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RESEARCH ARTICLE

Synthesis of copper particles and elimination of cupric ions by chemical reduction

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ABSTRACT

Development of enhanced methods for copper particles synthesis is crucial for the improvement of material science and technology. Therefore, in this study a successful synthesis of copper metal was achieved by chemical reduction. Ascorbic acid was used as a reducing agent. In the presence of soda, copper sulphate pentahydrated ($CuSO_4$, $5H_2O$) with acid ascorbic at 60 °C of temperature produced metallic copper powder with the total degradation (100%) of copper ions (Cu^{2+}). The presence of hydroxide ions (OH^-) is necessary to achieve and improve the chemical reduction reaction. Several parameters, as reducing agent volume, reaction temperature and soda quantity were investigated and checked their impact in this research study. The obtained powder was washed and dried in the fresh air then analysed by X-ray diffraction.

Keywords: Ascorbic acid, chemical reduction, ions, copper metal, copper sulphate, sodium hydroxide

1. INTRODUCTION

Water pollution by heavy metals has got a serious toxicological impact. For this reason, it is necessary to monitor industrial wastes contents as well as water designated for domestic consumption [1]. Among these metals, we find copper, which is an essential trace element for human metabolism. However, in small quantity, where the daily adult need for copper is about 0.2 mg [2]. WHO recommended a provisional guide value of 0.2 mg L^{-1} of copper concentration in domestic water [2]. Copper can be found in some natural water sources under ionic or complex forms at low concentrations less than 0.1 mg L^{-1} [2]. It can be also found as metallic deposits, electric and electronic household wastes and leachates of minerals. In addition, water piping corrosion generates from 0.5 to 0.1 mg L^{-1} of copper in water [2] [3] [4].

It already exists several methods of aqueous copper separation solutions. These methods are based on chemical precipitation phenomenon [5], ions exchange [6], biosorption [7], extraction [9] [10] or membrane separation [11].

Reduction method is largely used for metallic nanoparticles synthesis and in particular for copper. Different reducing agents have been used as sodium borohydride [12] and hydrazine [13]. Natural agents as ascorbic acid are used for copper ions (Cu^{2+}) reduction to metallic copper [14]. Reduction method has got a big advantage of cleaning up water from dissolved copper ions and transforming them to metallic particles that can be easily separated after settling.

2. MATERIALS AND METHODS

2.1. Preparation of solutions

Prepared solutions were made at the basis of distillate water of pH between 5.5 to 6.8 and conductivity from 3 to 5 µS cm^{-1}. In this study, the mass molar of the two prepared solutions are 249.69 g mol^{-1} and 176.13 g mol^{-1} for copper sulphate solution ($CuSO_4$, $5H_2O$) 0.2 M and ascorbic acid ($C_6H_8O_6$) consecutively.

A defined volume of acid ascorbic was heated to 60 °C in a laboratory bain-marie. Once the ascorbic acid was preheated, 10 mL of copper sulphate was added drop by drop agitated with a mechanical stirrer as shown in the scheme in Figure 1.

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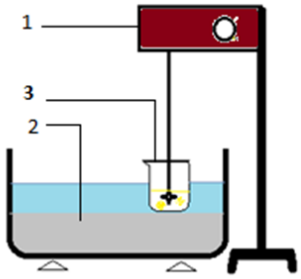

Fig 1. Experimental dispositive of the research study. 1: Mechanical stirrer 2: Laboratory bain-marie 3: Beaker (reactor)

The series of reactions of ions copper reduction until obtaining metallic copper are represented in the three following reactions (1), (2) and (3).

$$Cu^{2+} + C_6H_8O_6 \rightarrow Cu^{+} + C_6H_6O_6 + 2H^{+} \quad (1)$$

$$Cu^{+} + 2OH^{-} \rightarrow Cu(OH)_2 \quad (2)$$

$$Cu(OH)_2 + C_6H_8O_6 \rightarrow Cu + C_6H_6O_6 + 2H_2O \quad (3)$$

2.2. Analytical methods

During reaction and every 10 min, a sample was taken to determine copper ions concentration. The concentration was determined by calorimetric dosage with Titriplex III and the presence of Murexide ($C_8H_8N_6O_6$) as colour indicator. After 0.1 hr of reaction, the final solution was centrifuged at 6000 rpm for 5 min. The deposited solid was washed by distillate water then filtrated by standard paper filter. The obtained solid was dried in the open air. During drying process, the obtained powder was visually monitored. It did not show any sign of oxidation and the final obtained powder is illustrated in Figure 2.

For the optimal conditions, the prepared or obtained solid sample was analyzed by X-Ray Diffraction (XRD) for different solids characterization.

Fig 2. Metallic copper powder obtained after copper ions reduction

3. RESULTS AND DISCUSSION

3.1. Effect of acid ascorbic volume

In this section of the study, the variation of reducing agent volume was investigated and studied its impact on the copper ions production efficiency. Three different volumes of ascorbic acid were used 20, 50 and 60 mL. The attained results are represented in Figure 3.

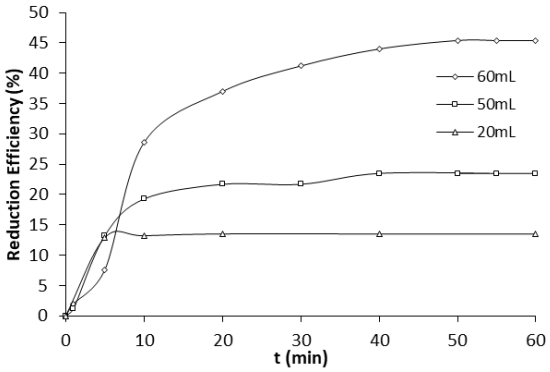

Fig 3. Copper ions reduction efficiency in function of ascorbic acid volume

The results show that 45.5% of copper ions were generated at 60 mL of ascorbic acid after about 60 min of reaction. The weakest efficiency was noticed at 20 mL of ascorbic acid. According to the obtained results, it can be seen that the copper reduction efficiency increases with the increase of reducing agent volume. This improvement of copper reduction can be explained by more ascorbic acid molecules which are available for reducing the same quantity of copper ions containing in the aqueous solution [15] [16].

The dried solid sample obtained at 60 mL of ascorbic acid was analysed and XRD results are illustrated in Figure 4, where it is clear that the two significant spectres correspond to pure metallic copper.

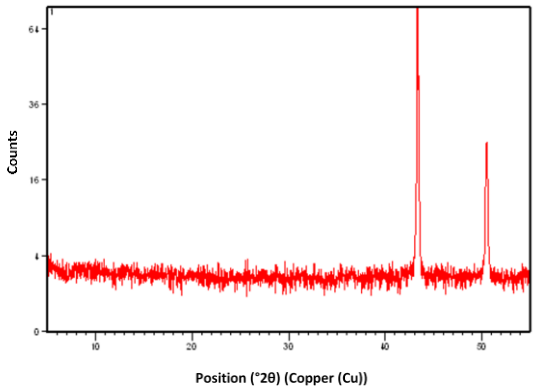

Fig 4. XRD Spectre obtained after copper ions reduction with 60 mL of ascorbic acid volume

3.2. Effect of temperature

To study the impact of temperature on the copper ions reduction, the same procedure was followed. However, the laboratory bain-marie temperature was varied.

The investigated temperatures were: 27, 40, 60 and 70 °C. The achieved results are summarised in Figure 5.

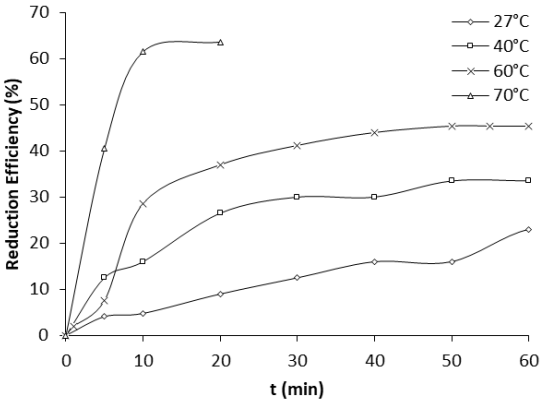

Fig 5. Copper ions reduction efficiency in function of bain-marie temperature

The results illustrated in Figure 5 show that the ions copper reduction is favoured by increasing temperature. In fact, the reduction efficiencies obtained after 60 min of reaction were 23, 33.5 and 45.4% at 27, 40, and 60 °C subsequently. The energy required to trigger copper ions reduction into copper particles declines with the temperature. Additionally, at higher temperatures, the probability of one molecule colliding and reacting with another increases [15]. In this study, the increase of temperature to 70 °C allowed having 63.6% of ions copper reduction efficiency after just 20 min of reaction confirming what was found in the literature [15]. However, under this temperature, water started to evaporate which leads to a decrease in treated water quantity and eventually the studied concentration of ascorbic acid as a reducing agent will be different from its initial value. For such reasons, the experiment was stopped once water evaporation started and it was judged that 60°C is the optimum temperature of copper reduction using 60 mL of ascorbic acid. In all tests, colour indicator gave pink colour indicating that the reaction has taken place.

3.3. Effect of copper ions reduction in an alkaline environment

According to ions copper reduction reactions (2) and (3), reduction can happen in an alkaline environment. Thereby for such reason, it is studied how much is affected reduction efficiency according to the volume of sodium hydroxide added. The experimental procedure was altered this time, where initially 10 mL of copper sulphate was mixed with 10 mL of sodium hydroxide of the same concentration 0.2M to form copper hydroxide ($Cu(OH)_2$). The measured pH of solution was 12.7. The mixture is then added to the preheated 60 mL of ascorbic acid drop by drop and agitated with a mechanical agitator as done in the first experiments. The results are shown in Figure 6.

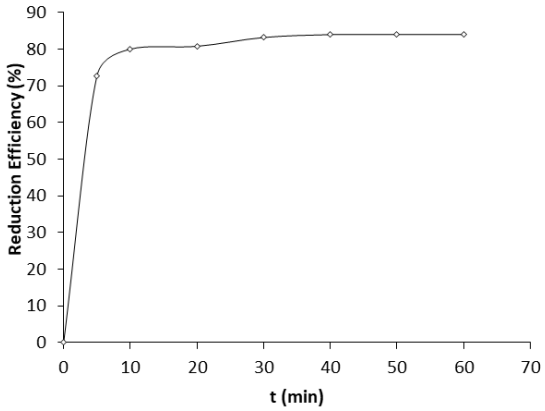

Fig 6. Copper ions reduction efficiency for 60 mL of ascorbic acid in an alkaline environment at 60 °C

As expected and with compliance with other researches, the addition of NaOH solution has dramatically impacted on the progress of copper chemical reduction reaction [16] [17] [18]. After 30 min of reaction, 84% of ions copper were reduced. However, according to Figure 3 and under the same conditions of ascorbic acid volume and temperature, reduction efficiency was only 41.2% after the same period of reaction without alkaline solution.

3.4. Effect of sodium hydroxide volume

To determine how the volume of sodium hydroxide can alter the reduction efficiency, many volumes were taken in consideration (10, 20, 30 and 40 mL) and the rest of conditions kept constant as in the previous section. The obtained results are illustrated in Figure 7.

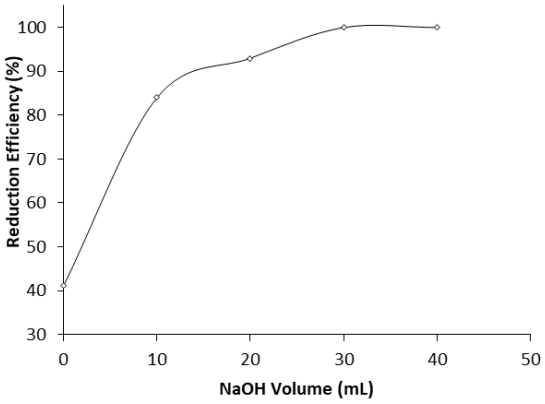

Fig 7. Copper ions reduction efficiency in function of sodium hydroxide volume for 60 mL of ascorbic acid volume at 60 °C of temperature

The results represented in Figure 7 indicated that a complete ions copper reduction was achieved with addition of 30 mL of NaOH. Therefore, it is definitely, ions copper reduction is better in an alkaline pH. However, it is difficult to explain the cause. Actually, no explanation was found in the literature. Probably, it can be explained by the initial transformation of copper ions to hydroxide particles which gives the advantage of their transformation to reduced particles.

4. CONCLUSION

The main objective of this research work was about investigation the possibility of copper elimination by chemical reduction using ascorbic acid as a reducing agent. This experimental study allowed to note that the chemical reduction of copper hydroxide can be achieved at 100% of removal efficiency using 60 mL of ascorbic acid and 30 mL of sodium hydroxide at 60 °C

REFERENCES

[1]. M. Di Benedetto, "Méthodes spectrométriques d'analyse et de caractérisation, Les Métaux Lourds", *National High School of Mines, Saint-Etienne, France*, pp. 4-48, 1997. Available: https://studylibfr.com/doc/2772848/methodes-spectrometriques-d-analyse-et-de-caracterisation (accessed on the 01 May 2020).

[2]. J. Rodier, B. Legube, and N. Merlet, "L'Analyse de l'eau, Contrôle et Interprétation", *Techniques et Ingénierie, Dunod, 9th edition*, pp. 1244, 2009.

[3]. J.M. Balet, "Gestion des déchets", *Aide-mémoire, Dunod, 2nd edition*, pp. 121, 2008.

[4]. Y. Andrès, C. Faur-Brasquet, C. Gerente, and P.L. Cloirec, "Techniques de l'Ingénieur w8000 Élimination des ions métalliques et des métalloïdes dans l'eau", *Techniques de l'Ingénieur*, pp. 5-6, 2007.

[5]. L. Youcef, and S. Achour, "Elimination Du Cuivre par Des Procèdes De Précipitation Chimique et d'adsorption", *Courier du Savoir, Biskra, Algeria.* Vol 7, pp. 59-67, 2006.

[6]. P. Rajec, L. Matel, J. Orechovska, J. Sucha, and I. Novak, "Sorption of radionuclides on inorganic sorbents, Journal of Radioanalytical and Nuclear Chemistry", Vol. 208(2), pp. 477-486, 2008.

[7]. S. Kadouche, "Utilisation des biomatériaux dans le traitement des eaux", *Ph.D. Thesis, Mouloud Mammeri University, Tizi Ouzou, Algeria*, pp. 9-11, pp. 112-126, 2013.

[8]. S. Ghali, "Etude de la carbonisation d'un précurseur végétal, les noyaux d'olives. Utilisation dans le traitement des eaux", *M. Eng. Thesis, 20 August University, Skikda, Algeria*, pp. 25-60, 2008.

[9]. A. Bendada, "Etude expérimentale et modélisation de L'élimination des cations métalliques de L'acide phosphorique issu du procédé Humide. Application aux cas de l'aluminium, le fer et le cuivre", *Ph.D. Thesis, Mentouri University, Constantine, Algeria*, pp. 32-35, pp. 64, 2005.

[10]. F. Ghebghoub, "Effet du diluant sur l'extraction du cuivre(II), cobalt(II) et nickel(II) par l'acide di-(2-ethylhexyl) phosphorique", *Ph.D. Thesis, Mohamed Khider University, Biskra, Algeria*, pp. 63-84, 2013.

[11]. M. Kermiche and S. Djerad, "Desalination and water treatment facilitated transport of copper through bulk liquid membrane containing di-2ethylhexyl phosphoric acid", *Taylor and Francis, London, UK*, pp. 261–269, 2011.

[12]. W. Hongshui, Q. Xueliang, C. Jianguo, and D. Shiyuan, "Preparation of silver nanoparticles by chemical reduction method", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 256, pp. 111-115, 2004.

[13]. V.Q. Khuong, V.D. Cao, T.B.T. Nguyen, and T.P.P. Nguyen, "Synthesis and characterization of metallic copper nanoparticles at room temperature by hydrazine reduction method", *Tap chi Khoa hoc va Cong nghe*, Vol 50 (3C), pp. 519-524, 2012.

[14]. W. Songping, "Preparation of fine copper powder using ascorbic acid as reducing agent and its application in MLCC", *Materials Letters*, Vol. 61(4-5), pp. 1125-1129, 2007.

[15]. A.R. Ramos, A.K.G. Tapia, C.M.N. Pinol, L.B.L. Ma, L.F. del Mundo, R.D. Manalo, and M.U. Herrera, "Effect of reaction temperatures and reactants concentrations on the antimicrobial characteristics of copper precipitates synthesized using L-ascorbic acid as reducing agent", *Journal of Science: Advanced Materials and Devices*, Vol. 4, pp. 66-71, 2019.

[16]. A. Khan, A. Rashid, R. Youmas, and R. Chong, "A chemical reduction approach to the synthesis of copper nanoparticles", *International Nano Letters*, Vol. 6, pp. 21-26, 2016.

[17]. T.M. Dung Dang, T.T. Thu Le, E. Fribourg-Blanc, and M.C. Dang, "Synthesis and optical properties of copper nanoparticles prepared by a chemical reduction method", *Advances in Natural Sciences: Nanoscience and Nanotechnology*, Vol. 2, pp.06, 2011.

[18]. Q.M. Liu, T. Yasunami, K. Kuruda, and M. Okido, "Preparation of Cu nanoparticles with ascorbic acid by aqueous solution reduction method", *Transactions of Nonferrous Metals Society of China*, Vol. 22, pp. 2198-2203, 2012.