Optical Properties of Copper Oxides (CuO) and Titanium Oxides (TiO_2) Nanoparticles

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Abstract – *This paper deals with the investigation of the optical properties of nanoparticles in the field of solar thermal systems. The contribution of renewable source of energy is increasing with the demand of energy in various fields like industries and technologies, this paper focuses on the working medium used in the direct solar absorbing collector where traditionally the water is used, whereas here the Nanofluids are to enhance the performance of the system. The Nanofluids selected are copper oxides and titanium oxides Nanoparticles with the varying volume fraction of 2PPM, 4PPM, and 6PPM. The performance of the Nanofluid is compared both theoretically and experimentally. For the theoretical study of Nanofluids, Rayleigh's scattering model is used.*

Key Words: solar thermal systems, direct solar absorbing collector, Rayleigh's scattering model.

1. INTRODUCTION

The depletion of the conventional energy is making researchers to develop the alternate source of energy which is said to be non-conventional energy. In which the level of contribution of this energy will play a vital role in years to come and they will be replacing the present energy generating sources, in which the solar energy can be used because of its availability. The solar energy absorbed by the earth surfaces is about 4×10^{24} J per year and so its researcher responsibility to use the maximum out it. As it is clear that solar absorbing collectors required replacement of working fluids where water as working fluid is not having a very good absorption rate when compared to the Nano fluids [1]. The Nanofluids role as working fluid is increasing its importance in the solar thermal systems for better energy absorption. The idea of Nanofluids was discussed in the names of metallic and non-metallic particles absorption were discussed [2]. The performance of Nanofluids mostly depends on its morphology such as its shape and size which is known to be optical properties of the Nanoparticles [3]. It is noted that the metallic particles in the base water such as water, which is suspended in particular volume fraction are having the impact with the energy absorption, they transfer the energy received from the surrounding to the medium around them. The existing particles in the fluids can absorb more energy and transfer convection heat [4]. The metal Nanoparticle is having the very good property of absorbing solar energy under the visible range, as the incident light frequency consists of oscillating frequency electrons, the localized scattering Plasmon resonance (LSPR) effect which is leading to the enhancement of light scattering and absorption[5][6].

Core and shell Nanoparticles with dielectric constant have good Plasmon absorption peaks are high and they are noble metals, whereby controlling the shell to the core ratio is proving the effective performance, similarly, the resonance peak can be shifted for the considerably[7].[8] Considering the importance of using Nanofluids titanium oxides, silicon oxides and zirconium carbide on the bases of water where the result shows it has the impact of solar stored energy compared to other Nanoparticles.[9] shows that the nanoparticles were able to absorb 95% of solar energy by investigation the optical properties of Nanofluids containing particles of graphite, copper, aluminium, and silver. The research has shown that the research with the weight percentage of 0.0005 at the height of 5cm of Nanofluids and under the radiation of 20×1000 Wm^{-2} at a temperature of 600k has the performance of 0.7 Said.et.al. [10] it also found the titanium oxides Nanofluids is performing better than aluminium Nanofluids and has better optical property. there has been researching showing that 10PPM of nanoparticles such as nickel is performing better than the copper nanoparticles with the same volume fraction, they have also investigated that Nickel with carbon coated at 40PPM can absorb the 100% energy than compared with the pure nickel[11].

[12] using graphene Nanoplatelets Nanofluids for low-temperature direct absorption solar collector has shown effective result where they have concluded that the suitable weight percentage and temperature of nanoparticles having optical properties and thermal conductivity has a strong absorption band within 200-300nm for the suitable environment used in the direct solar collector.

[13] with the favorable light absorption and heat transfer performance can lead to higher light absorption efficiency, it provides a new strategy to improve the solar energy harvesting using SiO_2/Ag binary fluid.

2. Methodology

There are three main steps in preparing Nanoparticles as they are single step direct evaporation technique, one-step chemical method and two-step method, are used where the single step direct evaporation technique is not used because it cannot be used in large scale industry and it can only be used in the low vapor pressure fluids. The single step Nanoparticles are based on VEROS (vapor evaporation running oil substrate) which was introduced in Japan around 20 years before [14]. One step chemical method is where it is used for the preparation of the stable copper nanoparticles with ethylene glycol [15]. The most common method to synthesise the Nanoparticles is two-step method various methods are used to prepare the nanoparticle and they dispersed into the water with the help of mechanical stirrer or sonication.

2.1 Materials

Commercial spherical shape CuO nanoparticles with 99.8% trace metals basis with a diameter of 15nm are used and the TiO_2 with 95.8% trace of metals basis with the diameter of 15nm is used and the distilled water is used as the deionized water as a base fluid in the Nanofluid. Hydrochloric acid is used to maintain the Ph value of the water.

2.2 Theoretical background

Transmittance to extinction coefficient conversion is done by using below formula

$$I(r) = I_O e^{-\sigma_{ext}\delta} \qquad (1)$$

According to Lambert beer Law, the intensity of the light at the distance 'r' can be written in the above format.

The extinction coefficient is a combination of the absorption and scattering coefficient as in below formula.

$$\sigma_{ext} = \sigma_{abs} + \sigma_{sca} \qquad (2)$$

Experimentally the extinction coefficient can be found by the use of UV- visible spectroscopyFig-1. And by using (1) the extinction coefficient value can be found.

Fig.1 UV-visible spectroscopy

2.3 Optical properties

When the electromagnetic waves come in contact with a non-homogeneity or an obstacle the light will take a change in direction it is due to the scattering of light, formally the light scattering theory is classified into two ways as they are Rayleigh's scattering model and Mie scattering theory.

The Rayleigh's scattering theory is used for the particle size where the α is less than "1" and here in this paper the particle size is less than "1" and so the Rayleigh scattering model is adopted the Rayleigh scattering model was very originally formulated for the small, dielectric(non-absorbing) and spherical particle in shape. The upper limit x given by Kerker is stating that the error for the Rayleigh's scattering model is less than 4% when the $\alpha<0.3$[16, 17].the spherical particle size is small compared to the incident wavelength cause the same uniform dielectric energy around and inside the particle so the uniformity of the dielectric flew cause the possibility for obtaining for its differential scattering cross section. An unpolarised incident equation is given by the Bohren and Huffman [18]

$$I_s = \frac{8\pi^4 N a^6}{r^2\lambda^4}\left|\frac{m^2-1}{m^2+2}\right|^2 (cos^2\Theta + 1)I_i \qquad (3)$$

This equation is used for the small spherical size nanoparticles and as initially said to find the extinction coefficient of the nanoparticles the Rayleigh's scattering Model is adopted which is proposed by [19].

Some of the assumption according to [19] are

1. Independent scattering.
2. All particle are of same size and spherical.
3. Particle is of very small size.
4. Lower concentration(0.6<% v/v)
5. Optical properties of Nanoparticles are of the same property as in bulk material.
6. Nanoparticle is of graphite or metal.

To find the particle size (α) of the nanoparticle is

$$\alpha = \frac{\pi \times d}{\lambda} \qquad (4)$$

Here the'd' is the diameter of the nanoparticle and the λ is the wavelength incident on the obstacle or non-homogeneity, similarly the units of the two terms should be same so the answer will be dimensionless (α). The commonly available dimension for the diameter for the Nanoparticles are around 10-55nm and the wavelength of the sunlight will be at least 10 times higher, so the measurement of the optical property of the nanoparticle basically dependents on two factors as they are absorption and scattering coefficient, and Rayleigh's approximation equation is found several standard papers.

$$Q_s = \frac{4}{3}\alpha^4 \left|\frac{m^2-1}{m^2+1}\right|^2 \quad (5)$$

$$Q_a = 4\alpha \mathrm{Im}\left[\frac{m^2-1}{m^2+2}\left\{1+\frac{\alpha^2}{15}\left(\frac{m^2-1}{m^2+2}\right)\frac{m^4+27m^2+38}{2m^2+3}\right\}\right] \quad (6)$$

The "α" particle parameter basically depend on the mainly the diameter of the nanoparticle and the wavelength of the incident light. The attenuation of the electromagnetic waves caused by the scattering and absorption will transverse the particle medium.

In homogeneous media, the absorption is the dominant one and the extinction coefficient is the sum of the absorption coefficient and scattering coefficient.

$$Q_{ext} = Q_{abs}+Q_{sca} \quad (7)$$

As a result, the above equation can be used to find the scattering efficiency with the help of equation (5) and with the help of equation (6) the absorption efficiency can be found. The sum of the value from the above equation from the absorption efficiency and scattering efficiency are the value of the extinction efficiency which is the imaginary part of the refractive index. In some case, the scattering efficiency will be negligible where the value of the scattering media will not having importance. Considering the particle size parameter the size of the nanoparticle can be calculated as

$$m = \frac{n_{particle}}{n_{fluid}} \quad (7)$$

If the scattering coefficient is at the negligible value then the scattering efficiency is omitted from the below equation (7).

$$\mu_{ext,nano} = \frac{3}{2}\frac{f_v(Qs+Qe)}{D} \quad (8)$$

$$\mu_{ext\ nano} = \frac{3}{2}\frac{f_v \times Q_s}{D} \quad (9)$$

It is said that under the near infrared and infrared zone is absorbed by the base fluids such as water so it is also playing a role in extinction coefficient. Therefore any absorption of the base fluid must be incorporated into the extinction coefficient of the Nanofluids. The following equation is used to obtain the extinction coefficient of base fluid.

$$\mu_{ext,base} = \frac{4\pi k_{base\ fluids}}{\lambda} \quad (10)$$

The $K_{base\ fluid}$ is a complex component of refractive index that varies with the function of the wavelength.

The total extinction coefficient of the Nanofluid is the sum of the extinction coefficient of the nanoparticle and extinction coefficient of the base fluids.

$$\mu_{ext,total} = \mu_{nano\ particle} + \mu_{base\ fluid} \quad (11)$$

In non-scattering homogeneous media, the loss in intensity due to absorption can be calculated by the as the light travels through the medium is given beer-lambert law

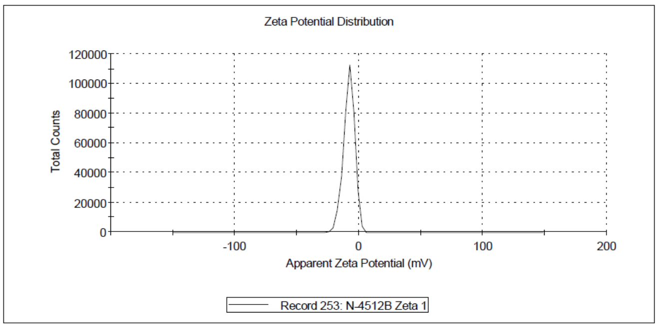
$$\frac{I}{I_o} = e^{-I.\sigma_{ext}} \quad (12)$$

3. Result and Discussion

3.1 stability analysis of Nanofluids

The sample were prepared with the best surfactants for better result of stability for the Nanofluids. The Nanofluids with surfactant were having good stability and it quite dispersed very after the mechanical stirring or sonication. Which help in avoid agglomeration or sedimentation on the bottom of the sample, similarly the particle was not sticking with each other.

A)



B)

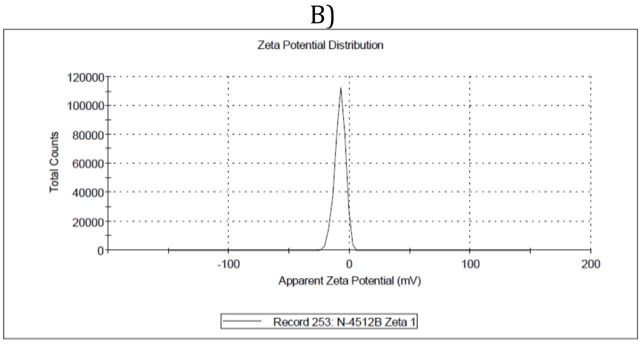


Fig-2 a) Zeta potential of copper oxide(CuO) b) Zeta potential of Titanium Oxides (TiO_2)

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Since the stability is important because most of properties are dependent on the stability. The optical property for the 6PPM Nanofluids were having good absorption so they were selected and then stability analysis, the 6PPM of copper oxide (CuO) is shown in figure (A) with value being -7.87mV and it is quite stable and similarly figure (B) is showing zeta potential for the titanium oxides (TiO_2) as 27.8mV which is good stability value. Usually, the zeta potential of the fluid which is in the range of the ±30mv is considered as good stability [21].

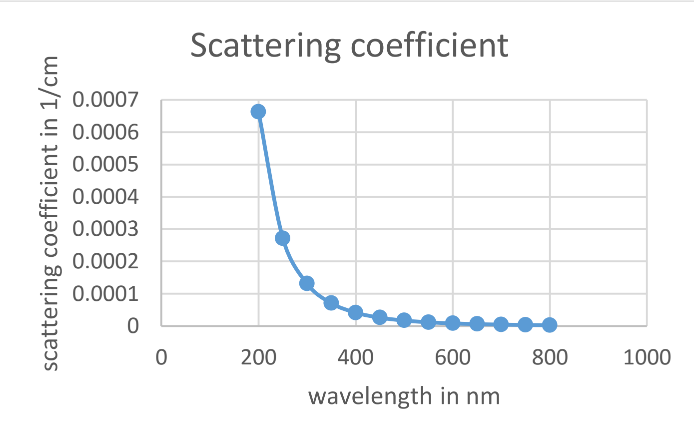
The stability of the colloidal system is determined from the total absorbed force of van der Waals and disposed of electrical double layer between particles which occurs due to Brownian motion. Usually, the charge particles such ions, which are opposite charge in suspension will attract each other and form sedimentation or agglomeration.

3.2 Optical properties of Copper oxides (CuO)

The copper oxide nanoparticles are suitable for the solar thermal systems as many standard papers result are stating and the copper oxides are having to stand out thermal conductivity which will help is absorbing to incident electromagnetic waves and expressed in terms of solar weighted fraction and it shows better results. The less concentration in the Nanofluids is also showing better the stability with a good amount of optical property.

3.2 Optical property of copper oxides (TiO_2) Nanofluids

The copper oxides Nanofluids is performing well where the nanoparticles with a diameter less than 10nm whose scattering coefficient are quite contributing to the extinction coefficient as it is high around the wavelength from 200nm to 500nm as shown in below graph.



. Fig-3 scattering coefficient is calculated by Rayleigh's scattering model.

The absorption coefficient is having an effective impact on the extinction coefficient, unlike the scattering coefficient where the value of the scattering coefficient is almost zero from the 500nm and 800nm wavelength region where the solar spectrum is laying at peak so while they enter the visible region its value turns into zero.

It's noteworthy to take the scattering coefficient is larger near the UV section. The increment of the volume concentration gives a larger scattering coefficient but it can be ignored after the most wavelength as its effect is not significant when the absorption is quite high and scattering value is relatively low.

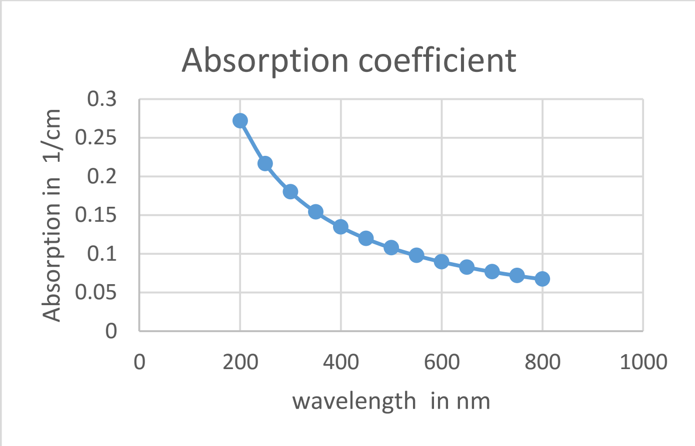


Fig-4 Absorption coefficient is calculated by Rayleigh's scattering Model.

The above graph stats that the absorption rate decrease from 500nm to 800nm region and the slope is reducing from 500nm as before 500nm under the UV region the absorption from the 200nm to the 500nm wavelength is having a high value which will increase the extinction coefficient. The total extinction coefficient will be plotted in below graph as shown.

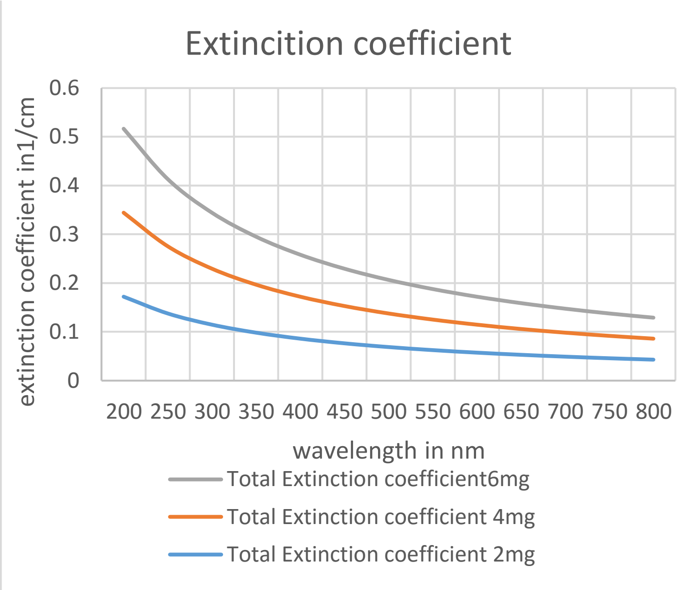


Fig-5 extinction coefficient of copper oxide nanoparticles using Rayleigh's scattering model for 2PPM,4PPM, and 6PPM.

3.3 Optical properties of Titanium Oxides (TiO_2) Nanofluids

The titanium oxides nanoparticles with the 15nm diameter are having quite a good scattering coefficient where the value of the scattering coefficient is high from the wavelength from 200nm to 500nm and it is having a significant role in the extinction coefficient as shown in the figure in 6.

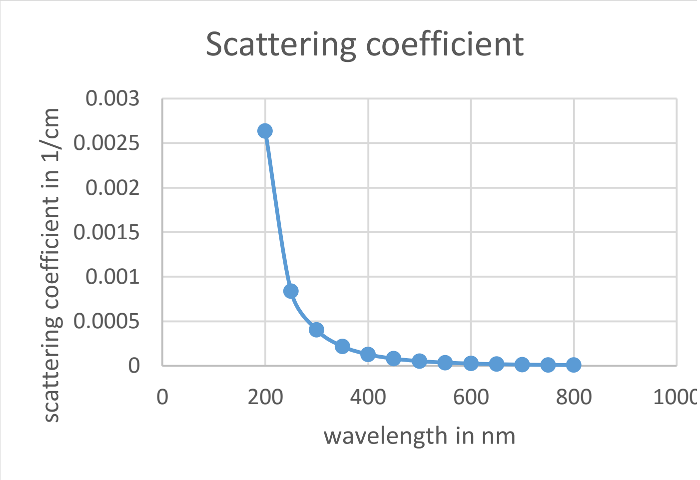


Fig-6 scattering coefficient is calculated by Rayleigh's scattering model.

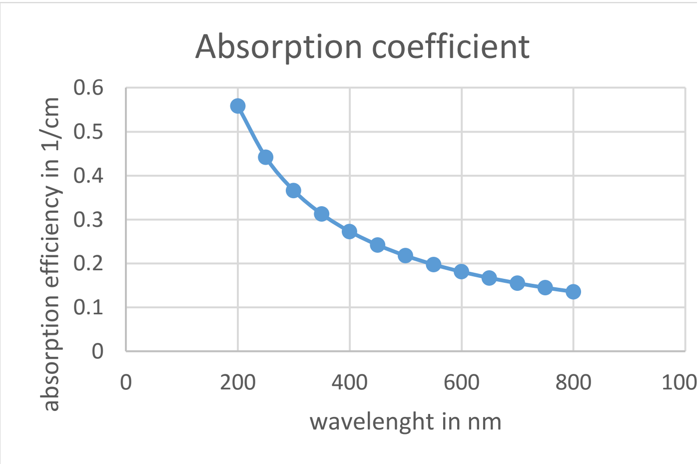


Fig-7 absorption coefficient is calculated by Rayleigh's scattering model.

The absorption coefficient for Titanium coefficient from 0.59 to 0.2 from the wavelength region of 200nm to 800nm and it is showing the titanium oxide is having a high absorption rate. As the curve is decreasing from the wavelength of 600nm as it is approaching near the visible region.

With varying volume fraction of 2PPM, 4PPM and 6PPM the titanium oxides in Rayleigh's scattering model proved to have good extinction coefficient values as shown in the Fig-8 below.

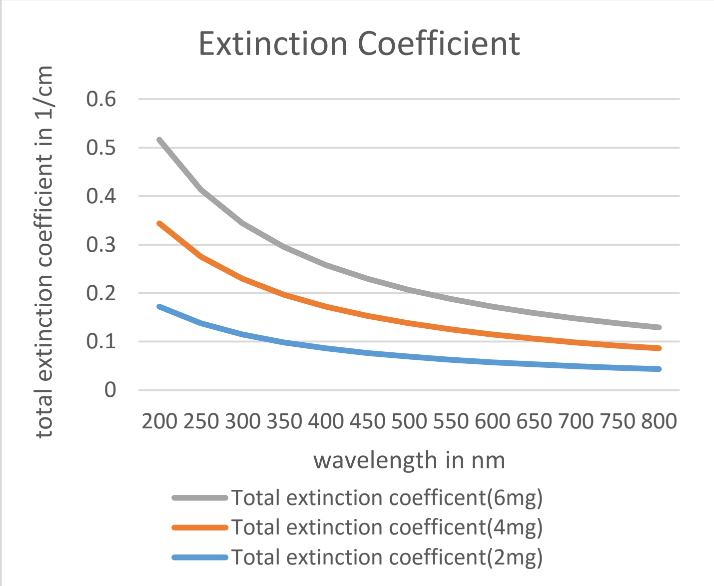


Fig-8 Extinction coefficient of the titanium coefficient, using Rayleigh's scattering model.

3.4 Experimental values in Copper oxides and Titanium oxides

The values of the extinction coefficient of copper oxides and titanium oxides are found using UV-visible spectroscopy.

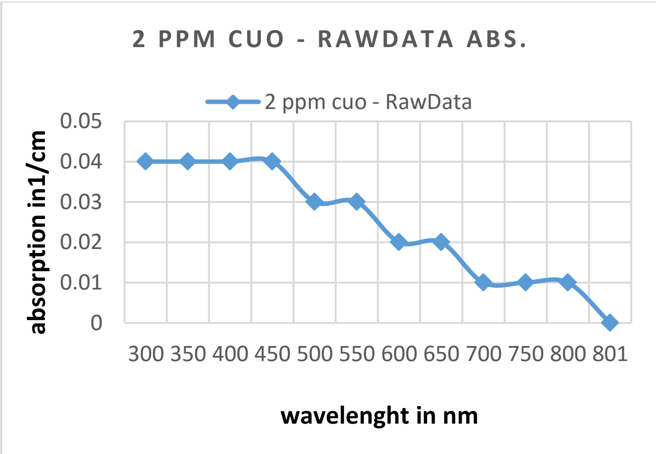


Fig-9 Absorption coefficient from UV-visible spectroscopy

The absorption value in the above graph is showing that copper oxides for from 0.04 to 0.01 around the wavelength in nm from the region of 300nm to 800nm. The level of volume concentration of the copper oxides are showing very good absorption with the electron density is high on the nanoparticle so there is a chance of different dielectric constant value for the nanoparticles

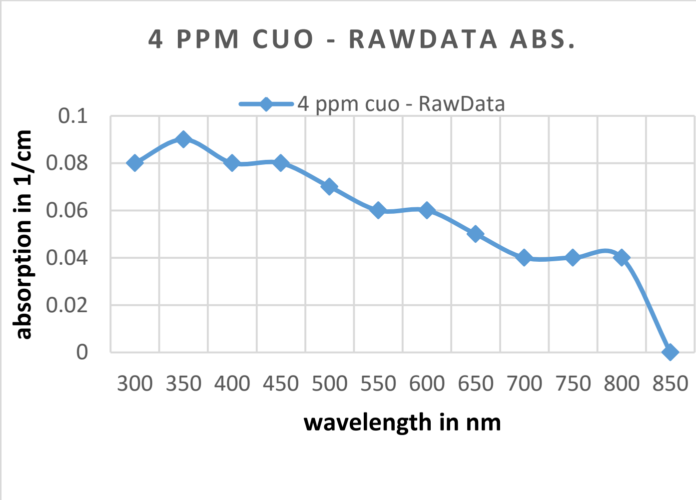


Fig-10 Extinction coefficient for the titanium coefficient for 4PPM.

The extinction coefficient of the copper oxides at 4PPM where from the wavelength region of 300nm to 800nm. Value of the absorption is high or peak at the 350.1nm as the value is about 0.095/cm. the absorption value decrease after 800nm as it is near the visible region.

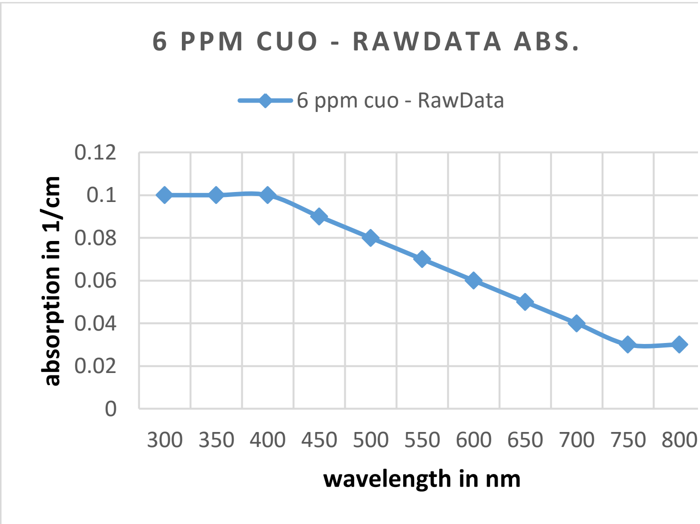


Fig-11 Extinction coefficient of copper oxides for 6PPM.

The extinction coefficient of copper oxides at 6PPM where the value is from 0.1 constant from 300nm to 420nm and it decreases as steep slope from wavelength region of 450nm to 750nm and at the 750nm 0.03 and it ends near the visible region.

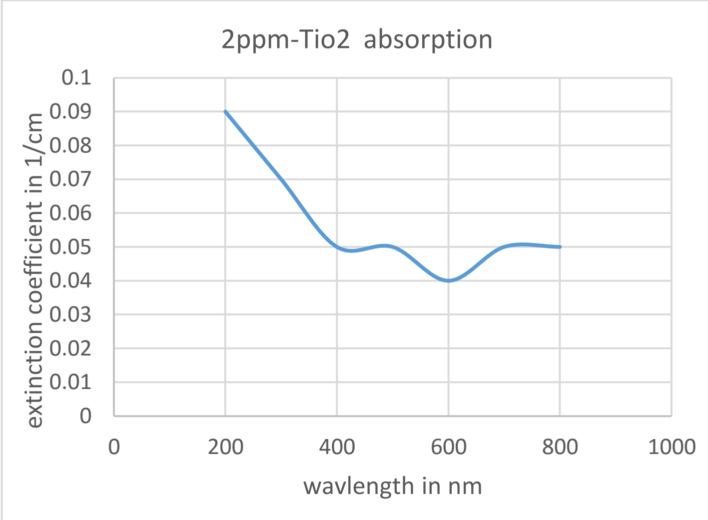


Fig-12 TiO_2 at 2PPM absorption coefficient found using UV-visible spectroscopy.

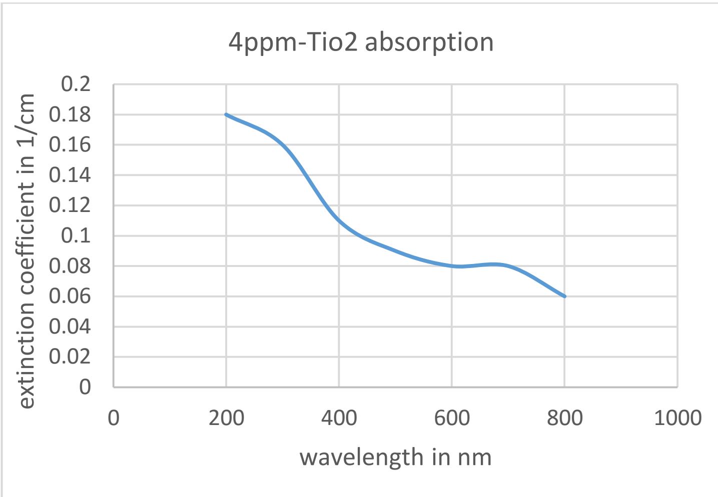


Fig-13 TiO_2 at 4PPM Absorption coefficient found using UV-visible spectroscopy.

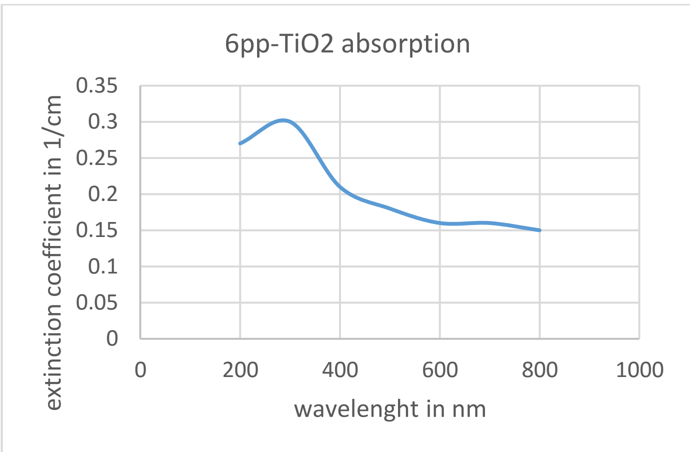


Fig-14 TiO_2 at 6PPM Absorption coefficient found using UV-visible spectroscopy.

Comparing the TiO_2 –water Nanofluids in varying volume fraction as 2PPM,4PPM and 6PPM where the titanium oxides Nanofluid in 6PPM was having good absorption and compare to the copper oxides the titanium oxides is having better absorption. The concentration of 6PPM for both copper oxides and titanium oxides has very good absorption rate within the range of 300nm to 550nm again it concluded that theoretical value is not coinciding with experimental value.

CONCLUSION

The work which was set to find the optical property of Nanofluids in both theoretical and experimentally.it is found that the experimental value is 10 times higher than the theoretical values and as a conclusion it proves that the TiO_2 nanoparticles is having very good optical property compared to CuO nanoparticles with water as the base fluids under which the volume fraction of 6PPM is having desirable result with the good stability. The stability of the nanoparticle can be improved by using desirable surfactant which will reflect in the value of zeta potential.

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