

Evaluating the Reaction Parameters' Effects on the Size and Shape of Synthesized Copper Nanoparticles based on Expert Design

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Abstract— In this study copper nanoparticles were synthesized by a chemical reduction method. In this method copper acetate was used as copper precursor and hydrazine and gelatin were used as a strong reducing agent and surface protecting agent, respectively. Reducing agent reduced copper ions to copper atoms and surface protecting agent avoided synthesized particles to join to each other. In this study we also used CCD, a design of experiment method, to predict the effect of reaction parameters on the size of synthesized particles. We changed reducing agent's concentration and surface protecting agent's concentration and pH of the reaction and studied the effect of these change on the final particle size. We also studied the purity of synthesized particles and proved that synthesized particles were completely pure with no oxygen molecules.

Keywords— Metals, Nanostructures, Electron Microscopy, Chemical Synthesis

I. INTRODUCTION

Nowadays metallic nanoparticles (NPs) have attracted so much attention because of their unique and different properties such as: high surface to volume ratio, low melting point, high thermal conductivity in comparison to their bulk state [1-5]. Metallic NPs can be used in many different fields such as heat transfer, catalysis, electronics and medicine [6-8]. Among metallic NPs, copper NPs have some outstanding characteristics that make them unique. These properties can be mentioned as their low cost, availability and having similar properties to noble and expensive metal NPs [7, 8]. Copper NPs can be applicable in preventing coatings against corrosion, electronics and catalysis [5, 8]. Gold and silver NPs had been used to fabricate electronic devices through printing conductive patterns, but because of their high cost, they were preferred to be substitute with copper NPs [9, 10].

Generally there are so many approaches to synthesize metal NPs. They can be divided into two main groups, physical and chemical approaches [7]. NPs' structure is made of atoms and molecules in chemical trends while in physical methods they are made by etching, cutting and abrasion of a piece of bulk metal. Chemical methods have many advantages comparing to physical methods like the low cost and availability of equipment.

In comparison with metal oxide NPs, pure metallic NPs show better performance in conductive inks. Silver NPs are good choice to be used in those mentioned inks since they are resistive against oxidation, [11]. Copper oxide is thermodynamically more stable than copper, so these NPs can be easily oxidized and oxide layer can be made on the surface of them in ambient temperature and pressure [3, 12]. To date, so many efforts have been done in order to solve this problem. The efforts can be categorized into three main groups. These methods are using an organic solvent [13, 14], inert atmosphere and surface protecting agents like polymers and inorganic legends [5, 15-17], respectively. From the view of environmental problems, the first method is not preferred because of high VOC value. The second method is also not available all the times, but the latter is a good choice to synthesize pure metal NPs.

Among different chemical methods to synthesize copper NPs, the chemical reduction method is the best from the point of different advantages like controlling the size and morphology of final NPs by varying the reaction parameters such as surface protecting agent's concentration, reducing agent's concentration, temperature, pH and so on [7, 18-20].

In this research we are going to synthesize pure copper NPs by chemical reduction method and using green surface protecting agents. We use central composite design as an experimental design method to evaluate the effect of reducing and surface protecting agents' concentration and the pH of the reaction on the size of synthesized copper NPs.

II. EXPERIMENTALS

A. Materials

Copper acetate monohydrate was used as copper precursor for the reduction reaction and was purchased from Merck. The concentration of the copper precursor was the same in different reaction mixtures. Gelatin, a green surface protecting agent, used to stabilize the synthesized NPs and was obtained from MP Company from the Netherlands. Hydrazine hydrate was purchased from Merck and used as the reducing agent. Ammonia was used to control the pH of the reaction and was purchased from Merck. All the materials were used as received with any further purification. The chemical structures of four mentioned materials are shown in the Figure 1. We also used distilled water as the synthesize matrix and ethanol as a solvent to disperse resulted copper particles in it. Ethanol was purchased from Hamoonteb Company from Iran.

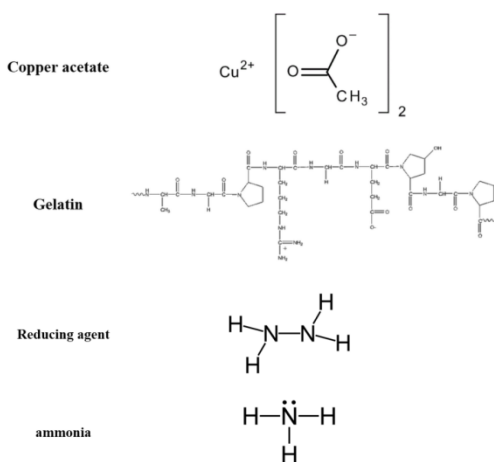


Fig. 1. Chemical structures of copper acetate, Gelatin, hydrazine and ammonia

B. Apparatus

To synthesize the copper NPs, magnetic multi-stirrer reactor was used. In this way all the different copper particles were synthesized simultaneously. Figure 2 shows the schematic illustration of the magnetic multi stirrer reactor.

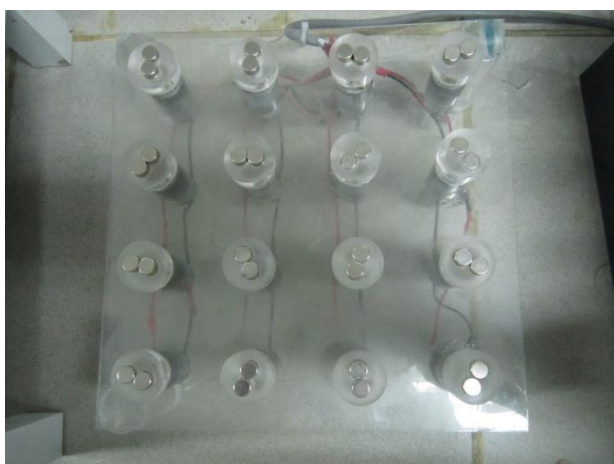


Fig. 2. Schematic illustration of the magnetic multi stirrer reactor

FESEM was used to evaluate the morphology of synthesized particles. In this research Σ IGMA/VP was used to take the FESEM photographs. The EDAX analysis was used to evaluate the presence of oxygen atoms on the surface of the copper particles. The EDAX measurements were done using the X-MAX Oxford apparatus. Dynamic Light scattering test was hired to investigate the average particle size of synthesized particles. Brookhaven ZET.PW32 model was used in this experiment. UV-Vis test was done to investigate the optical behavior of synthesized nanoparticles and to evaluate the Plasmon peak. The JENWAY 6715 UV-Vis spectrophotometer was used in this study.

C. Synthesis of copper nanoparticles

Copper nanoparticles were synthesized by the chemical reduction method. In this way, first of all, different amounts of gelatin were dissolved in hot water (60°C). When the entire

added gelatin was dissolved completely, the temperature of the solution was decreased to ambient temperature. While the solution was magnetically stirred, the copper acetate salt was added and the solution was mixed for 30 minutes. After stirring for 30 minutes and obtaining a homogenous solution, the pH of the solution was adjusted using ammonia-water solution to desired amount. When the pH was controlled, the solution was ready to introduce to the reducing agent. Different amounts of reducing agent were dropped into the reaction mixtures and after that the lids of the reaction reactors was closed to avoid entering further oxygen molecules.

The obvious color change was seen after stirring the mixture vigorously for three hours. The color of the reaction medium changed from light blue to dark blue then to yellow and reddish brown. The illustration of the color change is shown in Figure 3. After finishing the reaction, the mixture was centrifuged using 4000 rpm. The sediment was washed three times with ethanol and dispersed in it by the use of sonication. The mixture was sonicated for ten minutes using 150 watt power. The illustration of synthesis reaction is shown in Figure 4.

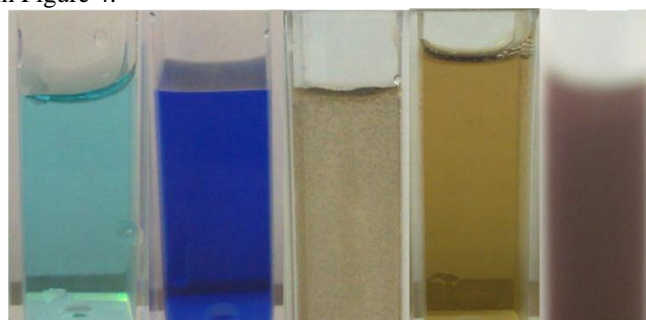


Fig. 3. Color change of the reaction mixture during reaction period

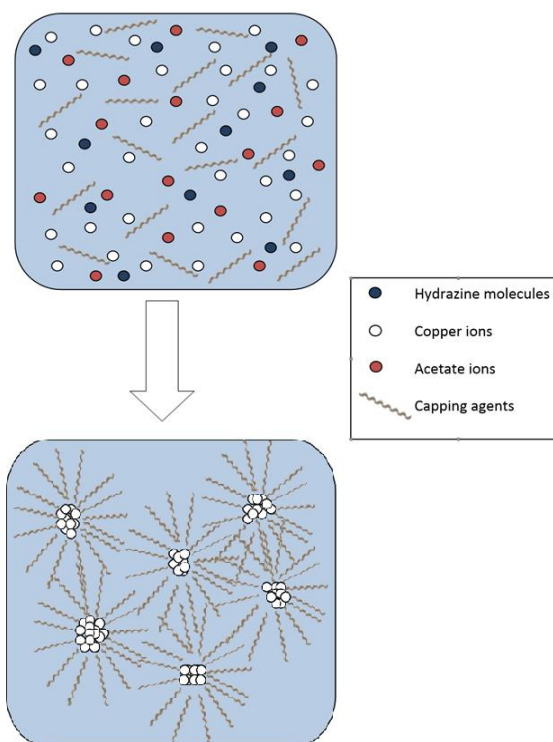


Fig. 4. Schematic show of what happens during synthesis reaction

D. Design of Experiments

In this research there are three factors with three levels and one response variable. The three levels of each factor are mentioned as -1, 0 and 1 and also the three factors are shown as X₁, X₂ and X₃ for gelatin concentration, hydrazine concentration and pH respectively. The process factors and their levels are represented in Table 1.

TABLE I. CCD PARAMETERS AND THEIR LEVELS

Parameter	Unit	Symbol	Levels		
			-1	0	+1
Gelatin	gr	X ₁	0.5	1	1.5
Reducing agent	ml	X ₂	6	8	10
pH	-	X ₃	8	9	10

Using this scientific design of experiment method results in 20 runs with six center points in a cube. This design of experiment method represents completely randomized experimental runs for mentioned factors and levels.

III. RESULTS AND DISCUSSIONS

A. Distribution of copper particles' size

A few ingredients should be used to synthesize the copper particles by the chemical reduction method. Among these materials, the first one is surface protecting agent which is so important and can affect on the particle size. Surface protecting agents can be absorbed on the surface of the made particles and stabilize them from joining different particles to each other followed by making bigger particles. In addition to their stabilizing function, they can also prevent the oxidizing of synthesized particles by protecting them against oxygen penetration. In this work we used gelatin as a green surface protecting agent and evaluated the effect of its concentration on the size of the synthesized particles. To discuss the effect of gelatin's concentration it was found that by increasing its concentration to a limited level, the size of the particles decreased. The reason for this can be discussed as below:

By adding more amount of surface protecting agent, its molecules can be more absorbed on the surface of the particles and limit the growth mechanism of particles followed by results in generating smaller particles. Increasing more and more the amount of gelatin concentrations makes some micelles and due to the incomplete absorption of the molecules on the surface of particles in this situation, the gelatin molecules cannot be effective and the particles' size begin to be bigger and bigger.

Reducing agent is another important material which is used in chemical reduction. When the reducing agent is introduced to reaction medium, the metallic salts change to metallic atoms and the charge of the salts becomes zero. By adding more reducing agent, other metallic ions reduce to atoms and join the made core and this mechanism is called growth mechanism. So it is clear that by adding more reducing agent, the number of made cores will increase and this factor causes producing small particles.

A CCD design of experiment method was used to obtain an optimum condition to synthesize the copper particles. Twenty different reaction runs were done in this method. The details of the different conditions for the chemical reduction reaction are shown in the Table 2.

TABLE II. DETAILS OF THE DIFFERENT DESIGNED CONDITIONS IN CCD METHOD FOR THE CHEMICAL REDUCTION REACTION

RunOrder	Gelatin(gr)	Hydrazine (cc)	pH	Average Particle Size
1	1	11.36	9	323.4
2	1.5	10	10	194.6
3	1	8	10.68	66.6
4	1.5	10	8	57.4
5	1	8	9	65.1
6	1	8	9	77.0
7	1	8	9	57.4
8	0.5	10	8	48.8
9	1.5	6	10	28.6
10	1	8	7.32	123.7
11	0.5	6	10	95.0
12	1	4.63	9	29.8
13	1.5	6	8	130.1
14	1	8	9	63.2
15	0.16	8	9	211.7
16	1	8	9	76.9
17	1	8	9	79.0
18	1.84	8	9	24.7
19	0.5	6	8	31.7
20	0.5	10	10	359.2

By using the CCD method, and using DLS method and evaluating the average particle size of each run, the results showed that the size of particles was related to three defined factors. The results showed that the size of particle sizes could be displayed as in equation 1. The SEM image of an individual run which has the smaller particle size is shown in Figure 5 and also the results of the DOE are shown in Figure 6.

(1)

$$S = 1981.46 + 773.395X_1 - 356.004.38X_2 - 238.265X_3 + 55.4444X_1^2 + 8.62716X_2^2 + 5.71170X_3^2 - 23.5X_1X_2 - 84.5X_1X_3 + 30.36X_2X_3$$

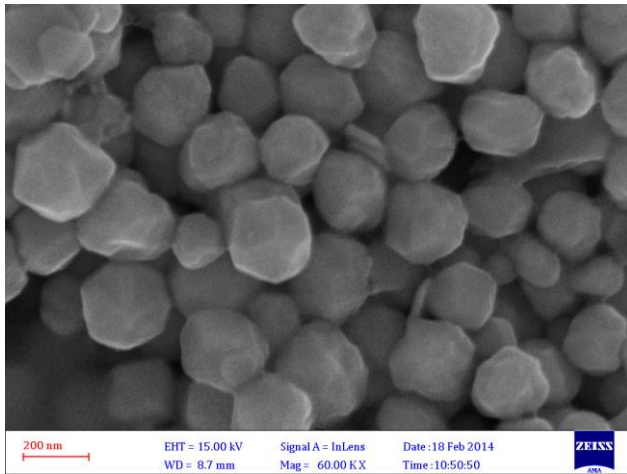


Fig. 5. SEM images of synthesized copper nanoparticles gained from 9th run

By adding reducing agent, the rate of nucleation process may become faster while the number of the nucleus becomes more. The pH value also can affect the particle size. By increasing the pH value, according to the equation 2, the rate of the nucleation reaction become fast and this increase in pH individually causes in decreasing the particle size. But as it can be seen these reason cannot be recognized when all the effects of three factors are being studied simultaneously. It can be explained more in this way that when a particular concentration of gelatin is used to synthesize copper NPs it may be in the zone that the concentration is excess and gelatin is not effective in decreasing particle sizes. In this way if we use more reducing agent, it should decrease the particle size because of formation more nucleus but in fact it cannot be seen. Because there are two different forces which one of them forces the particle size to be smaller while the other forces to increase particle size. In this way DOE just give a logical predict of the particle size with a non-done reaction.

$$\ln K_{eq} = nF\Delta E / RT \quad (2)$$

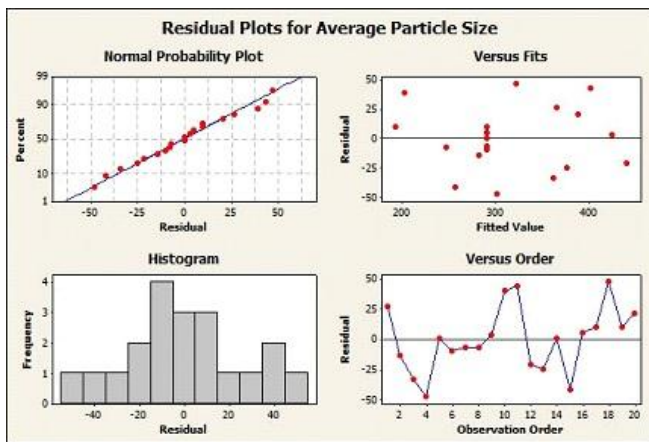


Fig. 6. Results of CCD design

Many researchers had investigated the effect of reaction parameters on the size of particles individually but the effect of reaction parameters had not been investigated simultaneously [12, 18, 19, 21-24]. The results of effects of parameters on the size of the particles are shown in Figures 7, 8 and 9. The relation between pH, reducing agent's concentration and particles size is shown in Figure 7. Figure 8 also shows the relation between pH, surface protecting agent's concentration and particle size and finally Figure 9 shows the relation between particle size, surface protecting agent and reducing agent's concentrations. As it can be clearly seen, a clear relation cannot be recognized between parameters and the final particle sizes. There are some common rules that can be used to predict the particle size but some of their effects may change when they become in contact with each other. For example it can be explained that by adding more surface protecting agent, the size of the particles decrease and reaches an optimum particle size. It should be noted that after this, the size of the particles increases again by adding more surface protecting agents.

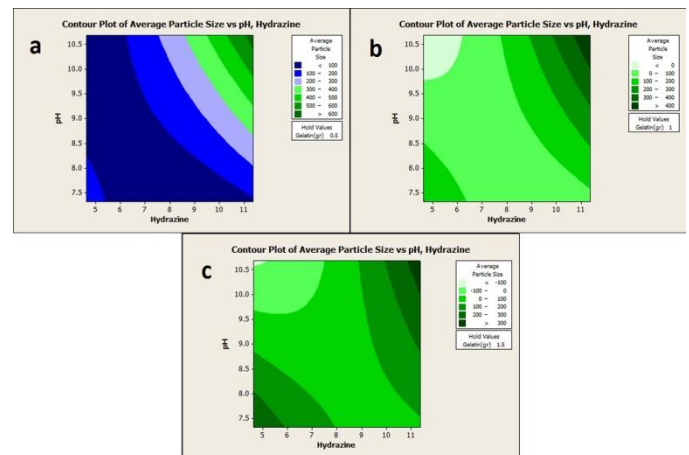


Fig. 7. Predicting of particle sizes (inside color bar) with the change of pH vs. hydrazine (cc) in different amounts of gelatin molecules: A) 0.5 gr, B) 1 gr, C) 1.5 gr

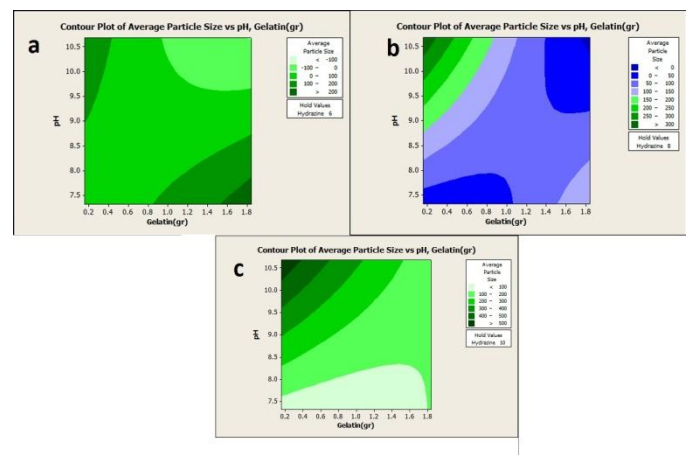


Fig. 8. Predicting of particle sizes (inside color bar) with the change of pH vs. gelatin (gr) in different amounts of hydrazine molecules: A) 6 cc, B) 8 cc, C) 10 cc

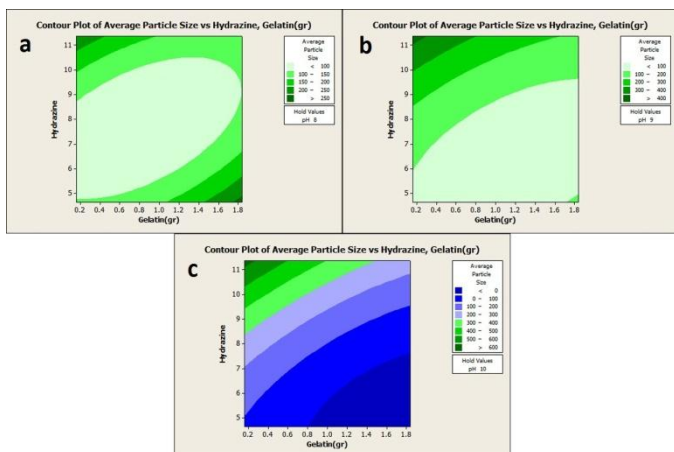


Fig. 9. Predicting of particle sizes (inside color bar) with the change of Hydrazine (cc) vs. gelatin (gr) in different pH values: A) 8, B) 9, C) 10

B. Oxidation of the copper particles

Synthesized particles were studied to investigate the oxidation behavior during and after the reaction. It is well known that copper particles can be oxidized very easily and this phenomenon was a big and challenging problem in synthesizing the copper particles. In this research, copper nanoparticles were obtained with almost no oxygen molecules on their surface and the synthesized particles were not oxidized after and during the reaction. The figure 10 shows EDAX analysis of synthesized copper nanoparticles in the fifth run of the DOE. We also recognized the map of oxygen and copper atoms on the surface of the synthesized particles. The figure 11 shows the map of these atoms. As it is clear in the Figure 10, there is no oxygen molecule on the surface of the particles. As it can be easily seen almost all the samples were pure and the percentage of oxygen was less than three percent.

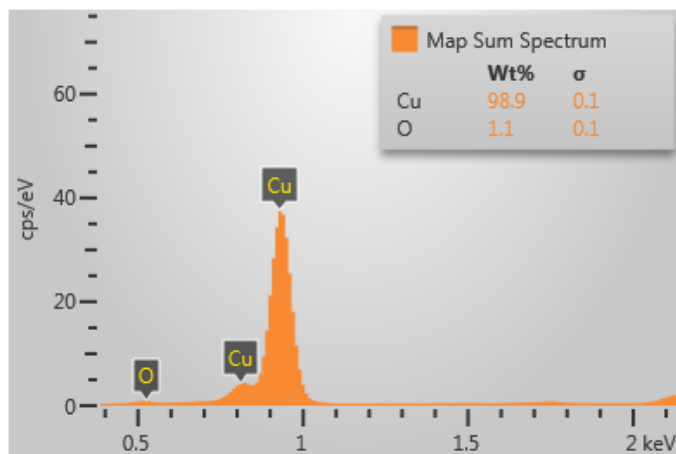


Fig. 10. EDAX analysis of synthesized copper nanoparticles

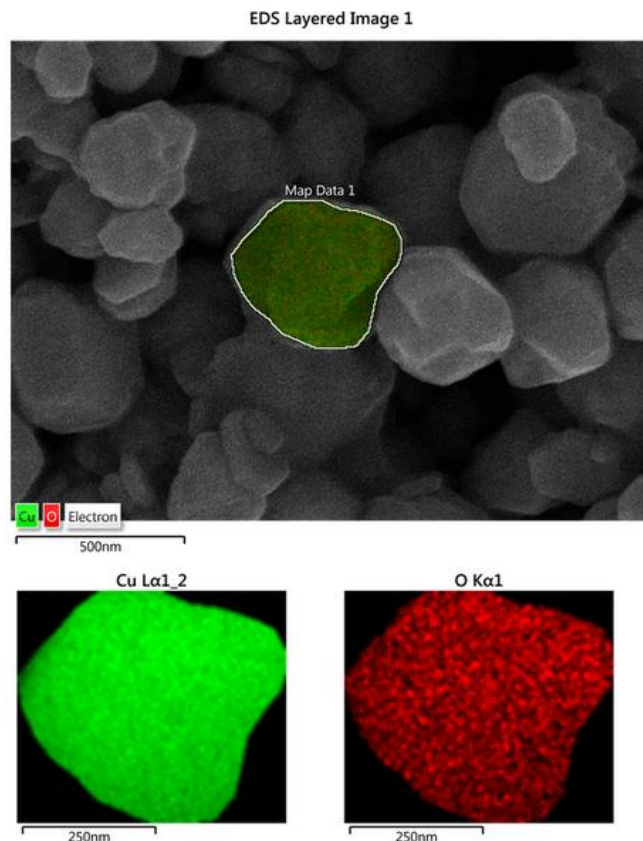


Fig. 11. Map of copper and oxygen atoms on the surface of synthesized copper nanoparticles

C. Formation of chemical bonds during reaction

In the beginning of the reaction, copper salts, surface protecting agent, reducing agent and ammonia molecules were in the reaction medium. In this case all the bonds between copper salts were electrostatically and ionic bonds. By completing the reaction and formation of copper atoms, the ionic bonds were being disappeared and new bonds were being formed between copper atoms and capping agent molecules.

D. Optical behavior of synthesized copper nanoparticles

The process of light absorption of organic molecules is usually attributed to the excitation of electrons in the molecular orbitals. Due to the lack of molecular orbitals of the metal nanoparticles, the absorption of light in this case is related to the phenomenon of surface plasmon resonance. It is known that sea of electrons in metallic nanoparticles float on the surface of a nanoparticle. In certain metal surfaces, light absorption leads to the resonance oscillation of the surface electrons.

Optical behavior of synthesized copper nanoparticles in this study is shown in figure 12. Figure 12 investigate the plasmon pick of copper nanoparticles that has been happened in the wavelength of 585 nm.

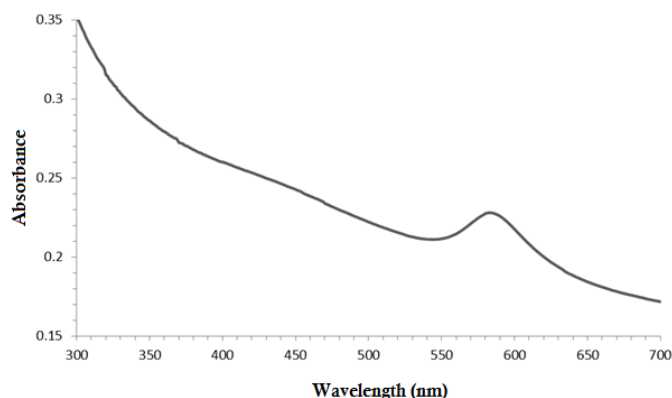


Fig. 12. Optical behavior of synthesized copper nanoparticles

IV. CONCLUSION

In this study, copper nanoparticles were synthesized by chemical reduction method. Gelatin a green surface protecting agent, hydrazine, ammonia and copper acetate precursor were used as reaction ingredients. The effects of reaction parameters like surface protecting agent's concentration, reducing agents concentration and the pH of reaction were studied by CCD design of experiment method.

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