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OPTIMISATION OF COPPER REMOVAL FROM DILUTED SOLUTIONS

FLORICA IMRE-LUCACI[a], SORIN-AUREL DORNEANU, PETRU ILEA

ABSTRACT. An experimental study concerning the copper removal from a simulated wastewater containing 10 ppm of Cu^{2+} ions was performed in a continuous flow electrochemical reactor equipped with a rectangular three-dimensional (3D) cathode made of reticulated vitreous carbon (RVC) with 100 ppi porosity. The influence of low supporting electrolyte concentrations and of the electrode polarisation potential was investigated. The reactor performance was evaluated considering the residual copper concentration and the specific energy consumption. After 90 min of electrolysis, the copper ion concentration was reduced to less than 0.1 ppm, permitting the discharge of the treated solutions to the drain system. With an operating cell voltage around 1.8 V, specific energy consumptions close to 0.18 kWh per cubic meter of treated wastewater was calculated.

Keywords: *removal, copper, reticulated vitreous carbon electrode, waste waters*

INTRODUCTION

Wastewaters containing heavy metal ions (HMI), such as cadmium, chromium, copper, gold, lead, nickel, silver, tin and zinc, are generated in large quantities during electroplating, manufacturing of microelectronic parts, mining and processing of photographic materials. For environmental and economic reasons, these toxic metals should be removed from wastewater before discharge [1, 2].

The maximum admitted concentrations (MAC) of heavy metals is strictly regulated in EU, imposing a rigorous control and treatment of wastewaters. These limits are in the domain 0.05 – 1 ppm for HMI [3]. In order to respect the MAC, the removal by cathodic deposition presents a clear, versatile and efficient method.

Depending on the heavy metals concentrations, the removal process can be done in different manners. For high concentration (grams per litre), two-dimensional cathodes can be used and the content of heavy metals can be reduced with one order magnitude. The resulting effluent can be reused in the process or it can be introduced in a new stage of chemical or electrochemical decontamination [2].

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[a] *Department of Physical Chemistry, "Babes-Bolyai" University, 11 Arany Janos, 400028 Cluj-Napoca, Romania;* [*] *fimre@chem.ubbcluj.ro*

For low concentrations, under hundreds milligrams per litre, three-dimensional (3D) electrodes must be used and the content of heavy metals can be reduced to levels that allow the discharge of the effluents in environment [4-11].

Preliminary tests concerning the removal of Cu (RCu) from diluted solutions of nitric acid lead to very low current efficiencies due to a very intense hydrogen evolution reaction (HER) but also due to the cathodic reduction of the nitrate and dissolved oxygen. In this context, an alternative method of RCu, able to minimize the specific energy consumption, was searched.

In this work, we present our results concerning the optimization of the copper removal and recovery process from synthetic diluted solutions containing ~ 10 mg/L (ppm) of Cu^{2+} and Na_2SO_4 or NaCl at low concentrations (< 15 mM) as supporting electrolyte. The prepared solutions were electrolyzed, potentiostatically and galvanostatically, in a continuous flow electrochemical reactor (ER), equipped with a 3D RVC electrode. The reactor performance was evaluated based on the final residual copper concentration (C_R) and the global specific energy consumption (W_S) for metric cube (m^3) of treated solution. The concentrations of HMI were measured by atomic adsorption spectroscopy (AAS).

RESULTS AND DISCUSSIONS

Removal studies

The studies concerning the electrochemical copper elimination from dilute solutions were performed using electrolyte volumes of 250 mL. During the whole period of the electrolysis experiments (90 minutes), electrolyte samples of ~ 5 mL were taken out every 5 minutes for copper concentration evaluation. The working electrode current ($I_{W.E.}$) and the mean cell voltage (E_C) were used to estimate W_S and the current efficiency ($C_{\mathbf{E}}$) for cooper recovery.

Potentiostatic removal of Cu from diluted chloride solutions

The influence of cathodic potential

The measurements' results concerning the influence of the cathodic potential ($\varepsilon_{W.E.}$) on E_C, W_S, $C_{\mathbf{E}}$ and C_R are presented in Table 1. These experiments were completed using 10 mM NaCl as supporting electrolyte and a volume flow rate (V_F) of 50 mL/min.

For a working electrode potential of –100 mV/RE, the system is swinging and it has a poor performance (low $C_{\mathbf{E}}$ and high W_S, respectively). Moreover, the oxygen evolved at the anode is reduced on the cathode, generating a significant parasitic current even in the absence of an intense copper electrodeposition process.

The increase of the cathodic polarization potential to –200 mV/RE induces the enhancement of $C_{\mathbf{E}}$ and, obviously, a decrease of W_S. Furthermore, the formation of a compact cathodic deposit of Cu inhibits the oxygen reduction reaction (RRO) and allows achieving the desired MAC level (< 0.1 ppm Cu^{2+}).

Table 1. Global electrolysis parameters obtained at different cathodic polarization potential (t = 90 min, C_{NaCl} = 10 mM; V_F = 50 mL/min).

$\varepsilon_{W.E.}$ [V/ER]	E_C [V]	W_S [kWh/m^3]	C_E [%]	C_R [ppm]
–0.100	2.17	0.81	2.57	0.626
–0.200	1.79	0.18	9.18	0.060
–0.300	2.16	0.52	3.81	0.059

A cathodic potential of –300 mV/RE is already excessive for RCu, producing a porous Cu deposit and a significant increase of W_S due to the RRO evolved on the anodes' surface.

In these conditions, it was decided to continue the experiments at a cathode polarization potential of –200 mV/RE.

Concerning the C_R, we observed that, after 90 min of electrolysis at $\varepsilon_{W.E.}$ of –100 mV, only 94 % of Cu is removed, without reaching concentrations below 0.1 ppm. Contrarily, at $\varepsilon_{W.E.}$ of –200 mV and –300 mV, around 99.4 % from the initial amount of Cu was removed, reaching C_R below 0.1 ppm.

The effect of the chloride concentration

Due to the low salinity of the used electrolyte solutions, the corresponding electric conductivities were very small and determine high values of W_S. In order to evaluate the influence of supporting electrolyte concentration, measurements have been made at different concentrations of NaCl, the corresponding results being presented in Table 2.

Table 2. Global electrolysis parameters at different C_{NaCl} values (t = 90 min, $\varepsilon_{W.E.}$ = –200 mV/ER; V_F = 50 mL/min).

C_{NaCl} [mM]	E_C [V]	W_S [kWh/m^3]	C_E [%]	C_R [ppm]
5	2.55	0.73	4.24	0.050
10	1.79	0.18	9.18	0.060
15	1.53	0.12	11.37	0.138

The increase of the NaCl concentration in the electrolyte increases the C_E and decreases W_S. Unfortunately, C_R doesn't reach the desired level because, in the presence of high concentration of Cl^- ions, the formation of Cu^+ ions complexes, $[CuCl_x]^{-(x-1)}$, and also the low solubility of CuCl compound inhibit RCu [12]. As a result, the presences of chloride ions have complex effects and a moderate concentration (~ 10 mM NaCl) represents an optimal compromise that includes a reasonable salinity value.

The influence of volume flow rate

In order to evaluate the positive effect of the mass transport intensification, several measurements were accomplished at different volume flow rates. In this context, the results concerning the influence of V_F on RCu are presented in Table 3. The evolutions in time of the copper concentration at different V_F values are also presented in Figure 1.

Table 3. Global electrolysis parameters at different volume flow rate (t = 90 min, C_{NaCl} = 10 mM, $\varepsilon_{W.E.}$ = –200 mV/ER).

V_F [mL/min]	E_C [V]	W_S [kWh/m^3]	C_E [%]	C_R [ppm]
25	1.97	0.35	5.56	0.682
50	1.79	0.18	9.18	0.060
75	1.90	0.29	6.05	0.069
100	1.97	0.49	4.37	0.053

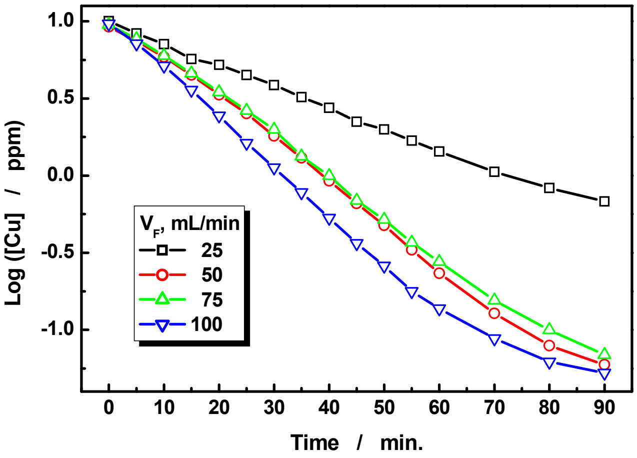

Figure 1. The evolution in time of the copper concentrations for different volume flow rates ($\varepsilon_{W.E.}$ = –200 mV/RE; C_{NaCl} = 10 mM).

At very low V_F values, the rate of RCu is also low and the Cu deposit is insufficient to inhibit RRO.

The increase of the volume flow rate intensifies Cu nucleation and a fast grows of the deposit, which inhibits RRO.

Anyway, the implicit increase of de oxygen quantity developed at the anode and its faster transport to the cathode produces a decrease of the C_E and an increase of W_S.

For volume flow rates higher than 25 mL/min, time values less than 90 min are required in order to attain 0.1 ppm Cu residual concentration (see Figure 1).

In these conditions, a flow rate of 50 mL/min is recommended.

Potentiostatic removal of copper from sulphate solutions

The influence of cathodic potential

The measurements' results concerning the influence of the cathodic potential on E_C, W_S, C_E and C_R are presented in Table 4. Based on preliminary tests (see next results), these experiments were completed using 7.5 mM Na_2SO_4 as supporting electrolyte and a volume flow rate of 50 mL/min.

Table 4. Global electrolysis parameters at different cathodic polarization (V_F = 50 mL/min; 7.5 mM Na_2SO_4).

$\varepsilon_{W.E.}$ [V/ER]	E_C [V]	W_S [kWh/m^3]	C_E [%]	C_R [ppm]
–0.100	1.51	0.15	8.84	0.858
–0.200	1.69	0.19	7.85	0.093
–0.300	2.05	0.33	5.37	0.079
–0.350	2.76	1.32	1.91	0.089

In sulphate solutions, the increase of the cathodic polarisation to more negative values induces an increase of the mean value of the recorded current and a decrease of C_E.

At $\varepsilon_{W.E.}$ values of –100 mV, –200 mV and –300 mV, the Cu deposit can inhibit RRO. For $\varepsilon_{W.E.}$ of –350 mV, the electrochemical system becomes lightly unstable (swinging) and a high amount of oxygen developed on anode is reduced at cathode, inducing the increase of the parasitic current and, consequently, the decrease of C_E.

In these conditions, we decided to continue the experiments at a cathodic polarization potential of –200 mV/RE because, at this value, the concentration of the Cu decrease bellow 0.1 ppm and reasonable energy consumption can be obtained.

The effect of Na_2SO_4 concentration

Because Na_2SO_4 is more toxic for environment that NaCl, we try to use the minimum amount of added sulphate. In order to evaluate the influence of Na_2SO_4 on RCu, several measurements have been made at low concentrations of supporting electrolyte, the corresponding results being presented in Table 5.

At low concentration of Na_2SO_4 (1.0 mM), the solution have a very low electric conductivity and, consequently, the W_s is very highly. The increase of Na_2SO_4 concentration induces a decrease of E_C, but the electrochemical system remains unstable due to the evolution of parasitic processes. Because, in the 7.5 mM Na_2SO_4 solution, the C_R decrease under 0.1 ppm and W_s is low, we decide to use this concentration for further experiments.

Table 5. Global electrolysis parameters at different C_{Na2SO4} values (t = 90 min; $\varepsilon_{W.E.}$ = –200 mV/RE; V_F = 50 mL/min)

C_{Na2SO4} [mM]	E_C [V]	W_S [kWh/m^3]	C_E [%]	C_R [ppm]
1.0	5.20	2.04	2.14	0.365
2.5	1.88	0.19	8.35	0.164
5.0	1.74	0.35	5.19	0.350
7.5	1,69	0.18	7.85	0.093
10.0	1.69	0.21	6.66	0.133

The influence of volume flow rate

In order to evaluate influence of electrolyte volume flow rate on RCu, measurements were accomplished at V_F values of 25, 50, 75, 100 mL/min, the obtained results being presented in Table 6. The evolutions in time of the copper concentration at different V_F values are also presented in Figure 2.

Table 6. Global electrolysis parameters at different volume flow rate (t = 90 min, $\varepsilon_{W.E.}$ = –200 mV/ER; 7.5 mM Na_2SO_4).

V_F [mL/min]	E_C [V]	W_S [kWh/m^3]	C_E [%]	C_R [ppm]
25	1.42	0.11	11.78	0.727
50	1.69	0.19	7.85	0.093
75	1.72	0.19	7.82	0.264
100	1.87	0.29	5.79	0.062

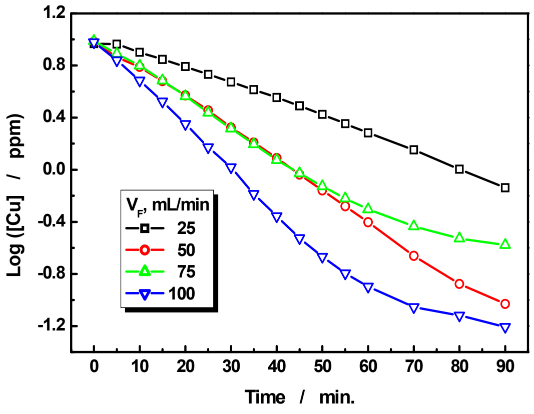

Figure 2. The evolution in time of the copper concentration for different volume flow rate ($\varepsilon_{W.E.}$ = –200 mV/RE; 7.5 mM Na_2SO_4)

At very low volume flow rates, RRO concurs with RCu and the Cu deposit is insufficient to inhibit RRO.

Based on the increase of V_F, the intensification of the mass transport allows Cu nucleation and a fast grow of the deposit, with positive effect on the RRO inhibition. Unfortunately, the implicit grow of de oxygen quantity evolved at the anode and its faster transport to the cathode induces a decrease of C_E and an increase of W_S.

Based on these observations, we concluded that a volume flow rate of 50 mL/min represents the optimal compromise for RCu.

Galvanostatic removal of copper from sulphate solutions

Based on the promising results obtained in potentiostatic conditions, we also decided to test RCu in galvanostatic mode.

The results concerning the influence of the imposed current on the RCu parameters are presented in Table 7. The measurements were done at current values of 25, 30 and 40 mA, at V_F = 50 mL/min and using 7.5 mM Na_2SO_4 as supporting electrolyte.

Table 7. Global electrolysis parameters evaluated for RCu in galvanostatic mode (V_F = 50 mL/min; 7.5 mM Na_2SO_4).

$I_{W.E.}$ [mA]	E_C [V]	W_S [kWh/m^3]	C_E [%]	C_R [ppm]
25	2.22	0.44	4.24	0.164
30	2.24	0.47	4.03	0.136
40	2.71	0.72	3.14	0.157

From the point of view of E_C, W_S and C_E, a current intensity of 25 mA is favourable to the RCu process but it isn't for C_R.

Using the same experiment time (90 min.), we observe that a volume flow rate of 50 mL/min is insufficient to reach the desired level of concentration (< 0.1 ppm).

CONCLUSIONS

The results of our researches concerning the removal of copper from diluted solutions allow us to take the following conclusions:

- For the potentiostatic RCu, a cathodic potential of –200 mV/ ER, a volume flow rate of 50 mL/minute and concentrations of 10 mM NaCl or 7.5 mM Na_2SO_4, respectively, represent the optimal values.
- Using the optimised parameters, MAC of Cu can be attained in the treated solutions.

- The evolution in time of the currents recorded in potentiostatic mode encouraged us to also test RCu in galvanostatic mode;
- The galvanostatic tests show us that increased volume flow rates and/or electrolyse time are required to attain the MAC. The optimisation of galvanostatic operating parameters involves additional experiments.

These promising obtained results prove the feasibility of copper removal from diluted solutions simulating wastewaters.

The validation of the obtained results requires additional measurements at scaling-up level, using pilot installation and real wastewaters samples.

EXPERIMENTAL SECTION

Reagents

The simulated solutions were prepared starting from analytical grade reagents ($CuSO_4$, NaCl and Na_2SO_4, all from Chimopar, Romania) and double-distilled water. The tested solution contained 10 mg/L Cu^{2+} and different concentrations of NaCl or Na_2SO_4.

Experimental setups

A Plexiglas home made electrochemical reactor (ER) previously described [2], a Reglo-Digital peristaltic pump (Ismatec, Switzerland) and a HP72 potentiostat (Wenking, Germany) were used for RCu tests.

A parallelepiped (L x W x H = 45 mm x 25mm x 25 mm) of 100 ppi RVC was used as working electrode. Four graphite cylindrical bars (Φ = 10 mm, L = 25 mm) were used as counter electrodes. Two $Ag/AgCl/KCl_{SAT}$ reference electrodes (RE) were used to record the cathode's and anode's potentials.

The LabView 6.1 software and a PCI 6024 E data acquisition board (National Instruments, USA) were used for process control.

The AAS measurements of Cu concentration in the electrolyte samples were performed with an Avanta PM Spectrometer (GBC, Australia).

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