

Synthesis, Spectroscopy Study of Copper (II) Sulphate Pentahydrate, Tetra-Amminocopper (II) Sulphate and Bis-Ethylenediamine Copper (II) Sulphate in the Catalytic Reduction of Nitrophenol Derivatives

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Abstract— The copper complex of the type; copper (II) sulphate pentahydrate, tetra-amminocopper (II) sulphate, and bis-ethylenediamine copper (II) sulphate complexes was synthesized and structurally characterized using Fourier transform infrared (FTIR). The test of the catalytic performance of the complexes were carried out in the reduction of 2-methyl-4-nitrophenol to 2-methyl-4-aminophenol using sodium borohydrate as reducing agent which reduce nitrophenol to nitrophenolate ion using 0.5 mg, 1 mg and 1.5 mg dose of catalyst. The result obtained shows that bis-ethylenediamine copper (II) sulphate has the highest performance with 65.3% followed by tetra-amminocopper (II) sulphate with 50.4% then copper (II) sulphate pentahydrate with 34.6%. The catalyst's recyclability and reproducibility activities revealed that the complexes are fairly effective as catalyst.

Keywords— Catalytic reduction, Derivatives of 4-Nitrophenol, Copper complexes.

I. INTRODUCTION

Copper complex have got a lot of interest due to their structural, magnetic, electron transfer and catalytic attributes (D.J Hodgson, 1975). Copper (II) compounds are typically stable and can be synthesised in water and the simple copper oxide can dissolves in mineral acids to provide the sequence of salts as the required starting material.

As a potential antitumor agent, ethylenediamine chelator can exhibit excellent antitumor activity and form water-soluble neutral complexes with transition metal ions. Comparing the chelating effects, ethylenediamine is more stable than ammonia ligands (D.R Mcmillin and K.M Mcnett, 1998). Polydentate ligand metal complexes are substantially more stable than the respective complexes of chemically identical monodentate ligands. (Chabera *et al.*, 2020). This increase in stability is called the chelate effect. A chelate compound stability depends on the size of the chelate rings. Complexes containing five-membered chelate rings with almost no strain are significantly more stable for ligands with a flexible organic substrate like ethylenediamine than complexes with six-membered chelate rings, which are much more reliable in comparison than complexes with four-membered or seven-membered rings (Chabera *et al.*, 2020).

The coordinate-covalent bond between a ligand and a metal is dynamic, which means that around the metal centre, ligands are constantly exchanging and re-coordinating. Both the metal and the ligand's identities determine which ligands preferentially bind over another one. (Shevick *et al.*, 2020). In addition, colour and magnetic properties are also due to the types of complexes that are formed (Li JX *et al.*, 2020). The coordination compounds that form are analysed using a variety of instruments and tools. The used of copper complex as catalyst has drawn less attention which generate a novel research interest in inorganic chemistry. Here, a series of copper complexes namely; copper (II) sulphate pentahydrate, tetra-ammino copper (II) sulphate and bis-ethylenediamine copper (II) sulphate were synthesized apply for catalysis study.

In this work, we present the synthesis, characterisation and catalytic activities of copper complexes as a model reaction to assessed the reduction of 2-methyl-4-nitrophenol to 2-methyl-4-aminophenol in presence of NaBH₄ which act as a reducing agent.

II. EXPERIMENTAL

Materials and Methods

All materials used in this study were bought and used without additional treatment as they were obtained. Molecular sieves (4Å) were used to distilled and dry the solvent before usage. The glassware used was cleaned and dried overnight in the oven. All process were carried out in an inert atmosphere of nitrogen. Using the FT-IR Frontier-Elmer 1800 Model spectrophotometer in the 4000-400cm⁻¹ range, FT-IR spectroscopy was used to identify products synthesised in particular by functional groups. In the scanning range of 200-800 nm, the Shimadzu model UV-Vis probe 1800 spectrophotometer was used to run a catalytic analysis.

Synthesis of Complexes

Copper (II) sulphate pentahydrate; $CuSO_4 \cdot 5H_2O$

In a 250 ML beaker, copper oxide (8 g. 0.1 mol) was placed and 120 ML of diluted sulphuric acid was added. In a bunsen burner, the mixture was warm to dissolve the black solid. The mixture was filtered and crystallized by taking 40 ML of the mixture via evaporation. The crystal was isolated and dried by suction filtration.

Tetra-amminocopper (II) sulphate ; $[Cu(NH_3)_4SO_4 \cdot H_2O]$

The residual copper sulphate solution (30 ML, 0.025 mol) was transferred in to a conical flask (250 ML) and diluted with small amounts of ammonia solution. To precipitate the dark-blue solid from the solution, ethanol was added. The compound was isolated by suction filtration, washed with ethanol and dried.

Bis-ethylenediamine copper (II) sulphate; $[Cu(en)_2SO_4 \cdot H_2O]$

The leftover copper sulphate solution (30 ML, 0.025 mol) was transferred in to a 250 ML conical flask and the dark blue / purple compound was obtained by adding ethylene diamine (10 percent). The compound was isolated by suction filtration, washed with ethanol and dried

Catalytic performance of the complexes (catalyst) in the reduction of nitrophenol derivative

Newly prepared solution of sodium borohydride ($NaBH_4$, 1mL, 0.2 mol) was added in to the solution of 2-methyl-4-nitrophenol (2-CH₃-4-NP, 3 mL, 0.01 mol) in a cell or cuvette. Distilled water was used to form the solution. After adding sodium borohydride ($NaBH_4$) solution, the colour of the mixture automatically changed to a deep-yellow colour. 1 mg of the catalyst was introduced to the reaction mixture and run the reaction in the scanning range of 200 nm to 600 nm. The end of the catalytic reduction was indicated by the appearance of colourless solution of the reacting mixture in the cuvette. UV-Vis spectrophotometer examined the performance of the reduction.

For each cycle, the nitrophenolate ion peak absorbance at $\lambda = 400$ nm was observed over a period of two (2) minutes at ambient temperature. A standard calibration curve was plotted based on six concentrations with correlation coefficient of $R^2=0.9947$ (Fig.1) of 2-methyl-4-nitrophenol solutions with sodium borohydride varying from 0.01-0.1 mM. The conversion percentage from 2-CH₃-4-NP to 2-CH₃-4-AP was obtained using the relation below;

$$\text{Percentage conversion} = \frac{\text{Initial Abs} - \text{Final Abs}}{\text{Initial Abs}} \times 100\%$$

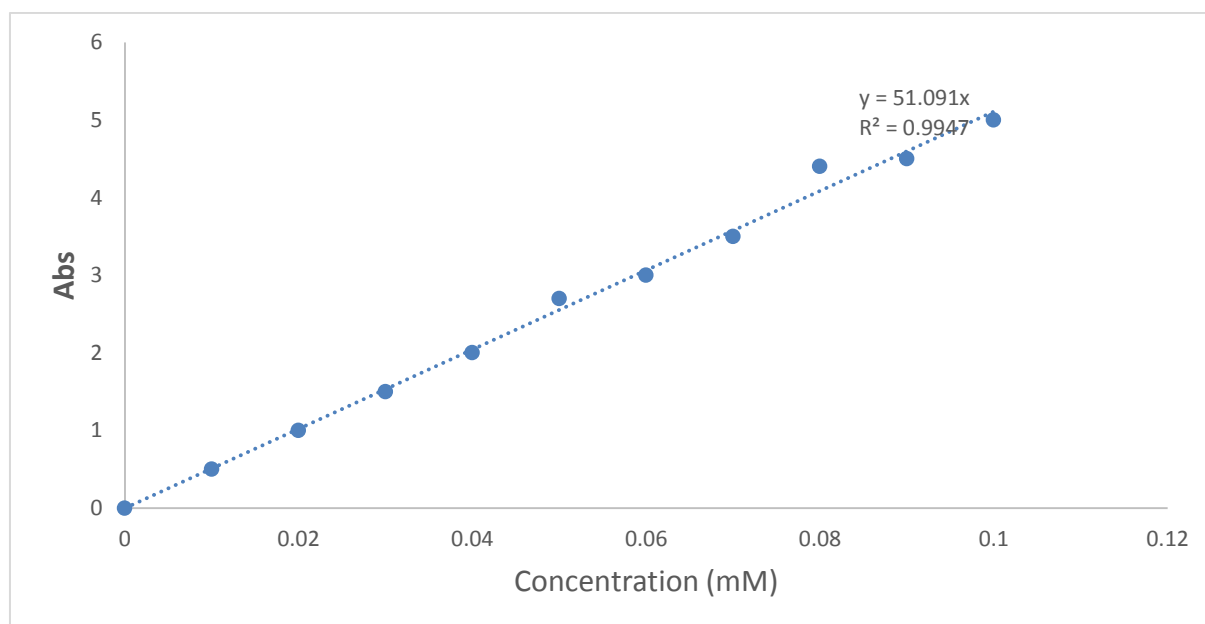


Figure. 1 Calibration curve of 2-methyl-4-nitrophenol at different concentrations

Recovery of the catalyst

By centrifugating the mixture for 40 min at 4000 rpm, the catalyst was restored. The catalyst was settled at the bottom of the centrifugation tube, after this time and obtained by decanting the solution. The recovered catalyst was rinsed with deionized water and dried for future analyses using a silica gel desiccator.

Recyclability test of the catalyst

Recycle tests have been carried out in order to test the reproducibility of the catalyst by performing the reaction under the same conditions. The recyclability test was carried by centrifugation of the mixture to remove the catalyst. The catalyst was extracted, rinsed using distilled water and dried in a desiccator. Equal dose of 2-CH₃-4-NP and a newly made NaBH₄ were applied in the subsequent experiment. The 2-CH₃-4-NP percentage conversion was assessed and relate with the previous test.

III. RESULTS AND DISCUSSION

The copper complex of the type; copper (II) sulphate pentahydrate, tetra-amminocopper (II) sulphate, and bis-ethylenediamine copper (II) sulphate were synthesized and characterized using Fourier transform infrared (FTIR) spectroscopy. Infrared spectra of the product obtained were performed on a Perkin Elmer 1600 FTIR spectrometer from 4000 cm⁻¹ to 400 cm⁻¹ range adopting potassium bromide (KBr) to identify the functional group

FT-IR analysis of Characterization of the complexes

TABLE 1. Selected FT-IR data for the C1, C2 and C3 complexes

Compound/Freq	V(N-H)	V(O-H)	V(S=O)
CuSO ₄ .5H ₂ O (C1)	-----	2062	1320
[Cu(NH ₃) ₄]SO ₄ .H ₂ O (C2)	3144	2251	1313
[Cu(en) ₂]SO ₄ .H ₂ O (C3)	3418	2264	1300

The complexes observed stretching frequency at 3144cm⁻¹ and 3418cm⁻¹ which was assigned to V(N-H) group of the [Cu(NH₃)₄]SO₄.H₂O and [Cu(en)₂]SO₄.H₂O respectively indicating the coordination of N-H groups link to copper (Nakamoto, K., 1986). Similarly, the stretching frequency observed at the peak of 2062 cm⁻¹, 2251cm⁻¹ and 2264cm⁻¹ for CuSO₄.5H₂O, [Cu(NH₃)₄]SO₄.H₂O and [Cu(en)₂]SO₄.H₂O respectively correspond to OH group presence in the complexes. A lower energy peak observed at 1320cm⁻¹, 1313 cm⁻¹ and 1300 cm⁻¹ for CuSO₄.5H₂O, [Cu(NH₃)₄]SO₄.H₂O and [Cu(en)₂]SO₄.H₂O respectively suggesting a sulfone groups V(S=O) link to copper complexes (Reddy *et. al.*, 2008). Table 1 above show the selected FT-IR data for the three complexes.

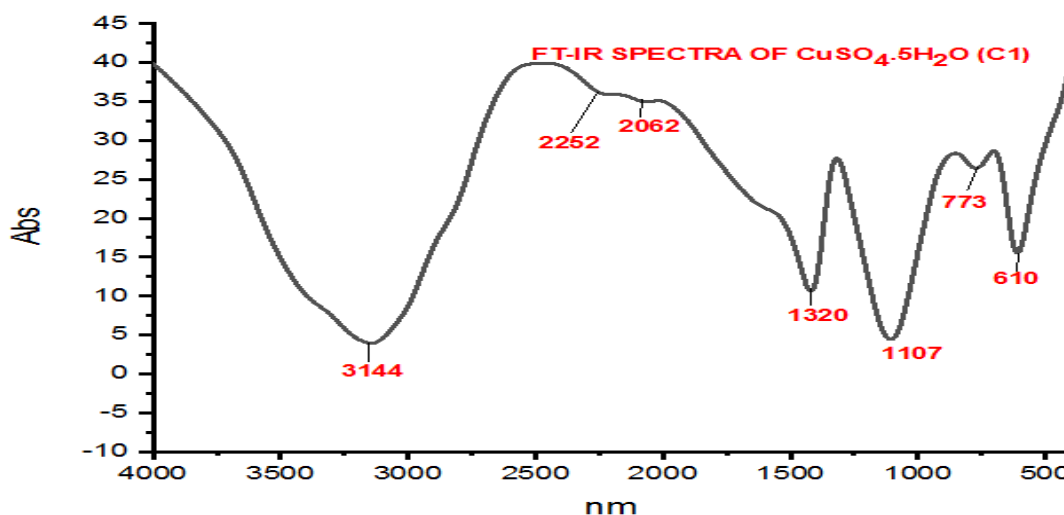


Figure 2. IR spectra of copper (II) sulphate pentahydrate

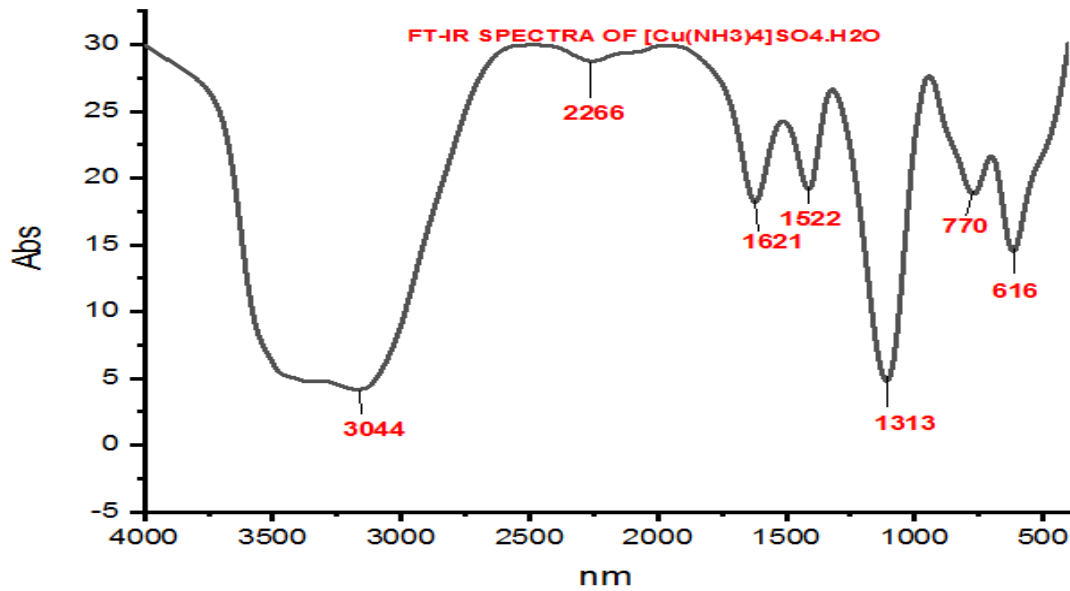


Figure 3. IR spectra of tetra-amminocopper (II) sulphate

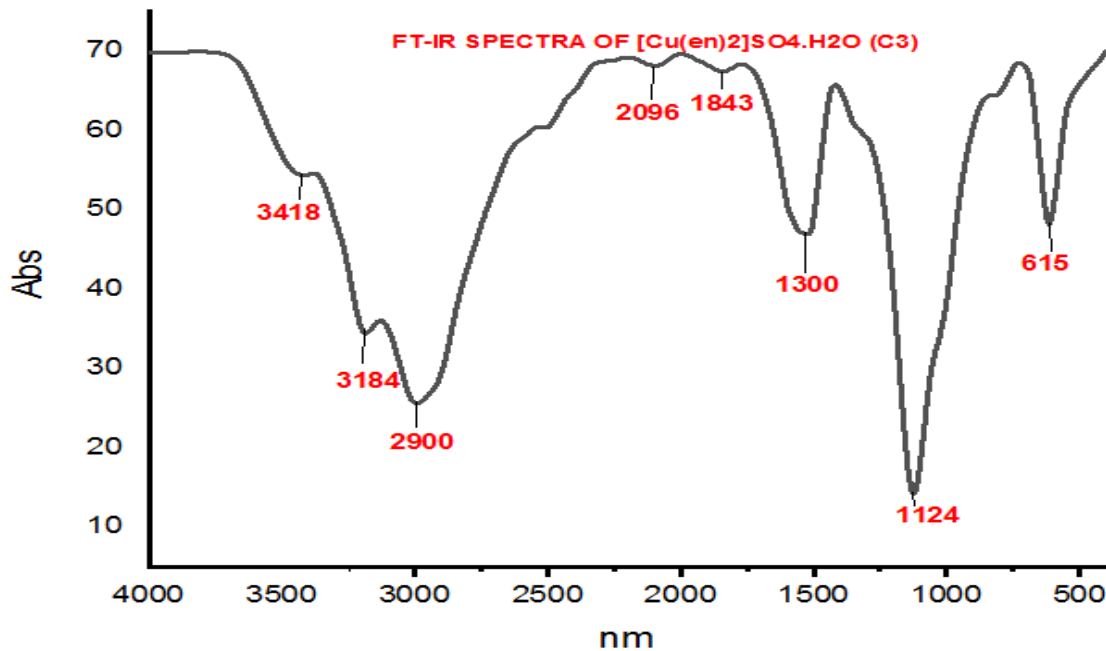


Figure 4. IR spectra of bis-ethylenediamine copper (II) sulphate

Catalytic activity of copper (II) sulphate pentahydrate, tetra-amminocopper (II) sulphate, and bis-ethylenediamine copper (II) sulphate complexes (catalysts) in the reduction of 2-methyl-4-nitrophenol

In order to test the catalytic activity of copper complex catalysts, a 2-methyl-4-nitrophenol reduction to 2-methyl-4-aminophenol was chosen as a model reaction. Using the kinetic parameters obtained from an aqueous solution using UV-Visible spectrophotometer, this reaction offers a consistent assessment of the catalysts. The catalytic performance of the copper complexes in the reduction of 2-methyl-4-NP at ambient temperature was examined in the existence of NaBH₄ during this study. The solution was yellowish in colour attributed to the generation of 4-nitrophenolate anion when 2-methyl-4-NP was mixed with NaBH₄, and has a maximum absorbance of 400 nm. Such peaks are very unique in the spectrum of UV-V is spectroscopy, as shown in scheme 7, 8 and 9 below. Once the catalyst was applied, the peak at 400 nm started to decrease while at the same time another peak around 300 nm emerged. The appearance of peak around 260 nm was due to the absorbance resulting in the formation of 2-methyl-4-AP. Time taken for the reaction was reported at 400 nm for complete disappearance of the peak. (Abdullahi *et al.*, 2020).

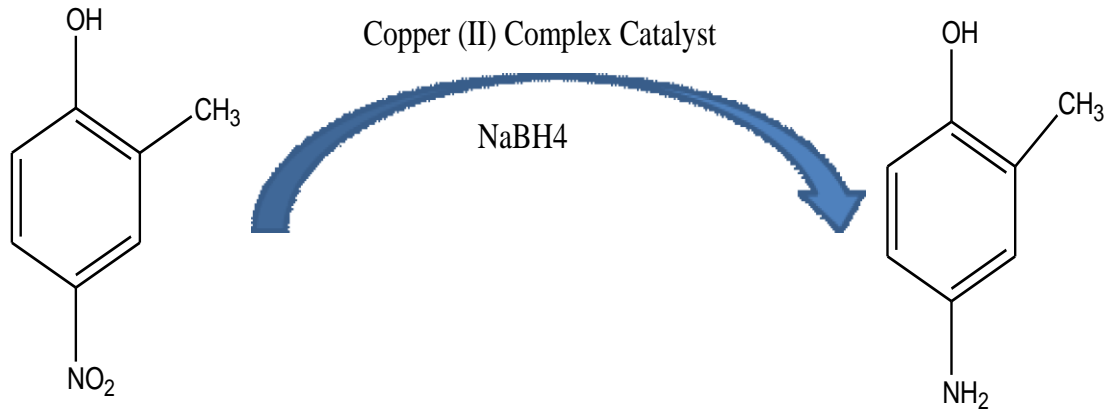


Figure 5. Reduction of 2-Methyl-4-Nitrophenol to 2-methyl-4-Aminophenol

TABLE 2. Comparing the performance of catalyst at different time and amount of catalyst used

Catalyst	Time (s)	Amount of catalyst added	% Conversion
CuSO ₄ .5H ₂ O	2	0.5mg	28.4%
	2	1mg	26.6%
	2	1.5mg	33.2%
Cu(NH ₃) ₄ SO ₄ .H ₂ O	2	0.5mg	39.2%
	2	1mg	43.4%
	2	1.5mg	45.6%
Cu(en) ₂ SO ₄ .H ₂ O	2	0.5mg	57.5%
	2	1mg	55.3%
	2	1.5mg	65.7%

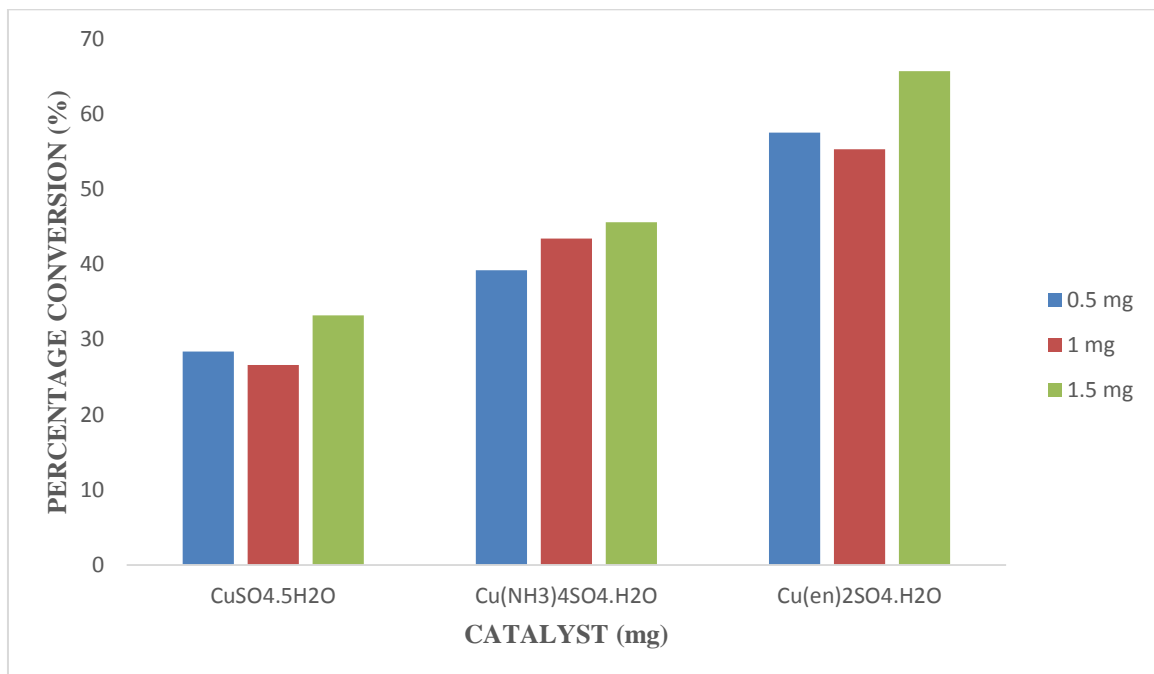


Figure 6. Graph showing catalytic performance of C1, C2 and C3 at different dose

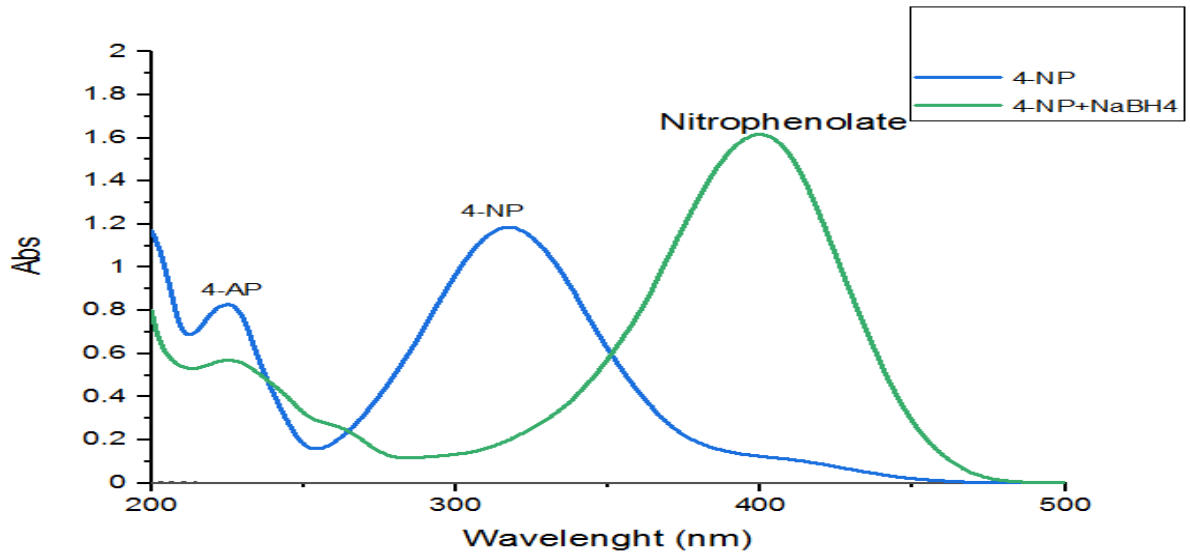


Figure 7. Model for the catalytic reduction of 2-methyl-4-nitrophenol using UV-Vis spectroscopy.

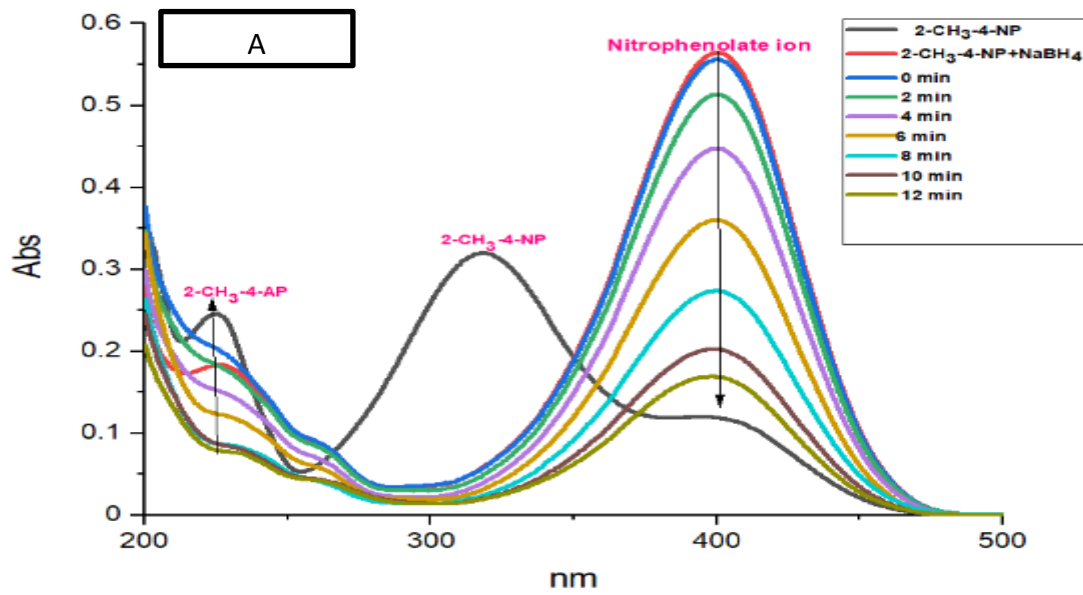


Figure 8. UV-Vis spectrum of the reduction of 2-methyl-4-NP catalysed by $Cu(en)_2SO_4 \cdot 5H_2O$

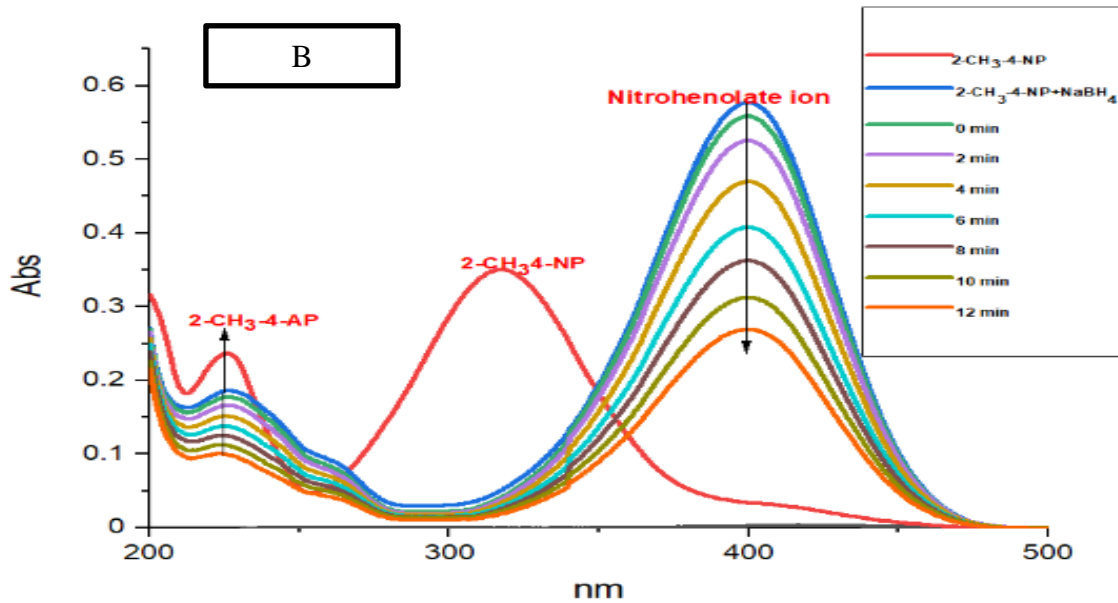


Figure 9. UV-Vis spectrum of the reduction of 2-methyl-4-NP catalysed by $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot 5\text{H}_2\text{O}$

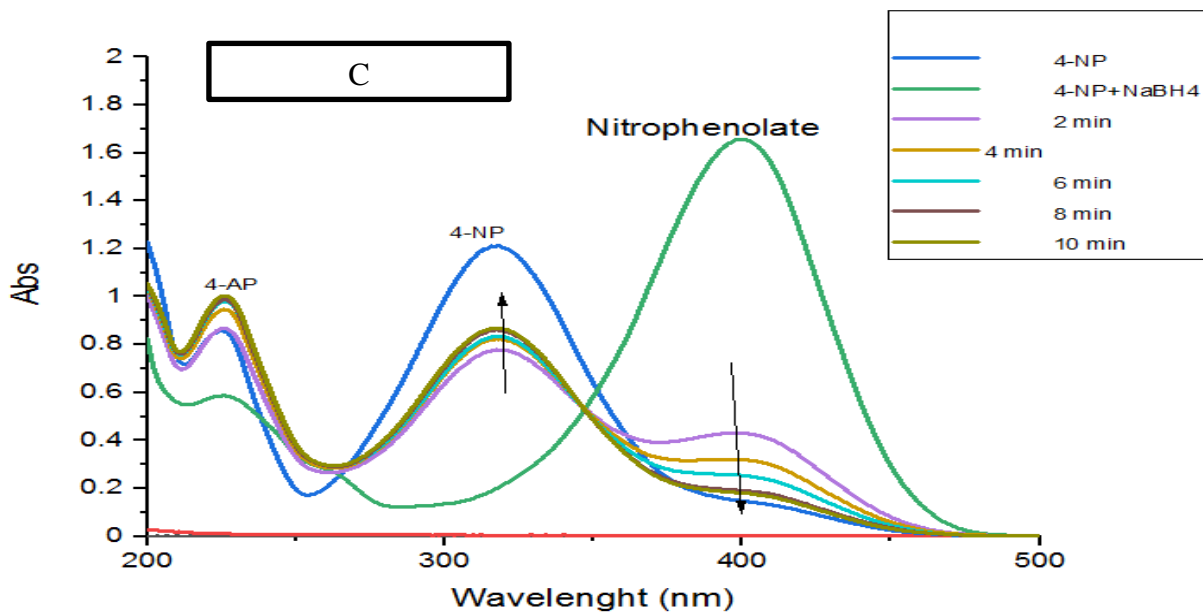


Figure 10. UV-Vis spectrum of the reduction of 2-methyl-4-NP catalysed by $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

IV. CONCLUSION

A complexes of Copper (II) sulphate pentahydrate, Tetra-amminocopper (II) sulphate and Bis-ethylenediamine copper (II) sulphate was successfully synthesized and characterized by Fourier transform infrared (FT-IR) spectroscopy. The synthesized complexes were effectively applied for catalytic reduction of 2-methyl-4-nitrophenol to 2-methyl-4-aminophenol using UV-Vis spectroscopy to monitor the catalytic performance of the catalyst. The results showed that Bis-ethylenediamine copper (II) sulphate has a highest performance with 65% (1.5mg) conversion followed by Tetra-amminocopper (II) sulphate with 45% (1.5mg) conversion. Copper (II) sulphate pentahydrate with 33% (1.5mg) conversion has a lower catalytic impact (weak catalyst). The result further suggest that Bis-ethylenediamine copper (II) sulphate has the potential of recovery, recyclability, and reproducibility followed by Tetra-amminocopper (II) sulphate with 1.5mg dose of catalyst.

Conflict of interest statement

Authors claim that there is no conflict of interest in them.

ACKNOWLEDGEMENT

The authors wishes to extend their appreciation to the Universiti Teknologi Malaysia for providing the research facilities. Further appreciation goes to Federal Government of Nigeria for providing TETFUND grant via Adamawa State University Mubi (ADSU Mubi), Adamawa State, to pursue MSc programmed.

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