

PURIFICATION OF ELECTROPLATING WASTE WATER USING A HYDROCYCLONE ELECTROLYTIC CELL

Guido RAJALO, Tamila PETROVSKAYA, Maya GLUSHKO, and
Viktor AHELİK

Keemia Instituut (Institute of Chemistry), Akadeemia tee 15, EE-0026 Tallinn, Eesti (Estonia)

Received 10 April 1996, accepted 3 June 1996

Abstract. A hydrocyclone electrolytic cell was applied for the purification of electroplating rinsewater. The kinetics of both the oxidation of cyanides and the deposition of copper was investigated. The process rate is influenced by diffusional resistance. An addition of sodium sulphate somewhat decreases the process rate and the current density, but significantly reduces energy consumption.

Key words: electroplating waste water, cyanide oxidation, copper recovery, electrolysis, hydrocyclone cell.

INTRODUCTION

Electrochemical technology is being successfully used today in many pollutant removal and recycling processes thanks to its selectivity, lower processing temperature and cost, a small amount of waste by-products, and amenability to automation [1–3]. The purification and recycling of electroplating waste waters is an area where electrochemistry is playing an important role.

The waste waters coming from electroplating processes contain very toxic complex cyanides of copper, zinc, iron, and other metals, as well as sodium cyanide. The purification of this kind of wastes has to solve two main problems: the oxidation of cyanides to less toxic compounds and the recycling of metals. Both of them can be fulfilled simultaneously by the use of the electrochemical method.

The rate of an electrochemical process depends in addition to electrical parameters on the diffusional mass transfer between the bulk of the liquid phase and the electrode surface. The diffusional resistance can be significantly reduced by the use of a turbulent swirling flow within the

cell [4]. Such a possibility is offered by a hydrocyclone cell (HCC) with a helical flow of the electrolyte between the electrodes. An electrochemical HCC has been developed and used for the electrodeposition of copper and silver from dilute solutions by Dhamo et al. [5].

In the present study an HCC was used for the purification of electroplating rinsewater. Both the electrooxidation of cyanides and the recovery of copper were investigated.

EXPERIMENTAL

The general arrangement of the experimental equipment is shown in Fig. 1. Experiments were carried out at batch recycle mode of operation using an electrochemical HCC, a well-stirred electrolyte tank ($V = 2.9 \text{ dm}^3$), and a rotary pump for electrolyte recirculation. The flow rate of the circulating electrolyte was regulated in a range from 10 to $40 \text{ cm}^3/\text{s}$ by means of a valve. The stainless steel wall of the HCC served as cathode. The 38 mm diameter of the graphite anode was situated at the centre of the hydrocyclone with a 50 mm inlet diameter. The anode, equipped with helical wings on the surface, was surrounded by a tube of cation-exchange membrane MKK (VNIKhT) 44 mm in diameter and 50 mm in height,

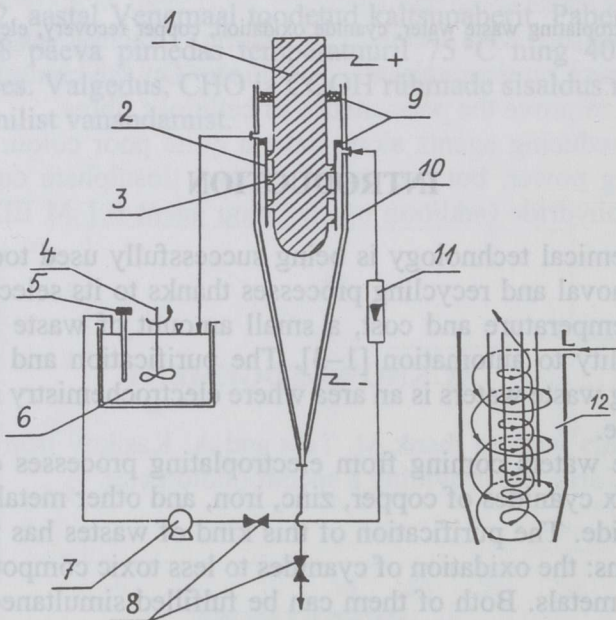


Fig. 1. Scheme of the experimental equipment. 1, anode; 2, membrane; 3, helical wing; 4, stirrer; 5, temperature regulation; 6, tank; 7, rotary pump; 8, valves; 9, Teflon gaskets; 10, hydrocyclone wall (cathode); 11, flowmeter; 12, scheme of the electrolyte flow.

acting simultaneously as the vortex finder of the hydrocyclone and the cell diaphragm. The electrolyte entered tangentially the top of the cathodic compartment between the cyclone wall and the membrane, flew at first helically downward and then upward through the anodic compartment, swirling round the anode (Fig. 1). The apex valve of the cyclone was kept closed, so the whole electrolyte flow was issued from the HCC and recirculated. The process time of batch experiments was varied from 1 to 10 h. During the experiment the current was kept constant at 1.4 A. The electrolyte temperature was 20–30°C.

Electroplating rinsewater containing 290 g/m³ copper, 20 g/m³ iron, 25 g/m³ sodium carbonate, and 220 g/l cyanide with pH 9.4 was used as electrolyte. In part of the experiments 35.5 g (0.25 mol) sodium sulphate was added to 1 dm³ electrolyte to increase electroconductivity. The samples for analysis were taken from the electrolyte at the beginning and at the end of the process.

The total cyanide concentration after distillation was determined by argentometric titration [6, 4500-CN C, D], the content of cyanides amenable to chlorination ('toxic' cyanides) by Bucksteeg's method binding the hexacyanoferrate ions with zinc acetate before distillation [7, p. 243]. Copper was determined by complexometric titration with murexide [8, pp. 62–63] and iron photometrically by means of sulphosalicylic acid [8, pp. 75–77], both after decomposing the cyanides.

RESULTS AND DISCUSSION

The following assumptions may be made for the description of the experimental process:

(1) The spiral movement of the electrolyte through the cathodic and anodic compartments of the HCC may be approximated to plug flow.

(2) The electrolyte reservoir has a constant volume and can be regarded as a perfectly stirred tank.

(3) The volume of the HCC is very small compared with that of the tank, therefore the change in the concentrations with time is very small as compared to the change in the length of the HCC.

The concentrations of cyanides and copper in the electrolyte vs. the process time at a current density 6.4 A/dm² are shown in Fig. 2a. All these experiments were performed with the above-described electroplating rinsewater. In Fig. 2b analogous concentration–time curves for the same rinsewater with an addition of 0.25 mol/dm³ sodium sulphate are shown. In both cases the oxidation of cyanides and the recovery of copper run rapidly in the beginning of the process, but are decelerated at a low concentration of reagents. A comparison of Fig. 2a and 2b shows that the addition of sodium sulphate somewhat decreases both the cyanide oxidation and copper deposition rates. The content of 'untoxic' cyanides (mainly hexacyanoferrate(III)) remains more or less unchanged.

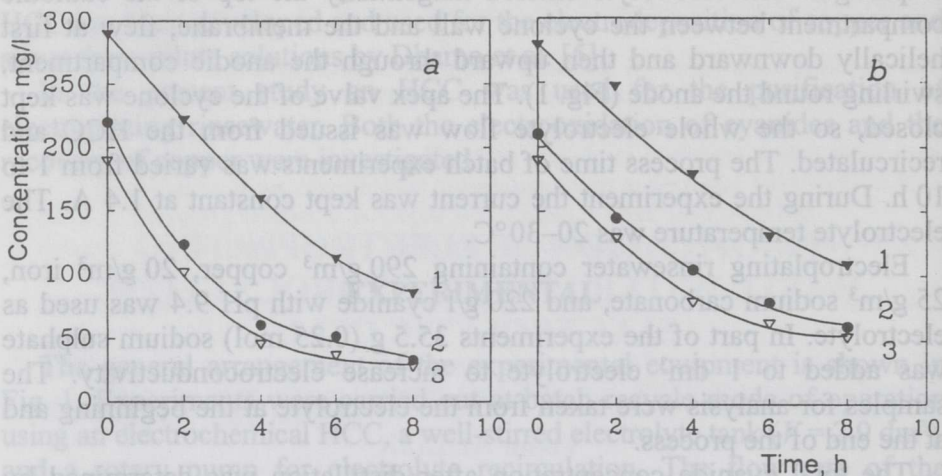


Fig. 2. Dependence of copper (1), total cyanide (2), and 'toxic' cyanide (3) concentration on time. Electroplating rinsewater (a) and rinsewater with Na_2SO_4 addition (b).

The process rate can be influenced by the rates of both the diffusional mass transfer and the chemical reaction. If the concentrations of the cyanides and copper are very low and hence the process is controlled by mass transfer, we can, according to the above-presented assumptions (1)–(3), describe the process as [5]

$$-dC(t)/dt = \tau_B^{-1} [1 - \exp(-K_L/Q)] C(t). \quad (1)$$

Integration of Eq. (1) gives a linear plot of $\ln(C(0)/C(t))$ against t . From the slope of the straight line we can calculate the volumetric mass transfer coefficient as

$$K_L = 2\pi RLK = -Q \ln [1 + \tau_B t^{-1} \ln(C(t)/C(0))], \quad (2)$$

where K is the mass transfer coefficient, m/s; R is the radius and L the length of the membrane, m; Q is the volumetric flow rate, m^3/s ; τ_B is the mean residence time of the electrolyte in the tank, s; t is the process time, s; $C(0)$ and $C(t)$ are the initial and end concentrations of the reacting component, respectively.

In Fig. 3 the linear plot $\ln(C(0)/C(t))$ vs. t and our experimental data obtained at constant current and electrolyte flows are shown. The experimental data points are close on the linear plot, demonstrating the adequacy of the above presumptions and Eq. (1).

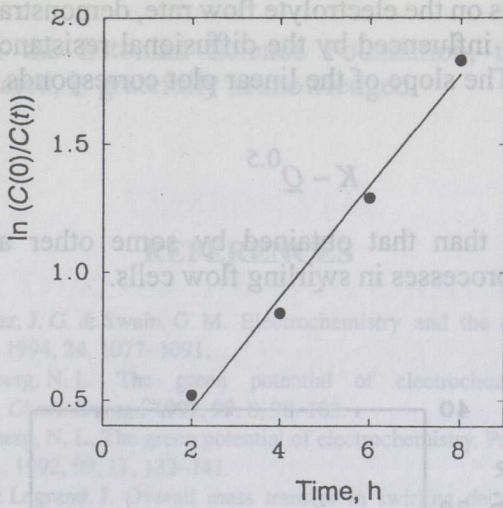


Fig. 3. Dependence of cyanide concentration ratio on time. $Q = 22 \pm 2 \text{ cm}^3/\text{s}$.

In case of a diffusion controlled isothermal electrochemical process the mass transfer coefficient depends on both the electrolyte flow rate and the cell voltage. In our experiments the current was kept constant. The cell voltage did not vary much. So it was possible to observe the influence of the electrolyte flow rate on the process rate.

In Fig. 4 the linear plot of $\ln K$ vs. $\ln Q$ for cyanide oxidation is presented. The mass transfer coefficient values were calculated from the

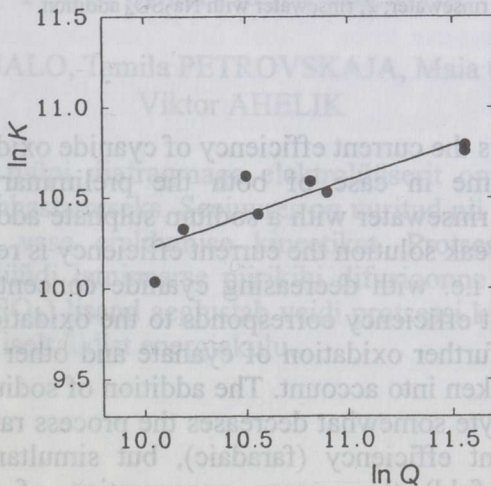


Fig. 4. Dependence of the mass transfer coefficient, K , on the flow rate, Q , at the oxidation of cyanides.

experimental data using Eq. (2). As can be seen, the mass transfer coefficient depends on the electrolyte flow rate, demonstrating the fact that the process rate is influenced by the diffusional resistance in the laminar electrolyte layer. The slope of the linear plot corresponds to the following expression:

$$K \sim Q^{0.5} \quad (3)$$

and is less steep than that obtained by some other authors [4, 5] at diffusion-limited processes in swirling flow cells.

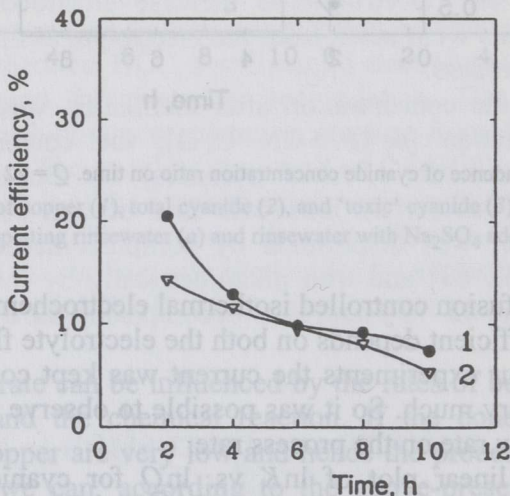


Fig. 5. Dependence of the current efficiency on time at the oxidation of cyanides. 1, electroplating rinsewater; 2, rinsewater with Na_2SO_4 addition.

Figure 5 displays the current efficiency of cyanide oxidation depending on the process time in case of both the preliminary electroplating rinsewater and the rinsewater with a sodium sulphate addition. As can be seen, in case of a weak solution the current efficiency is relatively low and decreases in time, i.e. with decreasing cyanide concentration. The low value of the current efficiency corresponds to the oxidation of cyanide to cyanate only, the further oxidation of cyanate and other electrochemical reactions are not taken into account. The addition of sodium sulphate as a supporting electrolyte somewhat decreases the process rate (cf. above) as well as the current efficiency (faradaic), but simultaneously reduces significantly (2–3-fold) the energy consumption of the process in connection with increasing the electroconductivity of the electrolyte and thus decreasing the cell voltage.

ACKNOWLEDGEMENT

A grant from the Estonian Science Foundation, under which the research was initiated, is gratefully acknowledged.

REFERENCES

1. Rajeshwar, K., Ibanez, J. G. & Swain, G. M. Electrochemistry and the environment. *J. Appl. Electrochem.*, 1994, **24**, 1077–1091.
2. Pletcher, D. & Weinberg, N. L. The green potential of electrochemistry. Part 1: The fundamentals. *Chem. Engng.*, 1992, **99**, 8, 98–103.
3. Pletcher, D. & Weinberg, N. L. The green potential of electrochemistry. Part 2: The applications. *Chem. Engng.*, 1992, **99**, 11, 132–141.
4. Legentilhomme, P. & Legrand, J. Overall mass transfer in swirling decaying flow in annular electrochemical cells. *J. Appl. Electrochem.*, 1990, **20**, 216–222.
5. Dharmo, N. An electrochemical hydrocyclone cell for the treatment of dilute solutions: Approximate plug-flow model for electrodeposition kinetics. *J. Appl. Electrochem.*, 1994, **24**, 745–750.
6. *Standard Methods for the Examination of Water and Wastewaters*. 17th. edn. American Public Health Association, 1992.
7. Lur'e, Yu. Yu. *Analiticheskaya khimiya promyshlennykh stochnykh vod*. Khimiya, Moscow, 1984 (in Russian).
8. Zhendareva, O. G. & Mukhina, Z. S. *Analiz gal'vanicheskikh vann*. Khimiya, Moscow, 1970 (in Russian).

GALVAANIKA HEITVEE PUHASTAMINE HÜDROTSÜKLONI TÜÜPI ELEKTROLÜUSERIGA

Guido RAJALO, Tamila PETROVSKAJA, Maia GLUŠKO,
Viktor AHELIK

Hüdrotsükloni tüüpi diafragmaga elektrolüüserit on rakendatud galvaanika heitvee puhastamiseks. Seejuures on uuritud nii tsüaniidide oksüdatsiooni kui ka vase eraldumise kineetikat. Protsessi üldist kiirust limiteerib elektrolüüdi laminaarse piirikihi difusioon takistus. Kande-elektrolüüdi (Na_2SO_4) lisand aeglustab veidi protsessi kiirust, kuid samal ajal vähendab oluliselt üldist energiakulu.