Research Article

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Effluent treatment using a bipolar electrochemical reactor with rotating cylinder electrodes of woven wire meshes

Javier M Grau and José M Bisang*

Abstract

BACKGROUND: The behaviour of a bipolar electrochemical reactor consisting of one or more rotating cylinder electrodes of woven wire meshes is reported using copper and cadmium deposition from dilute solutions as test reactions.

RESULTS: The best performance related to electrode number was determined for copper deposition and was achieved by an arrangement with two bipolar electrodes, for which the conversion in a single pass was approximately 47%. The specific energy consumption was 3.27 kWh kg^{-1} with a normalised space velocity of 23.05 h^{-1}. The copper powder obtained showed a nodular and dendritic surface morphology. This reactor configuration was also analysed for cadmium deposition, in which hydrogen evolution takes place simultaneously as a side cathodic reaction, considering the effect of flow rate and total current. The maximum conversion per pass for cadmium removal was 38.91%. In this case the reactor with two bipolar electrodes showed a performance similar to that of a monopolar reactor operated at a rotation speed three times higher.

CONCLUSION: A continuous electrochemical reactor with two rotating bipolar electrodes of woven wire meshes presents a good performance for copper or cadmium removal from dilute solutions.

Keywords: electrochemical reactor; mass transport; woven wire mesh; rotating cylinder electrode; three-dimensional electrode

NOMENCLATURE

B_i	ith bipolar electrode
C	terminal cathode
C_{in}	inlet concentration (mg dm^{-3})
I	current (A)
Q	volumetric flow rate (m^3 s^{-1})
t	time of experiment (min or h)
x	conversion (%)
β	current efficiency (%)
ω	rotation speed (rpm)

INTRODUCTION

Bipolar electrochemical reactors are very attractive for industrial practice owing to their simple electrical connection and they additionally have the advantage of a more economical way of using energy. The individual cells are connected in series, thus avoiding high currents and high voltage drops. They are usually applied with a stationary configuration of electrodes.[1,2] However, Sasaki and Ishikawa[3] studied copper deposition from dilute solutions with a rotating bipolar cell made up of disc electrodes with fins attached to the anode in order to promote turbulence and scrape the deposited metal. Furthermore, in order to vary the electrode potential by mechanically moving a cylindrical electrode through different potential regions, Nadebaum and Fahidy[4,5] employed a rotating bipolar electrode. In a previous paper from this laboratory[6] it was reported that a packed bed rotating cylinder electrode of woven wire meshes presents mass transport coefficients three times higher than those obtained with smooth electrodes because of the turbulence-promoting action of the meshes. However, the electrode thickness must be small in order to guarantee that the whole bed is working under limiting current conditions. The present paper examines the copper and cadmium deposition performance of an electrochemical reactor which makes use of the good mass transport conditions of a woven wire rotating packed bed of optimal bed thickness with a bipolar arrangement.

EXPERIMENTAL

Figure 1 shows the configuration of the electrodes used in this work. The terminal cathode and the bipolar electrodes are made by winding a 316 stainless steel woven wire mesh (60-mesh size) around a 316 stainless steel tube (1.4 mm thick). This tube works as a cathodic current feeder for the terminal cathode and as a partition wall for the bipolar electrodes in order to address the electrolyte flow from one reactor to the next in the bipolar stack. Likewise, the inner surface of the partition wall is the anodic side of the

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* Correspondence to: José M Bisang, Programa de Electroquímica Aplicada e Ingeniería Electroquímica (PRELINE), Facultad de Ingeniería Química, Universidad Nacional del Litoral, Santiago del Estero 2829, S3000AOM Santa Fe, Argentina. E-mail: jbisang@fiq.unl.edu.ar

Programa de Electroquímica Aplicada e Ingeniería Electroquímica (PRELINE), Facultad de Ingeniería Química, Universidad Nacional del Litoral, Santiago del Estero 2829, S3000AOM Santa Fe, Argentina

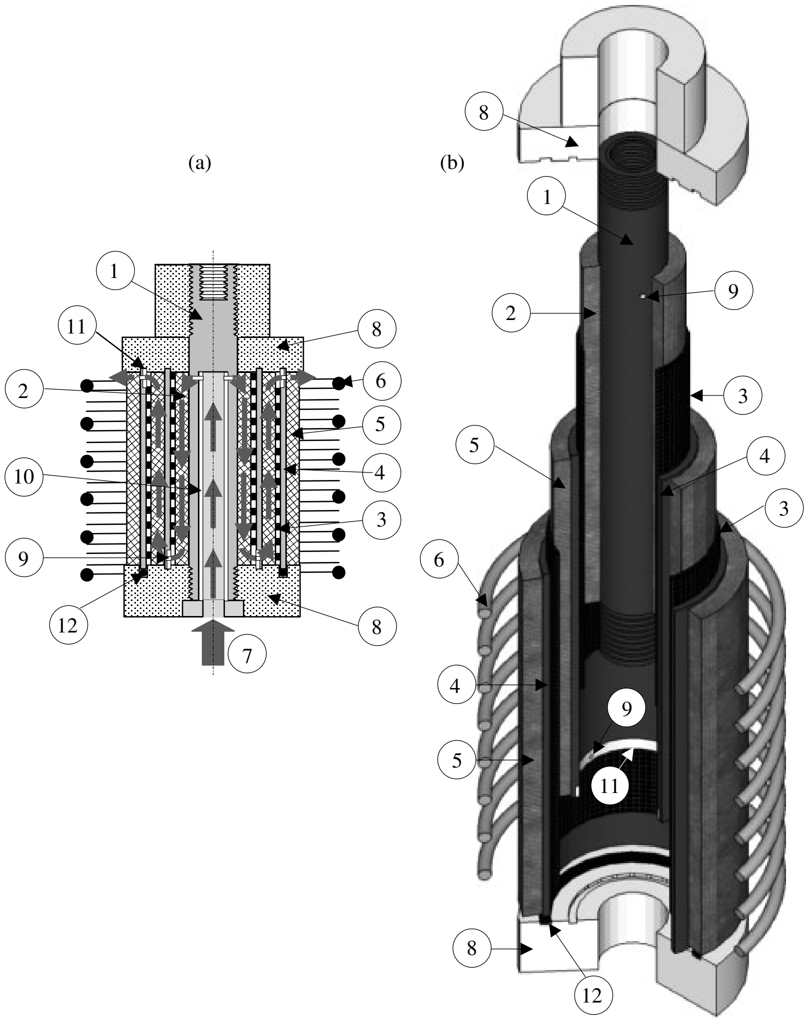

Figure 1. (a) Schematic and (b) exploded views of bipolar electrode assembly: 1, cathodic current feeder; 2, terminal cathode; 3, separator; 4, partition wall and anodic side of bipolar electrode; 5, cathodic part of bipolar electrode; 6, static terminal anode; 7, electrolyte flow path; 8, Teflon plates; 9, electrolyte port; 10, Teflon cylinder; 11, Teflon ring; 12, O-ring.

bipolar electrode, whereas its cathodic side is an ordered packing of woven wire meshes. Cylindrical plastic separators were used between each pair of electrodes. The height of the bipolar stack was 50 mm and two thicknesses were used for the cathodic packed beds, whose essential details are provided in Table 1. A concentric helical 316 stainless steel wire (2.25 mm diameter, 160 cm long) with an internal diameter of 65 mm was used as the terminal anode. However, when the number of bipolar electrodes was higher than two, the terminal anode was a concentric helical 316 stainless steel wire (3 mm diameter, 350 cm long) with an internal diameter of 103 mm. The cathodic current feeder also works as an electrolyte inlet to the bipolar stack. Ports in the cathodic current feeder and at each partition wall allow the flow of electrolyte through the bipolar electrodes. The design of the ports was critical and their construction represents a compromise between pressure drop and a minimum leakage current. After considering many different configurations, a design of symmetrically distributed ports, three of 2 mm diameter at the cathodic feeder, two of 1.75 mm diameter in the first partition wall, three of 1.5 mm diameter in the second partition wall, and so on, was found satisfactory. The ports are alternately located in the upper or lower part of the partition walls. Thus the electrolyte flows up in one bipolar electrode and down in the next. Preliminary experiments were carried out with a higher number of ports in the partition walls, but for the experiments on copper deposition the number was reduced to obtain a total transverse section of 4.7 mm^2 and thus achieve a low level of leakage current. For cadmium removal the transverse section of the ports was increased twofold to facilitate the exhaustion of gases, which reduces the leakage current owing to the increase in effective electrolyte resistivity. The region near the ports was covered with a Teflon ring so as to hinder its blockage due to metal deposition. The lower and upper parts of the bipolar stack were closed by Teflon plates in order to orientate the electrolyte flow through each sheet pack and also to diminish the leakage current. The upper end of the bipolar electrode arrangement was attached to the motor shaft and rotated at approximately 500 rpm, whereas the terminal anode was static. The experiments were performed in a cylindrical reactor (109 mm internal diameter, 150 mm high), which was made part of an electrolyte circulation system. Thus the solution flows from a thermostatted tank to the lower part of the current feeder of the terminal cathode, passes via a zigzag path through the bipolar electrodes, shown in Fig. 1, and is collected in another tank. It was not recycled so that the inlet metal concentration remained constant. The use of stainless

Table 1. Dimensions of bipolar stacks

		C	B_1	B_2	B_3	B_4
	Internal diameter[a] (mm)	10	22.4	35.1	47.7	60.5
Assembly I. Thickness of separator: 0.9 mm	External diameter (mm)	20.6	33.0	45.7	58.3	71.1
	Cathodic side thickness (mm)	3.9	3.9	3.9	3.9	3.9
	Cathodic mesh length (cm)	74	131	187	229	280
Assembly II. Thickness of separator: 2.1 mm	External diameter (mm)	18.2	30.6	43.3	55.9	68.7
	Cathodic side thickness (mm)	2.7	2.7	2.7	2.7	2.7
	Cathodic mesh length (cm)	43	70	96	133	163
Mesh size		60				
Specific surface area (m^{-1})		9214				
Wire diameter (mm)		0.17				
Distance between wires (mm)		0.253				
Thickness of partition wall (mm)		1.4				

[a] The current feeder for the terminal cathode or the partition wall for the bipolar electrodes is included.

steel as an anode produces the dissolution of iron as an anodic side reaction. After each experiment the solution was acidified and Fe(II) was oxidised by bubbling air through the solution for 48 h. Then the pH was adjusted to a value higher than 4 and the precipitate of Fe(III) was separated by filtration. Thus the solution was reused for a further experiment.

Two test reactions, copper and cadmium deposition, were employed to determine the reactor performance. For copper deposition, hydrogen evolution can be avoided by an appropriate choice of electrode potential, but cadmium deposition takes place simultaneously with hydrogen evolution.

RESULTS AND DISCUSSION

Copper deposition as test reaction

The supporting electrolyte was a solution of 1 mol dm^{-3} Na_2SO_4 and H_2SO_4 to obtain pH 2, with an inlet copper concentration of approximately 350 mg dm^{-3}. During the experiment, samples of solution were taken at intervals from the reactor outlet in order to determine the copper concentration by atomic absorption spectroscopy. The experiments were performed at 30 °C under galvanostatic control at 1 A. This current was chosen by performing a preliminary experiment under potentiostatic control with a rotating cylinder electrode composed of only the terminal cathode according to assembly I (Table 1). Thus, to avoid hydrogen evolution, the potential was controlled at −0.65 V *vs* SCE (saturated calomel electrode)[7] at the side of the cathode nearest the counter electrode, which represents the more negative cathodic potential value. In this experiment, performed at $Q = 4.373 \times 10^{-6}$ m^3 s^{-1} with an axial liquid flow velocity of 2.137×10^{-2} m s^{-1}, the current approached 1 A, giving for the terminal cathode a macrokinetic current density of 309 A m^{-2}.

Figure 2 shows the effect of the bipolar electrode number on the conversion and current efficiency for the two types of arrangement examined. It indicates that for a small number of bipolar electrodes the conversion increases linearly and the current efficiency is high. Thus the conversion for the reactor with one bipolar electrode is twice that for a monopolar reactor with only the terminal cathode, showing that the leakage current is minimal. However, when the number of bipolar electrodes is higher than three, both figures of merit decrease abruptly. Thus the optimal number of bipolar electrodes is two. This behaviour can be attributed to the accumulation of gases inside the stack, because the evacuation of gases evolved at the anodes becomes more difficult when the number of bipolar electrodes is increased. The full lines and full symbols in Fig. 2 correspond to the experimental results for the type II arrangement, which presents a lower thickness of cathodic bed and consequently a higher thickness of separator in order to restrict the possibility of short circuit between the two electrodes due to the formation of dendrites. It can be observed that assembly II shows the best performance, i.e. higher conversion and current efficiency, in spite of its lower surface area. This behaviour can be explained, for the current efficiency, by taking into account that assembly II presents a higher inter-electrode gap, which makes the arrival of oxygen for its reduction at the three-dimensional cathode more difficult. Likewise, both assemblies in Fig. 2 are compared for a given value of the volumetric flow rate. Thus the higher conversion for assembly II can be attributed to the increase, approximately 50%, in the electrolyte velocity due to a lower bed thickness, which favours the evacuation of gases.

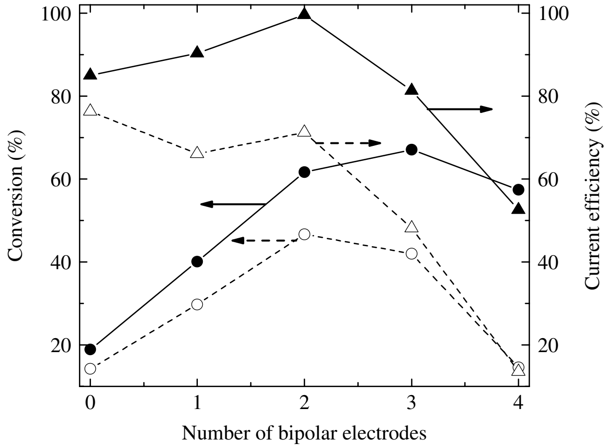

Figure 2. Conversion (●, ○) and current efficiency (▲, △) as a function of number of bipolar electrodes. Copper deposition. Full lines, separator thickness 2.1 mm, assembly II; broken lines, separator thickness 0.9 mm, assembly I. $Q = 4.373 \times 10^{-6}$ m^3 s^{-1}, $C_{in} \approx 350$ mg dm^{-3}, $\omega \approx 512$ rpm, $I = 1$ A.

To restrict the accumulation of gases inside the stack, an additional experiment was performed with a higher volumetric flow rate of electrolyte. Figure 3 shows the results for assembly

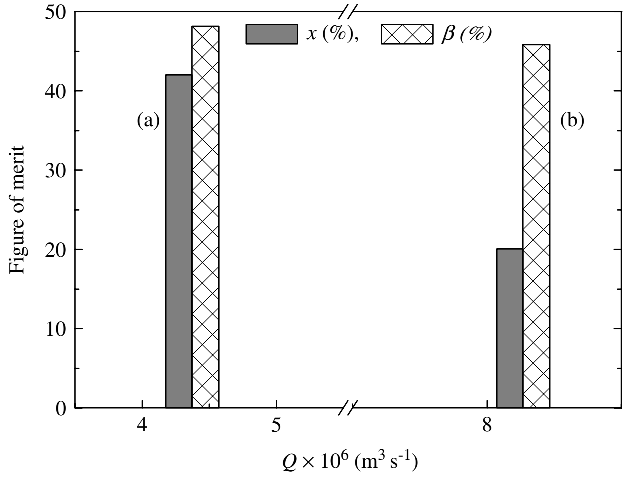

Figure 3. Comparison of conversion (x) and current efficiency (β) for a stack with three bipolar electrodes as a function of flow rate. Assembly I. (a) $C_{in} = 345$ mg dm^{-3}, $Q = 4.373 \times 10^{-6}$ m^3 s^{-1}; (b) $C_{in} = 364$ mg dm^{-3}, $Q = 8.268 \times 10^{-6}$ m^3 s^{-1}. $\omega \approx 512$ rpm, $I = 1$ A.

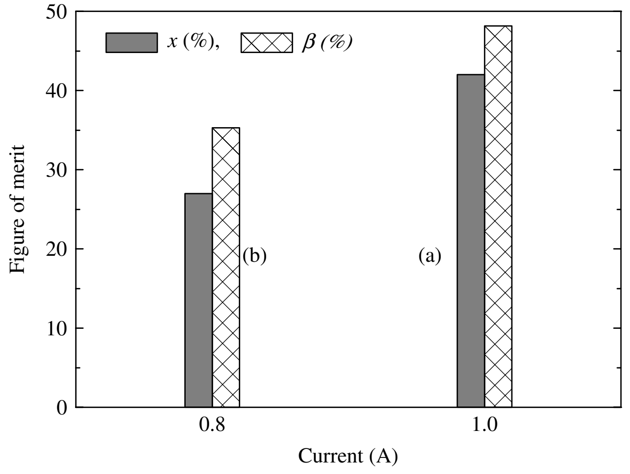

Figure 4. Comparison of conversion (x) and current efficiency (β) for a stack with three bipolar electrodes as a function of total current. Assembly I. (a) $C_{in} = 345$ mg dm^{-3}, $I = 1$ A; (b) $C_{in} = 315$ mg dm^{-3}, $I = 0.8$ A. $\omega \approx 512$ rpm, $Q = 4.373 \times 10^{-6}$ m^3 s^{-1}.

I. The increase in volumetric flow rate does not improve the performance of the stack; it can only be seen that the conversion decays owing to the decrease in electrolyte residence time, and the current efficiency is not modified. Likewise, the effect of total current is shown in Fig. 4 for assembly I, where a decrease in current does not increase the figures of merit of the stack. Taking into account Figs 2–4, a rotating stack with two bipolar electrodes operated at 1 A with an electrolyte volumetric flow rate of 4.373×10^{-6} m^3 s^{-1} presents the best performance. Under these operative conditions, Fig. 5 shows a long-term experiment of 13 h for a stack with two bipolar electrodes according to assembly II. Thus the inlet concentration as well as the conversion and current efficiency as a function of time are shown. During this time the conversion had a mean value of 47 ± 5% and the cell voltage was 6.2 ± 0.3 V with a current efficiency of 54 ± 5%. The specific energy consumption was 3.27 kWh kg^{-1} with a normalised space velocity of 23.05 h^{-1}. This value is slightly higher than that reported by Robinson and Walsh[8] for a rotating cylinder electrode reactor.

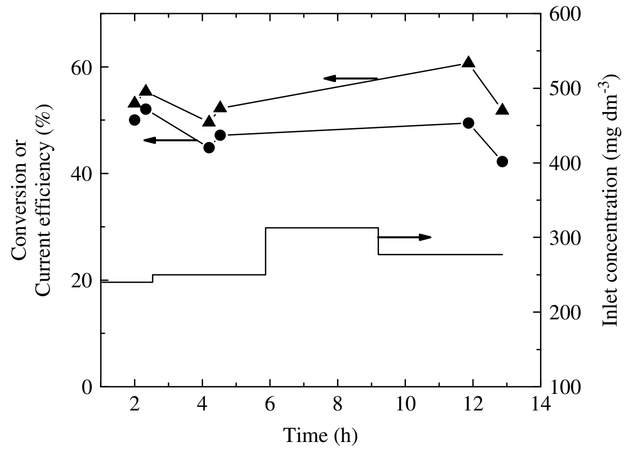

Figure 5. Conversion (●), current efficiency (▲) and inlet concentration as a function of time for a long-term experiment. Assembly II with two bipolar electrodes. $\omega \approx 520$ rpm, $I = 1$ A, $Q = 4.373 \times 10^{-6}$ m^3 s^{-1}.

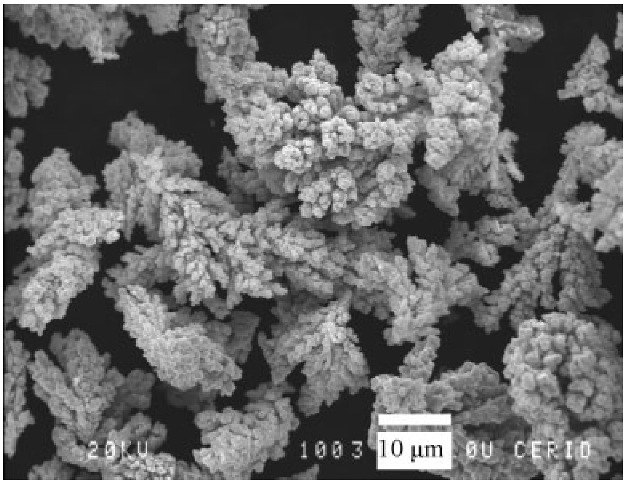

Figure 6. Scanning electron micrograph of copper powder obtained from experiment reported in Fig. 5.

The surface morphology of the electrodeposit obtained from the experiment reported in Fig. 5 was examined by scanning electron microscopy (SEM) and is shown in Fig. 6. It can be appreciated that the copper powder shows simultaneously nodular and dendritic characteristics, which can be attributed to the overpotential distribution along the bed thickness in the three-dimensional cathodes.

Cadmium deposition as test reaction

The supporting electrolyte was a solution of 1 mol dm^{-3} Na_2SO_4 at pH 7, with an inlet cadmium concentration lower than 650 mg dm^{-3}; the exact value is presented in each case. The rotating system with two bipolar electrodes according to assembly II was used for the experiment performed at 30 °C under galvanostatic control. During the experiment, samples of solution were taken at intervals from the reactor outlet in order to determine the cadmium concentration by complexometry. Because cadmium deposition takes place simultaneously with hydrogen evolution and it is not easy to formulate a relationship between the characteristic parameters of the process, a 2^2 factorial design of experiments was carried out with two levels for

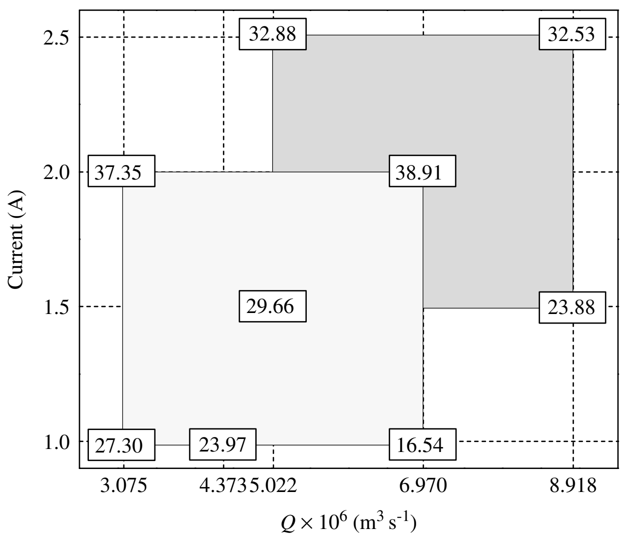

Figure 7. 2^2 factorial design analysis of fractional conversion for cadmium removal as a function of current and volumetric flow rate. Assembly II with two bipolar electrodes. $C_{in} \approx 650$ mg dm^{-3}, $t = 10$ min, $\omega \approx 530$ rpm.

current and volumetric flow rate. This procedure was repeated twice, shown in Fig. 7 by the light and dark grey squares, to determine the highest conversion for cadmium deposition with a bipolar rotating electrode. The results obtained after 10 min of electrolysis are shown in Fig. 7. Thus, for a given current and at low values of current, the conversion decreases when the volumetric flow rate increases owing to the reduction in electrolyte residence time. However, at higher currents a change in volumetric flow rate has a small effect on the conversion. Moreover, for a given volumetric flow rate the conversion shows a maximum, which is a consequence of two opposite effects as the current increases. Initially an increase in current increases the conversion, because the mass transport of cadmium ions to the electrode surface is augmented owing to the turbulence-promoting action of hydrogen evolution. Subsequently, however, the increase in current restricts the electrode surface area owing to the accumulation of gases inside the electrode. Thus the operation of the reactor at higher currents is not convenient.

The experimental results of the light grey square in Fig. 7 are correlated by the following equation:

$$x = 35.48 - 5\,925\,666Q + 0.32I + 3\,162\,888QI \qquad (1)$$

Taking into account Eqn (1) and Fig. 7, the best conditions for the deposition of cadmium in the present reactor are a current of 2 A with a volumetric flow rate of 6.97×10^{-6} m^3 s^{-1}, where the conversion is 38.91%. The current efficiency was 51%.

Figure 8 shows the conversion and current efficiency as a function of the inlet cadmium concentration to the reactor. It can be observed that the conversion shows a small decay when the concentration is lower than 150 mg dm^{-3}, whereas the current efficiency increases linearly with inlet concentration. The mean cell voltage was 10.2 V. For an inlet cadmium concentration of 353 mg dm^{-3} the space time yield was 5.76×10^{-4} kg m^{-3} s^{-1} with a specific energy consumption of 7.27 kWh kg^{-1}, which is higher than values obtained previously from experiments performed potentiostatically and consequently with a higher current efficiency.[9] The space time yield is similar to that reported for a continuous reactor with a smooth rotating cylinder electrode operated at 1500 rpm.[9] Thus it is possible to achieve a similar performance with a bipolar rotating electrode at a rotation speed three times lower.

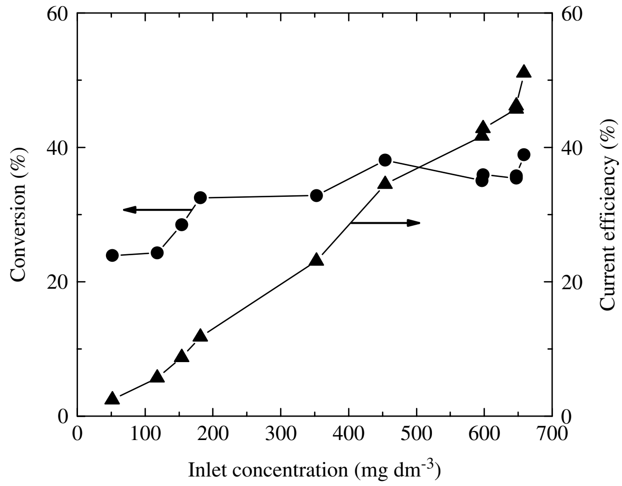

Figure 8. Conversion (●) and current efficiency (▲) as a function of inlet cadmium concentration. $Q = 6.970 \times 10^{-6}$ m^3 s^{-1}, $I = 2$ A, $\omega \approx 548$ rpm.

CONCLUSIONS

1. A rotating cylinder composed of two bipolar electrodes of woven wire meshes showed the best performance. For copper deposition, when the number of bipolar electrodes was higher than two, the figures of merit of the reactor decreased, probably because of the accumulation of gases inside the reactor.
2. The copper powder obtained showed a changing morphology of nodular or dendritic nature as a result of the overpotential distribution in the electrode.
3. For cadmium removal the performance of the reactor was quite similar to that of a monopolar rotating cylinder electrode operated at a rotation speed three times higher.

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