

ISSN 0975-413X CODEN (USA): PCHHAX

Der Pharma Chemica, 2016, 8(12):30-35 (http://derpharmachemica.com/archive.html)

Degradation of direct red-81 and direct yellow-27 by photolysis with UV-light and solar irradiation using C-N-codoped TiO₂

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ABSTRACT

Direct Red-81 ($C_{28}H_{19}N_5Na_2O_8S_2$) and Direct Yellow-27 ($C_{28}H_{19}N_5Na_2O_6S_4$) are non-biodegradable organic compound containing azo group and confirmed carcinogenic. Direct Red-81 and Direct Yellow-27 were degraded by photolysis method under 10 watt UV-light irradiation (λ =365 nm) and solar irradiationwith and without C-Ncodoped TiO₂ catalyst. The dyes solution was analyzed\by UV-Vis spectrophotometer at λ 300-800nm. The optimum mass of C-N-codoped TiO₂ catalyst was 10 mg. From those methods, concluding solar irradiation method enhanced better degradation than UV-light irradiation, Direct Red-81 and Direct Yellow-27 were degraded 17.37 % and 8.72 % by solar irradiation and the degradation percentage increased to 75.63 % and 71.52 % by the addition of C-Ncodoped TiO₂ catalyst for 120 minutes.

Keywords: Dye, Direct Red-81, Direct Yellow-27, Degradation, Photolysis, Catalyst, C-N-codoped TiO₂, Solar Irradiation

INTRODUCTION

Wastewater of industrial textile mostly contains *Direct Red-81* and *Direct Yellow-27* which are *non-biodegradable* compounds. It contains azo group andits carcinogenicity can cause kidney damage, cancer, and heart disease.Dyes in aquatic and human life can decrease sun-light exposure, while photosyntesis process and air solvation process will be decrease as effect. Evaluation is necessary to know pollution level which have been reached and wastewater treatment effectively, so negative effect of pollution can be prevent and anticipation before pollution goes worse. Hence, it needs effective treatments prevent dyes go to the streams which people use for life activity. Without treatments, it potentially be the reason of water pollution, means significantly decline the quality of water which is consumed by living-thing[1-4].

Treatments of dyes have been done by different techniques such as biodegradation, adsorption, coagulation, reverse osmosis, etc. Those techniques with non-desctructive properties are not compatible to remove waste because treatments change waste into another phase with the same side efffect[5]. In case, biodegradation is not work properly because it has high resistance to dyes moleculs, so it can split into corresponding aromatic amines by damage[6-8].

There are more efficient and promising techniquesto remove dyesfromtextilewastewatersuch as ozonolysis, sonolysis, UV-light irradiation, solar irradiation combined with catalysts to degrade or attack dyes compounds chains in dyes become well-disposed compunds which environmental friendly discharged into streams[8-9].

In previous work, Direct Red-23, Direct Violet and Yellow GCN have been degraded over sonolysis, ozonolysis and photolysis processwithUV-light and solarirradiation. The degradation processes were done with addition of N-doped TiO₂catalyst, while Yellow GCN has been degraded with addition of C-N-codoped TiO₂ catalyst.8 mg/L of Direct Red-23 and Direct Violet could be degraded by 39,378 % and 25,893 % after 120 minutes UV-Light irradiation by using 20 mg N-doped TiO₂ catalyst, andYellow GCNthe degradation percentage increase to 23,6% by using 10 mg C-N-codoped TiO₂ catalyst.It degreded Direct Red-23 over 62,696 % , Direct Violet only 62,5 % after 120 minutes solar irradiation by using 20 mg N-doped TiO₂ catalyst. While, yellow-GCN could be degraded18,7% after 120 minutes solar irradiation and the degradation percentage increase to 38,0% by using 10 mg C-N-codoped TiO₂ catalyst[8-10].

In this work, Direct Red-81 and Direct Yellow-27 are degraded by photolysis process with UV-light and solar irradiation using C-N-codoped TiO₂ as catalyst.

MATERIALS AND METHODS

Equipments and materials

Equipments which were used are Spectrophotometer UV-Vis (S.1000 Secomam Sarcelles, French), UV-lamp (Germicidal CE G 13 Base BFC11004, λ =365 nm, 10 Watt), irradiation box, analytical balance, centrifugewith 10.000 rpm, petridish, and other glasses equipment's.

Materials are *Direct Red-81* ($C_{28}H_{19}N_5Na_2O_8S_2$, Mr = 675 g/Mol) as Fig. 1, *Direct Yellow-27* ($C_{28}H_{19}N_5Na_2O_6S_4$, Mr = 695 g/Mol) as Fig. 2 were get from Silungkang textile-industry, double distilled water, and C-N-codoped TiO₂as catalysts were made in laboratory.



Fig. 1. Structure of Direct Red-81

Fig. 2. Structure of Direct Yellow-27

Degradation of Direct Red-81 and Direct Yellow-27by photolysis

Direct Red-81 solutions filled into petridish, degradationwas done by photolysis under UV-lamp (λ =365 nm, 10 Watt)andsolar irradiation within time variations. Absorbance of residue dyes-solution was measured by UV-Vis Spectrophotometer in its maximum wavelength to get percent of degradation. Same treatments were done to degradation of Direct Yellow-27 with addition of C-N-codoped TiO₂.

Effect of C-N-codoped TiO₂

Effect of C-N-*codoped* TiO_2mass to degradation of Direct Red-81 and Direct Yellow-27was learned by added variation mass (5-25 mg) of its into dyes solution which degradedby photolysis with UV lamp and solar irradiationwithin 2 hours. Absorbances of residue dyes-solution was measured by UV-Vis Spectrophotometer in its maximum wavelengthto get percent of degradation.

RESULTS AND DISCUSSION

Direct Red-81 and Direct Yellow-27 solutions were analyzed by UV-Vis Spectrophotometer. Fig.3 describe that 60 mg/ Direct Red-81 solutions absorbed light maximally at 398 nm (0,820AU) and 60 mg/L Direct Yellow-27 solutions absorbed light maximally at 510 nm (0,702 AU).



Fig. 3.Spectrum of (a)Direct Red-81and (b)Direct Yellow-27

Determination mass optimum of C-N-codoped TiO₂in degradation process

Fig. 4 shows that variation mass (in range of 5 to 25 mg) of C-N-codoped TiO₂catalyst affect to degradation percentage of Direct Red-81. From this figure, we can see that the optimumC-N-codoped TiO₂catalyst mass is 10 mg with 53.13% degradation of Direct Red-81. The photocatalysis plays important role in photodegradation process, due to producing the hydroxyl radical[11].



Fig. 4. Effect of C-N-codoped TiO₂ catalyst-massto degradation of Direct Red-81

Effect of degradation time

Fig. 5.showsthat increasing time of photolysis with UV-light irradiation as well as solar irradiation is followed by increasing degradation of Direct Red-81 andDirect Yellow-27.Direct Red-81 is more active in the area of visible light because it has a maximum absorbance at 508 nm unlike the case of Direct Yellow-27 is more active inUV light ($\lambda = 398$ nm). Hence Direct Red-81 is easier degraded than Direct Yellow-27 because it has much π bond in and also contain a lot of small energy bonding groups in its molecular structure (asFig. 2).It was observed as long as irradiation occured, it was equal to degradation process, in solar irradiation there was •OH as agentthat declined toxic compounds in the solution by attacked mostly double chains, such as N=N, C=C and C=N, and •OH be produced by UV-light and solar irradiation.



Fig. 5. Effect of degradation time to degradation percentage of Direct Red-81 and Direct Yellow-27, without catalyst (a).Solar irradiation(b). UV-lightirradiation



Effect of C-N-codoped TiO₂Catalyst inSolar Irradition and UV-LightIrradiation

Fig.6.(a)Effect of C-N-codoped TiO₂catalyst in Direct Red-81degradation by Solar irradiation, (b) UV-light irradiation



Fig. 6. (b)Effect of C-N-codoped TiO₂catalyst inDirect Yellow-27degradation by (a) Solar irradiation, (b) UV-light irradiation

When irradiation time increased, UV light exposed C-N-codoped TiO₂ for more, so producing OH• was increased. Fig. 6 shows that percent degradation of Direct Red-81 and Direct Yellow-27with the addition of catalyst is better

than without the addition of catalyst. It was evaluated that catalyst accelerated rate of reaction without including in the reaction. Degradation process was started by photoexcitation because UV-light adsorbed to C-N-*codoped* TiO₂surface, so electrons in C-N-*codoped* TiO₂excited from valence band to conduction band and produced hole (h_{vb}^+) in valance band then reacted with H₂O in the air to form OH⁻(OH•). Next process was electrons in conduction band (e_{cb}⁻) reacted to oxygen producing superoxide ion (O₂•⁻), then reacted with water forming OH•[12].



Effect of Light Source toDegradation Percentageof Direct Red-81 and Direct Yellow-27

Fig. 7Effect of light source to degradation percentage of (a) Direct Red-81 and(b) Direct Yellow-27 with addition of C-N-codoped TiO₂catalyst

Fig. 7 (a) and (b) shows that thesolar irradiation reached higher percentage of degradation, such as 75.63 % for Direct Red-81 and 71.52 % for Direct Yellow-27within 120 minutes. Solar irradiation can be use to degradate organic compounds in liquid phase, also it can be detracted by hidroxil ion (OH-) or its conjugate base H_2O_2 (HO₂-) becomes HO₂• radical and OH• which support degradation process. The degradation process can be optimize with addition of C-N-*codoped* TiO₂ catalystsby solar irradiation because C-N-*codoped* TiO₂ particles excited then *hole* (positif charge) in valance band (h⁺) on TiO₂ surface formed increasingly as well as OH• that degraded Direct Red-81 and Direct Yellow-27[12].

CONCLUSION

The degradation of Direct Red-81 and Direct Yellow-27 was obviously affected by the addition of catalyst and light source of irradiation. Solar irradiation method enhanced better degradation than UV-light irradiation. Direct Red-81 and Direct Yellow-27 were degraded 17.37 % and 8.72 % by UV-light irradiation and the degradation percentage increased to 75.63 % and 71.52 % by solar irradiation and with addition of C-N-codoped TiO₂ catalyst for 120 minutes.

Acknowledgements

We would like to express our gratitude to PUPT DP2M DIKTI Grand, Research Centre of Andalas University for all the support provided.

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