

# Removal of cadmium from dilute aqueous solutions with a rotating cylinder electrode of expanded metal

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**Abstract:** The removal of cadmium from dilute solutions using a continuous undivided electrochemical reactor with a rotating cylinder cathode of expanded metal is analysed. The effects of cathodic applied potential, size and orientation of expanded metal meshes and inlet cadmium concentration were ascertained. The results show that cadmium can be removed from dilute solutions (inlet concentration range 5–50 mg dm<sup>-3</sup>) with a high fractional conversion of between 35 and 40% depending on the operating conditions. Thus a minimal residual cadmium concentration of 3 mg dm<sup>-3</sup> was achieved. The specific energy consumption increases from 0.6 to 2 kWh mol<sup>-1</sup> as the cadmium concentration decreases.

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**Keywords:** electrochemistry; electrochemical engineering; effluent treatment; cadmium removal; rotating cylinder electrode; expanded metal

## NOTATION

$a_e$	Reactor specific surface area (m <sup>-1</sup> )
$A_s$	Electrode specific surface area (m <sup>-1</sup> )
$C_{in}$	Inlet concentration (mol m <sup>-3</sup> or mg dm <sup>-3</sup> )
$d_h$	Hydraulic diameter = $6\varepsilon/A_s$ (m)
$D$	Diffusion coefficient (m <sup>2</sup> s <sup>-1</sup> )
$E_s$	Specific energy consumption (w-s mol <sup>-1</sup> or kWh mol <sup>-1</sup> )
$E_{SCE}$	Cathode potential referred to saturated calomel electrode (V)
$F$	Faraday constant (C mol <sup>-1</sup> )
$h$	Interelectrode gap (m)
$i$	Current density (A m <sup>-2</sup> )
$I$	Total current (A)
$k$	Mass-transfer coefficient (m s <sup>-1</sup> )
$Q$	Volumetric flow rate (m <sup>3</sup> s <sup>-1</sup> )
$r_1$	Internal radius (m)
$r_2$	External radius (m)
$\bar{r}$	Mean radius = $\sqrt{(r_1^2 + r_2^2)}/2$ (m)
$Re_c$	Channel Reynolds number = $Q/h\varepsilon\nu$
$Re_r$	Rotating Reynolds number = $\omega r_2^2/\nu$
$s_n$	Normalized space velocity (s <sup>-1</sup> or h <sup>-1</sup> )
$Sc$	Schmidt number = $\nu/D$
$Sh$	Sherwood number = $kd_h/D$
$U$	Cell voltage (V)
$V$	Electrolyte volume within the reactor (m <sup>3</sup> )

$V_R$	Reactor volume (m <sup>3</sup> )
$x$	Fractional conversion
$\beta$	Current efficiency
$\varepsilon$	Porosity
$\nu$	Kinematic viscosity (m <sup>2</sup> s <sup>-1</sup> )
$\nu_e$	Charge number of the electrode reaction
$\rho$	Space time yield (mol m <sup>-3</sup> s <sup>-1</sup> )
$\omega$	Rotation speed (s <sup>-1</sup> or rpm)

## 1 INTRODUCTION

Cadmium provides plated surfaces with a good corrosion resistance, a high electrical conductivity and lubricity. These attractive features of the cadmium coatings are counteracted by the highly toxic nature of cadmium salts. Thus, the legal limitations concerning cadmium discharge in effluents are very stringent and the development of new technologies to correct the deleterious effect of the cadmium ions is necessary.

The electrolytic processing of dilute solutions requires the use of reactors with a high value of the product of the mass-transfer coefficient and the active electrode surface area in order to increase the space time yield. A strategy to achieve a combination of good mass-transfer conditions with a high degree fractional conversion is the use of the rotating

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cylinder electrode, which is recognized as a successful reactor for the cathodic removal of metals.<sup>1</sup> Likewise, the performance of the rotating electrodes can be enhanced by using a three-dimensional structure. Thus, Kreysa and Brandner<sup>2</sup> have performed the hydrodynamic characterization, mass-transfer studies and have analysed the reaction engineering behaviour of a rotating packed-bed electrochemical reactor. As test reactions, the reduction of ferricyanide on nickel plated steel spheres or silver deposition on graphite particles were used and high values of the normalized space velocity were reported. In previous works from this laboratory<sup>3-5</sup> the electrochemical cadmium removal was analysed and it was concluded that a continuous electrochemical reactor with a rotating electrode allows effective operation in the concentration range from 100 to 500 mg dm<sup>-3</sup>.

The present work continues the study of the electrochemical removal of cadmium from synthetic sulfate solutions with a cadmium concentration lower than 50 mg dm<sup>-3</sup> by using a three-dimensional rotating cathode of expanded metal sheets. A systematic study of the process variables is performed.

## 2 EXPERIMENTAL

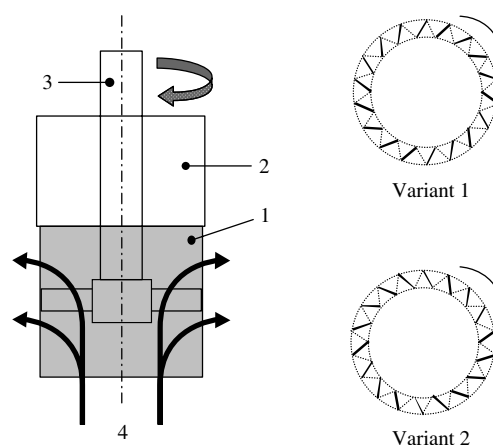
The experiments were performed in an undivided continuous reactor intercalated in a flow circuit system. The solution flowed from a thermostatted tank (30 °C) to the reactor, and was collected in another tank. It was not recycled so that the inlet cadmium concentration remained constant. The solution volume in the reactor was 1.3 dm<sup>3</sup> and the volumetric flow rate was  $4.373 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ .

The working electrode was a rotating cylinder made by ordered packing of sheets of expanded metal of stainless steel. The upper part of the electrode was bounded to a Teflon sleeve in order to orientate the electrolyte flow through the sheet pack. A perforated disc, centrally positioned and rendered inactive with an epoxy coating, was used as current feeder of the electrode. The sheets were arranged with the large diagonal parallel to the rotating shaft. There are two possibilities for the orientation of the mesh with regard to the direction of motion of the electrode, which are sketched in Fig 1. In variant 1 the strands of the expanded structure made an acute angle with the ground plane of the metal sheet. Thus, in variant 1, the expanded material contributes to deflecting the electrolyte towards the outer region of the electrode. Similar considerations of deflection have been made by Letord-Quéméré *et al*<sup>6</sup> for a stack of expanded metal in a flow channel and for gas-evolving electrodes.<sup>7</sup> Table 1 gives the geometrical characteristics of the expanded metal sheets and of the rotating electrodes. The three-dimensional electrodes were arranged with a perfect superposition of the expanded metal sheets, which defines straight interconnected pores perpendicular to the rotating shaft and diminishes the apparent thickness to 0.95 mm for the larger

mesh and 0.7 mm for the micromesh. Prior to each experiment the working electrode was washed with hydrochloric acid in an ultrasound cleaner in order to remove the cadmium deposit of the previous experiment. All experiments were performed at 30 °C under potentiostatic control for 70 min. The electrode reactions were the oxygen evolution at the anode and the cadmium deposition at the cathode. Likewise, hydrogen evolution and oxygen reduction took place as cathodic side reactions.

The supporting electrolyte was 1 M Na<sub>2</sub>SO<sub>4</sub> with a pH  $\cong$  7 at the reactor inlet. The inlet cadmium concentration was lower than 50 mg dm<sup>-3</sup>; the exact value was determined at each experiment. Likewise, during the experiment samples of solution were taken from the reactor outlet in order to determine the cadmium concentration by complexometry.<sup>8</sup>

Further details of the equipment employed, method of operation, data acquisition, reactions and reagents can be obtained from a previous work.<sup>5</sup>



**Figure 1.** Schematic view of the working electrode and of the orientations of the expanded metal structure. (1) Working electrode, (2) Teflon sleeve, (3) electrode shaft, (4) electrolyte flow rate produced by the electrode rotation.

**Table 1.** Geometrical parameters of the electrodes

Characteristic parameters of the expanded metals	Larger mesh	Micromesh
Long diagonal (mm)	10	6
Short diagonal (mm)	5	2.5
Long mesh aperture (mm)	8	4.5
Short mesh aperture (mm)	4	2
Thickness (mm)	0.36	0.3
Apparent thickness (mm)	1.2	0.9
Strand width (mm)	0.7	0.6
Surface area per unit volume of electrode, $A_s(\text{m}^{-1})$	$766 \pm 22$	$1600 \pm 27$
Surface area per unit net area	$0.92 \pm 0.03$	$1.44 \pm 0.02$
Internal diameter of the rotating electrode (mm)	35	35
Electrode length (mm)	33	38

### 3 EVALUATION OF THE REACTOR PERFORMANCE

The relevant equations required to analyse the performance of the electrochemical reactor, called 'figures of merit', are given below.

The current efficiency was calculated by:

$$\beta = \frac{\nu_e F Q C_{in} x}{I} \quad (1)$$

For a continuous reactor the space time yield in terms of the fractional conversion and assuming  $V = V_R$  is given by:

$$\rho = \frac{Q C_{in} x}{V} \quad (2)$$

Likewise, for a continuous stirred tank electrochemical reactor the fractional conversion is:

$$x = \frac{ka_e V / Q}{1 + ka_e V / Q} \quad (3)$$

and the normalized space velocity in terms of the fractional conversion is given by:

$$s_n = \frac{Q}{9V} \left( \frac{x}{1-x} \right) \quad (4)$$

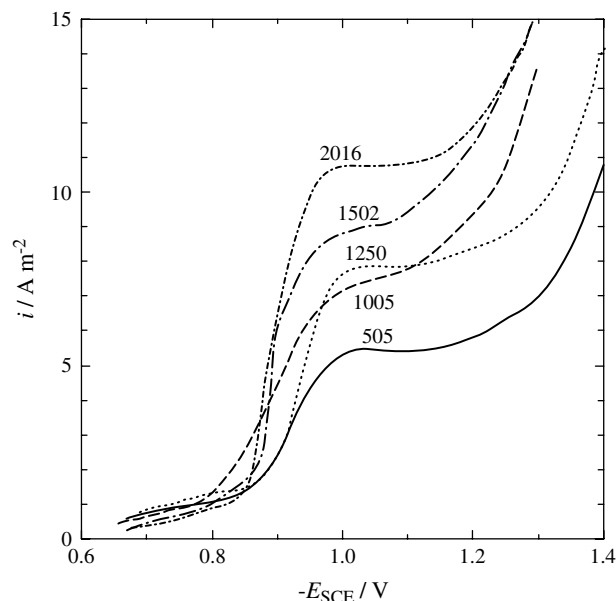
Furthermore, Eqn (5) allows the calculation of the specific energy consumption.

$$E_s = \frac{\nu_e F U}{\beta} \quad (5)$$

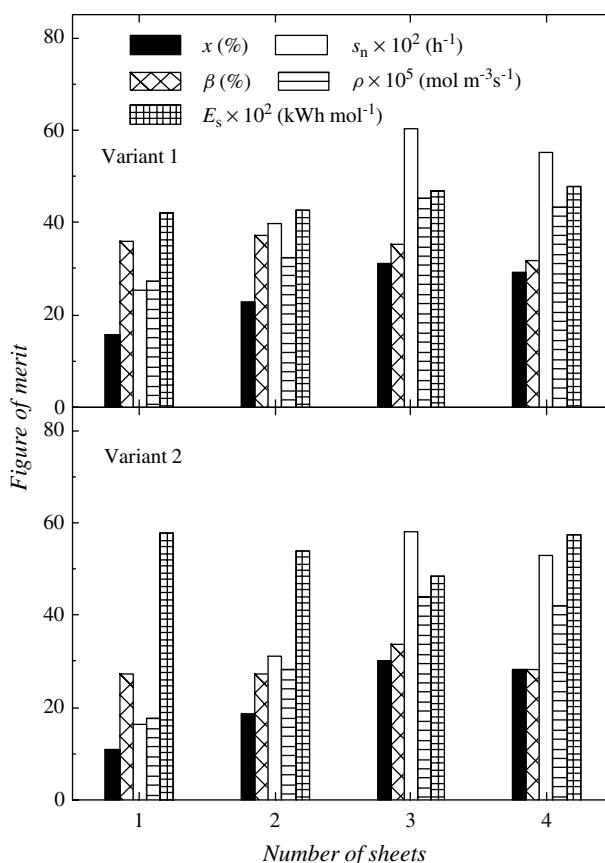
### 4 RESULTS AND DISCUSSION

Figure 2 shows typical polarization curves, obtained with a cadmium-plated copper rotating disc, at different rotation speeds for a cadmium concentration of  $43 \text{ mg dm}^{-3}$ . It can be seen that the cadmium deposition begins at  $-0.75 \text{ V}$ , which is in accordance with the equilibrium potential predicted by the Nernst equation, and achieves the limiting current density at approximately  $-0.95 \text{ V}$ . The current density shows a plateau over a narrow range of potentials, lower than  $0.15 \text{ V}$ , because of the onset of hydrogen evolution.

Figures 3–6 report the 'figures of merit' of the reactor as a function of the number of sheets for the two variants of the expanded structures at two cathodic potentials, which were adopted because in a previous work<sup>5</sup> the best conditions for cadmium deposition were obtained when the potential was in the range from  $-0.9 \text{ V}$  to  $-1.0 \text{ V}$ . Figures 3 and 4 correspond to the larger mesh and Figs 5 and 6 to the micromesh. Figures 3–6 show that the fractional conversion and consequently the normalized space velocity and the space time yield increase when the number of sheets is increased but approach to a maximum for three sheets. The values at  $-1.0 \text{ V}$  are higher than at  $-0.9 \text{ V}$ , this behaviour can be explained by taking into account that at more negative

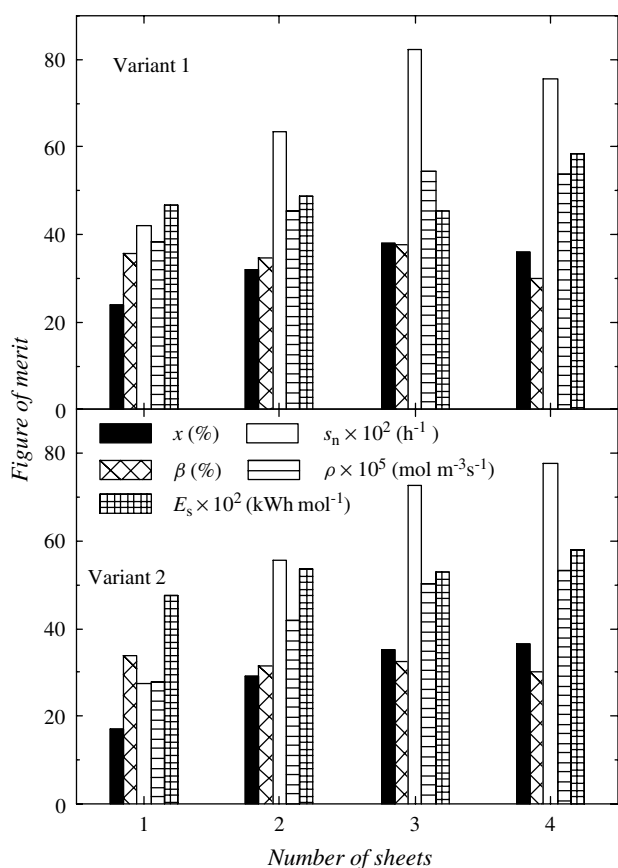


**Figure 2.** Current density as a function of the electrode potential for cadmium-coated rotating disc electrodes at different rotation speeds in rpm. Scan rate:  $1 \text{ mV s}^{-1}$ .  $T = 30^\circ \text{C}$ . Electrolyte:  $1 \text{ M Na}_2\text{SO}_4$ ,  $C_{\text{Cd}^{2+}} = 43 \text{ mg dm}^{-3}$ ,  $\text{pH} \cong 7$ .



**Figure 3.** 'Figures of merit' as a function of the number of sheets.  $\omega = 1000 \text{ rpm}$ ,  $Q = 4.373 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$ . Inlet cadmium concentration  $\cong 50 \text{ mg dm}^{-3}$ . Supporting electrolyte:  $1 \text{ M Na}_2\text{SO}_4$ . Inlet  $\text{pH} \cong 7$ .  $T = 30^\circ \text{C}$ . Larger mesh.  $E_{\text{SCE}} = -0.9 \text{ V}$ .

potentials the cadmium deposition will be enhanced by the turbulence-promoting action of the hydrogen evolution. The fractional conversion for micromesh

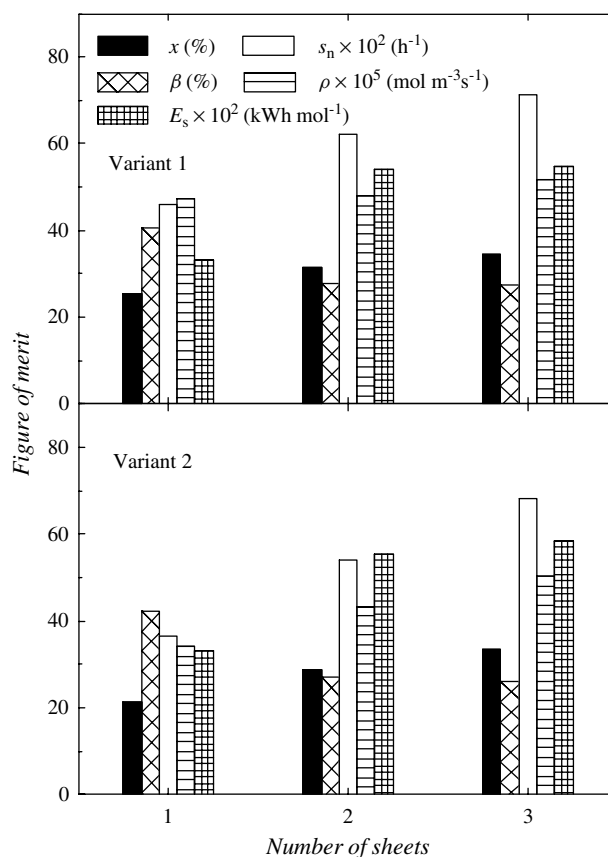


**Figure 4.** 'Figures of merit' as a function of the number of sheets. Larger mesh.  $E_{SCE} = -1.0\text{V}$ . Other parameters according to Fig 3.

electrodes is higher than for the larger mesh electrodes because of the higher value of the specific surface area. The effect of the number of sheets on the current efficiency is less important, with a tendency to decrease when the number of sheets is increased, which is more evident for micromesh electrodes. As expected, the specific energy consumption follows the inverse tendency of the current efficiency. Likewise, variant 1 always gives the best performance, due to the fact that the orientation of the strand of the expanded structure contributes to increasing the solution flow towards the outer region of the electrode.

Figures 3–6 also show that the best performance is obtained for a three-dimensional electrode of three sheets, which means a bed thickness parallel to the current flow of  $2.85 \times 10^{-3}\text{m}$  for the larger mesh and  $2.1 \times 10^{-3}\text{m}$  for the micromesh. These values of bed thickness are lower than those calculated taking into account a single reaction under limiting current conditions because the side reactions, eg oxygen reduction and hydrogen evolution, alter the potential distribution in the electrode, diminishing the optimal bed depth.<sup>9</sup>

Figure 7 compares the 'figures of merit' of the reactor for different values of the inlet cadmium concentration. It can be observed that the fractional conversion is always high, near 35%, and is independent of the orientation of the mesh when the cadmium concentration decreases. This behaviour can



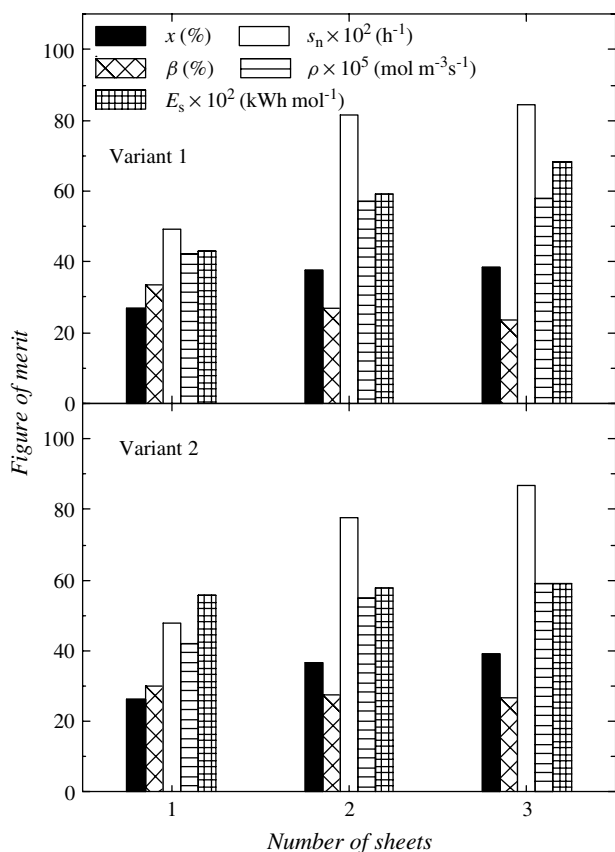
**Figure 5.** 'Figures of merit' as a function of the number of sheets. Micromesh.  $E_{SCE} = -0.9\text{V}$ . Other parameters according to Fig 3.

be explained by taking into account the enhancement in the mass transfer because of the bubble-induced convection produced by the hydrogen evolution, which is the predominant cathodic reaction at low values of the inlet cadmium concentration. Likewise, the low values of current efficiency yield an increase in the specific energy consumption when the cadmium concentration decreases. The normalized space velocity follows the same tendency as the fractional conversion.

## 5 COMPARISON WITH PREVIOUS STUDIES

Figure 8 compares some results of this study with a previous paper<sup>5</sup> where the recovery of cadmium by using a rotating cylinder electrode of stainless steel plate was analysed. The use of a three-dimensional electrode shows a sharp increase in the fractional conversion in spite of the lower value of the inlet cadmium concentration. However, the current efficiency decreases when the solutions are more dilute and the specific energy consumption is increased.

The mass-transfer coefficients have to be evaluated in order to discuss the results obtained experimentally. Kreysa<sup>10</sup> proposed the following expression to calculate the mass-transfer coefficient for a rotating packed

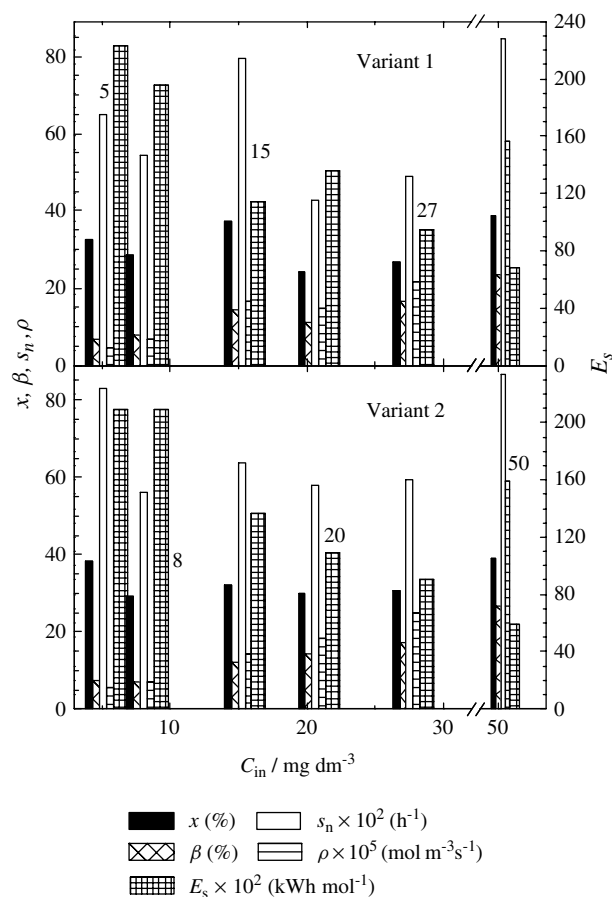


**Figure 6.** ‘Figures of merit’ as a function of the number of sheets. Micromesh.  $E_{SCE} = -1.0\text{ V}$ . Other parameters according to Fig 3.

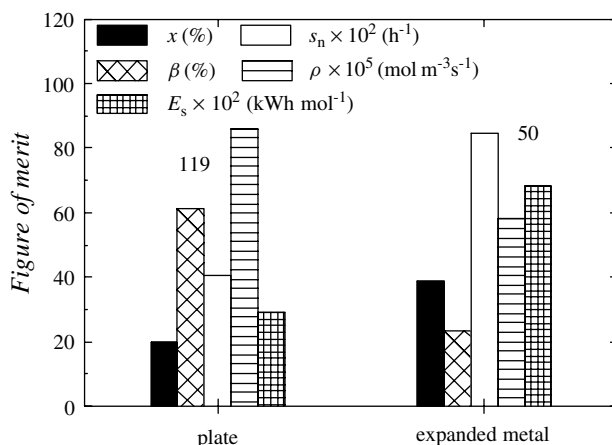
bed electrochemical reactor:

$$Sh = 0.454 Sc^{1/3} \left[ Re_c^2 + \left( Re_r \frac{d_h}{\varepsilon r} \right)^2 \right]^{0.290} \times \left( \frac{d_h}{r_2 - r_1} \right)^{1.116} \quad (6)$$

In the present study the contribution of the channel Reynolds number on the mass-transfer coefficient was neglected because the volumetric flow rate is small. On the other hand, the pattern of internal flow of our reactor is different from that used to obtain Eqn (6). Table 2 compares the mass-transfer coefficients according to Eqn (6) with the mean value of the experimental results calculated with Eqn (3) between the two variants for both types of expanded metals. It can be observed that the experimental mass-transfer coefficients are lower than the predicted ones but the concordance between them increases for the higher values of bed thickness. Also, both sets show the same tendency when the number of sheets is increased. The experimental and predicted mass-transfer coefficients for the micromesh electrode are lower than those for the larger mesh electrode. Thus, the better performance detected with the micromesh can be attributed to its higher specific surface area.



**Figure 7.** ‘Figures of merit’ as a function of the inlet cadmium concentration.  $E_{SCE} = -1.0\text{ V}$ . Three-dimensional cathode: three sheets of micromesh expanded metal. The numbers at each parameter set represent the inlet cadmium concentration. Other parameters according to Fig 3.



**Figure 8.** Comparison of the ‘figures of merit’ between a three-dimensional cathode of three sheets of micromesh expanded metal in variant 1 with a plate electrode, both as rotating cylinder electrodes.  $E_{SCE} = -1.0\text{ V}$ . The numbers at each parameter set represent the inlet cadmium concentration. Other parameters according to Fig 3.

## 6 CONCLUSIONS

These experimental results show that an electrochemical reactor with a rotating three-dimensional electrode of expanded metal offers an attractive alternative to

**Table 2.** Comparison between predicted and experimental mass-transfer coefficients

Number of sheets	$k \times 10^4 (\text{m s}^{-1})$			
	Larger mesh		Micromesh	
	Eqn (6)	Expt	Eqn (6)	Expt
1	11.41	4.18	9.49	3.31
2	5.49	3.48	4.52	2.66
3	3.63	2.94	2.97	1.87
4	2.74	2.15		

remove efficiently cadmium from very dilute aqueous solutions. Fractional conversion values twice as large were obtained using the rotating three-dimensional electrode than with a rotating plate, which can be attributed to three factors: (i) good mass-transfer conditions of the rotating cylinder electrode, (ii) high specific surface area of the expanded structures, and (iii) turbulence-promoting action of the hydrogen evolution as a side cathodic reaction. However, higher values of the specific energy consumption are necessary.

The approximate 40% fractional conversions observed for cadmium solutions ranging in concentration from 5 to 50 mg dm<sup>-3</sup> will give residual cadmium concentrations between 3 and 30 mg dm<sup>-3</sup>. These values are well above the legal discharge limits for this element, eg 0.1 mg dm<sup>-3</sup> in Argentina, so that further work is required before this system can be applied commercially. Another promising strategy may be to couple the electrochemical procedure with other removal methods.

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#### REFERENCES

- Walsh FC, The role of the rotating cylinder electrode reactor in metal ion removal, in *Electrochemistry for a Cleaner Environment*, ed by Genders D and Weinberg N. The Electroynthesis Company Inc, New York, pp 101–159 (1992).
- Kreysa G and Brandner R, Experiments with a rotating packed bed cell, in *Modern Concepts in Electrochemical Reactor Design, Extended Abstracts of the 31<sup>st</sup> ISE Meeting*, Venice, Italy. Vol 2: H8 (1980).
- Grau JM and Bisang JM, Cadmium removal from aqueous sulfate solutions by treatment with iron felts. *J Chem Technol Biotechnol* **73**:398–404 (1998).
- Grau JM and Bisang JM, Electrochemical removal of cadmium using a batch undivided reactor with a rotating cylinder electrode. *J Chem Technol Biotechnol* **76**:161–168 (2001).
- Grau JM and Bisang JM, Removal of cadmium and production of cadmium powder using a continuous undivided electrochemical reactor with a rotating cylinder electrode. *J Chem Technol Biotechnol* **77**:465–472 (2002).
- Letord-Quéméré MM, Legrand J and Coeuret F, Improvement of mass transfer in electrochemical cells by means of expanded materials. *IchemE Symp Ser* **98**:73–84 (1986).
- Elsner C and Coeuret F, Potential distribution along gas evolving electrodes. *J Appl Electrochem* **15**:567–574 (1985).
- Merck AG, Cadmio, in *Métodos complexométricos de valoración con titriplex*, 3rd edn, ed by Merck AG. Darmstadt, pp 23–24.
- Bisang JM, Theoretical and experimental studies of the effect of side reactions in copper deposition from dilute solutions on packed-bed electrodes. *J Appl Electrochem* **26**:135–142 (1996).
- Kreysa G, Elektrochemie mit dreidimensionalen Elektroden. *Chem-Ing-Tech* **55**:23–30 (1983).