RASĀYAN *J. Chem.*
Vol. 19 | No. 1 | 244-249 | January-March | 2026
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

SUSTAINABLE VISIBLE-LIGHT INDUCED NEUTRAL RED DYE DEGRADATION TO BENIGN PRODUCTS BY NANOSPHERES $Mn_2O_3/K_2S_2O_8$

R. Lakshminarayani[1,2] C. Malathi[1,✉], and Anusuikdev[3]

[1]Department of Chemistry, MSRIT (affiliated to VTU), Bangalore-560054, (Karnataka)India
[2]Department of Chemistry, MES PUC College, PBangalore-560003, (Karnataka)India
[3]Department of Chemistry, Presidency University, Italagur-YNK-560065, (Karnataka)India
✉Corresponding author: maalathichalla@msrit.edu

ABSTRACT

Sustainable visible light-induced neutral dye degradation to benign products of CO_2, H_2O, NO_3^-, was achieved by photocatalyst $Mn_2O_3/K_2S_2O_8$ combination in polluted water. In this photo, oxidative breakdown of dye, catalytic Mn_2O_3 bixbyite with $K_2S_2O_8$ system produced the prominent radicals OH^- and SO_4^{2-} that completely oxidized the dye molecules up to 89.5 per cent without leaving the intermediate carcinogenic phenazine products to meet the sustainable development goal of clean water and sanitation. The photo-responsive catalyst Mn_2O_3 nano spheres was synthesized by one-pot solution combustion method using a 1:1.5 ratio of bi-fuel mixer of glucose and urea derivative with Mn $(NO_3)_2H_2O$. It was characterized by PXRD, FESEM-EDX, UV-vis Spectro photometer and TGA. Optimization of the parameters' studies revealed that a 0.50g/L Mn_2O_3 dose, 0.08g/L of $K_2S_2O_8$ and 40 ppm neutral dye at a pH of 6 were suitable for the efficient neutral red dye photo degradation for 30min and followed pseudo-first order kinetics.

Keywords: Mn_2O_3 Nano Spheres, $K_2S_2O_8$ Oxidizing Agent, Visible Light, Photocatalytic Degradation, Neutral Dye, Benign Products.

RASĀYAN *J. Chem.*, Vol. 19, No.1, 2026

INTRODUCTION

Organic pollutants liberated from various industries like dyeing, etc., are highly toxic owing to develop a thin layer across the water surface leads to preventing sunlight penetration and utilizing the dissolved oxygen for their natural decomposition. In fact, the disintegration of the dye is either natural or the other catalytic methods like homo and heterogeneous, photo and bio, etc., with or without oxidizing agents, produce the intermediates which are more toxic than the pristine dye, cause to suffer from cancer, mutations, and teratogenic damages in the organisms. Among them, the photocatalytic degradation pathway gets a significant recognition on account of cost-effectiveness, green technique and advanced oxidation process in wastewater treatment.[2-9] However, mostly aimed chromophore degradation and left the toxic transient species as such, which is draw back in many research publications.[5,8] Those toxic intermediate species must be degraded to CO_2 and H_2O at the end, declaring prominently complete removal of the pollutant as to meet Sustainable Development Goal 6 (SDS) clean water and sanitation.[8-9] To achieve this, phenazine-based carcinogenic neutral red (NR) dye[4] used in textiles, food, and research laboratories, is subjected to visible-light-driven degradation by the multivalent bixbyite-Mn_2O_3 nano spheres with $K_2S_2O_8$ in this current study.

EXPERIMENTAL

Material and Methods

All chemicals were purchased from Sigma-Aldrich and Merck, and used as it is purchased. The bixbyite-(Mn_2O_3) nanospheres were produced by mixing a fuel consists of 1:1.5 ratio of glucose and urea derivative with manganese nitrate in 25ml of DDW and combusted at 470 ± 10 ℃.[6] The obtained black product was calcinated at 600 ℃ for 1 h and cooled to room temperature. Characterization of it was performed by Philips PW1050 X pert diffractometer (Cu-K = 1.5406 Å), UV-vis spectrophotometer (Systronics 2202), TGA (NETZSCH STA 449 F5) and FESEM - EDX (in JEOL version JSM-6390LV,

http://doi.org/10.31788/RJC.2026.1919555

SEM Tech solutions). Batch studies were evaluated using 20 ppm NR dye, 0.4g/L catalyst, 0.05 g/L of $K_2S_2O_8$ oxidizing agent at pH of 6± 0.2 for 60 min to optimize the degradation parameters; pH (4-10), Oxidizing agent (5-15mg), Catalyst (20-70mg) and NR dye concertation(20-100ppm) for 60 min[5,6,9] under irradiation of light (mercury vapor lamp). The left NR dye concentration in the solution was evaluated for 10-minute intervals up to 60 minutes by a UV-vis spectrophotometer and computed using the equation in Table-1.[5-6,9,10]

RESULTS AND DISCUSSION

Characterization of Bixbyite (Mn_2O_3) Nano Spheres

The diffractogram of the synthesized bixbyite Mn_2O_3nanospheres in Fig.-1a has exhibited at 2θ are 23.23°, 33.09°, 38.29°, 45.28°, 49.40°, 55.26°, and 65.86°, corresponding to the standard JCPDS card No. 41-1442 of cubic structure.[5,7] The average crystallite size was 45 nm from the Debye-Scherrer equation in Table-1. TGA -DSC analysis of Mn_2O_3 in Fig.-1b has shown a gradual decline, indicating that no impurities and no intermediate state, and a weight loss at 900˚C belongs to the loss of MnO. This thermogram revealed that temperature-induced phase transition from Mn_2O_3 to Mn_3O_4.[6,7] Figure-1 c, d, shows the FESEM images of the nano spheres, which together formed a network of interconnected porous structure, benefiting the application of adsorption and catalysis. The particle sizes, as shown in Fig. 1d, are between 54.0 - 85.5 nm and consistent with the crystallite size. The existence of the elemental structure in the synthesised Mn_2O_3 nano powder is expressed in Table-2, and the existence of carbon is from the surface adsorption of CO_2 during the synthesis.[6-8]

Table-1: Equations Used to Calculate the Studying Bixbyite Function

Function of material	Equation	Equation Parameters
Per cent of degradation	$\%\,Degradation = \frac{(A_0 - A_t)}{A_0}\ X\ 100$	A_0 = initial absorbance of the dye, and A_t = absorbance at time t and k = degradation rate constant [5,9,10].
Kinetic studies	$Ln\frac{A_t}{A_0} = -kt$	
Crystallite size	D = $\cos\frac{0.9\lambda}{\beta cos\theta}$ nm	The FWHM (β), λ = 0.154 nm, θ = angle, and D = crystallite size[6].
Band gap	$(\alpha h\nu) = A(h\nu - E_g)^n$	h=Plank constant, υ =frequency, α = constant. Electronegativity χ ≈ 5.68 eV, E_e = free electron energy vs NHE = 4.5 eV, Eg = band gap (eV), E_{VB} =valence band potential, E_{CB} = conduction band potential [10-12]
Valence Band Potential	$E_{VB} = E_g + E_{CB}$	
Conduction Band Potential	$E_{CB} = \chi - E_e - 0.5E_g$	

Optimisation Parameters for Photocatalytic Studies

The absorbance of the phenazine ring in NR is at 280 nm, and the substituents of $-N(CH_3)_2$ and NH_2 electron-donating group brought the bathochromic shift at 530 nm in the UV-vis spectrum.[4,13] The NR pollutant degradation per cent while optimising the parameters in batch studies is shown in Fig.-2. The involvement of radicals and NR dye is widely influenced by the pH of the medium, and Fig.-2 b reveals that pH 6 (77 % at 280 nm, 78 % at 530nm) is suitable for further studies. Similarly, the $K_2S_2O_8$ OA effect in Fig.-2c, declares the highest NR degradation is for 0.08g/L (81% at 280 nm,88 % at 530 nm), and further, a less significant improvement is observed. This saturation is due to the reactive radicals that may undergo self-quenching or be scavenged in the side reaction.[4-5,8-9] The active catalyst dose effect in Fig.-2d unveils that the highest dye photooxidative breakdown is at 0.5g/L (77.8 % at 280 nm, 87.8% at 530nm) and further decreases, perhaps less photon penetration due to the turbidity and agglomeration of the catalyst.[5,9,10] Figure-2e is related NR dye dose effect, suggesting that the maximum photochemical degradation percentage is attained at 40 ppm (77.5% at 280 nm, 90.6% at 530nm). This enhancement may be a good proportionality between the photocatalytic active sites and the light absorption, and further reduction of degradation is due to saturation of the catalyst surface.[8-10] The optimum time required to achieve 85.6 % NR completely transformed to benign products CO_2 and H_2O is 30 min (Fig.-2f), attributed to the better charge separation and production of reactive species required in photocatalysis.[9-10]

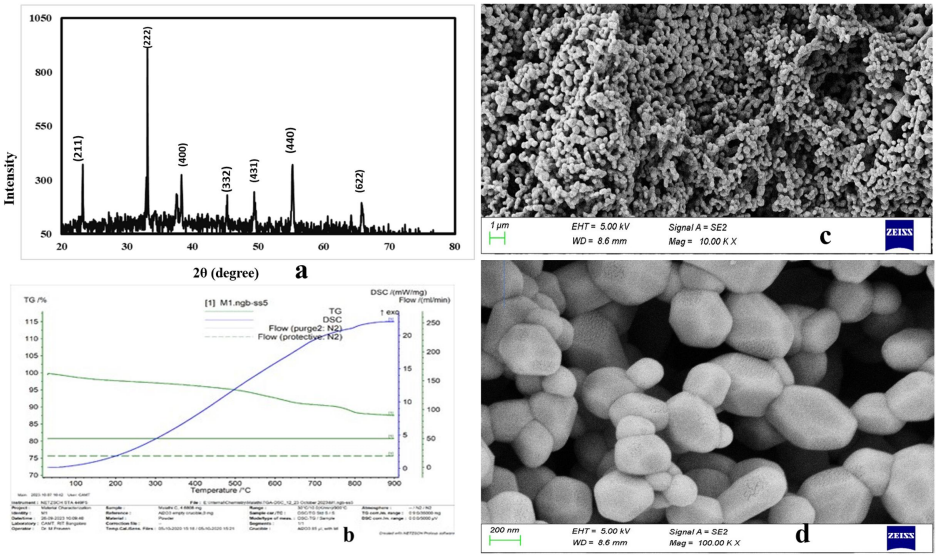

Fig.-1: Characterisation of Mn_2O_3 Nano Sphere (a) PXRD Diffractogram (b) TGA Analysis (c) FESEM Image of 1 µm -10KX Magnification (d) FESEM Image of 200 nm -100KX Magnification

Table-2: EDX Analysis of Mn_2O_3

Element	Weight%	Atomic%
C	4.68	11.38
O	29.36	53.57
Mn	65.95	35.04
Totals	100.00	100

Mechanism of Photocatalytic Degradation of NR Dye

The catalyst band gap plays a prime role in harvesting the light for the photodegradation of dyes. The band gap of Mn_2O_3 from the Tauc plot is 2.8 eV in Fig.-2a. The quantum confinement effect of nano-sized crystallites has led to a band gap shifted to the visible spectrum. Consequently, it absorbs visible light that assists in utilising it as the vis-light catalyst.[11] The equations used to compute the band gap and potentials are mentioned in Table-1. The compounds' potentials vs SHE that are involved in the photocatalyst-induced degradation are displayed in Table-3. The effect of Mn_2O_3 with and without $K_2S_2O_8$ oxidising agent is investigated and displayed in Fig.-3a, b. The Fig.-3a, confirms that Mn_2O_3 alone has achieved 60.08 % degradation at 530 nm for 60 min, indicating low photocatalytic activity driven by the h^+ majorly, $OH^{\bullet}/O_2^{\bullet}$ radicals (minorly)and no notable influence on the oxidation of the phenazine species at 280nm. On the other hand under the optimized conditions, Mn_2O_3 with $K_2S_2O_8$ OA together has exhibited synergistic enhancement in the catalytic performance of 82.15% and 85.6 % at 530and 280 nm for 30min respectively and further 89.5% for 60min (Fig.-3b) in the presence of vis -light irradiation due to the ROS species OH• and $SO_4^{\bullet-}$involved for NR photo oxidative decomposition at pH of 6 ± 0.1 which is confirmed from Table-3 as per electrodepotentials.[9,10] This highlights its potential application in environmental remediation. The photo degradation of NR dye has followed pseudo-first order kinetics (Fig.-3c, d and Table-4), and its mechanism is mentioned below.[9,10]

Mechanism of NR Dye Degradation by Mn_2O_3 Photo-Catalyst Alone[5,9,10]

$Mn_2O_3 + h\nu\ (visible) \longrightarrow Mn_2O_3\ (e_{CB}^-) + Mn_2O_3(h_{VB}^+)$

$O_2 + e_{CB}^- \longrightarrow O_2^{\bullet -}$

$H_2O + h_{VB}^+ \rightarrow OH^{\bullet} + H^+$

$Dye + h_{VB}^+{}_{(Major)} + OH^{\bullet}/O_2^{\bullet -}{}_{(minor)} \rightarrow$ Intermediate Phenazine ring + $CO_2 + H_2O$

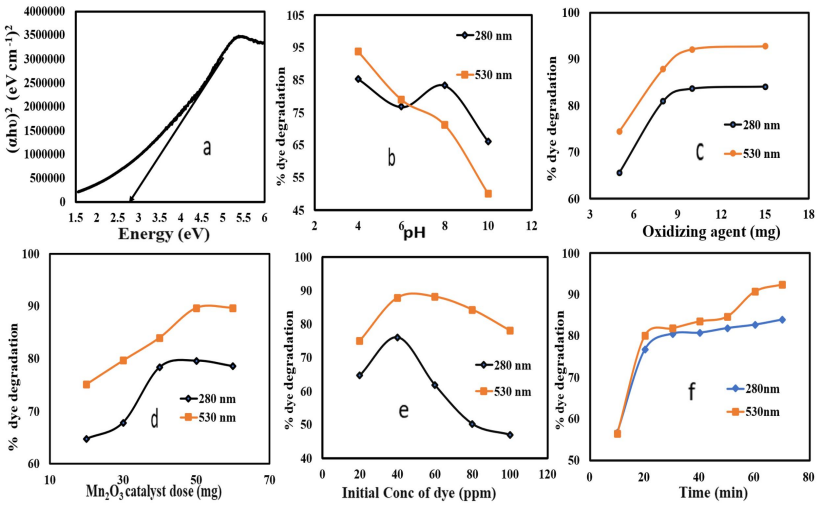

Fig.-2: Optical Properties and Optimisation of Neutral Red Dye Degradation Parameters. (a) Band Gap Analysis (b) pH Effect (c) Oxidizing Effect (d) Catalyst Dose Effect (e) NR Dye Concentration Effect (f) Time Effect

Table-3: Potential of the NR, Mn_2O_3 Nanosphere Catalyst, ROS[10-14]

Compounds	Potential (eV)
phenazine ring in NR (mid potential)	−0.64 to – 1.8 V
Mn_2O_3 nanosphere- E_{CB}	-0.22
Mn_2O_3 nanosphere- E_{VB}	+2.58
O_2 / $O_2^{\bullet-}$	-0.18 to -0.28
$SO_4^{\bullet-}$ radical	+1.44 to 2.43
H_2O/•OH radical	+ 2.73

Mechanism of NR Dye Degradation by Mn_2O_3 with $K_2S_2O_8$ Oxidising Agent [8,9-14]

$Mn_2O_3 + h\nu\ (visible) \longrightarrow Mn_2O_3\ (e_{CB}^-) + Mn_2O_3\ (h_{VB}^+)$

$S_2O_8^{2-} + e_{CB}^- \longrightarrow SO_4^{\bullet-} + SO_4^{2-}$

$h_{VB}^+ + H_2O \longrightarrow {}^{\bullet}OH + H^+$

$2SO_4^{2-} + 2h_{VB}^+ \longrightarrow SO_4^{\bullet-}(aqs) + SO_4^{\bullet-}(ads)$

$SO_4^{\bullet-}(aqs) + H_2O \longrightarrow {}^{+\bullet}OH + HSO_4^-$

$Dye + SO_4^{\bullet-} + {}^{\bullet}OH \longrightarrow CO_2 + NO_3^- + H_2O$

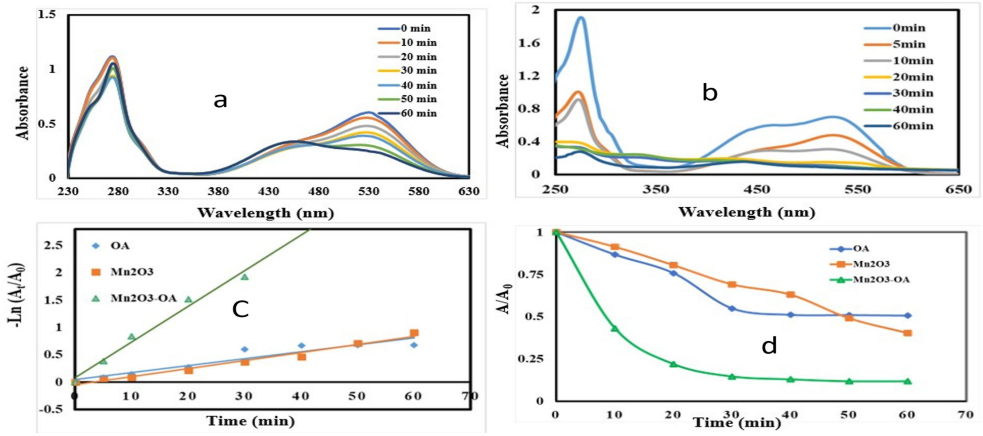

Fig.-3: Neutral Red Dye Degradation at the Optimised Parameters Under Visible Light, (a) Mn_2O_3 Catalyst (b) Mn_2O_3 Catalyst with $K_2S_2O_8$ Combination (c) Pseudo First Order Kinetic Model (d) A_t/A_0 vs Time

Table-4: Pseudo First Order Constants Under Different Conditions of NR Photodegradation

Catalyst	K (m^{-1})	R^2
$K_2S_2O_8$ (OA)	0.0128	0.895
Mn_2O_3	0.015	0.978
Mn_2O_3 -OA	0.0653	0.981

Regeneration of the catalyst has been performed in 1N HNO_3 solution at 60˚C for 30 min and washed with distilled water. After the washing, it is calcinated at 300˚C to remove any deposits on its surface. In its second and third cycles, it has exhibited an average of 66 % of degradation efficiency.

CONCLUSION

The Synthesised bixbyite Mn_2O_3nanosphere diffractogram corresponds to JCPDS card No. 41-1442. Its individual photocatalytic efficiency on the degradation of NR under visible light was 60.08 % at 530 nm, but it was unable to disintegrate the intermediate phenazine product, which is a carcinogenic compound. On contrary, bixbyite Mn_2O_3nanosphere with $K_2S_2O_8$ OA under visible light and optimized parameters at pH of 6± 0.1, has exhibited a synergistic effect on degradation of NR around 89.5% for 60 min and finally converted to benign CO_2, H_2O and nitrate products which is an ecofriendly approach to remove pollutants in wastewater stream results in environmental sustainability and meet SDS goals:6. This degradation of the dye has followed pseudo first order kinetics.

ACKNOWLEDGMENTS

The authors say thanks to IISC and CAMT @RIT for the characterisation of the material.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-6:Clean water and Sanitation*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

R. Lakshminarayani https://orcid.org/0009-0005-1633-8895
S. C. Malathi https://orcid.org/0000-0002-8985-9166
Anusukdev https://orcid.org/0000-0001-9755-5157

Cite this article as: R. Lakshminarayani *et al.*, *Rasayan J. Chem.*, 19(1), 244-249(2026), https://doi.org/10.317 88/RJC.2026.1919524.

REFERENCES

1. S.T. Fardood, F. Moradnia, F.Y. Zare, S. Heidarzadeh, M. Azad Majedi, A. Ramazani, M.Sillanpää, K.Nguyen, *Scientific Reports,* **14(1)**,6755 (2024), 10.1038/s41598-024-56666-2
2. P. Amruta, J.N. Sahu, A. K. Poonia, G. Prabir, *Chemical Engineering Research and Design*,**190,**667(2023), https://doi.org/10.1016/j.cherd.2023.01.014
3. S.S.Majani , M.A.Veena , C.M.Hemanth Kumar , B.Poojitha , S.Setty, M. Iqbal, C. Shivamallu, A.C. Cull, K.E.Hales, R.B. Paul , Raghavendra , K. Shiva Prasad, *Scientific Reports*, **15,**18081(2025), https://doi.org/10.1038/ s41598-025-97862-y
4. F. Mahfoozi, A. Mahmoudi, M. Reza Sazegar, K. Nazari, *Journal of Sol-Gel Science and Technology*, **100**, 170(2021), https://doi.org/10.1007/s10971-021-05627-6
5. Gulnaz Munir, Hamza Elsayed Ahmed Mohamed, Khaoula Hkiri, Suresh Ghotekar, Malik Maaza, *Inorganic Chemistry Communications,* **167**,112695(2024),https://doi.org/10.1016/j.inoche.2024.112695

6. R. Lakshmi Narayani, V. J. Angadi, S. Anu, C. Malathi, M. Shidaling, P.R. Deepthi, P. Mohan Kumar, M. Pasha, *Journal of Magnetism and Magnetic Materials*, **476,** 268(2019), https://doi.org/10.1016/j.jmmm.2018.12.072
7. K.K. Hazarika, G. Chiranjita, H. Saikia, B. Biraj Jyoti, B. Pankaj, *Molecular Catalysis*, **451** 153(2018), https://doi.org/10.1016/j.mcat.2017.12.012.
8. M.S.P. Yadav, N. Neghi, M. Kumar, G.K. Varghese, *Journal of Environmental Management*, **222,** 164(2018), https://doi.org/10.1016/j.jenvman.2018.05.052
9. S. Khan, T. Noor, N. Iqbal, L. Yaqoob, *ACS Omega*, **9(20),** 21751(2024), https://doi.org/10.1021/acsomega.4c00887
10. A.Mancuso, K.Monzillo, O. Sacco, L. Spiridigliozzi, V. Monfreda, A. Muscatello, G. Dell'Agli, S. Esposito, V. Vaiano, *Journal of Alloys and Compounds*, **1026**, 180435(2025), https://doi.org/10.1016/ j.jallcom.2025.180435
11. Mahsa, T. Mohammad, *Journal of Modern Optics*, **69,**1(2022), https://doi.org/10.1080/09500340.2022. 2095050
12. Jie Teng, Yuzhen Zhang, Pu Li, Guoshuai Liu, *Sustainable Horizons*, **16**,100156(2025), https://doi.org/10.1016/j.horiz.2025.100156
13. A Nixon Azariah, Sheela Berchmans, V. Yegnaraman, *Bulletin of Electrochemistry,* **14(10)**, 309(1998)
14. A. David Armstrong, R. E. Huie, L.Sergei, W.H. Koppenol, M. Gabor, P. Neta, D. Stanbury, S. Steenken, W. Peter. *BioInorganic Reaction Mechanisms*, **9(1-4)**, 59(2013), https://doi.org/10.1515/irm-2013-0005

[RJC-9555/2025]