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Formulation and characterization of high thermal conductivity copper nanofluids for a single step industrial heat transfer application system for microelectronics and automobiles

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Abstract

This research article investigate a novel method for the formulation of stable, non–agglomerated copper nanofluids by reducing copper sulphate pentahydrate with sodium hypophosphite chemical as a reducing agent in ethylene glycol as base power fluid by means of conventional heat transfer process in electronics, electrical and automobiles. This is an insitu, single step method, which gives very high yield of product with less time duration. The characterization of the nanofluid was done by particle size analyzer, x-ray diffraction (XRD), uv-visible (UV-VIS) analysis and Fourier transform infrared spectroscopy (FTIR) followed by thermal conductivity studies of nanofluid by the well known transient hot wire anemometer method.

Keywords: *Thermal conductivity; Sodium hypophosphite; Dilution; Nanofluids; Heat transfer efficiency; microelectronics; Transformers.*

INTRODUCTION

Cooling system of machineries and instruments has become one of the top technical challenges faced by hi-tech industries such as microelectronics, electrical transformer, automobiles, manufacturing and metrology. There is a wide requirement in these industrial fields to develop blended heat transfer fluids [1, 2] with significantly higher thermal conductivity than pure fluids. It is a well known fact that crystalline solids have a higher thermal conductivity by 1- 3 orders of magnitude than traditional homogeneous fluids like water, ethylene glycol, oil etc. Therefore the fluids containing suspended solid particles are highly expected to have a better thermal conductivity than pure fluids. Nanofluids [3], containing metallic or non–metallic nanoparticles and have attracted much research attention due to their excellent heat transfer efficiency through convection.

Nanofluids, which are having suspensions [4, 5] of nanometer sized small particles, have been proposed as a route for surpassing the performance of heat transfer liquids that are currently in use [6]. Recent experiments on homogeneous nanofluids have indicated that the significant increase in thermal conductivity could be achieved when compared with liquids without nanoparticles or larger size particles [7-10]. Nanofluids have attracted greatest interest on researchers recently because of their induced and enhanced thermal properties. For example 0.3 vol% copper nanoparticles dispersed in ethylene glycol is reported to increase its inherently poor thermal conductivity by 40% [7].

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At present, the copper nanofluids are prepared by dispersing the copper nanoparticles in the base fluid [8]. This is a step-by-step method, which involves agglomeration that takes place during the formulation process of drying, storage and transportation of nanoparticles. Agglomeration will result in settlement and clogging of the microchannels and hence the thermal conductivity will be decreased. There are several other methods that are similar to one-step physical processing method, in which copper vapour is directly condensed into nanoparticles by contact with a flowing low vapor pressure liquid [7] but this present processing method appears to be cost effective. By conventional polyol process [11], mono dispersed, non agglomerated copper nanoparticles are obtained since polyol acts as solvent and reducing agent but the major drawback of this method is that, the solution of the copper salt should be heated to its boiling point and kept under refluxing conditions for a long period of time [12]. In the aqueous chemical reduction method [13], though the rate of the reaction is high, however, agglomeration problem exists, as a consequence a decrease in the thermal conductivity of the nanofluid is observed in most of the cases. Hence development of new and novel method for the preparation of copper nanofluid is inevitable. With all these ideas in mind, an attempt has been made in the present investigation to synthesize and formulate the copper nanofluid by a novel single step method by using copper sulphate as a source for copper nanoparticles, ethylene glycol as base power fluid and sodium hypophosphite as reducing agent by means of conventional heat transfer method.

This single step method appears to be a unique one, where the preparation of copper nanoparticles is combined together with the preparation of nanofluids and hence the process of drying, storage, transportation and re-dispersion of copper nanoparticles is avoided and ultimately reduce the production cost as well. These aspects of this present study make this as novel process.

Experimental

Preparation of copper nanofluids

All the reagents and chemicals used for this investigation are analytical purity and were used without further purification. The beakers used in this procedure are cleaned by an ultrasonic cleaner (B2510) in an ultrasonic bath (MXB6). In this procedure, 25 ml of ethylene glycol (Merck) solution was taken in a 500 ml clean beaker and to this, 15 ml of (0.1M) concentrated copper sulphate pentahydrate (Merck), 50 ml of surfactant sodium lauryl sulphate (SLS) (Merck) and 100 ml water was added. Further few drops of kerosene were added to prevent immediate oxidation. The reaction mixture was subjected to magnetic stirring for 15 minutes in a magnetic stirrer cum heater (Remi). Then 30 ml of sodium hypophosphite (Merck) was added slowly and the magnetic stirring was continued for another 30 minutes. The colour of the mixture turned from blue to dark red after the reaction. Copper nanofluid was obtained after cooling the reaction mixture to room temperature. To hasten the reaction, few drops of dilute sulphuric acid were added drop by drop and this can be neutralised by the addition of an equivalent amount of dilute ammonia.

Chemical reaction involved is given in scheme 1

$$3NaH_2PO_2 + 3H_2O + CuSO_4 \longrightarrow 3NaH_2PO_3 + H_2SO_4 + 2H_2 + Cu^o$$

Scheme 1

Characterisation

Characterisation of the formulated copper nanofluid was done by particle size analyser, XRD, UV-Visible analysis, and FTIR techniques.

Particle size analysis

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The particle size of the copper nanofluids was carried out by particle size analyzer (cilas 1180). Before analysing of the particle size, the nanofluids are subjected to ultrasonication, to keep the particles in suspension and homogeneity to prevent agglomeration of the particles. The Mie theory and principles are followed for the analysis of particles by the particle size analyzer.

XRD

The XRD analysis was made for copper nanopowder on a D/max – X-ray diffractometer using Nickel – filtered CUKα radiation. The copper nanopowder was obtained after diluting and washing copper nanofluid by using absolute ethanol followed by centrifugation at 4000rpm for 60 minutes by using remi desktop centrifuge. The product thus obtained was washed with acetone and vacuum dried at 80^0C for 2 hrs.

The crystallite size can be found by applying Sherrer's equation

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

D - Crystallite size
λ - Wavelength of X-ray used
θ - Diffraction angle
β - Full width half maximum (FWHM)

FT-IR analysis

A 510P FT – IR Spectrometer was used to identify the presence of the copper nanoparticles in nanofluid solution. The nanofluids were centrifuged at 16,000 rpm for 60 minutes and supernatant alone used for FT – IR analysis.

UV analysis

The presence of copper shows characteristic absorption which was identified qualitatively by UV-VIS spectroscopy.

Transient hot wire method

The Thermal conductivity (K) is the intensive property of a material which relates its ability to conduct heat from surface to medium through convection. Hence determination of thermal conductivity is done by transient hot wire method [14-19].

A Transient hot wire system involves a wire (typically Platinum) suspended symmetrically in a liquid in a vertical cylindrical container. Briefly the method works by measuring the temperature/time response of the wire to an abrupt electrical impulse. The wire is used as both heater and thermometer and the thermal conductivity K is calculated from a derivation of Fourier’s Law which is given below

$$K = \frac{q}{4\pi(T_2 - T_1)} \ln\left(\frac{t_2}{t_1}\right)$$

where, q = applied electrical power
T_1 and T_2 are the temperatures at time t_1 and t_2

Results and discussions

Effect of concentration

The effect of copper sulphate concentration on the formation of copper nanoparticles is shown in Table 1. From the table it is strong evident that copper fluid of 0.1 M concentration seems to be quite effective for obtaining copper nanoparticle of desired particle size. This is mainly due to the fact that the growth and nucleation process do not take place simultaneously, as a result the distribution range of copper nanoparticle is narrow. But at higher concentrations (namely 0.3 M and 0.5 M), the nucleation and quantum growth of copper nanoparticles takes place simultaneously. Moreover some large particles grow continually and some growing particles do appear simultaneously within the copper nanofluid hence the distribution of copper nanoparticles is broadened. The results

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obtained were optimized and the particle diameter of copper nanofluid was further reduced by dilution, which is shown in Table 2.

Effect of dilution

Dilution plays an important role in the synthesis and formulation of copper nanofluids as the particle size can significantly be minimized by dilution (Table 2). The copper nanofluids of 0.1M empirical concentration are subjected to ultrasonication in order to keep the particles in homogeneous suspension and then the different diluted solutions of 0.1M concentration viz. 25 ml dilution, 50 ml dilution, 75 ml dilution, 100 ml dilution were measured by means of particle size analyzer. From the present investigation study it is observed that dilution of copper nanofluid (0.1M) by 100 ml water was quite most effective in reducing the size of the particle and prevents the agglomeration of particles again. As a consequence narrow size copper nanoparticles of 0.14 mu were obtained through this process.

Effect of pH

The pH plays a significant role in this synthesis of copper nanofluid. A low pH results in faster reaction time and hence a low pH is maintained throughout. As pH decreases, the time taken to obtain the copper nanoparticle also decreases. This trend can clearly be observed from Table 3. For example, when the pH is maintained at 8, the time taken to obtain copper nanoparticle is found to be 90 minutes. However, the copper nanoparticle could very well be obtained within 20 minutes, when the pH is maintained at 2. This behaviour may be explained due to the fact that, sodium hypophosphite performs the reduction of copper ions to copper, only if the pH is towards more acidic. The copper nanofluid thus obtained would be in a highly acidic state and therefore capable of corroding the engines when it is used as a coolant, hence the obtained copper nanofluid is neutralized with dilute ammonia, which reverts 'Cu' back to the basic state and capable of being used in engines and electronic cooling system without causing corrosion problem.

Effect of SLS

The introduction of (0.01M) SLS during the preparation of copper nanoparticles, keeps the nanoparticles suspended, retards the growth and re-agglomeration of the metal nanoparticles and thus it contributes to higher thermal conductivity.

Effect of reducing agent

Sodium hypophosphite ions favours the reduction of copper from +2 oxidation state to zero valent (0) state by adding 0.25M concentration sodium hypophosphite to copper sulphate pentahydrate in the ratio of 3:1.The copper nanofluid thus obtained is determined to be stable for more than three weeks in the stationary state and stable for more than 8 hrs under centrifugation at 4000 rpm without sedimentation.

The stabilization of the nanofluid is very important for industrial application as heat transfer medium. It has been tested at room temperature that the obtained nanofluid is stable for more than 3 weeks in the stationary state and more than 8 hrs under centrifugation at 4000 rpm without sedimentation. It could even be suspended for more than 2 weeks in stationary state at 120^{o}C. The stabilization ability of the obtained copper nanofluid is found to be better than that of the one prepared by the step-by-step conventional method, in which the nanofluid lasted for only one week in the stationary state at room temperature. Two factors seems to contribute to this improvement, one is the small size and hence better dispersion ability of copper nanoparticles and the other is due to the addition of the surfactant (SLS) which prevents the

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agglomeration and the growth of the metal nanoparticles.

By optimizing the various parameters such as concentration, pH, surfactant, dilution, addition of reducing agent, the minimal particle size was obtained. These trends can be observed in Figures 1(a) and (b), where the results were obtained for copper nanofluid of 0.1M concentration. For example, the particle sizes of the copper nanofluid before optimization were very large and the mean diameters were found to be 21.79 mu (Figure 1a). However, significant reduction in the mean particle diameters were observed after optimizing the various parameters, the minimum particle diameter d_{10} obtained by is 0.07 mu (70 nm), at d_{50} it is 0.14 mu (140 nm), at d_{80} it is 0.20 mu (200 nm) and the mean diameter is 0.16 mu (160 nm) (Figure 1b).

The XRD pattern of the sample is shown in Figure 2. Diffraction peaks can be indexed to those of pure face centred cubic (FCC) Cu (JCPDS, File No.04-0836), corresponding to the (1,1,1), (2,0,0) and (2,2,0) planes respectively. The crystallite size can be found by applying Sherrer's equation and the average crystallite size is found to be 130 nm. FT – IR spectra are taken for the analytical pure ethylene glycol (Figure 3) and copper nanofluid solution (Figure 4) respectively. It can be seen from the FT-IR analysis, that the spectrum corresponding to the copper nanofluid solution resembles the spectrum of pure ethylene glycol. There is no sign indicating the formation of oxidised products of ethylene glycol. This suggests that it is sodium hypophosphite and not ethylene glycol which acts as a reducing agent. Hence this method preserves the respective advantages of the polyol process and aqueous chemical reduction process. It is also determined to be a fast and novel method for preparation of several nanofluids.

The results of UV-VIS analysis is shown in Figure 5. As we get a peak at around 422.15 nm, in the visible region confirms the presence of copper. The Thermal conductivity of the copper nanofluid evaluated by transient hot wire method was found to be (0.6 Wm^{-1} k^{-1}) which is significantly larger than that of pure ethylene glycol whose thermal conductivity was (0.256 Wm^{-1} k^{-1}). Hence the copper nanofluid prepared in the present work can be efficiently used for electronic cooling system and heat transfer applications in large scale industries.

CONCLUSIONS

A novel single step method was developed for preparing copper nanofluids by reducing copper sulphate pentahydrate using sodium hypophosphite as reducing agent and ethylene glycol as base power fluid by means of conventional heating method. This method is determined to be an ideal method for the preparation of nanofluids than conventional methods like polyol process, step by step process and aqueous chemical reduction method. This method appears to be a unique one where in a single step non-agglomerated and stable suspension of copper nanofluid was obtained in a shorter time. The characterization of the obtained nanofluids was done by particle size analyzer, XRD, FT-IR, and UV-VIS spectroscopy. The minimum particle diameter d_{10} obtained for copper nanoparticle by optimizing the various parameters is found to be 70 nm, 140 nm at d_{50} , 200 nm at d_{80} and the mean diameter is 160 nm.

Thermal conductivity measurements of the obtained nanofluid were carried out by transient hot wire method in order to find the suitability of the nanofluid as an effective heat transfer medium for micro electronic system, electrical transformers and automobile industries. The experimental results reveal that copper nanofluid has a better thermal conductivity

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(0.6 Wm^{-1} k^{-1}) than pure ethylene glycol agent (0.256 Wm^{-1} k^{-1}) and suggest that it can be used as an effective coolant than conventional power fluids that are currently used for automobile industries, electrical transformers, electronics and microelectronic cooling system.

Table 1: *Effect of concentration on the size of copper nanoparticles before optimizing the parameters*

Concentration (M)	Diameter (mu)
0.1	0.74
0.3	2.46
0.5	5.35

Table 2: *Effect of dilution on the size of copper nanoparticles of 0.1M concentration*

Dilution (ml)	Particle size (mu)
25	0.66
50	0.52
75	0.26
100	0.14

Table 3: *Effect of pH on the time of synthesis of copper nanofluid*

pH	Time (minutes)
8	90
7	60
5	40
2	20

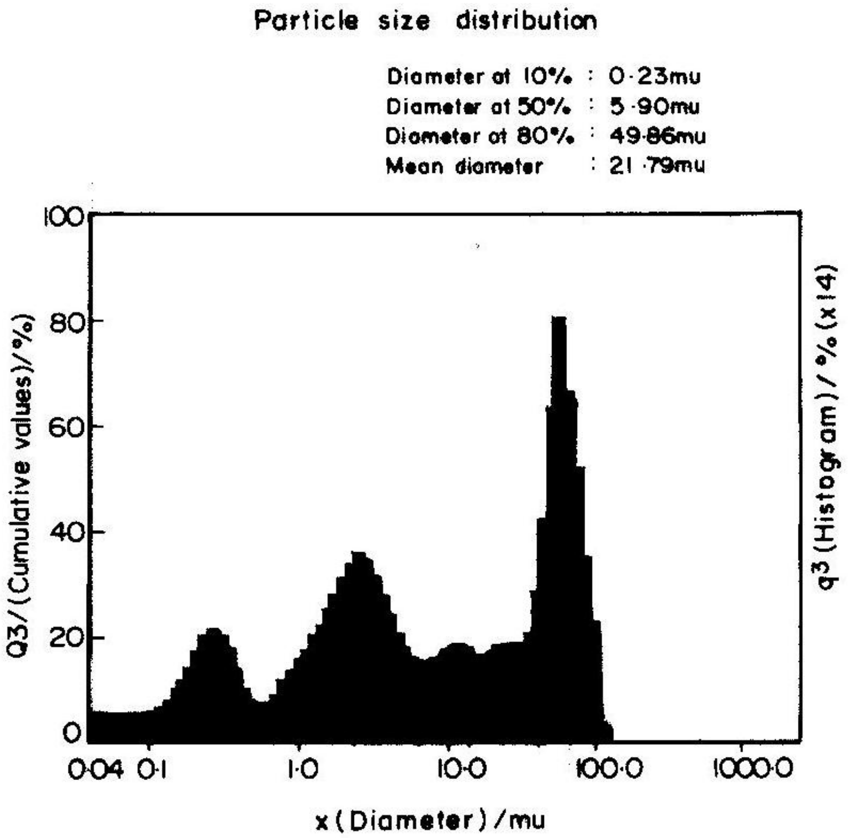

Fig. 1 (a). *Particle size analyzer results for copper nanofluid (I)*

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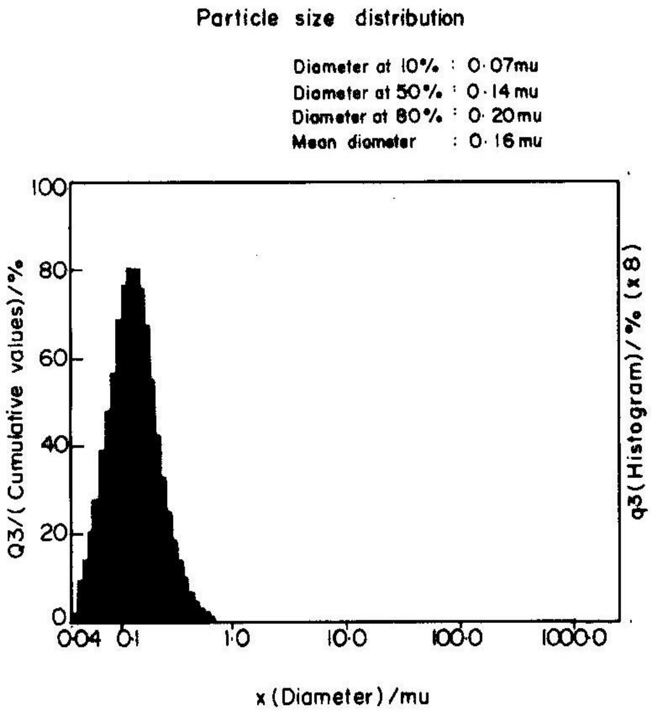

Fig. 1 (b). *Particle size analyzer results for copper nanofluid (II)*

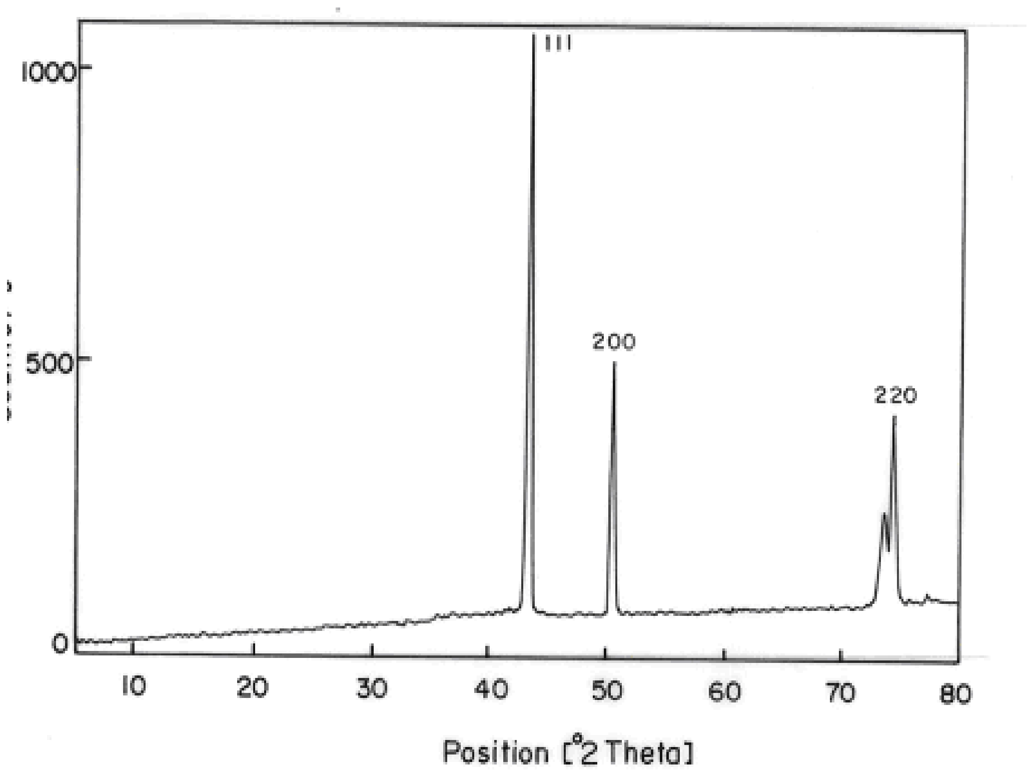

Fig. 2. *XRD Pattern for copper nanofluids*

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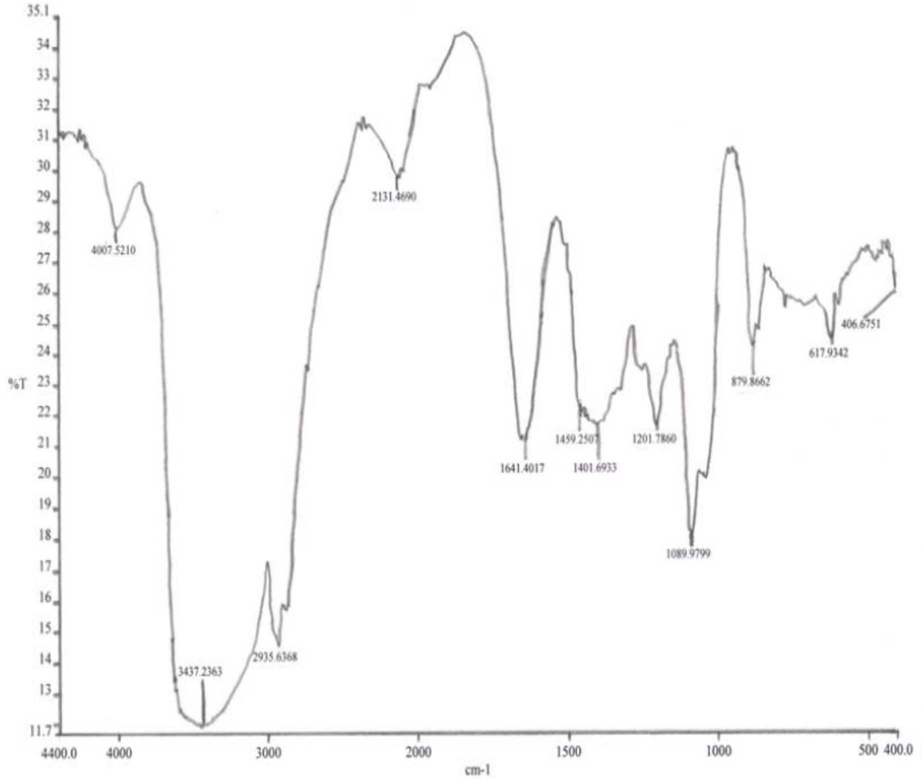

Fig. 3. FT – IR spectrum of ethylene glycol

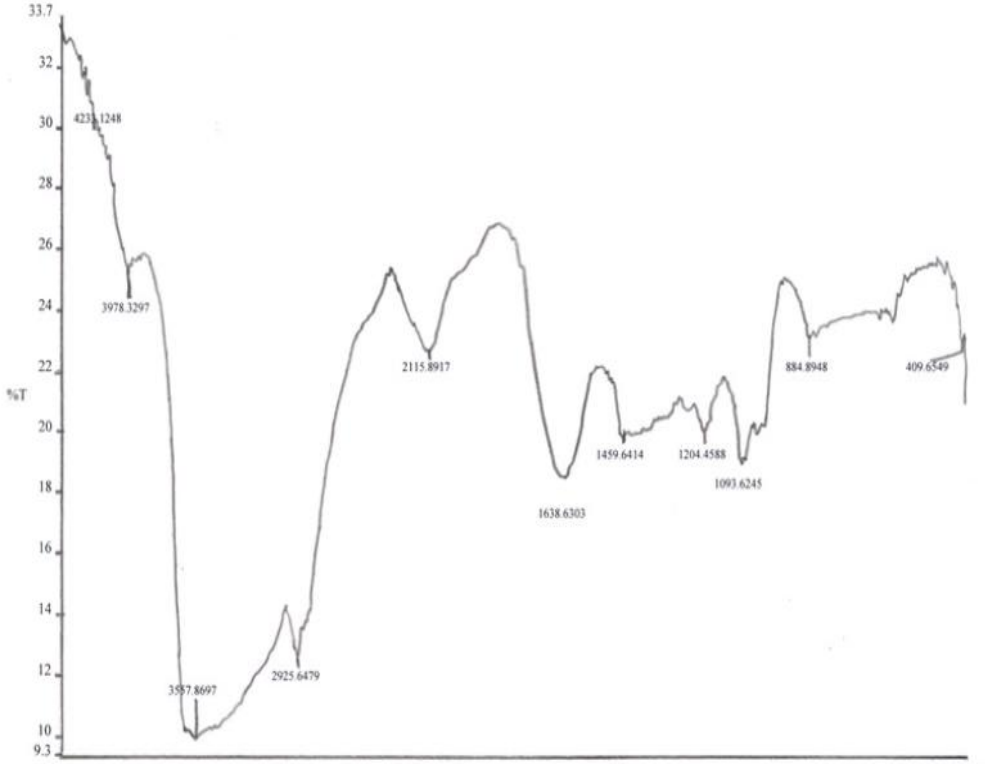

Fig. 4. FT-IR spectrum of copper nanofluids

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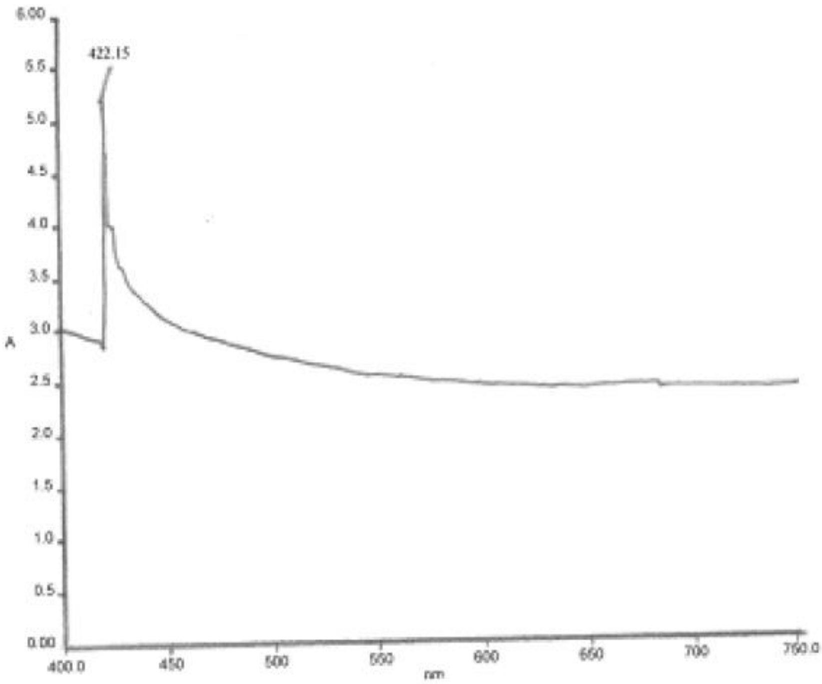

Fig. 5. *Analysis pattern of copper nanofluid by UV – Visible method*

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