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RESEARCH ARTICLE

Ecologically friendly production of copper powder and elimination of cupric ions from aqueous solutions using D-Glucose and ascorbic acid

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ABSTRACT

Copper(II) ions (Cu^{2+}) in copper sulfate solutions ($CuSO_4$) can be reduced with several carbohydrates to produce copper metal powder. In this study glucose was used as a reducing agent. The big challenge in this study was to find the optimum conditions for copper ions reduction because they were entwined with positive conditions for degradation and hydrolyses of sugar (D-glucose). For that reason, the impact of several parameters on these conditions was investigated in a series of experiments in this research study. The glucose concentration (0.2-1.6M), the temperature (30-70 °C), initial sodium hydroxide concentration (0.2-0.4M), the role of adding sulfuric acid (H_2SO_4) at different volumes (0.6-3 mL) and the addition of ascorbic acid at different doses (4-20 mL) were the considered key parameters that were studied in this research. The synthesis of copper was restricted due to organic acid build up and reactions of the degradation products and copper. Under optimum conditions using glucose as a reducing agent, maximum of 48% of copper ions were transformed to copper metal (Cu). By adding ascorbic acid at the end of the experiment process, reduction efficiency was 100% where total and complete copper reduction was achievable. Most of solid particles were analyzed and the characterization and nature of the produced solid was achieved by X-Ray Diffraction.

Keywords: Copper (II), glucose, ascorbic acid, copper metal synthesis, aqueous solution, X-ray diffraction analysis

1. INTRODUCTION

Hydrometallurgy has always a remarkable reputation in view of its ability to treat ores with lowest environmental pollution issues [1], [2]. One of the most important hydrometallurgy areas is metal compound recovery by precipitation or chemical reduction [3]. In the past years, a great interest for copper powder synthesis has improved because of its high demands and high quality characteristics [4]. It is know that copper ions can be reduced chemically by different carbohydrates as glucose, fructose and sucrose [5], [6].

In fact, copper ion (Cu^{2+}) is considered as an oxidant of ores (Kasaie et al 2016). It is also used in Fehling liquor destined to determine blood sugar level [8]. Furthermore, during reaction, copper ions containing in Fehling solution oxidize blood sugar giving carboxylic acid under its basic form (ion carboxylate) and brick red precipitate (Cu_2O) according to the following reaction [9], [10]:

$$R\text{-}CHO + 2Cu^{2+}_{(aq)} + 5HO^{-}_{(aq)} \rightarrow RCOO^{-} + Cu_2O_{(s)} + 3H_2O$$

The aldehyde group –CHO is present in the linear form of reducing sugars. Glucose is qualified as a reducing sugar, i.e. its open form D(+)-glucose can be oxidized selectively to glycolic acid or to ion gluconate according to solution pH. In this case, the reaction in an alkaline environment can be written as follows [11], [12]:

$$C_5H_{11}O_5CHO + 2Cu^{2+}_{(aq)} + 5HO^{-}_{(aq)} \rightarrow C_5H_{11}O_5COO^{-} + Cu_2O_{(s)} + 3H_2O$$

According to the reaction, it seems that glucose triggered only one step of reduction of copper ions where copper ion passed from Cu^{2+} to Cu^{+}. However, the ultimate objective of this study is synthesizing copper metallic powder from copper ions which requires two successive reductions [13]. For these reasons several experiments were conducted in this

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research study to determine optimal conditions for copper ions transformation.

The benefits of combinatorial approaches for better and complete metal recovery from aqueous solutions are unquestionable [14], [15]. The development of a new combination between two different reducing agent has improved copper ions reduction from copper sulfate solution [15], [16]. In addition of glucose, another known reducing agent was added to improve copper recovery efficiency.

2. MATERIALS AND METHODS

2.1. Preparation of solutions

The experiment was directed as follows: 10 mL of 0.8M glucose solution (pH of 6.5) was mixed with 10 mL of 0.3M sodium hydroxide (NaOH) i.e. 1.5 times the glucose concentration. (pH of NaOH solution was 12.9). The mixture was stirred mechanically in a bain-marie of 60°C as illustrated in the dispositive shown in Fig 1. After few minutes, the solution became clear yellow (pH of the mixture was 12) (Fig 2). According to the literature [17], [18], this color indicates that the glucose hydrolyze has taken place. After that, 10 mL of 0.2M copper sulfate ($CuSO_4$) was added drop by drop. After 10 min of the adding of $CuSO_4$, particles of brick color appeared (as shown in Fig 2b) indicating the creation of Cu_2O particles (at this level pH of the solution was 4). The next step was adding 0.6 mL (equivalent to 12 droplets) of pure sulfuric acid (H_2SO_4). pH of the final solution decreased to 1 and its color transformed to pink/brown as illustrated in Fig 2c.

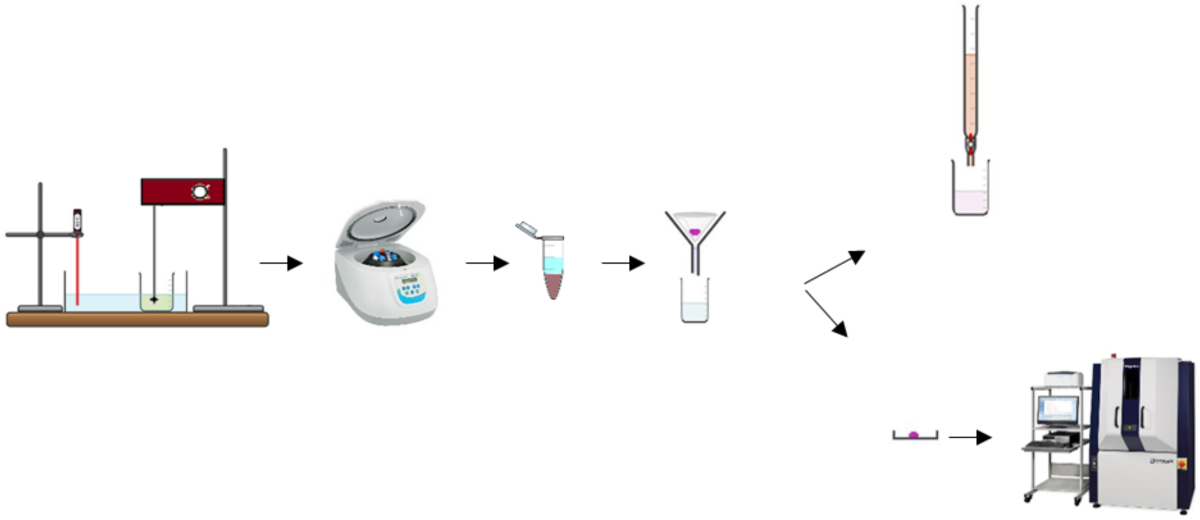

Fig 1. Schematic representative experimental dispositive of the research study.

(a) (b) (c)

Fig 2. Solution color variation during copper ions reduction using D-glucose in an alkaline environment (a) clear yellow solution, (b) brick color solution and (c) pink/brown solution

2.2. Analytical methods

The pink/brown solution obtained at the end of experiment was left for settling. The supernatant solution was taken to determine the remaining copper ions concentration. Ions quantity was determined by calorimetric dosage with Titriplex III and the presence of Murexide ($C_8H_8N_6O_6$) as color indicator. The solution was centrifuged at 6000 rpm for 05 min and the obtained solid particles were washed carefully by distillate water several times, filtrated using a standard paper filter and then dried in the open air. The ultimate powder was visually monitored and did not show any sign of oxidation. The characterization of solid powder was determined by X-ray diffraction (XRD) analysis.

3. RESULTS AND DISCUSSION

3.1. *Effect of glucose concentration*

10 mL of 0.2M copper sulfate and glucose volumes were kept constant while glucose concentration was varied as follows: 0.2M, 0.4M, 0.6M, 0.8M, and 1.6M corresponding to (glucose/Cu^{2+}) molar ratios of 1,2,3,4, and 8 subsequently. After settling, the final solution was dosed and the transformed copper ions were determined (Fig 3).

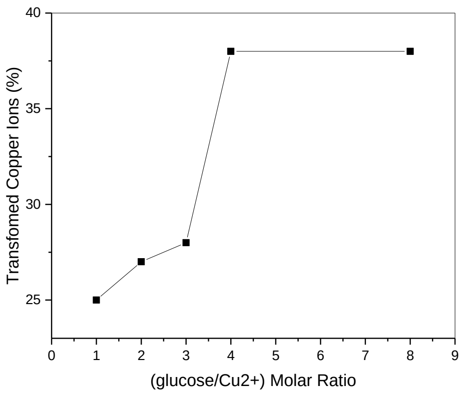

Fig3. Copper ions reduction efficiency in function of (glucose/Cu^{2+}) molar ratios

Results represented in the graph shown in figure 03 demonstrate that in all cases copper ions were partially reduced and transformed to copper solid. The best results were for 0.8M of initial glucose concentration (molar ratio of 4) where 38% of copper ions were reduced and deposited as dark pink solid particles. Molar ratios of 1, 2 and 3 showed copper ions reduction efficiency of 25, 27 and 28% consequently and the deposited solid was of brown color.

The increase of glucose concentration up to 1.6M (molar ratio of 8) did not show any advantage. Based on this result, it is evident that excessive electrons arising from glucose did not enhance copper ions reduction capacity [13]. However, the obtained deposited particles were of black color indicating the formation of copper monoxide (CuO) characterized by its coal color [19]. Therefore, at this concentration glucose oxidized copper ions instead of reducing them.

Consequently, glucose concentration is found of a great importance because it can orient to either a reduction or oxidation of copper ions containing in the aqueous solution. In order to determine the allotropic nature of the obtained solid particle, two samples of 2 and 4 molar ratios were analyzed by XRD. The obtained results are illustrated in Fig 4 and 5.

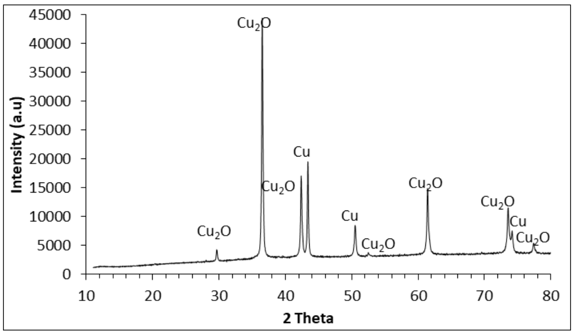

Fig 4. XRD specters of solid particles analysis obtained by 0.4M of glucose as reducing agent (glucose/Cu^{2+} molar ratio of 2)

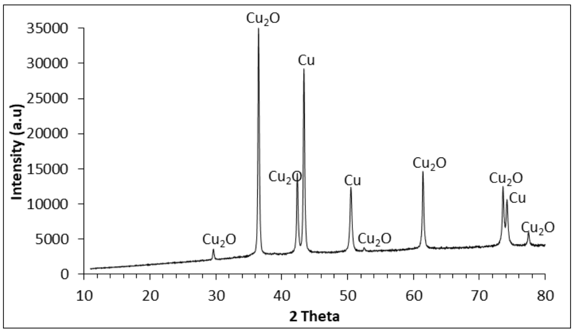

Fig 5. XRD specters of solid particles analysis obtained by 0.8M of glucose as reducing agent (glucose/Cu^{2+} molar ratio of 4)

The above results demonstrate that obtained solid particles given by both concentrations 0.4M and 0.8M of glucose are a mixture between copper metal (Cu) and cuprite (Cu_2O). Actually, there are few articles in the literature on the synthesis of copper metal using glucose; however, most of the literature studied the production of Cu_2O rather than Cu as confirmed in [6]. In addition, copper metal intensity peaks are lower than cuprite ones signifying weaker ability to transform copper ions to copper metal. However, glucose concentration played an important role of generated copper metal quantity. In fact, the peak observed a 42 in Fig 5 has got a bigger intensity than the one observed in Fig 4.

3.2. *Effect of temperature*

A range of temperatures was studied in this research to determine the optimum conditions for better copper metal synthesis from an aqueous solution. The different experiments were conducted under 30, 50, 60 and 70°C of temperature and 0.8M of glucose concentration. The rest of reactants concentrations and volumes were kept the same as the previous section. The obtained results are represented in Fig 6.

Results show that copper ions reduction using glucose as a reducing agent requires heat confirming previous studies in the literature [5, 20]. At nearly ambient temperature, 30 °C, the solution remained blue and did not change color. The dosage revealed very low transformation of copper ions. By increasing temperature, the quantity of produced solid particles has enhanced and became more important gradually.

Only a small increase of Cu^{2+} reduction was noticed for temperature increase from 30 °C to 50 °C. The maximum copper ions reduction efficiency was 48% obtained at 70 °C of temperature. Two samples of the best results, those of 60 and 70 °C, were analyzed and XRD specters are represented in Fig 7and 8 continuously.

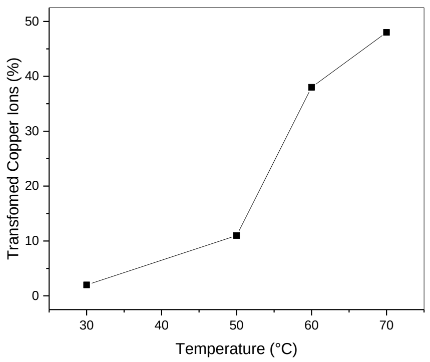

Fig 6. Copper ions reduction efficiency in function of reaction temperature

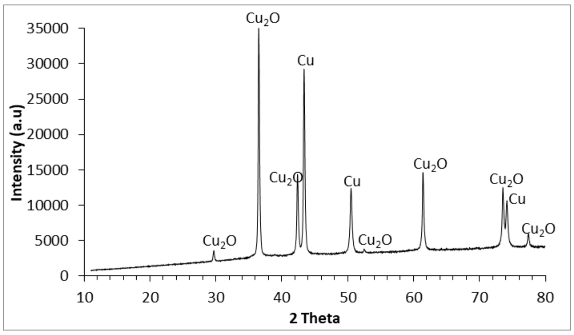

Fig 7. XRD specters of solid particles analysis obtained by 0.8M of glucose as reducing agent and 60 °C of reaction temperature

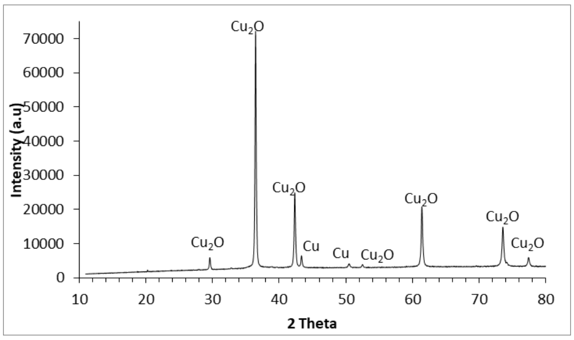

Fig 8. XRD specters of solid particles analysis obtained by 0.8M of glucose as reducing agent and 70 °C of reaction temperature

Comparing previous results, it is remarked that indeed temperature was in the favor of generating more solid particles; however, it did not act well to transform copper ions to metallic copper. At 70 °C, peaks which correspond to copper metal (Cu) are neglected compared to the ones of copper(I) oxide Cu_2O. On the other hand, the produced solid particles at 70 °C were more crystalline than the one of 60 °C. Furthermore, the temperature of 70 °C allowed the creation of crystallized precipitate formed mainly of Cu_2O. As a result, 60 °C of temperature was maintained for afterward experiments.

3.3. Effect of sodium hydroxide (NaOH) concentration

It is known that reduction of copper(II) to Cu by glucose requires high pH, where the metal species responds as insoluble oxides [13]. In this part of the study, 10 mL of three different sodium hydroxide concentrations were investigated: 0.2M, 0.3M and 0.4M, giving pH solution of 12.7, 12.9 and 13 respectively. The same experiences previously conducted were repeated using 10 mL of 0.8M glucose solution at 60 °C of temperature. Then, 10 mL of 0.2M copper sulfate ($CuSO_4$) was added to glucose-NaOH solution. In the three cases, when glucose was added to sodium hydroxide, pH of the mixture solution was nearly the same around 12. After adding $CuSO_4$, pH decreased to around 4, 4.5 and 5.5 for the different initial NaOH concentration 0.2M, 0.3M and 0.4M consecutively indication the consumption of OH^- ions. At this level of reduction, the color of the three solutions passes from yellow-green to brown-green. By adding the droplets of sulfuric acid (12 droplets equivalent to 0.6 mL), orange particles appeared demonstrating that a formation of Cu_2O has occurred. However, the particle color has instantly changed to pink-brown signifying that the second reduction has happened [18].

Solid particles obtained from the reaction under three different initial sodium hydroxide concentrations were analyzed and characterized by XRD. The results are illustrated in Fig 9, 10 and 11.

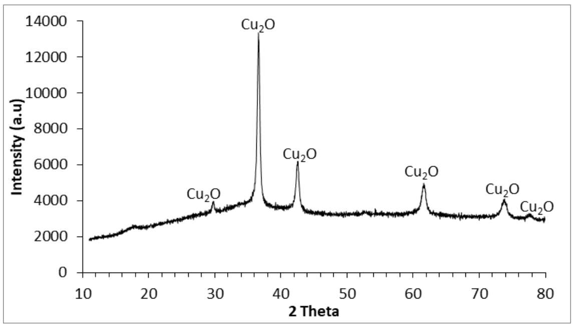

Fig 9. XRD specters of solid particles analysis obtained by 0.8M of glucose as reducing agent and 60 °C of reaction temperature and 0.2M of NaOH initial concentration

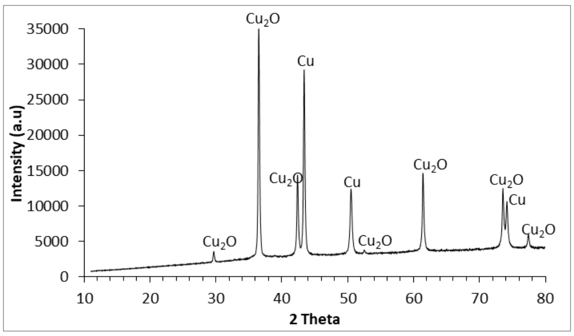

Fig 10. XRD specters of solid particles analysis obtained by 0.8M of glucose as reducing agent and 60 °C of reaction temperature and 0.3M of NaOH initial concentration

Fig 9 shows that the produced solid given by 0.2M of NaOH initial concentration is of amorphous form with the presence of cuprite (Cu_2O) particles only. By increasing sodium hydroxide initial concentrations, there was an apparition of metallic copper peaks with different intensities (Fig 10 and 11). Increasing the amount of NaOH resulted the decrease of Cu2+ reduction to Cu (Fig 11). From Fig 10, we can conclude that there are more important and stronger peaks corresponding to Cu showing that the optimum sodium hydroxide concentration for this experiment is 0.3M matching a solution of pH equal to 12.9. Although, considered pH in this study were close (12.7, 12.9 and 13); however, results were relatively different. As a result, pH is a key parameter to push the second copper ions reduction to occur.

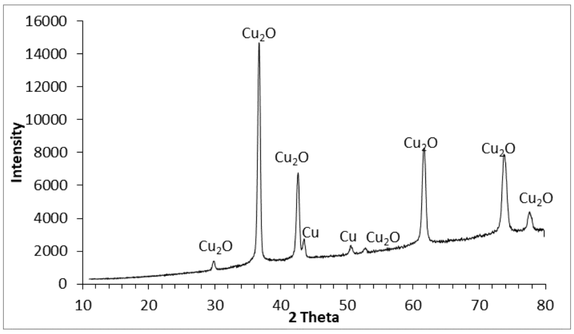

Fig 11. XRD specters of solid particles analysis obtained by 0.8M of glucose as reducing agent and 60 °C of reaction temperature and 0.4M of NaOH initial concentration

3.4. Effect of sulfuric acid volume

The objective of adding H_2SO_4 at the end of reaction was in order to promote the second reduction. When adding glucose solution to copper hydroxide solution, the mixture solution turns to orange color indicating the formation of Cu_2O particles and remains stable without changing its color even after a while. References [21] and [22] show the use of sulfuric acid for metals chemical reduction. The addition of sulfuric acid has provoked the change in color to dark pink. This color indicates that probably metallic copper has been produced. To determine the nature and characterize solid particles that were formed, two different sulfuric acid volumes were investigated, 0.6 mL (12 droplets) and 3 mL (60 droplets). The XRD results are shown in Fig 12 and 13 respectively.

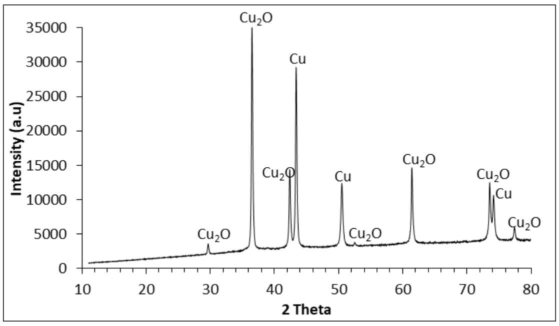

Fig 12. XRD specters of solid particles analysis obtained by adding 12 droplets of sulfuric acid H_2SO_4

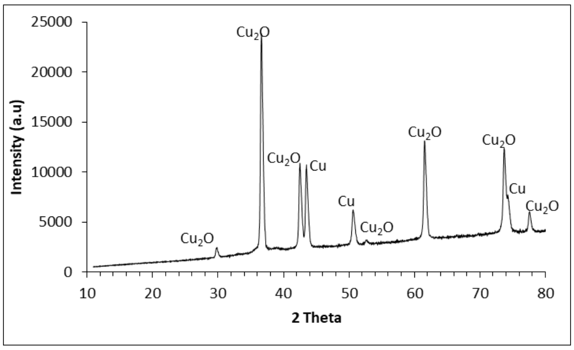

Fig 13. XRD specters of solid particles analysis obtained by adding 60 droplets of sulfuric acid H_2SO_4

The above results show that the concentration of sulfuric acid is a crucial parameter for copper ions reduction and copper metal synthesis. However, copper metal (Cu) peak intensity in Fig 12 (added H_2SO_4 volume is 0.6 mL) is more important than the one in Fig 13 (added H_2SO_4 volume is 3 mL). These results can be explained by the excessive use of acid, where copper can be solubilized in the acid solution [23].

3.5. Effect of adding ascorbic acid

It is perceived in all the previous experiments results that copper ions were not totally reduced to copper metal. For such reason, it is suggested that the second reduction reaction is difficult to achieve using glucose alone as a reducing agent. In the literature [24], glucose was used to reduce silver cations (Ag+) which requires only one reduction. The combination of two reducing agents seems to be a good idea to enhance copper ions reduction efficiency. Ascorbic acid is known to be an environmentally friendly reducing agent widely used for copper reduction from aqueous solutions [15, 25].

The experiment was conducted under the optimum conditions previously proved. 10 mL of glucose at 0.8M of concentration and 10 mL of NaOH 0.3M were heated up to 60 °C and mechanically mixed. 10 mL of $CuSO_4$ 0.2M was added to the mixture drop by drop. At the end of reaction, four different doses of ascorbic acid: 4, 10, 16 and 20 mL, were added. The obtained results are illustrated in Table 1.

Table 1. Impact of ascorbic acid addition on copper ions reduction to metallic copper. From Table 1, the addition of ascorbic acid has highly increased copper ions reduction efficiency. A complete Cu^{2+} degradation was achieved for 16 and 20 mL of ascorbic acid. The powder sample obtained by adding 16 mL of ascorbic acid was analyzed and the given XRD spectra is illustrated in Fig 14.

Table 1. Impact of ascorbic acid addition on copper ions reduction to metallic copper

Ascorbic acid volume (mL)	Transformed Cu^{2+} efficiency (%)	Observations
04	45	At the beginning, the supernatant solution was of dark green color and deposited solid particles were orange. After a week at ambient temperature, particles color changed to pink. After the change of color, Cu2+ dosage was redone and found that the total of copper ions were reduced
10	60	Pink solid particles were formed rapidly and the supernatant solution was light blue
16	100	Pink solid particles were formed rapidly and the supernatant solution was transparent
20	100	

Fig 14 shows that the produced solid is mainly formed by metallic copper (Cu) since the main important three pics correspond to copper metal particles. The presence of other copper species could not be verified because unfortunately spectrum could not be processed to eliminate noise and detect lower intensity peaks. Therefore, the addition of ascorbic acid has highly helped the reduction of copper ions and pushed the second reduction reaction to take place.

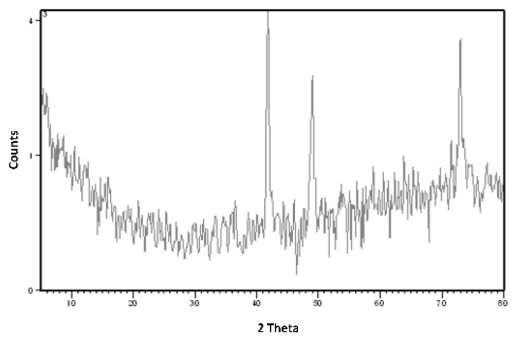

Fig 14. XRD specters of solid particles analysis obtained by adding 16 mL of ascorbic acid

4. CONCLUSIONS

Copper powder was synthesized from copper sulfate aqueous solution using glucose and ascorbic acid as a combination of reducing agents. Both reducers played an integrated role to obtain a total degradation of copper(II) ions. The first reduction reaction was conducted by glucose, where the second reduction was taken in charge after the addition of ascorbic acid. The initial glucose concentration affected significantly the efficiency of copper ions reduction. Increasing temperature to 70 °C, enhanced copper reduction efficiency. However, XRD analyses demonstrated that produced solid particles at this temperature was mainly composed of copper(I) oxide (Cu_2O). pH was a key parameter for Cu^{2+} ions reduction as well. Sodium hydroxide was added at different concentrations; however, a concentration of 0.3M headed to better results where copper metal peaks were more important and significant.

The addition of sulfuric acid did not help the second reduction to take place. Quite the opposite, when additional volume of H_2SO_4 was used, most of the powder was characterized by the presence of Cu_2O. Eventually, ascorbic acid was more effective by adding 16 mL at the end of reaction process, copper ions containing in the aqueous solution were completely transformed to solid particles. The nature of the formed product was confirmed by XRD analysis and it was mainly or totally made of copper metal. As a result, combination between the two reducing agents, glucose and ascorbic acid, can be affective approach to synthesis copper metal by chemical reduction and recover copper ions from polluted waters.

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