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Sol-gel Synthesis of Copper, Silver and Nickel Nanoparticles and Comparison of their Antibacterial activity

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ABSTRACT: The present study involves a novel microwave assisted synthesis of metal nanoparticles which was carried out using Geraniol as a reducing agent. In this method water is used as the medium for reduction. Nanoparticles were studied with a wide variety of capping reagents such as starch, PEG and Gelatin. The medium was kept alkaline during the reaction using 5% NaOH solution. Formation of Copper nanoparticles (CuNPs) was indicated by absorption band at 540nm whereas Silver nanoparticle (AgNPs) gave a band at 420nm, with nickel nanoparticles (NiNPs) the band appeared a 390nm. The variation in λ max value is due to nature of metal and size of metal nanoparticles, as a small nanoparticle absorbs at higher wavelength. The characterization of metal nanoparticles was done by TEM (Tunneling electron microscopy) and XRD (X-ray diffraction) studies. Antimicrobial studies were carried out to check the zone of inhibition around these particles and it was found that silver nanoparticles were most effective followed by copper and nickel nanoparticles.

Key words: Geraniol, microwave, antimicrobial, TEM

I. INTRODUCTION

Syntheses of metal nanoparticles have been an area of interest in recent past due to their unusual structural, electrical, optical and magnetic properties. These unique properties of nanoparticles can be tailored during the growth of nanoparticles as such properties generally depend upon particle size and surface area. New materials are being synthesized wherein researchers focus mainly on identifying materials with unique properties and applications, so the environmental implications of the synthetic processes are often not considered. So it is the need of the hour to develop certain methods of synthesis which have lesser detrimental effects on environment [1-5].

Green chemistry has been employed successfully in the preparation of highly functionalized products particularly in organic synthesis; efforts are being carried out to synthesize nanoparticles via greener routes. The development of high-precision, low-waste and greener methods of nanoparticle manufacturing will be crucial to their commercialization. In addition to providing enhanced research and development strategies, green chemistry can also play a prominent role in guiding the development of nanotechnology to provide the maximum benefit of these products for society and the environment [5-10].

Metallic nanoparticles of specific sizes and morphologies can be readily synthesized using chemical and physical methods. However, these methods employ toxic chemicals as reducing agents, organic solvents and non biodegradable stabilizing agents which are therefore potentially dangerous to the environment and biological systems. Moreover, most of these methods entail intricate controls or nonstandard conditions making them quite expensive. The biosynthesis of Nanoparticles has been proposed as a cost effective environmental friendly alternative to chemical and physical methods. Consequently, Nanomaterials have been synthesized using microorganisms and plant extracts. The use of plant extracts for Nanoparticles synthesis is advantageous over microorganisms due to elaborate process of maintaining cell cultures. Gold and silver Nanoparticles have been synthesized using various plant extracts including hibiscus (*Hibiscus rosa sinensis*) leaf extract, neem (*Azadirachta indica*) leaf broth, black tea leaf extracts, Indian gooseberry (*Emblica officinalis*) fruit extract, sun dried camphor (Cinnamomum camphora) leaves, and Aloe vera plant extract. The synthesis of metal nanoparticles using plant extracts has developed a rapid, cost-effective biosynthetic protocol for bulk synthesis of stable metallic nanoparticles. In the present work we have developed green synthesis of metal nanoparticles via a single-step, room-temperature reduction of metal ions using environmentally benign reagents [11-12].

Reduction using environmentally benign reluctant is a relatively new and green method for the synthesis of different metal Nanoparticles (Au, Ag, Pt, Pd, Cu, Fe etc) it is done by using commonly available sugars, e.g., glucose, fructose and sucrose and other available alkaloids having reducing properties. The process is highly reproducible, easy and bio friendly for the synthesis. Using this method it is intended to apply the three important R's of Green synthesis i.e. Reduce, Recycle and Reuse. In the present work, a low cost microwave assisted greener method has successfully been developed to prepare metal nanoparticles. The main target of this paper is to synthesize, characterize and to investigate their structural, morphological, and antibacterial properties [13-18].

II. EXPERIMENTAL PROCEDURE

A. Materials

All the chemicals used for synthesis of metal nanoparticles were of analytical grade (Merk), these have been used as such without any further purification. The Glassware used in the process was cleaned thoroughly first with chromic acid, then with 1% HNO_3 and finally many times with deionized water. Solution of metal ion was prepared by using Copper sulphate for CuNPs, Silver nitrate for AgNPs and Nickel chloride for NiNPs. A stock solution containing metal ion concentration of 1M was prepared and other solutions were made by diluting the stock solution using deionized water.

B. Preparations of Metal Nanoparticles

Different metal nanoparticles were synthesized using Geraniol as reductant with water as the medium for reduction in a microwave assisted process. Various capping agents such as starch, PEG and Gelatin were used for the stabilization of metal nanoparticles. The reaction mixture was heated using a kitchen microwave for about 5 minutes to attain the required temp for the reaction. The pH of the solution kept alkaline using 5% NaOH solution. Formation of metal Nanoparticles was indicated by change in color of the solution which is supported by the corresponding absorption bands at wavelength 540nm for Copper, 420 for silver and 390 for Nickel. The synthesized particles were washed several times with water and finally with alcohol. The effect of various parameters such as contact time, pH, concentration and heating method was also optimized (Fig. 1).

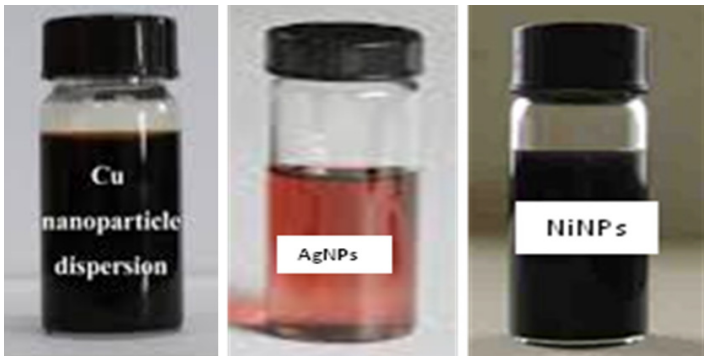

Fig. 1. Preparation of Cu, Ag and Ni nanoparticles.

C. Characterization Techniques

Characterization of synthesized nanoparticles was done by UV, IR, XRD and TEM analysis. The synthesis was carried out in batch experiments varying the concentration of metal ions, reducing agents, capping agents and pH regulators at room temperature. The common house hold oven was used for heating which requires a time of 10 to 20 seconds to reach the optimum temperature for synthesis. The optimization of size distribution and effect of various parameters such as contact time, pH, Concentration and heating method was also optimized.

D. Antibacterial tests

The antibacterial activity of metal nanoparticles was studied against *S. aureus* using spread plate technique [19-22]. In this method a culture of *S. aureus* bacteria was prepared in nutrient solution in a petridish. *S. aureus* organisms was inoculated into 20 mL sterilized nutrient solution and incubated at room temp for 12 hours. Four petridishes were prepared to check the antibacterial activity of the synthesized metal nanoparticles. A petridish containing blank solution was also taken as a reference(petridish 1), Colloidal solution containing copper nanoparticles was taken in petridish 2, a colloidal solution of silver in petridish 3 & finally the colloidal solution of nickel in petridish 4 and all these petridishes were incubated at room temperature for 12 hours.. After successful incubation the viable bacteria colonies were counted and antibacterial efficiency was calculated using the relation.

$$\%E = \frac{(A - B)}{B} \times 100$$

Where E is the antibacterial efficiency, A is the number of viable bacteria in the petridish, B is the number of viable bacteria in the petridish having metal nanoparticles prepared using different concentration.

III. RESULTS AND DISCUSSIONS

A. Formation of metal nanoparticles

A variety of reducing agents such as ascorbic acid, starch and geraniol have been used to synthesize metal nanoparticles. A capping agent is required when Ascorbic acid and Geraniol as reductant, however if starch is used as a reductant no capping agent is required. The reducing abilities of Geraniol was found to be better than other agents as nanoparticles are produced at a faster rate this may be due to the fact that Geraniol is a better reducing agent and starch act as a good capping agent. Role of pH is important in providing optimum condition for synthesis. Microwave assisted process provides a better means of attaining optimum temperature of the reaction. A comparison of traditional heating process with microwave assisted process revealed that it is more efficient and less time consuming way of doing the reaction [19-21].

B. Effect of Geraniol volume (ml) for the Nanoparticle Synthesis

Solutions at different concentrations of metal ions were used synthesizing various metal nanoparticles. Geraniol was added (2.0; 4.0 and 6.0ml) in the metal ion solution (0.1, 0.2, 0.4 & 0.8M). The nanoparticles prepared by reducing metal ions with 2.0; 4.0 and 6.0ml of Geraniol were yellowish brown or yellowish black colored giving characteristic absorption. The optimal concentration of Geraniol on the basis of UV absorption was chosen to be 4ml for a metal ion concentration of 0.4 M for Cu and Ni while O.2M for Ag (Fig. 2(a) & (b)).

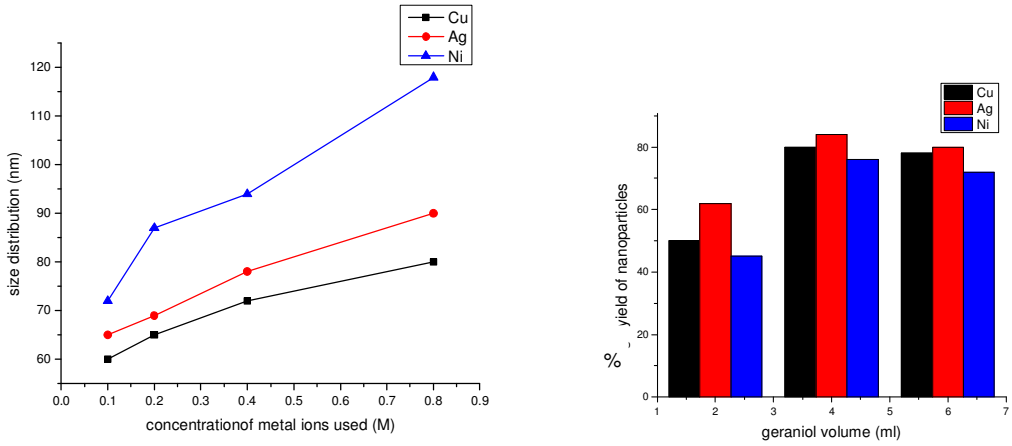

Fig. 2. Effect of (a) Concentration of metal ions (b) volume of Geraniol (reductant).

C. Structural Studies

The formation of Copper Nanoparticles was indicated by the change in color of solution, which is confirmed by UV spectrum which gave characteristic absorption in the region 540 nm for copper, 420nm for silver and 390nm for nickel. These values clearly indicate that various nanoparticles have been formed in the colloidal form (Fig. 3 (a), (b) & (c)).

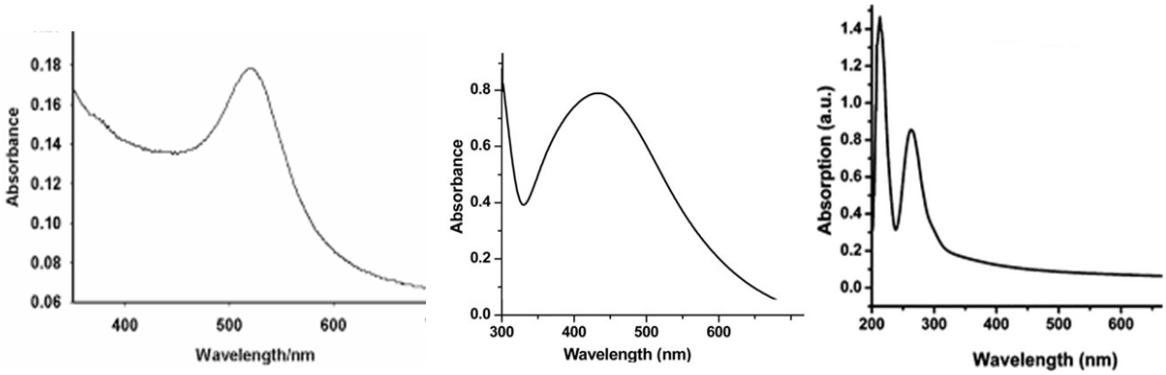

Fig. 3. UV spectra of Colloidal solution of (a) Cu (b) Ag and(c) Ni nanoparticles.

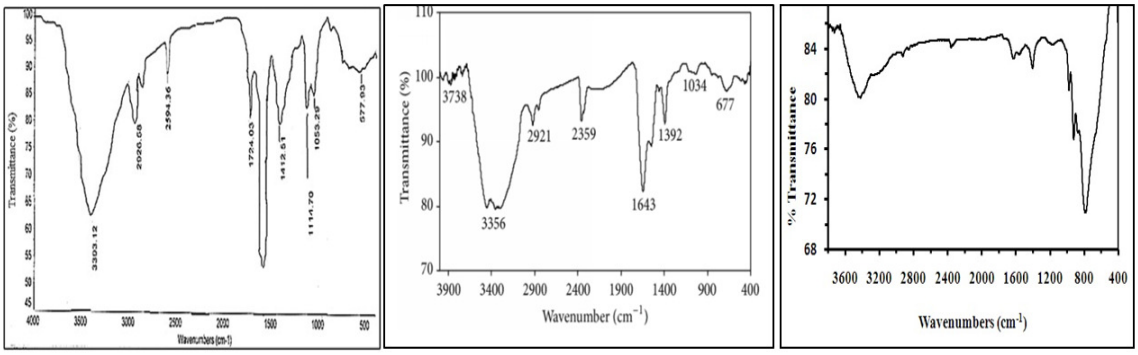

Fig. 3. FTIR Spectrum (a) Cu (b) Ag(c) Ni nanoparticles.

Separation of synthesized particles was done by ultracentrifugation (5000rpm) and the dried powder was analyzed by FTIR and XRD studies (Fig. 3 & 4) showed the characteristic bands. Diffraction patterns obtained in the XRD gives useful information about size and shape of unit cell and electron density in the unit cell. This information is obtained from peak position and peak intensities in the XRD Spectrum. The Analysis of synthesized nanoparticles was done with a drop coated on glass and the XRD spectrometer operating at a voltage of 40KV and current of 20mA with Cu K radiation [21-24].

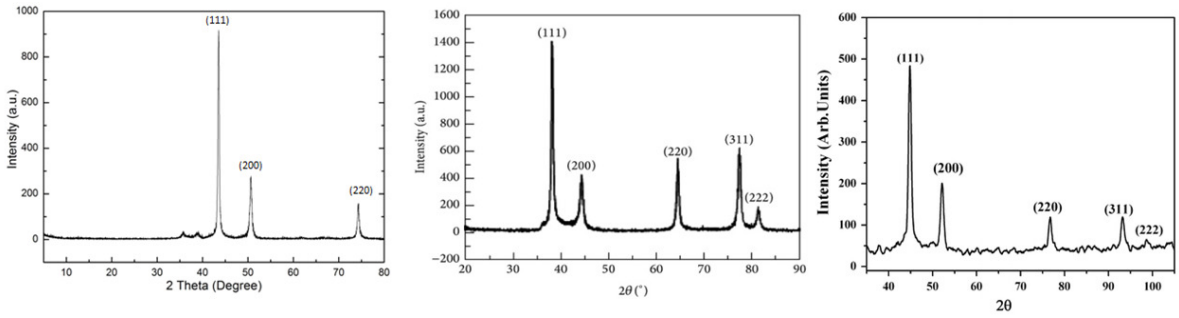

Fig. 4. XRD of Synthesized (a) Copper (b) Silver (c) Nickel Nanoparticles.

The final analysis pertaining to the determination of size of nanoparticles is the TEM Analysis (Fig. 5) and it was found that the particle size of copper Nanoparticles falls in the range 70-90nm ,silver nanoparticles in the range of 80-100nm and nickel particles in the range of 100-120nm.

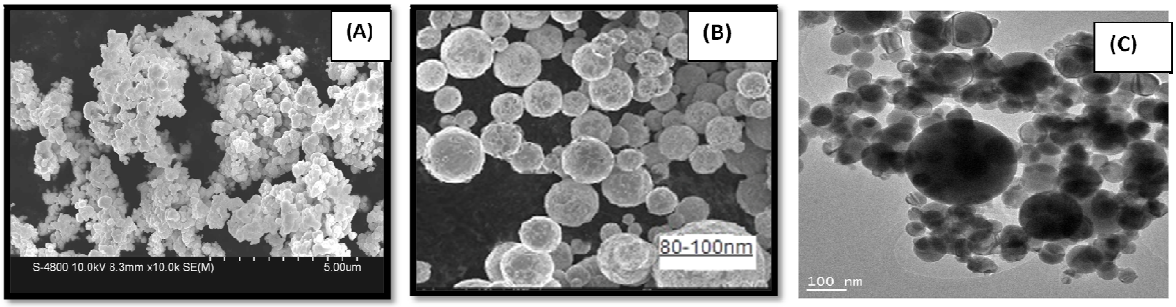

Fig. 5 (a) TEM images of (a) Cu (b) Ag (c) Ni Nanoparticles.

D. Antibacterial tests

The antibacterial activity of metal nanoparticles synthesized was investigated. The samples were tested for *S. aureus* incubated for 12 hrs using blank nutrient solution without metal nanoparticles {fig. 7(a)}, with copper nanoparticles {fig. 7(b)}, with silver nanoparticles {fig. 7(c)} and finally with nickel nanoparticles{fig. 7(d)}. It was observed that silver nanoparticles showed maximum antibacterial activity while nickel nanoparticles showed the least. It was also observe that as the concentration of metal ions increases from 0.1 to 0.8M the antibacterial activity of the all the type of nanoparticles enhances from about 25% to 80%.

This increased antibacterial activity is due to high concentration of metal ions used which produce nanoparticles of larger size, as the size distribution of nanoparticles increases from 50nm to 120 nm [25-33].

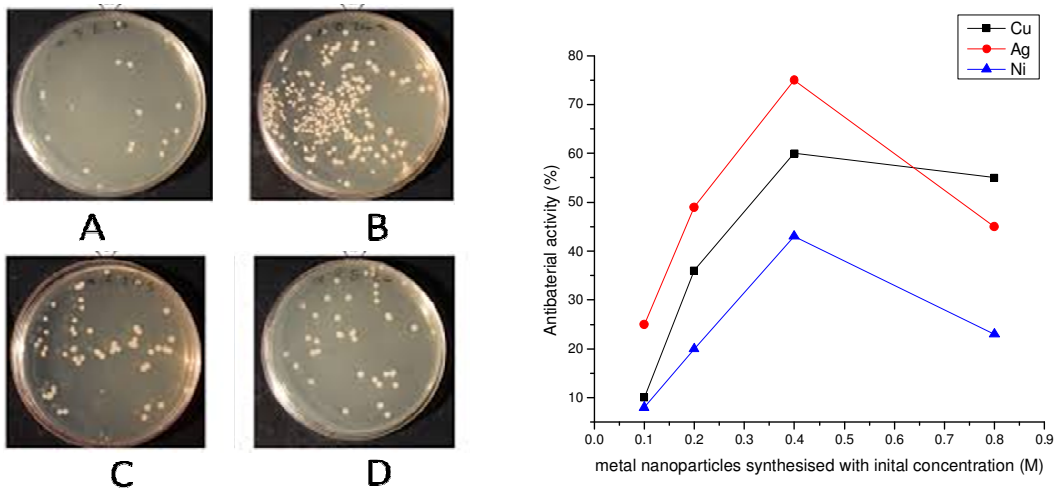

Fig. 6. (a) Antibacterial activity after incubation and Plot showing antibacterial efficiency using (a) blank solution (b) Cu (c) Ag (d) Ni Nanoparticles.

CONCLUSIONS

The present study successfully developed a green method for synthesizing metal nanoparticles in the size range 50-100nm using microwave assisted approach. The structural studies which include UV, IR, and TEM images indicate the formation of metal nanoparticles. UV analysis indicates that the value of λ-max increases as the size of the metal nanoparticles increases which in turn depends upon the concentration of copper ions taken in the solution. Antibacterial activity of copper, silver and nickel nanoparticles showed the size of the nanoparticles decides the antibacterial efficiency. The Experiments suggest that the synthesized particles can be used in future for water purification, Air Quality monitoring, removal of toxic ions from water samples and other adsorbent properties.

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