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Copper recovery from dilute solutions in the Falling-Film cell

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The removal of copper from dilute solutions is examined in electrochemical reactors where the electrolyte flows as a thin film in an inclined channel between a plane plate and a sheet of expanded metal (Falling-Film cell). Copper is recovered as a thin sheet from the plane plate. The results are compared with a known simplified model and the variations of the faradaic yield with the operating conditions are discussed.

Nomenclature

A_e	electrode surface area
b	width of inclined channel
$C(t)$	copper concentration at time t
C_0	initial copper concentration
d	interelectrode distance
$\bar{i}$	overall current density
$\bar{i}_L$	overall limiting current density
$\bar{k}_d$	overall mass transfer coefficient
L	length of the channel
Q_v	volumetric flow rate
Q_{vl}	volumetric flow rate per unit of channel width ($= Q_v/b$)
t	time
t_s	residence time in the reactor, defined by Equation 1
$\bar{u}_m$	mean flow velocity of the liquid film, defined by Equation 2
V	volume of electrolyte in the circuit
V_R	reactor volume
v_{sn}	normalized space velocity, defined by Equation 9
α	inclination angle with respect to the horizontal
η	instantaneous faradaic yield
$\bar{\eta}(t)$	time-averaged faradaic yield
ν_e	number of electrons exchanged in the electrochemical reaction

1. Introduction

The Falling-Film electrochemical cell which was recently proposed [1] uses the gravity flow of the electrolyte between the two electrodes, one of which is the inclined plane surface and the other a sheet of expanded metal conveniently positioned at a small distance from the plane surface, as shown in Fig. 1. When compared with other new cells this type of cell offers the following advantages: solutions of low electrical conductivity can be treated (small interelectrode distance), the overall hydrodynamics are greatly simplified (gravity flow only) and the gas produced may escape from the cell through the free surface of the film.

A previous paper [2] was concerned with the diffusional mass transfer at the two electrodes of the cell and with the empirical correlations of the overall mass transfer coefficients ($\bar{k}_d$) at the inclined plane plate. The experiments showed that, depending on the values of d (interelectrode distance) and of α (inclination angle of the planar electrode), three flow regimes may be distinguished through the variations of $\bar{k}_d$ with the flow-rate Q_v. Let us recall that the first of these flow regimes, corresponding

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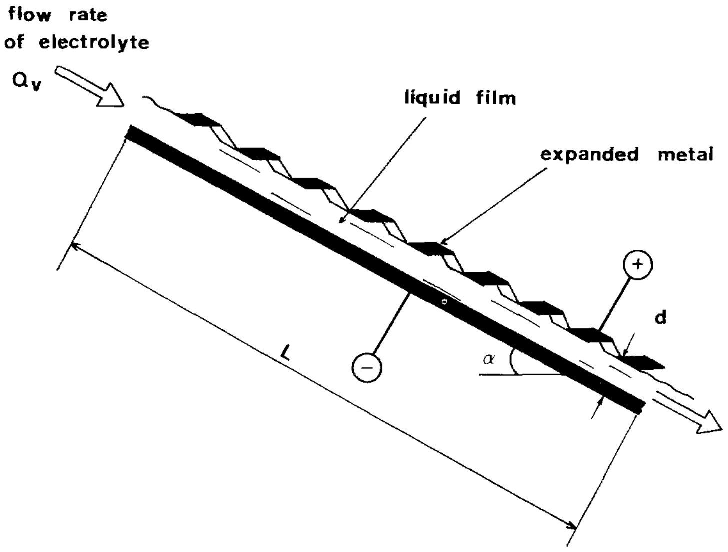

Fig. 1. Schematic view of the Falling-Film cell.

to small flow-rates, was called the capillary flow regime; this is such that $\bar{k}_d$ decreases when Q_v increases, thus allowing the ratio $\bar{k}_d/Q_v$ to present high values for small values of Q_v. As the space–time yield varies with this ratio[3], the Falling-Film cell is particularly suited to operation in the capillary flow regime.

The present work applies the Falling-Film cell to copper removal from dilute solutions simulating waste waters containing copper. Solutions with and without supporting electrolyte have been used. Copper removal is carried out in batch operations under galvanostatic conditions using two cells of different sizes. All of the experiments are performed in the conditions of the capillary flow regime.

2. Experimental details

The hydrodynamic circuit was similar to that described in [2]. The dimensions of the cells and their working conditions are given in Table 1. The chosen value of α (10°) was that for which the capillary flow regime is easily obtained and the value for Q_{vl} ($3.46\,\mathrm{cm^2\,s^{-1}}$) was such that this regime existed for the interelectrode distance adopted (i.e. 0.17 cm). ($Q_{vl} = Q_v/b$ represents the volumetric flow-rate per unit width of the plane plate.)

The plane surface acted as cathode and consisted of a planar sheet of stainless steel. The anode was a sheet of expanded stainless steel, the mesh of which had the following characteristic dimensions: large diagonal (LD, 1 cm) parallel to the general flow direction, small diagonal (CD, 0.5 cm)' normal to the flow and apparent mean thickness of the sheet (0.2 cm). The form and the definition of the mesh may be seen in [2].

Two classes of electrolyte were used:

(i) Solution type 1 contained abut $0.05\,\mathrm{g\,l^{-1}}$ copper (from $CuSO_4$) in 0.006 M H_2SO_4 and 0.1 M

Table 1. Geometric and hydrodynamic characteristics of the electrochemical cells

	Length L *(cm)*	*Width* b *(cm)*	Q_v *(l/h)*
Cell 1	24	10	125
Cell 2	100	13.8	172

Na_2SO_4; the sodium sulphate was added as an inhibitor of the chemical dissolution of the deposited copper.

(ii) Solution type 2 had a copper concentration varying between 0.2 and $1.0\,\mathrm{g\,l^{-1}}$; they were obtained by dissolving copper sulphate in demineralized water. The electrical conductivity of the different solutions varied between 5×10^{-4} and 3×10^{-3} Siemens depending on the experiments.

The experiments were carried out at ambient temperature (20-22° C). The imposed overall current density, $\bar{i}$, was varied in the study but was always chosen to be lower than the overall limiting current density, $\bar{i}_L$, which was calculated from the correlations established for the diffusional mass transfer [2]. Each experiment consisted of treating a given solution of concentration C_0 at a constant current density, and measuring at regular periods of time the copper concentration of the recirculated electrolyte by means of UV spectrophotometer or an atomic absorption spectrophotometer.

3. Results

3.1. *Variations of the concentration with time*

Figs 2 and 3 give the variations of the relative concentration $C(t)/C_0$ in the tank with time for the solution of type 1 ($C_0 = 0.05\,\mathrm{g\,l^{-1}}$, with supporting electrolyte) treated in cell 1 (Fig. 2) and in cell 2 (Fig. 3). Fig. 4 presents results obtained in cell 2 for solutions of type 2 (no supporting electrolyte). In Figs 2, 3 and 4 it appears that an increase of the current density leads to a better depletion of the copper concentration of a given solution. It can be also seen in Fig. 3 that an increase in $\bar{i}$ beyond $\bar{i} = 0.36\,\mathrm{mA\,cm^{-2}}$ does not produce a higher rate of depletion; this means that the limiting current density is approached.

The running time t is used as one of the abscissae in Figs 2–4 while the other scale gives the total cell residence time t_s. The time t_s is a parameter which allows a comparison of results obtained in cells of different size and with different volume, V, of electrolyte contained in the whole hydraulic circuit. The calculations of t_s are made using the equation

$$t_s = \left(\frac{L}{\bar{u}_m}\right)\left(\frac{Q_v}{V}\right)t \tag{1}$$

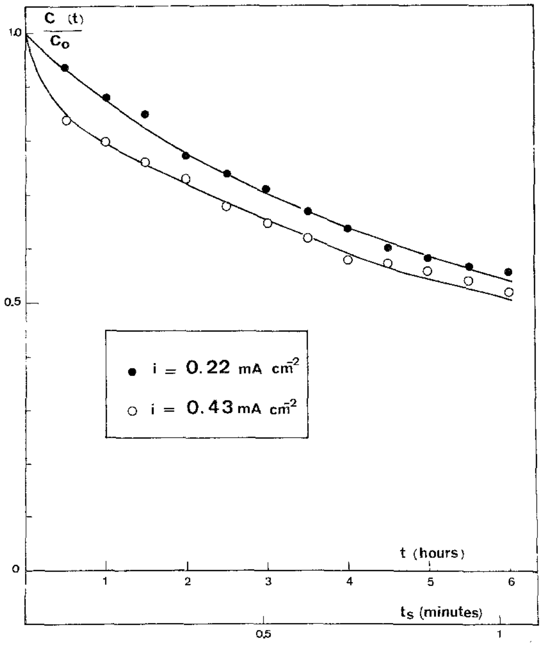

Fig. 2. Variations of the relative concentration $C(t)/C_0$ with time. Solution with supporting electrolyte (cell 1). $C_0 = 0.05\,\mathrm{g\,l^{-1}}$.

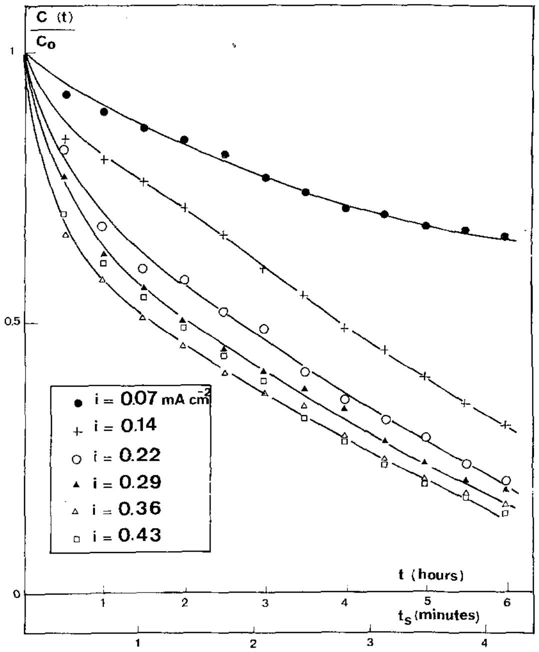

Fig. 3. Variations of the relative concentration $C(t)/C_0$ with time. Solution with supporting electrolyte (cell 2). $C_0 = 0.05\,\mathrm{g\,l^{-1}}$.

where $\bar{u}_m$ is the mean flow velocity of the liquid film. It has been shown [2] that, due to the capillary effect, the rigorous value of $\bar{u}_m$ is unknown, so that $\bar{u}_m$ can only be approximated by

$$\bar{u}_m \approx \frac{Q_v}{db} = 20.4\,\mathrm{cm\,s^{-1}} \tag{2}$$

The results obtained with cell 1 (Fig. 2) and with cell 2 (Fig. 3) are compared in Fig. 5 in the form of a plot of $C(t)/C_0$ versus t_s for two values of the current density. It is shown that for each current

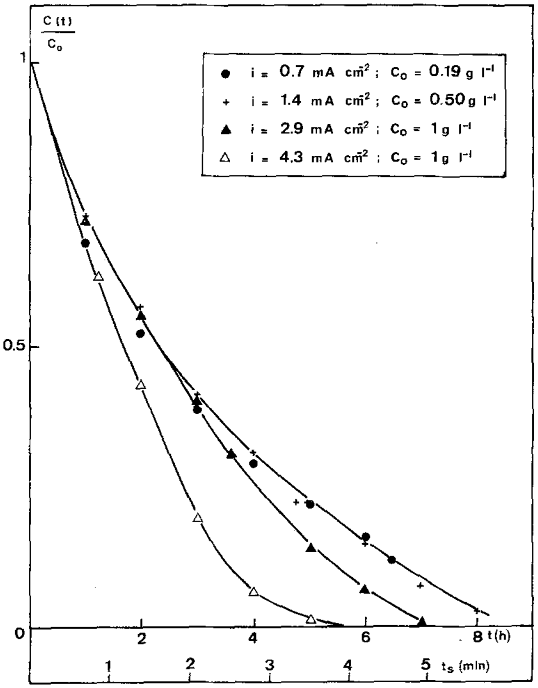

Fig. 4. Variations of the relative concentration $C(t)/C_0$ with time. Solution without supporting electrolyte (cell 2).

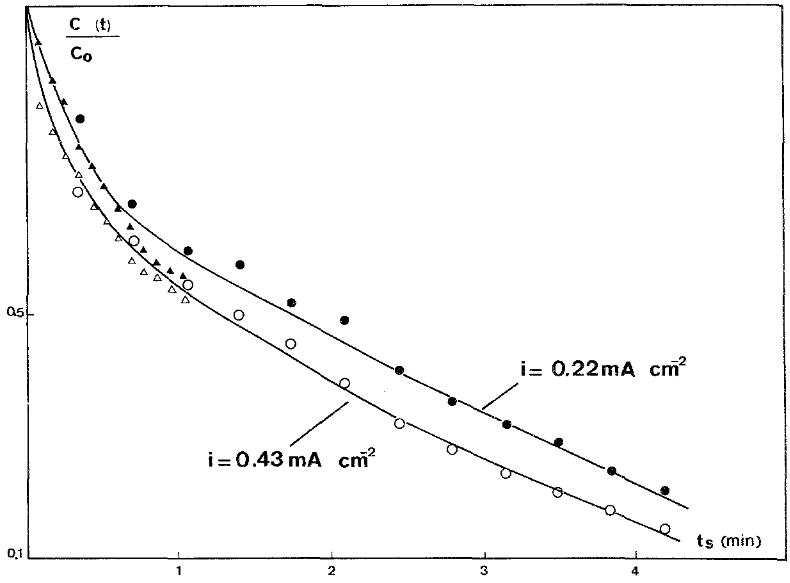

Fig. 5. Comparison of the results obtained in cell 1 and cell 2.

density the same curve describes the experimental values obtained with both cells; this is due to the fact that in the capillary flow regime, the flow may be considered as being of identical form all along the cell.

It is interesting to note that the copper concentration can be reduced to small values. For example, at $i = 4.3 \times 10^{-3}\,\mathrm{A\,cm^{-2}}$, a copper sulphate solution having an initial copper concentration $C_0 = 1.08\,\mathrm{g\,l^{-1}}$ contains $0.00012\,\mathrm{g\,l^{-1}}$ of copper after a total residence time $t_s = 5\,\mathrm{min}$ (this corresponds to the treatment of 20 litres during 7.5 h). Thus, industrial solutions containing copper at concentrations of a few grams per litre, and possibly without supporting electrolyte, may be treated in the Falling-Film cell with a depletion of copper which is very satisfactory. Industrial solutions having concentrations of this order of magnitude may be rinsing baths or waste waters. Another very important advantage is that the copper may be deposited as a thin sheet which is separated from the cathode after the experiment.

3.2. *Faradaic yield*

The experimental time variations of the concentration permit (for each intensity I) the determination of the time-averaged faradaic yield $\bar{\eta}(t)$ between $t = 0$ and t, i.e:

$$\bar{\eta}(t) = \frac{\text{mass of copper removed at } t}{\text{theoretical mass assuming a 100\% yield}} = \frac{(C_0 - C(t))V\nu_e F}{ItM} \tag{3}$$

where ν_e is the number of electrons in the electrochemical reaction ($\nu_e = 2$), F the Faraday number ($96\,487\,\mathrm{C\,mol^{-1}}$) and M the molar mass of copper. The concentrations C_0 and $C(t)$ are expressed in mass concentration.

Fig. 6 shows the time-variations of $\bar{\eta}(t)$ calculated for the treatment of solutions of type 1 in cell 2. It appears that $\bar{\eta}(t)$ decreases rapidly during the first 2 h and then the decrease with time is nearly linear. The higher the current density, the greater the decrease of $\bar{\eta}(t)$ with time. This result can be explained by the fact that for given hydrodynamic conditions ($\bar{k}_d$ fixed), the limiting current density

$$\bar{i}_L = \bar{k}_d \nu_e F C(t) \tag{4}$$

decreases proportionally with $C(t)$. Under galvanostatic conditions the operating current density $\bar{i}$

may become higher than $\bar{i}_L$, so that secondary reactions (such as H_2 evolution) occur, thus leading to a decrease in $\bar{\eta}(t)$.

For copper recovery, potentiostatic experiments [4] have shown that the faradaic yield decreases as the copper concentration is reduced in spite of the fact that $\bar{i} = \bar{i}_L$ at each instant. As noted before, one reason may be the simultaneous reduction of the hydrogen ions and it is known that the difference between the potentials corresponding respectively to the reduction of the cupric ions and to the hydrogen evolution decreases with decreasing copper concentration [5]. Another reason could be the chemical dissolution of copper in an acid medium when the coper concentration is of the order of a few p.p.m. [6].

The latter phenomenon is demonstrated by Fig. 7 which gives the variations of $\bar{\eta}(t)$ with $C(t)$ for both types of solution; it is seen that for copper concentrations smaller than 20 p.p.m., the faradaic yield is about 50–60% when the solution does not contain a supporting electrolyte and about 20 to 30% when a supporting electrolyte is present.

4. Discussion

Wragg and co-workers [7, 8] have developed models for the prediction of the time variations of the concentration in electrochemical reactor systems with continuous recirculation of the electrolyte: the cell is assumed to be either a perfectly mixed reactor [7] or a plug flow reactor [8]. In the capillary flow regime the Falling-Film cell presents a uniform flow over all the transfer surface thus approximating plug flow. The basic asumptions made in [7, 8] for the modelling of recirculating electrochemical systems are:

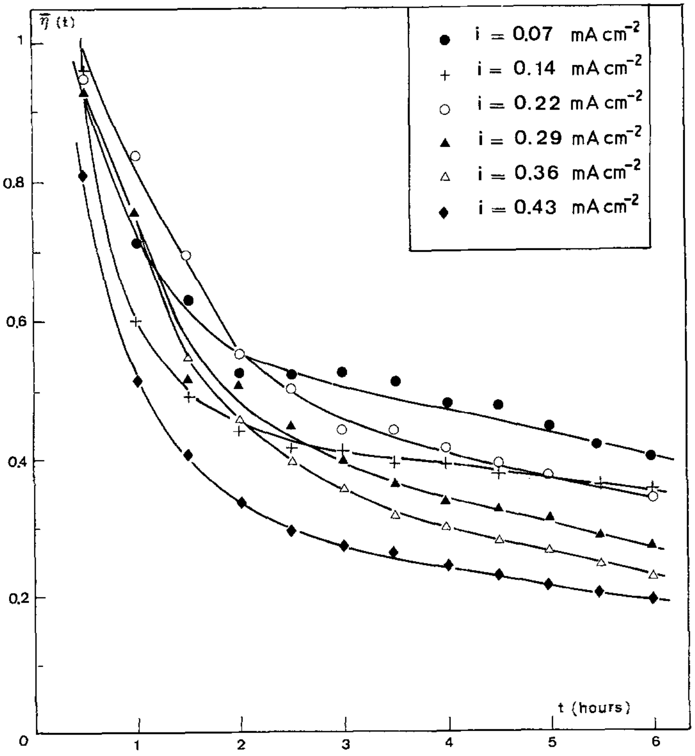

Fig. 6. Variations of the time-averaged faradaic yield $\bar{\eta}(t)$ for cell 2 (solution with supporting electrolyte).

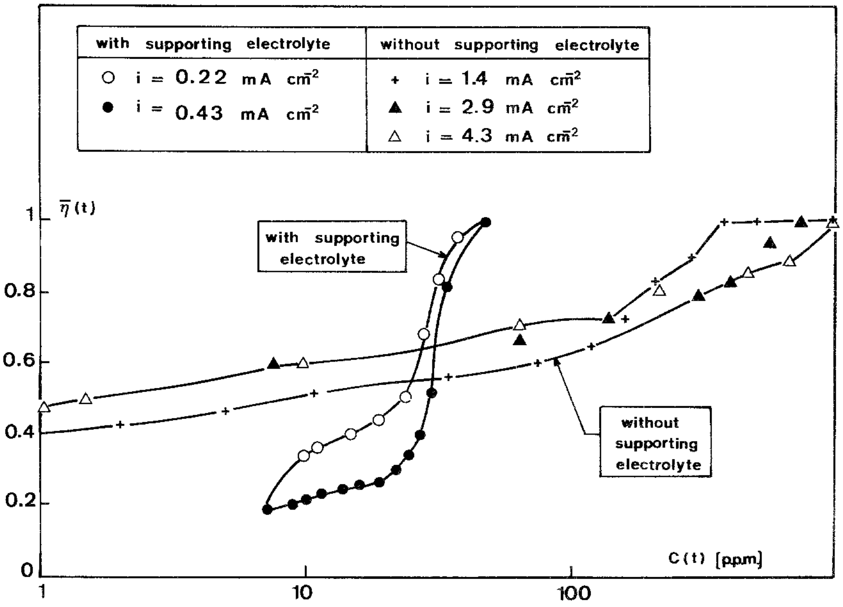

Fig. 7. Variations of $\bar{\eta}(t)$ with copper concentration.

(i) the reservoir is considered as perfectly mixed
(ii) the reactive ions are transported by convection and diffusion
(iii) the mass transfer coefficients $\bar{k}_d$ at the electrodes are constant throughout the reactor
(iv) the physical properties of the electrolyte are constant in space and time.

Assumption (ii) can be applied in the present case only for solutions of type 1. Under these conditions the mass balance in a differential element of the plug flow reactor leads to the following expression for $C(t)$:

$$C(t) = C_0 \exp\left\{-\left(\frac{Q_v}{V}\right)t\left[1 - \exp\left(-\frac{\bar{k}_d Ae}{Q_v}\right)\right]\right\} \tag{5}$$

if the volume V_R of the reactor may be considered as negligible when compared with the volume of the reservoir [8], which is the case in the present work. If the conversion X,

$$X = 1 - \exp\left(-\frac{\bar{k}_d Ae}{Q_v}\right)$$

per pass through the reactor is small, Equation 5 becomes

$$C(t) = C_0 \exp\left(-\left(\frac{k_d Ae}{V}\right)t\right] \tag{6}$$

It is seen in Fig. 6 that the copper depletion is maximum when $\bar{i}$ reaches the value 0.36 mA cm^{-2} which is almost equal to the limiting current density corresponding to C_0. For solutions of type 1 the relative concentrations $C(t)/C_0$ are reported versus time in a semilogarithmic plot (Fig. 8). For $\bar{i} \geqslant 0.36\,\text{mA}\,\text{cm}^{-2}$, $\bar{k}_d$ is deduced from the slope of the line and the obtained value, $\bar{k}_d = 1.3 \times 10^{-3}\,\text{cm}\,\text{s}^{-1}$, is in good accordance with the experimental value given by the method using the reduction of ferricyanide [2], although the physical properties of the electrolytes are different. For $\bar{i}$ smaller than the limiting current density (i.e. $\bar{i} < 0.36\,\text{mA}\,\text{cm}^{-2}$), Equation 6 may be written [8]:

$$C(t) = C_0 \exp\left[\left(-\frac{\lambda \bar{k}_d A_e}{V}\right) t\right] \tag{7}$$

The dimensionless parameter λ varies between 0 and 1 and represents the ratio $\bar{i}/\bar{i}_L$. By assuming that λ is independent of time and that $\bar{k}_d = 1.3 \times 10^{-3}\,\mathrm{cm\,s^{-1}}$, λ has been calculated from the slopes of the straight lines representing Equation 7 in Fig. 8. The experimental data are well represented by Equation 7 except for $\bar{i} = 0.29\,\mathrm{mA\,cm^{-2}}$ where the assumption that λ is independent of time does not seem to be valid.

The instantaneous faradaic yield, η, is defined by

$$\eta = \bar{\eta}(t) + t\left(\frac{\mathrm{d}\bar{\eta}(t)}{\mathrm{d}t}\right) \tag{8}$$

This can be calculated from the time-averaged faradaic yield $\bar{\eta}(t)$ curves of Fig. 6. The values obtained for η are plotted versus log $C(t)$ in Fig. 9 in a similar manner to the presentation used by Keating and Williams [9] for the comparison of the ESE cell with planar electrodes. Fig. 9 also displays the curve obtained in [4] for copper recovery in limiting diffusion conditions in a rectangular channel with turbulence promoters.

The Falling-Film cell appears as intermediate between the ESE cell and a classical cell with planar electrodes and without forced convection. For solutions of high electrical conductivities, a porous electrode like the ESE cell may be attractive because the surface area that is electrically active may be high, particularly when the copper concentration is low, as can be deduced from the definition of the electrochemical Thiele criteria for the effectiveness of porous electrodes [3]. On the contrary, the Falling-Film cell permits the treatment of solutions having low electrical conductivities.

Further comparison of the performance of the Falling-Film cell with that of other cells can be made through the normalized space velocity V_{sn} [10] representative of the ratio (productivity)/(investment cost). The volume (in litres) for waste water whose impurity concentration can be reduced by a factor of ten in 1 h in a reactor of 1-litre capacity is expressed as V_{sn}:

$$V_{sn} = \left(\frac{3600 I \eta}{(C_0 - C_s) V_R v_e F}\right)\left(\log \frac{C_0}{C_s}\right) \tag{9}$$

where C_0 and C_s are the initial and final concentration of impurities, respectively. The results obtained in the present work lead to values of V_{sn} which are between 6 and 12, i.e. of the same order

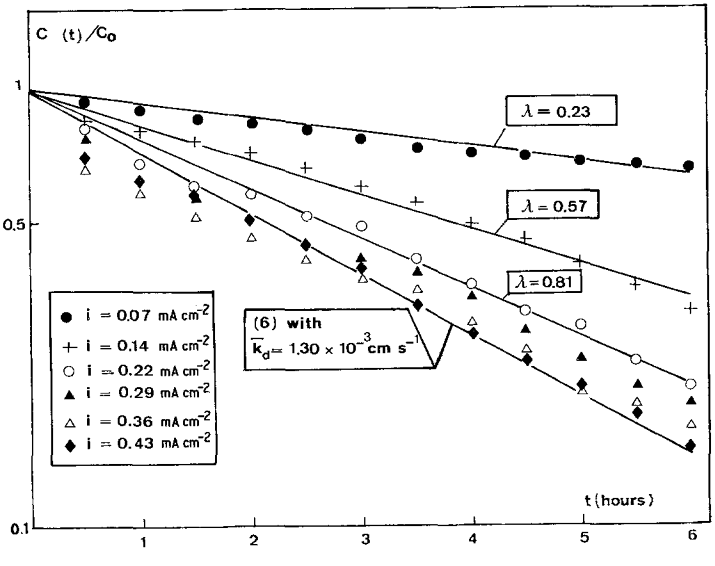

Fig. 8. Semilogarithmic plot of $C(t)/C_0$ versus time.

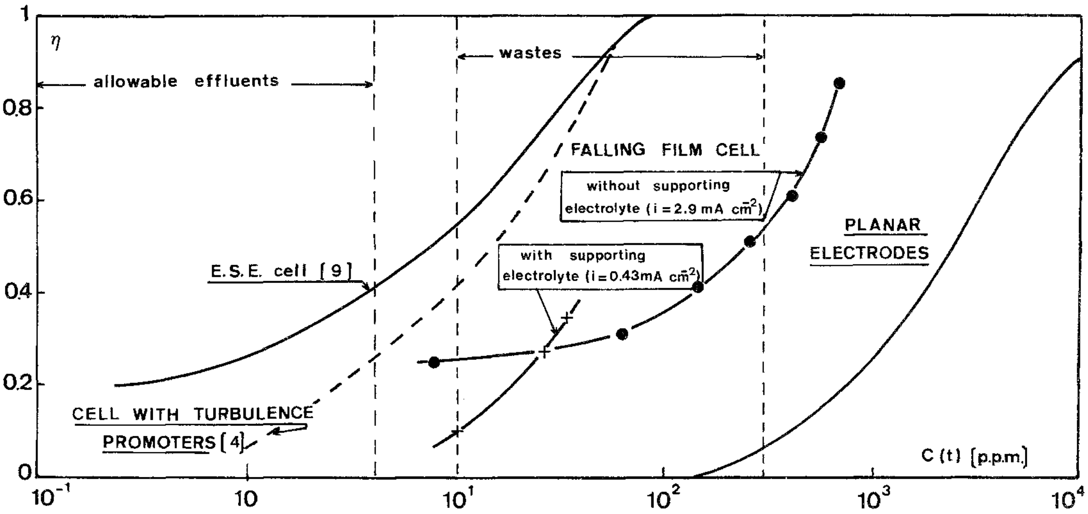

Fig. 9. Influence of the copper concentration on the instantaneous faradaic yield for various electrochemical cells.

as most other new cells [10]. It is the simplicity of the Falling-Film cell which is a particularly attractive feature for practical application.

5. Conclusions

Simulated industrial effluents containing copper have been treated to a final copper concentration as low as 0.1 p.p.m. depending on the operating current density and on the residence time in the cell. By using two cells of different sizes it has been shown that the performances of the Falling-Film cell working in the capillary flow regime seem to be independent of the dimensions of the flowing surface. The simplified model associating a plug flow electrochemical reactor with a perfectly mixed reservoir permits an explanation of the concentration–time relationships deduced experimentally under constant current densities. In spite of its simplicity, using gravity flow only, the Falling-Film cell has a performance similar to most of the more sophisticated new cells.

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