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Microwave assisted green synthesis of copper nanoparticles

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The production of copper nanoparticles using green chemical reductions in aqueous solution is reported without any gas protection or oxygen removal, by high speed microwave method with no harmful substances. Colloids of Cu NPs have been synthesized by two stabilizers: potato starch and polyvinylpyrrolidone (PVP). The sizes of nanoparticles obtained in starch and PVP were 35-90 nm and 9-20 nm respectively. L-ascorbic acid (vitamin C) has been used as a reducing agent for copper precursor as well as an antioxidant because of its high capability to scavenge oxygen molecules dissolved in water. Amount and speed of adding the reducing agent, concentration of stabilizer and pH are effective factors on amount and purity of Cu NPs, so in this study, some optimizations was done in order to find the conditions to get the maximum amount and purity in production of Cu NPs.

Keywords: Colloids, Cu NPs, Reductions, Stabilizers, UV/Vis spectroscopy

INTRODUCTION

Nano means so small that can be placed among the components of the world of biology and chemistry [1]. We apply the word “green” for environmentally safe and sustainable technologies.[2] Green synthesis of nanoparticles is a bottom-up method with a main reaction of oxidation and deduction. The Production of Metal nanoparticles using natural precursors seems to be very economical. So, it can be used as a valid and economical alternative for the large-scale production of metal nanoparticles [3]. Today, the study on colloidal nanometals is more interesting because of their varied applications originated from their chemical and physical traits [4], including electronic, spectroscopic, physical and chemical properties that differ from those in bulk substances and occur because of small size and thereupon great ratio of surface to volume [5]. Cu NPs attract our attention because of this metal abundance [6], and profitable properties (e.g., great electrical and thermal conductivity) as well as their cheaper availability than valuable noble metals such as gold and silver. [7]. Cu NPs have many applications in several fields such as catalysts, lubricants, next generation of thermal transfer nanofluids with higher conductivities, optical devices and electronic materials [4]. Cu is known to be an antibacterial and antifungal metal [7]. Cu NPs have been produced by various methods that most reported ones include electrochemical reduction, vapor deposition, photochemistry, γ-radiolysis, wet chemical reduction and thermal decomposition [5]. Two other important methods are sonochemical reduction and microwave irradiation [8]. Cu NPs productions usually need expensive tools and long duration to be completed [6]. Most of the chemical methods utilize harmful substances [5]. Chemical reduction in an aqueous solution needs to regulate and study some factors, such as reaction time, temperature, concentrations, reducing agent and Cu precursor and also the effect of mixing style on nucleation, growth and agglomeration phenomena and as a result on size distribution of nanoparticles [3]. Unlike some noble metals, like Pt, Ag, and Au, copper in stable and pure metallic form can hardly be obtained in aqueous solution using reduction of plain copper salts. It has been known that, copper in zero valence form can easily change into oxides and Cu NPs are very unstable in some solutions [4]. Without appropriate protections Cu NPs intensely aggregate [6]. Green synthesis of Cu NPs have been reported with different capping agents such as starch [9], PVP [10-12], gelatin [13, 14] and chitosan [15], or with plant extracts [16-21]. In this article green synthesis of Cu NPs is reported with two stabilizers, PVP and starch, with the help of microwave.

RESULTS AND DISCUSSION

By adding NaOH to a copper sulfate or nitrate solution, In the absence of stabilizer, blue sediment of $Cu(OH)_2$ will be generated.

$2Na+aq + 2OH-aq + Cu2+aq + SO42-aq \rightarrow Cu(OH)2\ s + SO42-aq + 2Na+aq$

$2Na^{+}aq + 2OH^{-}aq + Cu^{2+}aq + 2NO^{3-}aq \rightarrow Cu(OH)^{2}\ s + 2NO^{3-}aq + 2Na^{+}aq$

But in the presence of stabilizer no deposit is formed in container, because copper is enclosed by

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stabilizer molecules and interacts with them [22]. After adding ascorbic acid, it changes to Dehydroascorbic acid by detaching two H+ ions [4]. In the presence of OH- ions, electron transfer to copper ion and reduction of Cu2+ to Cu0 takes place.

In this study, the reduction process was executed in two ways: one-step process in the presence of starch and two-step process in the presence of PVP, which is because of the adding method of ascorbic acid that was *en masse* and dropwise respectively. (Fig.1)

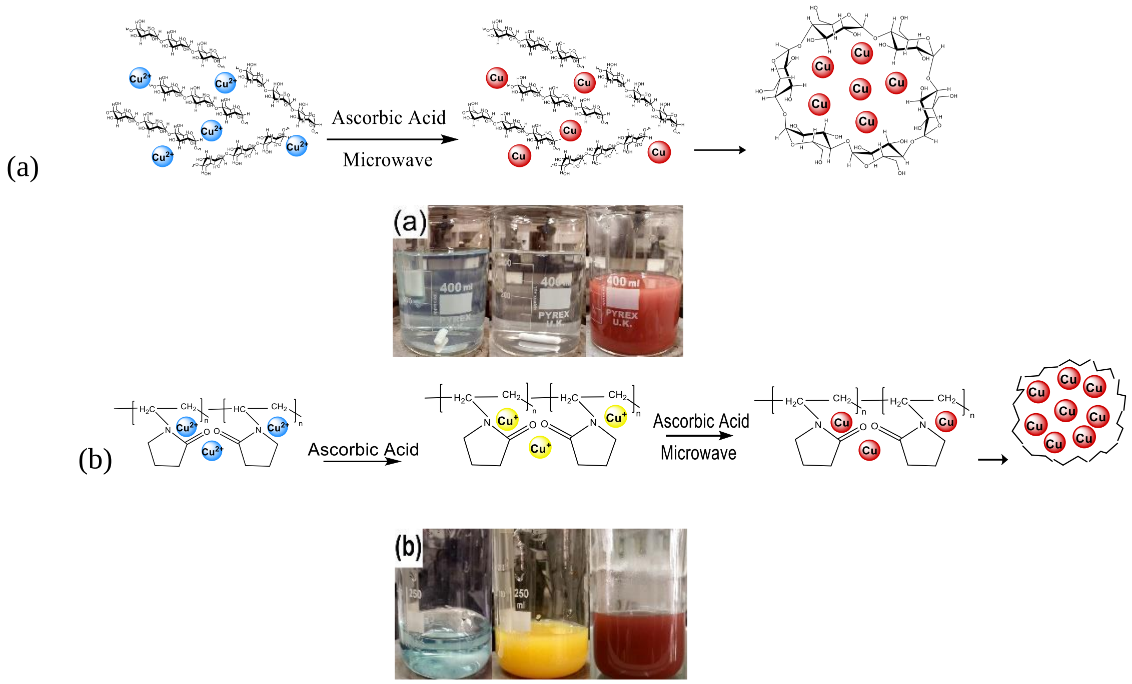

Fig. 1. Steps of Cu2+ reduction and formation of Cu NPs in a) starch solution and b) PVP solution

CHARACTERISTICS

Cu NPs coated with Starch and PVP synthesized had λmax of 591nm and 528nm respectively. SPR phenomenon causes the spectrophotometry to be a proper means for a qualitative interpretation of colloidal nanoparticles. This means that, the smaller λmax gets the smaller particle size becomes and absorption rate in λmax is an indication of the concentration and amount of nanoparticles [23]. Fig. 2 shows X-ray diffraction (XRD) patterns of Cu NPs. In this figure, three larger peaks of samples corresponded with standard pattern of copper and the average calculated particle sizes made in starch and PVP were 34.73 nm and 15 nm. Fig. 3 shows the Fourier transform-infrared (FT-IR) spectrum. In the case of Cu NPs produced in starch, the resulting peaks in the range of 3222.37 to 3777.05 are related to OH groups and from 1670.10 to 3777.05 are related to Carbonyl groups. Considering that the carbonyl groups of Cu NPs were in about similar ranges of ascorbic acid, but the peaks of OH groups in Cu NPs shows changes compared to ascorbic acid, it can be expressed that copper ions have received electrons required for the reduction process from the OH groups. . In the case of nanoparticles synthesized with PVP, similar issue exists and peaks at 3420.79, 1649.06, 2961.64 are respectively relevant to stretching OH groups, carbonyl groups and stretching C-H. Fig. 4 shows Field Emission-Scanning Electron Microscope (FE-SEM) images of Cu NPS. These images show that starch-coated Cu NPs were spherical and in a size range of 35 to 90 nm which in some cases, after centrifugation and drying, created larger nanoparticles. PVP-coated Cu NPs were spherical with small sizes between 9 and 20 nm and were uniform in size while no agglomeration was observed in them.

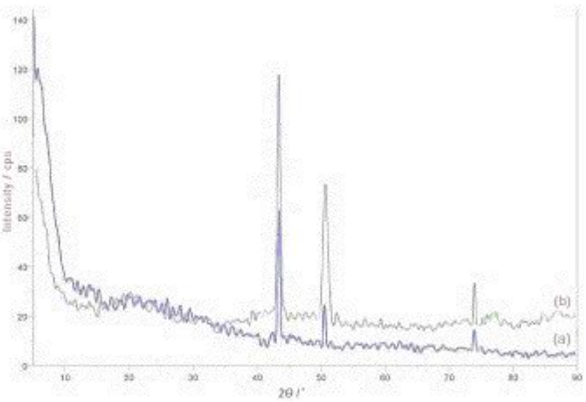

Fig. 2. XRD patterns of Cu NPs coated with a) starch and b) PVP

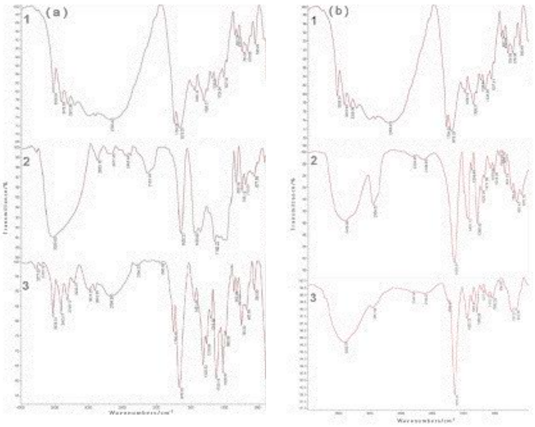

Fig. 3. FT-IR spectrum of a) ascorbic acid (1), starch (2) and starch capped Cu NPs (3), b) ascorbic acid (1),

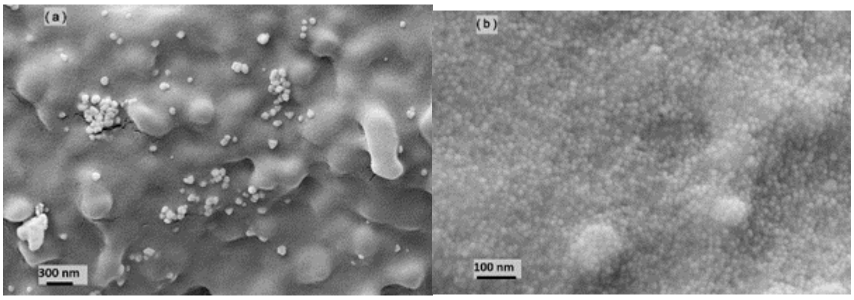

Fig. 4. FE-SEM images of Cu NPs coated with a) starch and b) PVP

The effects of pH on amount of Cu NPs production

Starch coated Cu NPs had very low concentrations in acidic pH values of 5 and 6. In pH values from 7 to 9 concentration increased. In pH = 10 concentration increased but Colloid was not completely pure and contained copper and copper oxide nanoparticles, so the color of colloid turned darker [12] to blackish red. The concentration of PVP coated Cu NPs in pH = 5, was so low that no peak was shown in UV-Vis spectroscopy. About pH values from 6 to 9 concentration increased. In pH values of 10 and 11 less amounts of particles were formed and existence of copper oxide particles was found out with the color of colloid turned to blackish red. However the best pH for producing Cu NPs was 9. NaOH is a catalyst and if enhances, the amount and uniformity of the Cu NPs increase, but if NaOH exceeds a certain amount, it will cause non-purity and even less concentration of Cu NPs (Fig. 5).

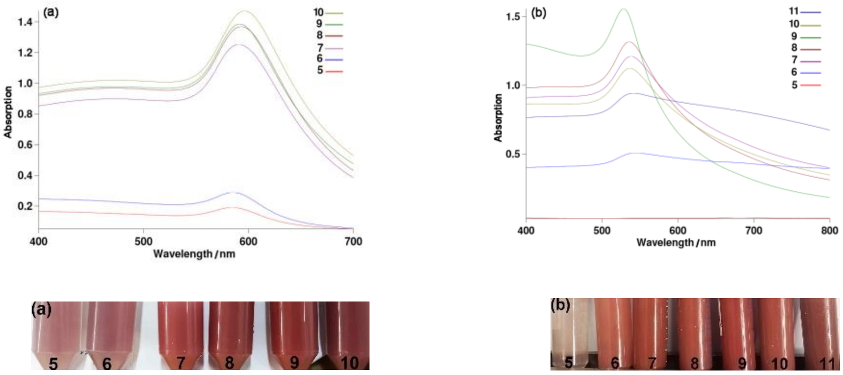

Fig. 5. The effect of pH on Cu NPs coated with a) starch and b) PVP

The effect of stabilizer on amount of Cu NPs production

By increasing the starch from 1% to 4% and PVP from 0.1 to 0.3 mM, the amount of NPs production increased but in 0.4 mM of PVP concentration extremely decreased. In fact, stabilizer is an essential factor in the formation of Cu NPs and its absence causes intensive aggregation and prevents the formation of nano-scaled particles. In literatures, its effect on lessening the particle size has been mentioned [5]. The result of this review shows the positive effect of stabilizers on the rate of NPs production. However, it should not exceed a certain range. The Type of stabilizer is an important factor which is the basis of this research. Glucose structure somewhat causes reduction feature in starch and in case of using it, less reducing agent is needed. But about PVP, more reductant should be used (Fig. 6).

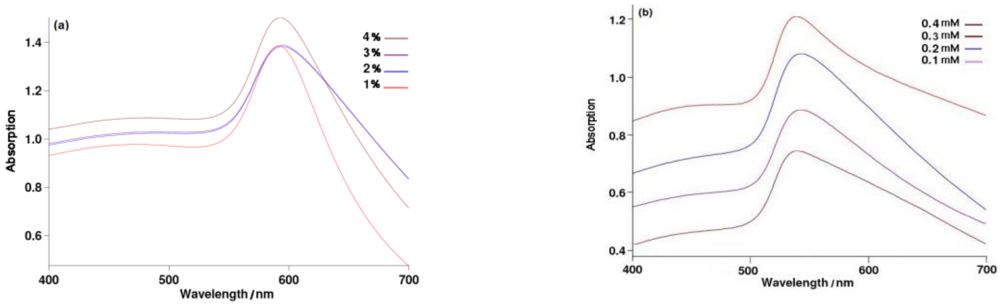

Fig. 6. The effect of stabilizer on Cu NPs a) coated with starch and b) coated with PVP.

The effect of reducing agent on amount Cu NPs production

In starch-coated Cu NPs, the best result was obtained when acid was added at once and in Cu NPs coated with PVP the best result was related to the addition of ascorbic acid dropwise at 2 cm3.min-1. Decreasing in speed of adding ascorbic acid caused a decrease in purity of colloid by formatio of copper oxide particles

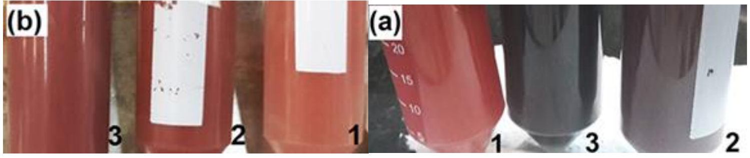

Fig. 7. The effect of adding speed of reducing agent 1) at once, 2) 2 cm3.min-1, 3) 1 cm3.min-1 on Cu NPs coated with a) starch and b) PVP.

In starch-capped Cu NPs, pH values of 7, 8 and 9 were chosen for this step. By increasing the acid from 0.2 cm3 to 1.2 cm3 the most amount of Cu NPs in pH=7 was produced with 0.6 cm3 acid. In pH = 8, the most concentration of nanoparticles was obtained with 0.8 cm3 acid and the most production in pH = 9 was made with 1 cm3 acid. It has been mentioned that increase in reducing agent leads to smaller nanoparticle production [13].In fact, in each pH, acid increase to a certain extent results in an increase in nanoparticle formation and the production rate will decline when more acid is added (Fig. 8).

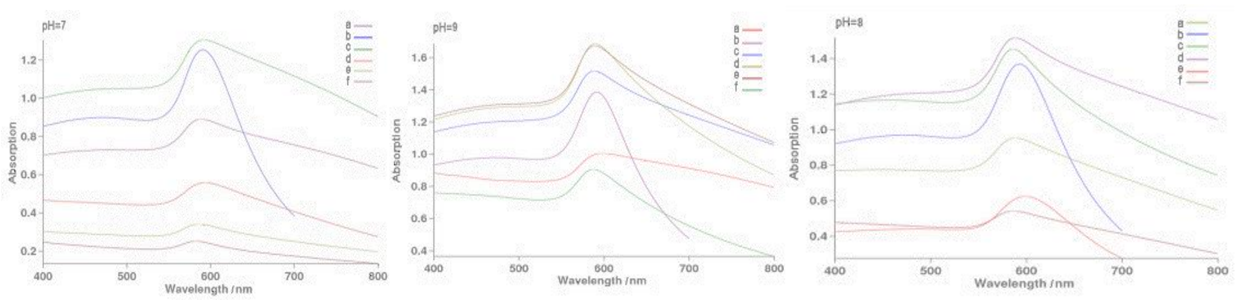

Fig. 8. The effect of ascorbic acid on amount of starch coated Cu NPs. a) 0.2 cm3, b) 0.5 cm3, c) 0.6 cm3, d) 0.8 cm3, e) 1 cm3, f) 1.2 cm3.

CONCLUSION

In this research Cu NPs have been synthesized in two stabilizers by a green chemistry method and minimum reaction time. Stability of colloidal Cu NPs was up to 2 months and powdered form was perfectly stable. In pH = 9, 4% starch and 0.3 mM PVP the highest purity and amount of production can be obtained. To achieve the most production, appropriate balance is needed between pH and reducing agent

EXPERIMENTAL

Materials

Anhydrous copper (II) sulfate ($CuSO_4$), copper (II) nitrate trihydrate ($Cu(NO_3)_2.3H_2O$), potato starch and L_ascorbic acid were purchased from Merck (Germany) and PVP-K25 (MW = 24000 g.mol-1) from Acros Organics (USA). All the materials were in analytical grade and used exactly in the form they were purchased with no further purifications. Deionized water was the solvent of systems.

Synthesize of nanoparticles

To produce Cu NPs with copper stabilizer, 3 cm3 of 0.01 M copper sulfate solution was added to 50 cm3 1% solution of potato starch (reached room temperature) and was stirred up for 10 minutes. Then, pH of the solution was adjusted to 9 by using NaOH, and 0.5 cm3 of 10% ascorbic acid solution was added while stirring up so pH reached about 3.5. The mixture changed from light blue to colorless. It was placed in a MicroSYNTH laboratory microwave (Milstone, Italy) at ambient pressure and full power for 2 minutes and then was stirred up in the presence of air for 10 minutes until the red colloid was formed which indicated the Cu NPs formation and the completion of the reaction.

To produce PVP-coated Cu NPs, 3 cm3 of 0.01M copper nitrate solution was added to 50 cm3 0.3 mM PVP solution and was stirred up at room temperature for 10 minutes. Then, pH of the solution was adjusted to 9 using NaOH, and 1 cm3 solution of 10% ascorbic acid was added dropwise while stirring up wherein the mixture turned from light blue to colorless and then yellow which was an indication of Copper(I) oxide (Cu_2O) formation. Then, it was placed in the same microwave conditions for 2 minutes. Then it was stirred up for 15 minutes in the presence of air until wine red colloidal solution was formed. For further investigations, colloids of Cu NPs were centrifuged at 11,000 rpm for 15 minutes, then was washed with deionized water (with 2 more times centrifugation and wash) and finally freeze-dried overnight whereby Nano-copper powder was collected.

Characterization

Surface Plasmon resonance (SPR) peaks of Colloids were checked using a UV-visible spectrophotometer (Conc 30, Varian) by CaryWinUV Scan software. The XRD pattern was recorded by a X-ray diffractometer (PST 300, Germany) with 2θ of 0.5° to 90° , the X-Ray source of a copper cathode ($\lambda = 0.154$ nm) and 2:1 symmetry scanning axis with RAYFLEX software. Review of results was performed with three larger peaks and the crystalline size was calculated by the means of Debye Scherer equation Eq. (1). FT-IR spectrum was recorded by a (NEXUS 870, USA) FT-IR spectrometer and Omnic Spectra software .Small and certain amounts of nanoparticles powders, ascorbic acid, starch and PVP were used for the formation of pellets and the results were compared. Size and morphology were investigated by a FE-SEM (Sigma, Zeiss, Germany).

$$D = \frac{K\lambda}{\beta\cos\theta}, \tag{1}$$

where D/m^{-10} is crystal size, β/rad is full width at half maximum of peak, λ/nm is the wavelength of X-ray, θ/° is the angle between the radiation and the sample and K is a constant.

The study of some effective factors on amount of Cu NPs production

In identical systems (1% starch and 0.5 cm3 ascorbic acid or 0.3 mM PVP and 1 cm3 ascorbic acid) the effect of pH was studied. Also, the effect of amounts of PVP and starch were examined in similar systems with only different amounts of stabilizers (about starch-coated Cu NPs, pH=9 and 0.5 cm^3 acid, and about PVP-coated Cu NPs, pH=7 and 1 cm3 acid). 3 different speeds of adding reducer (At once, 2 cm^3.min-1 and 1 cm3.min-1) were experimented for both stabilizers. Then, starch-coated Cu NPs were produced in 3 pH values chosen from previous steps and 1% starch. In each pH, different amounts of 10% ascorbic acid solution (0.2, 0.5, 0.6, 0.8, 1 and 1.2 cm^3) were added and the effect of acid was studied. Amount of Cu NPs were studied with the help of UV-visible spectroscopy.

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