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RETICULATED VITREOUS CARBON (RVC) ELECTRODE REACTOR FOR COPPER IONS REMOVAL FROM DILUTE SOLUTIONS

C. G. ILEA[*], S. DORNEANU[**], A. IMRE[*], P. ILEA[**]

"Babes-Bolyai" University, Faculty of Chemistry and Chemical Engineering
[*]Department of Chemical Engineering, [**]Department of Physical Chemistry
11 Arany Janos Str. 400028 Cluj-Napoca , Romania. E-mail:pilea@chem.ubbcluj.ro

ABSTRACT. The present work shows the results of a Cu^{2+} electroextraction test from a diluted solution (500 ppm) using an electrochemical reactor with a reticulated vitreous carbon cathode. This technique allows the recovery of approximately 90% of the copper ions from the solution. A mathematical model for the design of an electrochemical reactor for Cu^{2+} electroextraction was built. Using the geometric dimensions of the designed electrochemical reactor, a simulation of the electroextraction process was done in order to compare the calculated data with the experimental ones. A good agreement is observed and small differences were recorded only at the end of the experiment.

INTRODUCTION

Nowadays, metal ion removal from wastewaters is one of the main environmental issues and also one of the most important applications of cathodic treatment of aqueous effluents [1-2]. In this context, this research was focused on the electrochemical removal of copper from dilute wastewater. Copper is one of the main pollutants and it also has a great economical importance. Its recovery in a pure state is greatly desired and it can only be achieved using an electrochemical method. Due to the possibility of a high dilution of the wastewater, the electrochemical recovery method must use a mass transfer enhancement technique. Using a volumic cathode such as a **r**eticulated **v**itreous **c**arbon (RVC) cathode [3] is one of the widely used options. Therefore, the main objective of the following work is to study the perspective of copper ion removal from diluted wastewaters with the aid of a RVC electrode. This was done via an experimental research using a laboratory scale **e**lectrochemical **r**eactor (ER) equipped with a RVC cathode. The main experimental parameters of the process were identified and evaluated. Also, in order to design a continuous ER for wastewater processing, a mathematical model of the process was elaborated.

EXPERIMENTAL RESULTS

The experimental set-up includes a home-made cylindrical ER equipped with a cylindrical working electrode (RVC, 20 ppi, Φ_{out} = 24 mm, Φ_{in} = 14 mm, h = 12 mm) and a concentric cylindrical sieve acting as a counter electrode (lead with 1% Ag, Φ_{out} = 10 mm, Φ_{in} = 8 mm, h = 12 mm). The counter electrode is placed inside the working electrode as it can be observed in Figure 1.

Potentiostatic measurements at room temperature were performed using an analogical potentiostat controlled by a HP Kayak PC via a National Instruments PCI 6024E data acquisition board. LabView5.1® software (National Instruments)

was used for the experiment control and data acquisition. The synthetic electrolyte solution (500 ppm Cu^{2+}, 25℃) was recycled using a centrifugal pump.

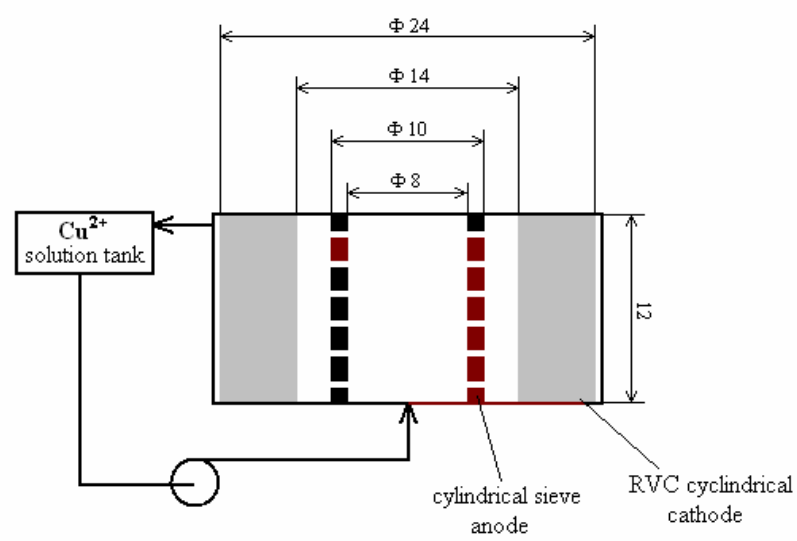

Figure 1. Scheme of the laboratory scale ER for the Cu^{2+} ions recovery

In order to estimate the concentration of copper ions, reduction limiting current measurements were performed using a Cu **r**otating **d**isk **e**lectrode (RDE). Figure 2 presents the calibration plot for the limiting current *vs.* Cu^{2+} electrolyte concentration recorded at different rotation velocities of the RDE.

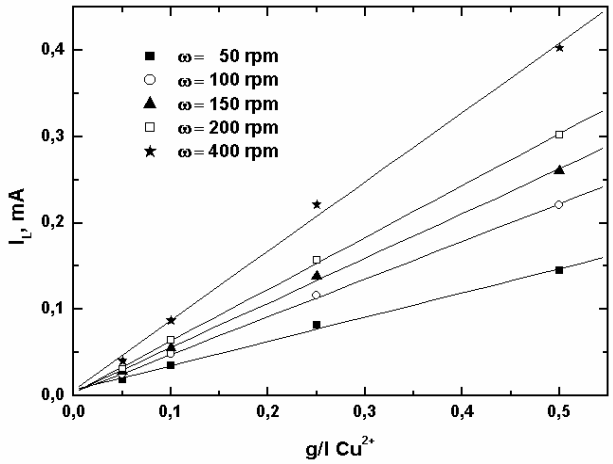

Figure 2. Limiting current *vs.* Cu^{2+} concentration calibration plot at different RDE rotation velocities, ω.

A Cu^{2+} electroextraction test was done with the experimental ER setup. Data for a series of successive cathodic extractions, performed in potentiostatic conditions (E = -0.400 V/SCE), are presented in the Table.1.

The results presented in Table 1 show that it is possible to decrease the Cu^{2+} concentration with one order of magnitude, simultaneously with a 15% decrease of the initial cell voltage.

Table.1.

Experimental results for successive cathodic extractions,
performed in potentiostatic conditions (E = -0.400 V/SCE);
volume of solution = 75mL, initial concentration of Cu^{2+} = 500 ppm.

Time (min)	Q (A s)	$C^{*}_{Cu^{2+}}$ (ppm)	Cell voltage (V)	Current efficiency (%)
15	30,36	388	4,0	84
30	37,31	271	3,9	71
45	42,82	141	3,7	69
60	33,27	51	3,4	62

*final concentration of Cu^{2+} ions

This test also shows that approximately 90% of the initial copper can be recovered during 60 minutes of electroextraction.

REACTOR DESIGN MODEL

A mathematical model was elaborated in order to obtain the geometric characteristics of a continuous ER for the recovery of Cu^{2+} ions from dilute wastewaters. The main purpose of this model is to design a proper cylindrical RVC cathode in order to achieve the desired conversion of the Cu^{2+} ions. The unknown variables of the model were: the mass transfer coefficient – k_m; the thickness of the **c**ylindrical **c**athode (CC) - δ; the length of the CC - L; the inner diameter of the CC – d_1. In order to uniquely determine their values, four equations must be used. Thus, the equations of the model are [4, 5, 7]:

1) *The Plug Flow Reactor design equation*:

$$X = 1 - e^{\frac{-k_m \cdot A_e \cdot L}{\bar{v}}}, \quad (1)$$

where X represents the desired conversion; A_e – the specific area of the RVC (20 ppi, 1038 m^2/m^3 [6]);

$$\bar{v} = \frac{V_f}{\frac{\pi}{4}\left[(d_1 + 2\cdot\delta)^2 - {d_1}^2\right]} \quad (2)$$

is the average velocity of the liquid flow inside the reactor and V_f is wastewater feed flow rate.

2) *The mass transfer equation*:

$$Sh = a \cdot Re^{b} \cdot Sc^{c}, \quad (3)$$

where $$Sh = \frac{k_m \cdot 2 \cdot \delta}{D_{Cu^{2+}}} \quad (4)$$

is the Sherwood number;

$$Re = \frac{\bar{v} \cdot 2 \cdot \delta}{\nu} \quad (5)$$

is the Reynolds number;

$$Sc = \frac{\nu}{D_{Cu^{2+}}} \quad (6)$$

is the Schmidt number; according to [4] the exponent values are: a = 1.44, b = 0.58, c = 1/3; the Cu^{2+} ion diffusion coefficient is $D_{Cu^{2+}} = 7.6 \cdot 10^{-10}$ (m^2/s); $\nu = 1.22 \cdot 10^{-6}$ (m^2/s) is the cinematic viscosity.

3) *The limiting current equation*:

$$\frac{I_L}{A_e \cdot V} = z \cdot F \cdot k_m \cdot c_{in}\ , \quad (7)$$

where I_L is the limiting current; V is the volume of the **CC**; z = 2 is the number of transferred electrons for the cathodic reaction; F = 96487 As/Eg, is the Faraday number; c_{in} = 500 ppm is the Cu^{2+} inlet concentration. The left term of the equation, representing the limiting current density, was experimentally determined and a value of 6,4 A/m^2 was used in order to solve the model.

4) *A dimensional restriction*:

In order to have a proper geometric shape of the reactor, the following restriction should be fulfilled:

$$d_1/\delta = 3.5. \quad (8)$$

The model was solved using the MATLAB® software for different values of conversions and wastewater feed flow rates. For all simulations, the determined value for the mass transfer coefficient was $k_m = 4.2 \cdot 10^{-6}$ m/s. The dependence of the reactor (cathode) length with respect to different desired conversion values, at different feed flow rates is presented in Figure 3. Figures 4 and 5 present the dependence of the cathode thickness and inner diameter, respectively, versus wastewater feed flow rate values at different desired conversions.

The data presented in figures 3-5 allow the design of an ER with an RVC cathode taking into consideration the initial concentration, the required conversion value and the mass transport parameters. Given the fact that each, the galvanostatic or the potetiostatic operation, has its own advantages and disadvantages, it is possible to determine the most advantageous alternative, based on the proposed model taking into account criteria like the duration of wastewater processing and/or the required energy consumption.

Using the geometric dimensions of the ER given by the design model, an electroextraction process simulation was done in order to compare the data with the experimental results. Figure 6 presents a comparison between the model based extraction simulation and the experimental data. A good agreement between them can be observed.

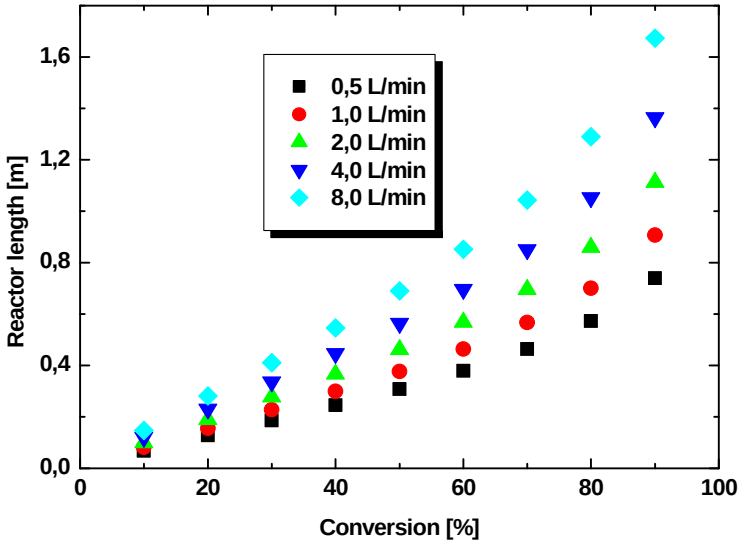

Figure 3. The influence of desired conversion on the reactor length at different feed flow rate values

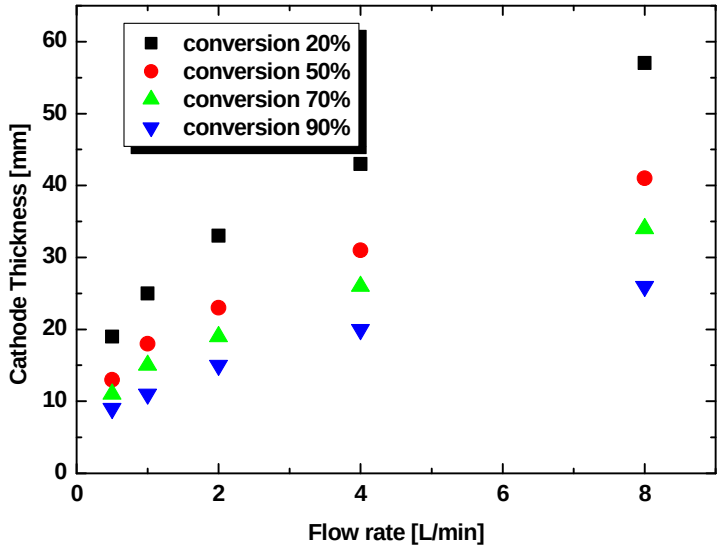

Figure 4. The influence of the feed flow rate on the RVC cathode thickness at different conversion values

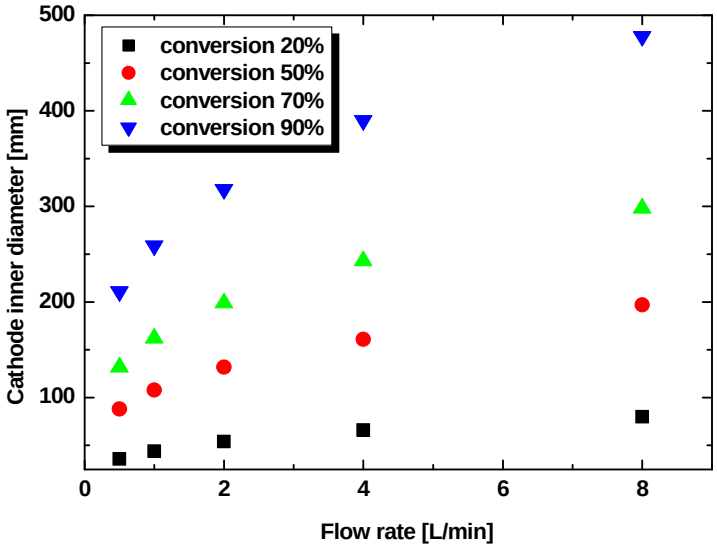

Figure 5. The influence of feed flow rate on the RVC cathode inner diameter for different conversion values

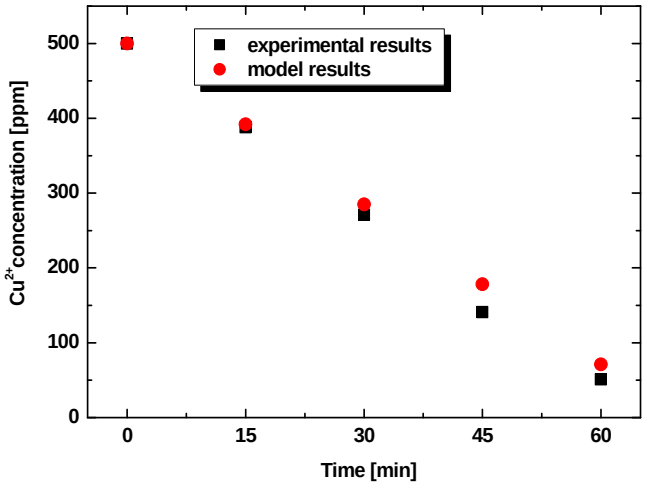

Figure 6. Comparison between experimental and mathematical model results

CONCLUSIONS

The model based design shows that reasonable dimensions for the ER can be obtained for the explored range of flow-rates at a desired conversion.

The reactor length increases with the desired conversion and the flow area, dependent on the inner diameter and the thickness of the RVC cathode. It also increases with the desired feed flow rate value.

Comparing the theoretical model with the experimental results, a good agreement is observed, only small differences being observed at the end of the experiment.

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