iJRASET
International Journal For Research in
Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH
IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 14 **Issue:** VII **Month of publication:** July 2026

DOI: https://doi.org/10.22214/ijraset.2026.84165

International Journal for Research in Applied Science & Engineering Technology (IJRASET)
ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor: 7.538
Volume 14 Issue VII July 2026- Available at www.ijraset.com

Photocatalytic activity of Ni (II) Complexes Derived from p-substituted Isonitrosoacetophenone-4 Phenylthiosemicarbazone as Catalyst for Degradation of Azo Dye

Shivani B. Malap[1], Sayali V. Kadam[2], Raju M. Patil[3]
Department of Chemistry, The Institute of Science, Dr. Homi Bhabha State University, 15, Madame Cama Road, Mumbai-400 032, India

Abstract: A series of p-substituted isonitrosoacetophenone-4-phenylthiosemicarbazone Ni(II) complexes were successfully synthesized and investigated for their photocatalytic potential in the degradation of the azo dye methyl orange, a common organic pollutant found in industrial wastewater. The synthesized complexes were thoroughly characterized using various physicochemical and spectroscopic techniques, including elemental analysis, molar conductance measurements, magnetic susceptibility studies, electronic absorption spectroscopy, Fourier-transform infrared (FTIR) spectroscopy, and thermogravimetric–differential thermal analysis (TG-DTA). The photocatalytic activity of the Ni(II) complexes was evaluated under heterogeneous catalytic conditions by monitoring the degradation of methyl orange under light irradiation. The influence of important operational parameters such as irradiation time, catalyst dosage, and catalyst reusability was systematically examined to optimize the degradation process. The results revealed that the synthesized Ni(II) complexes exhibited significant photocatalytic efficiency toward methyl orange degradation, leading to substantial dye removal within the studied time period. Furthermore, the catalysts retained considerable activity after repeated catalytic cycles, demonstrating good stability and reusability. Based on the experimental findings, a possible photocatalytic degradation mechanism involving the generation of reactive oxygen species has been proposed. These results suggest that the synthesized Ni(II) complexes can serve as effective and environmentally friendly photocatalysts for the treatment of dye-contaminated wastewater.

Keywords: Nickel metal complexes, Structural study, Photocatalytic activity, Methyl orange

I. INTRODUCTION

The rapid growth of industrial activities has led to the extensive release of synthetic dyes into aquatic environments, posing a serious threat to ecosystems and human health. Dyes are widely used in textile, paper, leather, cosmetics, food, and pharmaceutical industries because of their excellent coloring properties and chemical stability. However, a significant fraction of these dyes is discharged into wastewater during manufacturing and processing operations. Even at low concentrations, dyes can impart intense coloration to water bodies, reducing light penetration and disrupting photosynthetic processes in aquatic ecosystems. Methyl orange (MO), a widely used azo dye, is frequently detected in industrial effluents and poses serious environmental and health risks because of its persistence and potential carcinogenic nature [[1]–[3]].

The removal of methyl orange from wastewater has therefore attracted considerable research interest. Conventional treatment techniques such as adsorption, coagulation–flocculation, ultrafiltration, and electrochemical degradation have been employed for dye removal; however, these methods often suffer from limitations such as incomplete degradation, high operational costs, and the generation of secondary pollutants in the form of sludge [[4]–[6]]. Consequently, the development of efficient and environmentally sustainable approaches for dye remediation remains an important area of investigation.

Photocatalytic degradation has emerged as a promising strategy for the treatment of dye-contaminated wastewater because it can convert organic pollutants into less harmful or completely mineralized products under light irradiation [[7]]. The photocatalytic process involves the excitation of electrons from the valence band to the conduction band of a photocatalyst, generating electron–hole pairs that subsequently produce reactive oxygen species capable of degrading dye molecules [[8],[9]].

Despite significant progress, the rapid recombination of photogenerated charge carriers remains a major challenge that limits photocatalytic efficiency. Therefore, considerable efforts have been devoted to the development of novel photocatalysts with enhanced charge separation and visible-light activity [[10]–[12]]. In this context, transition metal complexes, particularly nickel(II) complexes, have gained attention owing to their favorable electronic properties, structural versatility, chemical stability, and catalytic potential [[13]–[18]]. The present study investigates the photocatalytic degradation of methyl orange using nickel(II) complexes under visible-light irradiation to evaluate their effectiveness as photocatalysts for wastewater treatment applications[[19]–[22]].

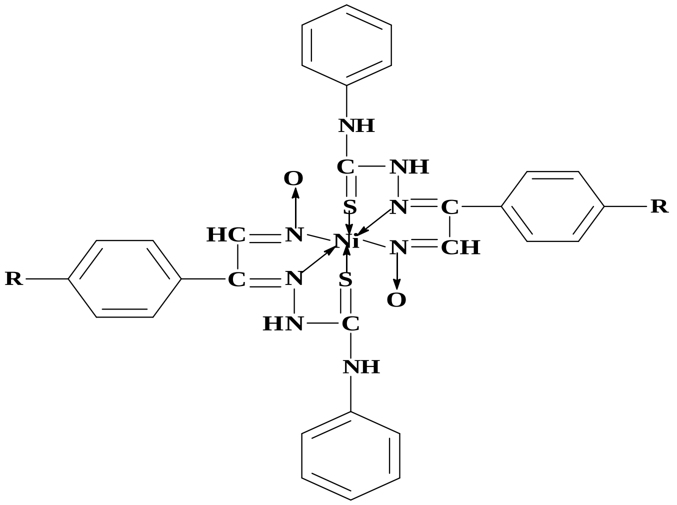
II. MATERIALS AND METHODS

Analytical reagent grade chemicals were used throughout the study. Nickel chloride hexahydrate ($NiCl_2 \cdot 6H_2O$) was obtained from SDFCL and used without further purification. Methyl Orange Dye was purchased from Sigma Aldrich. All solvents were purified and distilled by standard methods before use [[23]]. The thiosemicarbazone ligands were prepared via the condensation of 4-phenylthiosemicarbazide with para-substituted isonitrosoacetophenones and characterized in our laboratory[[24]].

A. Synthesis of Ni(II) complexes

The Ni(II) complexes of ligands were synthesized [[25]] by using an aqueous solution of Ni(II) chloride hexahydrate (1 mmol) and *p*-substituted isonitrosoacetophenones phenyl thiosemicarbazones(INAP-PTSC) (2 mmol). The preparation of nickel complexes was carried in 2:1 molar ratio. The complexes derived from p-substituted isonitrosoacetophenones phenyl thiosemicarbazone (INAP-PTSC) were prepared by dissolving 2 moles of ligands in 20 ml ethanol and 1 mole of $NiCl_2.6H_2O$ metal salt in 10 ml ethanol; NH_3 was added dropwise with constant stirring. The pH was maintained between 7-8 and stirred for 30 minutes. The solid mass was separated by filtration and washed repeatedly with ethanol and dried.

The nickel content of the synthesized complexes was estimated by complexometric titration using standard analytical procedures [[26]]. The molar conductance of the complexes was measured in 10^{-3} M DMF solutions using a EQUIP-TRONICS EQ-660A digital conductivity meter fitted with a magnetic stirrer and having a cell constant of 1. Room-temperature magnetic susceptibility measurements were carried out using a Gouy balance (Batra Trading Company, Model GMX-TR2), with $Hg[Co(SCN)_4]$ employed as the standard calibrant. The effective magnetic moments were calculated after applying diamagnetic corrections for the ligand moieties using Pascal's constants [[27]]. The electronic spectra of the nickel(II) complexes were recorded in DMF on a Shimadzu UV-1800A UV–Visible spectrophotometer. Thermal studies, including thermogravimetric (TG) and differential thermal analysis (DTA), were performed using a Rigaku Thermo Plus-8120 TG-DTA instrument. Fourier-transform infrared (FT-IR) spectra of the ligands and their corresponding metal complexes were obtained in the 4000–400 cm^{-1} region using an INFRA-3000 spectrometer and interpreted with reference to reported literature data [[28]]. The proposed structures of the nickel(II) complexes are depicted in given scheme.1



Where R= -H, $-CH_3$, $-OCH_3$, -OH, -Cl, $-NO_2$

Ni(II) Complex of Isonitrosoacetophenonephenylthiosemicarbazone

Scheme 1: Ni(II) complexes of Isonitrosoacetophenonephenylthiosemicarbazone

B. Preparation of Methyl orange dye solution:

The stock solution of methyl orange (MO) was prepared at a concentration of 100 ppm by dissolving 100 mg of the dye in 1000 mL of deionized water. A 10 ppm working solution was then prepared by transferring 50 mL of the stock solution into a 500 mL volumetric flask and making up the volume with deionized water. This diluted solution was employed for the photocatalytic degradation studies.

C. Photocatalytic activity:

The photocatalytic activity of the nickel(II) complexes was assessed through the degradation of methyl orange (MO) dye under illumination from a tungsten filament lamp. The degradation experiments were performed using a 10 ppm MO solution at different irradiation times (30, 60, 90, and 120 min) and with varying catalyst dosages (25, 50, 75, and 100 mg). The absorbance of the dye solution was recorded both before and after exposure to light, in the presence as well as the absence of the catalyst. Following irradiation, the catalyst was recovered by centrifugation, and the absorbance of the resulting supernatant was measured using a UV–Visible spectrophotometer at 480 nm. The percentage degradation efficiency was determined from the change in absorbance using the following equation:

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

Where A_0 and A_t denotes absorbance before and after photocatalytic degradation of Methylorange

III. RESULTS AND DISCUSSIONS

A. Photocatalytic Activity

For determination of λ_{max} Methyl orange dye was used of 100 ppm concentration (100 mg/L) and was found at 480 nm shown in Fig.2.

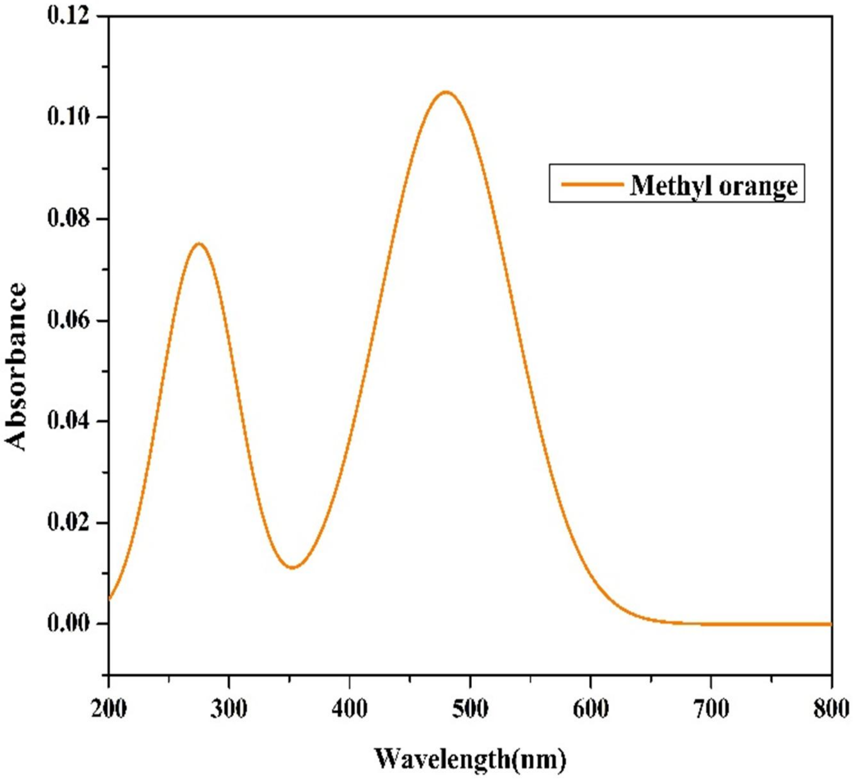


Fig. 1. Wavelength of maximum absorbance of Methyl orange dye λ_{max} 480 nm

B. Determination of initial absorbance (A_o):

For determination of initial absorbance (A_o) 10 ppm dye solution was used and absorbance obtained at A_o = 0.105 is shown in Fig.2

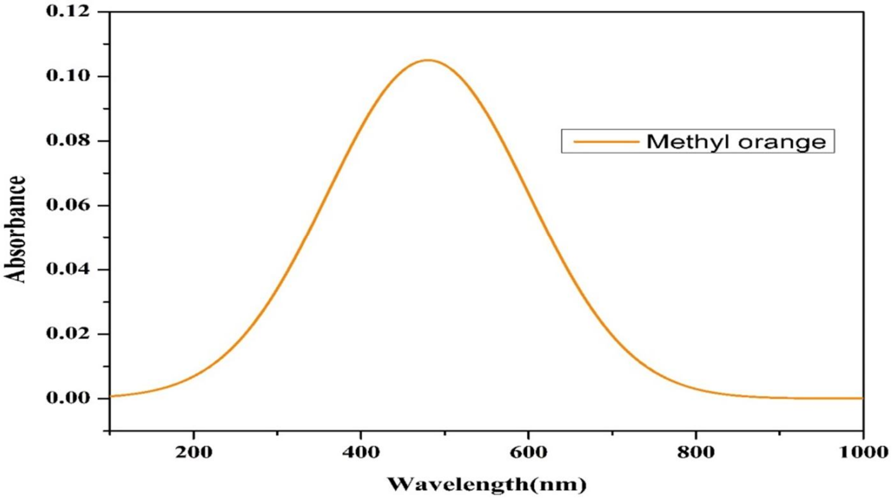


Fig.2. Initial absorbance (A_o) of Methyl Orange dye without light irradiation

C. Effect of time on degradation:

In first way keeping fixed concentration (10 ppm) of dye and 50 mg of complex with varying time interval 30,60 ,90 and 120 min, absorbance measured at wavelength 480 nm, which is tabulated in

Table *1* and represented in Fig.3 shown as below:

Table 1 : Effect of time on degradation

Sr. No	Complex	Time	Absorbance	% Degradation
1	NL1	30	0.097	7.61
		60	0.067	36.19
		90	0.037	64.76
		120	0.015	85.71
2	NL2	30	0.096	8.57
		60	0.065	38.09
		90	0.036	65.71
		120	0.014	86.66
3	NL3	30	0.095	9.52
		60	0.063	40.0
		90	0.035	66.66
		120	0.013	87.61
4	NL4	30	0.093	11.42
		60	0.062	40.95
		90	0.033	68.57
		120	0.013	87.61
5	NL5	30	0.092	12.38
		60	0.061	41.90
		90	0.031	70.47
		120	0.011	89.52
6	NL6	30	0.090	14.28
		60	0.058	44.76
		90	0.029	72.38
		120	0.010	90.47

L1= INAP-PTSC L2 = p-Me INAP-PTSC L3 = p-OMe INAP-PTSC,
L4 = p-OH INAP-PTSC L5 = p-Cl INAP-PTSC , L6 = p-NO_2 INAP

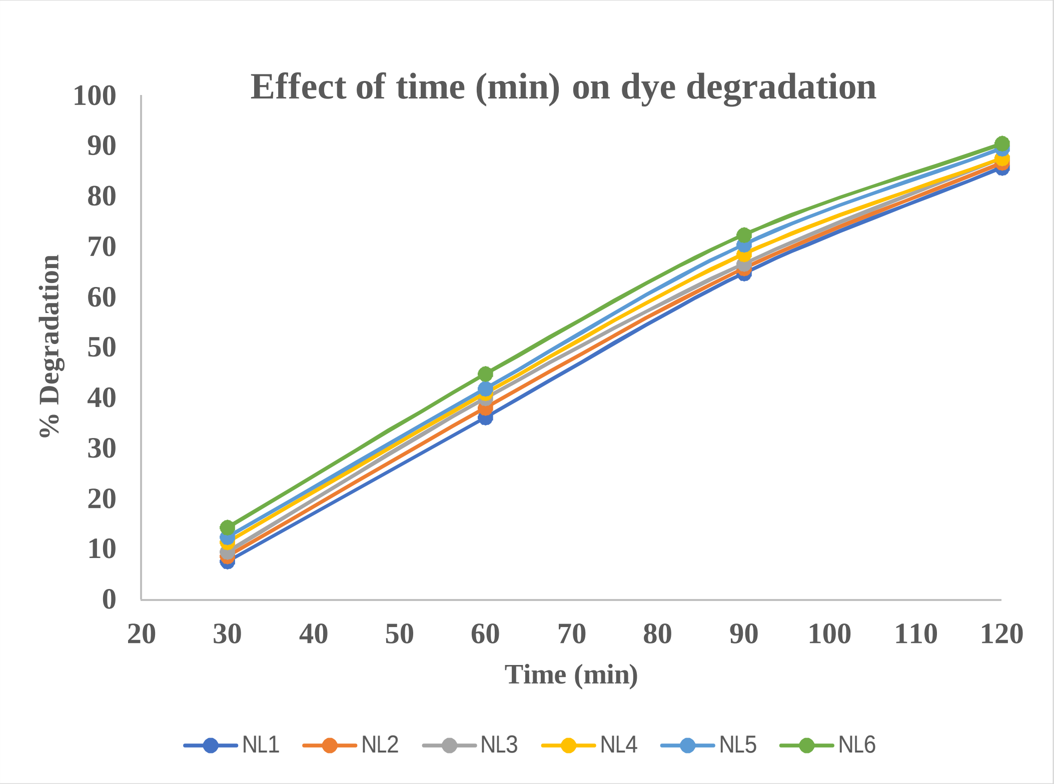


Fig.3. Effect of time (min) on dye degradation

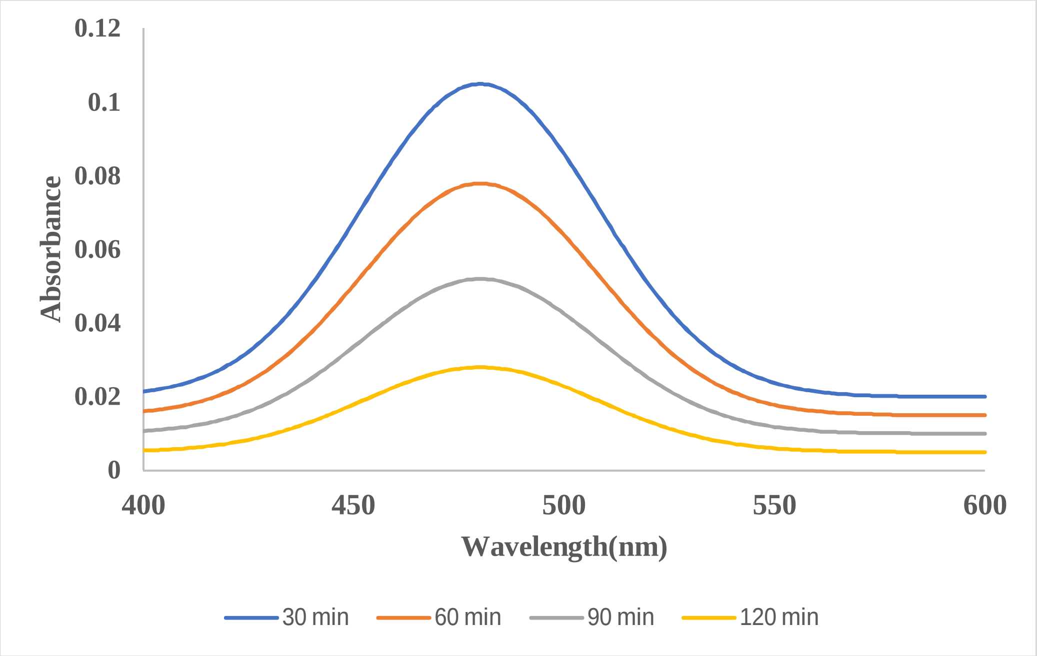


Fig. 4. UV–Vis absorption spectra of methyl orange solution recorded at different irradiation times (30–120 min) in the presence of the representative NL1 complex photocatalyst.

The gradual decrease in absorbance intensity at λ_{max} = 480 nm indicates the progressive photocatalytic degradation of methyl orange under light irradiation. The nickel complexes exhibited significant photocatalytic activity toward dye degradation, with degradation efficiency increasing progressively with irradiation time.

The percentage degradation ranged from 7.61-14.28% after 30 min, 36.19-44.26% after 60 min and 64.76–72.38% after 90 min of irradiation. A further increase in degradation efficiency was observed after 120 min, reaching 85.71–90.47%**.** These results demonstrate that prolonged irradiation enhances the photocatalytic performance of the nickel complex, resulting in more effective degradation of the dye.

D. Effect of amount of Catalyst on Degradation:

In second way by varying the amount of catalyst and fixed 10 ppm concentration of dye sample was irradiated with light for 120 minutes. After irradiation absorbance was measured and it was found to be increased. With increasing the amount of catalyst, the % dye degradation increased tabulated in (Table 2) and represented in Fig.5.

The percentage degradation of the dye increased with increasing catalyst dosage. The degradation efficiency ranged from 18.09–23.80%**,** 69.52-76.19%**,** 74.28-80.00%**,** and 77.14–81.90% at catalyst loadings of 25, 50, 75, and 100 mg**,** respectively. These results indicate that higher catalyst concentrations enhance the photocatalytic degradation of the dye.

Table 2. Effect of amount of Catalyst on Degradation

Sr.No	Complex	Amount	Absorbance	% Degradation
1	NL1	25	0.086	18.09
		50	0.032	69.52
		75	0.027	74.28
		100	0.024	77.14
2	NL2	25	0.085	19.04
		50	0.031	70.47
		75	0.026	75.23
		100	0.023	78.09
3	NL3	25	0.084	20.00
		50	0.030	71.42
		75	0.025	76.19
		100	0.022	79.04
4	NL4	25	0.083	20.95
		50	0.029	72.38
		75	0.024	77.14
		100	0.021	80.00
5	NL5	25	0.081	22.85
		50	0.027	74.28
		75	0.022	79.04
		100	0.020	80.95
6	NL6	25	0.080	23.80
		50	0.025	76.19
		75	0.021	80.00
		100	0.019	81.90

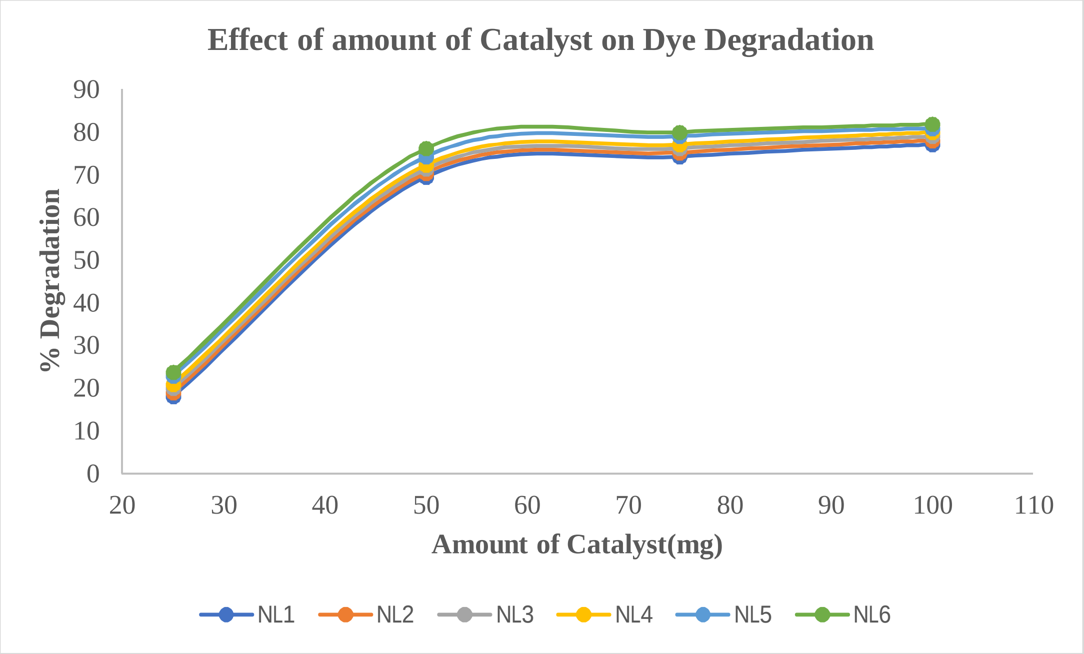


Fig.5. Effect of amount of catalyst on dye degradation

E. Reusability of Catalyst

The reusability of the representative NL1 complex (

Table *3*) was investigated through successive photocatalytic degradation cycles of Methyl Orange under optimized reaction conditions, employing a catalyst dosage of 50 mg, an irradiation time of 120 min, and a dye concentration of 10 ppm. After each cycle, the catalyst was recovered by filtration, washed thoroughly with distilled water and ethanol, dried, and reused in subsequent experiments. The results revealed a gradual decrease in the photocatalytic degradation efficiency of the NL1 complex with increasing number of cycles. This decline in activity may be attributed to the loss of catalyst during recovery, adsorption of degradation intermediates on the catalyst surface, and partial deactivation of active sites. Despite the reduction in degradation efficiency upon repeated use, the NL1 complex retained appreciable photocatalytic activity after several cycles, demonstrating good stability and reusability for the degradation of Methyl Orange under the investigated conditions.

Table 3. Efficiency of Representative NL1 Complex

No.of Catalytic cycle	Absorbance (At)	% Degradation
1	0.035	65.34
2	0.037	65.36
3	0.04	60.39
4	0.04	60.39
5	0.04	60.39

F. Mechanism for Dye Degradation

Upon exposure to visible light irradiation, the nickel complex absorbs photons and undergoes photoexcitation, resulting in the generation of electron–hole pairs. The efficient separation of these charge carriers enhances the photocatalytic activity of the complex and suppresses electron–hole recombination. The photogenerated electrons react with dissolved oxygen molecules to produce superoxide radical anions ($O_2^{\bullet-}$), while the photogenerated holes oxidize water molecules or surface hydroxyl groups to generate highly reactive hydroxyl radicals ($^{\bullet}OH$). The superoxide radicals may further react with H^+ ions to form hydroperoxyl radicals ($HO_2^{\bullet}$), which contribute to the formation of additional reactive oxygen species. These radicals, particularly $^{\bullet}OH$ and $^{\bullet}O_2^-$, play a crucial role in the oxidative degradation of Methyl Orange molecules. The reactive species attack the azo (–N=N–) bond and aromatic rings of the dye, resulting in cleavage of the chromophoric structure and progressive decomposition into smaller organic intermediates.

Further oxidation of these intermediates leads to their mineralization into environmentally benign products such as carbon dioxide, water, and inorganic ions. The synergistic action of hydroxyl and superoxide radicals significantly accelerates the degradation and decolorization of Methyl Orange. Therefore, the nickel complex acts as an efficient photocatalyst by facilitating charge separation and promoting the generation of reactive oxygen species responsible for dye degradation.

IV. CONCLUSION

The photocatalytic degradation of Methyl Orange was investigated using a series of nickel(II) complexes containing p-substituted isonitrosoacetophenones phenyl thiosemicarbazone ligands. All the synthesized complexes exhibited significant photocatalytic activity, achieving more than 85% degradation of Methyl Orange within 120 min of irradiation.

Among the investigated complexes**,** NL6, containing the p-nitro substituted ligand, displayed the highest photocatalytic activity. The enhanced performance of NL6 can be attributed to the strong electron-withdrawing nature of the nitro group, which facilitates efficient charge separation and suppresses electron–hole recombination. This promotes the generation of reactive oxygen species such as hydroxyl and superoxide radicals, leading to improved degradation of Methyl Orange. Similarly, the p-chloro substituted complex NL5 exhibited superior activity compared to the unsubstituted and electron-donating substituted analogues, further highlighting the beneficial effect of electron-withdrawing substituents on photocatalytic performance.

In contrast, complexes containing electron-donating substituents such as methyl, methoxy, and hydroxyl groups showed comparatively lower degradation efficiencies. Although these substituents may enhance electron density within the ligand framework, they are less effective in facilitating charge separation during the photocatalytic process. The unsubstituted complex NL1 displayed the lowest activity among the series.

The results demonstrate that the electronic properties of ligand substituents play a crucial role in determining the photocatalytic efficiency of nickel(II) complexes. The present study suggests that incorporation of electron-withdrawing groups into the ligand framework is an effective strategy for enhancing photocatalytic degradation of organic dyes. These nickel(II) complexes therefore represent promising candidates for the treatment of dye-contaminated wastewater and environmental remediation applications.

V. ACKNOWLEDGEMENT

Authors are grateful to The Institute of Science and Dr. Homi Bhabha State University, Mumbai for providing Instrumental and Laboratory Facilities.

REFERENCES

[1] Chowdhury, A. P.; Anantharaju, K. S.; Keshavamurthy, K.; Rokhum, S. L. Recent Advances in Efficient Photocatalytic Degradation Approaches for Azo Dyes. Journal of Chemistry 2023, 1–24. doi:10.1155/2023/9780955.

[2] Goswami, D.; Mukherjee, J.; Mondal, C.; Bhunia, B. Bioremediation of azo dye: A review on strategies, toxicity assessment, mechanisms, bottlenecks and prospects. Science of The Total Environment 2024, 954, 176426. doi:10.1016/j.scitotenv.2024.176426.

[3] Emmanuel, S. S.; Adesibikan, A. A.; Opatola, E. A.; Olawoyin, C. O. A pragmatic review on photocatalytic degradation of methyl orange dye pollutant using greenly biofunctionalized nanometallic materials: A focus on aquatic body. Applied Organometallic Chemistry 2023, 37(7). doi:10.1002/aoc.7108.

[4] Yaseen, D. A.; Scholz, M. Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review. International Journal of Environmental Science and Technology 2019, 16(2), 1193–1226. doi:10.1007/s13762-018-2130-z.

[5] Crini, G.; Lichtfouse, E. Advantages and disadvantages of techniques used for wastewater treatment. Environmental Chemistry Letters 2019, 17(1), 145–155. doi:10.1007/s10311-018-0785-9.

[6] Rueda-Marquez, J. J.; Levchuk, I.; Fernández Ibañez, P.; Sillanpää, M. A critical review on application of photocatalysis for toxicity reduction of real wastewaters. Journal of Cleaner Production 2020, 258, 120694. doi:10.1016/j.jclepro.2020.120694.

[7] Forgacs, E.; Cserháti, T.; Oros, G. Removal of synthetic dyes from wastewaters: a review. Environment International 2004, 30(7), 953–971. doi:10.1016/j.envint.2004.02.001.

[8] Chong, M. N.; Jin, B.; Chow, C. W. K.; Saint, C. Recent developments in photocatalytic water treatment technology: A review. Water Research 2010, 44(10), 2997–3027. doi:10.1016/j.watres.2010.02.039.

[9] Emmanuel, S. S.; Adesibikan, A. A.; Opatola, E. A.; Olawoyin, C. O. A pragmatic review on photocatalytic degradation of methyl orange dye pollutant using greenly biofunctionalized nanometallic materials: A focus on aquatic body. Applied Organometallic Chemistry 2023, 37(7). doi:10.1002/aoc.7108.

[10] Gadore, V.; Mishra, S. R.; Ahmaruzzaman, Md. Metal sulphides and their heterojunctions for photocatalytic degradation of organic dyes-A comprehensive review. Environmental Science and Pollution Research 2023, 30(39), 90410–90457. doi:10.1007/s11356-023-28753-w.

[11] Sarkodie, B.; Amesimeku, J.; Frimpong, C.; Howard, E. K.; Feng, Q.; Xu, Z. Photocatalytic degradation of dyes by novel electrospun nanofibers: A review. Chemosphere 2023, 313, 137654. doi:10.1016/j.chemosphere.2022.137654.

[12] Samarasinghe, L. V.; Muthukumaran, S.; Baskaran, K. Recent advances in visible light-activated photocatalysts for degradation of dyes: A comprehensive review. Chemosphere 2024, 349, 140818. doi:10.1016/j.chemosphere.2023.140818.

[13] Dhasade, V. S.; Janwadkar, S. P. Photocatalytic Activity of Some Mixed Ligand Metal Complexes as Heterogeneous Catalyst for Degradation of Azo Dye; J.Chemical Health Risks,2025.15,2080-2084.

[14] Ban, F.; Wei, Y.; Xin, J.; Ye, C.; Xiao, A. Research Progress on Photocatalytic Degradation of Methyl Orange Dye Wastewater by Light-assisted Composite-modified Ag_3PO_4. Chemistry Select 2024, 9(3). doi:10.1002/slct.202303252.

[15] Haleem, A.; Shafiq, A.; Chen, S.-Q.; Nazar, M. A Comprehensive Review on Adsorption, Photocatalytic and Chemical Degradation of Dyes and Nitro-Compounds over Different Kinds of Porous and Composite Materials. Molecules 2023, 28(3), 1081. doi:10.3390/molecules28031081.

[16] Krishnan, A.; Swarnalal, A.; Das, D.; Krishnan, M.; Saji, V. S.; Shibli, S. M. A. A review on transition metal oxides based photocatalysts for degradation of synthetic organic pollutants. Journal of Environmental Sciences 2024, 139, 389–417. doi:10.1016/j.jes.2023.02.051.

[17] Islam, M.; Kumar, S.; Saxena, N.; Nafees, A. Photocatalytic Degradation of Dyes Present in Industrial Effluents: A Review. ChemistrySelect 2023, 8(26). doi:10.1002/slct.202301048.

[18] Kisch, H. Semiconductor Photocatalysis—Mechanistic and Synthetic Aspects. Angewandte Chemie International Edition 2013, 52(3), 812–847. doi:10.1002/anie.201201200.

[19] Rueda-Marquez, J. J.; Levchuk, I.; Fernández Ibañez, P.; Sillanpää, M. A critical review on application of photocatalysis for toxicity reduction of real wastewaters. Journal of Cleaner Production 2020, 258, 120694. doi:10.1016/j.jclepro.2020.120694.

[20] Crini, G.; Lichtfouse, E. Advantages and disadvantages of techniques used for wastewater treatment. Environmental Chemistry Letters 2019, 17(1), 145–155. doi:10.1007/s10311-018-0785-9.

[21] Yaseen, D. A.; Scholz, M. Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review. International Journal of Environmental Science and Technology 2019, 16(2), 1193–1226. doi:10.1007/s13762-018-2130-z.

[22] Chong, M. N.; Jin, B.; Chow, C. W. K.; Saint, C. Recent developments in photocatalytic water treatment technology: A review. Water Research 2010, 44(10), 2997–3027. doi:10.1016/j.watres.2010.02.039.

[23] Armarego, W. L. F. .; Perrin, D. D. . Purification of Laboratory Chemicals; Butterworth Heinemann, 19971996.

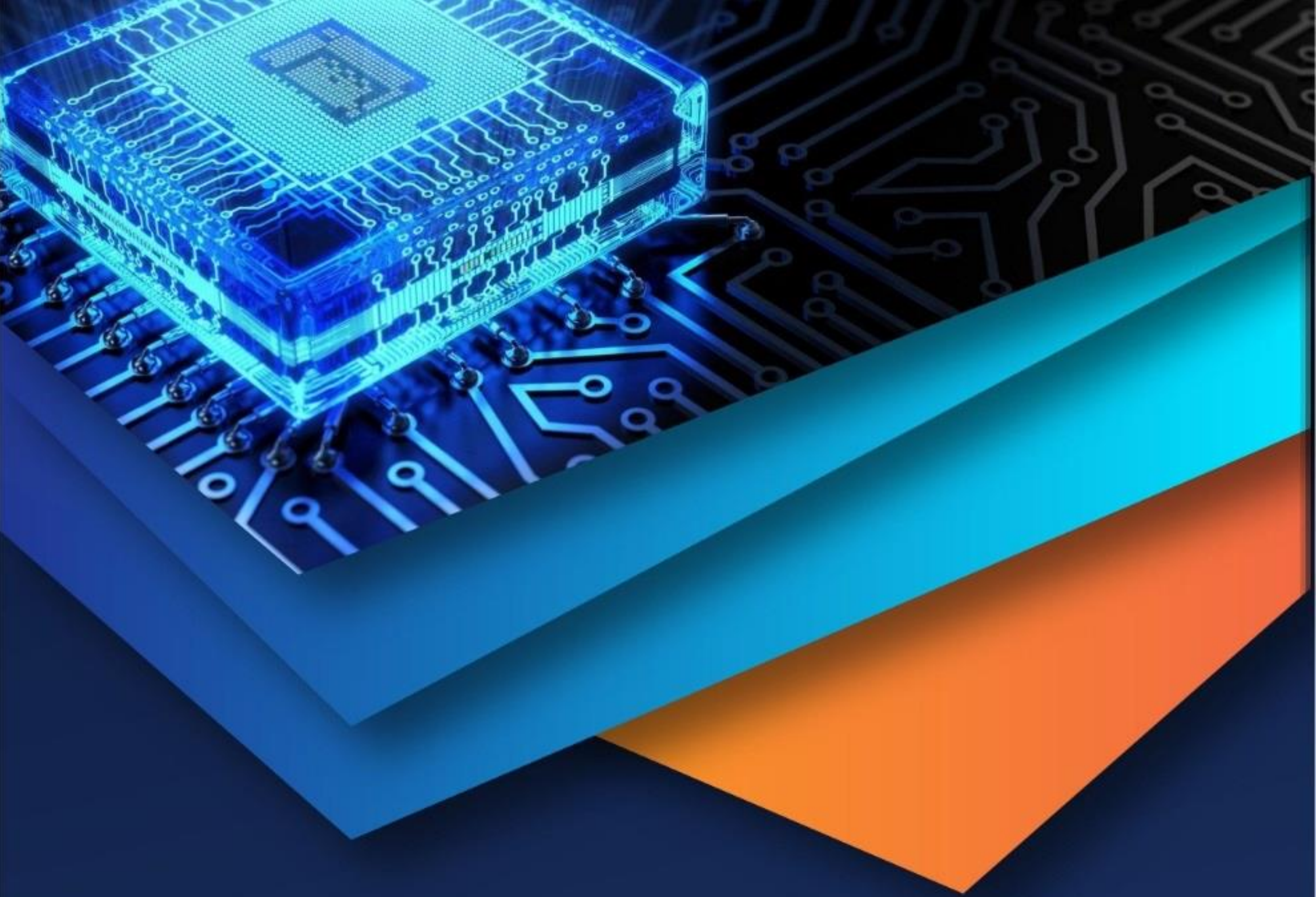
[24] Malap, S. B.; Patil, R. M. Synthesis, characterization and biological investigations of novel phenylthiosemicarbazones. Journal of the Indian Chemical Society 2025, 102(9), 101933. doi:10.1016/j.jics.2025.101933.

[25] Malap, S. B.; Patil, R. M. Nickel Complexes derived from Novel Phenylthiosemicarbazone ligands as Antimicrobial and Anticancer Agents: Synthesis, Characterization and Biological Investigations.International Journal of Innovative Research and Technology , 2026,12(10), 3531-3550.

[26] Vogel, A. I. .; Jeffery, G. H. .; Vogel, A. Israel. Vogel's Textbook of Quantitative Chemical Analysis; Longman Scientific & Technical ; Wiley, 1989.

[27] Datta R.L.; Syamal A. Elements of Magneto-Chemistry; 2nd ed.; Affiliated East West Press, New Delhi, 1993.

[28] Nakamoto, K. Infrared and Raman Spectra of Inorganic and Coordination Compounds. In Handbook of Vibrational Spectroscopy. Griffiths, P. R., Ed.; Wiley, 2001. doi:10.1002/0470027320.s4104.



INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY