Synthesis, Characterization, and Dye Degradation Study of Lanthanide (Ln, Ce, Pr, Nd) Metal Complexes

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Abstract

Dyes are widely used in textile, cosmetic, paint, ceramic, and plastic industries, contributing significantly to water pollution. Conventional dye removal methods, including chemical, biological, and physical techniques, often fall short due to inefficiency or secondary pollution. In this study, we synthesized and characterized metal complexes of lanthanum (La), cerium (Ce), praseodymium (Pr), and neodymium (Nd) using a Schiff base ligand, *N, N-bis (salicylaldehyde) para-phenylenediamine*. The synthesized complexes were analyzed using various spectroscopic techniques, including UV-Visible, FTIR, XRD, TGA, mass spectrometry, and elemental analysis, to confirm their structural integrity and coordination behavior.

The photocatalytic activity of these complexes was evaluated for the degradation of methylene blue (MB) dye under visible light irradiation. The results indicated that Ce-PBDP exhibited the highest photocatalytic efficiency, achieving nearly complete MB degradation within 50 minutes. Nd-PBDP and Pr-PBDP showed moderate efficiency, while Ln-PBDP was the least effective. The study highlights the potential of lanthanide-based metal complexes as efficient photocatalysts for dye degradation, offering a promising approach to wastewater treatment. Future research should focus on optimizing catalyst performance, stability, and scalability for real-world applications.

Keywords: Lanthanide complexes, Schiff base, dye degradation, photocatalysis, wastewater treatment, methylene blue

1. Introduction:

In many areas of the textile and dyeing industries, dyes are essential. The most commonly used dyes in these industries are more than 100,000 synthetic dyes that are sold commercially. With an annual production of over 7,105 tons, these dyes are typically made from two primary sources: coal tar and petroleum intermediates. (1),(2) dyes are used in various field such as textile, cosmetics, paints and pigment, ceramic and plastic industries and many more. Anything surrounding us is colorful, and much of this is because of dyes."

Konstantinou and Albanis observed that industrial dye substances and textile dyes represent one of the major categories of hazardous organic chemicals. The World Bank estimates that approximately 17–20% of water contamination is mostly attributed to the textile finishing and dyeing sectors. A study by Kant identified that 72 hazardous compounds in wastewater were exclusively generated by textile dyeing, with approximately 30 of these chemicals being non-treatable. (3)(4)

Today, Water pollution is a big environmental and social issue all around the world. According to the research of national environment engineering research institute (NEERI), Nagpur, it has been noted that around 70% of our river water has been contaminated by pollutant like dye and other chemicals. One of the major categories of contaminants discharged from textile industry wastewater is organic dyes. Numerous general techniques, including chemical, biological, and physical ones, are being investigated and used;

however, each has drawbacks. For example, physical techniques like reverse osmosis and adsorption on activated carbon do not result in full mineralization; instead, they simply proceed the pollutants from one phase to another, developing secondary pollution (5)

1.1 Chemistry of Lanthanides:

Lanthanides, a group of 15 elements from Lanthanum (La) to Lutetium (Lu), are known for their unique properties and wide range of applications. These elements belong to the f-block of the periodic table and are also referred to as rare earth elements. They exhibit a gradual filling of the 4f electron orbitals, which significantly influences their chemical behavior. (6)

One of the most notable characteristics of lanthanides is their common oxidation state of +3, though some can also exhibit +2 and +4 states. This trivalent state results from the loss of three 6s and 4f electrons, leading to similar ionic radii across the series, known as the lanthanide contraction. This contraction causes a slight decrease in ionic size from Lanthanum to Lutetium, affecting their chemical reactivity and coordination chemistry.

Lanthanides are typically silvery-white metals that are relatively reactive, especially at elevated temperatures. They tarnish quickly when exposed to air and react slowly with water, forming hydroxides. When reacting with acids, they form various salts and release hydrogen gas. The unique properties of lanthanides, such as their magnetic, optical, and catalytic abilities, arise from the shielded 4f electrons, which are less affected by the surrounding environment compared to d-block elements.

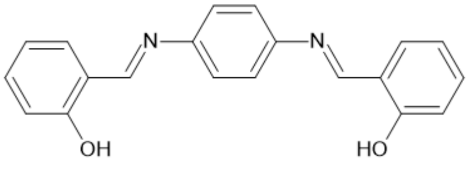
In terms of applications, lanthanides are essential in the production of high-strength magnets (e.g., neodymium magnets), phosphors for lighting and displays, catalysts in petroleum refining, and in various advanced materials. Their ability to form coordination complexes with diverse ligands makes them valuable in chemical research and industrial processes, including the photodegradation of pollutants and luminescent materials.

Recent research is concentrating on creating metal complexes that can photodegrade pollutants using solar energy, a renewable resource. Due to the ability to create unique combinations using various organic ligands and metal centers, coordination complexes provide greater structural flexibility than other materials. Sun et al. have reported the Co(II) complex with multi dentate O-donor or N-donor ligands as an active catalyst against the photodegradation of methylene blue and rhodamine blue. (7)

2. Materials and method:

2.1 Ligand preparation

The ligand was prepared with minor modifications to the method prescribed by in Shamin Ahemad khan, et al (8) Synthesis of Schiff base – 1:2 mole of Para phenylenediamine and Salicylaldehyde dissolve in Ethanol than reflux for 3 h at 70 ^{0}C- 80 ^{0}C for 3 hours, after 3 h cooling in ice cold water yellowish orange product separates out. Wash with several time with ethanol and dried in a vacuum desiccator over calcium chloride and obtain bright orange color product. (84% yield)



p-Phenylenebis(2-hydroxyphenylazo)benzene

2.2 Synthesis of Metal Complex:

1 mole metal chloride salt of Ln, Ce, Nd and Pr are dissolve in Methanol and 1 mole Schiff base dissolve in DMSO, metal Chloride add drop wise manner in ligand solution and stir for 30 minute and after reflux for 3 h on cooling metal complex separate out (yield = 59 %)

Table :- 1 Analytical Data and Some Physical Properties of the Ligand and Metal Complexes

Complex	**Color**	**Formula weight**	**Molecular formula**	**m.p**	**Elemental analysis**				
					C	H	N	O	Metal
PBDP	Bright Orange	316.38	$C_{20}H_{16}N_2O_2$	160 ^{0}C	75.93	5.10	8.86	10.11	
Ln-PBDP	Orange	879.76	$[Ln(C_{20}H_{16}N_2O_2)_2](H_2O)_6$	300 ^{0}C	56.63	15.51	6.37	15.39	15.80
Ce-PBDP	Brick Red	899.0	$[Ce(C_{20}H_{16}N_2O_2)_2](H_2O)_7$	300 ^{0}C	53.45	16.24	6.23	17.13	15.59
Pr-PBDP	Yellow	899.78	$[Pr(C_{20}H_{16}N_2O_2)_2]H_2O)7$	220 ^{o}C	53.44	16.24	6.23	17.12	15.66
Nd-PBDP	Orange	903.11	$[Nd(C_{20}H_{16}N_2O_2)_2\ (H_2O)_7]$	290 ^{o}C	53.16	16.16	6.20	17.01	15.97

3.0 Characterization

3.1 UV-Visible Spectroscopy

The UV-Visible spectral analysis of the ligand (Schiff base) and its metal complexes (Lanthanum, Cerium, Praseodymium, and Neodymium) reveals significant electronic transitions. The Schiff base shows π-π* transitions, while the Cerium and Lanthanum complexes exhibit both LMCT and d-d transitions. Praseodymium and Neodymium complexes display n-π* and f-f- transitions. These findings confirm the successful coordination of the ligand with metal ions, highlighting the distinct electronic structures and interactions within the complexes. The observed transitions reflect the versatile coordination behavior and provide insights into the electronic properties of the synthesized complexes.

Table: - 2 UV-Visible Spectroscopy data of the Ligand and Metal Complexes

Chelate	**λ (nm)**	**cm^{-1}**	**Band Assignments**
Schiff base	**243** **252**	**41152.26** **39682.54**	***π*- *π* *** ***π*- *π* ***
Cerium	**380.9**	**26252.25**	**n- *π* ***
	331.8	**30134.18**	**LMCT**
	318.7	**31380.12**	**LMCT**

	285.7	**35006.64**	**d-d**
Lanthanum	**375.6**	**26623.02**	**LMCT**
	333.2	**30018.01**	**LMCT**
	266.3	**37500.00**	**LMCT**
Praseodymium	**276.6**	**36150.62**	**π- π ***
	371.6	**26906.99**	**n-π* f-f-**
Neodymium	**371.6**	**26906.99**	**n-π* f-f-**

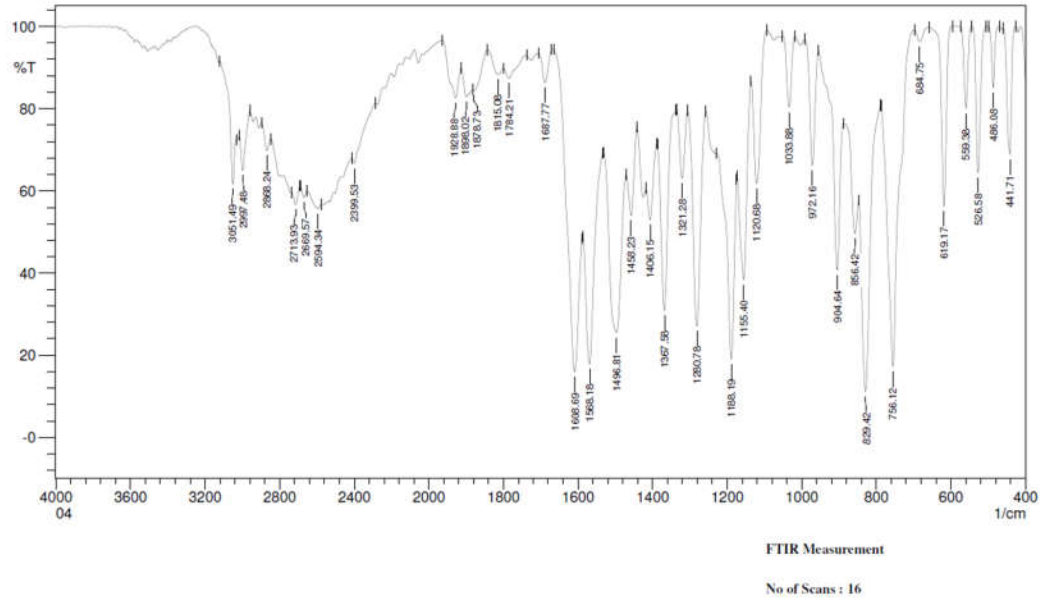
3.2 Infrared Spectroscopy

The IR spectra of the Schiff base and Ln (III) metal complexes (Ln-PBDP, Ce-PBDP, and Nd-PBDP) were obtained in the 4000 – 400 cm^{-1} region using KBr pellets. The N-H stretching band at 3412.08 cm^{-1} in the ligand shifts to lower wave numbers in the metal complexes, indicating coordination. The C=N stretching frequencies ranged between 1606 cm^{-1} and 1687.77 cm^{-1}, while aromatic C-N stretching frequencies were recorded between 1321.28 cm^{-1} and 1499.81 cm^{-1}. Peaks between 800-850 cm^{-1} correspond to triazine ring modes. The ν(M-N) stretching frequencies in Ln-PBDP, Ce-PBDP, and Nd-PBDP range from 480.94 cm^{-1} to 665.46 cm^{-1}, indicating metal-nitrogen coordination. A broad band near 3150 – 3500 cm^{-1} corresponds to $-NH_2$ or =NH stretching modes. These results confirm successful coordination of metal ions with the ligand.

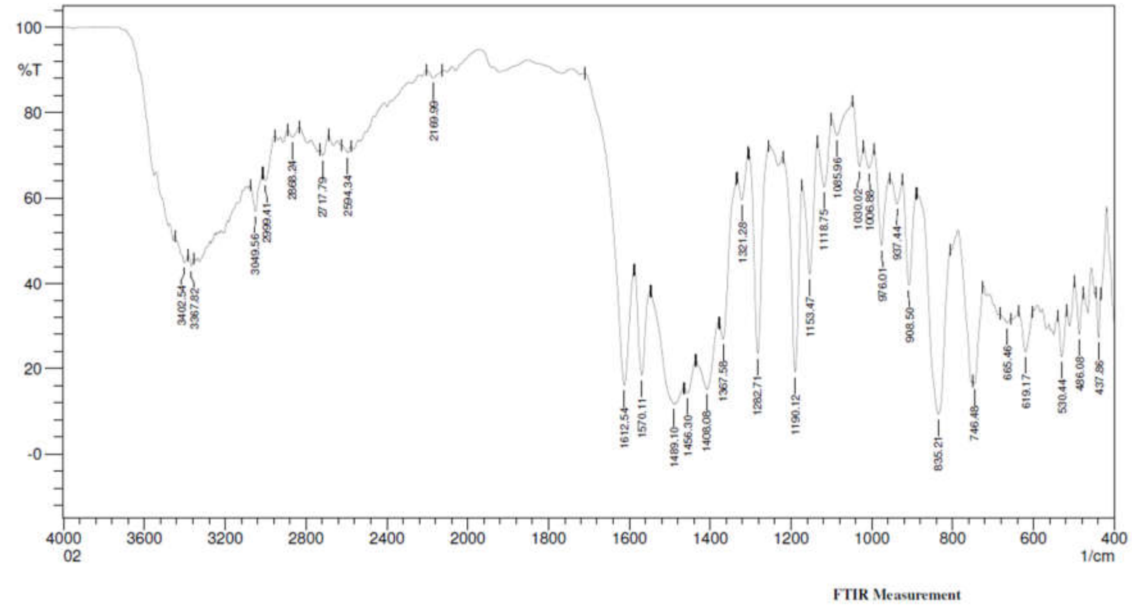
Table :- 3 IR spectroscopy data of the Ligand and Metal Complexes

Compound	Ar(C-H) stretching (cm-1)	ν(N-H) Stretching (cm-1)	C=N Stretching (cm-1)	Ar(C-N) Stretching (cm-1)	-OH Stretching (cm-1)	ν(M-N) (cm-1)
PBDP	3051.49 cm^{-1}		1687.77 cm^{-1} –	1499.81 cm^{-1} and 1321.28 cm^{-1}	3051– 3500 cm^{-1}	----
Ln-PBDP	3049.56 cm^{-}	3402.54 cm^{-1} and 3387.82 cm^{-1}	1612.54 cm^{-1}	1489.10 cm^{-1} and 1408.08 cm^{-1}	3402.54 cm^{-1}	619.17 cm^{-1} and 665.46 cm^{-1}
Ce-PBDP	3050-3100 cm^{-1}	3425.16 cm^{-1}	1643.41 cm^{-1}	1491 cm^{-1} and ~1456 cm^{-1}	3578.07 cm^{-}	525.96 cm^{-1} 489.94 cm^{-1}
Nd-PBDP	2983 cm^{-1}	3339 cm^{-1}	~1606 cm^{-}	1491 cm^{-1} and ~1450 cm^{-1}	3339 cm^{-1}	617 cm^{-1}
Pr-PBDP	3052 cm^{-1}, 2995 cm^{-1}	1492 cm^{-1}, 1467 cm^{-1}	1492 cm^{-1}, 1467 cm^{-1}	1570 cm^{-1}, 1607 cm^{-1}	3646 cm^{-1}	648 cm^{-1}

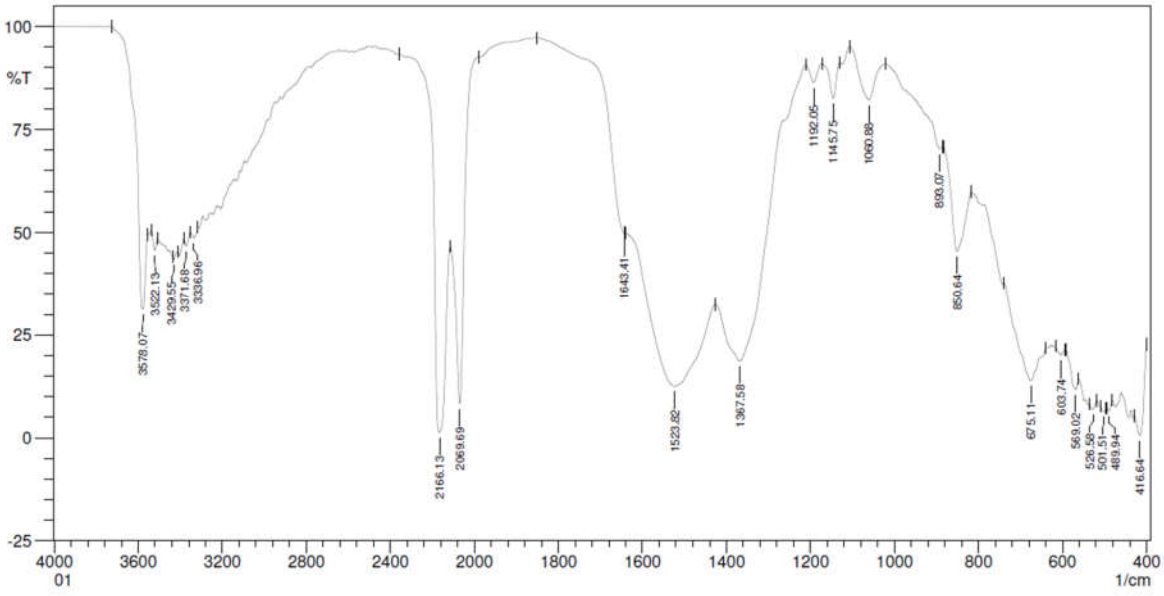
3.2.1 IR SPECTRA OF LIGAND



3.2.2 IR SPECTRA OF Ln-PBDP



3.2.3 IR SPECTRA OF Ce-PBDP

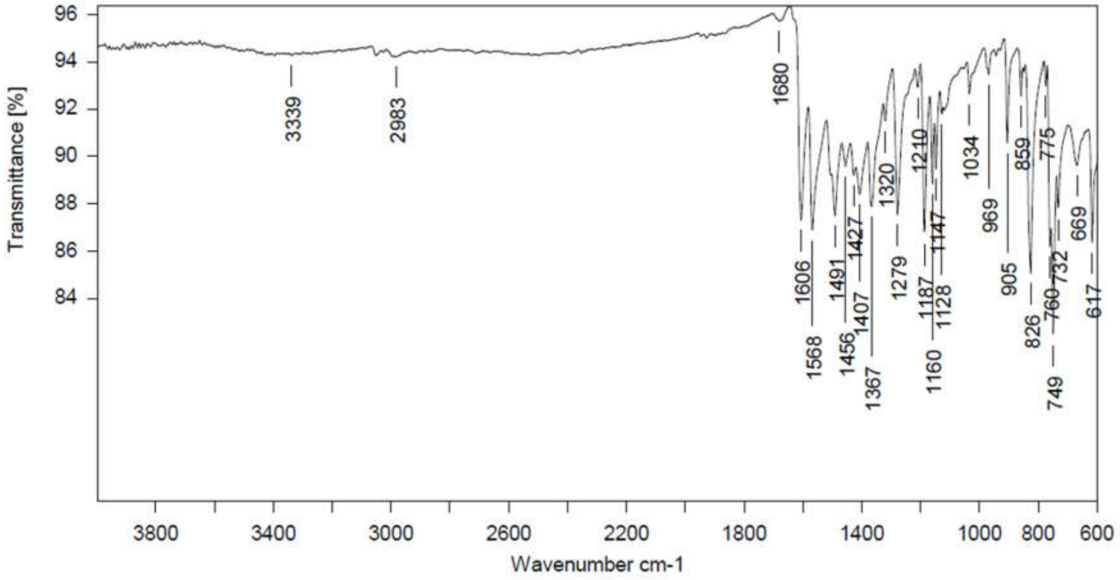


FTIR Measurement

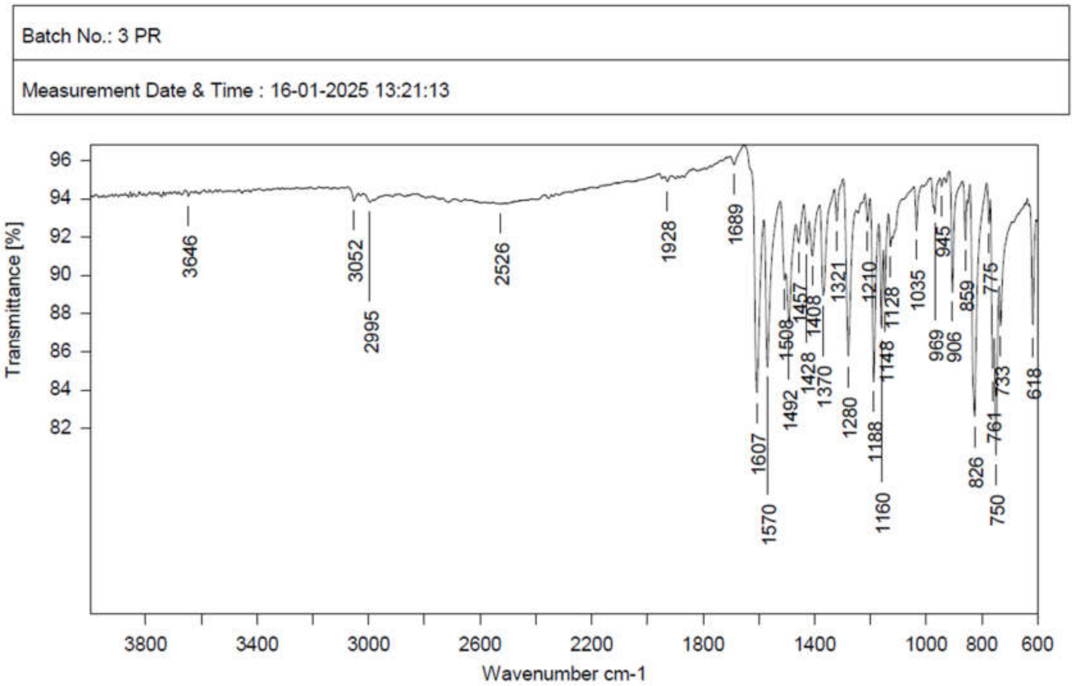
3.2.4 IR SPECTRA OF Nd-PBDP

Batch No.: 4 ND

Measurement Date & Time : 16-01-2025 13:24:11



3.2.5 IR SPECTRA OF Pb-PBDP



3.3 MASS Spectroscopy

The mass spectrometry analysis of the ligand (Schiff base) and its metal complexes (Lanthanum, Cerium, Praseodymium, and Neodymium) provides comprehensive insights into their fragmentation pathways. Mass spectrometry is a powerful analytical technique that measures the mass-to-charge ratio of ions. This method helps in identifying the molecular structure and composition of compounds by observing the fragmentation patterns of the molecular ions. The key findings are summarized as follows:

Table :- 4 Mass Spectroscopy data of the Ligand and Metal Complexes

Compound	Major Fragment's	m/z value (Calculated)	m/z value (Found)
Ligand	**$[C_{16}H_{14}N_2O]^+$**	**274.36**	**274.27**
Lanthanum	**$[C_6H_4N_2O_2]^+$**	**178.88**	**178.85**
	$[C_{19}H_{16}N_2OLa]^+$	**320.83**	**320.80**
	$[C_{25}H_{23}N_4O_2La]^+$	**608.87**	**608.85**
	$[C_{28}H_{26}N_4O_3La]^+$	**686.45**	**686.43**
Cerium	**$[C_6H_4N_2O_2]^+$**	**178.97**	**178.97**
	$[C_{24}H_{18}N_4O]^+$	**368.65**	**368.65**
	$[C_{28}H_{25}N_4O_4Ce]^+$	**802.49**	**802.49**
Praseodymium	**$[C_6H_4N_2O_2]^+$**	**178.98**	**178.97**
	$[C_{24}H_{18}N_4O]^+$	**368.67**	**368.65**
	$[C_{28}H_{25}N_4O_4Pr]^+$	**802.52**	**802.49**
Neodymium	**$[C_6H_4N_2O_2]^+$**	**178.99**	**178.81**
	$[C_{24}H_{18}N_4O]^+$	**368.70**	**368.76**
	$[C_{28}H_{25}N_4O_4Nd]^+$	**802.55**	**802.52**

4.0 Experimental section:

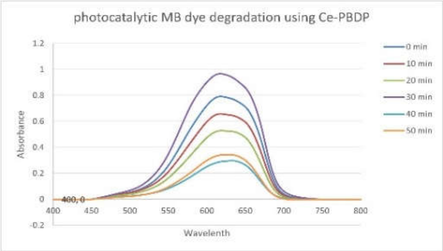
The photocatalytic degradation of methylene blue (MB) dye in an aqueous medium was investigated under visible light irradiation using metal complexes of lanthanum (Ln), cerium (Ce), Praseodymium (Pr), and neodymium (Nd). The progress of dye degradation was analyzed spectrophotometrically to evaluate both decolorization and mineralization efficiency. The influence of key parameters, such as irradiation duration and catalyst concentration, on the degradation rate was systematically examined.

A stock solution of MB (1.2×10^{-5} mol/L) was prepared using Millipore water for experimental studies. The photodegradation reactions were conducted under natural sunlight, with 50 mL of the dye solution mixed with 5 mg of the respective metal complex in a continuously stirred glass beaker. Prior to light exposure, the solutions were kept in the dark for one hour to attain adsorption-desorption equilibrium. (9)(10)

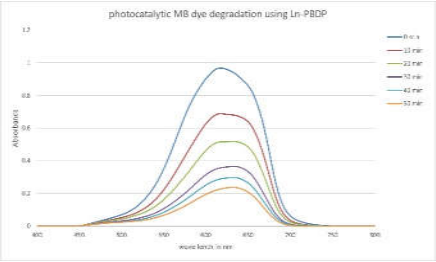
The effect of irradiation time on MB degradation was assessed over a period of 10 to 50 minutes. At fixed intervals of 10 minutes, aliquots were withdrawn using a syringe, filtered through a 0.22 µm Millipore membrane, and analyzed using a UV-Visible spectrophotometer to measure dye concentration. The absorbance spectra were recorded within the 400–800 nm range to monitor photodegradation efficiency. The photocatalytic activity of each metal complex was evaluated based on temporal changes in dye concentration, and the results were graphically represented.

5.0 Results:

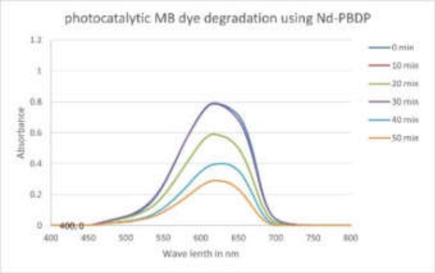
5.1 UV-Visible absorption spectra showing the photocatalytic degradation of methylene blue (MB) dye over time using metal complex as a photocatalyst under light irradiation.



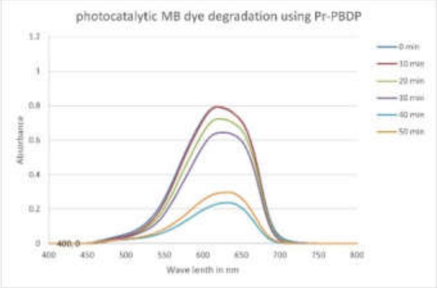
2. Ce-PBDP



1. Ln-PBDP



3. Nd-PBDP



3. Pr-PBDP

5.1

Results Analysis:

Catalyst	Initial Absorbance at 0 min (MB)	Degradation Efficiency	Performance Summary
Ce-PBDP	Strong absorbance peak at ~660 nm	Fastest degradation; significant reduction in absorbance with near-complete MB removal within 50 minutes.	Most efficient photocatalyst.
Nd-PBDP	Strong absorbance peak at ~660 nm	Moderate efficiency; MB concentration decreases significantly but not completely removed by 50 minutes.	Slightly more effective than Pr-PBDP.
Pr-PBDP	Strong absorbance peak at ~660 nm	Similar to Nd-PBDP but slightly less effective; some MB remains after 50 minutes.	Comparable to Nd-PBDP but slightly less efficient.
Ln-PBDP	Strong absorbance peak at ~660 nm	Slowest degradation; MB concentration remains relatively high even after 50 minutes.	Least effective catalyst.

The Result table shows the photocatalytic degradation efficiency of different Ln-PBDP catalysts for methylene blue (MB) dye removal, evaluated by UV-Vis spectroscopy at 660 nm.

- Ce-PBDP exhibited the fastest degradation, achieving near-complete removal of MB within 50 minutes, making it the most efficient photocatalyst.
- Nd-PBDP showed moderate degradation efficiency, with significant MB removal but some residue remaining at 50 minutes.
- Pr-PBDP performed similarly to Nd-PBDP but was slightly less effective, indicating comparable photocatalytic activity.
- Ln-PBDP had the slowest degradation, with high residual MB even after 50 minutes, making it the least efficient catalyst.

This analysis confirms that **Ce-PBDP is the most promising photocatalyst** for MB degradation among the tested materials.

6.0 Conclusion :

The study showed that Ce-PBDP had the highest photocatalytic efficiency, achieving nearly complete MB degradation within 50 minutes. Nd-PBDP and Pr-PBDP showed moderate efficiency, while Ln-PBDP was the least effective. The results suggest that Ce-based catalysts are the most promising for wastewater treatment due to their superior light absorption and charge separation. Future work should focus on optimizing catalyst performance and stability.

7.0 Acknowledgment

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