ISSN 0973-3450 (Print)
JUC Vol. 15(3), 23-29 (2019). Periodicity 2-Monthly
ISSN 2319-8036 (Online)

JOURNAL OF ULTRA CHEMISTRY
An International Open Free Access Peer Reviewed Research Journal of Chemical Sciences and Chemical Engineering
website:- www.journalofchemistry.org
Estd. 2005

Extraction optimization of cupric ions by cloud point

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http://dx.doi.org/10.22147/juc/150301

Acceptance Date 04th Febuary, 2019, Online Publication Date 02th May, 2019

Abstract

Several pre-concentration and separation techniques are known, as well as the cloud point extraction (CPE). In order to optimize the operation of a coacervate extraction process, it is extremely important to take into account, on the one hand, the choice of the surfactant, which must be the most efficient and, on the other hand; and to know well the evolution of the factors that governs the effectiveness of this technique.

Investigations on the extraction of cupric ions by Triton X-100, the ionic liquid denoted LIM and the potassium nitrate (KNO_3) were produced using the technique of extraction by cloud point (coacervat). The extraction experiments showed that the cupric ions were extracted with the following optimal parameters: pH 2.0; Concentration of LIM equal to 0.08M; Triton X-100 mass ratio equal to 0.1%; KNO_3 mass ratio equal to 1%; at ambient temperature.

Key words: Copper (II), Cloud point extraction, Ionic liquid, Nonionic surfactant.

Introduction

The separation and recovery of heavy metal cations from effluent streams is becoming a major challenge for several industrial plants due to the environmental requirement in terms of metal ion pollution. Heavy metals pose a serious global environmental concern because of their toxicity, abundance and persistence in the environment, and accumulation in aquatic habitats. Cu is an important micronutrient required for good health. It is considered essential not only for mammals, but also for plants. However, a high concentration of Cu is toxic. As a result, the determination of its traces is crucial for the natural protection of water. Thus, many processes have already been used, such as liquid-liquid extraction[1], solid phase extraction[2], precipitation[3] and cloud point extraction (CPE)[4-6] should be used. CPE, a kind of micellar systems, has attracted considerable attention because it is in line with the principles of

"green chemistry". The cloud point extraction process results from phase separation induced by the well-known temperature presented by micellar solutions of nonionic surfactants. Accordingly, any metal ion which interacts directly with surface-active micelles or after complexation with a hydrophobic chelating ligand can be extracted from the stock solution by a CPE method. Its use has been very promising for several reasons, the first being that it is a purely aqueous process in the absence of organic solvents; the second is that the extraction phase is dispersed in the form of micelles.

In the aqueous phase, it's about promoting the interaction between the two phases without the need for external force.

This work was based on a parametric study, making it possible to optimize the conditions for extracting copper (II) from an aqueous solution containing a non-ionic surfactant Triton X-100 and an extracting agent which is an ionic liquid based on imidazolium di- (2-ethylhexyl) phosphate "LIM".

Research Methodology/ Experimental Procedure:

Reagents :

Copper nitrate trihydrate and nitric acid of purity ≥ 69% (Merck), Triton X-100 (4-otylphenol polyethoxylate) and sodium hydroxide (Fluka), Ethanol (Biochem Chemopharma), Potassium nitrate (Gerhard Buchman). Ultra-pure water was prepared in the laboratory.

Apparatus :

pH measurements were performed by a HANNA HI 1131 pH meter. The quantitation of the Cu (II) was determined by a flame atomic absorption spectrophotometer type PERKIN ELMER Pin AAcle 900H. The stirring was carried out by a magnetic stirrer type VELP. The weightings were made with an electronic analytical balance type Carat Series OHAUS Item: PAJ1003. The ultra-pure water was prepared by the YOUNG LIN distiller. The volumes were taken using Accumax micropipettes of 100 and 1000 µL. The extraction experiments were carried out in 20 mL graduated test tubes. The preparation of the solutions was carried out in 100, 200 mL volumetric flasks.

Methodology :

All the manipulations carried out during this work are based on the extraction by cloud point of the Cu (II) ions by the Triton X-100 and the pre-prepared imidazolium ionic liquid denoted LIM [9]. To do this, several extraction experiments were carried out in order to identify the different parameters governing this extraction process.

The issue is to analyze the effects of the factors below by varying each factor while maintaining the others constant.

Effect of the initial pH was tested from several solutions containing 2% Triton X-100, 20% KNO_3 and 0.1M LIM and the aqueous solution of Cu (II) at 10^{-4}M. The whole was dissolved in a volume of 15 mL. The pH adjustment was carried out by adding the aqueous solutions of sodium hydroxide NaOH (1M) or nitric acid (0.5M) following the method shown in Fig 1.

Effect of the initial concentration of the ionic liquid LIM at different concentrations (0.01 -0.02 -0.04 -0.06 -0.08-0.10 M) following the general procedure (see Fig. 1).

Effect of the Triton X-100 level was achieved by the addition of Triton X-100 at various mass ratios of 0.1 to 10%, with 20% KNO_3 and 0.08 M LIM according to Fig 1.

Effect of ionic strength (KNO_3) was realized by introducing varying mass ratios of 0.1 to 20% KNO_3 according to the above scheme.

Extraction time was achieved by mixing 1% KNO_3, 0.1% Triton X-100 and 0.08M LIM. according to the above scheme. The time of extraction is varied from 1 min to 48 hours at ambient temperature.

Results and Discussion

The extraction of the cupric ions by cloud point is a liquid-liquid extraction process which consists in causing the metal ion present in a diluted phase (aqueous, low in Triton X-100) in another phase

called coacervate (rich in Triton X-100) using an extractant (LIM). In order to optimize the Cu (II) extraction conditions by Triton X-100, LIM and KNO_3, an experimental study was carried out by varying a single parameter with respect to the others which are kept constant.

Effect of pH :

The initial pH of the mixture (Triton X-100, KNO_3, and LIM) is an important factor in the control of the movement of cupric ions (from one phase to another). Indeed, the pH can act simultaneously on the predominance of Cu (II) species present in aqueous solution. The fig. 1 illustrates the distribution of the various complexes of the cupric ion. The free form Cu (II) then prevails in acidic pH.

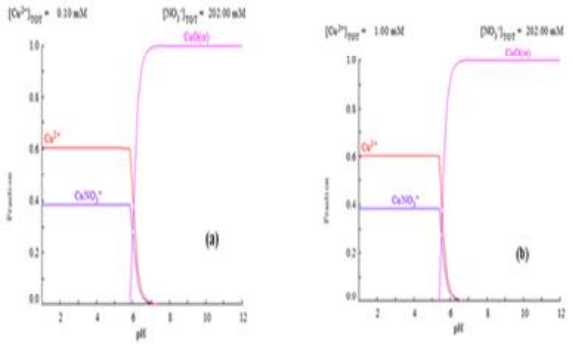

Fig.1. Predominance of copper species in nitrate medium as a function of pH: (a) For a concentration of cupric ions 10^{-4} M; (b) for a concentration of cupric ions 10^{-3} M.

In addition, the study of the effect of the initial pH on Cu (II) extraction was carried out in making extractions at pH ranging from 2 to 10. The results obtained are summarized in Fig 2.

According to Fig. 2, the extraction yield of the Cu (II) ions reaches its maximum at pH 2. It is 81.4%. Above this pH, the extraction yield decreases and becomes almost constant in a pH range between 4 and 10. The minimum extraction obtained is 10.6%. It is carried out by the actual pH of the initial solution which is 5.67 (without pH adjustment).

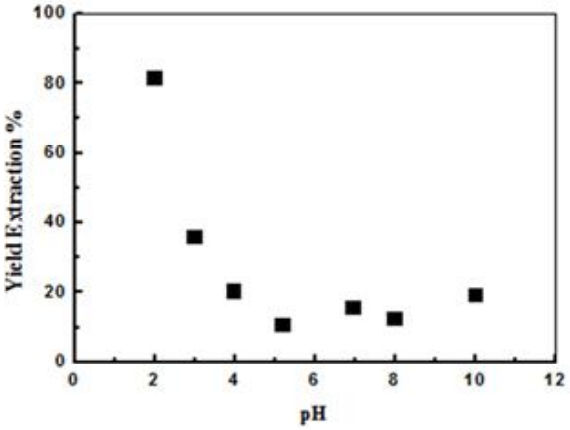

Fig. 2. Effect of the initial pH on the extraction yield of Cu (II)

Moreover, the extraction quantities: volume fraction of coacervate, factor concentration, and partition coefficient are described in Fig 3.

According to the latter, the partition coefficient ($K_{C/D}$) and concentration factor (F_C) have the same evolution. It is noted that the maximum of $K_{C/D}$ and F_C is obtained at pH equal to 2. They are respectively equal to 4.37 and 0.81. Beyond this pH, they decrease until reaching the bearing from pH 4. Minimum of $K_{C/D}$ and F_C are of the order of 0.10 and 0.11 respectively. While, the volume fraction of the coacervate phase increases progressively that the pH passes from acid medium to basic medium. The highest volume fraction is 0.03, concretized at pH 8.0.

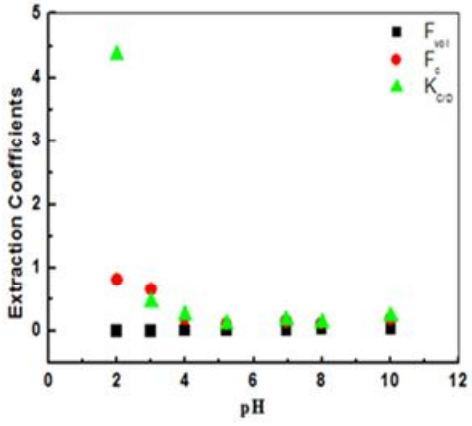

Fig. 3. Variation of the extraction quantities of Cu (II) as a function of pH.

Effect of ionic liquid concentration :

The choice of the carrier is a determining criterion in the extraction. Indeed, the conveying agent or the extractant forms complexes with the metal which must be soluble in the organic phase and insoluble in the aqueous phase. For this purpose, the extractant selected is an imidazolium ionic liquid, noted LIM. The study of its effect on extraction is carried out by varying its concentration from 0.01 M to 0.10 M while maintaining the pH constant at 2. Figure 4 shows the influence of the LIM concentration on the yield of the extraction of Cu(II).

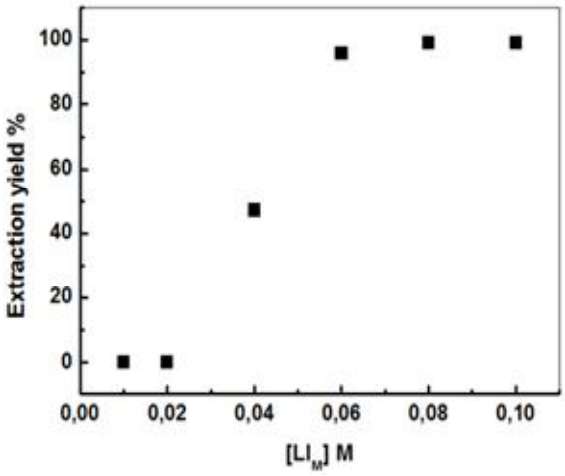

Fig. 4. Extraction yield as a function of the LIM concentration.

It is noted that the extraction yield increases by increasing the concentration of the ionic liquid. In addition, it can be seen that at low concentrations ([LIM] ≤ 0.02 mol L^{-1}) there is no extraction of the metal ions. The best Extraction is carried out with 0.08 mol L^{-1} of LIM was 99.2%. On the other hand, according to Fig. 5, a typical behavior of the evolution of $K_{C/D}$ and of F_C identical to that of the extraction yields with respect to the concentration of LIM. The maximum of $K_{C/D}$ and F_C respectively is 127.9 and 0.99 with a concentration of LIM equal to 0.08M. As for the volume fraction, no remark is observed. The variation in F_{vol} increases with increasing LIM.

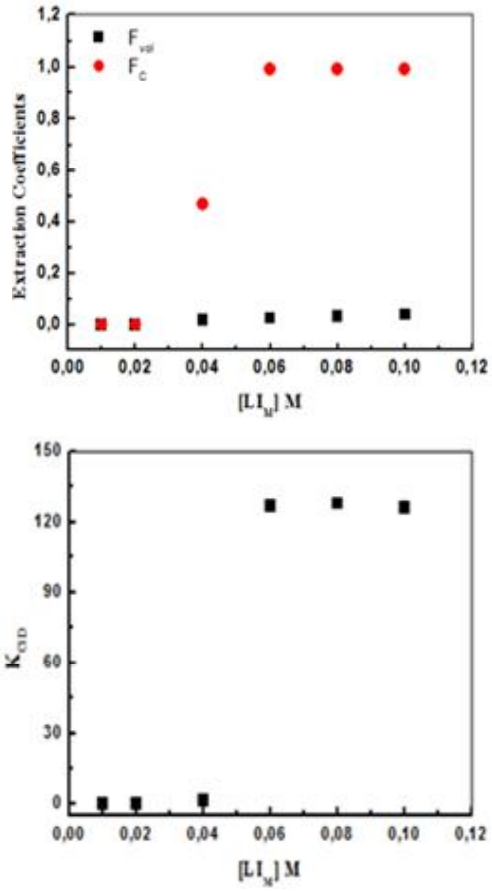

Fig. 5. Variation of the extraction quantities of Cu (II) as a function of LIM concentration. Volume fraction of coacervate (F_{vol}), concentration factor (F_C), partition coefficient ($K_{C/D}$).

Effect of amount of surfactant :

The surfactant plays a very important role in the design of the process by CPE. The surfactant used in this work is the Triton X-100. It finds a wide field of application especially in biomedical (DNA separation)[7,8].

Thus, the analysis of its effect is paramount. Thus, the analysis of its effect is important. Its rate varied from 0.1 to 10%, while maintaining the pH of 2.0 and the concentration of LIM equal to 0.08 M.

Fig. 6 shows an identical variation of the yield Extraction factor, partition coefficient and

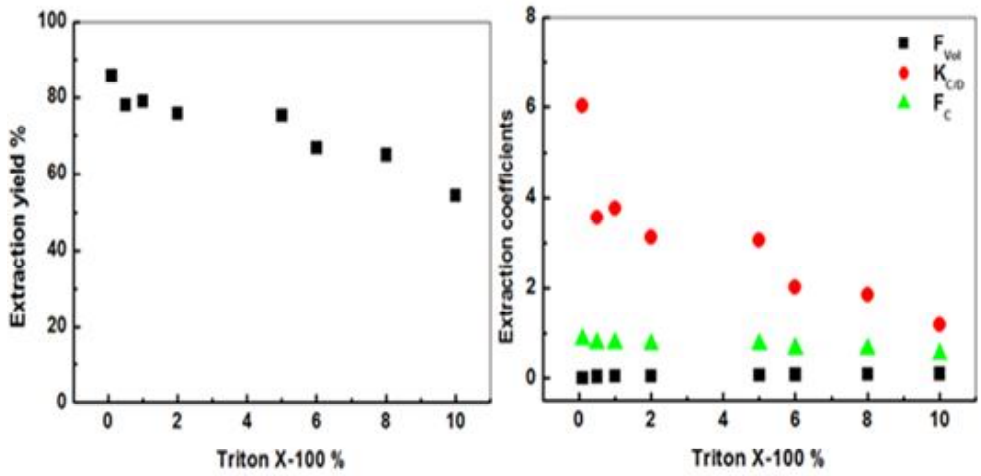

Fig 6. Variation of the extraction quantities of Cu (II) as a function of mass Triton X-100. Volume fraction of coacervate (F_{vol}), concentration factor (F_C), partition coefficient ($K_{C/D}$).

concentration factor with respect to the Mass of Triton X-100, contrary to that observed with the volume fraction. The Extraction yield, $K_{C/D}$ and F_C decreased in a range of 0.1 to 10% surfactant. The yield decreases from 85.8% to 54%, the partition coefficient decreases from 6.02 to 1.18 and the concentration factor decreases from 0.85 to 0.54. On the other hand, F_{vol} increases from 0.01 to 0.1 in the same field of study.

Effect of ionic strength (KNO_3) :

The influence of ionic strength on the Cu (II) extraction synthesized ionic liquids, was studied by adding potassium nitrate (KNO_3). The effects of this salt at different rates on the Cu (II) extraction yield were evaluated.

The effect of the nature of the added salt is studied by fixing the mass ratio of Triton X-100 to 0.1%, the LIM concentration at 0.08 M and the pH at 2 and varying its mass ratio from 0.1 to 20%. Fig. 7 shows an increase in extraction yield from 0.1 to 10% KNO_3 and then a decrease from 1 to 10% KNO_3 and then a decrease of 1 to 10%. The results are shown in Fig. 7.

The influence of ionic strength on the Cu (II) extraction synthesized ionic liquids, was studied by adding potassium nitrate (KNO_3). The effects of this salt at different rates on the Cu (II) extraction yield were evaluated. The results showed that the yield

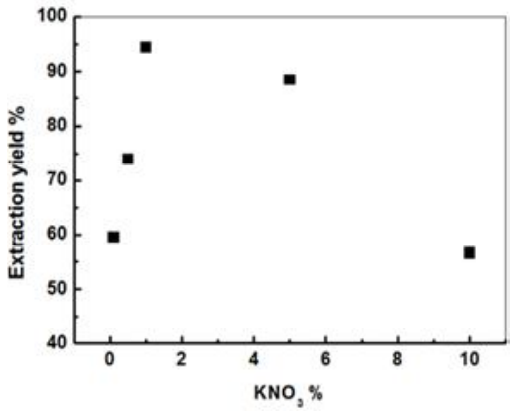

Fig. 7. Effect of the quantity of the added KNO_3 on the extraction yield of Cu (II).

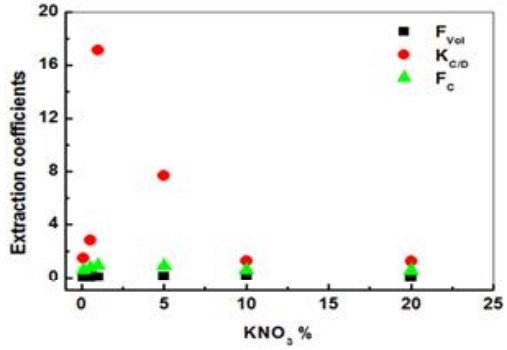

Fig. 8. Variation of the extraction quantities of Cu (II) as a function of the mass ratio of KNO_3.

increases to an optimum of 94.73% at a rate of 2%, followed by a decrease. On the other hand, according to Fig. 8, a typical behavior of the evolution of F_C identical to that of the extraction yields with respect to the mass ratio of KNO_3. The maximum of F_C is 0.94 with 1% KNO_3. Moreover, the partition coefficient increases rapidly, between 0.1 to 1% of salt to reach the maximum of 17.1 [9].

Then, it decreases until a 10% level of KNO_3 is obtained. At this stage, the $K_{C/D}$ is of the order of 1.25. Finally, the volume fraction of the coacervate phase increases gradually between 0.1 and 10% of salt to arrive at an extremum which is 0.13. Then it drops between 10 and 20% KNO_3.

Effect of extraction time :

The extraction time of the Cu (II) ions is one of the most important parameters.

It was studied by varying the rest time from one minute to 48 hours the samples taken at pH equal to 2 and comprising 0.1% (w/w%) of Triton X-100, 0.08M of LIM and 1% (w/w%) of KNO_3.

Fig. 9 shows the variation of the extraction yield as a function of the time. It shows that Cu (II) extraction is instantaneous. From the first minute, 93.24% of cupric ions are extracted. Optimum 94.30 is achieved after 6 hours.

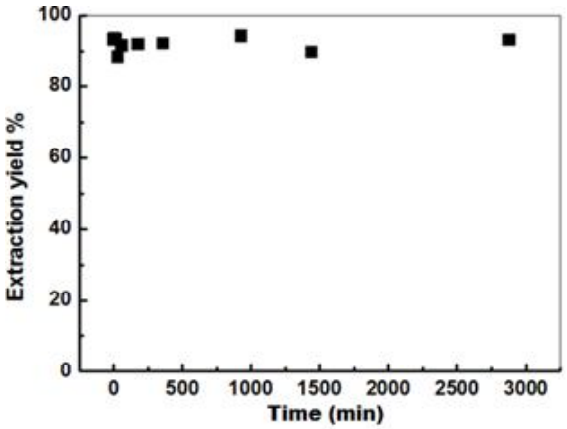

Fig. 9. The evolution of the extraction yield of Cu (II) as a function of the rest time of the mixture.

Fig. 10 shows an identical partition concentration factor with respect to the mass of TritonX-100, contrary to that observed with the volume fraction and coefficient distribution in the same field of study.

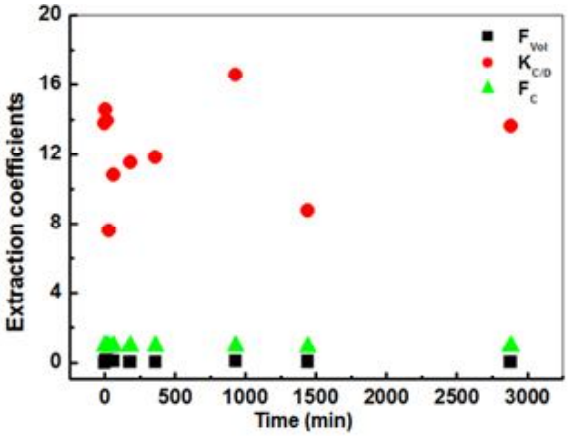

Fig. 10. Variation of the extraction quantities of Cu (II) ions as a function of extraction time.

Conclusion

Coacervate extraction of the metal cations was carried out using a nonionic surfactant, which makes it possible to obtain two distinct phases: a phase rich in surfactant named coacervat and another poor in surfactant called diluted, and a liquid which acts as a complexing agent for these ions.

Indeed, investigations on the extraction of cupric ions by Triton X-100, the ionic liquid denoted LIM and the potassium nitrate (KNO_3) were produced using the technique of extraction by cloud point (coacervat).

The extraction experiments showed that the cupric ions are extracted with the following optimal parameters: pH 2.0; Concentration of LIM equal to 0.08M; Triton X-100 mass ratio equal to 0.1%; KNO_3 mass ratio equal to 1%; at ambient temperature.

The reaction of extraction of cupric ions by coacervat is instantaneous. From the first minute, a good yield of 93.2% (almost the maximum) was obtained.

Under these optimal conditions, coacervate extraction makes it possible to extract 5000 times the maximum permissible concentration of Cu (II) in

industrial effluents in a single operation and with no energy input (no heating).

The efficiency of the separation then depends on the partition coefficient of the complex between the water and the micellar phase. In most cases, the work was ducts with a trace analysis objective, the point of cloud extraction being used as a pre-concentration step[9].

Acknowledgement

We gratefully acknowledge the ATRST-Algeria for the financial support.

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