SINDH UNIVERSITY RESEARCH JOURNAL (SCIENCE SERIES)
ISSN (Print) 1813-1743, ISSN (online) 2791-0547
Vol. 57:02 (2025).
Doi: https://doi.org/10.26692/surjss.v57i02.7297

Synthesis, characterization of Cu(II)/ Ni(II) complexes metal ions derived from flexible (4, 4’-Dimethyl-2,2’-Bipyridine) ligand and their photo degradation applications.

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***Cite this*:**
Fayaz Ahmed Keerio, Ambreen Shah, & M. Younis Talpur, Synthesis, characterization of Cu(II)/ Ni(II) complexes metal ions derived from flexible (4, 4’-Dimethyl-2,2’-Bipyridine) ligand and their photo degradation applications Sindh Uni. Res.J. (SS) 57.02, 2025

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ABSTRACT

Newly developed metal ligand (M-L) coordination complexes were synthesized by various methods for research and commercial uses, which shown significant improvement over time. A newer flexible, bipyridine-based Cu (II) and Ni (II) metal complexes formed from 2,2’-bipyridine-4,4’-dicarboxylic acid, using the metal-coupling reaction. The structure of the new M-L complexes was analyzed using various spectroscopic techniques, including FT-IR, UV/Vis, SEM, and EDS. The newly synthesized compound 2,2’-bipyridine-4,4’-dicarboxylic acid[(BPyCOOH)] showed weak to medium-intensity bands in the 1730 cm^{-1} range, attributed to aromatic carboxylate stretching vibrations. These metal complexes were employed as photo-catalysts for the photo degradation of methylene blue in an aqueous solution. The photocatalytic experiments revealed that the Cu(II) complex exhibited the best photocatalytic performance than Ni(II) complex, degrading 88% of methylene blue (MB) at 26°C. The photo-degradation activity was observed under UV light and in darkness. The kinetics of the photo degradation of methylene blue were investigated with optimized parameters in the presence of nan catalysts. The rate constants (k) for the metal ions [(BPyCOO)Cu] and [(BPyCOO)Ni] were measured to be 0.0481 and 0.0212, respectively. These results indicate a pseudo-first-order reaction with a higher rate constant for [(BPyCOO)Cu] compared to [(BPyCOO)Ni].

Keywords: Metal complexes, synthesis, FT-IR, UV-Vis, SEM, photo-degradation reaction.

INTRODUCTION

The synthesis of new types of complexes remains an important focus in today's chemical sciences due to their promising applications in various fields such as microelectronics, nonlinear optics, porous materials, catalysis, and luminescence (Hui, Xu. et al., 2012; Yamanoi, Y., 2024). These metallic complexes also exhibit significant supramolecular structures in crystalline morphology which enabled by noncovalent interactions such as hydrogen bonds and van der Waals forces (Mingming, C.,et al., 2006; Yuan-Ping, W & Sizhuo, Y., 2021).However, it remains a challenge the chemists for newer synthesis , especially those focused on crystal engineering, to create complexes with specifically focused supramolecular compound that exhibit some metallic properties (Imteaz A. &Sung, H. J., 2017 ; Xiuyan, D. et al., 2022).

Bipyridine compounds, also known as bipyridyl compounds, are a class of compounds in which two pyridine rings fused together, each containing five carbon atoms and one nitrogen atom (Su-Ping, L., et al., 2017; Thach Ngoc, T. et al., 2021). The general chemical formula of bipyridine is $C_{10}H_8N_2$. These compounds have been broadly studied and used in various fields such as coordination chemistry, organic synthesis, and materials science (Sadaf, Y. et al., 2024).

For the synthesis of these complex structures requires careful selection of metal ions, primary ligands, auxiliary or co-ligands, and optimization of reaction conditions such as pH, temperature, and solvent selection. All parameters provide some important feature of complex and play a crucial role in the self-assembly process to generate the desired supramolecular based structures (Sergio, N. et al., 2022). The selection of ligands and co-ligands is particularly important as N-donor and O-donor bridging and chelating ligands are usually used in the synthesis of target complexes (Tahere, K. et al., 2021). These ligands, when coordinated with transition metal ions, can form complexes with specific co-ordination bonding properties (Guoshuai, L. 2017; Weili W.et al., 2022).

Water pollution especially that caused by organic dyes, is a major environmental hazard on a global scale (Hanbing, R.et al., 2016; Jakob, B.., et al., 2021). The aromatic based complex structures helpful that organic dyes are often resistant to degradation for conventional biological treatments and are stable in aqueous systems (Christopher, K. P.et al., 2013; Anna, M.et al., 2022). Standard industrial wastewater treatment methods such as adsorption and coagulation often fail to completely eliminate these pollutants or convert them to less harmful forms (Jia-Wei. et al., (2017); Fatemeh, H. et al., 2018). Although chemical and membrane filtration methods are effective but they are expensive and may also produce toxic materials as byproducts forms (Jiajia, Wei. et al., 2023; Mohamed, A. H. et al., 2023).

Certain these limitations, coordination complexes are increasingly being explored by synthetic chemists as photo catalysts for dye degradation because they generate highly reactive transition species that effectively degrade dyes under mild conditions at low cost (Satyanarayan, P., 2018; Wu, W. P., et al., 2019., Shailendra, Y. et al., 2024;).

In this research, we focus on the synthesis of a novel ligand,2,2'-bipyridine-4,4'-dicarboxylic acid[(BPyCOOH)], derived from 4,4'-dimethyl-2,2'-bipyridine, and its corresponding Cu(II) and Ni(II) metal complexes. These complexes exhibit flexibility at the nitrogen heteroatom sites and possess potential for diverse coordination geometries. This enables them to form robust supramolecular structures with notable catalytic features. Structural characterization of these complexes confirms their coordination behavior, and their photocatalytic activities were evaluated by monitoring the photo degradation of methylene blue under UV light and dark conditions. The findings demonstrate their potential as effective and eco-friendly materials for wastewater treatment applications (Long, P., et al., 2003; Luca, M., et al., 2021).

2. EXPERIMENTAL

2.1 Materials and Methods

Reagents and Chemicals

Following analytical grade reagents used such as 4-methylpyridine(C_6H_7N), phosphorus trichloride (PCl_3), Potassium per magnate ($KMnO_4$), Sulfuric acid (H_2SO_4),copper acetate $(CH_3COO)_2Cu$, nickel acetate $(CH_3COO)_2Ni$, acetic acid (CH_3COOH), dimethyl sulfoxide (DMSO),n-hexane (n-C_6H_{14}), methyl alcohol (CH_3OH), ethyl alcohol (C_2H_5OH), were bought from E. Merck, Germany.

2.2 Synthesis of (2,2'-bipyridine-4,4'-dicarboxylic acid) Copper Complex:

The compound (4,4'-dimethyl 2,2'-bipyridine) was initially prepared from 4-methyl pyridine (picolines) using the well-known Kröhnke method (Telmo N. F. et al., 2024), then (4, 4'-Dimethyl-2,2'-bipyridine**)** oxidized into 2,2'-bipyridine 4,4'-dicarboxylic acid [(BPyCOOH)], which followed the subsequent procedure for the synthesis of metal complex:

(0.05 M) 2,2'-bipyridine 4,4'-dicarboxylic acid [(BPyCOOH)],(0.3 mL) and copper acetate (0.37 mL) were dissolved in a mixture of 15 mL of acetic acid and 30 mL of acetone. The mixture was heated until it became clear at room temperature. Refluxed the mixture for 6 hrs with continuous stirring. The solution was poured into 100 mL of chilled water. Filtered and dried the precipitate in oven. Recrystallized the precipitates in methyl alcohol and n-hexane.

This same procedure was also used to synthesize nickel metal complexes with the same reagents.

2.4 Characterization:

Elemental microanalysis was carried out by instrument (Elemental Micro-Analysis Ltd, U.K). The FT-IR were obtained on a new Infrared instrument (Nicolet Avatar 330 FT-IR (Thermo Nicolet Electron Corporation, USA), having ranged between 4000-600 cm^{-1}.

Spectrophotometric studies were carried out on a double beam Hitachi 220 spectrophotometer (Tokyo, Japan), with dual 1 cm silica cuvettes within 185-700 nm. Scanning Electron Microscopy with Energy Dispersive X-Ray analysis (SEM-EDX) was conducted on a Phenom-World instrument.

3. RESULTS AND DISCUSSION

The carboxylate ligand and its derived metal complexes exhibited values closely matching theoretical predictions, as confirmed by C, H, N analysis. Both the carboxylate ligand and its metal complexes demonstrated good solubility in polar solvents such as acetone (CH_3COCH_3), chloroform ($CHCl_3$), tetra hydro furan (THF), anddimethyl sulfoxide (DMSO).

Initially, the compound 2,2'-bipyridines, 4,4’-dicarboxylic acid[(BPyCOOH)] is synthesized and its FTIR spectrum also confirmed its characterized peak at 1730 cm⁻¹ range, due to carboxylate bond. The FTIR spectrum of 2,2’-bipyridine-4,4’-dicarboxylic acid is shown in **(Fig. 1).**

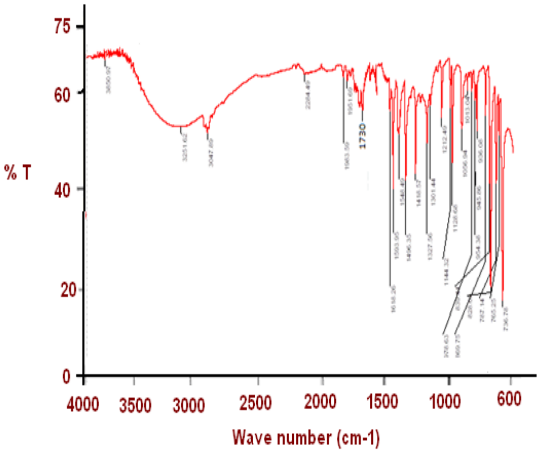


Fig. 1: FT-IR Spectrum of 2,2’-bipyridine-4,4’-dicarboxylic acid [(BPyCOOH)].

Then, a metal complex [(BPyCOO)Cu] showed weak to medium-intensity bands in the 3047.45 cm⁻¹ range, attributed to aromatic C-H stretching vibrations. These complexes displayed a distinctive peak around 1618-1548 cm⁻¹ because of υC=N stretching vibrations**.** The copper-oxide bond, one of the strongest bonds in the spectrum of Copper metal complex, appeared at 619.32 cm⁻¹. Some M-O stretching vibrations also appeared at 864.16 cm⁻¹ and 932.35 cm⁻¹, indicating new coordination bonds of M-L bonding.

Spectrophotometric analyses in dimethyl sulfoxide (DMSO) revealed two primary absorption bands in 2,2'-bipyridines, 4,4’- dicarboxylic acid [(BPyCOOH)]. First band appeared at372 nm which attributed to π–π* transitions due to benzene and naphthalene ring structure. Second band appeared at 483 nm, due to π–π* transitions of the conjugated C=N bending in the bipyridine ring, **(Fig. 2)**.

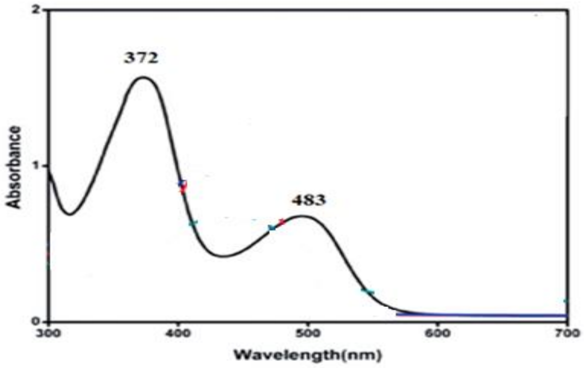
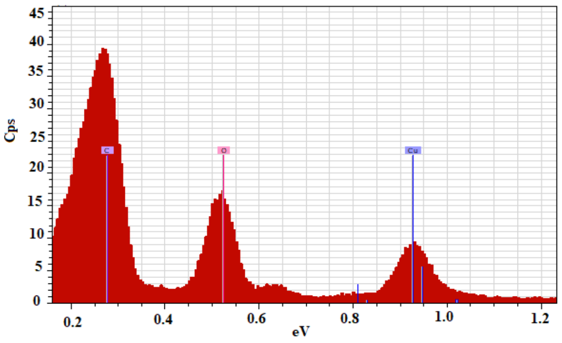


Fig. 2:UV. Vis Spectrum of (2,2’-bipyridine 4,4’-’-dicarboxylic acid) [(BPyCOOH).

The EDS spectrum of the carboxylate copper metal complex solution showed weight percentages for carbon, copper, and oxygen, with peaks at respective atomic weights: Carbon (C) at 47.04%, Copper (Cu) at 23.10%, and Oxygen (O) at 29.86% in the Cu(II) metal complex **(Fig. 3).**



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Spectrum: Acquisition

Element   Series   unn. C norm. C Atom. C Error
                   [wt.%]  [wt.%]  [at.%]   [%]
-----------------------------------------------
Carbon   K-series  47.04   47.04   63.72  14.4
Oxygen   K-series  29.86   29.86   30.36   9.3
Copper   L-series  23.10   23.10    5.92   7.3
-----------------------------------------------
            Total: 100.00  100.00  100.00
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Fig.3: EDS spectrum of (2,2’-bipyridine 4,4’-’-dicarboxylic acid) Copper [(BPyCOO)Cu] complex.

These results aligned with previously reported studies (Tahere, K. et al., 2021).

SEM images presented the morphology of all synthesized compounds at various magnifications. Both the copper metal complex [(BPyCOO)Cu] and the nickel metal complex [(BPyCOO)Ni] were analyzed by SEM spectroscopy, revealing a clear difference in their morphology. The copper metal complex [(BPyCOO)Cu] exhibited agglomerated spherical shapes, forming scattered clusters **(Fig. 4).**

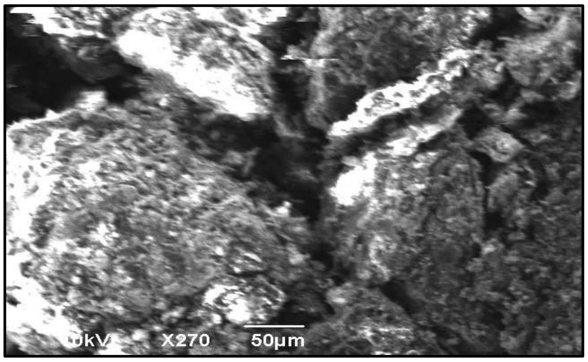

Fig. 4: SEM image of (2,2bipridine 4, 4'-dicarboxylic acid) Copper complex

In contrast, the nickel metal complex [(BPyCOO)Ni] displayed an aggregated cylindrical morphology. The images also verified that the nanoparticle sizes were smaller, in the micrometer range, and crystalline in structure **(Fig. 5).**

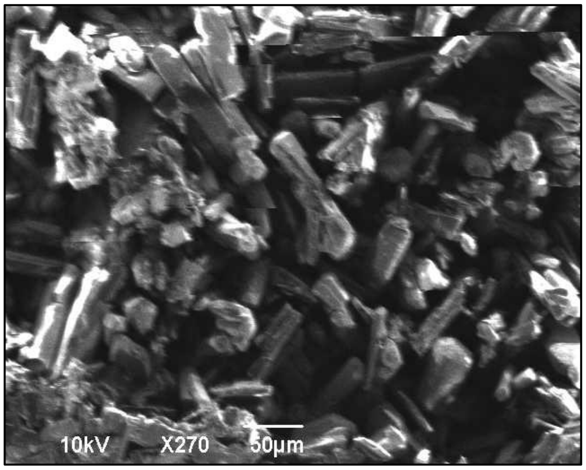

Fig. 5: SEM image of (2,2bipridine 4, 4'-dicarboxylic acid) Nickel complex

Photo Degradation Activity

Photo degradation, a method that uses light energy, typically from ultraviolet (UV) or visible light (Hanbing, R.,et al., 2016), to break down complex organic pollutants into simpler, less harmful compounds, was especially effective for treating water contaminated with dyes, pharmaceuticals, pesticides, and other organic pollutants resistant to conventional degradation methods (Christopher, K. P. et al., 2013).

The photocatalytic activity for [(BPyCOO)Cu] and nickel metal complex [(BPyCOO)Ni] was considered for the degradation of methylene blue (MB) along with UV lights. The schematic diagram of photo degradation of methylene blue with 2,2'-bipyridines, 4,4'-dicarboxylic Acid Cu(II) metal complex, **(Fig. 6)**.

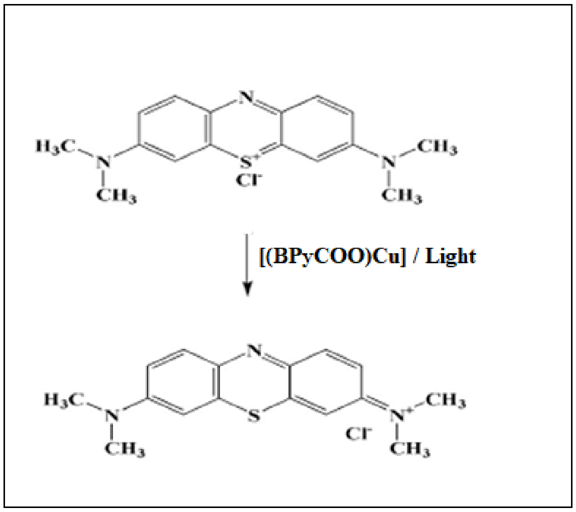

Fig. 6: Schematic diagram of photo degradation of methylene blue with 2,2'-bipyridines, 4,4'-dicarboxylic Acid Cu(II) metal complex.

It was experimental proved that once only UV light was exposed, the degradation (%) was relatively low (16.3%), under UV light only, but the addition of (Cu/Ni complexes) along UV lights observed a drastic improvement in the degradation percentage of organic dyes. The reactivity of methylene blue dye with the Cu and Ni complexes were optimized by examining the effects of pH, dye concentration of methylene blue (MB), catalyst dosage, and irradiation time. Based on experimental observations, it was concluded that the first concentration of methylene blue (MB) dyes were selected as 20 mg/L, with a catalyst dosage of 0.5 g and optimized pH = 10. This setup showed a successful photocatalytic degradation process at 40 minutes of UV light irradiation at 26°C**.**

After optimization, the photo catalytic degradation of methylene blue was conducted with both metal complexes under UV light as well as in the dark, with data shown in **(Fig. 7-8).**

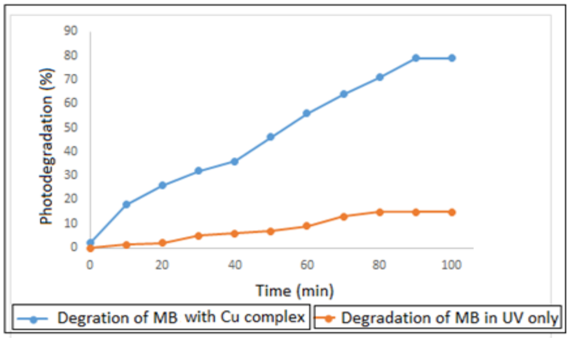

Fig.7: Effect of irradiation time (0–100 min) with and without Cu complex: Initial concentration of dye = 20 mg/L, catalyst dosage = 0.5 g, pH = 10; irradiation time (0–100 min) at constant temperature.

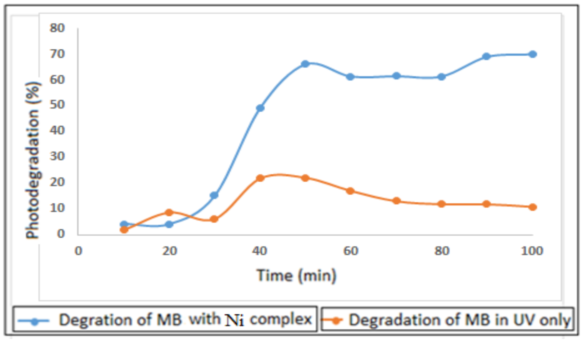

Fig.8: Effect of irradiation time (0–100 min) with and without Ni complex: Initial concentration of dye = 20 mg/L, catalyst dosage = 0.5 g, pH = 10; irradiation time (10–100 min) at constant temperature.

The kinetics of the photocatalytic degradation of methylene blue was investigated using optimized parameters in the presence of metal complexes, as a catalysts. The rate constants (k) for [(BPyCOO)Cu] and [(BPyCOO)Ni] metal ions were determined to be 0.0481 and 0.0212, respectively **(Fig. 9).**

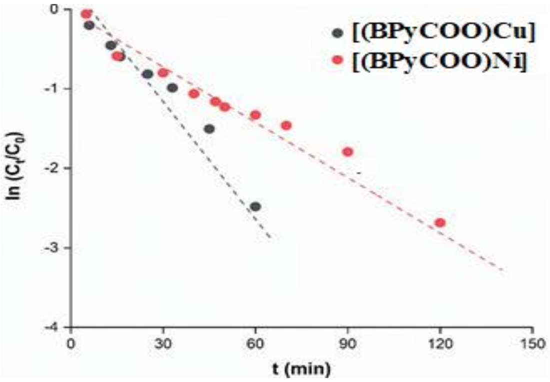

Fig.9: Kinetics of the photo catalytic degradation of methylene blue with copper and nickel metal complexes.

Photo degradation activity was observed under both UV light and dark conditions, and the reaction kinetics were studied for both metal complexes. These results are consistent with the findings of other researchers (Su-Ping, Luo.,. et al., 2017; Yuan-Ping, & Sizhuo, Y. 2021).

4. CONCLUSION

This study established new coordination metal ligand (M-L) complexes 2,2'-bipyridine-4,4'-dicarboxylic acid [(BPyCOOH)] was formed from 4-methyl pyridine using the Kröhnke method and then it was further reacted with Cu(II) and Ni(II) ion salts in a metal coupling reaction to form a flexible bipyridine-based metal complexes. The structure of the new M-L complexes was elucidated using different spectroscopic techniques (FTIR, UV/Vis, SEM, EDS). As an application, the photocatalytic degradation of methylene blue was carried out in the presence of M-L complexes. The kinetics of the photocatalytic degradation of methylene blue was analyzed for the Cu(II)/Ni(II) metal complexes, which demonstrated effective photocatalytic activity.

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