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Green synthesis and characterization of copper nanoparticles using *Eryngium campestre* leaf extract

M. Khodaie, N. Ghasemi*

Department of Chemistry, Arak Branch, Islamic Azad University, Arak, Iran

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Metal oxides nanoparticles are increasingly used in various fields, including medical, food, consumer, health care, and industrial purposes, due to their unique physical and chemical properties, their unique size-dependent properties make these materials efficient for many areas of human activities. So in the past few decades, Nanotechnology has become an attractive research area. Synthesis of nanoparticles by chemical and physical methods has many disadvantages, such as need advanced equipment, solution instability and use harmful and toxic chemicals compounds during the synthesis that will have many harmful effects on environment and humans. Bio synthesis of nanoparticles compared to the other synthesis routes is more efficient, because plant sources are more available and affordable in addition, compounds which are used in this method are eco-friendly and non-toxic. The present study aims to optimize and biosynthesize copper nanoparticles using an aqueous extract of *Eryngium campestre* (Sulang) plants and copper nitrate. Effective factors on the formation of nanoparticles, including pH, salt concentration of copper nitrate, time and temperature were studied and optimized using ultraviolet spectrophotometer. Particle size and stabilizing chemical compounds of the obtained nanoparticles were investigated by VEGA TESCAN scanning electron microscope (SEM), Fourier transform infrared spectroscopy (FTIR), (Bruker optics Germany), X-ray diffraction spectroscopy (XRD), (Philips X-Ray Diffraction), and Energy-dispersive X-ray spectroscopy (EDX).

According to the results, the optimum conditions for synthesis of copper nanoparticles was pH = 6, t = 35 ° C for 80 minutes, and the average size of the nanoparticles was obtained between 50 - 60 nanometers.

Keywords: green synthesis; Copper Nanoparticles; Eryngium Campestre

INTRODUCTION

In the last few decades, synthesis of nanoparticles and research about them have attracted many attentions of scientists in various fields of applied sciences [1]. Nanotechnology is the study and development of materials at atomic, molecular and macromolecular scales that leads to manipulate the structures and convert them to 1–100 nm scales [2]. From this definition, it is clear that quantum mechanics effects have a great importance [3]. In recent years, using metal nanoparticles have found many applications in new technologies, metal nanoparticles are of interest because of their unique features such as Surface Plasmon Resonance[4], optical properties [5], suitable catalytic performance[6], and high Surface-area-to-volume ratio and controlled porosity [7], etc. Metal nanostructures due to their outstanding size dependence properties are among the most studied nanomaterials. In particular, metals nanoparticles show an interesting optical behavior, known as surface plasmon resonance [8,9]. Plasmon resonance is the collective oscillation of conduction electrons and occurs when the frequency of incident light matches with the resonance frequency of the free electrons[10]. For example, copper nanoparticles due to their quantum size and wide high effective surface area have unique physical and chemical properties that play an important role in today's industrial world. Due to the conductor and semiconductor ability this substance has many applications in electronics and electrical industries. In general, the approaches to synthesis these nanoparticles can largely be divided into two categories; top-down and bottom-up techniques. In the first method, a piece of the base material is achieved during a physical processes such as milling, and in the second method, the nanoparticles synthesized through electrochemical methods, vapor phase synthesis, photolysis, chemical reduction, etc. [11]. These methods are very expensive and many harmful, toxic and very hazardous chemicals compounds are used to synthesis nanoparticles [12] which causes some biological and environmental issues [13]. For this reason, scientists and nano-chemists are looking for new and alternative, eco-friendly methods for the synthesis of nanoparticles [14]. Nowadays, Nanotechnology has been significantly changed in the synthesis of nanoparticles. Using plant and plant extracts can be a suitable choice for the synthesis of nanoparticles in large scale [15] and it is also very environmentally-friendly [16]. some advantages of using plants in the

* To whom all correspondence should be sent:
E-mail: n-ghasemi@iau-arak.ac.ir

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synthesis of nanoparticles is ease of using, biosecurity, a wide variety of effective metabolites in ion reduction, produce high purity nanoparticles, low response time and completeness reaction. Use of living organisms, such as microorganisms (such as fungi, bacteria and yeasts), as well as macroorganisms (such as plants, algae, etc.) as an intermediary agent in the synthesis of nanoparticles from inorganic compounds, are another way besides chemical and physical methods for nanoparticles production [17,18].

Remarkable growth in this up-and-coming technology has opened new applied and fundamental frontiers. Nanotechnology has a rapid development in number of areas such as health care, cosmetics, food and feed, environmental health, mechanics, optics, biomedical sciences, chemical industries, electronics, drug-gene delivery ,space industries, energy science, optoelectronics, reprography ,catalysis, , single electron transistors, nonlinear optical devices light emitters, , and photo electrochemical applications [19,20].

In the present study, the bio-synthesis of copper nanoparticles by *Eryngium Campestre* leaf extract has been investigated. The reason for this choice is that the *Eryngium Campestre* extract contains flavonoid phenolic compounds, Gallic acid, quercetin, natural antioxidants, which can be used as reducing agents for copper ions. In this study, the effects of concentration of copper nitrate and pH, temperature and time reaction, were investigated, eventually, synthesized nanoparticles were evaluated by ultraviolet (UV-vis) spectroscopy, scanning lectron microscopy (SEM), X-ray diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDX) and infrared Fourier transform (FTIR) spectroscopy.

EXPERIMENTAL DETAILS

Materials

Fresh leaves of Eryngium Campestre plant, copper nitrate (from Merck Co. , with a purity of 99.99%). Hydrochloric acid solution (0.1N) and Sodium hydroxide solution (0.1N) for pH adjusting .Doubly distilled water was used in all the experiments.

Collection of leaves plant

In this study, fresh leaves of Eryngium Campestre have been collected from Mazandaran-Iran suburbs, washed with deionized water several times, dried and powdered for further experiments (Figure 1).

Preparation of leaf extract

All glass wares have been properly washed with distilled water and dried in oven. 10 g of dried leaves were dipped in a conical flask, and bring to a final volume of 100 mL with deionized water .Then the resulting mixture was boiled in a water bath for 20 minutes and the obtained extract was cooled and filtered using filter paper and it was kept at 4 °C for later use [21].

Fig. 1. The fresh leaves of *Eryngium campestre.*

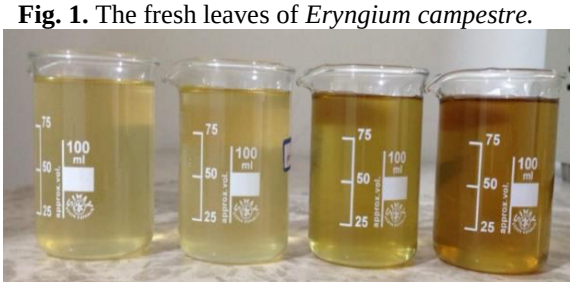

Fig. 2. Green synthesized copper nanoparticles using (*Eryngium campestre*) leaf extract.

Synthesis of copper nanoparticles

For green synthesis of copper nanoparticles (CuNPs), 10 ml of extract was mixed with 90 ml aqueous solution of copper nitrate (5 mM) and stirred continuously for 15 min at room temperature (25°c), the color of solution became darker (Figure 2) which is related to surface plasmon resonance of copper nanoparticles, and it is an evidence for the successful synthesis of these nanoparticles [22]. Then the solution was centrifuged with stirring rate of 10,000 rpm for 20 min and dispersed in double distilled water to remove any unwanted biological materials. Synthesized nanoparticles were confirmed by UV-Visible spectroscopy in the range between 500-700 nm. In this study, the experimental parameters (concentration of nitrate salt, pH, temperature and time) were investigated and optimum conditions were determined using absorption spectra taken by spectrophotometer.

Presence of copper nanoparticles were investigated by different techniques such as(UV-vis) spectrometry, scanning electron microscope (SEM), X-Ray Diffraction (XRD), Energy-dispersive X-ray spectroscopy (EDX) and Fourier transform infrared spectrometry (FTIR).

Effective parameters on synthesis rate, size and shape of copper nanoparticles. Optimization of copper nitrate concentration

In this study, different solutions of copper nitrate with different concentration were prepared in order

to investigate the effect of copper nitrate concentration. 10 ml of extracts were added to 45 ml of various concentrations of copper nitrate solutions (1-3-5-10 mM) at room temperature (25˚C). After 30 minutes, spectrophotometer spectra were taken from each and it was observed that absorption increased with concentration increasing.

Analysis were performed for all samples and the maximum absorption were observed at the wavelength range of 500-700 nm using UV–visible spectrophotometer, then selected as the optimum concentration.

pH optimization of the reaction

pH is an important parameter which is affected on copper nanoparticles reduction. Shape and size of the copper nanoparticles were dependent on pH of the solution. In order to optimize the pH value, five solutions were prepared. 10 ml of extracts were added to 90 ml of copper nitrate solutions at room temperature (25°c) for 30 minutes with optimal concentration then set the pH of the solutions (3, 5, 6, 7 and 9) by using 0.1N HCl and 0.1N NaOH.

Absorbance of the resulting solutions were measured using UV-vis spectroscopy.

Temperature optimization of the reaction

Although, it is possible to achieve copper nanoparticles using herbal extract at room temperature, but the reaction temperature was also evaluated to obtain better nanoparticles. So five solutions were prepared by mixing 10 ml of extract and 90 ml of copper nitrate with optimal concentration and pH then separately reached up to temperatures of 25°C, 35 °C, 50 °C and 60 °C for 30 minutes. The absorbance of the resulting solutions were measured by UV–vis spectra

Optimization of time

In order to optimize the time, some solutions with optimal concentration, pH and temperature were prepared. The absorbance of the solutions was measured using UV–Vis spectroscopy then the optimum reaction time was selected.

UV–VIS spectra analysis

UV–vis Analysis is an important way to confirm the formation of metal (Cu) nanoparticles in colloidal solutions. UV-Vis measurements were carried out using Perkin-Elmer spectrophotometer from 500-700 nm.

XRD analysis

The powder X-ray diffraction (XRD) analysis was performed by philips model pw1730, powder diffractometer using monochromatic Cu, radiation ($\theta = 1.5406$ Å) operating at a voltage of at 40 kV and a current of 25 mA at room temperature(25°c). The diffraction angle is from 2θ in the range of 10°–80°. Different phases available in the synthesized samples were determined by X′ pert high score software with search and match facility. XRD patterns were analyzed to determine peak intensity, position and width. Full-width at half-maximum (FWHM) data was used with the Scherrer's formula to determine mean particle size [23].

Scherrer's equation [24,25].

$D = K\lambda / \beta \cos \theta$

Where:

D = is the crystallite size of CuNPs.

λ = is the wavelength of x-ray source (0.1541 nm) used in XRD.

β = is the full width at half maximum of the diffraction peak.

K = is the Scherrer constant with value from 0.9 to 1. θ = the Bragg angle.

Morphology

The morphology and copper nanoparticles size were investigated by means of scanning electron microscopy (SEM). A thin layer of Au was coated to make the samples conductive. Then the samples were characterized at an accelerating voltage of 20 KV carried out by VEGA TESCAN SEM.

EDX analysis of copper nanoparticles

To evaluate the formation of copper nanoparticles Energy-dispersive X-ray spectrometry were used. EDX observations were carried out by VEGA TESCAN. In the X-ray range the energy of a single photon is just adequate to produce a measurable voltage pulse X-ray, the charge pulse is converted to a voltage pulse by a charge-sensitive preamplifier. A semiconductor substance is used to detect the x-rays together with processing electronics to analyses the spectrum [26].

FTIR analysis

The infrared (FT-IR) spectra of CuNPs was carried out through the potassium bromide (KBr) pellet (FTIR grade) method. The chemical composition of the synthesized copper nanoparticles were studied by Bruker alpha-series FTIR spectroscopy.

RESULTS

UV–VIS analysis

Cu nanoparticles show the maximum absorbance at 570 nm. The absorption bands of copper nanoparticles have been reported in the range of 550–600 nm [27,28]. Appearance of this peak, assigned to the Surface Plasmon Resonance band, has been recorded for various metal nanoparticles with different size range[29]. Formation of Surface Plasmon Resonance is due to the particle shape, size

and interaction with the medium and the degree of charge transfer between the particle and the medium.

Concentration of copper nitrate

As we mentioned above, absorption increased when concentration increased, but the absorption reduced at higher concentration, which is related to the nanoparticles aggregation and reduction of the synthesized nanoparticles, so the optimum concentration of 5 mM was selected. (Figure 3).

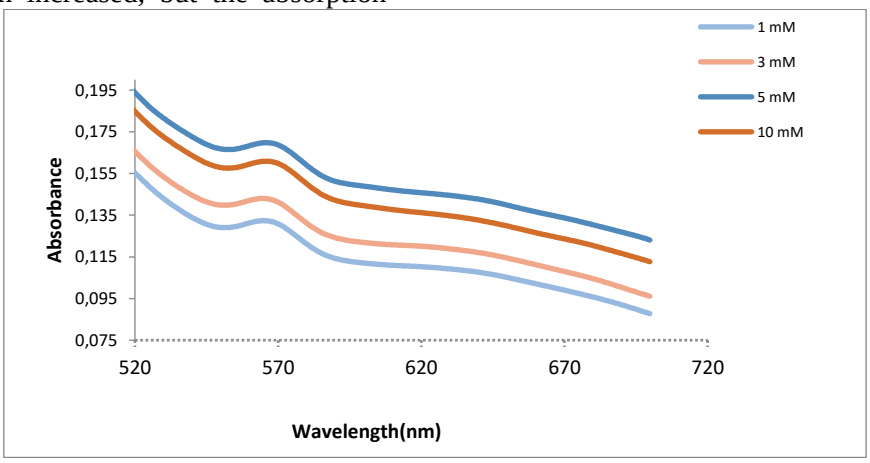

Fig. 3. Effect of copper nitrate concentration on green synthesized CuNPs using (*Eryngium campestre*) leaf extract (temperature =25°c, time = 30 minutes).

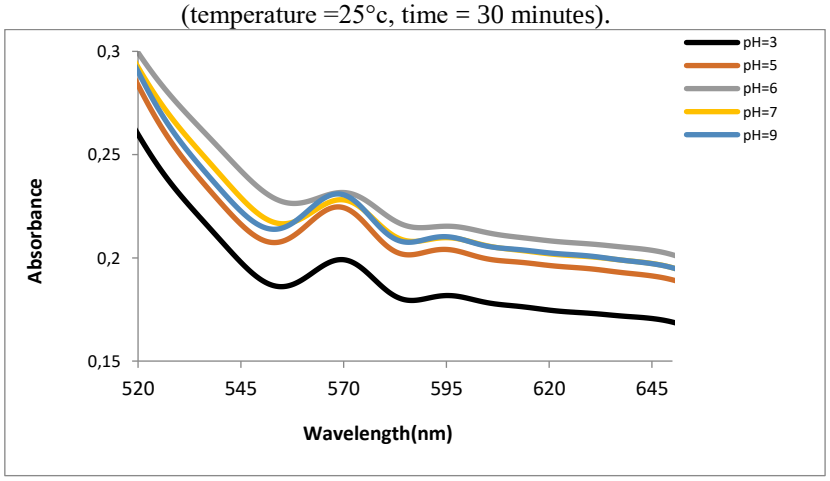

Fig. 4. Effect of pH on green synthesized CuNPs using (*Eryngium campestre*) leaf extract (copper nitrate concentration = 5mM, pH=4, temperature =25°c, time= 30 minutes).

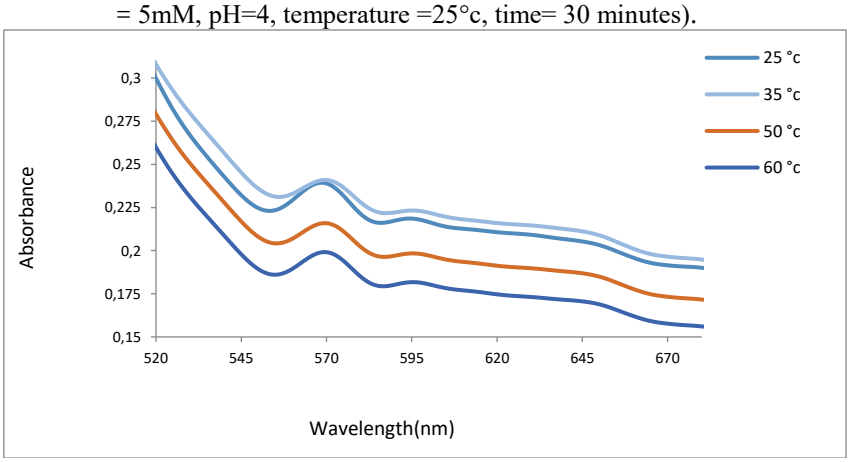

Fig. 5. Effect of temperature on green synthesized CuNPs using (*Eryngium campestre*) leaf extract (copper nitrate concentration =5mM pH =6, time= 30 minutes.

pH

Initially, the acidity of each solution was about 4, after analyzing, it was found that the absorption changed slightly at PH = 3, but, while pH increased to 6, the absorption of the solution increased, which is related to the amount of the synthesized

nanoparticles in the solution. Therefore, pH =6 was considered as optimum pH (Figure 4).

Temperature

It was observed that with increasing reaction temperature, the adsorption of surface Plasmon resonance increased significantly, but this process continued up to 35 °C and absorption decreased at higher temperature, so 35 °C was selected as optimum temperature (Figure 5).

Time

To study the effect of time on the reaction completion, the reactions were monitored from 5 to 120 min. It was observed that absorption was very low in the first 5 minutes, but there have not been significant changes after 30 minutes, so optimum time of 30 minutes was selected.

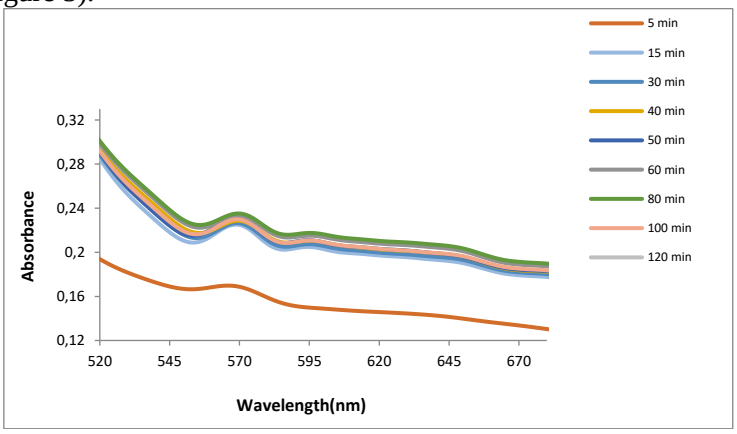

Fig. 6. Effect of Time on green synthesized CuNPs using (*Eryngium campestre*) leaf extract (copper nitrate concentration =5mM pH =6, temperature=35°C).

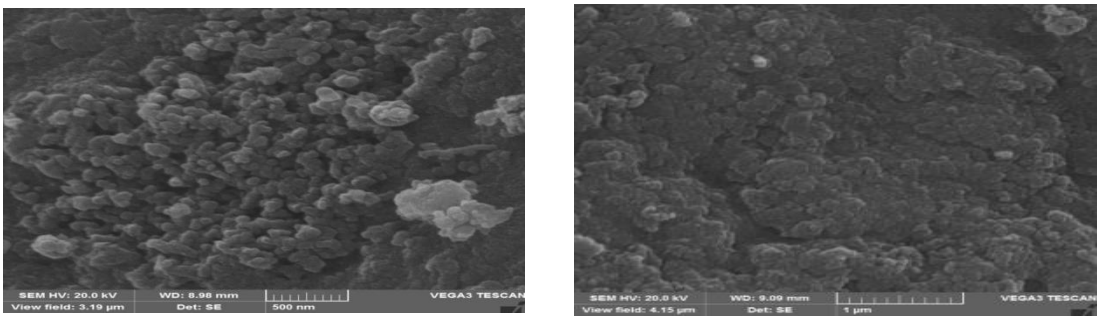

Fig. 7. SEM micrograph of synthesized CuNPs using (*Eryngium campestre*) leaf extract at two magnifications (copper nitrate concentration =5mM, pH =6, temperature=35°c, time= 35 minutes).

SEM analysis

Due to the Surface Plasmon Resonance, copper nanoparticles show the highest absorption peaks value. The images were estimated 1 µm–500 nanoscale magnitudes which clearly show the average size of diameter ranges between 50 and 60 nanometers (Figure 7).

EDX Analysis

Figure 8 shows the EDX spectra of CuNPs synthesized at room temperature to confirm the presence of copper atoms in copper nanoparticles. The presence of the copper can be observed in the graph which is obtained from EDX analysis. The EDX analysis showed signs of carbon, oxygen and Nitrogen. These peaks belong to the bio-molecules in the plant extracts. The presence of oxygen's peak along with the Cu signal, suggested that the CuNPs

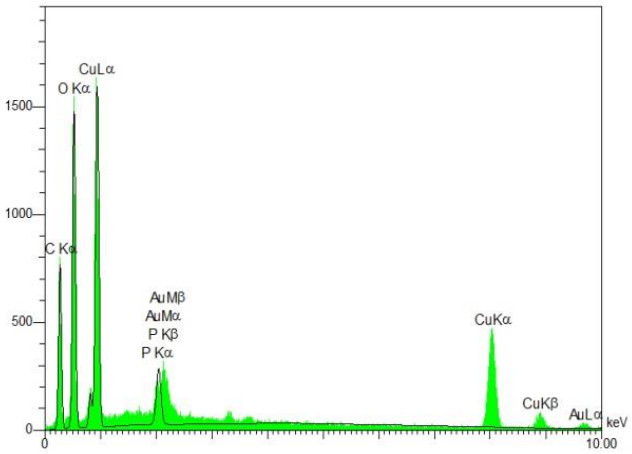

Fig. 8. EDX analysis of synthesized CuNPs using (*Eryngium campestre*) leaf extract (copper nitrate concentration =5mM pH =6, Temperature=35°c, time= 80 minutes).

were capped by phytoconstituents through oxygen atoms and the presence of trace amount of carbon demonstrated the involvement of plant phytochemical groups in reduction and capping of the synthesized CuNPs [30,31].

XRD

Sharp peaks in this pattern confirms the synthesis of copper nanoparticles and it is consistent with the standard peak of copper metallic nanocrystals. Diffraction pattern has 11 peaks, the diffraction peaks at 2θ values of 35.96 and 38.79. After comparing the standard ICCD with number of 05-0661, it can be said that the synthesized material is copper nanoparticles and the nanoparticle structure is monoclonal. The average size of the crystalline particles of copper nanoparticles was calculated using Debye-worker formula. It was estimated to be about 50 nanometers which is consistent with the results of the optical microscope (Figure 9).

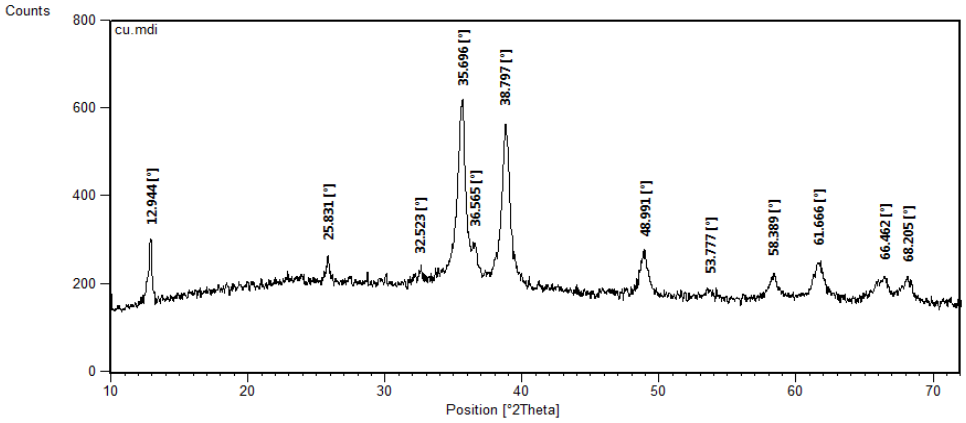

Fig. 9. XRD pattern of synthesized CuNPs using (*Eryngium campestre*) leaf extract (copper nitrate concentration =5mM pH =6, Temperature=35°c, time= 80 minutes)

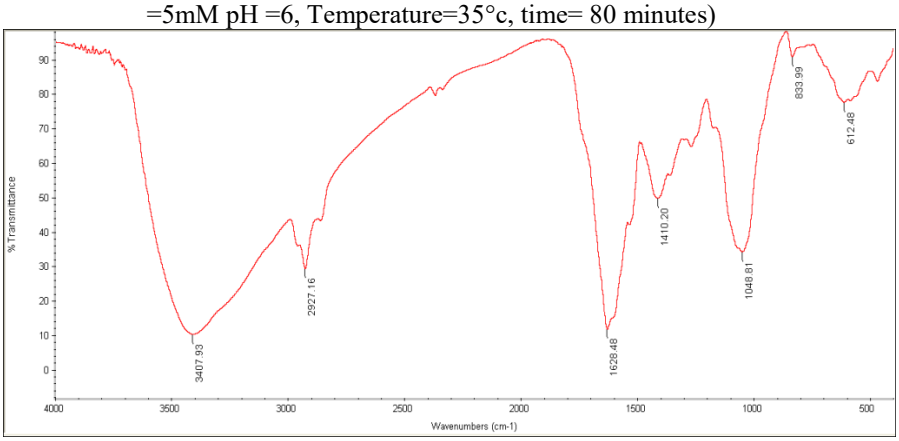

Fig. 10. FT-IR analysis of synthesized CuNPs using (*Eryngium campestre*) leaf extract (copper nitrate concentration =5mM pH =6, Temperature=35°c, time= 80 minutes).

FTIR analysis

The chemical composition of the synthesized copper nanoparticles were studied by using FTIR spectrometer. The dried powders were characterized in the range of 600-4000 cm-1 using KBr pellet method. To investigate the functional groups of CuNPs and herbal extract, absorption band at 1628 cm^{-1} and 1048 cm^{-1} results due to the stretching of the N–H bond of amino groups and indicative of bonded hydroxyl (-OH) group at 3407 cm^{-1} , A peak 2927cm^{-1} indicates C=O group of carboxylic acids. The peak at 833 cm^{-1} and 612 cm^{-1} indicative of Alkynes and Alkyl halides. FTIR study indicates that the carboxyl (C=O), hydroxyl (-OH) and amine (N-H) groups of herbal extract are mainly involved in the reduction of Cu to Cu nanoparticles (Figure 10).

CONCLUSIONS

In this study, synthesis of copper nanoparticles was investigated using (Eryngium Campestre) Leaf Extract. Four parameters including copper nitrate concentration, pH, temperature and time were investigated and optimum condition using absorption spectra taken by spectrophotometer. It is generally recognized that UV- Visible spectroscopy could be used to examine the size and shape of copper nanoparticles .The absorption peak at 570 nm showed the presence of copper nanoparticles. According to the results, the synthesis of copper

nanoparticles was completed under these conditions; pH = 6, T = 35 °C and t = 80 minutes which showed that the synthesis has a high velocity without high temperatures requirements.

The basis of the synthesis of nanoparticles is the reduction of their salt ions and, in fact, the neutralization of electrical charge. To determine the size and morphology of the copper nanoparticles, a mixture of extract and salt of copper nitrate was collected by observing optimized parameters by centrifugation with stirring rate of 10000 rpm, and photographed by scanning electron microscopy. The image was estimated at the magnitude of the 500 nanoscale which showed that the average size of the particles between 50 and 60 nanometers.

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