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PARTICULATE BED CATHODE FOR COPPER ION REMOVAL FROM WASTEWATERS.
Part II: A correlation between copper recovery, current efficiency and energy consumption

ANCA MIHAELA MIHAI[1], LIVIU ONICIU[2]

[1] *Department of Chemistry, North University of Baia Mare, 4800, Baia Mare, Romania*
[2] *Department of Physical Chemistry, University "Babes-Bolyai", 3400 Cluj-Napoca, Romania*

ABSTRACT. An analysis based on current efficiency and energy consumption for Cu^{2+} recovery from wastewater, using a copper particulate bed cathode, was attempted. The influence of current intensity on the Cu^{2+} recovery and current efficiency was comparatively examined in order to establish the optimal value of electrolysis current. Additionally, the optimal value of electrolysis time was established based on an economic evaluation.

The investigated method was proved to be efficient for Cu^{2+} removal from wastewater. Thus, after 140 minutes of galvanostatic electrolysis (at 0.25 A) the Cu^{2+} level (10^{-2} M) of 1.5 L of wastewater was reduced with 80%, with a 34.7 % current efficiency. The optimal experimental configuration for the process was attained using a copper powder cathode (10 g, in 0.2 - 0.125 cm size range), a stainless steel sieve as current feeder, and an electrolyte circulation speed of 2 cm/s.

INTRODUCTION

The electrochemical treatment of industrial wastewaters can be considered an efficient method if high efficiency of extraction and current are ensured simultaneously.

It has been shown that fluidized bed of conducting particles in a stream of electrolyte has good performances in metallic ions recovery from dilute solutions [1-5].

In the first part of the study [6], the influence of technological parameters (cathode weight, range size of copper powder used for cathode construction, intensity of the electrolysis current, type of current feeder and electrolyte flow rate) on the extraction efficiency of Cu^{2+} from a wastewater from a metallurgical plant in Baia Mare, has been examined. The analysis of the experimental results indicated the following values as being the optimal ones: current intensity, 2 A; current feeder with the shape of a sieve placed at the bottom of the electrolysis cell and supporting a cathode made of copper powder from the 0.2-0.125 cm size range; cathode weight of 10 g; electrolyte flow rate of 2 cm s^{-1}. The correlation of these parameters led, after 100 minutes of galvanostatic electrolysis, to an extraction efficiency of 92%.

The present paper aims to analyze the copper recovery process from wastewaters, from the point of view of current efficiency.

EXPERIMENTAL

The composition of the studied wastewater is indicated in table 1. The experimental set-up was identical to that used in the first part of this study [6]. Basically, it has the following construction: the electrolyte flows from the bottom to the top of a three electrode cell, made of a glass with an internal diameter of 6 cm and a length of 25 cm. For an optimum bed expansion, the electrolyte flow rate, measured by a rotameter, was adjusted at 2 cm/s.

Table 1.

Composition of the used wastewater.

Volume of processed electrolyte	Concentration of metallic ions (g/l)			Concentration of sulfuric acid, (g/l)
	Cu^{2+}	Zn^{2+}	Pb^{2+}	
1,5 L	0.2	0.12	Traces	25

The cathode, made of 10g copper powder from 0.2-0.125 cm size range, has been placed at the bottom of the cell on a stainless steel sieve, which represented both the support of the cathode and the current feeder. Copper powder was pretreated by cleaning in dilute nitric acid, rinsing in water and drying in an oven. Before use, it was rinsed in dilute sulfuric acid to remove any oxide coating.

The anode, placed at the upper part of the cell was a stainless steel circular plate of 3-cm diameter. A calomel electrode, functioning as reference electrode, was placed above the bed. A potentiostat (HA 320, Hokuto Penko Ltd.) was used to supply electric power and to monitor the potential difference between working and reference electrode.

In all experiments, an atom absorption spectrophotometer (AAS PERKIN-ELMER Spectrometer, model 3300/5100 PC) was used to monitor periodically the Cu^{2+} concentrations.

The experiments were repeated in the same conditions by three times. In all tests, the final results represent an average of the three experimental results.

For an accurate evaluation of the electrolysis global efficiency, the values of extracted copper used for current efficiency calculation were the same as those used for extraction efficiency calculation.

Current efficiency was calculated using the following relation:

$$r(\%) = \frac{Q_t}{Q_p} 100 \tag{1}$$

where:

Q_t – the charge consumption to extract a certain copper quantity, [C]; it was estimated from the Faraday's law.

Q_p – the practical charge consumption to extract a certain quantity of copper, [C]; it was calculated as the product between the current intensity and the electrolysis time.

RESULTS AND DISCUSSIONS

As previous results indicated [6], the increase of the electrolysis current intensity determined the increase of the extraction efficiency of copper ions (Figure 1). A significant increasing of the copper recovery occurred when the electrolysis current intensity was changed from 1 A to 2 A. Consequently, in the following discussion we will consider only these values for the electrolysis current intensity.

Values of Q_t and Q_p, calculated from the Faraday's law and as the product between the current intensity and the electrolysis time, respectively, were substituted in relation (1) in order to obtain the variation of the current efficiency with electrolysis time (Figure 2).

From Figure 2, it can be noticed that the electrolysis efficiency varies inversely proportional with the electrolysis time and the current intensity. Contrarily, the extraction efficiency increased with the electrolysis current increasing. The maximum value of current efficiency was obtained during the first 10 minutes of electrolysis: 22.8 % at 1 A and 16.7 % at 2 A.

After 100 minutes of electrolysis the current efficiency decreased to 12.4 % at 1 A and 6.9 % at 2 A.

The small values of current efficiency showed that the energy consumption for copper extraction is higher than the gain developed by the recovered copper. A plausible explanation could be formulated if the side process (hydrogen discharge) is taken into consideration.

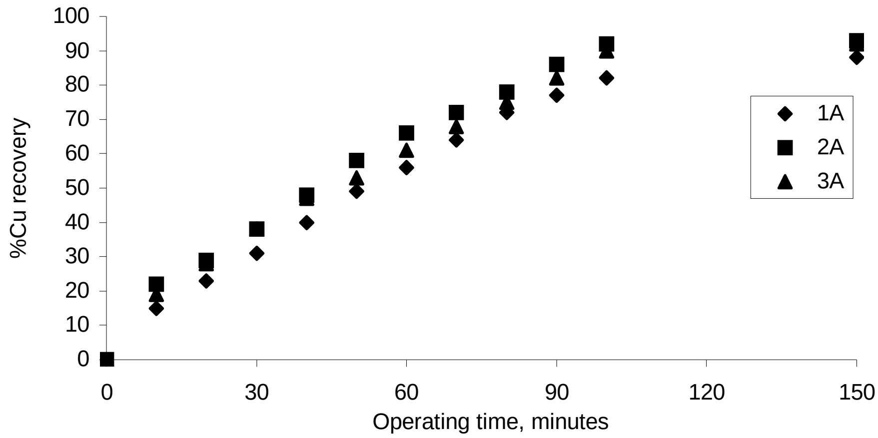

Figure 1. The variation of copper recovery with the electrolysis time for various intensities of the electrolysis current. Experimental conditions: acidified electrolyte (Table 1); cathode made of powder copper in 0.2-0.125 cm size range; cathode weight, 10 g; electrolyte circulation speed 2 cm/s (optimal fluidization); current feeder, stainless steel sieve.

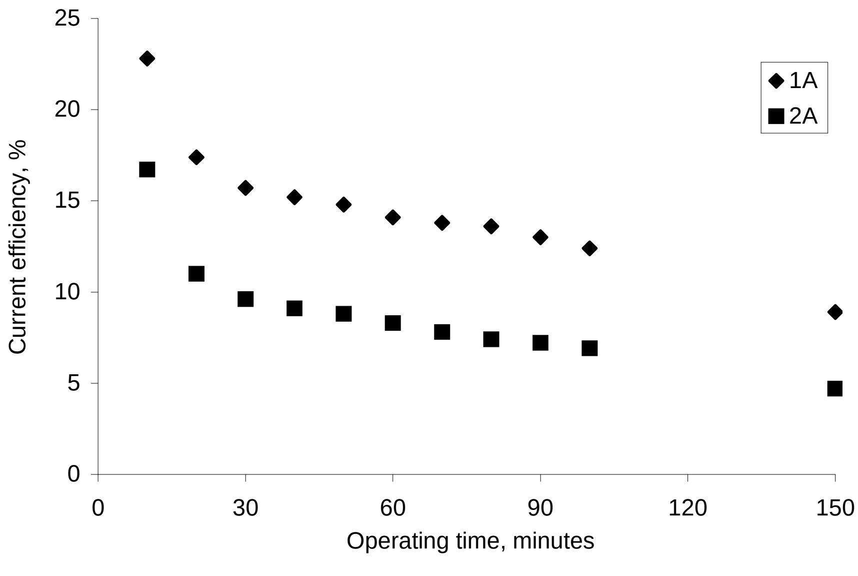

Figure 2. The variation of current efficiency with the electrolysis time for various intensities of electrolysis current. Experimental conditions, as mentioned in figure 1.

Therefore, considering the contrary effects on the copper extraction and current efficiency, induced by the increase of current intensity and time of electrolysis, it was necessary to find values of these parameters to ensure simultaneously high copper recovery and current efficiency. Thus, further it was examined the influence of lower values of current intensity on copper recovery efficiency (Figure 3) and current efficiency (Figure 4).

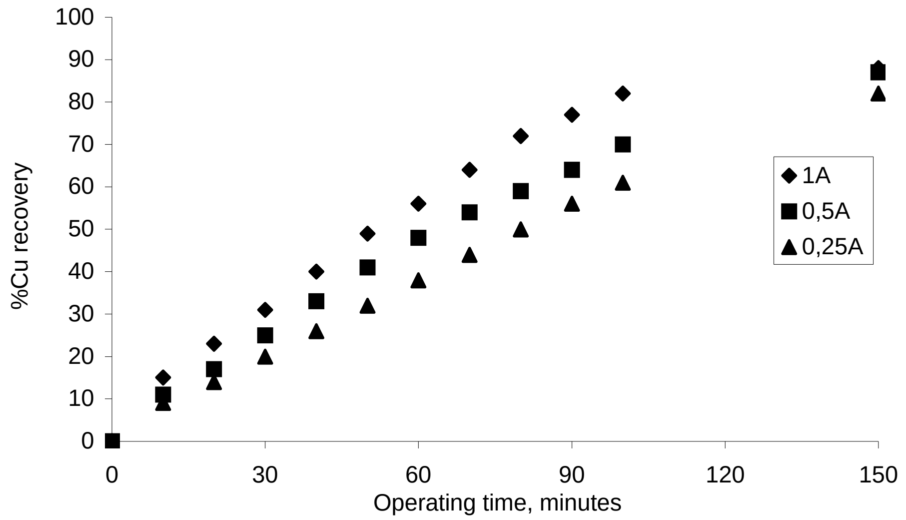

Figure 3. The variation of copper recovery efficiency with the electrolysis time for various intensities of electrolysis current. Experimental conditions, as mentioned in figure 1.

Based on the above-presented results, several conclusions can be stated:

(i) Along with the decrease of electrolysis current intensity, the extraction efficiency also decreased. For example, after 100 minute of electrolysis, a four-time current intensity decrease (from 1 A to 0.25 A) led to a decrease of extraction efficiency by 1.34 times, from 82 % to 61 %.

(ii) The decrease of electrolysis current determines the increase of the necessary operating time to obtain the same extraction efficiency. For example, to obtain a copper extraction percentage of 80 %, the four time current intensity decrease (from 1 A to 0.25 A) required a prolongation of 1.4 times of the electrolysis time (from 100 minutes to 140 minutes).

(iii) The decrease of electrolysis current intensity determines the increase of current efficiency. For example, after 100 minute electrolysis, the four time decrease in electrolysis current intensity (from 1 A to 0.25 A) led to 2.98 times increase of current efficiency (from 12.4 % to 37 %). Simultaneously, the maximum current efficiency corresponding to the first 10 minutes of electrolysis increased 2.39 times (from 22.8% to 54.7%).

Correlating all experimental data, it can estimate that, in order to decrease the energy consumption related to the process, it is more convenient to choose an operating intensity of 0.25 A (instead of 2 A), concomitantly with the prolongation of electrolysis time.

To ensure simultaneously high copper extraction and current efficiency, the following values ot the experimental parameters were considered optimal: current intensity of 0.25 A; current feeder, stainless steel sieve; cathode made of copper powder in 0.2-0.125 cm range size; cathode weight, 10 g, acidified electrolyte (Table 1); electrolyte circulation speed of 2 cm/s.

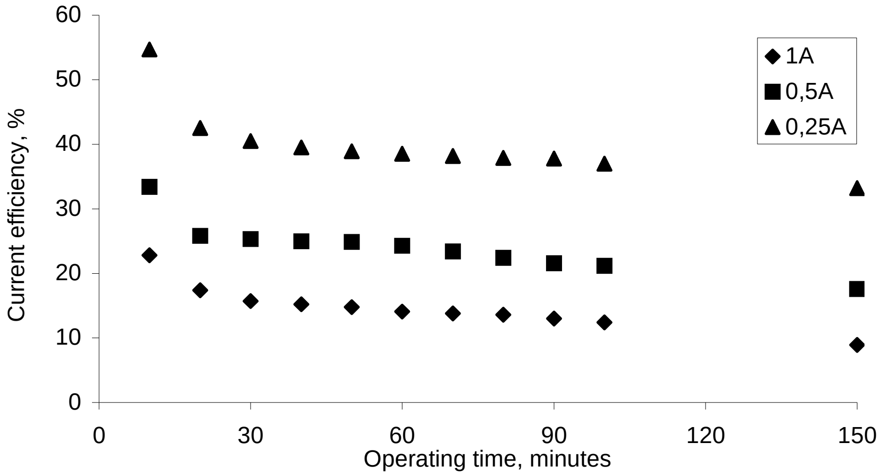

Figure 4. The variation of current efficiency with the electrolysis time for various intensities of electrolysis current. Experimental conditions, as mentioned in figure 1.

The optimal electrolysis time and, implicitly, the copper recovery percentage could be done on the basis of an economic analysis, taking into account the concomitant fulfillment of the following requirements:

- a high extraction and current efficiency;
- a maximum profit, mainly determined by the worth of the extracted copper.

An estimation of the profit requires preliminary calculations of income and expenses, involved by the electrolysis process performed under the optimal experimental conditions, already established.

I. *The income* was calculated on the basis of the following relation:

$$\text{Whole income} = \frac{v \cdot C_o \cdot \%Cu \cdot 10^{-3} \cdot 1.578}{100} \qquad (2)$$

where:

Whole income – the income obtained by the processing 1 L of electrolyte, [$/l];

v - volume of processed electrolyte, [1 L];

C_0 - initial copper concentration in the electrolyte, [g/l];

%Cu - copper extraction efficiency;

1.578 - price of electrolytic copper in March 2000, [$/Kg]

II. *Expenses* were calculated taking into account the materials consumed at a laboratory scale:

- The electrolyte is wastewater and does not require any processing expense,
- The copper powder used for the cathode can be obtained as waste material from the copper powder-processing department from the same metallurgical plant;
- The electrolyte circulation pump;
- The power source used for electrolysis;

Observing that solely expenses related to the energy consumption of the pump and electrolysis power source occur, these were calculated according to the relation (3):

$$\text{Whole expenses} = \frac{0.044(W_p + W_e)}{v} = \frac{0.044(P_p t + \eta_e It10^{-3})}{v} \qquad (3)$$

where:

Whole expenses – expenses for the processing of 1 L electrolyte, [$/l];

W_p – pump energy consumption to ensure electrolyte circulation with a speed of 2 cm/s (optimal fluidization), [KWh];

W_e – energy consumption of electrolysis power source, [KWh];

0.044 – cost of 1KWh, value applied to industrial consumers in March 2000, [$/KWh];

v – volume of processed electrolyte, [1.5 L];

P_t – pump electric power, [kW]; $P_p = 10^{-3}$ kW;

t –pump operating time equal to electrolysis time, [h].

I – electrolysis current intensity, [0,25 A];

η_e – the necessary overpotential for copper ions discharge at the cathode, [V]; it was determined in the following manner: in a cell filled with the investigated electrolyte were placed a copper and a calomel electrode. From the value of potential difference measured by a voltmeter (0.55 V) the potential value of the calomel electrode (0.244 V) was subtracted, and the value of 0.256 V was obtained. To compensate the possible loss occurring in the system, we preferred the value 0.3 V for η_e.

The values of Profit, correlated with current efficiency, copper extraction efficiency and electrolysis time, are presented in Table 2.

Table 2.

The variation of Cu extraction efficiency, current efficiency and profit with the electrolysis time. Experimental conditions: intensity of electrolysis current 0.25 A; for other experimental conditions see figure 1.

Electrolysis time (minutes)	Cu extraction efficiency (%)	Current efficiency (%)	Profit (10^5 \$/L)
0	0	0	0
10	9	54.7	2.3
20	14	42.5	3.3
30	20	40.5	4.7
40	26	39.5	6
50	32	38.9	7.4
60	38	38.5	8.7
70	44	38.2	10.1
80	50	37.9	11.5
90	56	37.8	12.8
100	61	37	13.9
110	66	36.4	14.9
120	71	35.9	16
130	75	35	16.7
140	80	34.7	17.8
150	82	33.2	17.8
160	84	31.9	17.9
180	87	29.3	17.8
200	88	26.7	17.1
220	88	24.3	16

In order to choose the optimum electrolysis time, on the same plot it was represented the variation of Cu extraction efficiency (%Cu recovery), current efficiency (r,%) and profit (Profit, $/L) with the electrolysis time (Figure 5).

The choice of a 60-minute electrolysis time, obtained by the intersection of curve r (%) and %Cu, would lead to a current efficiency of 38.5 %, a Cu extraction efficiency of 38 % and a profit of $8.7 \cdot 10^{-5}$ $/L. Although the condition to achieve a high current efficiency is fulfilled, after the recovery of only 38 % of the initial copper, the Cu^{2+} concentration in wastewater remains 124 mg/l.

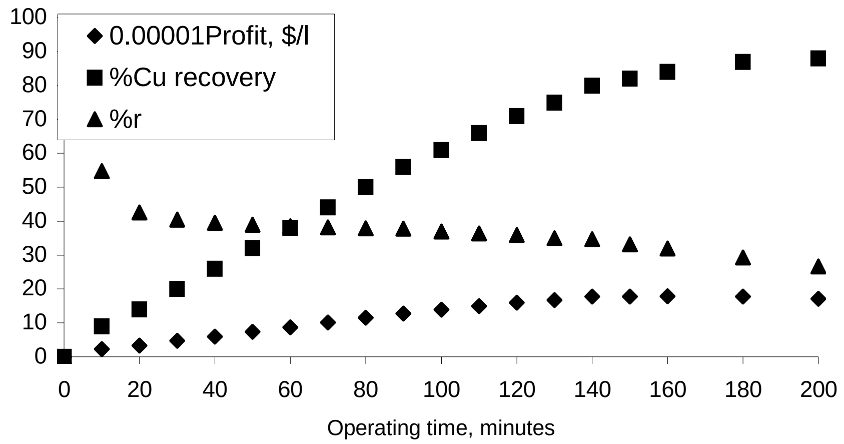

Figure 5. The variation of Cu extraction efficiency (%Cu recovery), current efficiency (r, %) and profit ($/L) with the electrolysis time. Experimental conditions: intensity of electrolytic current 0.25 A; for other experimental conditions see figure 1.

This value is higher than the value admitted by the Romanian reglementation (10 mg/L) [7]. An increase of Cu extraction efficiencappears necessary, even this will involve a decrease of the current efficiency.

More appropriate seems to be an electrolysis time of 140-minutes, which assures a Cu recovery efficiency of 80 %, a current efficiency of 34.7 % and a profit of $17.8{\cdot}10^{-5}$ $/L. To attain the level of Cu^{2+} concentration corresponding to the maximum admitted imposed by the Romanian reglementation (10 mg/l), a 95% Cu extraction efficiency should be achieved. It results that a single electrolysis stage, being limited by technological and economical reasons (long processing time and high- consumption of energy), appears to be unsatisfactory. To further lower the Cu^{2+} concentration, a second electrolysis stage will be necessary, either the use of a different Cu^{2+} extraction method should be considered.

Summarizing, it can be stated that after 140 minutes of galvanostatic electrolysis (0.25 A), using a 10 g fluidized cathode (made of copper powder in 0.2 - 0.125 cm range size), a Cu extraction efficiency of 80 % with a 34.7 % current efficiency can be attained, when 1.5 L of wastewater (containing 0.2 g Cu^{2+}/L) were processed with an electrolyte circulating speed of 2 cm s^{-1}. In the same time, a $17.8{\cdot}10^{-5}$ $/L profit was estimated.

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