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ANTIBACTERIAL AND OPTICAL PROPERTIES OF GREEN SYNTHESIZED COPPER DOPED COBALT OXIDE NANOPARTICLES

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Abstract: In the present study, Copper doped Cobalt Oxide ($CuCo_2O_4$) nanoparticles were successfully biosynthesized using aqueous leaf extracts of Eclipta Alba and characterized using various techniques such as UV-visible spectrophotometry, Fourier transform infrared spectrometry (FTIR) and Scanning electron microscopy (SEM) coupled with Energy dispersive X-Ray (EDX) and X-Ray Diffraction (XRD). The spectroscopic method confirmed that the formation of $CuCo_2O_4$ nanoparticles and the microscopic technique confirms the morphology of the nanoparticles. Antibacterial property of the synthesized nanoparticles was measured by disc diffusion method. The Optical absorption spectrum shows the optical properties of the nanoparticles. To analyse the behaviour of molecular interaction in the nanofluid the ultrasonic velocity, density and viscosity were calculated using Ultrasonic interferometer. From which the thermodynamical parameters like adiabatic compressibility, free length and acoustic impedance were computed.

Index Terms - Eclipta Alba, Antibacterial activity, Molecular Interaction, Thermodynamic Parameters, Ultrasonic technique

I. INTRODUCTION

In recent years, the use of green nanoparticles has been addressed in playing a significant role in medicine, agriculture and solar cell fields. Therefore, obtaining new synthesis methods using biological systems for the fabrication of nanoparticles can pave a promising pathway for biomedical and nanotechnology-based industries [1–4]. Different low-cost and low-environmental impact approaches for preparing nanoparticles have emerged as alternatives to traditional synthetic processes. One of the most considered techniques is the synthesis of nanoparticles using organisms. Among all organisms, plants appear to be the best candidates for this and they are appropriate for the up-scaled bio-production of nanoparticles [5]. Nanoparticles synthesized by extracts are more stable and the rate of production is faster than in the case of microorganisms. In addition, extracts of medicinal plants are often utilized as stabilizing and reducing materials in the production of metallic nanoparticles [6].

Metal nanoparticles find applications in microelectronics, sensors, catalysis, and various areas of nanotechnology. These particles are found to have advantages arising due to their small size, large surface area, chemical and optical properties, and good electrical conductivity. Among them, copper doped cobalt oxide nanoparticles ($CuCo_2O_4$) have acquired great interest in research fields, such as solar cells, biodiesel, photocatalysis, water pollutant removal, supercapacitors, electrocatalysis, etc., due to their desirable properties, such as low cost, nontoxicity, and easy preparation [7]. With the aim of synthesizing copper doped cobalt oxide nanoparticles, a complete green approach was adopted using aqueous leaf extracts of plant Eclipta Alba, as an effective stabilizing and chelating agent. The fact that there was neither the use of organic/inorganic solvents and nor the use of any surfactants making the process as an eco friendly and green. The interface of medicinal plants and biosynthesis of nanoparticles provides an exciting opportunity for wide range of biomedical applications [8]. In the present study, we are reporting the synthesis of copper doped cobalt oxide nanoparticles using Eclipta Alba leaves extract and characterized using XRD, UV, FTIR, SEM, EDX, and antibacterial studies. Thermodynamic properties of the prepared nanofluid were explained using ultrasonic technique under various temperatures.

II. MATERIALS AND METHODS

The chemical used for this study are of AR grade, cobaltous chloride hexahydrate ($CoCl_2.6H_2O$) and cupric sulphate pentahydrate ($CuSo_4.5H_2o$) was purchased from HiMedia Laboratories Pvt. Ltd., Mumbai and Avantor performance materials India Ltd., Maharashtra. Fresh leaves of Eclipta Alba were collected from Paddy fields.

2.1 Preparation of leaf extract

The Eclipta Alba leaves were washed thoroughly under running tap water and then with distilled water. The plant material was then mixed with 400 ml of distilled water and the mixture was boiled for 30 minutes to get 150 ml of leaf extract. The extract was then cooled and filtered through Whatman no. 1 filter paper.

2.2 Preparation of nanoparticles

For the synthesis of cobalt oxide nanoparticles, the freshly prepared leaf extract of 100ml was added to the 1 molar concentrated cobaltous chloride and cupric sulphate pentahydrate. The mixture was stirred over 3 hours at room temperature. After that, the solution was allowed to settle for overnight and the supernatant solution was then discarded carefully. Washing with distilled water and ethanol was carried out to remove the by-products, impurities and un-react particles that were bound to the nanoparticles. This process was repeated for 5 days. The obtained precipitate was dried using hot air oven at 120^0C for 3 hours. The derived Copper doped Cobalt oxide nanoparticles were grained and calcined at 500^0C for 3 hours. Finally, a fine nanopowder was obtained, and collected for further characterization studies.

III. RESULTS AND DISCUSSION

3.1 Characterization of $CuCo_2O_4$ nanoparticles

3.1.1 X- Ray Diffraction (XRD) Studies

Fig.1 shows the XRD Pattern of $CuCo_2O_4$ nanoparticles. XRD analysis was done on instrument (Diffractometer system=XPERT-PRO) by using Cu K_α radiation. The confirmation of successful synthesis of copper doped cobalt oxide nanoparticles was done by powder x-ray diffraction (XRD). The obtained diffraction pattern had some sharp peaks which indicate that the synthesized nanoparticles were well crystalline and these are located at the 2θ values of 16.50, 31.54, 37.08, 45.02, 54.98, 59.61 and 65.40 and their (hkl) planes are (111), (220), (311), (400), (442), (511) and (440) respectively. The average crystallite size (D) was calculated using Debye-Scherrer's formula. The average crystallite size of $CuCo_2O_4$ was found to be 25 nm.

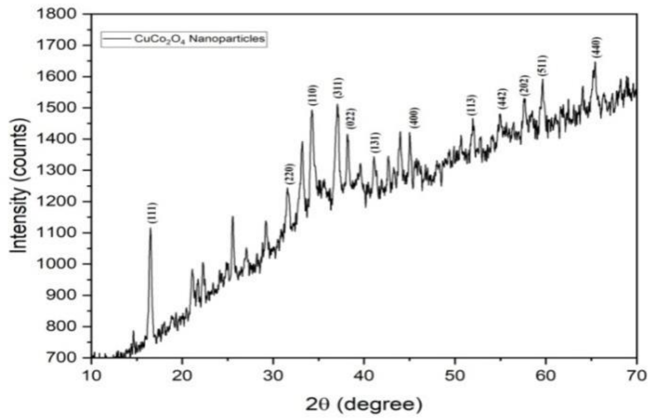


Fig.1 XRD Pattern of $CuCo_2O_4$ Nanoparticles

3.1.2 Ultraviolet – Visible Spectroscopy (UV) Studies

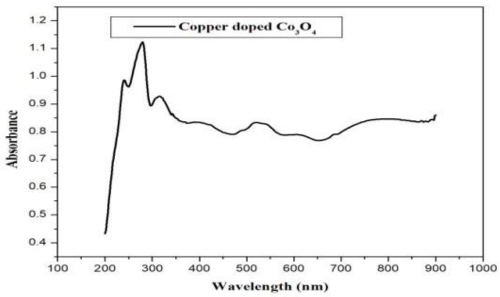


Fig. 2(a), UV Spectrum of $CuCo_2O_4$

The optical spectrum of $CuCo_2O_4$ nanoparticles was depicted in the Fig. 2(a). The graph shows a maximum absorbance at 280 nm, after that it gets decreases with increase in wavelength this may due to the excitation of surface plasmons in the nanocomposite. Band gap of materials was estimated from absorption coefficient (α) and photon energy (hν) using the following relation [10].

$$(\alpha h\nu) = A\,(h\nu - E_g)^{n} \qquad (3.1)$$

Fig. 2 (b), shows the plot of $(\alpha h\nu)^2$ versus photon energy (hν). The value of band gap of Copper doped cobalt nanoparticles was measured by extrapolating the intercept line on the photon energy (hν) axis gives direct band gap (E_g) of 2.279 eV, which confirms the semiconducting properties of the nanoparticles.

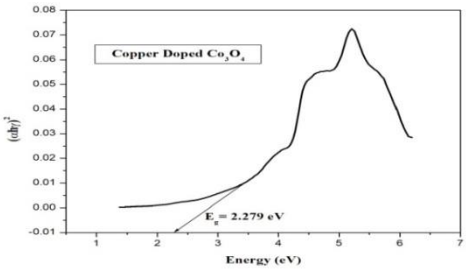
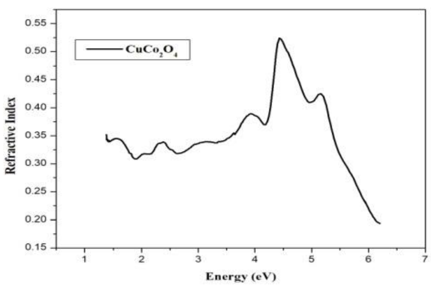


Fig. 2(b), Direct Band gap of $CuCo_2O_4$

Refractive index and extinction coefficient values against photon energy plot of $CuCo_2o_4$ nanoparticles are shown in Fig. 2(c) and 2(d) respectively. From the image, the refractive index is found to increase with an increase in photon energy.



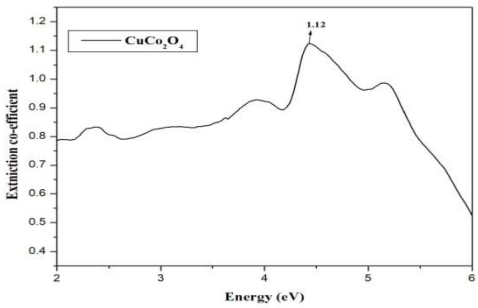
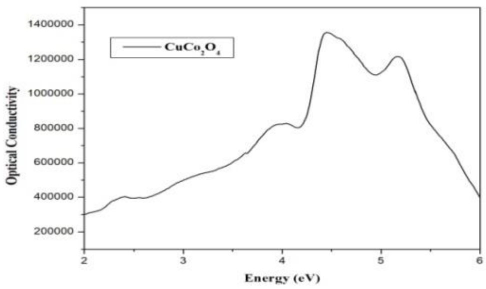


Fig. 2(c), Refractive Index of $CuCo_2O_4$ Fig. 2(d), Extinction Coefficient of $CuCo_2O_4$

In general, refractive index of the semiconductor is a measure of its transparency to incident spectral radiation. The assessment of the refractive index of the optical material is notably important for applications in integrated optical devices. The extinction coefficient of $CuCo_2O_4$ nanoparticles increases with increase in the photon energy. The observed extinction coefficient values are very low (1.12) in the absorption region, and it specifies the smoothness of the surface and homogeneity of the particles [11].

A graph is plotted for optical and electrical conductivity of the nanoparticles as a function of energy and is shown in figure 2(e) and 2(f). The free charges are described by optical conductivity. The increase in optical conductivity with incident photon energy shows good optical response of the material. The higher value of photo conductivity shows a very good photo response of the nanoparticles.



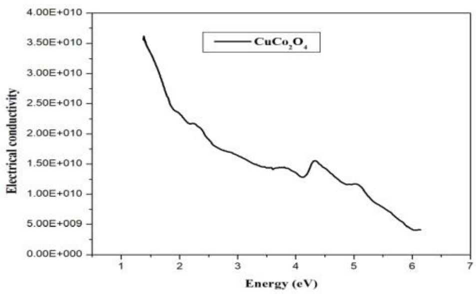


Fig. 2(e), Optical conductivity of $CuCo_2O_4$ Fig. 2(f), Electrical conductivity of $CuCo_2O_4$

From the Fig. 2(g), the high value of transmittance and low absorption in the visible region indicate that the nanoparticle is suitable for nonlinear optical applications. Fig. 2(h) shows the variation of reflectance as a function of photon energy for copper doped cobalt oxide nanoparticles.

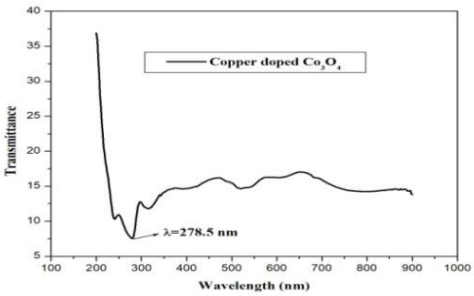


Fig. 2(g), Transmittance of $CuCo_2O_4$

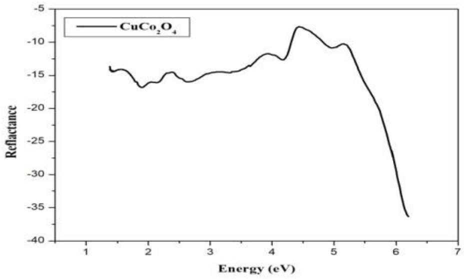


Fig. 2(h), Reflectance of $CuCo_2O_4$

Very low reflectance is observed in the entire visible, and also near IR which reveal that the prepared nanoparticles are appropriate to use as an antireflection coating in solar thermal devices [12]. From the calculated optical parameters, it was confirmed that the green synthesized copper doped cobalt oxide nanoparticles can be used in semiconductor devices such as photo amplifier, photovoltaic cell, photo electronic devices, and photo detectors.

3.1.3 Fourier transforms infrared spectroscopy (FTIR) analysis

In molecules and crystals, the atoms or ions are connected by chemical bonds. These systems can be set into vibration depending on the elements and type of bond present. This vibrational frequency determined by the mass of atoms and bond strengths. The mechanical vibrations are at very high frequencies ranging from 10^{12} to 10^{14} Hz, which is in the Infrared (IR) regions of the electromagnetic spectrum. When vibrational frequencies are in resonance, impinging beam of infrared electromagnetic radiation is coupled. These absorption frequencies represent vibrations of the chemical bond, specific type of bond and the group of atoms involved in the vibration [13].

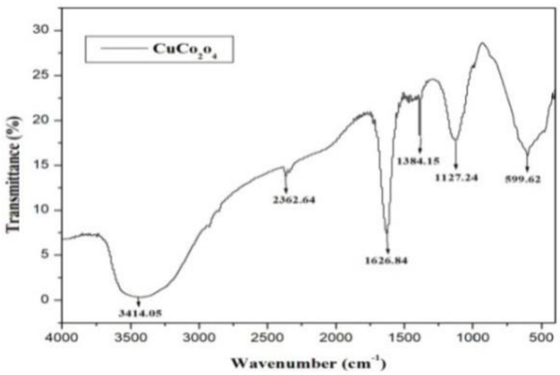


Fig. 3, FTIR spectrum of $CuCo_2O_4$ nanoparticles

FTIR analysis was performed to sort out the potential functional groups of the bio-molecules in the Eclipta Alba leaves extract involved in the formation of copper doped cobalt oxide nanoparticles; it was given in Fig. 3. The broad band around 3414 cm^{-1}, corresponding to the stretching vibrations of the hydroxide groups due to the moisture present in the sample and is assigned to O-H bond. Bond at 2362 cm^{-1} ascribed to presence of Co_2 in the air medium. Strong bands presents at 1625 cm^{-1} and 1387 cm^{-1}, which are characteristics of the asymmetric Coo^- and symmetric Coo^- stretching vibrational modes. A sharp band at 599 cm^{-1} attributed to the fingerprint stretching vibrations of metal oxide bonds of $CuCo_2O_4$ nanoparticles.

3.1.4 Scanning Electron Microscopic (SEM) studies

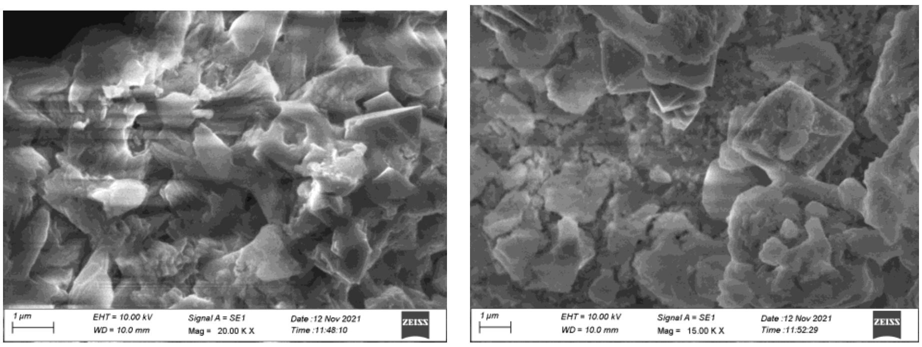


Fig. 4, SEM images of $CuCo_2O_4$ nanoparticles

The morphological characteristics of the gained copper doped cobalt nanoparticles are discovered with the Scanning electron microscopy and are shown in Figure 4. SEM images of $CuCo_2O_4$ sample reveals that all the nanoparticles are displayed an irregular arrangement prismatic shape.

3.1.5 Energy Dispersive X-ray (EDX) spectroscopy Analysis

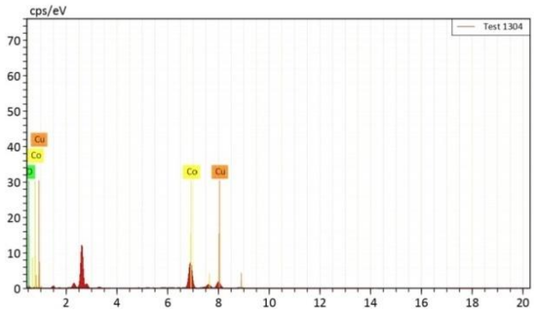


Fig. 5, EDX spectrum of $CuCo_2O_4$ nanoparticles

The chemical composition and purity of the as prepared copper doped cobalt oxide nanoparticle was investigated by using energy dispersive X-ray (EDX) spectroscopy it was shown in Figure 5.Only Oxygen, Copper and Cobalt elements was existed in the sample. The atomic percentages of Cu, Co and O were found to be 18.74%, 52.22% and 29.04%, respectively.

3.1.6 Antibacterial Activity

An antibacterial study of copper doped cobalt oxide nanoparticle was carried out by using disc diffusion method, nanoparticles have small size with high surface area and hence it possesses strong antibacterial activities. The synthesized nanoparticles showed remarkable antibacterial activities against Staphylococcus aureus, Pseudomonas aeruginosa and K.Pneumoniae. Figure 6 shows the results of antibacterial studies of $CuCo_2O_4$ nanoparticles using disc diffusion method. Table 1 represents the Zone of inhibition of $CuCo_2O_4$ nanoparticles using disc diffusion method.

Fig. 6, Antibacterial activity of $CuCo_2O_4$ nanoparticles

Table1. Results of antibacterial activity of $CuCo_2O_4$ nanoparticles

Name of the Bacteria	$CuCo_2O_4$-NPs	Standard
Staphylococcus aureus	30	20
Pseudomonas aeruginosa	30	26
K. Pneumoniae	35	25

3.2 Characterization of $CuCo_2O_4$ Nanofluid

3.2.1 Preparation of nanofluid

Preparation of stable nanofluid with uniform dispersion is an important requirement for improving heat transfer performance of conventional fluids and nanofluid needs to be prepared in a systematic and careful manner. Three methods available for preparation of stable nanofluids are

i. Surfactant addition to the base fluid.
ii. Acid treatment of base fluid.
iii. Ultrasonic mixing of nano powder in base liquid.

Thermo physical properties of nanofluids are affected with the use of surfactants and acid treatment may cause material degradation after some days of continuous usage of nanofluids in practical applications. The ultrasonication method is an approved technique for dispersing the aggregated nanoparticles [14].

In the present study ultrasonicator is used for preparation of nanofluid with minimum aggregation of nanoparticles and improved dispersion behavior. Prepared dry $CuCo_2O_4$ nanoparticles are mixed with propylene glycol as base fluid in nanofluid preparation. The quantity of nanoparticles required for preparation of nanofluid of different volume concentrations is calculated using weight percentage equation. A sensitive balance (Wensar, resolution-0.001 g) is used to weigh the nanoparticles very accurately. Ultrasonication was applied for 1-2h to mix calculated amount of nanoparticles in base fluid using ultrasonic Cleaner (Smiledrive, Voltage- 220-240 V, frequency- 50Hz). The $CuCo_2O_4$ nanofluid thus prepared was kept for observation and no particle settlement was observed at the bottom of the flask even after twenty four hours. During the experimentation, the time taken to complete the experiment is less than the time required for first sedimentation to take place and hence surfactants are not mixed in the nanofluid. Five different volume concentrations of 0.1%, 0.2%, 0.3%, 0.4% and 0.5% were used in the study it was shown in the figure 7.

Fig. 7, Image of prepared $CuCo_2O_4$ nanofluid

3.2.2 Thermodynamic Properties of nanofluid

Investigation based on the behavior of propagation of ultrasonic waves in nanofluid is now rather well established as an effective means for examining certain physical properties of the materials. The data obtained from the experiments are used to compute thermodynamic parameters and their variation with concentration of the nanoparticles in the base fluid are useful in understanding the nature of molecular interaction between them, in terms of physical parameters. The measured values of ultrasonic velocity (U), density (ρ) and viscosity (η) have been used to calculate the thermodynamic parameters like adiabatic compressibility (β_a), free length (L_f) and acoustic impedance (Z) using the following equations [15]. The velocities of ultrasonic waves in the nanofluid have been measured using an ultrasonic interferometer working at a fixed frequency of 2MHz supplied by Mittal Enterprises New Delhi. The density is measured using a 5cc specific gravity bottle. The viscosity of the pure propylene glycol and $CuCo_2O_4$ nanofluid were measured using an Ostwald's Viscometer.

$$\beta_a = 1/ (U^2 \rho) \quad (3.2)$$

$$L_f = K_T (\beta_a)^{1/2} \quad (3.3)$$

$$Z = \rho U \quad (3.4)$$

The study of physico chemical behaviour of the nanofluid is very much essential and it gives information regarding the interaction properties of the molecules in that system. In our system ultrasonic velocity starts decreasing with increasing concentration of the nanoparticles in the base fluid for low temperatures and vice versa, which is shown in figure 8 (a) from which the authors concluded that the intermolecular interaction of the nanofluid changes from strong to weak when the temperature of the system increases from lower to higher region. Similar behaviour was observed in the case of acoustic impedance, it was depicted in fig 8 (b).

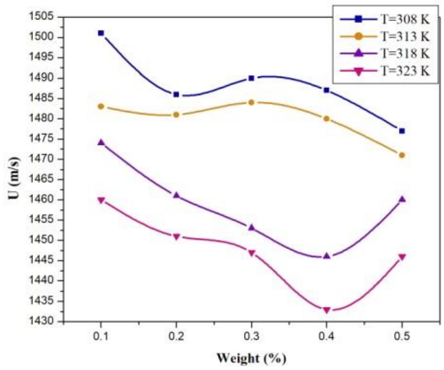


Fig. 8 (a), Velocity of $CuCo_2O_4$ nanofluid

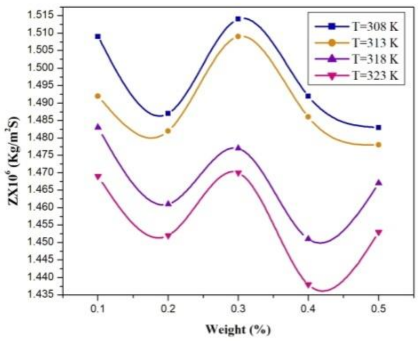


Fig. 8 (b), Impedance of $CuCo_2O_4$ nanofluid

From the variation of β_a with mole fraction Fig. 8 (c), it is observed that β_a decreases with increase in mole fraction at the system is in high temperature and vice versa, which gives the information regarding the associations or disassociation of the components. As the temperature increases, β_a increases, may be because of expansion of liquids. Similar behaviour is observed in the variation of free length (L_f) shown in Fig. 8 (d). This indicates the looser packing of molecules and hence the interaction becomes weak [16]. Thus from the variations of β_a and L_f it was confirmed that the interaction between the nanofluid become stronger to weaker when the temperature of the system increased.

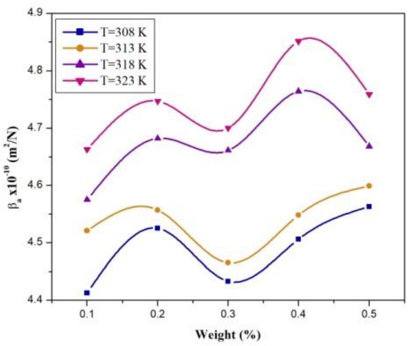


Fig. 8 (c), Compressibility of $CuCo_2O_4$ nanofluid

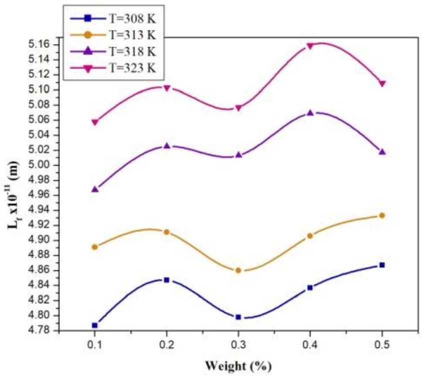


Fig. 8 (d), Free length of $CuCo_2O_4$ nanofluid

IV. CONCLUSION

The successful preparation of copper doped cobalt oxide nanoparticles have been achieved by sol gel method using biomaterial. The sharp peaks in XRD fairly indicate the crystalline size of the title substance. Optical studies shows the band gap and the optical parameters of the system, from which it was concluded that the prepared nanoparticles can be used in semiconductor devices such as photo amplifier, photovoltaic cell, photo electronic devices, and photo detectors. FTIR studies confirm that the functional group and mode of vibrations present in the sample. SEM and EDX image shows the morphology and the purity of the nanoparticle. Antibacterial study gives the knowledge about the strong antibacterial activity of the $CuCo_2O_4$ nanoparticles. From the study of thermodynamic properties, it was confirmed that the interaction between the $CuCo_2O_4$ nanofluid become stronger to weaker when the temperature of the system increased.

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