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Phyto-formulation of Stabilized CuO Nanoparticles from Copper Acetate Precursor with the Aqueous Extract of Azadirachtin indica Leaves.

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Abstract: *In recent times, nanoparticles of copper oxide (CuO-NPs) are being considered one of the celebrated and resourceful nanoparticles with their physicochemical characteristics and their vast application in nanoscience. An environmentally modest methodology was embraced in the preparation of aqueous neem (Azadirachtin indica) leaves stabilized CuO-NPs. They were characterized by FT-IR, TEM-ImageJ software that reflects the heterogeneous particles distribution with the setting conditions (image J) of (81.4222) distance in pixels, known distance of 500 pixels, the aspect ratio of 1.0, and unit scale of (0.1628 pixels/nm). Ten nanoparticles were identified and calculated for the mean area, standard deviation, and dispersity indices with the actual mean area of 1245.755 ± 9.4263 nm^2 and mean dispersity index of 1387.78 ± 319.98 (>1; polydispersity). Technically, a zeta potential of -17.8 mV justifies the stability and the dispersion of CuO-NPs in the system. Hence, these outcomes could enhance the characteristics studies, manipulations, and applications of CuO-NPs in the nearest future.*

Keywords: Copper nanoparticles, neem leaves, phytochemicals, FTIR and TEM-imageJ.

1. INTRODUCTION

Nanotechnology centers mostly on the formation, preparation, and control of the structure and size of the particles with measurements below 100 nm [1]. It relates with the principles of producing nanosized particles at a specific dimension making a rising sensation of interest in health, biological and chemical sciences. Nanoparticles completely demonstrate unique characteristics that are dependent on some explicit factors like size, shape, high surface to volume proportion, and direction [2], [3]. Notwithstanding, the categories depending on their sources are metallic and bimetallic nanoparticles, their oxides, and other inorganic sources [4]. Faraday recognized the potentials of the metallic nanoparticles as Mie theorized the quantitative implication of their coloration [5]. Metal nanoparticles are used in catalysis, sensors, and optoelectronics because they rely on their electrical, therapeutic, magnetic, and catalytic potentials [6]. Nanoparticles of copper, zinc, gold, magnesium, silver, and titanium nanoparticles are specifically important with their antimicrobial efficacies (Bacillus subtilis and Staphylococcus aureus), medical applications, dental materials, water treatment, sunscreen moisturizers, and coatings [4]. As of late, metal, metal oxides, clay, silicate, and polymer nanoparticles have been integrated and utilized in a few applications. The magnitude of their sizes and the high surface region has improved their utilization and expansion in material science [7]. Their properties are size-related concerning the nature of their immediate environment. Hence, the necessary and desired properties can be acquired by changing the surroundings of nanoparticles which offer higher reactivity and yet may bring about bunch arrangement which will affect their fundamental properties [8]. Copper-based nanoparticles especially retain imminent applications in medicine (antimicrobial agents), nanofluids, lubricants, and conductive materials [9]. The merits of copper-based nanoparticles are because of the lower cost of copper, the physicochemical stability, and the simplicity of blending with other polymers [10]. Various outcomes have been achieved concerning the combination and reliability of copper nanoparticles. However, it will be necessary to generate information that will bridge the copper oxide characteristics with various stabilizing systems at different conditions. Phyto-synthesis illustrates the production of nanoparticles in reaction with plant phytochemicals in preventing possible agglomeration of the nanoparticles [1]. The plant Phyto-constituents integrate the proteins with organic catalysts that are engaged with the normal decrease of the substrates. Some selected plant extracts have successfully been employed as reductants in the production of active nanoparticles [11]. This approach could be profitable over the microbial method because of the maintenance and stability of the plant cells and tissues. It has been indicated that numerous plants can effectively take up and bio-reduce metal particles from soils and matrices during detoxification procedure and treatment forming insoluble complexes with the metal particle as nanoparticles [12]. For instance, the extract of magnolia leaf was applied for the production of copper nanoparticles as capping and reducing agent [13]. Utilizing $CuSO_4$ as a substrate, copper nanoparticles were established to be produced with tamarind juice, milk, butter, and lime juice as stabilizing or capping agents in an acidic system [14]. Artabotrys odoratissimus has been likewise adopted as a reducing and capping agent for the copper nanoparticles with CuSO4 at 95°C, to the particle size range of 109 to 135 nm [15]. The deployment of nerium oleander with L-ascorbic acid as a reducer and stabilizer has been accounted for in a publication [16]. Datura metel leaf extract was used at room temperature to produce nanoparticles [17]. Processed starch from potato has been accounted for as a capping agent for copper nanoparticles with the influence of an anti-oxidant (L-ascorbic acid) and a catalyst (NaOH) [18]. There is tremendous enthusiasm for metal nanoparticles with regards to their unpredicted physic-chemical properties uncovered at the nanoscale level. Factors in terms of as pH, reaction time, the precursor's concentration, temperature, and catalyst do eventually affect their physico-chemical parameters [1]. The active components of aqueous neem leaves extract as azadirachtin, Nimbin, and trace others could thereby enhance the stability and preparation of copper nanoparticles [19]. In this work, the synthesis, selective characterizations, and dispersion of the oxide of copper nanoparticles with an aqueous fraction of neem leaf extract as an organic stabilizing agent was evaluated.

2. EXPERIMENTAL

Material Copper Nitrate (Precursor), deionized water, fresh neem leaves, magnetic stirrer, blender, burette, beakers, magnetic stirrer, and heater.

2.1 Neem leaves aqueous extract

Some fresh matured leaves of neem leaves were harvested and washed with deionized water. 25g of the fresh and washed leaves were blended with heating in deionized water (100 ml) in a beaker. The mixture was heated at 50ºC for 3 min. under a reflux system and reduced pressure in a rotary evaporator to produce a greenish color extract. Then the extract was cooled and centrifuged at 10000 rpm and filtered. The filtrate was filled in a 50ml burette capacity.

2.2 Synthesis and precipitation of CuO-NPs

20 mg of Copper nitrate was weighed into 50 ml deionized water and with the temperature of the magnetic stirrer at 65ºC and continuous stirring, the aqueous extract of the neem leaves in a burette was being added dropwise into the solution of copper nitrate till light green color forms indicating the precipitation of copper in water. The mixture after 24 hours was further centrifuged at 4000 rpm for 3 min. The recovered and dried precipitate at 100ºC for 2hours in an oven and preserved in an airtight container for subsequent uses.

2.3 Characterization

Copper nanoparticles dispersed in the neem leave aqueous extract was characterized with UV-visible spectrometry, FTIR, polydispersity index, zeta potential, electron microscopy (TEM) - image J, and descriptive statistics of the nanoparticles. UV-visible spectrophotometry UV absorbance spectroscopy has been an exceptionally helpful method for identifying the chemical nature of the metallic NPs because the absorbance position and wavelength of the spectra are responsive to the molecule size. At 217 nm, the maximum absorption of azadirachtin was ascertained [20].

2.4 FT-IR

The FT-IR spectra of both the neem aqueous extract and the CuO-NPs were analyzed.

2.5 Dispersity index of CuO-NPs with aqueous neem extract

This is the measure of the heterogeneity of particle sizes in a mixture. It was estimated by (PDI=Standard deviation × 100%) [21].

2.5 Zeta potential determination

This is an electrostatic charge on molecules that detect and anticipate the associations between particles in suspension. This was conducted by laser doppler electrophoresis technique [22].

2.6 TEM-image J analysis

Conditions of 81.4222, definite distance of 500 nm, pixel aspect ratio of 1 and scale of 0.1628pixels per nanometer were applied.

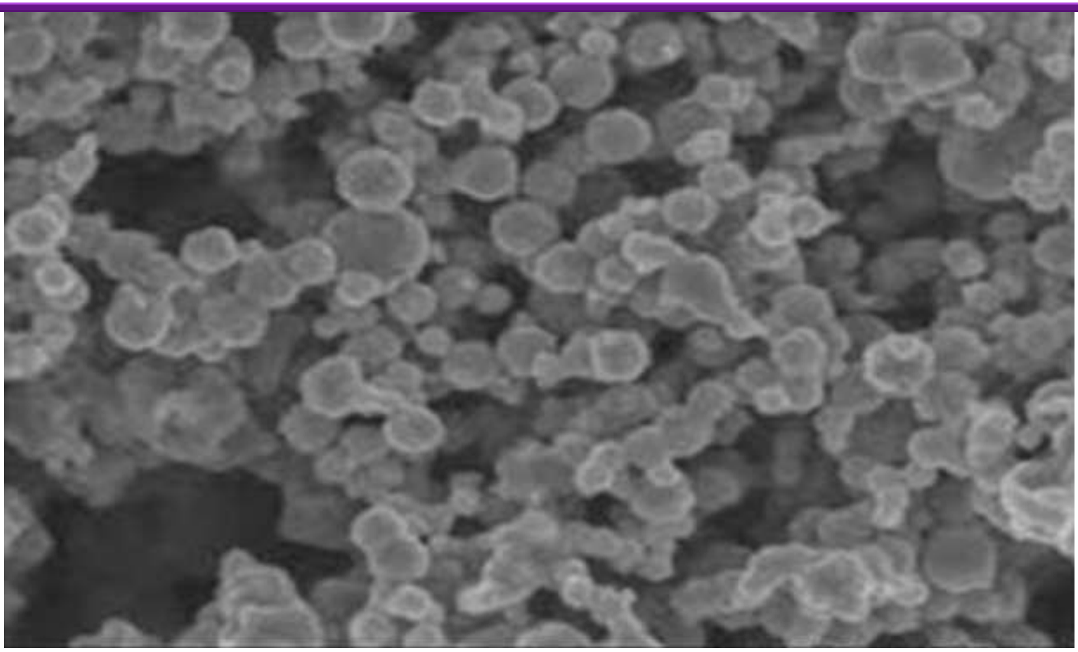

Figure 1. The transmission electron microscopy (TEM) of the precipitated CuO-NPs in aqueous extract of neem

2.7 Descriptive statistics

The mean areas, standard deviations, and the dispersity of ten repeated CuO-NPs with neem leave aqueous powder extract was estimated using Excel RealStats-2003.

3. RESULTS AND DISCUSSION

The scheme below depicts the process adopted in generating CuO-NPs from copper acetate precursor against the neem leaves aqueous extract.

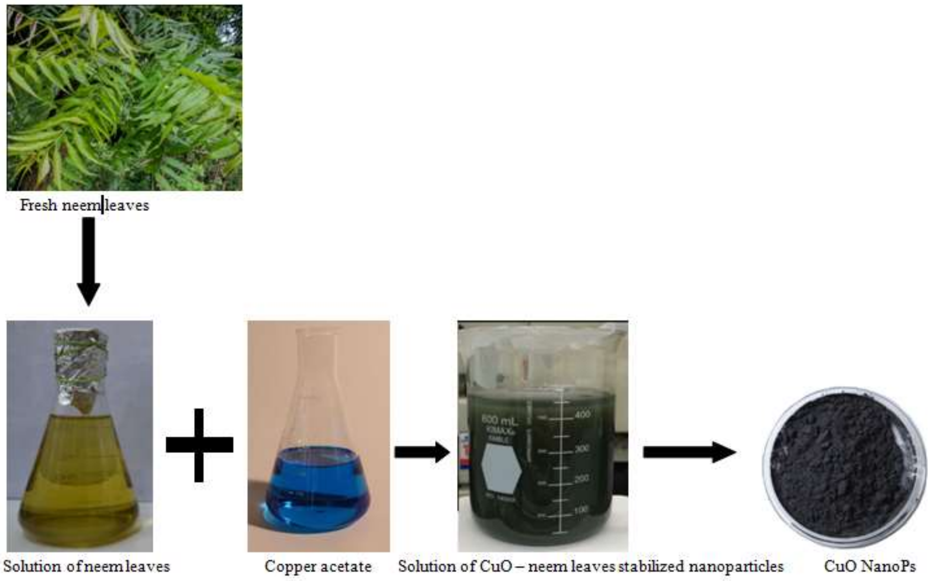

Figure 2. Synthesis of CuO neem leaves stabilized nanoparticles

The UV-spectrum of the neem leaves extracts exhibited a pronounced absorption peak at 217 nm, which is attributed to the azadirachtin active component with the leaves. Similarly, the absorption peak observed at 533 nm can be confidently assigned to the formation of CuO-NPs as the absorption band for CuO-NPs has been reported to be between 500-600 nm [7].

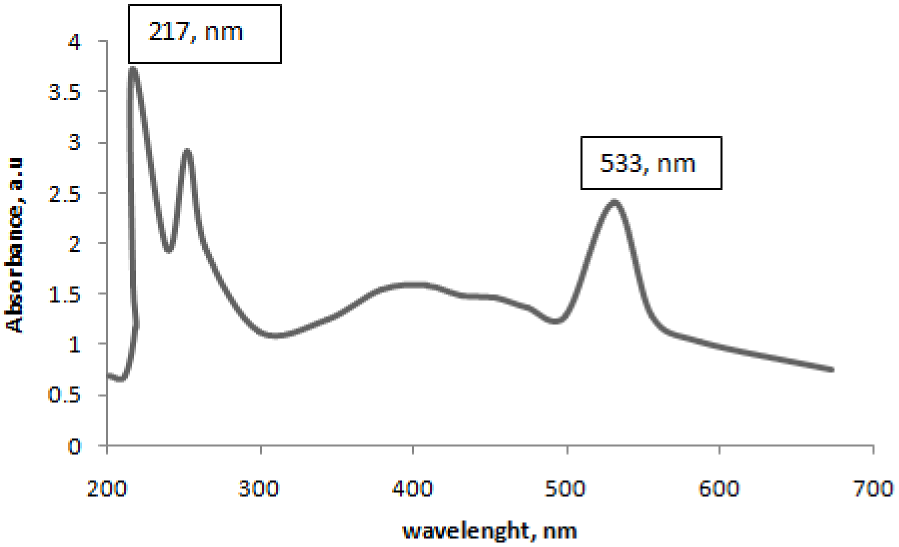

Figure 3. UV absorption spectrum of azadirachtin and nimbin in aqueous neem leaves

IR- spectrum with the leave aqueous extract in Figure 4A, reveals the availability of O-H stretching at 3,260 cm^{-1}, C=C bond at 1620 cm^{-1}, C-H stretching at 2685 cm^{-1}, and substituted methyl group at 1,103 cm^{-1}. An observed band at 2,191 cm^{-1} is for the stretching by an ester carbonyl group, at 1,665 cm^{-1} for C=N and 1,525 cm^{-1} for C=C stretching vibration with the aromatic conformation of the chlorophyll. The identified bands are directly accredited with the activity of terpenes and chlorophyll in the aqueous Azadirachta indica leave. Figure 4B shows the FTIR spectrum of the freshly prepared cupric oxide sample material. The bands at 2,937 and 3,291 cm^{-1} belong to the symmetric and asymmetric stretching vibration of the O-H bond respectively. The band appearances at 649 and 1,116 cm^{-1} signify dissimilar modes of bending vibration of the Cu-O bond. The stretching mode of vibration with the Cu-O bonding at 638 cm^{-1}. Similarly, the FT-IR output of Phyto-synthesized nanoparticles of copper oxide encapsulated with the aqueous leave extract of neem (Azadirachta indica) as stabilizing and reducing agent in Fig 4C declares a band at 3,636 cm^{-1} by O-H stretching from alcohols and phenols. 1,431 cm^{-1} is the N-H group as the primary amine. 1,200 cm^{-1} are C-O with phenol, acid, and flavonoids. 698 cm-1 connects with the metallic copper that was bound and saturated with either or jointly with the phenolic acid, flavonoids, or carboxylic acid found in the aqueous extract of the leaves.

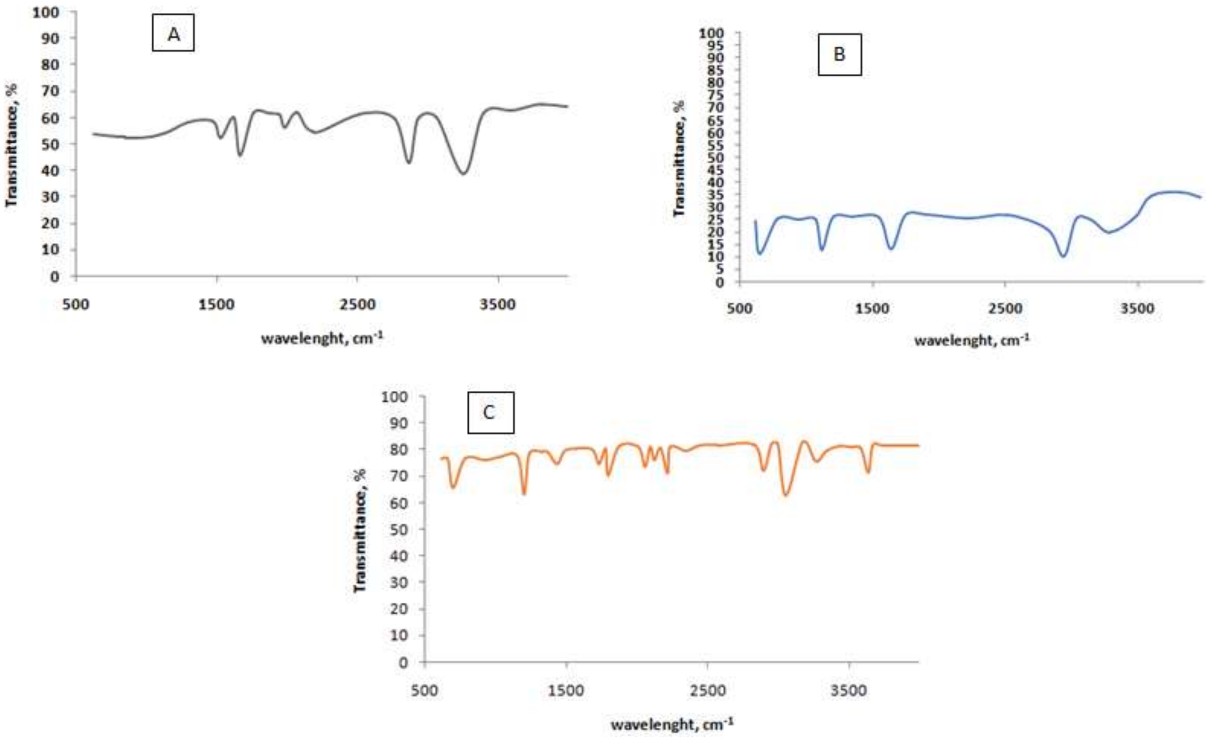

Figure 4. FT-IR of the neem leave aqueous extracts (A), cupric oxide (B) and CuO-NPs stabilized with aqueous neem leaves extract (C).

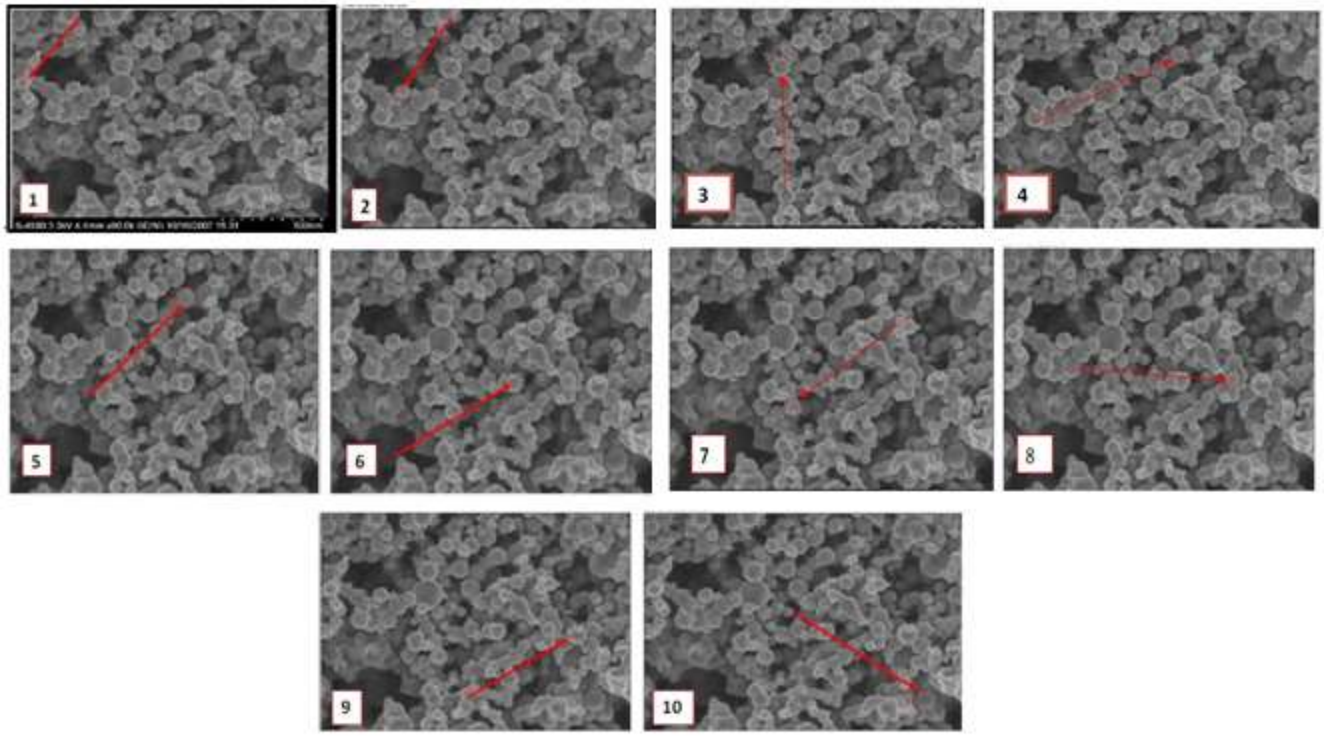

Figure 5. TEM-imageJ of ten (10) identified CuO-NPs stabilized with neem leaves aqueous extract.

The area distributions of the individual CuO neem extract stabilized nanoparticles were statistically justified in Table 1. Thence, the actual mean area of the nanoparticles was estimated to be 124.58 ± 9.43 nm^2, where 9.43 nm^2 is the definite standard deviation across the particles. The dispersity index of the entire nanoparticles against the stabilizing extract is 1387.78 ± 319.98, where 319.98 is the level of deviation in this regard. This established the nature of the nanoparticle distribution to be polydispersed and heterogeneous [23].

Table 1. Descriptive statistics of the aqueous neem leaves stabilized CuO-NPs.

S/N	Average Mean area (nm^2)	Standard Deviation (nm)	Dispersity Index
1	138.643	16.585	1658.5
2	125.500	14.235	1423.5
3	122.382	15.228	1522.8
4	114.080	9.989	998.9
5	118.542	9.979	997.9
6	130.603	15.380	1538.0
7	128.832	13.352	1335.2
8	129.282	11.884	1188.4
9	131.387	20.339	2033.9
10	106.504	11.807	1180.7
Actual mean value	124.5755 ± 9.4263		1387.78 ± 319.98

Moreover, the dispersion with the Phyto-reduced CuO-NPs was affirmed by the zeta potential with the level of the electrostatic interactions amongst the adjoining, correspondingly charged nano-particles. The high size of zeta potential worth shows the incredible steadiness of NPs24. In this case, the potential (zeta) with the aqueous neem extract stabilized CuO-NPs were suspected as a sharp peak at -17.8 mV, suggesting the high stabilities of Phyto-synthesized NPs under the operating conditions.

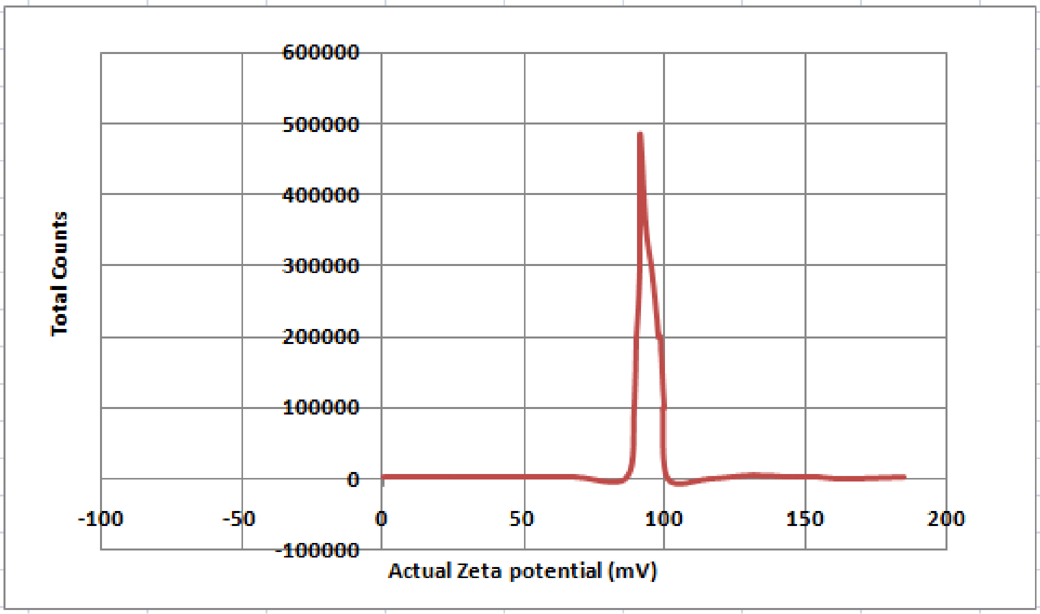

Figure 6. Zeta potential distribution of synthesized neem stabilized CuO-NPs

4.0 CONCLUSION

Copper nanoparticles are useful and valuable metal nanoparticles. They have been successfully prepared with a reduced and stabilizing potential of phytochemicals with Azadirachta indica aqueous leaves extract which is cheap, simple, and environmentally balanced. The magnitudes of the average mean area with the polydispersity percentage factor with the generated CuO-NPs to be in a heterogeneous stabilizing system. Similarly, the utilization of neem leaves aqueous extract as a reducing agent against the copper ion was optimally enhanced in terms of cost, synthesis, and sustainability. Nanoparticles of this nature are much safer and friendly than conventional chemical methods.

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