



# Photocatalytic Activity of Some Mixed Ligand Metal Complexes as Heterogeneous Catalyst for Degradation of Azo Dye

Vina S. Dhasade\* and Suhas P. Janwadkar

Department of Chemistry, Sonopant Dandekar Arts, V. S. Apte Commerce and M. H. Mehta Science College Palghar-401404 Maharashtra, India

(Received: 24 July 2025    Revised: 29 August 2025    Accepted: 30 September 2025)

## KEYWORDS

Nickel mixed ligand complexes, Structural study, Photocatalytic activity, Eriochrome black-T dye

## ABSTRACT

A series of ternary mixed ligand complexes of Ni(II) metal having general molecular formula is  $[\text{Ni}(\text{PCIINAP})(\text{aa})\cdot 2\text{H}_2\text{O}]$ ; where PCIINAP is sodium salt of *p*-chloroisnitrosoacetophenone and aa is a L-amino acids like alanine, valine, leucine, methionine and phenylalanine were prepared. These complexes were characterised by several physico-chemical techniques such as elemental analysis, molar conductance determination, magnetic susceptibility measurements, electronic absorption spectral studies, IR studies and TG-DTA analysis. The photocatalytic activity of the synthesized Ni(II) complexes were studied as a heterogeneous catalyst for degradation of Eriochrome black-T dye.

## 1. Introduction

Various harmful organic dyes originating from industrial pharmaceutical, textile and other processes are regularly discharged into the environment. Among these, azo dyes represent the largest class of synthetic dyes used commercially. Due to their extensive application in the textile industry, the release of azo dyes into natural water bodies poses serious environmental concerns, as they are highly toxic and potentially carcinogenic to aquatic life and other living organisms [1-6], therefore, it's become very important task to degrade azo dyes eco-friendly [7-16]. Heterogeneous catalysts [17-24] are used for degradation of dye molecule from aqueous solution under UV or Visible light by photocatalytic action. Eriochrome Black-T (EBT) is one of the important azo dyes which is widely used in dyeing silk, wool, nylon, multifibre and complexometric titration for an estimation of ions like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Zn}^{2+}$ .

Eriochrome Black T (EBT) is considered a highly hazardous azo dye and its degradation intermediate, naphthoquinone, is known to exhibit even greater carcinogenic potential. Therefore, it has become very serious matter for effective treatment of wastewater containing EBT dye but a rare work has been reported in the literature on the effective decolorization of such dye [25]. Complexes and also their oxides plays important role to degrade dye molecule by photocatalytic action [26,27]. Heterogeneous photocatalysts, especially using nickel(II) metal ligand

complexes due to its non-chemical reactivity, non-toxicity and easy recovery by filtration methods it has been widely used for effective photocatalytic degradation of dye.

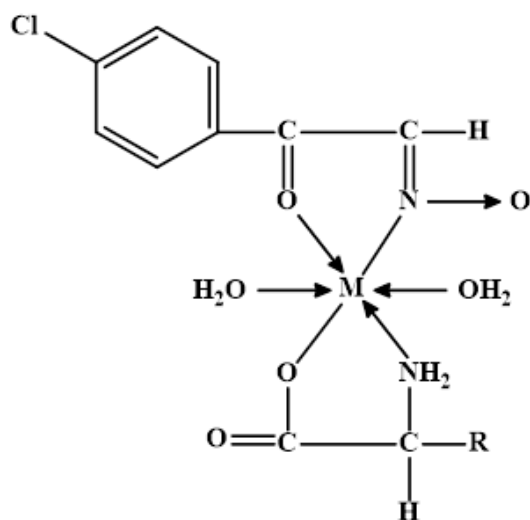
## 2. Methods

Chemicals and reagents used were of AR grade. L-series of amino acids such as alanine, valine, methionine, leucine, and phenylalanine were used of HIMEDIA. The sodium salt of *p*-chloroisnitrosoacetophenone was prepared by reported method in the literature [28]. All required solvents were distilled and purified by standard procedures.

**Synthesis of Ni(II) complexes:** The Ni(II) complexes were synthesized by using an aqueous solution of Ni(II) sulphate heptahydrate (1 mmol) and sodium salt of *p*-chloroisnitrosoacetophenone (1 mmol). The mixture was stirred and kept on heating mental for refluxing 30 min after that an aqueous solution of the sodium salt of amino acid (1 mmol) is added. The final mixture (1:1:1 molar) was again heated and refluxed for 3 h. The solid Ni(II) complexes were obtained are cooled, filtered and washed with ice-cold water followed by 1:1 ethanol:water solvent system. The complexes were dried and weighed. Nickel content in the complexes was determined by complexometrically as per standard procedures [29]. The elemental analysis was carried out at the microanalytical laboratory Sophisticated Analytical Instrument Facility IIT, Mumbai, India. The molar conductance values were measured in DMF solution of  $10^{-3}$  M concentration on a



EQUIP-TRONICS EQ-664ACM-180 digital conductivity meter with magnetic stirrer (cell constant = 1.0 cm<sup>-1</sup>). Magnetic susceptibilities data measured at room temperature by using Gouy's balance Batra Trading Company Model GMX-TR2 with Hg[Co(SCN)<sub>4</sub>] as a calibrant. Effective magnetic moments were calculated [30] after applying diamagnetic corrections for the ligand components using Pascal's constants. Electronic absorption spectra of the complexes were recorded in DMF on a Shimadzu UV-1800 spectrophotometer. Thermal Analysis (TG and DTA) of all the metal complexes were recorded on a Rigaku Thermo Plus-8120 TG-DTA instrument. Infrared spectra of all the ligands and their metal complexes interpreted [31] and recorded on Agilent Technologies, ATR-Model-Cary 630, Instrument S/N-MY18122007 Spectrometer in the 4000-400 cm<sup>-1</sup> region. The chemical structure of Ni(II) complexes is shown in Fig.1.



where,

R = (CH<sub>3</sub>) for alanine

R = (CH<sub>3</sub>)<sub>2</sub> for valine

R = CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub> for leucine

R = (CH<sub>2</sub>)<sub>2</sub>SCH<sub>3</sub> for methionine

R = CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub> for phenylalanine

Fig. 1: Structure of nickel(II) complexes

**Preparation of EBT dye solution:** Weighed 100 mg of EBT dye dissolved in 1000 mL with deionized water to prepare 100 ppm solution of dye. A 10 ppm solution was prepared from stock to taken 50 mL of 100 ppm solution

dilute to 500 mL deionized water. The 10 ppm dye sample solution was used for photocatalytic degradation of dye.

**Photocatalytic activity:** The photocatalytic dye degradation efficiency of the nickel(II) complexes were studied by the degradation of Eriochrome black T (EBT) in presence of Tungsten filament lamp. The photocatalytic degradation was investigated by different time interval (30, 60 and 90 min), concentration of dye (10 ppm) and various amount of catalyst (25, 50, 75 and 100 mg). Absorbance was measured by both before and after irradiation of light on dye sample with and without catalyst. After irradiation, the catalyst was separated by centrifugation and the absorbance of supernatant solution of EBT dye sample was determined by using UV-Visible spectrophotometer at wavelength of 530 nm. The photocatalytic efficiency (%) was calculated using the following formula:

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

where A<sub>0</sub> and A<sub>t</sub> are the absorbance of EBT dye sample before and after the photocatalytic reaction.

### 3. Results

**Photocatalytic activity:** For determination of λ<sub>max</sub> EBT dye was used of 100 ppm concentration (100 mg/L) and was found at 530 nm shown in Fig. 2.

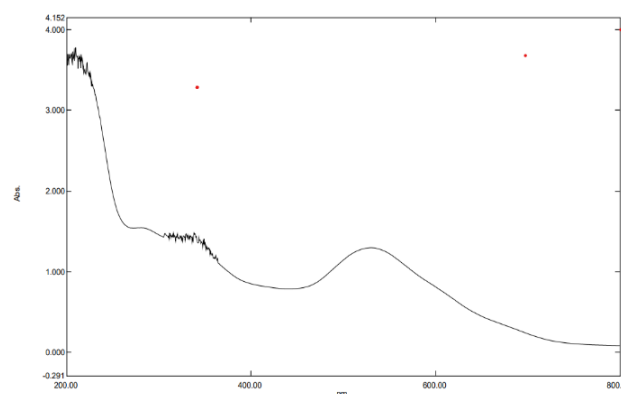


Fig. 2: Wavelength of maximum absorbance of EBT dye λ<sub>max</sub> 530 nm

**Determination of initial absorbance (A<sub>0</sub>):** For determination of initial absorbance (A<sub>0</sub>) 10 ppm dye solution was used and absorbance obtained at A<sub>0</sub> = 0.101 is shown in Fig. 3.

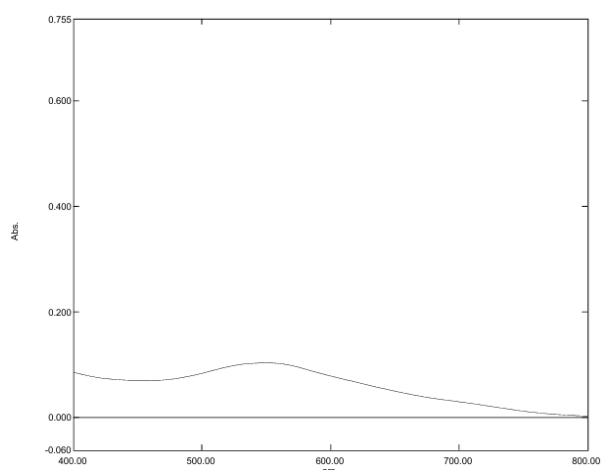


Fig. 3: Initial absorbance ( $A_0$ ) of EBT dye without light irradiation

**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 and 90 min, absorbance measured at wavelength 530 nm, which is tabulated in

Table-1 and represented in Fig.4 shown as below:

Table-1

S. No.	Complex	Time (min)	Abs. ( $A_t$ )	% Degrad.
1.	Ni(PCIINAP)(A)-2H <sub>2</sub> O	30	0.098	2.97
		60	0.068	32.67
		90	0.038	62.37
		90	0.038	62.37
2.	Ni(PCIINAP)(B)-2H <sub>2</sub> O	30	0.097	3.90
		60	0.066	34.65
		90	0.037	63.36
3.	Ni(PCIINAP)(C)-2H <sub>2</sub> O	30	0.095	5.94
		60	0.065	35.64
		90	0.035	65.34
4.	Ni(PCIINAP)(D)-2H <sub>2</sub> O	30	0.094	6.93
		60	0.063	37.62
		90	0.033	67.32
5.	Ni(PCIINAP)(E)-2H <sub>2</sub> O	30	0.092	8.91
		60	0.062	38.61
		90	0.032	68.31

where A = Alanine; B = Valine; C = Leucine; D = Methionine; and E = Phenylalanine.

In this study, the percentage degradation of the dye sample increased with time. The observed degradation ranged from 2.97% to 8.91% at 30 min, 32.67% to 38.61% at 60 min and 62.37% to 68.31% at 90 min, respectively.

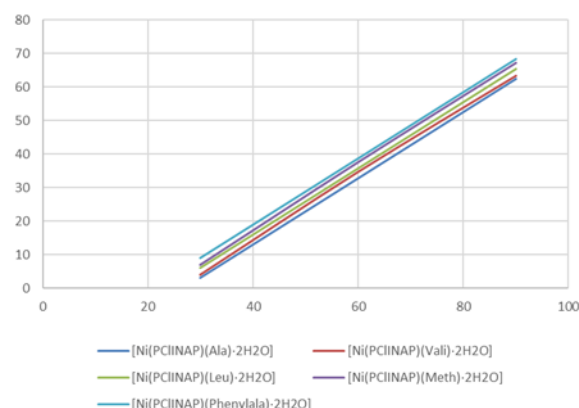


Fig. 4: Effect of time (min) on dye degradation

**Effect of catalyst amount:** By varying the amount of catalyst and fixed 10 ppm concentration of dye sample was irradiated with light for 90 min. After irradiation, the absorbance of the dye solution was measured. Using the absorbance values, the percentage of dye degradation was calculated. The degradation rate increased with the amount of catalyst used and the results are summarized in Table-2 and illustrated in Fig. 5 below:

Table-2

S. No.	Complex	Time (min)	Abs. ( $A_t$ )	% Degrad.
1.	Ni(PCIINAP)(A)-2H <sub>2</sub> O	25	0.092	8.91
		50	0.038	62.37
		75	0.036	64.35
		100	0.028	72.27
2.	Ni(PCIINAP)(B)-2H <sub>2</sub> O	25	0.091	9.90
		50	0.037	63.36
		75	0.035	65.34
		100	0.026	74.25
3.	Ni(PCIINAP)(C)-2H <sub>2</sub> O	25	0.090	10.89
		50	0.035	65.34
		75	0.034	66.33
		100	0.025	75.24
4.	Ni(PCIINAP)(D)-2H <sub>2</sub> O	25	0.088	12.87
		50	0.033	67.32
		75	0.030	70.29
		100	0.023	77.22
5.	Ni(PCIINAP)(E)-2H <sub>2</sub> O	25	0.086	14.85
		50	0.032	68.31
		75	0.027	73.26
		100	0.021	79.20

where A = Alanine; B = Valine; C = Leucine; D = Methionine; and E = Phenylalanine.

In this study, the percentage degradation of dye sample was found to increase with the increasing amount of catalyst. The degradation ranged from 8.91% to 14.85% at 25 mg, 62.37% to 68.31% at 50 mg, 64.35% to 73.26%



at 75 mg, and 72.27% to 79.20% at 100 mg of catalyst, respectively.

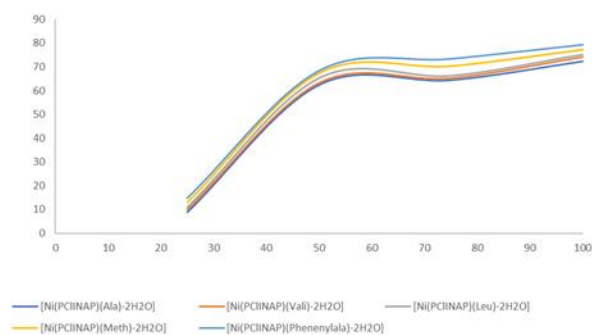


Fig. 5: Effect of amount of catalyst on dye degradation

In representative  $[\text{Ni}(\text{PCIINAP})(\text{Leu})\cdot 2\text{H}_2\text{O}]$  complex before irradiation with light by dye sample was higher coloured intensity as shown in Fig. 6a, but after irradiation with light the degradation of dye molecule is clearly seen in Fig. 6b by changing its decreasing colour intensity. This indicates degradation of dye by supporting decreasing absorbance value of solution.



Fig. 6: Before irradiation and after irradiation with light using  $[\text{Ni}(\text{PCIINAP})(\text{Leu})\cdot 2\text{H}_2\text{O}]$  complex

**Reusability of catalyst:** To evaluate the sustainability of the catalyst, catalytic cycle experiments were performed under fixed conditions: a reaction time of 90 min, a dye concentration of 10 ppm and 50 mg of catalyst. The study revealed that the efficiency of the representative nickel complex,  $[\text{Ni}(\text{PCIINAP})(\text{Leu})\cdot 2\text{H}_2\text{O}]$ , gradually decreased with successive catalytic cycles, indicating a decline in catalytic activity over repeated use.

Table-3

No. of catalytic cycle	Absorbance ( $A_t$ )	% Degrad.
1	0.035	65.34
2	0.037	63.36
3	0.040	60.39
4	0.040	60.39
5	0.040	60.39

**Mechanism for dye degradation:** When a complex is exposed to the light, it absorbs photons, which causes charge separation at the interface, which enhances photocatalytic activity. The EBT dye molecule interact with light and produces excited dye molecules as a result of this interaction. The excited dye molecules then combine with oxygen to produce positive dye radicals and negative  $\text{O}_2^-$  radicals. Further, the negative radicals react with  $\text{H}^+$  ions set free from  $\text{H}_2\text{O}$  to form superoxide radicals ( $^{\bullet}\text{OOH}$ ), which are responsible for destruction of the dye molecules [32]. The adsorption of  $\text{O}_2^-$  from  $\text{H}_2\text{O}$  is facilitated by photogenerated holes, which decrease recombination with electrons and the surface of OH groups. The photoformed electrons then causes reduction of  $\text{O}_2$  to  $\text{O}_2^-$  species, which can then mix with  $\text{H}_2\text{O}$  to produce additional oxygenated radicals, primarily hydroxyl ( $^{\bullet}\text{OH}$ ) radicals. The rate of dye molecule breakdown is substantially increased by both hydroxide and superoxide radicals and consequently, EBT dye decolorizes efficiently.

## Conclusion

The size and branching of the side chains in amino acids such as L-alanine, L-valine and L-leucine influence their adsorption behaviour and interaction with the photocatalyst surface, thereby affecting the overall dye degradation efficiency. In contrast, L-methionine, which contains a sulfur heteroatom, introduces different binding properties due to its unique side chain chemistry. Among all the synthesized nickel(II) metal complexes,  $[\text{Ni}(\text{PCIINAP})(\text{Phenylala})\cdot 2\text{H}_2\text{O}]$  exhibited the highest percentage of



dye degradation. This can be attributed to the presence of the aromatic phenyl ring in phenylalanine, which introduces a hydrophobic region and a  $\pi$ -electron system. The aromaticity of phenylalanine promotes stronger  $\pi$ - $\pi$  interactions with both the photocatalyst surface and the dye molecules, thereby enhancing degradation efficiency. Furthermore, the incorporation of phenylalanine into a dipeptide structure has been reported to influence biodegradation rates. The specific effect of nickel metal complexes of amino acids on photocatalytic performance also depends on factors such as the photocatalyst material, the type of dye used, and the reaction conditions. Further research is required to fully understand the complex interplay between amino acid side chains and photocatalytic dye degradation mechanisms.

#### Acknowledgements

The authors are thankful to sophisticated Analytical Instrument Facility, IIT-Bombay, Mumbai for providing instrumental facility for studies. Thanks are also due to The Institute of Science, Mumbai for TGA and DTA thermal analysis.

#### References

1. C.I. Pearce, J.R. Lloyd, J.T. Guthrie, *Dyes Pigments*, 58(3), 2003, 179-196.
2. R. Gong, Y. Sun, J. Chen, H. Liu, C. Yang, *Dyes Pigments*, 67(3), 2005, 175-181.
3. P.K. Malik, *Dyes Pigments*, 56(3), 2003, 239-249.
4. N. Bensalah, M.A. Quiroz Alfaro, C.A. Martínez-Huitle, *Chem. Eng. J.*, 149(1-3), 2009, 348-352.
5. R. Aplin, T.D. Waite, *Water Sci. Technol.*, 42(5-6), 2000, 345-354.
6. M.A. Rauf, S.S. Ashraf, *Chem. Eng. J.*, 151 (2009) 10-18.
7. M.A. Rauf, M.A. Meetani, Hisaidee, *Desalination*, 276, 2011, 13-27.
8. S. Gul and O.O. Yildirln, *Chem. Eng. J.*, 155, 2009, 684-690.
9. V.T.T. Nhu, D. Q. Minh, N.N. Duy, N.Q. Hien, *Int. J. Environ. Agric. Biotechnol.*, 2(1), 2017, 529-538.
10. X. Chen, Z. Wu, D. Liu, Z. Gao, *Nanoscale Res. Lett.*, 12, 2017, 143.
11. I.K. Konstantinou and T.A. Albanis, *Appl. Catal. B. Environ.*, 49, 2004, 1-14.
12. S.B. Narde, R.B. Lanjewar, S.M. Gadegone, M.R. Lanjewar, *Der Pharma Chemica*, 9(7), 2017, 115-120.
13. Z.M. Zangi, H. Ganjidoust, B. Ayati, *Desalin. Water Treatment*, 63, 2017, 262-274.
14. V. Marinovic, D. Ljubas, L. Curkovic, *The Holistic Approach Environ.*, 7(1), 2017, 3- 14.
15. P. Dhathshanamurthi, B. Subash and M. Shanthi, *Mater. Sci. Semiconductor Process.*, 35, 2015, 22-29.
16. M. Shanthi and V. Kuzhalosai, *Indian J. Chem.*, 51A, 2012, 428-434.
17. O. Sacco, M. Stoller, V. Vaiano, P. Ciambelli, A. Chianese, D. Sannino, *Int. J. Photoenergy*, 2012, 626759 (2012).
18. B.K. Avasarala, S.R. Tirukkavalluri, S. Bojja, *J. Environ. Anal. Toxicol.*, 6, 2016, 1-8.
19. Q. Li, Z. Guan, D. Wu, X. Zhao, S. Bao, B. Tian, and J. Zhang, *ACS Sustain. Chem. Eng.*, 5(8), 2017, 6958-6968.
20. Y. Liu, R. Wang, Z. Yang, H. Du, Y. Jiang, C. Shen, K. Liang, A. Xu, *Chinese J. Catalysis*, 36, 2015, 2135-2144.
21. S.K. Kansal, M. Singh, D. Sud, *J. Hazard. Mater.*, 141(3), 2007, 581-590.
22. M.A. Fox, M.T. Dulay, *Chem. Rev.*, 93, 1993, 341-357.
23. R. Sarkhanpour, O. Tavakoli, S. Ghiyasi, M. Reza Saeb, R. Borja, *J. Resid. Sci. Technol.*, 14, 2017, 44-58.
24. S. Ahmed, M.G. Rasul, W. Martens, R. Brown, M.A. Hashib, *Water, Air, Soil Pollutant*, 215, 2011, 3-29.
25. S.K. Kansal, S. Sood, A. Umar, S.K. Mehta, *J. Alloys Compds.*, 581(25), 2013, 392-397.
26. R.S. Joseyphus, R. Reshma, D. Arish, V. Elumalai, *Results Chemistry*, 4, 2022, 100583.
27. M.Y. Nassar, H.M. Aly, E.A. Abdelrahman, M.E. Moustafa, *J. Mol. Struct.*, 1143, 2017, 462-471.
28. F.J. Welcher, *Organic Analytical Reagents*, De Van Nostrand, New York, vol. 3, (1955) p. 279.
29. A.I. Vogels, *A Text Book of Quantitative Inorganic Analysis*, 3rd Edition, ELBS, Longmans Green, London, 1961.
30. R.L. Datta, A. Syamal, *Elements of Magnetochemistry*, 2nd Edition, Affiliated East-West Press Pvt. Ltd., New Delhi, 2004.
31. K. Nakamoto, *Infrared and Raman spectra of Inorganic and coordination compounds*, 4th Edition, John-Wiley & Sons, New York, 1986.
32. B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, *Chemosphere*, 46, 2002, 1173-1181.