Copper (II) Complexes: Synthesis, Characterization and Catalytic Performance in the Reduction of 4-nitrophenol

Nur Alwani Abdullah and Mohamad Shazwan Shah Jamil*

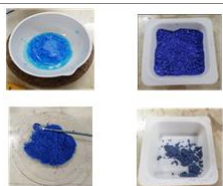*Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia*
Corresponding Author: shazwan.shah@utm.my

GRAPHICAL ABSTRACT

Physical appearance of copper (II) complexes

ABSTRACT

The unique characteristic of the copper (II) complexes renders many of their complexes suited for various catalysis reactions. In this study, four copper (II) complexes namely copper (II) sulphate pentahydrate (Cu-L1), tetraamminecopper (II) sulphate (Cu-L2), bis-ethylenediaminecopper (II) sulphate (Cu-L3) and copper (II) acetylacetonate (Cu-L4) were successfully synthesized and characterized by using Fourier Transform Infrared Spectroscopy and UV-Vis Spectroscopy. All complexes were synthesized by direct chemical reaction of starting material with corresponding ligand solution (sulphuric acid, ammonia solution, ethylenediamine solution and acetylacetone). These ligand solutions have been chosen in order to study the chelate effect between monodentate and bidentate ligands. Ligand solution was added in excess to obtained a more complete reaction and prevent localize supersaturation from occur. Cu-L1 acts as one of the catalyst in the reduction reaction of 4-nitrophenol (4-NP) and also being used as precursor to synthesis Cu-L2 and Cu-L3 and copper oxide nanoparticles (CuO-NPs). CuO-NPs were synthesized in a simple, efficient, and cheap method via solid state thermal decomposition. The synthesized complexes were used as catalyst in the reduction of 4-nitrophenol to 4-aminophenol in aqueous phase in the presence of sodium borohydride (NaBH$_4$). In this work, all the complexes show great performance on catalytic activity with (90.-97.3) % of percentage conversion. The reaction time for the reduction of 4-nitrophenol was between 18-34 min for each different complex.

Keywords: Copper(II) complexes, copper oxide nanoparticles, reduction, 4-nitrophenol

1.   INTRODUCTION

4-nitrophenol (4-NP) and other nitro-aromatic compounds are common by-product in the production of pesticides, pharmaceutical products, petrochemical compounds, paper, herbicides and synthetic dye [1]. The concentrations of nitrophenols presence in wastewater are 6700 mg/L. Due to its solubility and stability, 4-NP pollutes agricultural and industrial waters [2]. US Environmental Protection Agency has considered 4-NP is a dangerous waste and major pollutant that can affect mainly the liver, kidney, central nervous system, and blood [3]. Therefore, the removal of this compound from the aqueous media is essential. Many of these methods have been employed, such as adsorption [4], electro-chemical therapy [5], electrolytic reduction [6], homogenous catalytic transfer of hydrogen [7] and heterogeneous catalytic transfer of hydrogen [8]. The simplest way to decrease 4-NP is to use selective hydrogen in the present of sodium borohydride (NaBH$_4$) [9]. 4-AP is an important compound used in corrosion inhibitors, analgesic and antipyretic drugs, photographic developers, anti-corrosion grains and hair dyeing agents [3].

Owing to their wide potential applications, copper (II) complexes have been lately the subject of substantial scientific interest due to their low cost and better stability compared to other metal. Copper catalysts could replace precious metal complexes in many industrial processes involved in pharmaceutical, photodegradation of dye and polymer productions. This is of major importance in view of societal concerns relating to environmental and sustainable chemistry [10]. Therefore in this study, copper (II) complexes with were synthesized and characterized to study the catalytic activity in reduction of 4-nitrophenol with the presence of NaBH$_4$ as reducing agent. This application was chosen because it was easy to be monitored by using only UV-Vis Spectrophotometer and do not required longer period. CuO nanoparticles which derived from its complex also were prepared thorough solid state-thermal decomposition to compare the efficiency as catalyst with synthesized complexes in this this model reaction.

2.   EXPERIMENTAL

All the chemicals and reagents used in this study were commercially purchased and used, as received without further purification. All glassware were washed and dried overnight in an oven. The products obtained were collected using vacuum filtration and dried in air overnight before characterization. The synthesized products were characterized by Fourier Transform Infrared (FTIR) and UV-Vis Spectroscopies. The infrared spectra were obtained using the FTIR

Frontier-Elmer 1800 Model spectrophotometer in the range of 4000-400 cm^{-1}. The UV-Vis spectra were recorded in distilled water/dichloromethane solutions using a Shimadzu model UV-Vis probe 1800 spectrophotometer in the range of 400-1000 nm. The efficiency of synthesized products were evaluated for the reduction of 4-nitrophenol in the presence of sodium borohydride ($NaBH_4$).

2.1. Preparation of copper (II) sulphate pentahydrate (Cu-L1)

8 g of copper oxide was weighed and mixed with 100 ml dilute sulphuric acid. The mixture was gently boiled to dissolve the black solid. During heating, the solution turns to blue solution and then it was filtered while it is still hot by gravitational filtration. Next, 50 ml of the filtered solution was separated in an empty beaker to be used for the preparation of Cu-L2 and Cu-L3 in the next experiment procedure and the remaining filtered solution was placed into evaporating basin for further crystallization process. The remaining solution was boiled very gently to evaporate it until it being concentrated enough to crystallized upon cooling. The crystals then were isolated by suction filtration. The crystal washed thoroughly with small amount of cold water and 5 ml of absolute ethanol. Next, the crystal was collected and spread on the watch glass to allow it to dry in air. Then the dry crystal solid was kept in sample vial and weighted the product. The weight was recorded.

2.2. Preparation of tetraaminecopper (II) sulphate monohydrate (Cu-L2)

25 ml (0.021 mol.) of the residual Cu-L1 from 2.1 was poured into a conical flask of 250 ml and dilute ammonia was added in small portions then the flask was swirled after each addition. Initially a light blue solid (Cu $(OH)_2$) will form, but it re-dissolve as more ammonia is added and the solution becomes dark blue. When the entire solid re-dissolved, 100 ml of absolute ethanol was added into the conical flask and the solution was stirred using glass rod. The solution precipitated a dark blue solid and this is the desire product. The dark blue solid was isolated by suction filtration. The solid was washed thoroughly with a little ethanol. The product was collected and stored in sample vial.

2.3. Preparation of bis-ethylenediaminecopper (II) sulphate monohydrate (Cu-L3)

The following procedure was same as in 2.2, but use ethylenediamine instead of ammonia for the ligand solution. To obtain a dark blue / purple mixture, an excess dilute ethylenediamine solution (10%) given was used. The dark blue compound was isolated exactly as the ammonia complex by suction filtration. The solution was poured into the filter to remove all the liquid from dark blue solid then being washed thoroughly with little ethanol. The solid was transferred into the watch glass and spread it over to let it dry in the air. The product was weighed and stored in sample vial.

2.4 Preparation of copper (II) acetylacetonate (Cu-L4)

4 g of hydrated copper (II) chloride was weighted out and dissolve in 25 mL of distilled water. 5 mL of acetylacetone in 10mL of methanol was added drop wise to the solution over a period of 20 minutes. Constant stirring was maintained throughout the addition of acetylacetone-methanol. A solution of 6.8 g sodium acetate in 15 mL of distilled water was prepared. This solution was added to the resulting copper-acetylacetonate solution over a period of 5 minutes. The mixture was heated on a hot plate to ~80°C for 15 minutes. The contents of the flask should be briskly and continuously stirred. The mixture leaved to cool to room temperature before being put ice bath. The resulting precipitate was filter off by suction filtration then was stored in the vial. Next, 1.0 g of the dried crude product was weighed for further recrystallization. A small filter funnel placed in the neck of the flask to serve as a reflux condenser and boil on a water bath for 5 minutes. The solution was decant away carefully into a clean 100 mL Erlenmeyer flask. 5mL of methanol was added and the solution was reheated. The solution was cooled to room temperature until crystal solid being observed. The crystals were filtered by suction filtration, washed with some cold methanol and suction dry using the water pump.

2.5 Preparation of CuO nanoparticles

0.5 g of Cu-L1 was weighed and put into a crucible. The complex then was calcine in hot air furnace to 500°C for 3 hours. The product was allowed to be cooled and after 3 hours of cooling, the complex was washed with 2 M ammonium hydroxide solution to extract phosphate ion and dried for 2 hours in 100°C oven. CuO-NPs was supposedly to be characterized by XRD powder diffraction and X-ray diffractometer however due to the time constraint, it cannot be done and the product after calcination was assumed as CuO-NPs by referring to research by [11].

2.6 Characterization of copper (II) complexes

The synthesized copper (II) complexes were characterized by UV-Vis and FTIR Spectroscopy. The UV-Vis spectra were recorded using a Shimadzu model UV-Vis probe 1800 spectrophotometer in the range of 400-1000 nm. The infrared spectra were obtained using Frontier-Elmer 1800 Model spectrophotometer in the range of 4000- 400 cm^{-1}.

2.7 Catalytic performance of the catalyst in the reduction of 4-nitrophenol

A freshly 30 mM (0.01135 g) reducing agent,$NaBH_4$ was prepared in 10 ml volumetric flask and 1 mM (0.00695 g) of 4-nitrophenol was prepared in 50 ml volumetric flask. Both solutions were prepared using distilled water. The 4-NP solution then was diluted to concentration ranging (0.02 mM-0.10 mM). A standard calibration curve was plotted based on five concentrations of 4-NP solutions. Next, 3 ml of 4-NP was mixed with 0.3 ml $NaBH_4$ solution in a quartz cuvette with 1.0 cm path length and 4 mL volume. Then 1 mg catalyst was added to the mixture, and the initial yellow color of the solution turned to colorless as the reaction proceeded. The progress of the reduction was evaluated by UV-Vis spectrophotometer in the scanning range between 200 nm to 500 nm. The absorbance for the 4-nitrophenolate ion peak at $\lambda = 400$ nm was recorded in every cycling over 2 min at room temperature. The percentage of conversion from 4-NP to 4-AP was determined by calculation from the absorbance data using the following equation:

$$\text{Percentage Conversion} = (\text{Initial Abs-Final Abs}) / (\text{Initial Abs}) \times 100 \qquad (1)$$

2.8 Isolation of product

After the conversion was completed, the product was isolated by the following procedure. Firstly, the product was diluted with diethyl ether (30 mL) and separated using liquid-liquid extraction. The extraction steps were repeated three times. Then each diethyl ether fractions containing the product (4-AP) were combined together. Anhydrous sodium sulphate (Na_2SO_4) was then added to the fractions solution to absorb all the water content. Then, diethyl ether was evaporated using a rotary evaporator leaving only 4-AP inside the beaker. The product was then compared to 4-aminophenol standard via Fourier Transform Infrared Spectroscopy (FTIR).

3. RESULTS AND DISCUSSION

3.1. Preparation of copper (II) complexes

In this research, Cu-L1, Cu-L2, Cu-L3, Cu-L4 and CuO-NPs were successfully synthesized. All of these complexes are stable in air and moisture. The percentage yield was quite low due to difficulties in optimizing all the reaction condition such as temperature and solution concentration. Instead of that, some of the products were inevitably lose during physical manipulation involved in isolating the product from reaction mixture throughout the gravitational filtration step.

3.1.1 Preparation of copper (II) sulphate pentahydrate (Cu-L1)

Cu-L1 was prepared by direct chemical reaction between copper oxide and sulphuric acid by gently heating. During heating process, the black solution turns to blue indicated that the copper oxide dissolve and then continue for crystallization process by evaporating the blue solution until it being concentrated enough to allow the formation of crystal solid. Blue crystal solid was obtained upon cooling. The structure of the solid pentahydrate reveals a polymeric structure wherein copper is octahedral but bound to four water ligand. The Cu (II) (H$_2$O)$_4$ centers are interconnected by sulphate anions to form chains. The mass of product obtained was 7.637 g with percentage yield 48.4 %. The yield is low due to half of the solution during preparation procedure was being used to prepare Cu-L2 and Cu-L3.

3.1.2 Preparation of tetraaminecopper (II) sulphate (Cu-L2)

For this part, Cu-L1 was used as the starting material to synthesis Cu-L2 by chemically reacted with ammonia solution. Excess ammonia solution was added drop wise into the solution to obtained a more complete reaction and prevent localize supersaturation from occur. The reaction of ammonia with Cu-L1 involves two steps process in which in the first step, copper (II) hydroxide was formed which light blue in color. The copper (II) hydroxide dissolved as excess quantities of ammonia were added forming dark blue complex. Cu-L2 has square pyramidal geometrical structure. Product yield for Cu-L2 was 5.373 g with percentage yield, 65.4 %.

3.1.3 Preparation of bis-ethylenediaminecopper (II) sulphate (Cu-L3)

Cu-L3 was prepared by reaction of Cu-L1 with excess dilute ethylenediamine solution. Ethanol was used during the preparation procedure, but it is an indirect participant in the reaction. The used of ethanol helps to decreases the solubility of ionic compounds and increased the product yield. Dark blue solid salt was collected with mass 5.584 g with percentage yield 69.5 %. Cu-L3 has square pyramidal geometry.

3.1.4 Preparation of copper (II) acetylacetonate (Cu-L4)

As for the preparation of Cu-L4, when hydrated copper (II) chloride was mixed with acetylacetone in methanol solution, a greyish violet precipitate formed which is copper (II) acetylacetonate. The hydrated copper (II) chloride dissociates in aqueous solution to give free Cu^{2+} ions which can react with acetylacetonate to form complex. The geometrical structure for copper acetylacetonate complex is a square planar. Heating of Cu-L4 solution is carried out in water bath because the boiling point of methanol is low and can evaporate easily. This is to ensure that Cu-L4 complex can dissolve well in methanol in order to obtain a pure product. For recrystallization of Cu-L4 complexes, the solutions are placed in ice bath to fasten the process of crystallization of the complex. The weight of product obtained is 5.823 g with percentage yield 91.7%.

3.2 Preparation of CuO nanoparticles

CuO nanoparticle was successfully synthesized through calcination using Cu-L1 as precursor at 10°C min-1 to 500°C in the limited supply oxygen. This process was to bring out a thermal decomposition for water molecules. Characterization by TGA and XRD could not be performed due to time restriction. The temperature for calcination was set up based on [11]. The solid nanoparticles were stored in the desiccator over silica gel to avoid it from being oxidized.

3.3 Characterization of copper (II) complexes

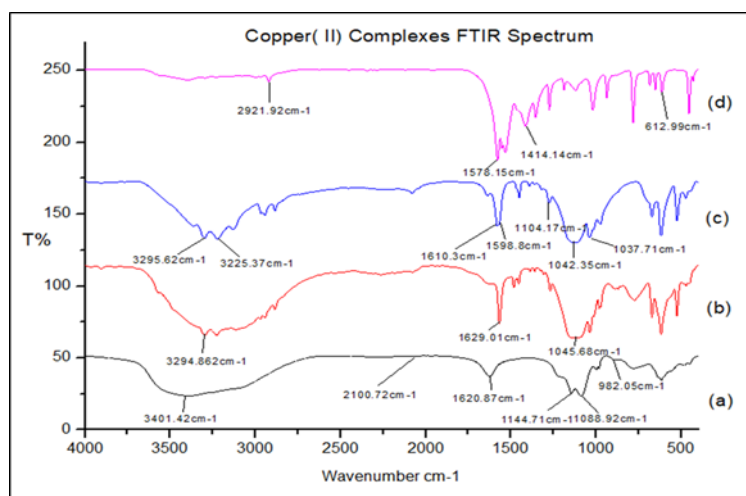### 3.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 1.FTIR spectrums for (a) Cu-L1, (b) Cu-L2, (c) Cu-L3 and (d) Cu-L4

Spectrum (a) was referring to Cu-L^1. The absorption band at 3420.42 cm^{-1} was assigned to (O-H stretch). Weak absorption band at 2100.72 cm^{-1} attribute to a combination of the bending and rocking mode of water. In the addition, O-H bending band at 1620.87cm^{-1} was due to interaction of water molecules with copper ions [12]. The characteristic bands of inorganic sulphate were observed at 1144.7 cm^{-1} and 1088.9cm-1. For (b), the IR spectrum shows a few peaks represent NH$_3$ ligands. The characteristic bands of inorganic sulphate were observed at 1144.7 cm-1 and 1088.9cm-1. For (b), the IR spectrum show a few peaks represent NH$_3$ ligands which were bonded to the central atom, Cu^{2+} at 3294.86 cm^{-1} (N-Hstretch) and 1629.0 cm^{-1} (N-H bend). The absorption band for N-H stretch shows a strong and quite broad showing that there was a possibility that it is superimposed to the hydroxyl group from the water molecules. Besides, band at 1045.7cm-1 indicates the present of S=O.

In spectrum (c), C-N stretching was found at 1104 cm^{-1}while C-C stretching is at 1037.71 cm^{-1}.N-H stretches were observed at 3295.6 cm^{-1} and 3225.4.1 cm^{-1} while for N-H bending at 1580.3cm-1 and 1569.9 cm^{-1}. A strong absorption band indicates the present of S=O was observed at1042.4 cm^{-1}. For spectrum (d), a weak absorption band was observed

at 2921.5 cm^{-1} indicates the vibrational band for C-H. The asymmetric C=C stretching in the chelated rings of Cu-L4 is strongly coupled to C-H in-plane bending and methyl deformation are observed as a strong band in the IR spectrum at 1578.2 cm^{-1}. In the addition, the medium IR band at 1414 cm^{-1} for the Cu-L4 complex is attributed to C=O coupled to methyl group CH$_3$. The 613 cm^{-1} band in the IR spectrum of Cu-L4 is assigned to the metal-ligand of asymmetric O=Cu=O stretching mode which is in agreement with the [13].

3.3.2 UV-Vis Spectroscopy

Based on Figure 2, the spectrum shows that there was only one maximum absorption peak observed for the all complexes except for Cu-L4 that formed two absorption peaks. Each of the peaks refers to the electronic transition of one non-bonding electrons which excited from the lower to higher energy state in $3d^9$ of Cu^{2+}. All the complexes exhibit paramagnetic properties since they have one unpaired electron in *d*-orbital. Cu-L1 absorb light at 809.5 nm which in the infrared region. Cu-L2, Cu-L3 and Cu-L4 absorbed light in visible light region and shows broad band at 586.0 nm, 550.5 nm, and 657.0 nm due to *d-d* transitions. A shoulder was formed in Cu-L4 spectrum indicating a blue shifted to lower wavelength due to charge transfer from metal to ligand (MLCT).
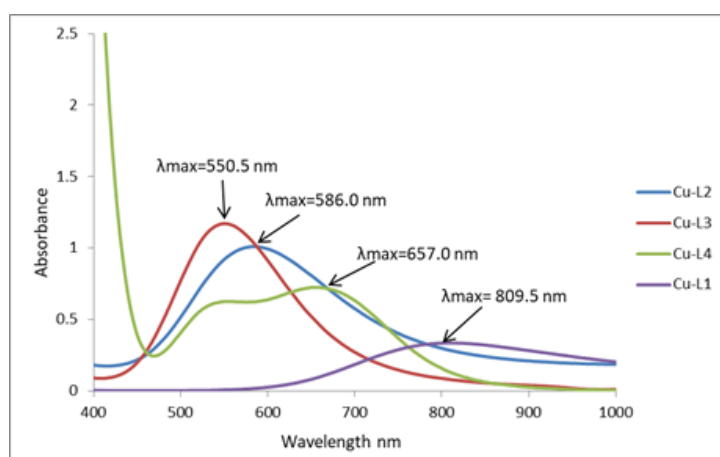

Figure 2. UV-Vis spectrums of Cu-L1, Cu-L2, Cu-L3 and Cu-L4

Using the wavelength data obtained from the curve, molar extinction coefficient was calculated for all of the complexes as shown in table below using formula A=εcl where A=absorbance, ε= molar extinction coefficient, c=concentration and l= path length. Molar extinction coefficient is used to determine the relative strength of light absorbing function (chromophores). Cu-L3 has the highest molar extinction coefficient followed by Cu-L2, Cu-L4 and Cu-L1 with value of (16.8, 50.5, 58.6, 36.2) M^{-1} cm^{-1} respectively. Based on this calculation, Cu-L3 has the highest strength of light absorbing function followed by Cu-L2, Cu-L4 and Cu-L1. Table 1 shows the calculated value of ε and crystal field energy (Δ^o).

Table 1. Molar extinction coefficient and crystal field energy of complexes

Complexes	λmax (nm)	Absorbance	Molar Extinction Coefficient (M^{-1}cm^{-1})	Δ^o J/s^{-1}
Cu-L^1	809.5	0.336	16.8	2.4534×10^{-19}
Cu-L^2	586.0	1.010	50.5	3.3891×10^{-19}
Cu-L^3	550.5	1.171	58.6	3.6078×10^{-19}
Cu-L^4	657.0	0.724	36.2	3.0228×10^{-19}
	554.5	0.626	31.3	3.5816×10^{-19}

3.4 Catalytic performances of the catalysts in reduction of 4-nitrophenol

When 4-nitrophenol was mixed with NaBH$_4$, the solution turned to yellowish and a maximum absorption of 400 nm was observed, which indicates the anion formation for 4- nitrophenolate. The peaks are very distinctive in the UV spectrum. After catalyst was added, the peak was decreased at 400 nm, while a new peak of around 294 nm appeared simultaneously. The new maximum of peak was observed due to a reaction product absorption of 4-aminophenol. The time to completely disappear the peak was recorded at 400 nm. The time taken for 4-nitrophenol to reduce at wavelength 400 nm is directly proportional to the catalyst's catalytic performance. Figure 3 shows the catalytic activity of catalyst in reduction of 4-nitrophenol to 4-AP in the presence of reducing agent (NaBH$_4$) over 16 minutes.
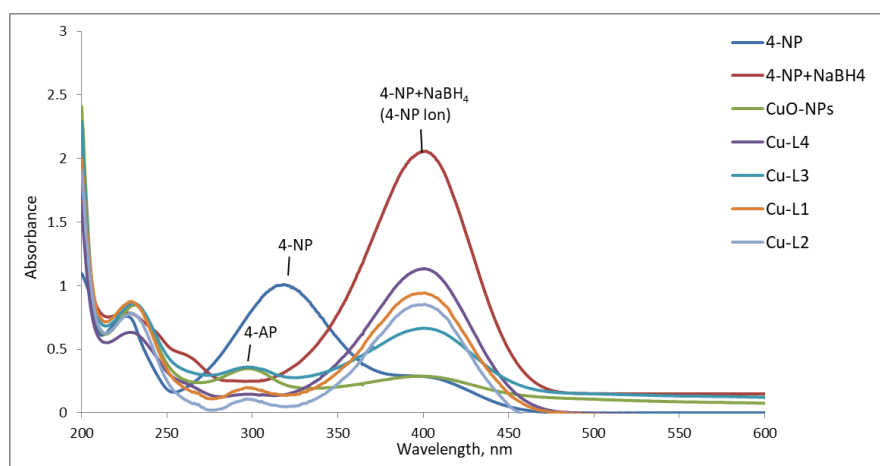

Figure 3. Catalytic activity of catalyst in reduction of 4-nitrophenol to 4-aminophenol over 16 min (0.10 mM 4-NP, 0.03 mM NaBH$_4$ and 1 mg catalyst)

According to the spectrum, CuO-NPs have the highest catalytic activity about 85.7% of 4-NP reduced to 4-AP over 16 minutes. CuO-NPs have relatively higher surface area compare to those copper (II) complexes. Increase in surface area will also increase the catalytic activity [14]. Meanwhile, the catalytic activity if Cu-L4 was the lowest (45.0 %). This might be due to the presence of methyl group which increase the sizes of complex thus decrease the surface area. Having higher molecular weight can lower the rate of reaction [15]. In the addition, Cu-L4 was slightly soluble in 4-NP so it cannot disperse and react well in the solution. This might be one of the factors that lowered the rate of reaction.

Cu-L3 has the second highest percentage of conversion 67.7 %, followed by Cu-L2 (58.5%) and Cu-L1 (54.0%). All these three complexes were dissolved in 4-NP solution right through after added into mixture solution and formed precipitate at the end of the reaction. Cu –L3 has slightly higher conversion since it can chelate to central copper atom which enhances its stability. Catalyst with higher stability will increase the rate of reaction because it has lower potential to dissociated or break during the reaction. Table 2 below shows the overall percentage conversion of 4-NP to 4-AP. All the catalyst give high yield of percentage conversion despite takes longer times than CuO-NPs to reduce 4-NP.

Table 2. Overall percentage conversion and reaction time for reduction of 4-NP to 4-AP

Type of catalyst	Reaction Time(min)	Initial Absorbance	Final Absorbance	Overall Percentage Conversion (%)
Cu-L1	30	1.946	0.145	92.5%
Cu-L2	28	1.954	0.152	92.2%
Cu-L3	24	1.901	0.117	93.8%
Cu-L4	34	1.929	0.175	90.0%
CuO-NPs	18	1.970	0.054	97.3%

For quantitative analysis, a calibration curve was constructed with 4-nitrophenol solution. A positive linear regression equation obtained was $y= 8.66x + 0.0748$ with correlation coefficient of 0.997 in the concentration range of 0.02–0.10 mM as shown in Figure 4. There were strong relationship between absorbance and concentration of 4-nitrophenol solution by referring to correlation coefficient obtained from the graph. Increase in concentration will increase the intensity of light absorption function (chromophores) thus increase the absorbance.
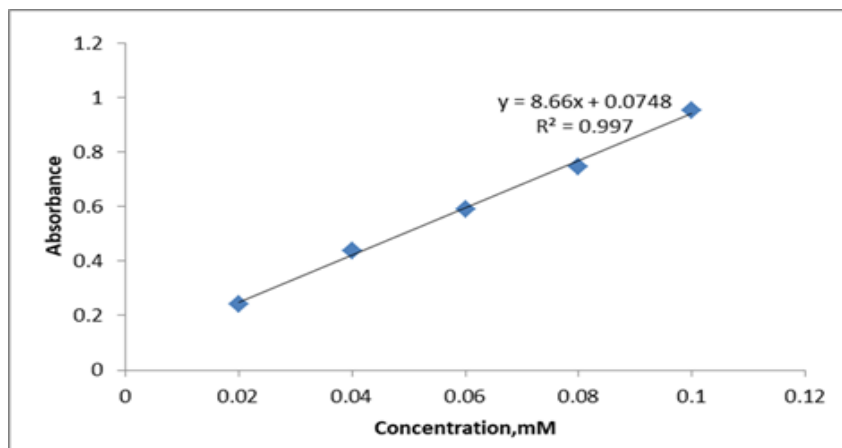

Figure 4. Standard calibration curve for 4-nitrophenol (0.02 mM-0.10 mM) against absorbance

3.5   Isolation of product

4-AP was successfully isolated and characterized by FTIR to determine the successful conversion of 4-NP to 4-AP. Figure 5 below shows the comparison of isolated 4-AP with respect to the standard.
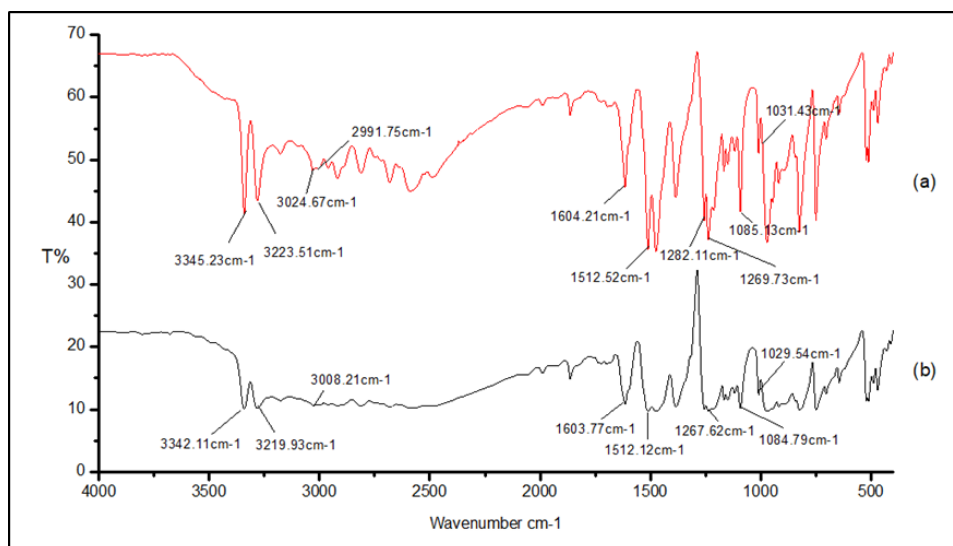

Figure 5. FTIR spectra for (a) 4-aminophenol standard (b) 4-aminophenol product

Based on the spectrum above, spectra (a), characteristic absorption peaks of 4-aminophenol shows the two N-H bands at 3340 and 3282 cm^{-1}, emerging from the broadband of the phenolic OH. Vibration peaks at 2991.8 - 3024.6 cm^{-1} were due to C-H stretching vibration peaks in the 4-aminophenol standard. In the addition, the absorption peak at 1604.2 cm^{-1} was due to N-H bending of aromatic amine and C=C group stretching . The absorption peak at 1515.5 cm^{-1} was due to C-C in aromatic ring stretching vibration peak. Absorption of vibration peak at 1031.4 – 1085.1 cm^{-1} indicate present of C-O band and absorption peak at 1269.7 -1282.11 cm^{-1} represent stretching vibration of C-N.

Meanwhile, most of the major peak in 4-aminophenol standard were found in the product of 4-aminophenol in (b). However it is a little bit differ in terms of intensity of absorption band due to the present of impurities or oxidization of the pellet when exposed in air. The absorption band were observed at 3219.9-3342.1 cm^{-1} represent the N-H band turn up from phenolic group, 3008.2 cm^{-1} (C-H stretch), 1603.8 cm^{-1} (N-H bending), 1512.1 cm^{-1} (C-C aromatic), 1267.6 cm^{-1} (C-N stretch) and 1029.5 cm^{-1} – 1084.8 cm^{-1} indicates C-O band. Overall, there was no major change in absorption peak of the product 4- aminophenol from reduction reaction with respect to its standard.

4. CONCLUSION

In conclusion, Cu-L1, Cu-L2, Cu-L3, Cu-L4 was successfully synthesized by direct chemical reaction of starting material with corresponding ligand solution, sulphuric acid (L1), ammonia solution (L2), ethylenediamine solution (L3) and acetylacetonate solution (L4). Characterization by FTIR spectroscopy confirms the presence of characteristic group for each of the complexes. UV-Vis spectroscopy shows *d-d* transition occurs for all the complexes due to electronic configuration of copper $3d^9$. For Cu-L4 a shoulder shifted to the lower wavelength observed that confirms the charge was transfer from *d* orbital of the metal to an empty orbital in the ligand (MLCT). CuO nanoparticles were also successfully prepared by solid state thermal decomposition of Cu-L1. The study of catalytic activity in reduction of 4-nitrophenol to 4-aminophenol shows that CuO nanoparticles has the highest percentage conversion (97.3%) over 18 minute compared to other complexes.

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