UV Induced Photodegradation of Direct Green dye by Tb-doped $La_{10}Si_6O_{27}$ Catalyst

Rajender Boddula
Center for Advanced Materials (CAM), Qatar University,Doha, Qatar.
rajender.boddula@qu.edu.qa

Ramachandra Naik
Department of Physics, New Horizon College of Engineering,Bangalore, India.
rcnaikphysics@gmail.com

Naveen Kumar A
Department of Physics, South East Asian College of Engineering and Technology, VTU,Bangalore, Karnataka, India
naveenphysics12@gmail.com

Ramyakrishna Pothu
College of Chemistry and Chemical Engineering, Hunan University,Changsha, China
research.ramyakrishna@gmail.com

Ahmed Bahgat Radwan
Center for Advanced Materials (CAM), Qatar University,Doha, Qatar
ahmedbahgat@qu.edu.qa

Noora Al-Qahtani
Center for Advanced Materials (CAM), Qatar University,Doha, Qatar
noora.alqahtani@qu.edu.qa

Abstract

Due to the expansion of industry, the world's population growth has led to increased air and water contamination. Because they are poisonous and non-biodegradable, organic dyes are a significant source of this contamination. Studies have concentrated on photocatalysts to transform organic dyes into innocuous compounds in order to lessen the harm that organic colours cause. In this study, solution combustion technique was employed to prepare rare-earth metal (terbium (Tb)) doped lanthanum silicate phosphor ($La_{10}Si_6O_{27}$) using lanthanum nitrate and fumed silica were utilized as precursors, oxalyldihydrazide was used as fuel, and terbium nitrate was used as a dopant. The photocatalytic activities for the Direct Green-23 (DG23) dye degradation under UV irradiation were studied and found that 59.05% of dyes degraded at 120 min. These findings shows that, $La_{10}Si_6O_{27}$ is a promising material for industrial dye degradation since 59.05% of the dyes were absorbed by the material in 120 min.

Keywords: Water treatment; Photodegradation; Direct Green-23 (DG23) dye; Toxic pollutant; Nanophosphors

1 Introduction

Dyes have been used in many trades to colour their articles, in textiles, food, paper, plastics, elastic, carpet and beauty care products. Amid the generation and utilization of distinctive coloration matters, until 10% of utilized colours are released as wastewater, making an assortment of natural and wellbeing issues. Colouring wastewater stemming is popular as deeply adulterated wastewaters because it holds complete colour, exaggerated chemical oxygen demand/synthetic oxygen request (COD), sour pH, harmful overpowering metals, and different harmful contaminants. The most

necessary and largest shade forged inside the manufacturing is the azo colour draw, that are acknowledged apiece posture of azo-groups (–N = N–) in relationship accompanying fragrant rings (naphthalene and/or benzene). Direct green 23 (DG23) dye (molecular formula: $C_{45}H_{33}N_7Na_4O_{16}S_4$; Figure 1) is one of the azo colours, which is recognized as one of the foremost hazardous banner since of their long career in water. This applies in specific to organic azides that have existed stimulated for one growth of mineral salts or dependable acids. Poisonous gasses are formed by mixing matters concerning this course accompanying acids, aldehydes, amides, carbamates, cyanides, not organic fluorides, halogenated organics, isocyanates, ketones, metals, nitrides, peroxides, phenols, epoxides, acyl halides, and hard oxidizing or lessening controllers.

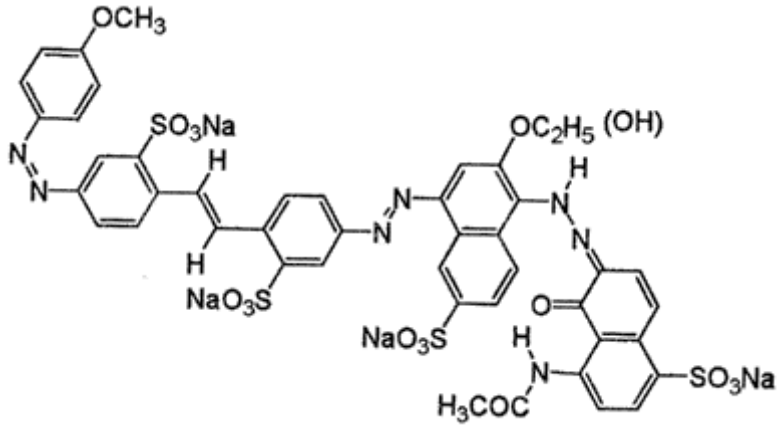

Fig. 1: Chemical structure of DG23 dye

Combustible gasses are formed by mixing matters in this place bunch accompanying being basic metals. Dangerous consolidation can occur with something complete oxidizing professionals, ingot salts, peroxides, and sulphides. As recently, all governments are disturbed be following accurate to halt this in a way color wastewater to the open waterways, except that it is medicated suitably. The primary objective of wastewater treatment features is to ensure people and the biological system from destructive and harmful components found in wastewater (Saeed et al. (2018); Maavia et al. (2019)). Water treatment facilities were planned to speed up the normal prepare of filtering water since the common prepare is over-burden. These facilities are utilized to treat the wastewater in different ways and after that send the filtered water back into the environment. Heterogeneous photocatalysis is considered an emerging destructive innovation that leads to the entire mineralization of assorted natural contaminants, in which the degradation of the sullying compound broken up in water happens by the activity of semiconductor materials illuminated by light, primarily bright (Nagaraj et al. (2021); Priya et al. (2020)). A few of the foremost used photocatalyst metallic semiconductor materials are TiO_2, ZnO, Fe_2O_3, WO_3, BiOCl, and g-C_3N_4, as well as a few blends of these have been examined (Nemiwal et al. (2021); Aslam et al. (2019a) (2019b); Farooq et al. (2019); Michael et al. (2019)). Nowadays, rare-earth doped metal oxide nanocomposites were gotten to be exceptionally one of a kind and tend to appear plenteous execution in all sorts of areas such as biological, electrochemical, and photocatalytic, etc (Naveen Kumar et al. (2020) and (2021)).

Lanthanum silicate ($La_{10}Si_6O_{27}$) nanophosphor is demonstrated to be an amazing multifunctional material for photoluminescence, photocatalytic and electrochemical applications. Its precious stone structure is hexagonal oxy-apatite with a space bunch P63/m, and shaped due to covalent and confined silicate tetrahedra (SiO_4). There are two locales named 6h which obliges seven La cations 4f which

obliges nine-coordinated locales. NMR spectroscopy and Raman spectroscopy have illustrated that the interstitial oxide particles in $La_{10}Si_6O_{27}$ contribute to expanded conductivity. Tb^{3+} particles have demonstrated to be incredible activator for doping into the cross section of $La_{10}Si_6O_{27}$ which comes about within the upgraded execution as a multifunctional material. To date, a composition of material, synthetic and natural means have happened itemized to empty colour from wastewater. Distinctive methods were checked for the banishing of various sorts of poisons from water to a degree advanced corrosion for effluents situation of material banner, blend of various composites for situation of water holding hurtful metals and taking advantage of nanomaterials as a stimulant for photodegradation of material effluents.

In this manner, the point of the show think about was to test Tb^{3+} doped $La_{10}Si_6O_{27}$ by the joining of 5 mol% Tb^{3+} for improved photocatalytic application for the evacuation of a material anionic DG23 dye from wastewater was performed beneath UV light for the length of 120 min to explore the photocatalytic action of $La_{10}Si_6O_{27}$:Tb^{3+} (5 mol%). This report demonstrates 5 mol% Tb^{3+} doped $La_{10}Si_6O_{27}$ may be a UV photocatalyst for wastewater treatment.

2 Experimental

Stoichiometric sums of crude materials required for the planning have been procured from Sigma Aldrich with 99% immaculateness and analytical reagent grade. Terbium nitrate (Tb $(NO_3)_3$) as a dopant, lanthanum nitrate (La $(NO_3)_3 \cdot 6H_2O$) as an oxidizer, smouldered silica and oxalyldihydrazide ($C_2H_6N_4O_2$) as a fuel were broken up in refined water taken in a container. 5 mol % Tb^{3+} doped lanthanum silicate ($La_{10}Si_6O_{27}$:Tb^{3+}) have been arranged as per the stoichiometric proportions and by keeping up the fuel to oxidizer proportion solidarity by arrangement combustion method. Container was kept in pre-warmed suppress heater of temperature 450 ºC where combustion takes put. Lack of hydration and seething of the response blend happens with the freedom of gigantic sum of vaporous items coming about in arrangement of the specified Tb^{3+} doped $La_{10}Si_6O_{27}$ nanomaterials by the substitution of La/Si destinations by Tb^{3+} particles. Last item gotten have been crushed and collected in an discuss tight holder.

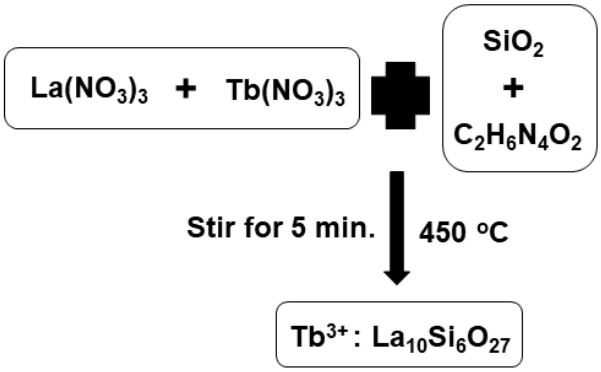

Fig. 2: Synthesis procedure of Tb^{3+} doped $La_{10}Si_6O_{27}$ material

The chemical responses for the union of have and one of the mole rates of Tb doped as appeared underneath.

$$10\,La(NO_3)_3.6H_2O + 6\,SiO_2 + 15\,C_2H_6N_4O_2 + 5\,Tb(NO_3)_3.6H_2O \rightarrow La_{9.95}Si_6O_{27}Tb_{0.5} + 105\,H_2O + 30\,CO_2 + 45\,N_2$$

3 Results and Discussion

Tb^{3+} doped $La_{10}Si_6O_{27}$ nanophosphors are characterized by FT-IR, XRD, UV-DRS, and TEM techniques (Naveen Kumar et al., 2021). Photocatalytic exercises were completed activity resorting

to the UV–Visible spectrophotometer show 2600 from Shimadzu. In arrange to debase the DG23 dye color within the nearness of UV radiation, a photocatalytic explore was completed activity on the devised 5 mol% Tb^{3+} doped test. A 250 ml color arrangement containing 20 ppm of the dye colors was made as the stock arrangement. In a circular glass reactor, catalyst measurements of 0.06 g were connected to the color arrangement. The response blend was attractively unsettled and uncovered to a 400W mercury light with a 254 nm wavelength whereas being lit up by UV radiation. A pyrex glass container was utilized for the tests. The response blend was exposed to UV radiation within the open discuss for to 120 min, and 5 ml of the sample arrangement were taken out and observed within the UV–Visible extend of 200–800 nm at 15 min interims.

The photodegradation of DG23 dye solution was utilized to gage the photocatalytic movement of 5 mol% Tb^{3+} doped test beneath UV light. It was taken in a circular glass reactor, kept underneath the UV source of mercury vapor light by keeping up the separate of 23 cm to maintain a strategic distance from the warm on a test (Satish Kumar et al. (2009)). Firstly, the explore was conducted in dim condition for DG23 color. No alter was watched as the color did not experience any degradation (Shams et al. (2019)). This was ascribed to the characteristic of the catalyst, which has less crystallite estimate, great charge transport capacity, and a more noteworthy number of oxygen opportunities due to doping. These properties make the material potential for photocatalytic applications (Shahbazi et al. (2017)). Figure 3 appears its absorbance spectra which shows most extreme retention at 621 nm. It appears rate degradation with regard to time up to 120 min. It was watched from the chart that; rate debasement is about 59.05% after 120 min of light.

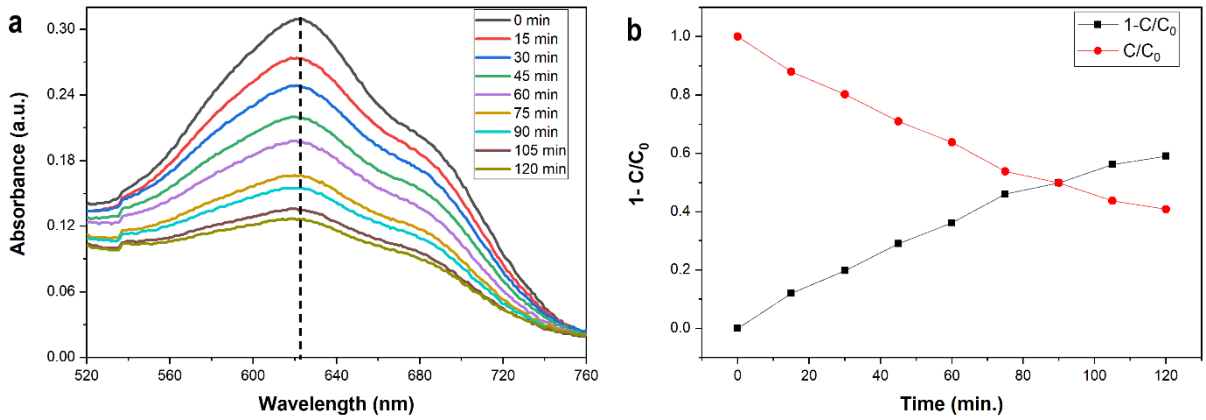

Fig. 3: a) DG23 dye degradation and **b)** time span vs 1-C/C_0 for the DG23 dye decolorization over Tb^{3+} doped $La_{10}Si_6O_{27}$ UV photo catalyst

Table 1 appears the nitty gritty investigation of debasement handle beneath UV light. Rate degradation was calculated utilizing the condition (i),

$$\% D = \frac{C_o - C}{C_o} \times 100 \qquad (i)$$

Where, C_o is the introductory colour concentration and C is the colour concentration after photo decolorization with regard to time. It presents C/C_o for the decolorization of DG23 dye with UV light, which clearly appear that, the degradation has been moved forward with time and achieved most extreme for 120 min. In arrange to decide the arrange of energy, log C/C_o have been assessed utilizing the condition (ii).

$$log\frac{C}{C_o} = -Kt \qquad (ii)$$

Where, K=first arrange rate steady, C_o = color concentration at t = min and C = color concentration amid testing (Prathap Kumar et al. (2021)). The linearity between log C/C_o and K was watched, which appears the primary arrange energy. The esteem of K was found to be 0.007419 min^{-1} for DG23 appeared within the Table 1.

Table 1: DG23 degradation percentage over 5 mol% Tb^{3+} doped $La_{10}Si_6O_{27}$ photocatalyst under UV light (20ppm DG23 + 0.06 g of photocatalyst + UV light, slope rate = 0.007419 min^{-1})

t	C	C/C_o	log C/C_o	-log C/C_o	%D
0	20	1	0	0	0
15	17.6	0.88	-0.055517328	0.055517328	12
30	16.06	0.803	-0.095284455	0.095284455	19.7
45	14.19	0.7095	-0.1490476	0.1490476	29.05
60	12.77	0.6385	-0.194839098	0.194839098	36.15
75	10.77	0.5385	-0.268814292	0.268814292	46.15
90	10	0.5	-0.301029996	0.301029996	50
105	8.77	0.4385	-0.358030402	0.358030402	56.15
120	8.19	0.4095	-0.387746094	0.387746094	59.05

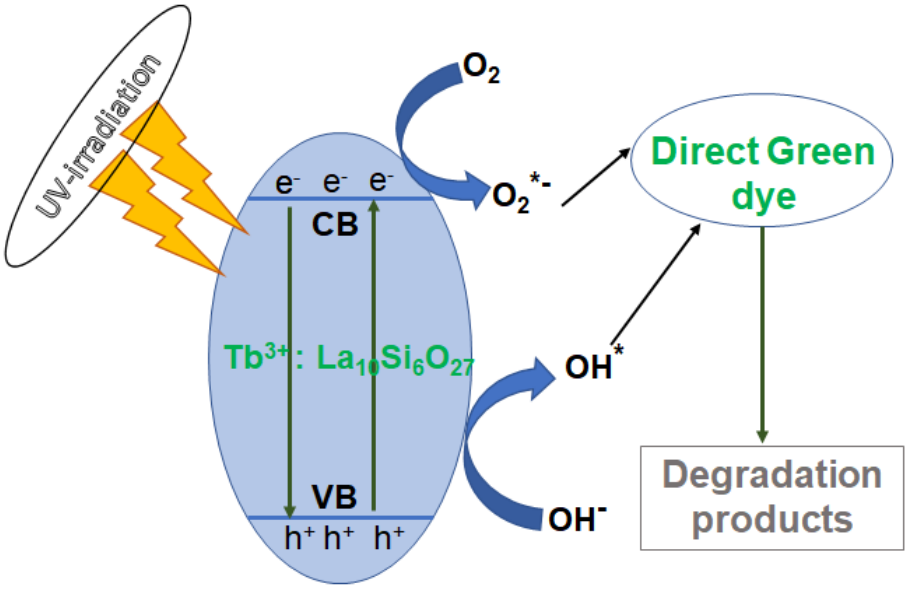

Fig. 4: Mechanism of DG23 dye degradation over 5 mol% Tb^{3+} doped $La_{10}Si_6O_{27}$ photocatalytic activity under UV light illumination

Figure 3b appears the analysed debasement half-life in which 50% color debasement has been recognized in 90 min. From these comes about, it can be concluded that 5 mol% Tb^{3+} doped $La_{10}Si_6O_{27}$ could be a potential photocatalyst for DG23 dye decolorization with more photo-decolorization capacity due to electron gap recombination, era of hydroxyl and superoxide radicals. In expansion, dynamic photo energized electrons and holes too degrades the color particles as appeared in Figure 4. When 5 mol% Tb^{3+} doped $La_{10}Si_6O_{27}$ was uncovered to the radiation, electrons

from valence band hops to conduction band and gaps are made in valence band (Naveen Kumar et al. (2021)). These electrons will move towards surface and produces anion radicals (O_2*−) from atomic oxygen, while gaps will oxidize the color or deliver hydroxyl radicals (OH*) from adsorbed water atoms. The adsorbed color atoms are oxidized by these dynamic radicals.

4 Conclusion

In summary, we have successfully synthesized a 5 mol% Tb doped $La_{10}Si_6O_{27}$ nanophosphor by combustion method. To examine the photocatalytic degradation of DG23 dye over nanophosphor beneath UV light. DG23 photodegradation over 5 mol% Tb doped $La_{10}Si_6O_{27}$ catalyst exhibited superior photocatalytic efficiency and found to be first-order rate reaction with rate constant is 0.007419 min^{-1}. 50% DG23 dye degradation half-life has been detected in 90 min and 59.05% after 120 min of UV light. These findings are very useful for cleaning the industrial wastewater applications.

Acknowledgements

This work was supported by Qatar University through a National Capacity Building Program Grant (NCBP), [QUCP-CAM-2022-463]. The publication of the article was funded by Qatar National Library. Statements made herein are solely the responsibility of the authors.

References

Aslam, et al. (2021). Synthesis of Non-Toxic Fe2 (WO4) 3 Photocatalyst with Efficient Performance. *Current Analytical Chemistry, 17*(5), 628-639.

Aslam, et al. (2019a). Synthesis of novel g-C3N4 microrods: A metal-free visible-light-driven photocatalyst. *Materials Science for Energy Technologies, 2*(3), 401-407.

Aslam, et al. (2019b). Synthesis of WO3· H2O spherical particles for efficient photocatalytic properties under visible light source. Materials Science for Energy Technologies, 2(2), 187-193.

Farooq, et al. (2019). Improved photocatalytic performance of reduced zinc oxide (ZnO) novel morphology of astray like microstructure under solar light irradiation. *Materials Science for Energy Technologies, 2*(2), 181-186.

Maavia, et al. (2019). Facile synthesis of g-C3N4/CdWO4 with excellent photocatalytic performance for the degradation of Minocycline. *Materials Science for Energy Technologies, 2*(2), 258-266.

Micheal, et al. (2019). Assembled composite of hematite iron oxide on sponge-like BiOCl with enhanced photocatalytic activity. *Materials Science for Energy Technologies, 2*(1), 104-111.

Nagaraj, et al. (2021). A Facile synthesis of anatase Ni2+ doped TiO2 nanorods with highly improved visible-light photocatalytic performance. *Current Analytical Chemistry, 17*(2), 279-284.

Nantharak, et al. (2017). Effect of local structure of Sm3+ in MgAl2O4:Sm3+ phosphors prepared by thermal decomposition of triethanolamine complexes on their luminescence property, *Journal of Alloys and Compounds, 701*, 1019-1026.

Naveen et al. (2020). Photoluminescence and electrochemical performances of Eu3+doped La10Si6O27 nanophosphor: Display and electrochemical sensor applications, *Applied Surface Science Advances 1*, 100026.

Naveen et al. (2021a). La10Si6O27:Tb3+ nanomaterial; its photocatalytic and electrochemical sensor activities on Disperse Orange and Fast Blue dyes, *Sensors International, 2*, 100076.

Naveen, et al. (2021b). Photoluminescence, photocatalytic and electrochemical performance of La10Si6O27:Sm3+ nanophosphor: It's applications in display, photocatalytic and electrochemical sensor, *Applied Surface Science Advances, 4*, 100070.

Nemiwal, M., Zhang, T. C. & Kumar, D. (2021). Recent progress in g-C_3N_4, TiO_2 and ZnO based photocatalysts for dye degradation: Strategies to improve photocatalytic activity, *Science of The Total Environment, 767*, 144896.

Pratapkumar, et al. (2021). Structural, photocatalytic and electrochemical studies on facile combustion synthesized low-cost nano chromium (III) doped polycrystalline magnesium aluminate spinels, *Journal of Science: Advanced Materials and Devices, 6*(3), 462-471

Priya, et al. (2020). A study of photocatalytic and photoelectrochemical activity of as-synthesized WO3/g-C3N4 composite photocatalysts for AO7 degradation. *Materials Science for Energy Technologies, 3*, 43-50.

Saeed, et al. (2018). Ag@Mn_xO_y: an effective catalyst for photo-degradation of rhodamine B dye. Environmental chemistry letters, 16(1), 287-294.

Sathish et al. (2009). Visible light assisted photocatalytic degradation of acid red 88 using Au-ZnO nanophotocatalysts, *Water Science and Technology*, *60*(6), 1589–1596.

Shahbazi, H., Shokrollahi, H. & Alhaji, A. (2017). Optimizing the gel-casting parameters in synthesis of MgAl2O4 spinel, *Journal of Alloys and Compounds, 712*, 732-741.

Shams, et al. (2019). Facile and Eco-Benign Synthesis of Au@Fe_2o_3 Nanocomposite: Efficient Photocatalytic, Antibacterial And Antioxidant Agent, *Journal of Photochemistry and Photobiology B: Biology*, *199*, 111632.

Cite as: Boddula R., Naik R., Kumar A.N., Pothu R., Radwan A.B. & Al-Qahtani N., "UV Induced Photodegradation of Direct Green dye by Tb-doped $La_{10}Si_6O_{27}$ Catalyst", *The 2nd International Conference on Civil Infrastructure and Construction (CIC 2023)*, Doha, Qatar, 5-8 February 2023, DOI: https://doi.org/10.29117/cic.2023.0179