Removal of cadmium and production of cadmium powder using a continuous undivided electrochemical reactor with a rotating cylinder electrode

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Abstract: The behaviour of a continuous undivided electrochemical reactor with a rotating cylinder electrode under potentiostatic control is examined for the abatement of cadmium from synthetic sodium sulfate solutions with Cd(II) concentrations lower than $500 \, \text{mg dm}^{-3}$ at a reactor inlet pH $\cong 7$. The process was designed to convert the metal ions in solution to metal powder, which settles to the conical of the reactor and may be removed at intervals as a sludge by opening a drop valve. The effect of applied potential, inlet cadmium concentration, rotation speed and hydrogen evolution as side cathodic reaction on the 'figures of merit' of the reactor are analysed. The best results were obtained for cathode potentials in the range from $-0.9 \, \text{V}$ to $-1.0 \, \text{V}$ against the saturated calomel electrode. Therefore, when the rotation speed was $1000 \, \text{rpm}$ the space time yield and the normalized space velocity were $0.64 \times 10^{-2} \, \text{mol m}^{-3} \text{s}^{-1}$ and $0.89 \, \text{h}^{-1}$ respectively, while the fractional conversion per pass was 35% with a current efficiency higher than 74%. The surface morphology of the deposits as a function of the process variables is also reported.
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NOTATION

a_e	Specific surface area (m^{-1})
C_{in}	Inlet concentration (mol m^{-3} or mg dm^{-3})
E_s	Specific energy consumption (w-s mol^{-1} or kWh mol^{-1})
E_{SCE}	Cathode potential referred to saturated calomel electrode (V)
F	Faraday constant (C mol^{-1})
I	Total current (A)
k	Mass transfer coefficient (m s^{-1})
Q	Volumetric flow rate ($\text{m}^3 \text{s}^{-1}$)
Re	Reynolds number
s_n	Normalized space velocity (s^{-1} or h^{-1})
t	Time (min)
U	Cell voltage (V)
V	Electrolyte volume within the reactor (m^3)
V_R	Reactor volume (m^3)
x	Fractional conversion
β	Current efficiency
λ	Parameter defined by eqn (4)
v_e	Charge number of the electrode reaction
ρ	Space time yield ($\text{mol m}^{-3} \text{s}^{-1}$)
ω	Rotation speed (rpm)

1 INTRODUCTION

Waste streams containing low concentrations of cadmium are produced from processes such as cadmium electroplating, zinc electrowinning, metal-pickling processes and recycling of waste batteries. The legal limitations concerning cadmium discharge in effluents are very stringent due to the highly toxic nature of cadmium salts, which necessitates the development of technologies that may prevent or correct the deleterious effect of cadmium ions.

There are many possible methods of cadmium recovery including ion exchange and solvent extraction,[1,2] adsorption,[3,4] coupling between biosorption and electrolysis[5] and electrolysis.[6–11] Considering the electrolytic method for the removal of metals, the rotating cylinder electrode[12] represents a successful reactor, which presents high mass-transfer conditions

at a two-dimensional cathode whose surface area is increased by the metal deposition and additionally is able to achieve continuous product extraction.

The electrochemical removal of cadmium was studied in previous works[13,14] carried out in this laboratory. Thus, in an earlier work[14] the behaviour of a batch reactor with a rotating cylinder electrode in cadmium removal was analysed and promising results were obtained. This work prompted the current study, where the performance of a continuous reactor is reported and a systematic study of the process variables performed.

2 EXPERIMENTAL

The experiments were performed in an undivided continuous reactor, 109 mm internal diameter and 201 mm total height with a conical bottom, 55 mm high and 52° angle of inclination to the base, in order to remove at intervals the deposit as a sludge by opening a drop valve. The solution volume in the reactor was 1.067 dm³. 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 flow circuit system also included a centrifugal pump, a flowmeter, a diaphragm valve and a needle valve. The working electrode was a rotating cylinder made of 316 stainless steel, which consists of an active electrode area, 37.9 mm in diameter and 30.5 mm long, bounded by Teflon sleeves, 39 mm in diameter and 30 mm long. The sleeves protrude by a small distance from the cathode and form a right angle with it, thereby preventing a sharp increase in the current density near the edges, which may lead to a localized dendritic growth of the electrodeposit. Likewise, the recess depth of the cathode is small in order to minimize hydrodynamic edge effects produced by the insulator sleeves. As a counterelectrode three platinum wires, 1 mm in diameter and 90 mm long, placed symmetrically were used. The working electrode and the counterelectrode were concentric, thereby assuring a uniform primary current distribution. The interelectrode gap was 11 mm. As reference, a saturated calomel electrode was used and the potentials are referred to this electrode. Prior to the experiments, the surface of the working electrode was carefully polished with silicon carbide paper 600; it was washed with tap water followed by distilled water. 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. Hydrogen evolution and oxygen reduction took place as cathodic side reactions. At high cadmium levels the oxygen reduction can be considered negligible, because of the low value of the oxygen concentration, but becomes more important at low metal concentration.

The supporting electrolyte was 1 M Na₂SO₄ with a pH ≅ 7 at the reactor inlet. In order to prevent hydrogen evolution as a side cathodic reaction, high pH values must be adopted. Cadmium hydroxide however precipitates at pH ≅ 8.7 for a cadmium concentration in solution of 500 mg dm⁻³, and the precipitation occurs at higher pH as the cadmium concentration decreases. When the current is applied the pH inside the reactor decreases because the generation of hydrogen ions by the anodic reaction is higher than the production of hydroxyl ions by the hydrogen evolution. Thus, the pH at the outlet reactor was close to 4 and cadmium hydroxide precipitation was hindered.

During the experiment, samples of solution were taken from the reactor outlet in order to determine the cadmium concentration by complexometry.[15]

3 REACTOR PERFORMANCE

In this section the relevant equations required to analyse the performance of the rotating cylinder electrode and to compare the experimental results with previous studies of cadmium deposition or with other cells for metal ion removal, called 'figures of merit', will be introduced.

The current efficiency was calculated by:

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

The space time yield is the amount of product which can be produced within a unit volume reactor per unit time. For a continuous reactor the space time yield in terms of the fractional conversion and assuming $V = V_R$ is given by:

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

The normalized space velocity, s_n, is a figure of merit frequently used to compare electrochemical reactors for the treatment of waste waters. s_n is the volume of waste water in which the reactant concentration is reduced by 90% in a unit volume reactor per unit time. The calculation of s_n however requires the adoption of a mathematical model to represent the electrochemical reactor. For a continuous reactor with a rotating cylinder electrode the electrolyte is assumed to be well-mixed. Thus, the fractional conversion is given by:

$$x = \frac{\lambda}{1 + \lambda} \qquad (3)$$

where

$$\lambda = \frac{k a_e V}{Q} \qquad (4)$$

and the normalized space velocity is

$$s_n = \frac{k a_e}{9} \qquad (5)$$

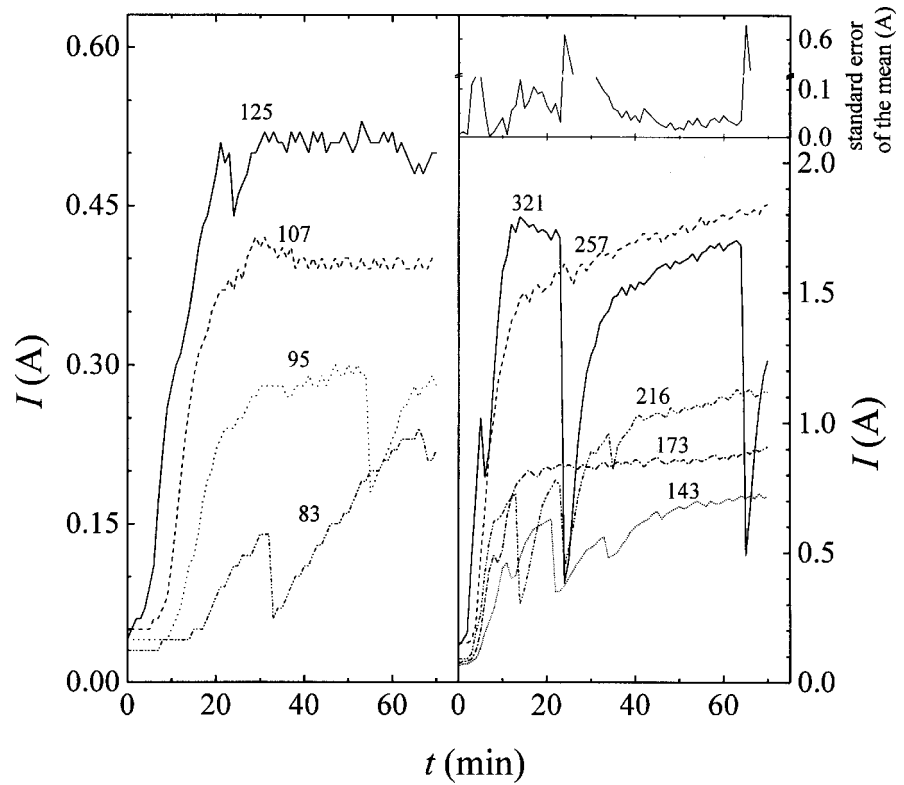Combining eqns (3)–(5) yields the normalized space

Figure 1. Current as a function of time at different cadmium concentration. $E_{SCE} = -1.0$ V. $\omega = 1000$ rpm. Supporting electrolyte: 1 M Na_2SO_4. Inlet pH $\cong$ 7. T = 30 °C. The numbers at each curve represent the outlet cadmium concentration. Inset: standard error of the mean for two experiments performed with an inlet cadmium concentration $\cong 500$ mg dm^{-3}.

velocity in terms of the fractional conversion:

$$s_n = \frac{Q}{9V}\left(\frac{x}{1-x}\right) \qquad (6)$$

Likewise, the specific energy consumption is given by:

$$E_s = \frac{v_e F U}{\beta} \qquad (7)$$

4 RESULTS AND DISCUSSION

Figure 1 shows the current as a function of time at different concentrations performed at -1.0 V. The initial current is low but the current increases with time because the metal deposition increases the electrode surface area, but after a time the deposit is detached from the cathode, the current decreases because the electrode is under potentiostatic control. Afterwards the current increases again as metal deposition recommences. This behaviour is more evident for high cadmium concentrations and allows removal of the cadmium as a metal powder without the use of a scraper.

Figure 1 also shows that, although the deposition of the metal increases the surface area of the electrode, the current reaches a constant value that stays while the deposit does not break away, which would indicate that saturation at the surface has been achieved. These pseudo-stationary values were used to perform the calculations reported in this work.

The standard error of the mean for two experiments performed under similar conditions is included as an inset in Fig 1. It can be observed that the reproduci-
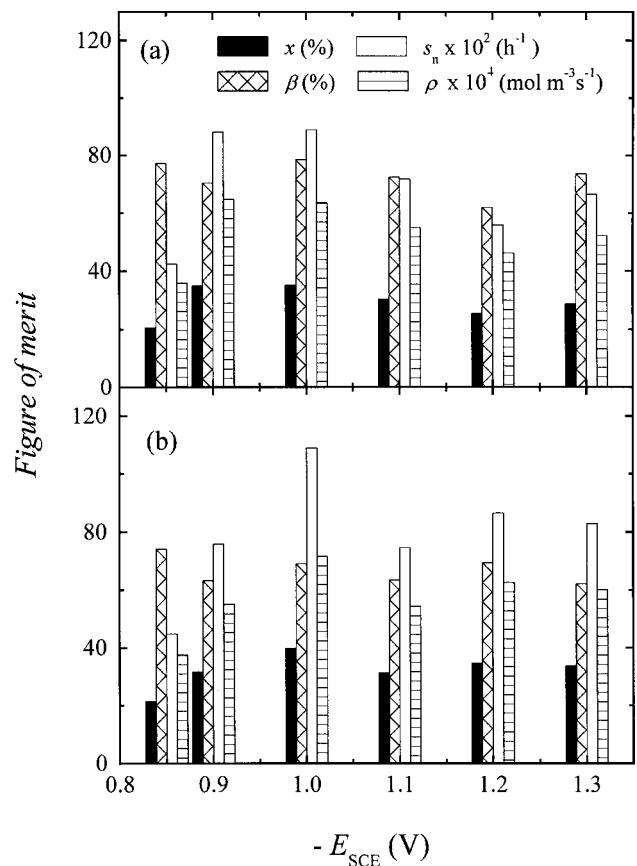

Figure 2. 'Figures of merit' as a function of the applied potential. (a) $\omega = 1000$ rpm, (b) $\omega = 1500$ rpm. $Q = 4.373 \times 10^{-6}$ m^3 s^{-1}. Inlet cadmium concentration $\cong 500$ mg dm^{-3}. Supporting electrolyte: 1 M Na_2SO_4. Inlet pH $\cong$ 7. T = 30 °C.
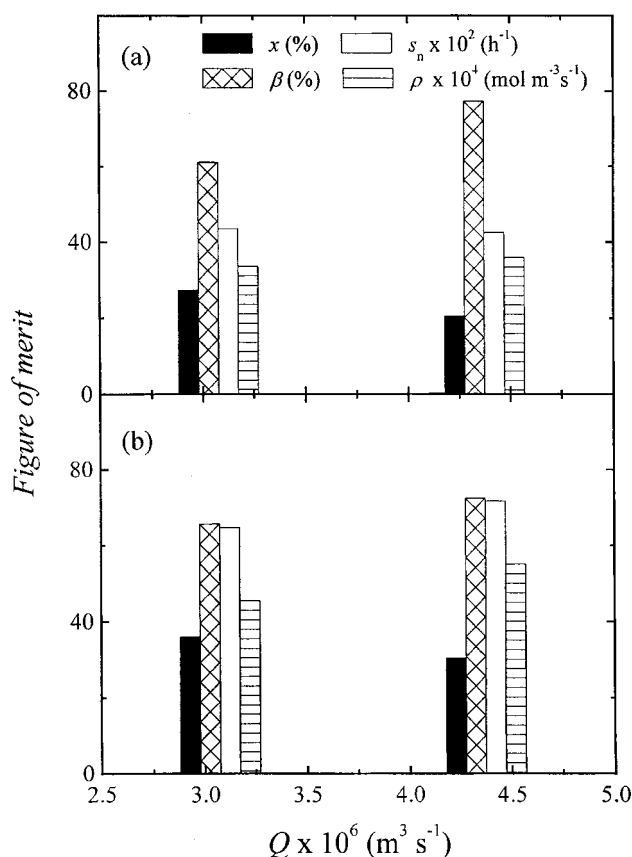
Figure 3. 'Figures of merit' as a function of the volumetric flow rate. (a) $E_{SCE} = -0.85\,V$, (b) $E_{SCE} = -1.1\,V$. $\omega = 1000\,rpm$. First set of values: $Q = 3.075 \times 10^{-6}\,m^3 s^{-1}$. Second set of values: $Q = 4.373 \times 10^{-6}\,m^3 s^{-1}$. Inlet cadmium concentration $\cong 500\,mg\,dm^{-3}$. Supporting electrolyte: 1 M Na_2SO_4. Inlet pH $\cong$ 7. T = 30 °C.

Figure 4. 'Figures of merit' as a function of the inlet cadmium concentration. (a) $E_{SCE} = -0.9\,V$, (b) $E_{SCE} = -1.0\,V$. $\omega = 1000\,rpm$. $Q = 4.373 \times 10^{-6}\,m^3 s^{-1}$. The number at each set value represents the inlet cadmium concentration. Supporting electrolyte: 1 M Na_2SO_4. Inlet pH $\cong$ 7. T = 30 °C.

bility of the experiments is acceptable, high deviations are only observed when the deposit is detached from the electrode.

Figure 2 compares the 'figures of merit' of the reactor for different applied potentials to the cathode at two values of the rotation speed. It can be observed that the conversion and consequently the normalized space velocity and the space time yield achieve a maximum when the potential is in the range from -0.9 to $-1\,V$. This behaviour may be explained by taking into account that for all potentials at a stainless steel cathode the cadmium deposition takes place simultaneously with the hydrogen evolution and both reactions are highly coupled. According to eqns (3) and (4), for a given value of the residence time an increase in the fractional conversion is produced by an increase of either the mass-transfer coefficient or the specific surface area, or both. In order to analyse the mass-transfer coefficient the combined effect of the forced convection, due to the rotation speed, and the bubble-induced convection, due to the hydrogen evolution, must be taken into account. It must be emphasized that the volumetric flow rate is relatively slow, and does not contribute significantly to mass transfer enhancement. At potentials more negative than $-0.85\,V$ the cadmium deposition is mass-transfer controlled[13] and at potentials still more negative the
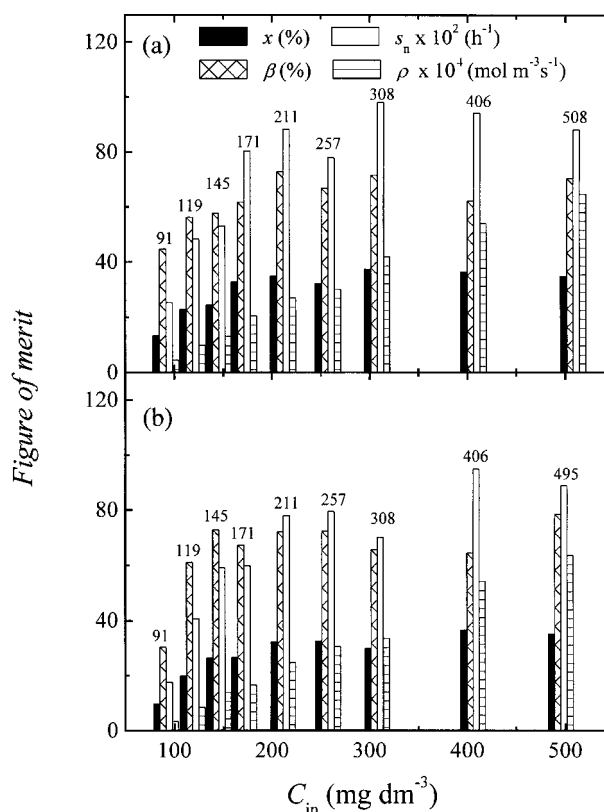
cadmium deposition will be enhanced by the turbulence-promoting action of the hydrogen evolution, which takes place mainly at the regions of the electrode not covered with cadmium. In the same way, the specific surface area of the electrode will be also increased due to the metal deposition. Thus, it is expected that the increase in both mass-transfer coefficient and specific surface area produce an increase in the fractional conversion as the potential becomes more negative. The experimental evidence however shows that this behaviour is not detected at very negative potentials, presumably because at low potentials the electrode surface coated with cadmium is increased, the hydrogen evolution is hindered, and low values of fractional conversion are measured. Further research however is required to elucidate better the interaction between both reactions. The current efficiency is $70 \pm 5\%$, with a slight tendency to decrease when the potential becomes more negative. The loss of current efficiency for the cadmium removal may be mainly attributed to the cathodic side reactions, ie hydrogen evolution and reduction of oxygen. The effect of the redissolution of the cadmium detached from the cathode on the current efficiency is minor because the cadmium sponge dissolves very slowly in dilute sulfuric acid[16] but more rapidly if the sponge is oxidized.

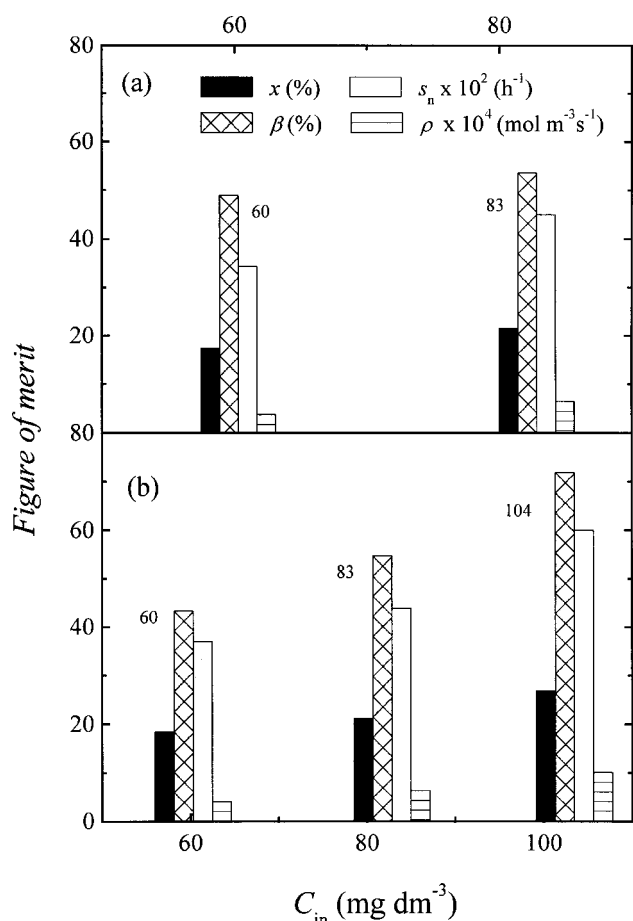Figure 3 shows the 'figures of merit' of the reactor as

Figure 5. 'Figures of merit' as a function of the inlet cadmium concentration. (a) $E_{SCE}=-0.9\,V$, (b) $E_{SCE}=-1.0\,V$. $\omega=1750\,rpm$. $Q=4.373\times10^{-6}\,m^3s^{-1}$. The numbers at each parameter set represent the inlet cadmium concentration. Supporting electrolyte: $1\,M\ Na_2SO_4$. Inlet pH $\cong 7$. T$=30\,°C$.

Figure 6. Part (a): Specific energy consumption as a function of the inlet cadmium concentration. ($\blacksquare$): $E_{SCE}=-0.9\,V$, $\omega=1000\,rpm$ and $Q=4.373\times10^{-6}\,m^3s^{-1}$, ($\bigcirc$): $E_{SCE}=-1.0\,V$, $\omega=1000\,rpm$ and $Q=4.373\times10^{-6}\,m^3s^{-1}$, ($\blacktriangle$): $E_{SCE}=-0.9\,V$, $\omega=1750\,rpm$ and $Q=4.373\times10^{-6}\,m^3s^{-1}$, ($\blacktriangledown$): $E_{SCE}=-1.0\,V$, $\omega=1750\,rpm$ and $Q=4.373\times10^{-6}\,m^3s^{-1}$, ($\blacklozenge$): $E_{SCE}=-1.0\,V$, $\omega=1000\,rpm$ and $Q=3.075\times10^{-6}\,m^3s^{-1}$. Part (b): Specific energy consumption as a function of the applied potential. ($\blacksquare$): $\omega=1000\,rpm$ and $Q=4.373\times10^{-6}\,m^3s^{-1}$, ($\bullet$): $\omega=1000\,rpm$ and $Q=3.075\times10^{-6}\,m^3s^{-1}$, ($\blacktriangle$): $\omega=1500\,rpm$ and $Q=4.373\times10^{-6}\,m^3s^{-1}$. Inlet cadmium concentration for Part (b) $\cong 500\,mg\,dm^{-3}$. Bars: standard error of the mean. Supporting electrolyte: $1\,M\ Na_2SO_4$. Inlet pH $\cong 7$. T$=30\,°C$.

a function of the volumetric flow rate for two values of the applied potential. As expected, the conversion decreases with the increase in the volumetric flow rate but the normalized space velocity and the space time yield increase.

Figure 4 compares the 'figures of merit' of the reactor for different values of the inlet cadmium concentration at two potentials. It can be observed that the conversion is high, near 35% in a large range of inlet concentration and decreases when the concentration is lower than $150\,mg\,dm^{-3}$. The normalized space velocity and the space time yield show the same tendency. The current efficiency also decays for the lower values of concentration.

In order to increase the fractional conversion for low values of the inlet concentration some experiments were performed at a higher rotation speed. Figure 5 reports the 'figures of merit' when the rotation speed was 1750 rpm at $-0.9\,V$ and $-1\,V$. As expected, the fractional conversion was increased to values near 20%, but low values of the current efficiency were again measured. Gabe and Walsh[9] report that the current efficiency for cadmium deposition lies in the range of 50–80%, which is consistent with the values reported here.
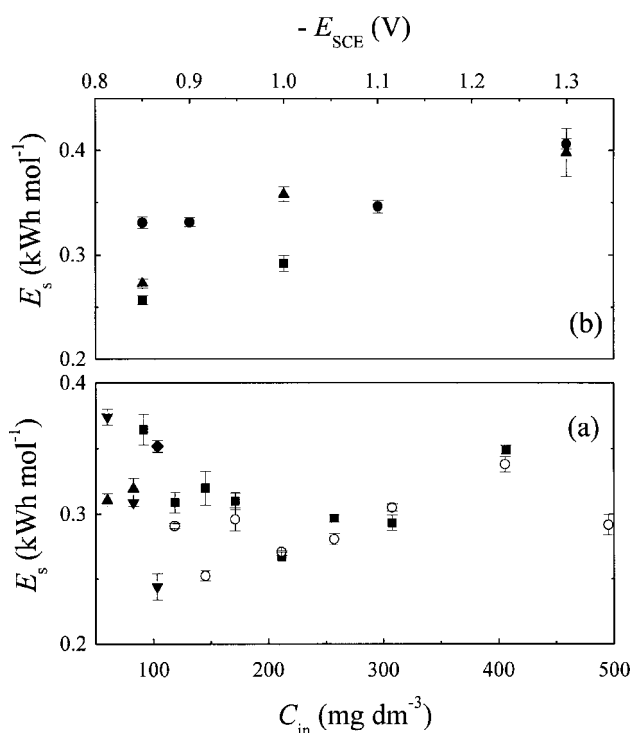
Figure 6 shows the specific energy consumption as a function of the inlet cadmium concentration, part (a), and as a function of the applied potential, part (b), for different values of angular velocities and volumetric flow rates. At high concentration E_s is near $0.3\,kWh$ mol^{-1} but at lower concentration higher values are observed, with a greater scattering of the results. This increase is because of the decrease in the current efficiency at lower concentrations. Likewise, as expected, an increase in E_s with the applied potential was measured. The specific energy consumption is similar to previous values[14] reported for a batch reactor.

The surface morphology of the electrodeposited cadmium powders at different values of applied potential and inlet cadmium concentration, obtained at 1000 rpm, was examined by scanning electron microscopy (SEM) and the results are shown in Fig 7. The comparison of micrographs (a) with (b) shows the effect of the variation of the concentration on the morphology of the deposit. Rough deposits, without a dendritic nature, were obtained for the dilute solutions. For more concentrated solutions, case (b), the presence of incipient dendrites was detected. This behaviour agrees with the previous finding[17] due to the
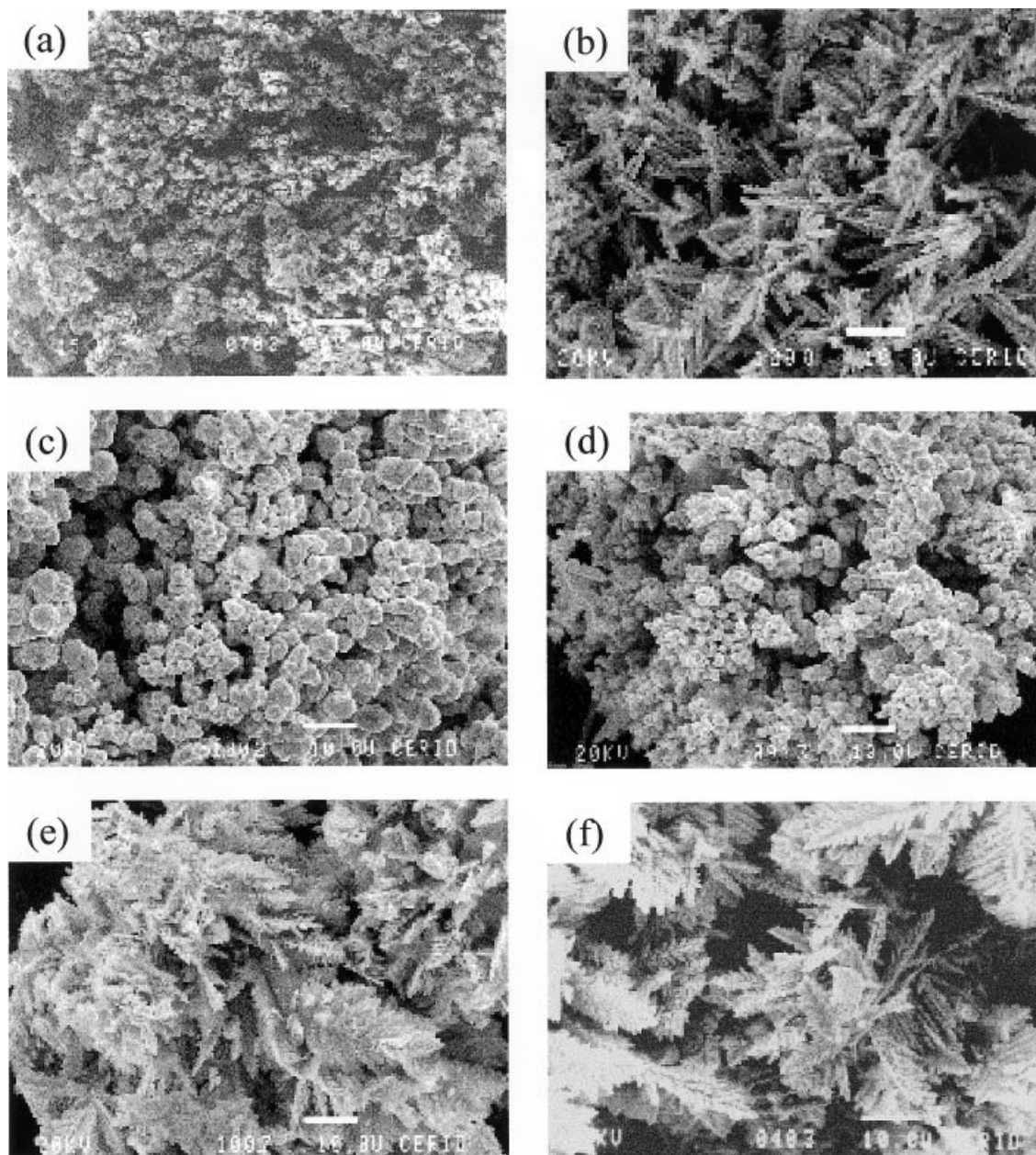
Figure 7. Scanning-electron micrographs of cadmium powders at different values of inlet cadmium concentration and potentials. (a) $E_{SCE} = -0.9\,V$, $C_{in} = 91.4\,mg\,dm^{-3}$ and $Q = 4.373 \times 10^{-6}\,m^3\,s^{-1}$, (b) $E_{SCE} = -0.9\,V$, $C_{in} = 406.3\,mg\,dm^{-3}$ and $Q = 4.373 \times 10^{-6}\,m^3\,s^{-1}$, (c) $E_{SCE} = -0.85\,V$, $C_{in} = 479.3\,mg\,dm^{-3}$ and $Q = 3.075 \times 10^{-6}\,m^3\,s^{-1}$, (d) $E_{SCE} = -0.9\,V$, $C_{in} = 495.22\,mg\,dm^{-3}$ and $Q = 3.075 \times 10^{-6}\,m^3\,s^{-1}$, (e) $E_{SCE} = -1.1\,V$, $C_{in} = 493.67\,mg\,dm^{-3}$ and $Q = 3.075 \times 10^{-6}\,m^3\,s^{-1}$, (f) $E_{SCE} = -1.3\,V$, $C_{in} = 493.67\,mg\,dm^{-3}$ and $Q = 3.075 \times 10^{-6}\,m^3\,s^{-1}$. Supporting electrolyte: 1 M Na_2SO_4. Inlet pH $\cong$ 7. T = 30 °C. $\omega = 1000$ rpm. Magnification: $\times 1200$.

fact that the transition potential for powdery deposition becomes more negative when the metal concentration in the electrolytic solution decreases. Likewise, the examination of micrographs (c) to (f) gives the effect of the applied potential. For the more negative values of potential the deposits showed similar surface morphology, due to the fact that the deposition process takes place at limiting current, but the cadmium dendrites increase the feather-like appearance as the potential is lowered. Calusaru[17] reported the same surface morphology for cadmium deposits obtained from more concentrated solutions. It can be observed however that the deposit at $-0.85\,V$ is also

very rough but with a different morphology, characterized by the presence of nodules.

5 COMPARISON WITH PREVIOUS STUDIES

The comparison of the experimental data with previous studies will be performed by analysing the mass-transfer coefficient. For the electrodeposition of metal powders the interfacial area effective for mass transfer cannot be accurately determined. For this reason, in the present work the mass transfer rates are reported in terms of transfer coefficients based on a unit volume of reactor, ka_e, rather than on a unit of
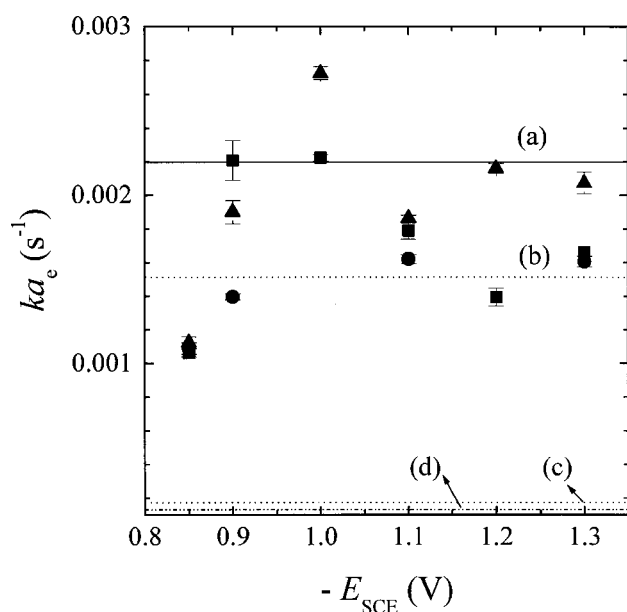
Figure 8. Variation of ka_e with the applied potential. (■): $\omega=1000$ rpm and $Q=4.373\times10^{-6}$ m^{3}s^{-1}, (●): $\omega=1000$ rpm ($Re=67757$) and $Q=3.075\times10^{-6}$ m^{3}s^{-1}, (▲): $\omega=1500$ rpm ($Re=101635$) and $Q=4.373\times10^{-6}$ m^{3}s^{-1}. Bars: standard error of the mean. Holland expression, (a): $\omega=1500$ rpm, (b): $\omega=1000$ rpm. Eisenberg *et al* expression, (c): $\omega=1500$ rpm, (d): $\omega=1000$ rpm. Inlet cadmium concentration $\cong$ 500 mg dm^{-3}. Supporting electrolyte: 1 M Na$_2$SO$_4$. Inlet pH $\cong$ 7. T=30 °C.

interfacial area, k. This is not a problem because for engineering calculations only the product of k and a_e is necessary. In this work the ka_e values were calculated from the fractional conversion using eqns (3) and (4). Figure 8 shows ka_e values as a function of the cathode potential for different values of rotation speed and volumetric flow rate. Figure 8 also records the mass-transfer coefficients according to the Holland expression,[18] which is usually accepted for metal powder deposits.[19] For comparison, the mass-transfer coefficients calculated with the correlation of Eisenberg *et al*,[20] which is valid for smooth electrodes, are also included in Fig 8. It can be observed that the measured mass-transfer coefficients agree with the predictions of the Holland equation for the more negative values of potential and, within the accuracy normally expected for this type of measurement, the ka_e values are independent of the volumetric flow rate. When the potential is in the range from -0.9 V to -1.0 V however the mass-transfer coefficients are higher than the predicted values. The enhancement in the mass transfer can be attributed to the bubble-induced convection produced by the hydrogen evolution.

6 CONCLUSIONS

The following conclusions may be drawn:

(i) Cadmium removal from dilute aqueous solutions, in the concentration range from 100 to 500 mg dm^{-3}, can be achieved efficiently in a continuous electrochemical reactor with a rotating cylinder electrode.

(ii) The maximum cadmium removal in the fractional conversion, in the normalized space velocity and in the space time yield, is achieved in the potential range from -0.9 V to -1.0 V against the saturated calomel electrode, where the cadmium deposition takes place with high values of current efficiency.

(iii) Hydrogen evolution, as a side cathodic reaction, has a beneficial effect, in a potential range, on the performance of the reactor.

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