



Copper reduction by ascorbate under diluted and concentrated state

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Received 6 October 2022; Accepted 29 January 2023

ABSTRACT

In this study, the complexity of sodium ascorbate as a reducing reagent for copper by executing reactions with different ascorbate concentrations at 30°C and a copper concentration at 5 mM was emphasized. It was found that increasing the molar ratio of $n_{\text{ascorbate}}/n_{\text{Cu}^{2+}}$ from 1:1 to 10:1 prolonged the time for the completion of the reduction from 30 to 300 min, respectively. The reactions were investigated by the cyclic voltammetry method and the products were characterized by scanning electron microscopy and X-ray diffraction analyses. The synthesized materials obtained with molar ratios of 1:1 and 10:1 were composed of 55.47% Cu + 44.53% Cu₂O (labeled as As1) and 73.66% Cu + 26.34% Cu₂O (labeled as As10), respectively. Both products were tested for their ability to discolor Basic Red 29 via the Fenton reaction. The discoloration of the dye was more rapid with As1, due to the higher Cu₂O content.

Keywords: Ascorbate; Copper reduction; Concentration effect; Reduction mechanism; Fenton process

1. Introduction

The huge utilization of metals, fossil fuels and other resources of the planet which are extracted and transformed via aggressive processes caused significant environmental damages [1–4]. The last decades have witnessed a considerable development in the field of green chemistry, which projected new approaches for human development and the use of natural products. In the field of chemistry, the synthesis of metals is increasingly oriented toward the utilization of environmentally friendly products to respond to the increased demand for green chemistry and sustainable processes. Copper is one of the most studied metals in literature because of its interesting characteristics. In the framework of synthesis, copper was fabricated by different techniques such as chemical, electrochemical, photochemical, and thermal methods [5,6]. Reduction is a chemical method using reducing reagents such as hydrazine, glycerol, hydroxylamine hydrochloride, and borohydride. These products are strong reductants but are harmful to the environment. Ascorbic acid was

envisaged as a green, renewable, and inexpensive reducing agent [7–9]. Ascorbic acid was also studied in the framework of its oxidation by different elements [10,11] but its reactivity was not yet clearly identified. This probably comes from the various forms into which it can be transformed, such as ascorbate anion, ascorbate free radical, and dehydroascorbic acid. This may also explain, why despite numerous reports, there is still no generally accepted mechanism for its oxidation taking place concurrently with the reduction process of the metal in which it is involved. The most accepted proposal is that the metal ion interacts with ascorbate through an initial electron transfer that results in the reduction of the metallic cation and the oxidation of ascorbate. In this mechanism, ascorbate is transformed into dehydroascorbic acid (A) by the release of protons, and the metal ion is reduced to a lower valence state. The difficulty of obtaining a single mechanism is also associated with the wide variety of conditions used in literature, such as different pHs, temperatures, aerated and non-aerated media, buffered and non-buffered solutions, the presence and absence of metals, and their nature [12,13].

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In our previous studies, sodium ascorbate was used as a green reagent for the reduction of copper [14,15]. The obtained product was found to be very active as a catalyst in a heterogeneous Fenton-like process. During the investigation of the effects of the operating conditions on copper reduction, it was noticed that the higher the concentration of ascorbate, the slower the reduction reaction. The mechanism of copper reduction by ascorbate in a concentrated state has received little attention in the literature. Generally, increasing the concentration of the reducing reagent improved the kinetics of the reduction reaction of the metallic cation. However, the contrary was observed in this case. Among the extensive studies dealing with the reduction of copper by ascorbate, only two papers were found [16,17] in which this effect was invoked without being explained.

In this study, the reduction of copper by sodium ascorbate at different concentrations is reported. The aim is not to propose a mechanism since there are still mechanistic interrogations about its reactivity, but to draw attention to a phenomenon that was ignored as it may allow for further deeper investigations.

2. Materials and methods

Solutions of copper cations and sodium ascorbate were prepared by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (99 wt.%, Sigma-Aldrich) and sodium ascorbate (100 wt.%, Riedel-de Haën) separately in deionized water. The experiments were carried out under atmospheric pressure, 30°C, and 250 rpm. In a typical experiment, 50 mL of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at 5 mM (0.25 mmol) was mixed with the same volume of sodium ascorbate at different concentrations. At the end of the experiment, the concentration of Cu^{2+} species remaining in the supernatant was analyzed by titration with ethylene diamine tetra acetic acid disodium salt (EDTA) using murexide as an indicator [18].

Cyclic voltammetry (CV) measurements were performed on the Potentiostat/Galvanostat (Biologic Science) model SP-300. The experiments were conducted in a three-electrode cell of 100 mL capacity under air at 30°C. The system consisted of a glassy carbon as the working electrode, Pt wire as the counter electrode, and Ag/AgCl/in 3 M KCl as the reference electrode. 10 cycles with a scanning rate of 50 mV/s were applied for each CV measurement.

During the experiments, the pH of the solutions was measured using a pH metre (model BOECO BT-600).

X-ray diffraction patterns used to identify the phase constitution were obtained with a Rigaku Ultima IV X-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) in step mode between 20° and 80°, using a step size of 0.02°/s. The surface morphology was examined by a FEI Quanta 250 FEG SEM.

The products were tested in the discoloration process of a cationic dye, Basic Red 29 (BR) with molecular formula $\text{C}_{19}\text{H}_{17}\text{ClN}_4\text{S}$. The concentration of BR 29 was determined using a Jenway 6705 UV/Vis spectrometer at 510 nm. Samples of BR 29 solution at different time intervals were measured in an optical quartz cell. The discoloration efficiency of BR 29 was calculated from the difference between the initial absorbance (A_0) and the absorbance at different time intervals (A_t):

$$\text{Discoloration efficiency (\%)} = \left(\frac{A_0 - A_t}{A_0} \right) \times 100 \quad (1)$$

3. Results and discussion

3.1. Images and copper dosage

Fig. 1a–c show camera photos taken during copper reduction by sodium ascorbate at 5–10 and 50 mM, respectively, at different time intervals at 30°C and 250 rpm. It can be seen that the time for completing the experiments was 30 min for 5 mM, 60 min for 10 mM, and 300 min for 50 mM. The yellow color instantaneously appeared upon mixing the two solutions. The transformation of the yellow suspension into orange, indicating the formation of Cu_2O occurred after 10 min with 5 mM and 20 min with 10 mM, while the orange color was absent with 50 mM. For the last case, the yellow suspension lasted upto 60 min and was transformed slowly to green–brown after 120 min, which darkened with time until the appearance of a red–brown suspension at 300 min. Clearly, the kinetics of the reduction of copper were slowed down by increasing the concentration of ascorbate. After the reactions, the particles were filtered and the soluble copper remaining in the supernatant was analyzed thereby, the percentage of the reduced copper was calculated. The values obtained were 80.62%, 93.87%, and 98.63% of copper reduced with ascorbate at 5, 10, and 50 mM, respectively (Fig. 2).

3.2. Cyclic voltammetry

The advantage of the cyclic voltammetry method is that both oxidative and reductive processes can be observed in one scan. The experiments were carried out by mixing copper sulfate at 5 mM with ascorbate at 5, 7, 10, 20, 30, and 50 mM. The intermediate concentrations: 7–20 and 30 mM were added because the shift in voltammetric curves when ascorbate concentration increased from 5 M to 50 mM was abrupt and no cathodic and anodic peaks were observed with 50 mM.

Fig. 3a shows a cyclic voltammogram of copper reduction by ascorbate at the concentrations of 5–7 and 10 mM. The cathodic peaks observed at -0.315 V and -0.313 V with ascorbate concentrations of 5 and 7 mM, respectively, correspond to the redox couple (Cu^{2+}/Cu , $E = 0.34 \text{ V}$) (Table 1). However, the value of potential shifted to -0.234 V with ascorbate at 10 mM and the anodic peak of ascorbate oxidation broadened. The current intensity of both cathodic and anodic peaks remarkably decreased as the concentration of ascorbate increased.

At higher ascorbate concentrations (20–30 and 50 mM), the cyclic voltammogram shows no detectable oxidation peak of ascorbate or reduction of copper (Fig. 3b). This makes the use of the cyclic voltammetric method for concentrated solutions not viable because its reliability is not ensured in this case. This problem was likely due to the electrodes being fouled by oxidation products. Nevertheless, the clear shift in peaks when comparing the curves of the low ascorbate concentrations used (7 mM compared to 5 mM) confirmed the delay in the progress of the reaction that was visually observed.

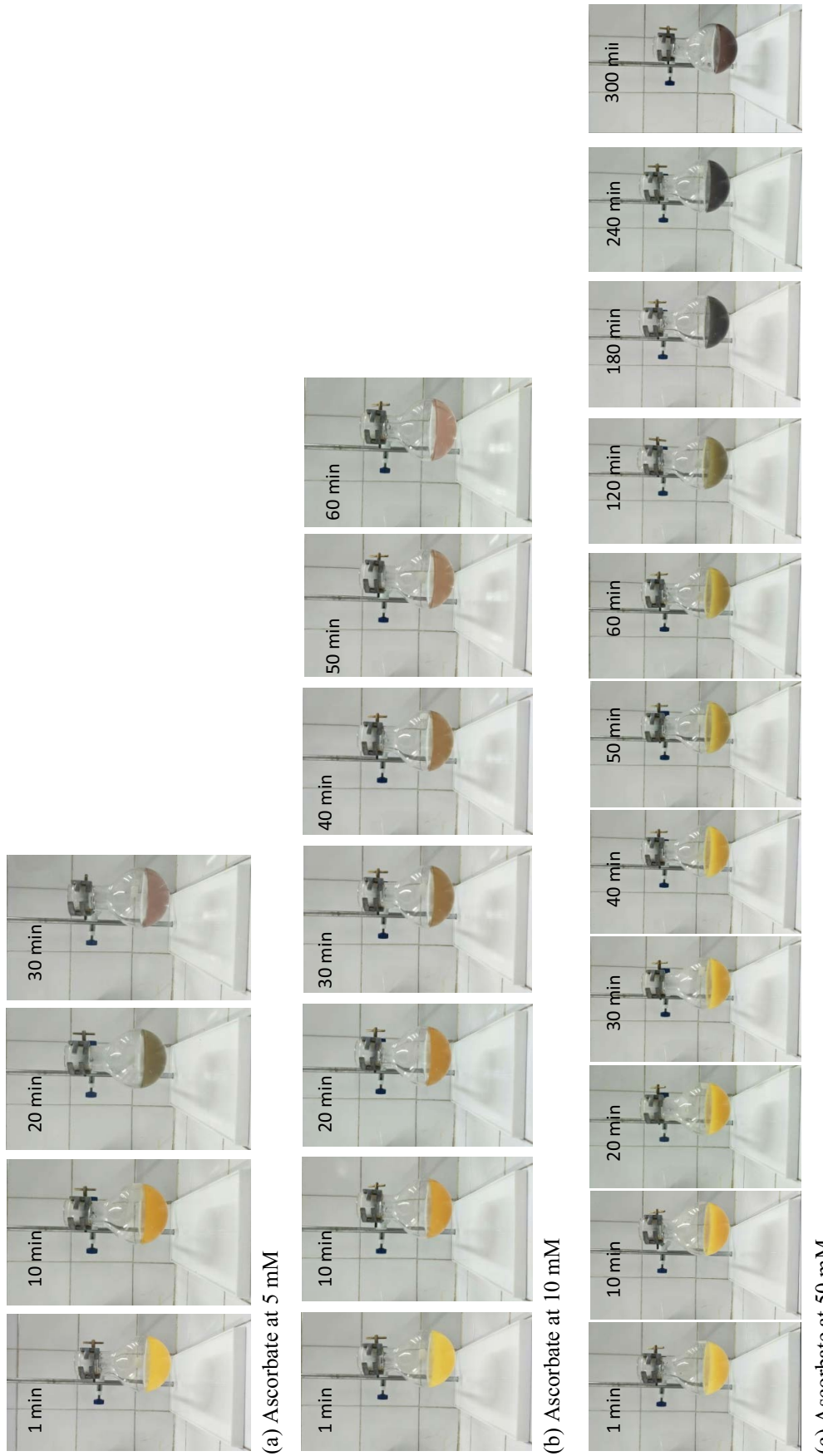


Fig. 1. Steps of copper (5 mM) reduction by ascorbate at different concentrations. Operation conditions: 30°C, 100 rpm.

3.3. pH measurements

The pH was monitored during the reduction of copper by ascorbate at 5 and 50 mM, respectively (Fig. 4). The initial pH value of copper sulfate solution at 5 mM was 5.3 and those of ascorbate solutions were 7.11 for 5 mM and 7.54 for 50 mM. After mixing, a decrease in pH to 3 and 4.78, respectively, was observed. In both cases, the decrease in pH value was very fast; 2 min with ascorbate at 50 mM, and 5 min for 5 mM after which they stabilized.

The decrease in pH values indicated the release of protons, and their stabilization indicated their non-consumption in subsequent steps and/or the presence of acidic products. This fast pH variation was however accompanied by slow progress in copper reduction. It took 30 min for ascorbate at 5 mM and 300 min for ascorbate at 50 mM to complete the reduction.

3.4. SEM and XRD analyses

Fig. 5a–d shows SEM images and XRD analyses of the samples synthesized with ascorbate at 5 and 50 mM, respectively.

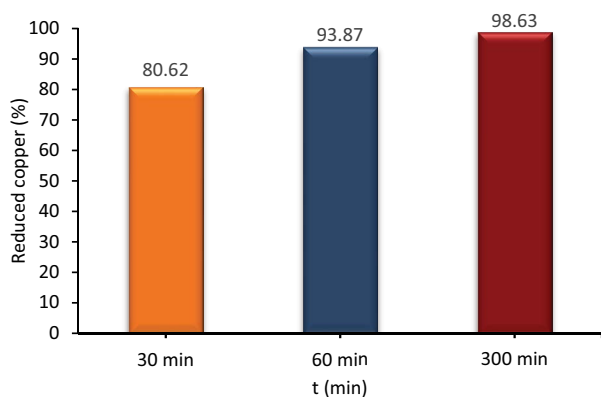


Fig. 2. Percentages of the reduced copper (5 mM) analyzed at the end of the experiments conducted with sodium ascorbate at 5 mM (orange), 10 mM (blue), and 50 mM (red) at 30°C and 250 rpm.

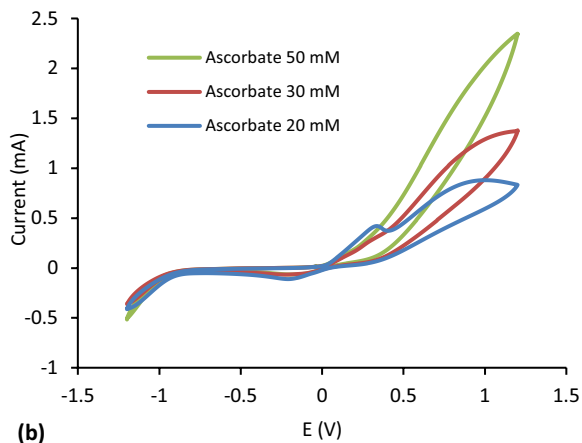
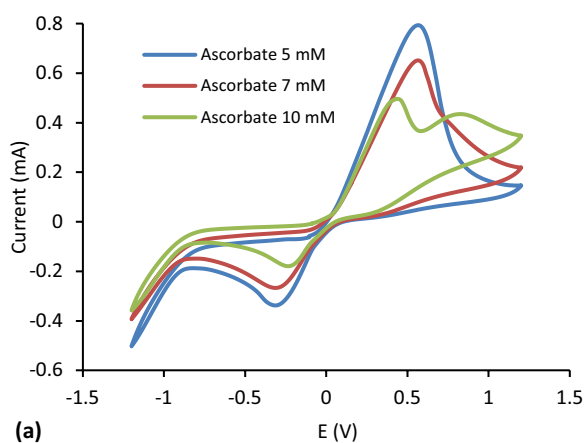


Fig. 3. Cyclic voltammograms of copper (5 mM) reduction by sodium ascorbate at 5, 7, and 10 mM (a) 20, 30, and 50 mM (b) at 30°C and 250 rpm.

It can be seen that the sample produced under equimolar conditions (5 mM) exhibited spherical particles with different diameters varying within the ranges of 0.8–3.5 μm and 170–400 nm (Fig. 5a). On the contrary, the particles obtained with 50 mM were smaller with sizes varying between 160 and 400 nm (Fig. 5c). In this case, the size was more uniform with the absence of the large particles. Thus, diluted ascorbate solution allowed for a fast reduction reaction with the formation of large particles, while concentrated ascorbate prolonged the reaction time and formed fine particles.

Table 1

Data obtained from the voltammograms at different ascorbate concentrations

	I_c	E_c	I_A	E_A
Ascorbate at 5 mM	-0.337 mA	-0.315 V	0.793 mA	0.566 V
Ascorbate at 7 mM	-0.267 mA	-0.313 V	0.651 mA	0.565 V
Ascorbate at 10 mM	-0.179 mA	-0.234 V	0.496 mA	0.438 V
Ascorbate at 20 mM	-0.110 mA	-0.208 V	0.420 mA	0.336 V

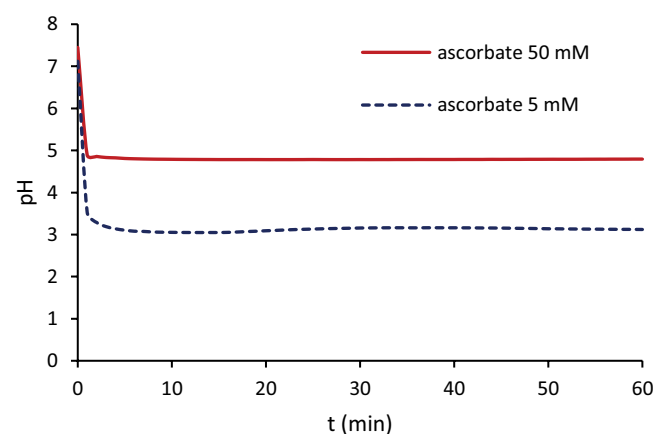


Fig. 4. pH variation during the reduction of copper by ascorbate at 5 and 50 mM at 30°C and 250 rpm.

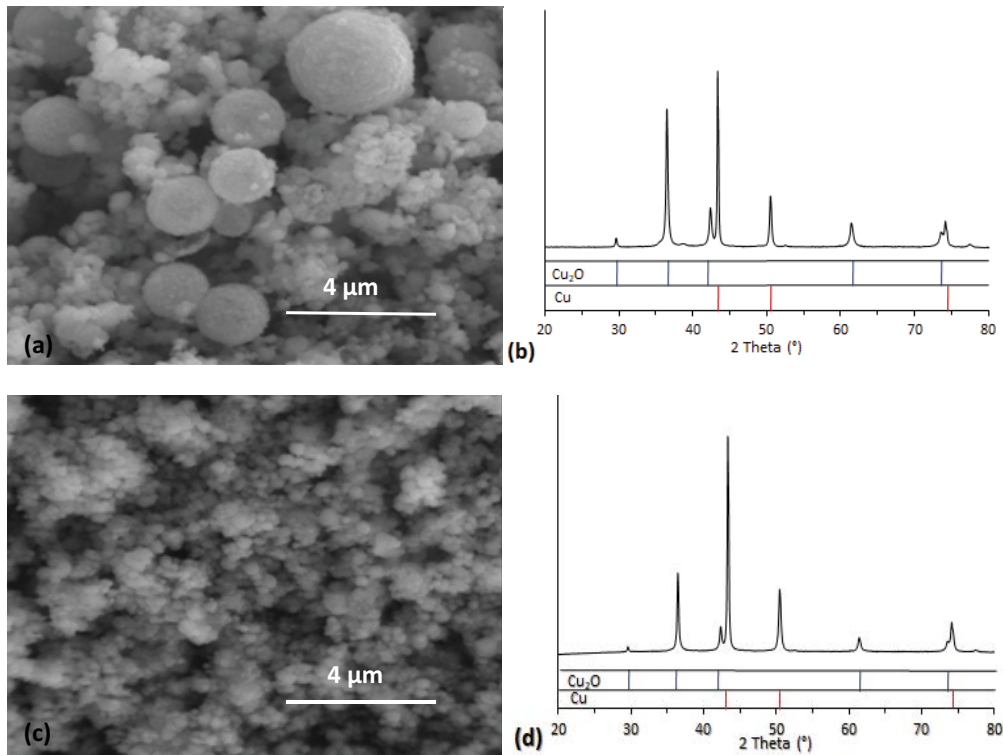


Fig. 5. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses for the samples obtained after reduction of copper with ascorbate at 5 mM (a, b) and 50 mM (c, d) at 30°C and 250 rpm.

XRD analysis shows the formation of Cu ($2\theta = 43.3^\circ, 50.4^\circ, 74.1^\circ$) and Cu_2O ($2\theta = 29.6^\circ, 36.5^\circ, 42.4^\circ, 61.4^\circ, 73.6^\circ$) on both samples, but the proportion of Cu was lower on the sample synthesized with ascorbate at 5 mM (55.47% Cu + 44.53% Cu_2O) (Fig. 5b) than that synthesized with ascorbate at 50 mM (73.66% Cu + 26.34% Cu_2O) (Fig. 5d).

This is logical since the ratio of 1:1 is generally not sufficient to ensure a total reduction of copper. However, the ratio of 10:1 also showed the presence of Cu_2O despite the high ascorbate concentration used. This may be due to the fact that the long reaction time (300 min) in an aqueous medium has promoted the exposure of the formed particles to water molecules, dissolved oxygen, and other species, leading to their partial reoxidation.

3.5. Effect of temperature

The experiments were conducted with copper and ascorbate concentrations of 5 mM under the agitation of 250 rpm and the synthesis temperature was varied within the range from 30°C to 60°C.

The results show that the particle formation time was shortened with increasing temperature. At 60°C, for example, the reaction ended only after 20 min. Furthermore, Cu content increased with the increasing temperature (Fig. 6). At 30°C the product was formed by 55.47% Cu + 44.53% Cu_2O , while at 60°C it was composed by 83.48% Cu + 16.52% Cu_2O (Fig. 7).

On the other hand, SEM images clearly show finer particles obtained at 60°C (400 nm), while those obtained at 30°C have dimensions ranging between 0.8 and 3.5 μm .

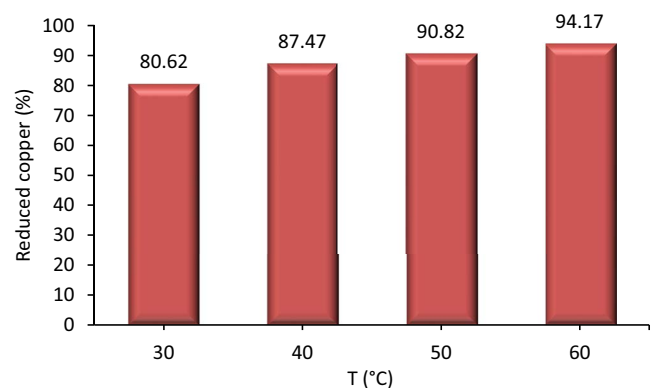


Fig. 6. Effect of temperature on copper reduction by ascorbate. Operating conditions: $C_{\text{Cu}} = C_{\text{As}} = 5$ mM, $V_{\text{Cu}} = V_{\text{as}} = 50$ mL, 250 rpm, $t = 60$ min.

The study of the subsequent parameters was carried out at 60°C because it allowed the reduction of a high percentage of copper in a short time.

3.6. Effect of pH

The experiments were carried out by varying the pH of the CuSO_4 solution (3–5.3 and 12) using sulfuric acid and sodium hydroxide. The experiments were conducted at 60°C and 250 rpm with both reagents at 5 mM.

XRD analysis shows that the samples prepared with CuSO_4 at pH 3 and 5.3 were mainly formed of metallic

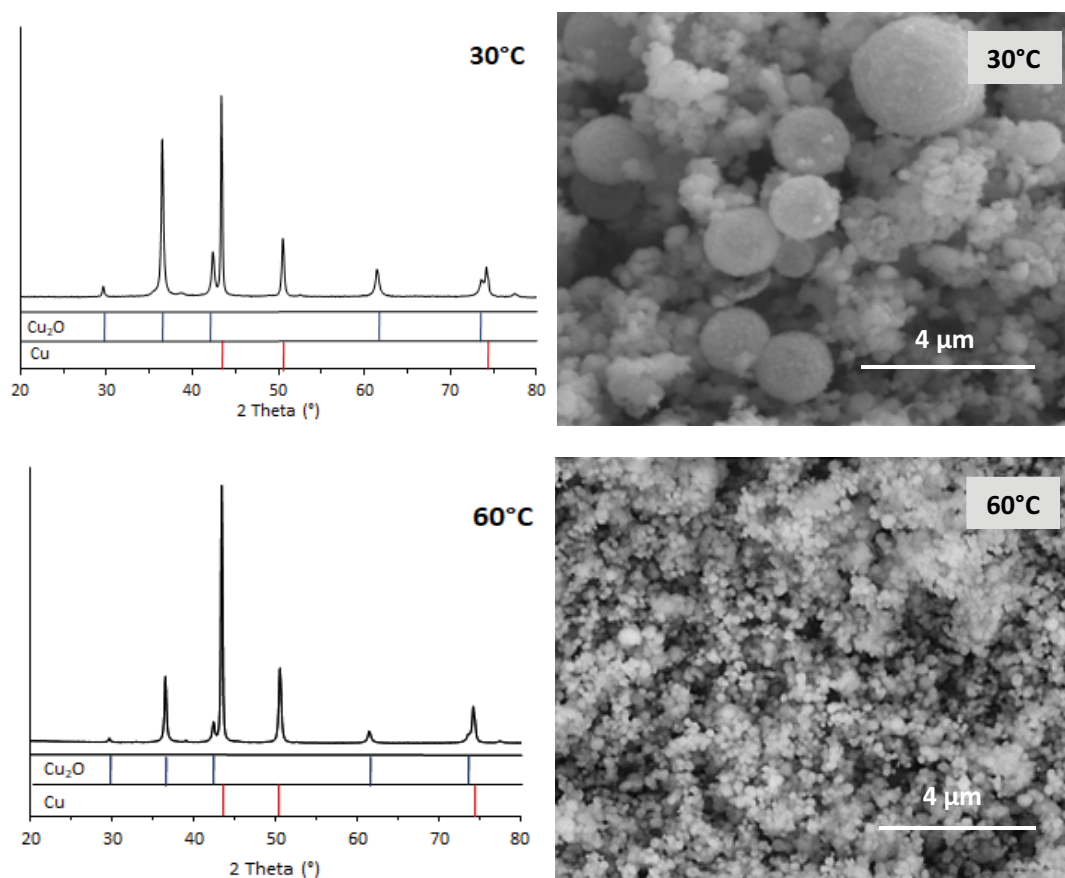
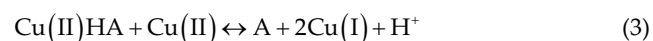


Fig. 7. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses of copper samples obtained at 30 and 60°C. Operating conditions: $C_{Cu} = C_{As} = 5$ mM, $V_{Cu} = V_{as} = 50$ mL, 250 rpm, $t = 60$ min.

copper 87.62% Cu + 12.38% Cu_2O and 83.48% Cu + 16.52% Cu_2O , respectively, while the sample prepared with $CuSO_4$ at pH 12 was exclusively composed of Cu_2O (Fig. 8).

SEM images show that increasing the pH of the $CuSO_4$ solution decreased the particle size of the obtained product. At pH 3 the particles were non-agglomerated and polyhedral in shape, with a mean size of about 2 μm while those obtained at pH 5.3 and 12 were finer with a mean size of about 400 nm and 135 nm, respectively.

In the literature, a number of different mechanistic proposals have been advanced to explain the reduction results of copper by ascorbate. The reaction is not simple due to the complexity of the ascorbate anion and appears to follow several routes depending on the conditions used. Weissberger et al. [19] suggested a mechanism involving an initial formation of a metal complex between copper and ascorbate anion, followed by a rate-determining electron transfer from the ascorbate anion to the metal ion:



Martell [20] suggested that once the complex is formed, it dissociates in a fast step to a lower valence metal.

Smith and Martell [16] reported the value of the stability constant of copper-ascorbate in stoichiometric condition (1:1) equal to $10^{1.6}$ which is considered as a weak value. Thus, ascorbate in the presence of copper tends to form weak chelates that are easily dissociated in the solution. However, no data was reported about the value of stability constant when the molar ratio $n_{Asc}/n_{Cu^{2+}}$ increased. Nevertheless, Martell [20] reported that the rate of ascorbate oxidation by copper decreased with increasing the stability of complexes without indicating what could be the cause of this stability.

Ascorbate is known as a chelating agent which may modify its coordination to the copper center upon the increase in its concentration by bringing a large number of donor groups coordinated to the metal ion. These coordinated bonds are probably more difficult to break in this case than in a diluted ascorbate solution. It is also known that the rate of any reaction is influenced by the geometric properties of the reagents [20]. Steric factor as an additional cause could affect the rate of the reaction [20] and this factor is linked to the orientation and dimension of the ligand [21]. In fact, ascorbate is a quite large molecule ($r = 341$ pm vs. 72 pm for Cu^{2+}). When ascorbate at 50 mM was used, the molar ratio was 10: 1 and an excess of large ascorbate ions remained in the solution. It is possible that this excess of organic molecules caused bulkiness in the solution, thus sterically preventing the progress of the reduction as shown in Fig. 1c.

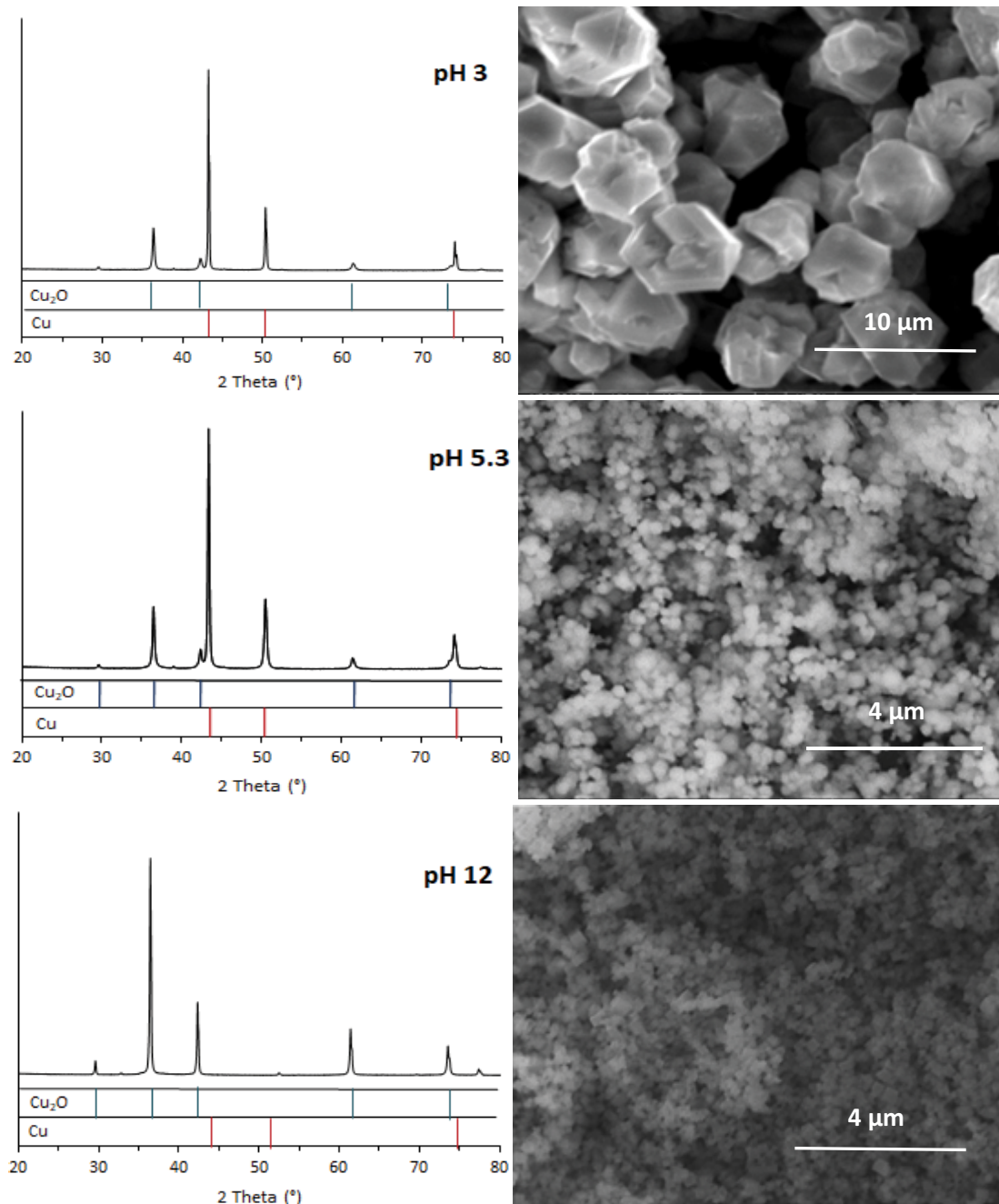


Fig. 8. X-ray diffraction (XRD) patterns and scanning electron microscopy (SEM) images of the samples obtained at pH = 3, 5.3, and 12. Operating conditions: $C_{Cu} = C_{As} = 5$ mM, $V_{Cu} = V_{as} = 50$ mL, 250 rpm, 60°C, $t = 60$ min.

What is worth noting is that diluted ascorbate produced large particles despite the rapidity of the reaction, which ended after just 30 min. Diluted medium seems to favor the agglomeration and growth process.

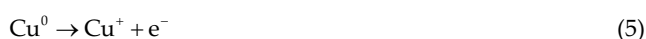
On the contrary, with concentrated ascorbate, the particles remained small despite the 5 h reaction time during which the particles could have easily agglomerated. But this fact did not occur. The oxidation product of ascorbate (dehydroascorbic acid "A") was longer considered inactive. However, the contrary was found by certain authors. In fact, the degradation of ascorbate was found to continue

beyond dehydroascorbic acid which was found to be unstable in water since its lactone ring opens spontaneously to form 2,3-diketogulonic acid (DKG) [22]. In the presence of oxidizing elements, such as copper, DKG may further be degraded up to 50 products such as 4,5,5,6-tetrahydroxy-2,3-di-ketohexanoic acid (THDH), and threonic acid ($C_4H_8O_5$) via decarboxylation reactions during which an oxygen atom is consumed by each reaction [23–25]. These products are thought to possess a reducing character [23]. This may explain the high reduction efficiency obtained in a stoichiometric condition, where normally a weak yield

should be obtained because of the mild reducing power of ascorbate.

3.7. Application of copper in the discoloration reaction of Basic Red 29

In our previous studies [14,15] it was observed that copper in an acidic medium produced H_2O_2 in situ via the reduction of the dissolved oxygen in water by the metal:



and that the formed H_2O_2 was transformed into reactive oxygen species such as $\cdot OH$ by the Fenton reaction [26]:

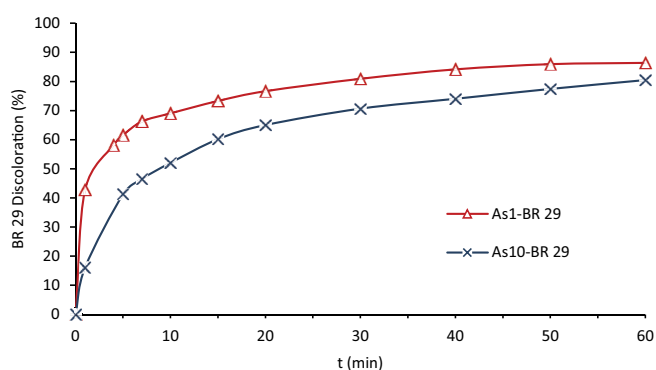
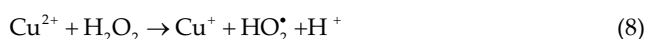


Fig.9. Application of As1 and As10 in the discoloration of Basic Red 29. Operation conditions: $m_{\text{copper}} = 30$ mg, $C_{\text{BR 29}} = 5 \times 10^{-5}$ M, pH 3, 40°C, 100 rpm.

The $\cdot OH$ is an unselective powerful oxidant that is primarily responsible for the degradation of organic pollutants. It was observed that a solid composed of Cu and Cu_2O was more efficient than Cu alone [14]. In the present study, the two products synthesized with ascorbate under equimolar condition $n_{\text{ascorbate}}/n_{\text{Cu}^{2+}} = 1$ (labeled as As1) and excess ascorbate $n_{\text{ascorbate}}/n_{\text{Cu}^{2+}} = 10$ (labeled as As10), were tested in the discoloration process of a cationic dye (Basic Red 29) in order to investigate the effect of the composition on their activities. The experiments were conducted by mixing under magnetic stirring (100 rpm), 30 mg of the samples with 100 mL of BR 29 solution at 5.10^{-5} M acidified at pH 3 and heated at 40°C by a temperature-controlled water bath.

The results obtained with As1 show a rapid discoloration rate at the beginning of the reaction, where 42.79% were registered after just 1 min. The reaction rate remained fast for up to 7 min after which it decreased, attaining 86.37% after 60 min (Fig. 9).

Under the same conditions, the discoloration of BR 29 proceeded more slowly with As10 when compared to As1 where 16.12% were registered after 1 min and increased continuously up to 80.49% attained after 60 min. It should be noted that the discoloration occurred through the *in-situ* production of hydrogen peroxide which is safer and cost-effective than the classical Fenton process, where external H_2O_2 addition is needed [14,15].

Fig. 10 shows the UV-Vis spectra of the dye registered during its discoloration in the presence of both products, where a fast decrease in peak intensity is clearly seen with As1 after just 1 min of reaction.

The discoloration followed a pseudo-first-order kinetic at the beginning of the reaction up to 10 min, where the calculation of rate constants gave the values of 0.0892 and 0.0404 min^{-1} for As1 and As10, respectively. In the first stage of the reaction, the discoloration process in the presence of As1 was two times more rapid than that with As10.

As1 is composed by a mixture of large and small particles, while As10 is composed of fine particles that provided higher surface area, but despite that, its activity in dye discoloration was lower than that of As1. These results may be related to their compositions. In fact, As1 and As10 are formed by 55.47% Cu + 44.53% Cu_2O and 73.66% Cu + 26.34%

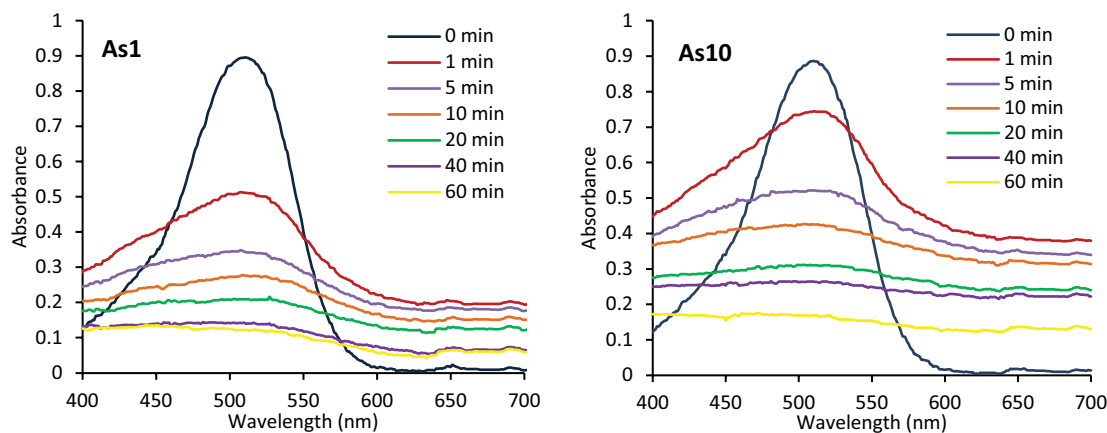


Fig. 10. UV-Vis spectra of BR 29 discoloration in the presence of As1 and As10. Operation conditions: $m_{\text{copper}} = 30$ mg, $C_{\text{BR 29}} = 5 \times 10^{-5}$ M, pH 3, 40°C, 100 rpm.

Cu₂O, respectively. In our previous study, Hamidani et al. [14] found that increasing the proportion of Cu₂O, improved the activity of Cu-Cu₂O in the Fenton process. This may explain the superior results obtained with As1 compared to As10.

From the results, one can conclude that the conditions used for the synthesis of copper affected the surface characteristics and the activity of the obtained products. In fact, using ascorbate in a concentrated state led to an increase in the time for the completion of the reduction reaction. This long reaction time led to form fine particles with uniform size and high content of metallic copper.

Depending on the utilization of the solid, the high content of copper may be beneficial or not in the process in which it is involved. In the Fenton reaction, it is the solid which contains a high proportion of Cu₂O that exhibits superior activity. On the other hand, the easiness by which copper was synthesized under ambient conditions in the framework of a green process makes this method greatly interesting. However, sodium ascorbate as a reducing reagent has a particular behavior, especially in a concentrated state which makes it very attractive and an exciting candidate for further studies.

4. Conclusions

This paper aims to shed light on ascorbate reactivity in a concentrated state that was not sufficiently considered in the literature. Generally increasing the concentration of the reducing reagent improves the kinetics of any reduction reaction, but the contrary was observed in this case. In fact, the time for the completion of copper reduction increased in the same order as the ratio $n_{\text{ascorbate}}/n_{\text{Cu}^{2+}}$. When the ratio ($n_{\text{ascorbate}}/n_{\text{Cu}^{2+}} = 1:1$) the reduction ended after 30 min and when it was 10:1, the reaction was completed after 300 min. It is difficult to interpret certainly these results since several factors may be the cause such as the formation of stable complexes, congestion of the reactive medium caused by the presence of large ascorbate anions, the multitude of secondary (side) reactions of the excess ascorbate producing a high number of products which interfere with the progress of copper reduction.

Both solids were tested in a discoloration process of Basic Red 29. The reaction rate in the presence of the sample synthesized under equimolar conditions was two times higher than that registered with the sample synthesized with a molar ratio of 10:1. The high content of Cu₂O formed on the first sample was the cause of such a result.

This study aimed to use a green and sustainable process in the synthesis of copper, emphasizing the unusual behavior of ascorbate as a reducing agent. Despite the fact that ascorbate is a common and natural product that is largely used, its reactivity remains complex and very interesting which needs further studies to be elucidated.

Acknowledgements

This work is supported by the Ministry of Higher Education and Scientific Research of Algeria (PRFU Project N°A16N01UN230120180003) through The General Directorate of Scientific Research and Technological

Development (GDSRTD). The authors would like to thank Pr Zougar S. for CV measurements.

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