



Electrochemical And Photocatalytic Studies of Novel Azo Ligand and Their Metal Complexes; Synthesis, Characterization and Biological Evaluation

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ABSTRACT:

The Novel Azo Dye ligand, 4-[(2E)-3-(6-nitro-1,3-benzothiazol-2-yl)triaz-2-en-1-yl]benzoic acid (NBA) and its Co(II), Ni(II) and Cu(II) complexes have been synthesized. The newly synthesized compounds characterized using physicochemical techniques. XRD pattern indicate crystalline nature of metal complexes. A modified electrode [Co(NBA)₂(H₂O)₂]/GCE was prepared by using the synthesized Co(II) complex to assess electrocatalytic properties by cyclic voltammetry (CV) studies. The [Co(NBA)₂(H₂O)₂]/GCE found to have excellent electrocatalytic activity with 4.599 μM/L limit of detection (LOD) with a linear range of 10–60 μM/L and R² = 0.9982 confirming the surface diffusion control of the electrochemical process. The [Co(NBA)₂(H₂O)₂]/GCE found efficient in detection of ascorbic acid in different concentrations. Furthermore, the synthesized compounds evaluated for antidiabetic activities exhibiting promising results. The catalytic efficiency of the synthesized metal complexes was assessed through the photodegradation of Methyl Red dye under visible light. The Photocatalytic efficiency of Co(II) and Ni(II) complexes reported to degrade methyl red by 71.58 and 72.13% respectively.

1. Introduction

Azo dyes are synthetic compounds featuring an –N=N– bond, primarily derived from aromatic amine substrates such as nitro and nitroso groups. The azo dye derivatives are significant colorants, which are widely employed in pharmaceuticals, textiles, printing, optics and food processing. The industries availability, affordability, stability and perceived safety of azo dye compounds contribute to their desirability as food additives [1-4]. Azo dye derivatives demonstrate notable antitumor [5], antiulcer [6], antifungal [7], antibacterial [8], anthelmintic [9], anti-inflammatory [10], anticonvulsant [11], antitubercular [12], antidepressant [13], antihypertensive [14], anticoagulant [15], and antiviral

[16] activities. Furthermore, azo dye metal chelates are increasingly valued in catalysis, pharmaceuticals and various industrial applications with their transition metal complexes exhibiting biological activity.

Cyclic Voltammetry is a recognized, facile, cost-effective and reliable electrochemical technique for redox studies and elements present in the impure sample detection. This potentiodynamic method investigates the electrochemical properties of analytes in solution or absorbed on the electrode surface [17]. Ascorbic acid (AA) a vital dietary component and potent antioxidant [18] possesses therapeutic benefits for various conditions including fever, fatigue, gum swelling, joint pain and impaired wound healing influences key physiological



processes. However, its electrochemical activity can interfere with the detection of the other analytes. Ascorbic acid undergo oxidation readily may cause peak overlap with other substances. The oxidation potential and resultant current peak in the cyclic voltammogram are directly correlated with its concentration. Therefore, this method is sensitive to ascorbic acid detection even in the presence of interfering substances.

A number of substituted azo dye ligand and their 3d metal complexes have been synthesized in our laboratory and these complexes used to prepare modified electrode for detecting biologically important molecules and in addition biological activity also been evaluated. In continuation of this, we report here the synthesis of a new azo dye ligand and its transition metal complexes, their biological evaluation, dye degradation and the subsequently detection of ascorbic acid using a [Co(NBA)₂(H₂O)₂]/GCE electrode.

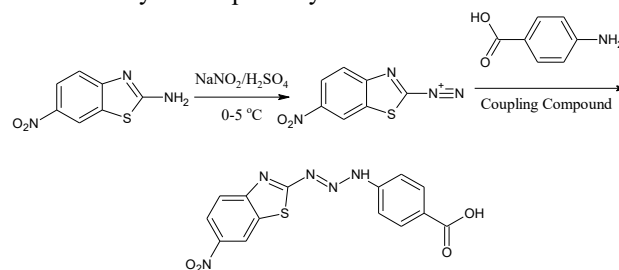
2. Experimental Methodology

2.1. Materials and Methods

All Chemicals and solvents used in this study were analytical grade and purchased from Sd-fine and Hi-Media. Ligand and metal complexes melting points were determined using an electrothermal melting point apparatus with a digital thermometer and the values are uncorrected. FT-IR spectra of the synthesized ligand and its metal complexes were recorded on a Shimadzu Spectrometer serial no: A224159 (Made in Japan) in Sahyadri Science College, Shivamogga-577203, Karnataka, India. UV-Vis absorbance was recorded using Systronics UV-Vis Double Beam Spectrophotometer 2206TS in Sahyadri Science College, Shivamogga-577203, Karnataka, India. ¹H and ¹³C NMR spectra of ligand were obtained using a JEOL spectrometer at a frequency of 400 MHz in Mangalore University, Mangalore-574199, Karnataka, India. Mass spectra obtained from Mysore University, Mysore – 570001, Karnataka, India. XRD patterns were obtained using Bruker D8 advance and SEM by Zeiss model-EVO LS 15. Cyclic voltammetry analysis was performed using CH instrument electrochemical analyzer (USA) at Sahyadri Science College, Shivamogga – 577203, Karnataka, India.

2.2. Azo dye ligand synthesis

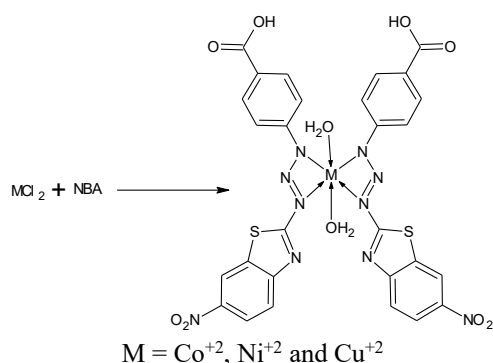
In a conical flask, solution of 0.002 mol of 2-amino-6-nitrobenzothiazole and 4N HCl dissolved in 10 mL of distilled water. Maintained the reaction mixture in an ice bath with continuous stirring for 2-hours. Simultaneously, 0.002 mol of NaNO₂ were dissolved in a separate flask using H₂SO₄ and maintained in an ice bath for 30 minutes. Subsequently, the NaNO₂ solution was carefully added to the conical flask with continuous stirring to avoid disruption. Following a 2-hour dissolution of 4-aminobenzoic acid in KOH solution under ice cold conditions, the solution was transferred to a previously prepared solution in a conical flask, stirring continued for an additional hour. Neutralization was achieved using NaHCO₃, following which the precipitate was generated, which was filtered, recrystallized and dried. The synthetic pathway is showed in Scheme-1.



Scheme 1: Synthesized 4-[(1E)-3-(6-nitro-1,3-benzothiazol-2-yl)triaz-1-en-1-yl]benzoic acid (NBA)

2.3. Synthesis of Metal Complexes

The synthesized ligand (NBA) (0.002 mol), dissolved in hot absolute ethanol and stirred. The solution of metal chlorides (Co, Ni and Cu) (0.001 mol) in absolute ethanol was prepared and added to the ligand solution. The reaction mixture was refluxed for 5 hours on a water bath. After that the excess solvent was removed by evaporation. The synthesized product was permitted to cool at ambient temperature. The resulting precipitate was subsequently filtered, washed and dried. Scheme 2 illustrates the synthetic pathway and the proposed structure of the metal complexes.



Scheme 2: Structure of metal Complexes

2.4. Electrochemistry

The electrocatalytic properties of synthesized metal complexes determined by preparing novel modified electrode. A saturated solution of metal complexes in isopropanol was prepared by sonication, was drop-coated onto a glassy carbon electrode (GCE). Cyclic voltammetry employed the GCE as the working electrode, an Ag/AgCl as reference electrode and a platinum wire counter electrode in a phosphate buffer solution was used to study the electrocatalytic activity. Redox reactions of ascorbic acid were induced by cycling the potential applied to the working electrode and the resulting current response correlated to ascorbic acid concentration via peak currents and calibration curves enabled quantitative analysis. This method provides rapid sensitive ascorbic acid detection with broad applicability [19-20].

2.4. Photocatalytic Activity

Methyl red (MR) degradation under natural sunlight was used to evaluate photocatalytic activity. A 50 mg photocatalyst sample was dispersed in 100 mL of aqueous MR solution. Prior to irradiation, the suspensions were magnetically stirred in the dark for 15 minutes to establish MR adsorption-desorption equilibrium. At predetermined intervals, 3mL aliquots were withdrawn, centrifuged to remove particles and MR concentration was determined by absorbance measurement observed at the characteristic wavelength using Systronics 2206TS UV-Vis double Beam Spectrophotometer [21-22].

2.5. Antidiabetic activity

α -Amylase inhibitory activity

α -Amylase inhibition assays were conducted according to the method detailed in Gharge et al., 2024 [23]. Porcine pancreatic α -amylase (1 U/mL; SRL, Bangalore, India) was prepared in 0.1 M phosphate-buffered saline (pH 6.9) at a concentration of 100 μ L. Enzymes sample at concentrations range from 0 to 100 μ g/mL underwent a 10-minute pre-incubation at 37 $^{\circ}$ C. The reaction commenced upon the addition of 0.1% starch substrate to the incubation mixture. Following 10-minute incubation period, the reaction mixture was quenched by the addition of 250 μ L of dinitrosalicylic acid (DNS) reagent (1% 3,5-dinitrosalicylic acid, 0.2% phenol, 0.05% Na_2SO_3 and 1% NaOH in aqueous solution). The reaction was quenched by maintaining the reaction mixture in a boiling water bath for 10 minutes. Subsequently, 250 μ L of a 40% potassium sodium tartrate solution was introduced. Following cooling to ambient temperature in a cold-water bath, absorbance was measured at 540 nm. The percentage inhibition was determined using the formula $(\text{OD of blank} - \text{OD of test}) / \text{OD of blank} \times 100$, and the results were expressed as IC_{50} values with acarbose serving as a positive control.

α -Glucosidase inhibitory activity

The α -glucosidase inhibitory activity of the samples using the methodology [24]. Specifically, 50 μ L of 1 U/mL yeast α -glucosidase (SRL, Bangalore, India) in 50 mM phosphate buffer (pH 6.9) was pre-incubated with varying sample concentrations (0-100 μ g/mL) for 10 minutes at 37 $^{\circ}$ C. The reaction was initiated by adding 50 μ L of 5 mM p-nitrophenyl- α -D-glucopyranoside in phosphate buffer, incubated for 30 minutes at 37 $^{\circ}$ C and subsequently quenched with 1 M Na_2CO_3 . Absorbance was measured at 405 nm. Inhibition percentage was determined using the formula $(\text{OD of blank} - \text{OD of test}) / \text{OD of Blank} \times 100$ and results are reported as IC_{50} values with acarbose serving as a positive control.

3. Results and Discussion

3.1. Chemistry

The novel azo dye ligand and its metal complexes exhibited stability at ambient temperature and solubility in ethanol, methanol, DMF, chloroform and DMSO. Elemental analysis data corroborated calculated values, as presented in Table 1.



Table 1 Physical properties and analytical data of the NBA and its metal complexes

Compounds	Mol.Wt	Calculated CHN values in (%)				Melting Point (°C)
		M	C	H	N	
NBA	344.04	-	48.98 (48.67)	2.64 (2.47)	20.40 (20.19)	183
[Co(NBA) ₂ (H ₂ O) ₂]	778.46	7.55 (7.43)	43.14 (42.89)	2.59 (2.47)	17.97 (17.86)	261
[Ni(NBA) ₂ (H ₂ O) ₂]	778.88	7.53 (7.45)	43.09 (42.57)	2.57 (2.43)	17.91 (17.79)	257
[Cu(NBA) ₂ (H ₂ O) ₂]	783.28	8.10 (7.95)	42.58 (42.37)	2.47 (2.34)	17.66 (17.53)	263

3.2. ¹H NMR Spectral Studies

The aromatic protons in the ¹H NMR spectrum of NBA appeared as multiplets in the region 7.6 – 8.5 ppm. A singlet observed at 4.9 ppm, corresponding to the NH proton. An additional sharp singlet at 12.8 ppm is an indicative of an aromatic OH as showed in the spectrum Figure 1.

The ¹³C NMR spectrum of the NBA exhibited fourteen distinct carbon chemical environments, resonating between 100 and 171 ppm. The C=O group exhibited a resonance at 171.81 ppm, while the remaining benzene ring carbons resonated between 112 and 140 ppm. Literature data corroborates the proposed molecular structure, with the ¹H and ¹³C NMR spectra showing excellent agreement. The ¹³C NMR spectral data are showed in Figure 2.

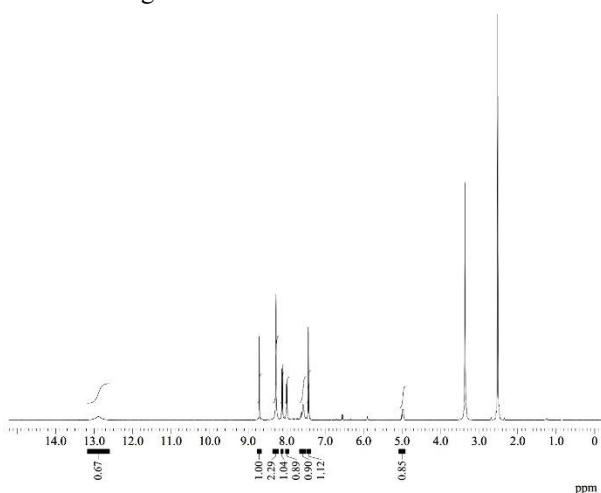


Figure 1 ¹H NMR spectrum of NBA

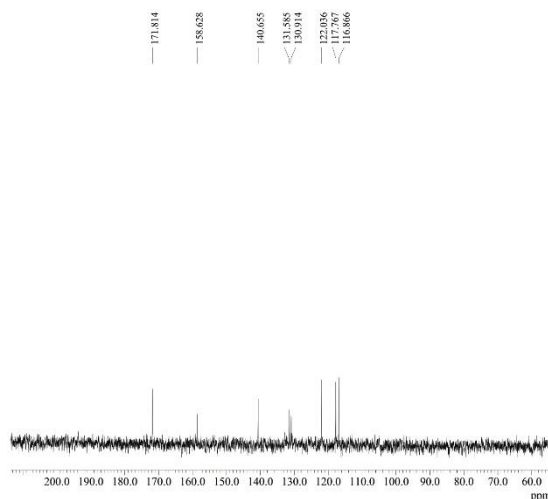


Figure 2 ¹³C Spectrum of NBA

3.3. Mass Spectral Studies

Mass spectral analysis of the synthesized ligand and its metal complexes was performed. The molecular ion peak in the ligand (NBA) mass spectrum, observed at *m/z* 344.04 (cal. 343.41) confirms the proposed molecular formula showed in Figure 3. Molecular ion peaks for the Co(II), Ni(II) and Cu(II) complexes were detected at *m/z* 778.46 (cal. 779.53), 778.88 (cal. 779.34) and 783.28 (cal. 784.17) respectively supporting the proposed 1:2 (M:L) stoichiometric ratio. Observed spectral data are consistent with the proposed molecular structures.

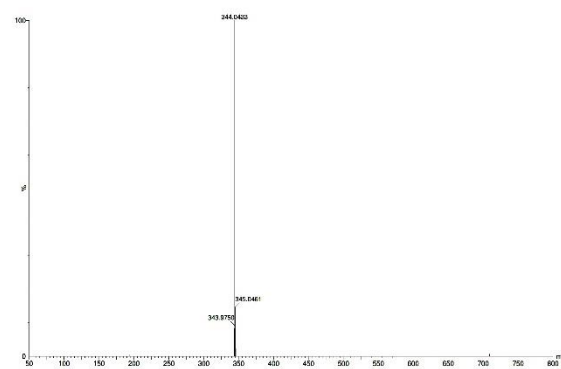


Figure 3 Mass spectrum of NBA

3.4. IR Spectral Studies

Infrared spectroscopy proved essential in identifying the functional groups of the synthesized ligand (NBA) and its metal complexes. The infrared spectra of NBA and its metal complexes recorded using KBr pellets in the 4000 – 350 cm⁻¹ wavelength range are presented in Figure 4.



The data placed in Table 2 indicate the –OH stretching vibration at 3430 cm^{-1} . The –OH stretching bands appeared at nearly identical regions across all complexes with minor shifts $20 - 30\text{ cm}^{-1}$ to higher frequencies. The –N=N– stretching was observed around 2027 cm^{-1} exhibiting similar minor shifts of $30 - 40\text{ cm}^{-1}$ to higher frequencies across all complexes. The C=O stretching remained at approximately 1649 cm^{-1} in all complexes showing no significant shifts. The involvement of the ligand and metal ion via –N=N– group in complex formation is supported by appearing new bands in the region $427 - 470\text{ cm}^{-1}$ which are assigned to M–N vibration modes.

Table 2 FTIR spectral data (cm^{-1}) of NBA and its metal complexes

Compounds	$\nu(\text{OH})$	$\nu(\text{N}=\text{N})$	$\nu(\text{C}=\text{O})$	$\nu(\text{M}-\text{N})$
NBA	3430	2027	1649	-
$[\text{Co}(\text{NBA})_2(\text{H}_2\text{O})_2]$	3467	2048	1645	470
$[\text{Ni}(\text{NBA})_2(\text{H}_2\text{O})_2]$	3452	2041	1641	441
$[\text{Cu}(\text{NBA})_2(\text{H}_2\text{O})_2]$	3445	2034	1643	427

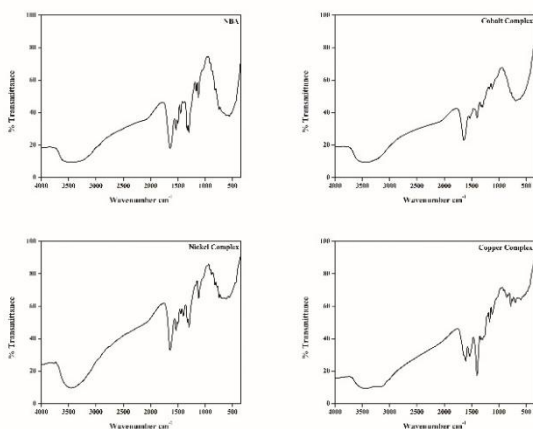


Figure 4 FT-IR spectra of NBA and its metal complexes

3.5. Electronic Spectral and Magnetic moment analysis

The electronic spectra of the synthesized Schiff base ligand and its metal complexes represented in Figure 5. With the numerical values detailed in Table 3. The NBA compound exhibits an absorption band at $26,666\text{ cm}^{-1}$ attributed to charge transfer transition. The $[\text{Co}(\text{NBA})_2(\text{H}_2\text{O})_2]$ complex displays two bands at $16,260\text{ cm}^{-1}$ and $14,836\text{ cm}^{-1}$ corresponding to

${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ transitions respectively. The magnetic moment of 3.80 BM and electronic transition suggest an octahedral geometry. The $[\text{Ni}(\text{NBA})_2(\text{H}_2\text{O})_2]$ complex exhibits transitions at $14,306\text{ cm}^{-1}$, $13,368\text{ cm}^{-1}$ and $10,499\text{ cm}^{-1}$ assigned to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{P})$, ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$ and ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ transition respectively. The observed magnetic moment of 2.75 BM indicated an octahedral geometry. The $[\text{Cu}(\text{NBA})_2(\text{H}_2\text{O})_2]$ complex shows a broad band at $10,030\text{ cm}^{-1}$ corresponds to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ consistent with an octahedral geometry and a magnetic moment of 1.78 BM.

Table 3 Electronic absorption spectral bands

Compounds	λ (nm)	Transitions (cm^{-1})	Magnetic Moment (BM)
NBA	374	26,666	-
$[\text{Co}(\text{NBA})_2(\text{H}_2\text{O})_2]$	615	16,260	3.80
	674	14,836	
$[\text{Ni}(\text{NBA})_2(\text{H}_2\text{O})_2]$	699	14,306	2.75
	748	13,368	
	957	10,449	
$[\text{Cu}(\text{NBA})_2(\text{H}_2\text{O})_2]$	997	10,030	1.78

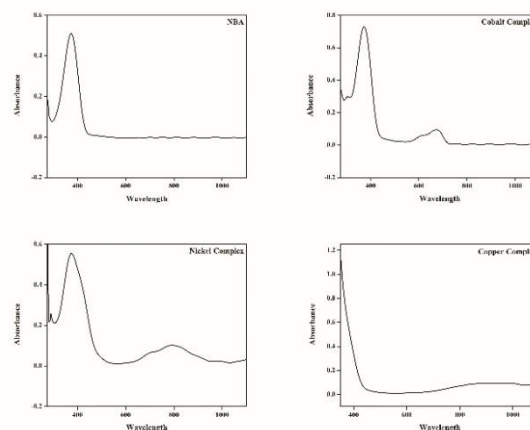


Figure 5 Electronic absorption spectra of NBA and its metal complexes

3.6. X-ray diffraction studies

X-ray diffraction patterns of the metal complexes were recorded over a 2θ range of $0-80^\circ$ as shown in Figure 6. The calculated lattice parameter $a=b=c$ of Co(II) 16.44, Ni(II) 15.23 and Cu(II) 16.77. The sharp peaks observed indicates the crystalline nature of the metal complexes. [25].

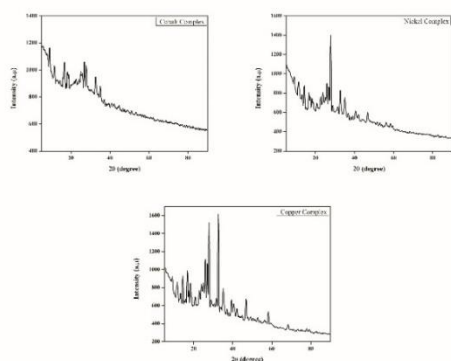


Figure 6 Power XRD of NBA and its metal complexes

4. Electrochemical Studies

4.1 Electrochemical detection of different electrodes

Electrochemical properties of the synthesized compounds have been studied by determining their electrochemical sensing ability. For which a modified electrode is prepared by dissolving synthesized compounds with isopropanol and coated a layer on the surface of glassy carbon electrode (GCE). The redox potential obtained by modified electrode was compared with redox potential of GCE. The solution of ascorbic acid (AA) in pH 7 of phosphate buffer solution was prepared in which both GCE and modified electrode placed and electrochemical detection was determined. Among the synthesized metal complexes $[\text{Co}(\text{NBA})_2(\text{H}_2\text{O})_2]/\text{GCE}$ found more suitable, therefore modified electrode $[\text{Co}(\text{NBA})_2(\text{H}_2\text{O})_2]/\text{GCE}$ has been used for further studies. The results in a significantly increased peak current as illustrated in Figure 7.

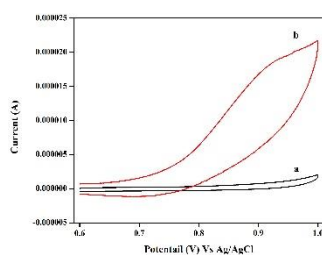


Figure 7 Cyclic Voltammograms of (a) bare electrode and (b) $[\text{Co}(\text{NBA})_2(\text{H}_2\text{O})_2]/\text{GCE}$ with AA $10 \mu\text{M/L}$ at a scan rate = 50 mV/s

4.2. Electrochemical detection of Ascorbic Acid at different concentration

Cyclic Voltammetry (CV) was used to determine Ascorbic acid (AA) concentration in pH 7 PBS using a

$[\text{Co}(\text{NBA})_2(\text{H}_2\text{O})_2]/\text{GCE}$. Figure 8. Show the CV of the modified GCE with and without AA recorded at a 50 mV/s scan rate. The bare GCE has no characteristic peaks between 0.6 and 1.0 V in PBS. However, the $[\text{Co}(\text{NBA})_2(\text{H}_2\text{O})_2]/\text{GCE}$ exhibited a well-defined peak upon AA addition. The AA oxidation peak current increased significantly at $[\text{Co}(\text{NBA})_2(\text{H}_2\text{O})_2]/\text{GCE}$ demonstrating superior electrocatalytic activity for AA oxidation compared to the unmodified GCE. Analytical parameters for AA detection using the modified GCE include a $4.599 \mu\text{M/L}$ detection limit. The linear regression equation is $y = 6.466 \times 10^{-8} (\text{AA}) + 1.0765 \times 10^{-5}$ ($R^2 = 0.9982$). Each calibration graph data point represents the mean of independent measurements [26].

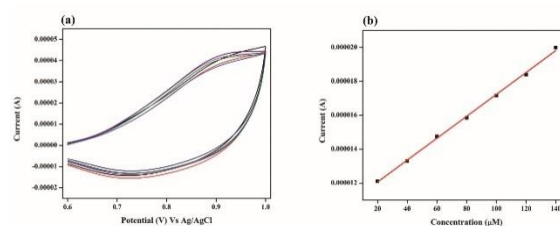


Figure 8 Cyclic Voltammetry of $[\text{Co}(\text{NBA})_2(\text{H}_2\text{O})_2]/\text{GCE}$ was performed at (a) varying concentrations from 10 to $60 \mu\text{M/L}$ and (b) a linear correlation between peak current and concentration was established in PBS (pH 7) at a scan rate of 50 mV/s

4.3. Different Scan rate of Ascorbic acid

Cyclic Voltammetry investigated the impact of scan rate on the peak currents of AA using $[\text{Co}(\text{NBA})_2(\text{H}_2\text{O})_2]/\text{GCE}$. Measurements were performed at a scan rate from 0.01 to 0.09 V/s in pH 7 PBS as illustrated in Figure 9. The peak current demonstrates a linear correlation with $R^2 = 0.9958$ confirming the surface diffusion control of the electrochemical process [27].

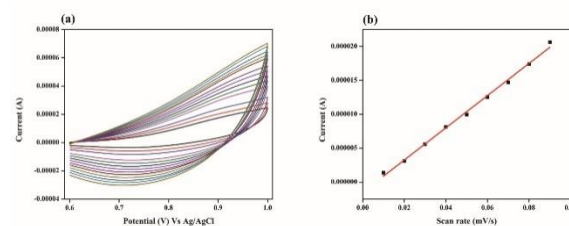


Fig. 9. Ascorbic acid concentrations were varied; Scan rates ranged from 0.01 to 0.09 mV/s (a) A calibration graph depicting the square root of the scan rate vs peak current is shown in the inset and (b) presents a linear



graph of peak current vs scan rate for the modified electrode.

Table 4 Comparison of present work with literature for the detection of ascorbic acid

Electrodes	Detection method	Linear range (μM)	LOD ($\mu\text{M/L}$)	Reference
Gr/CuPc/PANI	CV	0.5 - 0.12	0.06	28
GCE/MWCNT/PdPc	CV	0.3 - 2.4	1.0	29
Azo-bridged-CuPc polymer/GCE	CV	5 - 120	1.66	30
Co(NBA) ₂ (H ₂ O) ₂ /GCE	CV	10 - 60	4.599	This Work

5. Photocatalytic Studies

Photocatalytic activity of synthesized Co(II), Ni(II) and Cu(II) metal complexes was assessed via irradiation under natural sunlight. Graphically Figure 10. depicts methyl red dye absorption maxima observed at 363.43, 361.43 and 360.94 nm for synthesized Co(II), Ni(II) and Cu(II) complexes respectively. Increased irradiation time correlated with decreased methyl red absorbance in the presence of the synthesized metal complexes. Co(II), Ni(II) and Cu(II) complexes respectively exhibited 71.58, 72.13 and 59.19% of degradation efficiency against methyl red respectively. Therefore, Co(II) and Ni(II) complexes demonstrated superior photodegradation performance when compared to Cu(II) complex [31].

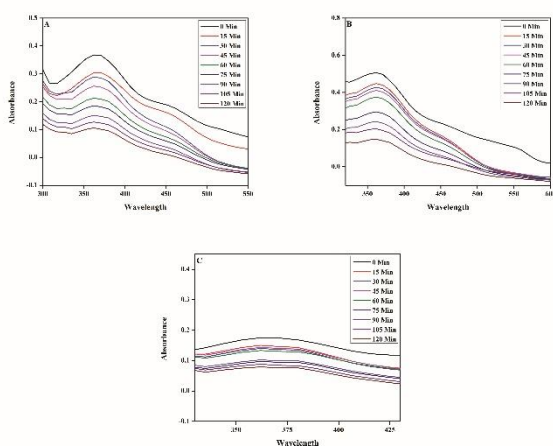


Figure 10 Photodegradation of methyl red with Co(II), Ni(II) and Cu(II) complexes

6. Antidiabetic activity

The antidiabetic activity of the synthesized ligand and its metal complexes was determined using the IC₅₀ method as described in the procedure section. Alpha-amylase and alpha-glucosidase enzyme activity was screened and the results are tabulated in Table 5 and comparatively illustrated in Figure 11. The [Co(NBA)₂(H₂O)₂] and [Ni(NBA)₂(H₂O)₂] complexes exhibited promising activity compared to the uncoordinated ligand and the standard [32].

Table 5 α -Amylase inhibition property of Samples in IC₅₀ ($\mu\text{g/mL}$)

Sample Name	α -Amylase inhibition (IC ₅₀ $\mu\text{g/mL}$)	α -Glucosidase inhibition (IC ₅₀ $\mu\text{g/mL}$)
NBA	105.19	59.59
[Co(NBA) ₂ (H ₂ O) ₂]	147.75	91.92
[Ni(NBA) ₂ (H ₂ O) ₂]	118.24	90.70
[Cu(NBA) ₂ (H ₂ O) ₂]	105.19	68.17
Std (Acarbose)	32.35	26.70

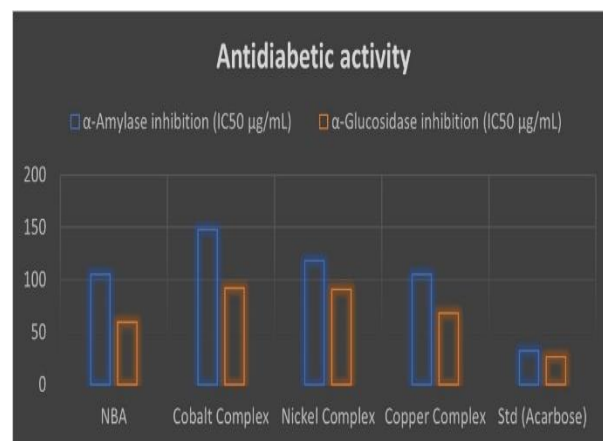


Figure 11 Antifungal activity of NBA and its metal complexes

7. Conclusion

The study emphasis on synthesis and characterization of the biologically active Co(II), Ni(II) and Cu(II) complexes of the novel 4-[(2E)-3-(6-nitro-1,3-benzothiazol-2-yl)triaz-2-en-1-yl]benzoic acid (NBA). The ligand acts as bidentate and the spectral study show an octahedral geometry for metal complexes. [Co(NBA)₂(H₂O)₂]/GCE prepared by incorporating the synthesized metal complexes exhibited excellent electrocatalytic activity at varying concentrations and has a low limit of detection (LOD) of 4.599 $\mu\text{M/L}$ with $R^2 = 0.9982$. The photocatalytic degradation efficiency of the synthesized metal complexes evaluated where methyl



red (MR) found to undergo most effective degradation when compared to other dyes. Results also indicate that the Co(II) and Ni(II) complexes exhibited a 71.58 and 72.13% degradation efficiency respectively. In addition, the ligand showed significant antidiabetic activity. However, its metal complexes exhibited pronounced antidiabetic activity.

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