionysiou, *Sep. Purif. Technol.*, **2015**, 156, 1011-1018.