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To Study Photocatalytic Efficiency of Chiral Mixed Ligand Zinc (II) Metal Complexes as Heterogeneous Catalyst for Degradation of Azo Dye

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Abstract

Novel Chiral mixed ligand complexes of Zn (II) metal having general molecular formula is [ZnPClINAP) (aa).2H_2O]; where PClINAP is sodium salt of p-chloroisonitrosoacetophenone and aa is a L- Amino Acids such as Alanine, Valine, Leucine, Methionine and Phenylalanine were prepared. Characterisation of complexes done by various physico-chemical techniques like elemental analysis, molar conductance determination, magnetic susceptibility measurements, electronic absorption spectral studies and also supported by IR and TG-DTA analysis with specific optical rotations. The photocatalytic activity of these metal complexes were studied as a heterogeneous catalyst for degradation of Eriochrome Black T (EBT) dye.

Keywords: Chiral zinc metal mixed ligand complexes, Characterisation study, Photocatalytic activity, Dye degradation.

Introduction

Azo Dyes are widely used in textile so due to disposal of such dyes in an environment like in water bodies are very hazardous effect on all living organisms[1-5], therefore, it's become very important to degrade azo dyes[6-15]. Heterogeneous catalyst[16-23] were 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 Ca^{2+}, Mg^{2+} and Zn^{2+}. EBT is one of the very hazardous dye also their intermediate product Naphthaquinone is more carcinogenic. Therefore, it has become very serious situation for effective treatment of wastewater containing EBT Dye but, a very few work has been investigated in the literature on the effective decolorization of such dye[24]. Complexes and also their oxides play important role to degrade dye molecule by photocatalytic action[25,26]. Heterogeneous photocatalysts, especially using Zn (II) metal ligand complexes because of its nonchemical reactivity, non-toxicity and easy recovery by filtration methods Zinc metal complexes has been widely used for effective photocatalytic degradation of azo dye.

Experimental

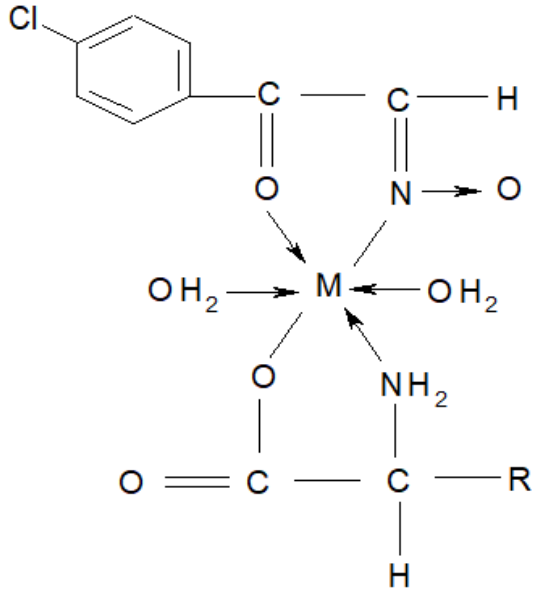
Materials and Methods

Chemicals were used are of AR grade. All L- amino acids were used of HIMEDIA. The sodium salt of p-chloroisonitrosoacetophenone was prepared by reported method in the literature[27]. All required solvents were distilled and purified by standard procedures.

Synthesis of Complexes

The Zinc complexes were synthesized by using an aqueous solution of Znic (II) sulphate heptahydrate (1mmol) and sodium salt of p-chloroisonitrosoacetophenone (1 mmol). The mixture was stirred and kept on heating mental for refluxing 30 minutes after that an aqueous solution of the sodium salt of amino acid (1 mmol) is added. The final mixture (1:1:1 molar proportion) was again heated and refluxed for three hours on heating mental. The solid 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.

Presence of Zinc metal content in the complexes was determined complexometrically by standard procedures[28]. The elemental analysis was carried out at the microanalytical laboratory SAIF I.I.T., Mumbai. For determination of molar conductance values DMF solution of 10^{-3} M concentration were used and measured on a EQUIP-TRONICS EQ-664ACM-180 digital conductivity meter with magnetic stirrer (cell constant = 1.0 cm^{-1}). Magnetic properties measured at room temperature by using Gouy's balance Batra Trading Company Model GMX-TR2 with $Hg[Co(SCN)_4]$ as a calibrant. Effective magnetic moments were calculated[29] after applying diamagnetic corrections for the ligand components using Pascal's constants all zinc complexes shows diamagnetic in nature. All complexes shows levorotatory optical rotation . For electronic absorption spectral study 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. FTIR spectra of all the ligands and their metal complexes interpretation[30] and recorded on using an IRAffinity-1S FTIR SPECTROPHOTOMETER SHIMADZU, SERIAL NO. A221354, SHIMADZU CORP. 00525 in the region 4000–400 cm^{-1}. From all above analysis results geometry of complexes indicated octahedral in nature. The chemical structure of CML Zn (II) complexes is shown in Fig.1.



Where, R = (CH_3) for Alanine
R = $(CH_3)_2$ for Valine
R = $CH_2CH(CH_3)_2$ for Leucine
R = $(CH_2)_2SCH_3$ for Methionine
R = $CH_2C_6H_5$ for Phenylalanine

Fig. 1: Chemical structure of the Chiral Mixed Ligand Zn (II) complexes

Preparation of Eriochrome Black T (EBT) Dye Solution

A] Preparation of 100 ppm solution - 100 mg of EBT dye dissolved in 1000 mL with deionized water.

B] Preparation of 10 ppm solution- Dilute 50 mL solution in 500 mL deionized water from 100 ppm to prepare 10 ppm dye solution. This 10 ppm sample solution was used for photocatalytic degradation study.

Photocatalytic activity

Photocatalytic degradation of EBT dye by Zinc metal complexes have been studied in presence of Tungsten filament 40-W lamp. This degradation was investigated by different time interval (30 min. 60 min. and 90 min.), concentration of Dye (10 ppm) and various amount of catalyst (25mg, 50 mg, 75 mg and 100 mg) respectively. Absorbance was measured by both, before and after irradiation of light on the dye sample with and without catalyst. After irradiation, the catalyst was separated by centrifugation and the absorbance of supernant solution of dye sample was recorded on a Shimadzu UV-1800 spectrophotometer at wavelength of 530 nm. The % of dye degradation was calculated using the formula,

$$\% \text{ Degradation} = \frac{Ao - At}{Ao} X\ 100$$

Where A_o and A_t are the absorbance of EBT dye sample before and after the photocatalytic reaction.

Results and Discussion

Photocatalytic Activity

Determination of Maximum Absorbance Wavelength (λ_{max}) of EBT Dye

For determination of λ_{max} 100 ppm concentration (100 mg/L) EBT Dye solution were used and it was found at λ_{max} 530 nm shown in Fig.2.

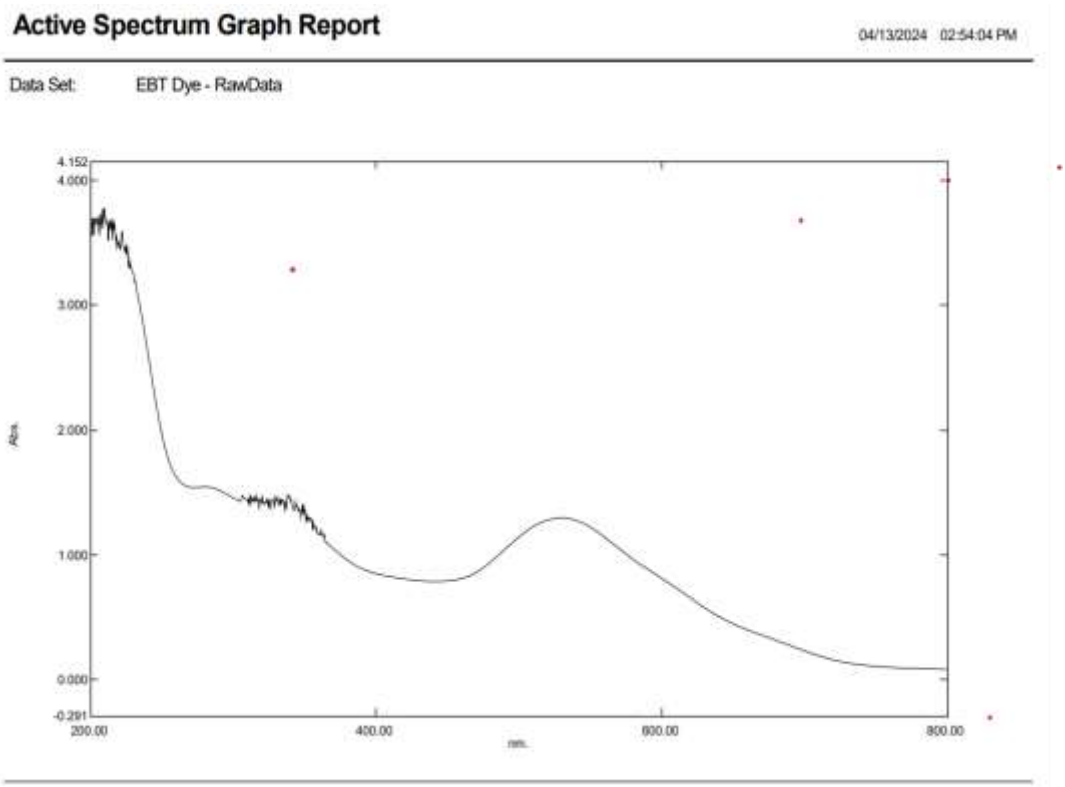


Fig.2: Wavelength of maximum absorbance of EBT Dye λ_{max} 530 nm

Determination of Initial Absorbance (A_o)

For determination of Initial Absorbance (A_o) 10 ppm dye solution was used and absorbance obtained (A_o = 0.101) shown in Fig.3.

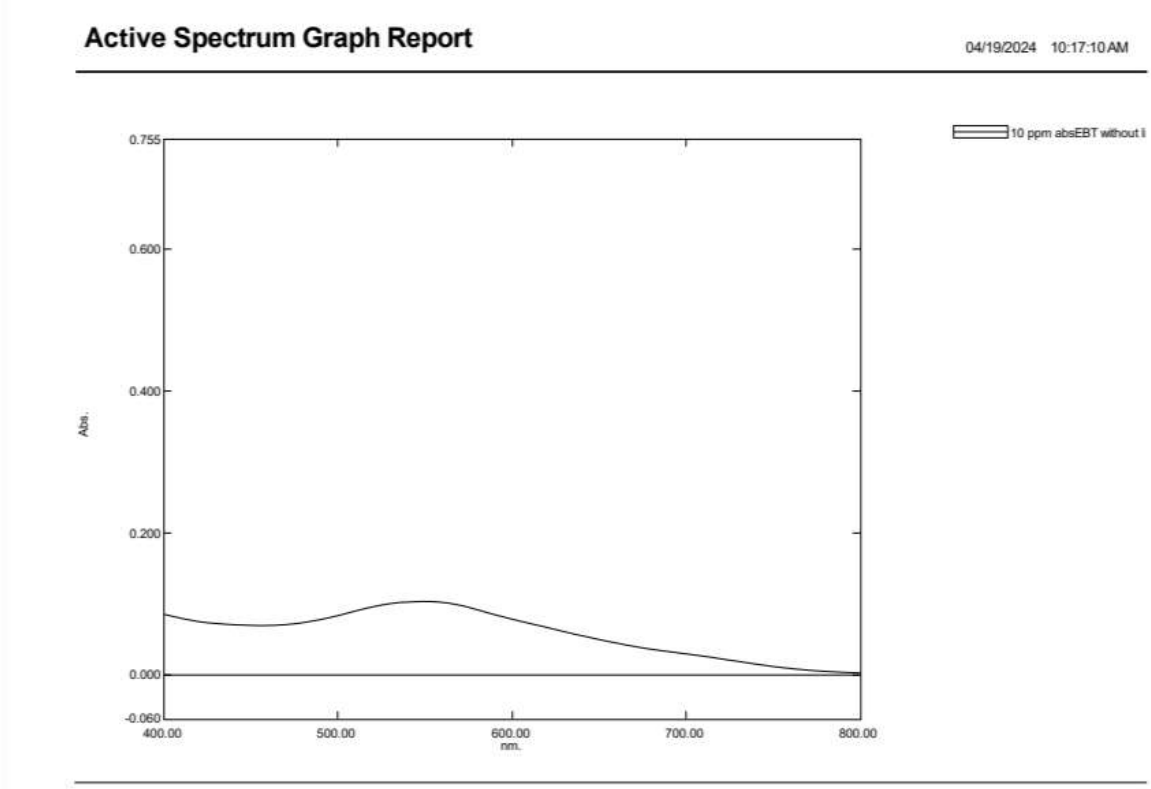


Fig.3: Initial Absorbance (Ao) of EBT Dye Without Light Irradiation

To study the photocatalytic activity of complexes used as heterogenous catalyst in two ways

I] Effect of Time on Degradation:

In First way keeping fixed concentration (10 ppm) of dye and 50 mg amount of complex with varying time interval 30 minutes, 60 minutes and 90 minutes absorbance measured at wavelength 530 nm. Which is tabulated in (Table-1) and represented in curve (Fig.4) shown as below,

Table 1: Effect of Time on Dye Degradation

Sr. No.	Catalyst	Time (min.)	Absorbance (A_t)	Degradation %
1	[Zn(PClINAP)(Ala)·2H_2O]	30	0.043	57.42
		60	0.037	63.36
		90	0.032	68.31
2	[Zn(PClINAP)(Vali)·2H_2O]	30	0.042	58.41
		60	0.036	64.35
		90	0.030	70.29
3	[Zn(PClINAP)(Leu)·2H_2O]	30	0.039	61.38
		60	0.034	66.33
		90	0.027	73.26
		30	0.038	62.37

4	[Zn(PClINAP)(Meth)·2H$_2$O]	60	0.032	68.31
		90	0.025	75.24
5	[Zn(PClINAP)(Phenylala)·2H$_2$O]	30	0.036	64.35
		60	0.030	70.29
		90	0.024	76.23

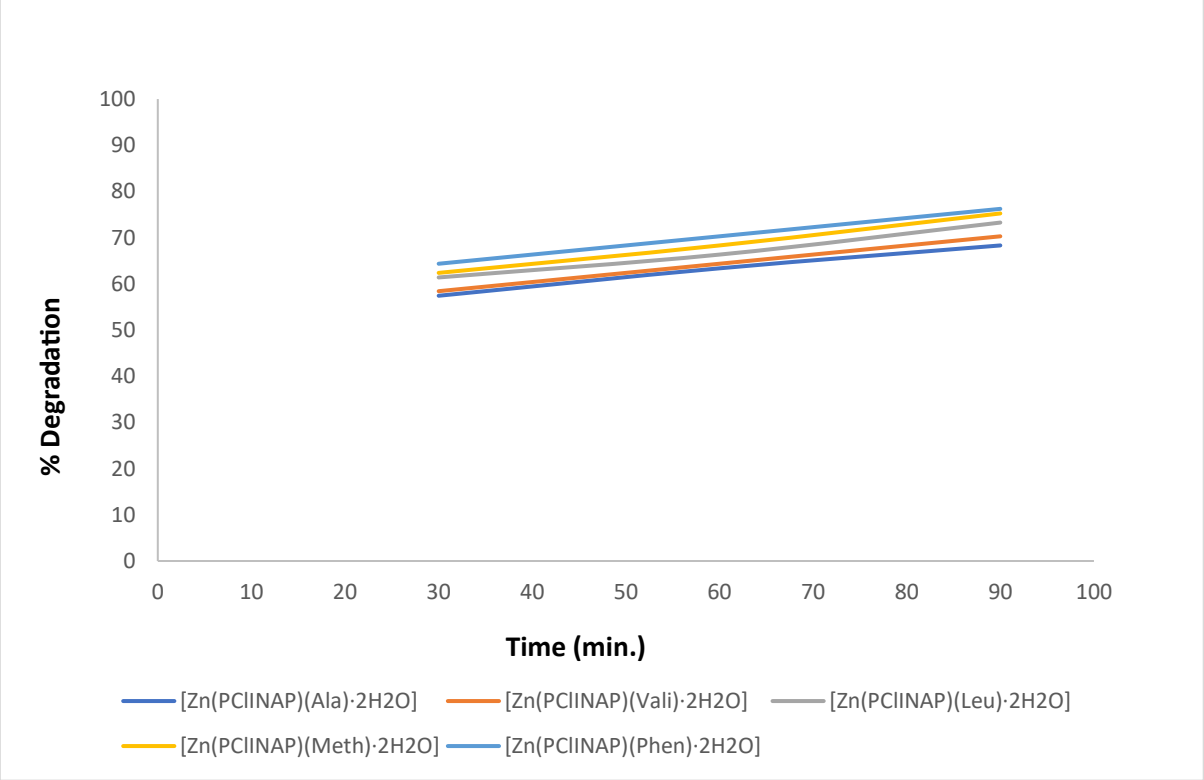


Fig. 4: Effect of Time on Dye Degradation

In this study percentage of degradation of dye sample increases with increasing time. At time 30 minutes range of % degradation obtained 57.42 - 64.35 %, for 60 minutes shown 63.36 – 7.29 % degradation and 90 minutes shown 68.31 – 76.23 % degradation respectively.

II] 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 90 minutes. After irradiation absorbance was measured and it was found to be increased. With increasing the amount of catalyst, the % dye degradation increased. Which is tabulated in (Table-2) and represented in Fig.5 shown as below,

Table:2 Effect of amount of Catalyst on Dye Degradation

Sr. No.	Catalyst	Amount mg	Absorbance (At)	Degradation %
1	[Zn(PClINAP)(Ala)·2H$_2$O]	25	0.087	13.86
		50	0.032	68.31
		75	0.028	72.27

		100	0.024	76.23
2	[Zn(PClINAP)(Vali)·2H$_2$O]	25	0.086	14.85
		50	0.030	70.29
		75	0.027	73.26
		100	0.023	77.22
3	[Zn(PClINAP)(Leu)·2H$_2$O]	25	0.085	15.84
		50	0.027	73.26
		75	0.025	75.24
		100	0.022	78.21
4	[Zn(PClINAP)(Meth)·2H$_2$O]	25	0.083	17.82
		50	0.025	75.24
		75	0.023	77.22
		100	0.021	79.20
5	[Zn(PClINAP)(Phenylala)·2H$_2$O]	25	0.082	18.81
		50	0.024	76.23
		75	0.020	80. 19
		100	0.018	82.17

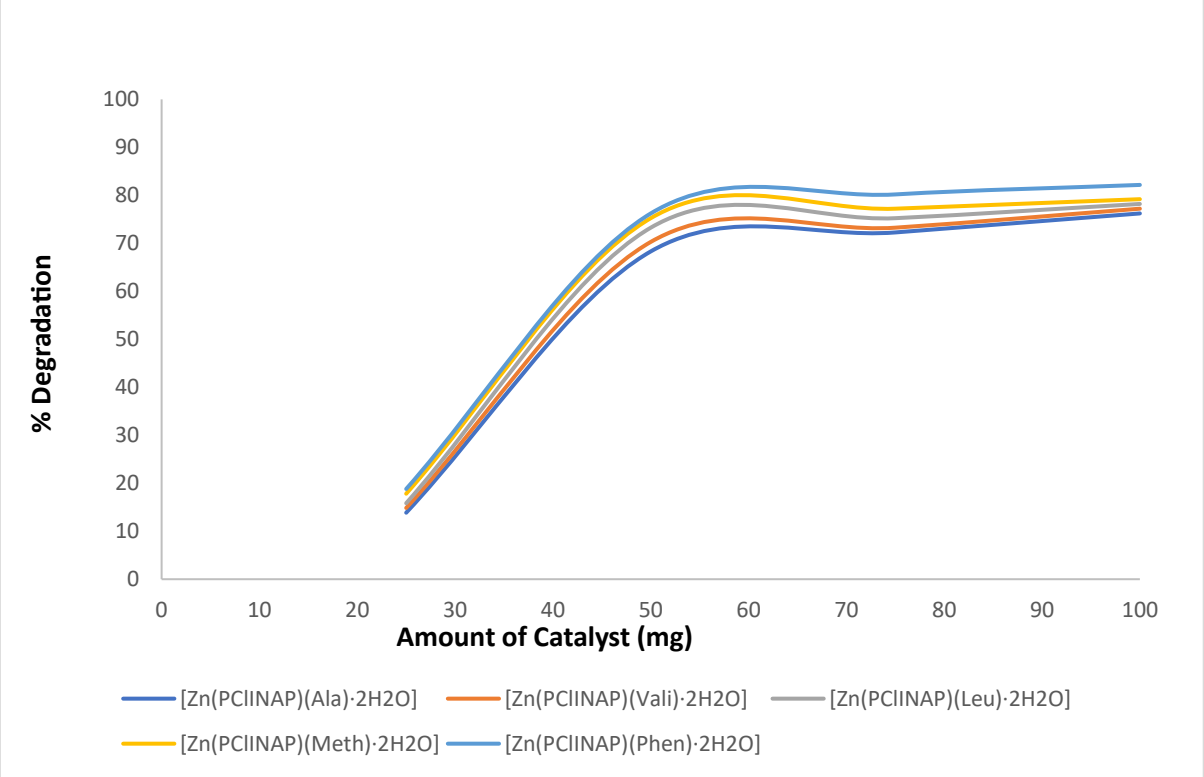


Fig. 5: Effect of amount of Catalyst on Dye Degradation

The 25 mg amount of catalyst shown range 8.91 – 14.85 % degradation, 50 mg catalyst 62.37 – 68.31 % dye degradation, 75 mg catalyst 64.35 – 73.26 % dye degradation and 100 mg catalyst 72.27 – 79.20 % dye degradation respectively.

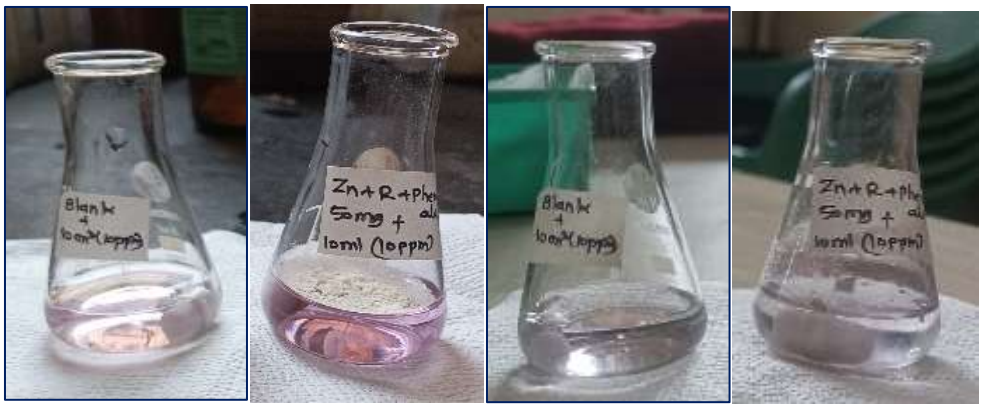


Fig. 6: Before Irradiation with Ligh [Zn(PClINAP)(Phenylala)·2H₂O]

Fig. 7: After Irradiation with Light [Ni(PClINAP)(Phenylala)·2H₂O]

In representative [Zn(PClINAP)(Phynylala)·2H₂O] complex before irradiation with light dye sample was higher coloured intensity as shown in Fig. 6, but after irradiation with light the degradation of dye molecule is clearly seen in Fig. 7 by changing its decreasing colour intensity. This indicates degradation of dye by supporting data obtained decreasing absorbance value of solution.

When a complex is exposed to 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 O_2 radicals. Further, the negative radical reacts with H^+ ions set free from H_2O to form superoxide radicals (OOH), which are responsible for the dye molecule's destruction[31-32]. The adsorption of O_2 from H_2O is facilitated by photogenerated holes, which decrease recombination with electrons, and the surface of OH groups. The photo-formed electrons then reduction of O_2 to O_2^- species, which can then mix with H_2O to produce additional oxygenated radicals, primarily hydroxyl (OH•) radicals. The rate of dye molecule breakdown is substantially increased by both hydroxide and superoxide radicals, and consequently, EBT dye decolorizes efficiently.

Reusability of Catalyst

To find out the sustainability of the present catalyst were checked by performing catalytic cycles. For this study keeping concentration of dye 10 ppm solution , 50mg of catalyst and 90 min. time interval were used has shown that the representative Zinc complex [Zn(PClINAP)(Phenylala)·2H₂O] effectiveness has decreased with number of catalytic cycles.

No. of Catalytic Cycle	Absorbance (At)	% D
1	0.024	76.24
2	0.028	72.27
3	0.031	69.30
4	0.031	69.30
5	0.031	69.30

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Conclusion

The structure of amino acids, side chains plays an important role to affect the adsorption and interaction of the photocatalyst surface and due to this degradation efficiency alter. In L-Methionine amino acid

contains heteroatoms like Sulphur has introduced in different binding properties. Among all Zinc metal complexes [Zn(PClINAP).Phenylala.2H_2O] shown higher percent of dye degradation. Because in the structure of phenylalanine aromatic phenyl ring introduces a hydrophobic and π-electron region. This aromaticity can lead to stronger interactions with both the photocatalyst and dye molecules, accelerated deterioration. The presence of phenylalanine in a dipeptide structure has also been shown to affect biodegradation rates. The specific impact of Zinc metal complexes of amino acids will also depend on the photocatalyst material the dye used and the reaction conditions. Further research is needed for completely understand the complex interplays between, amino acids side chains and photocatalytic dye degradation.

References

1. Renmin Gong, Yingzhi Sun, Jian Chen, Huijun Liu, Chao Yang, Effect of chemical modification on dye adsorption capacity of peanut hull, *Dyes and Pigments,* 67(3), **2005,** 175-181, https://doi.org/10.1016/j.dyepig.2004.12.003
2. P.K. Malik, Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36, *Dyes and Pigments*, 56(3), **2003**, 239-249, https://doi.org/10.1016/S0143-7208(02)00159-6
3. N. Bensalah, M.A. Quiroz Alfaro, C.A. Martínez-Huitle, Electrochemical treatment of synthetic wastewaters containing Alphazurine A dye, *Chemical Engineering Journal,* 149 (1-3), **2009**, 348-352, https://doi.org/10.1016/j.cej.2008.11.031
4. R. Aplin, T.D. Waite, Comparison of three advanced oxidation processes for degradation of textile dyes, *Water Science and Technology*, 42 (5-6), **2000**, 345–354, https://doi.org/10.2166/wst.2000.0534.
5. M.A. Rauf, S.S. Ashraf, Fundamental principles, and application of heterogeneous photocatalytic degradation of dyes in solution, Chem. Eng. J. 151 **(2009)** 10–18, https://doi.org/10.1016/j.cej.2009.02.026.
6. M.A. Rauf, M.A. Meetani and S. Hisaidee, An overview on the photocatalytic degradation of azo dyes in the presence of TiO2 doped with selective transition metals, *Desalination*, ,276, **2011**,13-27;doi:10.1016/j.desal 2011.03.071.
7. S. Gul, and O. Ozcan Yildlrln, Degradation of Reactive Red 194 and reactive yellow 145 azo dyes by O3 and H2O2/UV-C process, *Chemical Engineering Journal*, 155, **2009,**684-690.
8. Vo Thi Thu Nhu, Do Quang Minh, Nguyen Ngoe Duy and Nguyen Quoc Hien, Photocatalytic degradation of Azo dye (methyl Red) in water under visible light using Ag-Ni/TiO2 synthesized by γ Irradiation method, *International Journal of Environment Agriculture and Biotechnology*, 2 (1), **2017,** 529-538.
9. Xiaoqing chen, Zhansheng Wu, Dandan Liu and Zhenzhen Gao, Preparation of ZnO photocatalyst for the efficient and rapid photo catalytic degration of azo dyes, *Nanoscale Research letters*, 12, **2017,**143.
10. I. K.Konstantinou and T. A.Albanis, TiO2 assisted photocatalytic degradation of azo dyes in aqueous solution: Kinet ics and mechanistic investigations A review, *Applied Catalysis B.Environmental*, 49, **2004,** 1-14.
11. S.B Narde, R.B Lanjewar, S.M Gadegone, M.R Lanjewar, Photocatalytic Degradation of Azo Dye Congo Red Using Ni0.6Co0.4Fe2o4 as Photocatalyst, Der Pharma Chemica, 9(7), **2017,**115-120.
12. Z. M. Zangi, H. Ganjidoust, B. Ayati, Analysis of photocatalytic degradation of azo dyes under sunlight with response surface method, *Desalination and Water Treatment*, 63, **2017,** 262–274.
13. V. Marinovic, D. Ljubas, L. Curkovic, Effects of concentration and UV radiation wavelengths on phot-

olytic and photocatalytic degradation of azo dyes aqueous solutions by sol-gel TiO2 films, *The Holistic Approach to Environment*, 7 (1), **2017**, 3- 14.

14. P. Dhatshanamurthi, B.Subash and M.Shanthi, Investigation on UV A light photocatalytic degradation of an azo dye in the presence of CdO/TiO2 coupled semiconductor, *Materials Science in Semiconductor Processing*, 35, **2015,** 22-29.
15. M.Shanthi and V.Kuzhalosai, Photo-catalytic degradation of an azo dye acid Red 27 in aqueous solution using nano ZnO, *Indian Journal of Chemistry*, 51A, **2012,** 428-434.
16. O. Sacco, M. Stoller, Vincenzo, Vaiano, Paolo Ciambelli, Angelo Chianese, and Diana Sannino, Photocatalytic degradation of organic dyes under visible light on N-doped TiO2 photo catalysts, *International Journal of Photoenergy*, **2012,**1-8 (2012Doi:10.1155/20121626759.
17. B. K. Avasarala, S. R. Tirukkovalluri and S. Bojja, Magnesium doped Titania for photocatalytic degradation of dyes in visible light, *Journal of Environmental and Analytical Toxicology*, 6, **2016,**1-8.
18. Qiaoying Li, Zhipeng Guan, Di Wu, Xiuge Zhao, Shenyuan Bao, Baozhu Tian and Jinlong Zhang, Z Scheme BiOCl-Au-CdS Heterostructure with Enhanced Sunlight Driven Photocatalytic Activity in Degrading Water Dyes and Anti biotics, *ACS Sustainable Chemistry Engineering*, **2017**, DOI: 10.1021/acssuschemeng.7b01157.
19. Yanan Liu, Ruixia Wang, Zhengkun Yang, Hong Du, Yifan Jiang, Congcong Shen, Kuang Liang, Anwu Xu, Enhanced visible-light photocatalytic activity of Z-scheme graphitic carbon nitride/oxygen vacancy-rich zinc oxide hybrid photocatalysts, *Chinese Journal of Catalysis*,36, **2015,** 2135–2144.
20. S.K.Kansal, M.Singh and D.Sud, Studies on photodegradation of two commercial dyes in aquesous phase using different photo catalysts, *Journal of Hazardous Materials*, 141(3), **2007** 581-590.
21. M.A. Fox, and M.T. Dulay, Heterogeneous photocatalysis, *Chem. Rev.* 93, **1993**, 341.
22. R. Sarkhanpour, O. Tavakoli, S. Ghiyasi, M. Reza Saeb, R. Borja, Photocatalytic Degradation of a Chemical Industry Wastewater: Search for Higher Efficiency, *Journal of Residuals Science & Technology*, 14, **2017**, 44-58, doi: 10.14355/jrst.2017.1404.006.
23. S. Ahmed, M.G.Rasul, W. Martens, R. Brown and M.A.Hashib, Advances in Heterogeneous photocatalytic degradation of phenols and Dyes in wastewater: *A reivew Water, Air, Soil Pollutant*, 215, **2011**, 3-29.
24. S. K. Kansal , S. Sood, Ahmad Umar , S.K. Mehta Photocatalytic degradation of Eriochrome Black T dye using well-crystalline anatase TiO_2 nanoparticles, *Journal of Alloys and Compounds* 581 (25), **2013,** 392-397 https://doi.org/10.1016/j.jallcom.2013.07.069.
25. R.S.Joseyphus, R. Reshma, D.Arish, V. Elumalai, Antimicrobial, photocatalytic action and molecular docking studies of imidazole-based Schiff base complexes, Results in Chemistry, 100583 (4) **2022**, 1-11, https://doi.org/10.1016/j.rechem.2022.100583.
26. M.Y. Nassar, H.M. Aly, E.A. Abdelrahman, M.E. Moustafa, Synthesis, characterization, and biological activity of some novel Schiff bases and their Co(II) and Ni(II) complexes: A new route for Co 3 O 4 and NiO nanoparticles for photocatalytic degradation of MB dye, J. Mol. Struct. 1143 **2017**, 462–471, https://doi.org/10.1016/j.molstruc.2017.04.118.
27. F.J. Welcher, Organic Analytical Reagents, De Van Nostrand, New York, 3, 1955; 279.
28. A. I. Vogels, A Text Book of Quantitative Inorganic Analysis, 3rd Edition, ELBS, Longmans Green, London, **1961**.
29. R. L. Datta, and A. Syamal, Elements of Magnetochemistry, 2nd Edition, Affiliated East-West Press Pvt. Ltd., New Delhi, **2004**.

30. K. Nakamoto, Infrared and Raman spectra of Inorganic and coordination compounds, 4th ED., John-Wiley & Sons, New York, **1986**.
31. B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, Solar light induced and TiO 2 assisted degradation of textile dye reactive blue 4, Chemosphere 46 , **2002**, 1173–1181, https://doi.org/10.1016/s0045-6535(01)00284-3.
32. He Fang , Hu Wenrong, Biodegradation mechanisms and kinetics of azo dye 4BS by a microbial consortium, Chemosphere 57 (4), **2004,** 293-301, https://doi.org/10.1016/j.chemosphere.2004.06.03