Original Article

Electrocoalescence of emulsions in raffinate from the solvent extraction phase under AC electrical fields

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A B S T R A C T

Raffinate is an aqueous acid phase with low copper content obtained in the solvent extraction phase (SX). This solution, which drags a significant amount of the organic phase that forms an oil-in-water (O/W) emulsion, is recycled back to the leaching phase as an irrigation solution. In addition, the formation of emulsions can cause operational problems in the leaching phase. To solve these problems, this work is aimed to employ electrocoalescence under AC electrical fields to enhance demulsification of the emulsions that formed. The main objectives of this work were to select the most appropriate electrode and conduct laboratory tests based on a 2³ factorial design to determine the variables that have the most significant effect on electrocoalescence. The variables considered were distance, frequency and voltage, while TOC removal and actual power were the response variables. The distance between electrodes is the most important parameter affecting TOC removal. In relation to actual power, the voltage applied was more significant than the distance between electrodes, the frequency and the interactions among variables. The tests to determine the optimal type of electrode identified rectangular steel plate electrodes as providing the best results. The operational parameters: a voltage of 30 V, a frequency of 400 Hz and an electrode distance of 14 cm showed the greatest efficiency. Considering these results, it is demonstrated that electrocoalescence enhances demulsification of O/W emulsions in raffinate from solvent extraction in copper processing.

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1. Introduction

Chile is the world’s largest copper producer. According to the Chilean Copper Commission, fine copper production in 2015 was over 5760 kMT (29.9% of world production) [1]. Approximately 20% of the production is obtained by hydrometallurgical processing. After the heap leaching phase, an organic solution containing the extractant is employed in the solvent extraction phase (SX) to collect the copper from the

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PLS (pregnant leach solution, an acid solution rich in copper sulfate) [2]. Two phases are generated in solvent extraction: (i) a copper-bearing organic phase that is stripped of its copper in the next step and (ii) an aqueous acid phase, termed raffinate, with low copper content. Raffinate is recycled back to the leaching step of the hydrometallurgical process as irrigation solution [3].

Raffinate carries a significant amount of the organic phase, which forms an oil-in-water emulsion (O/W) [4], representing a loss of organic extractant. This is a high-cost solution, making it important to reduce drag-out losses. The formation of emulsions in raffinate not only represents a loss of organic extractant, but can also cause several operational problems in the leaching phase that adversely affect the efficiency of the global process, such as loss of porosity and permeability in the ore heap, irrigation system plugging and water loss [5].

An emulsion is a mixture of two liquids that are normally immiscible. The liquid being dispersed is in the dispersed phase, while the liquid in which it is dispersed is in the continuous phase. There are two types of emulsions: oil-in-water (O/W) and water-in-oil (W/O). Although emulsions are widely used in many industrial fields, such as explosives in mining, emulsion formation in solvent extraction is especially undesirable [6].

Given the composition of the feed solution, it can be understood that its behavior is closely related to the nature and colloidal characteristics of clay–silica systems in the operating conditions: low pH, ionic strength and high particle concentration [7]. Work done with this system, it is concluded that at a pH of approximately 3 the repulsive forces are reduced, promoting the aggregation and disintegration stabilization of the system [8,9]. Under these conditions, colloidal silica can overcome the repulsive barrier effect between particles, joining and forming three-dimensional networks that capture traces of organic reagent generating organic entrainment in the refining, and, on the other hand, the generation of waste.

In this case, the formation of the emulsion is favored by the characteristics of the feed solution in the SX process, since it contains impurities such as silica and clays (mainly kaolinite), which bind to the processed mineral and creep with the flow of PLS from the leaching stack [10–12].

To reduce the formation of emulsions and, consequently reduce organic extractant loss, it is necessary to develop and evaluate efficient easily-implemented low-cost separation techniques. There are now heat-based chemical demulsification [13,14], physical [15,16], membrane filtration separation [17,18] and electrocoalescence methods. In general, the mentioned methods present technological and operational difficulties, which involve the incorporation of unit operations to the conventional hydrometallurgical train, or the addition of reagents whose effects on downstream processes are unknown. In the case of coalescence, is a natural phenomenon by which two or more bubbles or droplets merge during contact to form a single bubble or droplet. An electrical field can be applied to increase the separation phase (coalescence rate) in emulsions. This technique is known as electrocoalescence [19–22]. Application of an electrical field increases the size of the bubbles or droplets and thus enhances their settling velocity and reduces the separation time [23]. Compared to other techniques, electrocoalescence is one of the most energy efficient since its application reduces the use of heat and the amount of chemical demulsifiers, which makes it more environmentally friendly [24].

We therefore propose employing electrocoalescence to enhance demulsification of O/W emulsions in raffinate, as a little invasive technique, with the potential to be incorporated simply and circumstantially in the hydrometallurgical process. The main goal of this work is to show the results of applying this technique with alternate current (AC) to raffinate from solvent extraction (SX). To do this, the most suitable type of electrode in terms of shape and material was determined, along with the impact, through scaled laboratory tests. Besides, laboratory tests based on a $2^3$ factorial design were conducted to determine the most influential operational variables.

2. Theory

The phenomenon of coalescence has been studied extensively theoretically and experimentally [25–30]. Publications have described several models to determine breakup and collision frequencies, the size distribution of bubbles and coalescence efficiency [31]. Coalescence is considered a complex phenomenon, since it involves interactions of bubbles not only with the continuous phase, but also among the bubbles themselves once they are brought together by the external flow or by bodily forces [32]. Given our limited understanding of this phenomenon, there are no accurate models in the literature that take into account all the mechanisms and the wide range of possible conditions [33]. However, it is well known that contact and collision is the most important condition for coalescence. Collisions among bubbles are usually caused by their relative velocities [34], which are due to a variety of mechanisms: turbulence fluctuation, viscous shear stress, capture in turbulent eddies, buoyancy and wake interactions [31].

Film drainage, as proposed by Shinnar and Church [35], is the most extended model for coalescence. The model divides coalescence into three stages: (1) a liquid film forms when two bubbles near each other due to overpressure, (2) the liquid film drains sequentially until reaching a critical thickness, and (3) the film ruptures, resulting in coalescence.

Electrocoalescence increases the size of bubbles, thus enhancing their settling velocity and reducing separation time. The main mechanism for bubble growth due to the application of an electrical field to an emulsion is dipole induction. Electrical fields are widely applied in the petroleum industry to demulsify W/O emulsions [36–38]. However, electrocoalescence in O/W emulsions has not been heavily studied. It is thought that demulsification of O/W emulsions under a low electrical field is mainly induced by electrophoresis of the bubbles toward the electrodes. However, the physical effect of a low electrical field on an emulsion is not clearly understood [6]. Alternate current (AC), direct current and pulsed DC electrical fields have been used to enhance coalescence. It has been demonstrated that the two fields act according to different mechanisms in separating phases [39]. The first works were carried out using DC fields, which appear to be more effective.
for coalescence due to the capacity to maintain continuously high electrical field force. Owe Berg et al. [40] experimentally found that coalescence efficiency is proportional to electrical field strength when it is low, while it is proportional to the square of the strength when electrical field strength is high. In addition, a level of critical field strength was determined above which two bubbles coalescence partially rather than fully. Applying a constant DC electrical field causes the bubbles to line up into chains in the direction of the electrical field. Mahtre et al. [41] noted that chain formation reduces electrocoalescence efficiency and can result in short-circuits caused by electrodes. Hamlin et al. [42] showed that complete coalescence patterns can involute to non-coalescence patterns by varying the strength of the DC electrical field. They also studied the effect on conductivity and demonstrated that the size of the daughter bubbles is independent of ionic conductivity.

Bailes and Lakai [43] employed pulsed DC electrical fields for first time to avoid the problems generated by using DC fields, and reported more efficient coalescence can be achieved than is possible with DC or AC fields. They demonstrated that chains are continuously disrupted in pulsed DC fields, thus increasing the collision rate between bubbles. Since this pioneering work, there have been several works using pulsed DC electrical fields [20–22,36,44–48]. The influence of electrical field parameters such as strength, frequency, amplitude and waveform has been investigated. Williams and Baileys [49] also stated that separation efficiency improves with increasing field strength, but if the field strength is too high it increases the probability that secondary bubbles form during coalescence [50,51]. Bailes and Dowling [52] showed that the coalescence rate depends on pulse amplitude, shape and frequency, and that all of these parameters have optimal values. The effects of frequency have been studied by Joos and Snaddon [53], Bailes [54] and Midtgard [55], among other authors. The influence of the field waveform has been studied by several authors [20,24,56].

3. Experimental set-up and procedure

The emulsion comes from a raffinate tank as the result of solvent extraction in a copper mine. The O/W emulsion employed presented an initial TOC of 388 mg/L. A batch cell system under the application of a constant voltage and variable frequency and vice versa generated by an alternate current source and applied through two electrodes. The experimental cell used in this work is shown in Fig. 1. The AC power source has an adjustable output voltage up to 1000 V and a frequency resolution up to 1 Hz. The power source is equipped with devices to measure voltage, current, frequency and frequency factor. The cell is made of acrylic to facilitate viewing coalescence. The volume of the cell is about 1000 mL. Fig. 2 shows the cell set-up employed for the experimental tests.

It is important to define the electrode type (material and shape) since an inert conducting material is necessary that does not affect the chemical properties of the emulsion. The electrodes employed for the experimental tests were made of graphite and stainless steel, and were in the form of cylindrical rods and plates. Several tests were conducted with varying voltage and frequency to determine the most appropriate electrode material and shape. Effectiveness was determined by comparing measurements of power, turbidity and total organic carbon (TOC). The electrodes were kept in constant separation.

A 2³ full factorial design was carried out to determine the influence of the variables distance, frequency and voltage on electrocoalescence. Fig. 3 shows the factorial design. Total organic carbon (TOC), the amount of carbon found in an organic compound, and turbidity were measured for all tests to evaluate the efficiency of electrocoalescence. TOC can be considered as a non-specific indicator of water quality. Thus, it was selected as a useful method to determine the efficiency of the process. TOC measurement was performed according to standard method 5310. Turbidity measurement was performed according standard method 2130 [57].

The sampling procedure consisted of collecting small fractions of aqueous solution using a 10 mL syringe. The extraction point was located between the two electrodes to ensure the representativeness of the sample.

4. Results

4.1. Electrode selection

Three electrode types were tested: (i) cylindrical graphite rods, (ii) cylindrical stainless steel rods and (iii) rectangular stainless steel plates. The laboratory tests to select the most suitable electrode involved varying the frequency while maintaining the voltage constant at 20 V, and varying the
voltage while maintaining the frequency constant at 60 Hz. The operational time was an hour for both tests and the electrodes were at a distance of 14 cm from each other. The final result was obtained by comparing the results of actual power, turbidity and total organic carbon (TOC) among the three electrode types.

Fig. 4a shows the results related to actual power. Frequency increased from 50 Hz up to 400 Hz in 1 h. As shown in the figure, an increase in frequency decreases actual power considerably. The rectangular stainless steel plate electrode provided the most significant reduction in actual power. Fig. 4b shows the results of actual power in function of voltage. Voltage ranged from 10 V to 40 V. With all three electrodes, the application of higher voltage increases actual power. The rectangular stainless steel plate electrode consumes more power because the area of the active electrical field is larger. A turning point appears for the three electrodes from which the power begins to decrease as voltage increases, especially with the steel plates. This phenomenon can be explained by impedance generated in the emulsion.

Fig. 5a shows the percentage of turbidity removal in function of frequency. The best result was provided by the steel plates, with 79.4% of turbidity removed. Fig. 5b shows the variation in the removal of turbidity. As noted above, the steel plate electrodes are more effective than the others. These results are attributed to coalescence between bubbles in the organic phase.

TOC removal efficiency was measured for the three electrodes. Fig. 6a shows the effect on TOC removal of varying frequency. The highest of TOC removal at around 31% was with steel plate electrodes. Similar results were obtained by varying voltage instead of frequency (Fig. 6b). Based on these results, the stainless steel plate electrode is the most suitable configuration for further electrocoalescence tests.

4.2. Factorial design

Laboratory tests based on a $2^3$ factorial design were conducted to determine the influence of the factors and their interaction on the process. The variables chosen were: distance ($X_1$), frequency ($X_2$) and voltage ($X_3$). Minimum and maximum levels for each factor (Table 1) were chosen according to data from previous experiments to select electrodes.

The factorial design was evaluated using the percentage of TOC removal and actual power as response variables. Table 2 shows the experimental matrix and the response variables of the factorial design.
Fig. 4 – Actual power: (left) constant voltage of 20 V and (right) constant frequency of 60 Hz.

Fig. 5 – Turbidity removal: (left) constant voltage of 20 V and (right) constant frequency of 60 Hz.

Fig. 6 – TOC removal: (left) at a constant voltage of 20 V, and (right) at a constant frequency of 60 Hz.

| Table 1 – Factors and levels used in the factorial design. |
|---------------------------------|----------|----------|
| Variables                      | Low (−) | High (+)|
| $X_1$: Distance (cm)           | 10       | 14       |
| $X_2$: Frequency (Hz)          | 60       | 400      |
| $X_3$: Voltage (V)             | 10       | 30       |

4.2.1. Modeling of the effects
A lineal polynomial model was defined to fit the response through Eq. (1):

$$y = a_{00} + a_{10}X_1 + a_{20}X_2 + a_{30}X_3 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3$$  (1)

where y is the response expressed as TOC removal or actual power; $X_1$, $X_2$ and $X_3$ represent distance, frequency and voltage, respectively. The subsets of regression coefficients ($a_{10}$, $a_{20}$, $a_{30}$) and ($a_{12}$, $a_{13}$, $a_{23}$) represent lineal and interaction effects of the model, respectively, and $a_{00}$ is a constant coefficient. The values of the regression coefficients for the response variables are presented in Table 3.

4.2.2. Statistical validation of the models
The significance of the regression process can be evaluated by the ratio between the media of the square of regression ($MS_{reg}$) and the media of the square of residuals ($MS_{res}$) and by comparing these variation sources using the F test. The F test is the inverse of the Fisher distribution, $F_{inv}(α, p − 1, n − p)$, and must be less than the ratio $MS_{reg}/MS_{res}$ to affirm that the model is
well-adjusted with the data, with a probability of $(1 - \alpha)$ [58]. The results of the F test, shown in Table 4, indicate that the predicted and observed values for both models are not significantly different (models of TOC removal and actual power are well fitted to the data, with a probability of 81% and 95%, respectively).

The coefficient of determination $R^2$ was calculated for each model. The $R^2$ value is a measure of the model fitting. A value of 1 indicates a perfect prediction, so the closer the value is to 1, the better. In this case, the values for TOC removal and actual power were 0.94 and 0.997, respectively. This means that 6% and 0.3%, respectively, of the total response variation cannot be explained by the model [59]. Therefore, the fit between the model and the experimental results is very good for both, TOC removal and actual power.

### 4.2.3. Test of the regression coefficients

The significance test of each regression coefficient can be evaluated by using the inverse function of the Student’s distribution ($t_{inv} (\alpha/2, n - p)$). The value must be less than $|t_0|$ to affirm that the variable associated with the coefficient contributes significantly to the model [58]. The results for the response variables are shown in Tables 5 and 6.

Table 5 shows the effects of the variables on the TOC removal. The variables with greater effect, arranged in decreasing order, are: $X_1$ (distance), $X_{23}$ (frequency × voltage), $X_2$ (frequency), $X_3$ (voltage), $X_4$ (distance × frequency), $X_5$ (distance × voltage), $X_6$ (frequency × voltage), and $X_7$ (distance × frequency × voltage).
$X_{13}$ (distance × voltage) and $X_3$ (voltage). On the other hand, the maximum TOC removal value, within the studied range, was 61.4%. This value was obtained with the following parameters: distance 14 cm, frequency 400 Hz and voltage 30 V.

As can be observed in Table 6, effects of the variables on the TOC removal, the variables with greater influence, in decreasing order, are: $X_{23}$ (frequency × voltage), $X_3$ (voltage) and $X_{13}$ (distance × voltage). The minimum actual power, within the studied range, was 27.5 Wh with the following parameters: distance 14 cm, frequency 400 Hz and voltage 10 V.

5. Conclusions

This work studies electrocoalescence of O/W emulsions in raffinate from the solvent extraction phase of copper extraction under alternate current. The work is divided into two parts: (i) selection of the most suitable electrode by comparing three types (cylindrical graphite rods, cylindrical stainless steel rods and rectangular stainless steel plates) and (ii) evaluation of the influence of three variables (distance between electrodes, frequency and voltage) on electrocoalescence efficiency through an experimental model with a $2^3$ factorial design. The results of the first part indicate that the rectangular stainless steel plate performed best with respect to turbidity and TOC removal. In the second part, the percentage of TOC removal and actual power were chosen as response variables. The variables with more effect on electrocoalescence efficiency were separation between electrodes and the combination of applied voltage and frequency. The best results were obtained with a voltage of 30 V, a frequency of 400 Hz and a distance of 14 cm between electrodes. This configuration provides an actual power of 77.9 Wh and a TOC removal rate of 60.6%. To summarize, experiments based on a factorial design have shown that efficiency is improved by increasing distance between electrodes and the product of voltage and frequency. The results demonstrate that the application of alternate current electrical fields enhances demulsification of O/W emulsions and generates less contaminated aqueous solutions for reuse in leaching. There is a room for improvement as the evaluation of alternative methods to determine the efficiency, for example, through image processing. Besides, it is recommended to develop experiments on a larger scale to characterize the behavior of the system before implementing the technique on an industrial scale.

Conflicts of interest

The authors declare no conflicts of interest.

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