

Electrolytic removal of lead using a flow-through cell with a reticulated vitreous carbon cathode

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Received 25 March 1997; revised 16 June 1997

The aim of this work was to establish an electrolytic method for the removal of lead from wastewater using a three-dimensional, reticulated vitreous carbon cathode. During the development of the experimental setup, particular attention was paid to the electrolyte flow rate and to the cathode porosity. The electrolytic cell employed potential values in such a way that the lead reduction reaction occurred under mass transport control. The potentials were determined by hydrodynamic voltammetry using a borate/nitrate solution as the supporting electrolyte on a vitreous carbon rotating disc electrode. The cell proved to be efficient in removing lead and was able to reduce the levels of this metal to 0.1 mg dm^{-3} in 20 min of recirculation, using the ratio catholyte volume/cathode volume equal to 0.027. The best configuration for this removal was a cathode porosity of 80 ppi and a solution flow rate of $240 \text{ dm}^3 \text{ h}^{-1}$.

Keywords: effluent lead removal, wastewater, electrolytic cell for metal removal, reticulated vitreous carbon (RVC), flow-through cell

1. Introduction

Increasing legal pressures are forcing industry to accept responsibility for waste treatment or storage in an attempt to minimize pollution. The permanent responsibility to care for waste materials, 'from cradle-to-grave' is encouraging not only a move towards zero-effluent discharge but also towards the adoption of solutions at the source of effluents rather than at the end of the industrial process.

Electrochemical technology offers an efficient means of controlling pollution as it provides removal of heavy metals via redox reactions. The literature on metal ion removal from aqueous solutions using porous electrode cells is extensive [1–13]. By flowing simulated effluents containing metal ions through porous cathodes, it is possible to achieve both high mass transfer rates and large surface areas for the electrochemical reaction. Metals in such solutions are reduced at the inner surface of the porous electrodes as the electrolyte is percolated through the cell.

In this paper we present an electrolytic cell with a porous cathode of reticulated vitreous carbon (RVC) which was designed to remove metal ions from aqueous streams and was used in this study for the removal of lead. Both the electrolyte flow rate and the cathode porosity were optimized in order to maximize the capacity of lead removal.

The toxicity of lead has been known for many years, and the clinical symptoms of prolonged exposure to a lead-contaminated environment are well defined [14, 15]. Lead enters waterways via effluent discharges from electroplating, metal finishing, ex-

plosive producing and battery manufacturing industries. As result of its high toxicity, the concentration of Pb(II) and other highly toxic metallic ions such as cadmium, chromium and mercury in drinking water is restricted to several ppb [16]. Unfortunately, studies for lead removal has received few attention. Wang and Dewald [8] electrodeposited lead at a flow-through reticulated vitreous carbon electrode accompanied by a simultaneous anodic stripping voltammetry for monitoring of effluents. More recently an elegant study carried out by Ponce de Leon and Pletcher [17] reported the results obtained for the removing of Pb(II) from different pH 2 aqueous media. The experiments were conducted at a flow-by cell with RCV electrode. Even considering the knowledge gained by perusal of these papers, we have, therefore, become interested in investigating the performance of a flow-through cell with a RVC cathode using solutions with characteristics closer to those presented by a real aqueous waste from electroplating industry. Drag-out from lead plating bath to the rinsing water tank result in a borate/nitrate solution of Pb(II) with pH ranging from 4 to 6.

The choice of RVC for the porous cathode is based on the observations that this material (a) is chemically and electrochemically inert over a wide range of potentials and also with a wide variety of chemicals, (b) has a high specific surface area within the porous structure that is accessible to electrochemically active species, (c) has a high fluid permeability, (d) is easily shaped as required by cell design considerations, and (e) has good mechanical resistance [18].

2. Experimental details

The development of the electrolytic cell for Pb(II) removal was carried out in two stages. Initially, a voltammetric study of the Pb(II) reduction reaction on a glassy carbon rotating disc electrode was performed in order to determine the range of potentials over which this reaction is controlled by mass-transfer. Subsequently, a potential value within this interval was selected and applied to a flow-through electrolytic cell containing a reticulated vitreous carbon cathode. The electrolyte flow rate and the cathode porosity were varied to establish the best conditions for lead removal.

2.1. Apparatus

All electrochemical experiments were performed using a PAR model 273A potentiostat/galvanostat system controlled by the software PAR model 270/250 (both from EG & G). In both stages, three-electrode cells were used, as described below. A model AA 12/1475 Varian spectrometer was employed to determine the Pb(II) concentration, using an air/acetylene flame.

2.2. Chemicals and materials

All reagents were of analytical grade and did not undergo further purification. Distilled and deionized water was used to prepare all solutions. The Pb(II) solution was prepared daily from Pb(NO₃)₂ using boric acid (0.5 M) plus sodium nitrate (0.05 M) as supporting electrolyte. The resulting solution presented pH 4.8. The atomic absorption standards were prepared from a Titrisol standard solution (Merck). The reticulated vitreous carbon (RVC) was purchased from Electrosynthesis, and a Nafion[®] 417 membrane was supplied by DuPont.

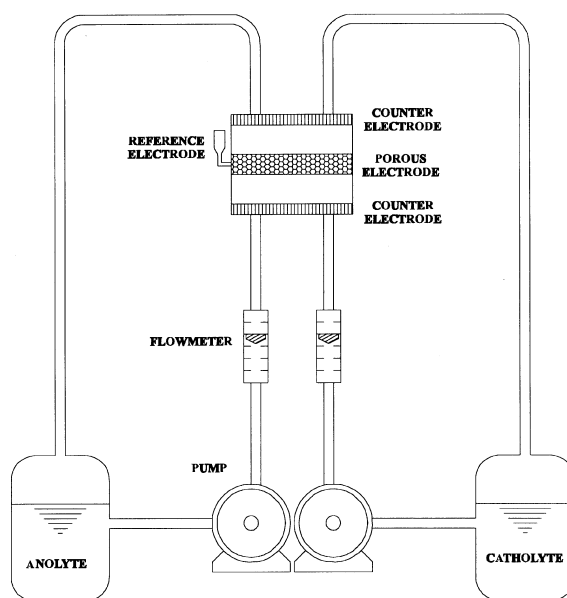
2.3. Hydrodynamic voltammetry

The hydrodynamic voltammetric experiments were carried out in a conventional three-electrode cell with separated compartments for each electrode. A glassy carbon rotating disc electrode (GCRDE) model 616 (PARC) was used as working electrode. A large-surface platinum counter-electrode, and a saturated calomel reference electrode (SCE) within a Luggin capillary were also used. The glassy carbon electrode was polished to a mirror-like surface using 1.0, 0.3 and 0.04 μm alumina slurries, consecutively, on polishing cloths. The current-voltage curves were obtained in buffered 50 mg dm⁻³ Pb(II) solutions, pH 4.8, for several rotations (41.9, 94.2, 167.5, 261.8 and 376.9 rad s⁻¹) by cycling the working electrode potential (one cycle) between 0.0 V and -1.0 V at 2 mV s⁻¹. All experiments were carried out at room temperature (around 298 K).

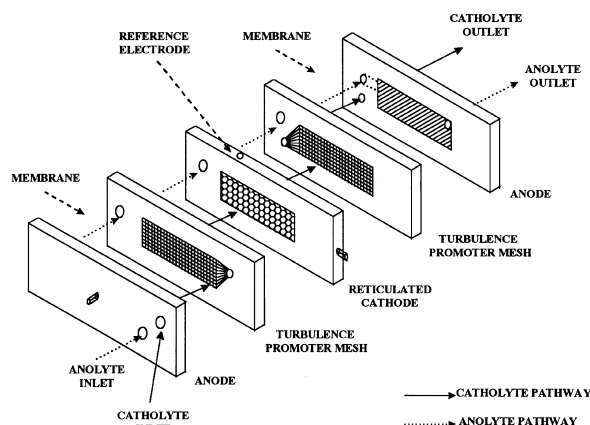
2.4. Flow-through cell configuration

The dual continuous-flow cell design is shown schematically in Fig. 1(a). The system consisted of an electrochemical cell, two 4.0 dm³ PVC reservoirs for catholyte and anolyte, two recirculation pumps, and two sets of flowmeters, with a flow range from 60 to 600 dm³ h⁻¹, for controlling the catholyte and anolyte flow rates. These components were connected together by polyvinylchloride and polyethylene tubes.

The electrochemical cell shown in Figure 1b was made from five Nylon[®] plates (13 cm × 30 cm × 1.25 cm) mounted in a 'sandwich' form. The cell was divided into one cathodic and two interlinked anodic compartments, separated by a Nafion[®] 417 membrane. The cathodic chamber was mounted between two turbulence promoters. To prevent electrolyte leakage, rubber joints were placed between each of the cell components. The cathodic compart-



(a)



(b)

Fig. 1. (a) Dual continuous-flow cell design. (b) Electrolytic cell for lead removal.

ment consisted of a rectangular frame of Nylon in which a block of reticulated vitreous carbon (5.0 cm × 15.0 cm × 1.25 cm) was fixed. The electrical contact was made by a stainless steel plate located on one of the inner sides of the frame, and welded to a copper wire (4 mm diam.), and cemented to the RVC with a conducting silver cement. Two stainless steel sheets (5.0 cm × 15.0 cm × 0.05 cm), each located in a 1.0 cm deep cavity within the end plates (Fig. 1(b)), comprised the anodes. Copper wires were soldered to the two plates of the stainless steel anode to provide the electrical contact. A saturated calomel reference electrode within a Teflon® Luggin capillary entered the catholyte compartment through a hole drilled in the upper side of the RVC cathode-containing frame. The cell had two electrolyte entrances and two electrolyte exits. In this system, the electrolytes flow separately and simultaneously in a closed circuit through the catholyte and anolyte compartments.

2.5. Procedure

After assembling the electrochemical cell, the flow system was loaded with 3.5 dm³ of catholyte and anolyte, each in a separate reservoir. The catholyte consisted of a buffered 0.5 M boric acid, 0.05 M sodium nitrate and 46 mg dm⁻³ of Pb(II) as an average value of metal concentration (see Table 1 for real values). As stated earlier the pH of the resulting solution was 4.8. The anolyte composition was the same as the catholyte, but without Pb(II). The flow rates of both electrolytes were adjusted to the same value (60, 120 or 240 dm³ h⁻¹). Then, a constant potential of -0.8 V vs SCE was applied to the cell from a potentiostatic power supply, in the controlled-potential mode. As observed in the preliminary hydrodynamic voltammetric study, the reduction of the Pb(II) at this potential is mass transport-controlled. At predetermined intervals, the solution leaving the cathodic compartment was sampled, and the remaining Pb(II) concentration was quantified by atomic absorption spectrometry in order to monitor the effectiveness of electrolysis. The above procedure was also used to examine the efficiency of RVC cathodes of different porosities (20, 45, 60 and 80 ppi).

3. Results and discussion

As stated earlier, the development of the electrolytic cell for Pb(II) removal was accomplished in two

phases. In order to determine the appropriate reduction potential for the removal of Pb(II) ions from the chosen medium under conditions of turbulence, a preliminary hydrodynamic voltammetric study was carried out. Subsequently, this potential was applied to the electrolytic cell under several combinations of electrolyte flow rate and RVC cathode porosity.

3.1. Preliminary hydrodynamic voltammetric experiments

Figure 2 shows a series of voltammograms obtained in the hydrodynamic mode for a solution containing 50 mg dm⁻³ of Pb(II) in 0.5 M boric acid and 0.05 M sodium nitrate. The potential was cycled between 0.0 and -1.0 V on a glassy carbon rotating disc electrode (area 0.1257 cm²) at 2 mV s⁻¹ using five different rotation rates (41.9, 94.2, 167.5, 261.8 and 376.9 rad s⁻¹). As can be seen, in the forward cathodic scan all the curves show waves for the reduction of Pb(II) to Pb, with a well-defined limiting current plateaux extending over a potential range of at least 400 mV. The value of the limiting current was dependent on the GCRDE rotation rate. This behaviour is characteristic of a mass-transfer controlled process. In the cathodic region of the reverse scan (sweep), the current magnitude after the limiting current plateaux was higher than that registered in the forward scan. This feature is to be expected for a system involving nucleation and growth of a metal phase on the carbon electrode. In the reverse sweep, an oxidation peak current was also observed at -0.4 V in all voltammograms. Despite the fact that the voltammograms from Fig. 2 show well defined flat plateaux of mass transport controlled currents, shifting the potential lower limit to more negative values, the currents still increased, probably due to roughening of the lead deposits. The increase in the electrode area results in greater currents for lead reduction and hydrogen evolution.

Application of the Levich equation is an appropriate test to verify whether an electrode process is under mass transfer control [19]. The limiting currents measured at the midpoint of the plateaux (-0.8 V) were plotted as a function of the square root of rotation rate (I against $f^{1/2}$) as shown in the inset of Fig. 2. The plot was linear, confirming that, lead deposition became mass transport controlled at potentials more negative than -0.6 V. In this case hydrogen evolution amplifies the response without apparently changing its shape.

Table 1. Initial Pb(II) concentrations for each experiment and the electrolysis times for 90% and 99% of the concentration reduction

	60 dm ³ h ⁻¹			120 dm ³ h ⁻¹			240 dm ³ h ⁻¹		
	C(0) /mg dm ⁻³	t _{90%} /min	t _{99%} /min	C(0) /mg dm ⁻³	t _{90%} /min	t _{99%} /min	C(0) /mg dm ⁻³	t _{90%} /min	t _{99%} /min
20 ppi	45.0	39.8	112.2	48.3	56.0	137.2	36.7	29.1	79.7
45 ppi	45.0	18.4	42.3	51.7	17.1	39.6	46.7	11.8	24.4
60 ppi	45.0	19.2	28.2	51.7	13.4	28.0	41.7	9.8	24.7
80 ppi	51.7	8.9	17.8	45.0	8.2	15.5	43.3	8.8	13.4

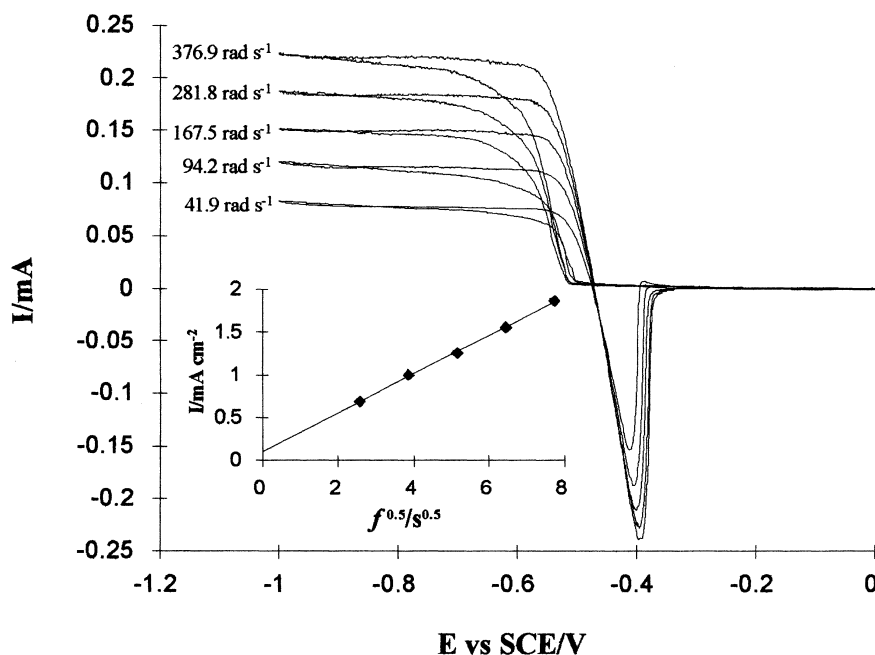


Fig. 2. Series of voltammograms obtained with a glassy carbon rotating disc electrode. Solution of $50\ mg\ dm^{-3}$ of $Pb(II)$ in $0.5\ M$ of boric acid and $0.05\ M$ of sodium nitrate. Potential range 0 to $-1.0\ V$ vs SCE. Scan rate $2\ mV\ s^{-1}$. Rotation rates indicated on the graph. Inset: Levich plot of (I_L vs $f^{1/2}$) for the limiting currents shown.

3.2. Efficiency of $Pb(II)$ removal by the recirculating flow-through cell

In flow-through cell performance studies, the removal of $Pb(II)$ was conducted in the recirculating mode. The depletion of lead concentration by potentiostatic electrolysis at the reticulated carbon cathodes was evaluated by measuring the remaining $Pb(II)$ concentration in the catholyte compartment solution as a function of the electrolysis time. The levels of lead were quantified by atomic absorption spectrometry. The initial $Pb(II)$ concentration in the catholyte, shown in Table 1, was added to $3.5\ dm^3$ of a solution with the same composition as that used in the preliminary experiments; the anolyte ($0.5\ M$ boric acid plus $0.05\ M$ sodium nitrate) contained no lead. A potential of $-0.8\ V$ vs SCE was applied at the RVC cathode for the electrodeposition of lead. This potential value was the midpoint of the limiting current plateaux obtained in the experiments with the GCRDE. Thus, as long as the hydrodynamic boundary layer with the RVC electrode is equal to or greater than that at GCRDE, this potential will result in mass transfer limited operation. Twelve experiments resulting from the combination of RVC cathode porosity (20, 45, 60 and 80 ppi) and electrolyte flow rate ($60, 120$ and $240\ dm^3\ h^{-1}$) were carried out.

Table 1 shows the initial values of lead concentration, $C(0)$, and the time for 90% and for 99% of removal with respect to the twelve experiments. The $Pb(II)$ concentration decreased to 1% from the initial value after an electrolysis time of 13 to 130 min, depending on the RVC cathode porosity. The time of electrolysis for concentration reduction of 99% is 2.2 ± 0.3 times greater than that for 90% of reduc-

tion. This is an evidence of a mass transport controlled process. According to Pletcher *et al.* [6] controlled potential electrolysis at a reticulated cathode, carried out under mass transfer control, may be modelled as

$$\ln \frac{C(t)}{C(0)} = Kt \quad (1)$$

where $C(t)$ is the concentration of the metallic ion as a function of the time of electrolysis, and K will be defined later. Simple calculations using Equation 1 show that the value for the ratio $t_{99\%}/t_{90\%}$ is equal 2 for a mass transport controlled reduction reaction.

Figure 3 illustrates the decrease in normalized $Pb(II)$ concentrations [$C(t)/C(0)$] with the length of electrolysis, using different RVC cathode porosities (20, 40, 60 and 80 ppi), at a catholyte flow rate of $240\ dm^3\ h^{-1}$. All the curves had the same profile in which the lead ion concentration dropped nearly exponentially with the time. To reach 90 or 99% of concentration reduction, the electrolysis demanded less time for higher porosities. This behaviour reflects differences in the specific surface areas of RVC cathodes, since an increase in RVC porosity results in a larger area being available for the electrodeposition. In the conditions of the experiments shown in Fig. 3, a concentration of $0.1\ mg\ dm^{-3}$, which corresponds to a 99.8% reduction, was achieved in 20, 30, 40 and 120 min using sponges of 80, 60, 45 and 20 ppi, respectively.

The influence of electrolyte flow rate on the effectiveness of electrolysis is also depicted in Fig. 4, which shows the normalized concentration in order to make the comparison easier. The data show that as the flow rate increases the reduction of $Pb(II)$ becomes more effective. This behaviour was attributed to a

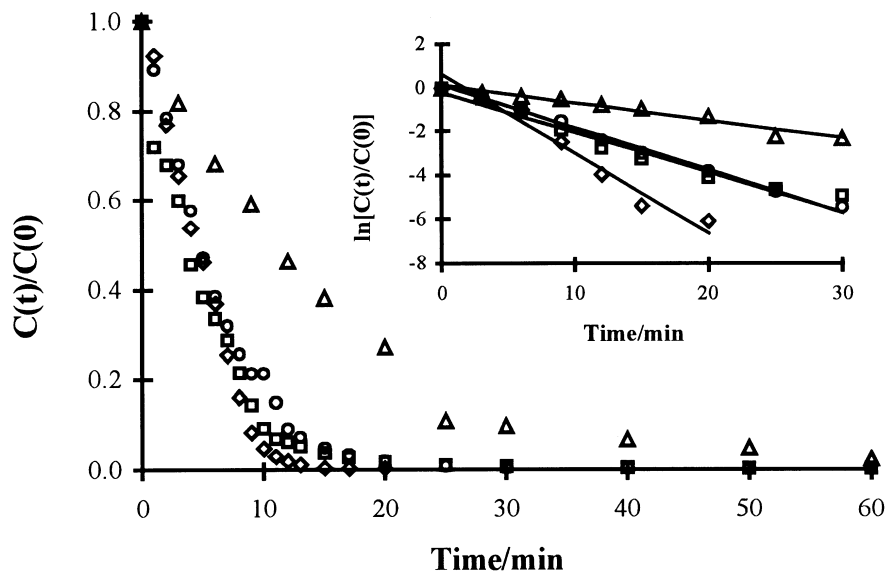


Fig. 3. Normalized concentration $[C(t)/C(0)]$ against time curves, obtained for a $240 \text{ dm}^3 \text{ h}^{-1}$ flow rate and cathode porosities of (Δ) 20, (\circ) 45, (\square) 60 and (\diamond) 80 ppi. Initial Pb(II) concentrations shown in Table 1. Potential -0.8 V vs SCE. Inset: Plots of $\ln[C(t)/C(0)]$ against time for the data shown.

greater rate of mass transport of Pb(II) due to an increase in the electrolyte flow rate.

Although the plots of $C(t)/C(0)$ as a function of electrolysis time were apparently exponential, the expectation of linearity for $\ln[C(t)/C(0)]$ against time was confirmed only for the first 30 min of electrolysis. For longer times, when greater than 90% of the lead had been removed, a slight deviation from linearity occurs. The reason for that is the probable loss of current efficiency as lead is being removed. The electrolytic process of lead removal shows an increasing current efficiency for higher values of foam porosity and flow rate, despite some discrepancies. Table 2 shows the current efficiency for 90 and 99% of lead removal. The remarkable difference between the two values, for each operating condition of the cell, is due to the lead concentration drop. As lead ions are removed, the current for hydrogen evolution

becomes more significant relative to the current for Pb(II) reduction and reduces the efficiency. The loss of efficiency as lead is removed is the reason for the deviation from linearity in the plots of $\ln[C(t)/C(0)]$ against time. For this reason these plots (insets from Figs. 3 and 4) were limited to times of 30 min. A low deviation from linearity was also observed for the first five minutes of the experiments. This is presumably related to the nucleation process that takes place in the early moments of polarization. Voltammograms of Fig. 2 show that hysteresis of the nucleation process extends over about 300 mV at a scan rate of 2 mV s^{-1} . A similar nucleation process also occurs on the RVC cathodes causing some delay in the lead layer growth.

As stated earlier, controlled potential electrolysis at a reticulated cathode in a recycle mode follows Equation 1. In that expression K is defined as:

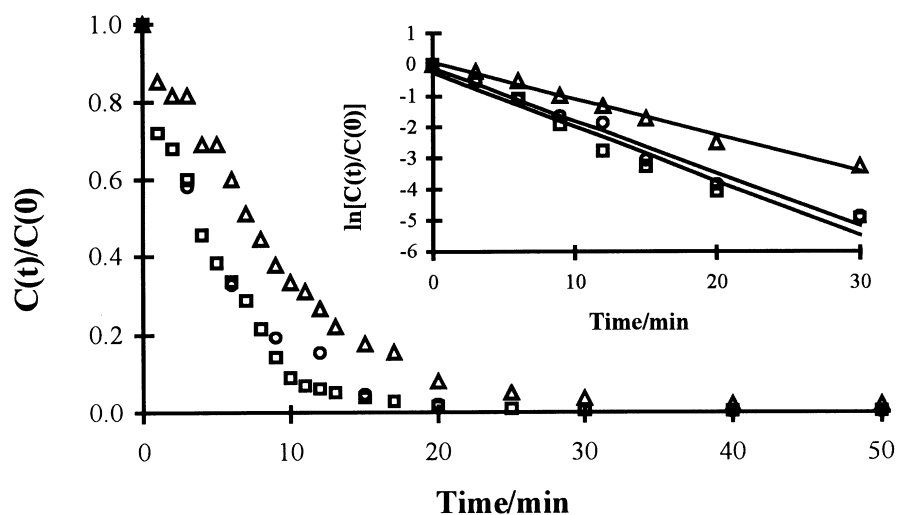


Fig. 4. Normalized concentration $[C(t)/C(0)]$ against time curves, obtained for a 60 ppi cathode porosity and flow rates of (Δ) 60, (\circ) 120 and (\square) $240 \text{ dm}^3 \text{ h}^{-1}$. Initial Pb(II) concentrations shown in Table 1. Potential -0.8 V vs SCE. Inset: Plots of $\ln[C(t)/C(0)]$ against time for the data shown.

Table 2. Current efficiency of the electrolytic cell for 90% and 99% of lead removal considering the operating conditions used in this study

	60 dm ³ h ⁻¹		120 dm ³ h ⁻¹		240 dm ³ h ⁻¹	
	Eff _{90%} /%	Eff _{99%} /%	Eff _{90%} /%	Eff _{99%} /%	Eff _{90%} /%	Eff _{99%} /%
20 ppi	4.6	1.8	18.0	13.7	4.9	2.0
45 ppi	11.5	4.8	12.3	5.8	16.3	8.4
60 ppi	10.4	3.2	15.8	8.4	17.3	7.6
80 ppi	22.3	12.5	21.3	12.8	19.0	14.1

Table 3. Values of $k_m A_e$ and k_m taken from the slopes of the $\ln[C(t)/C(0)]$ against time plots from the details in the Figs 3 and 4

Flow rate /dm ⁻³ h ⁻¹	Cathode Porosity/ppi – Cathode Area/cm ² .cm ⁻³							
	20 – 11.2		45 – 27.2		60 – 37.4		80 – 51.2	
	$k_m A_e$ /s ⁻¹	$k_m \times 10^3$ /cm s ⁻¹	$k_m A_e$ /s ⁻¹	$k_m \times 10^3$ /cm s ⁻¹	$k_m A_e$ /s ⁻¹	$k_m \times 10^3$ /cm s ⁻¹	$k_m A_e$ /s ⁻¹	$k_m \times 10^3$ /cm s ⁻¹
60	0.031	2.83	0.080	3.00	0.074	2.00	0.136	2.67
120	0.025	2.17	0.080	3.00	0.105	2.83	0.191	3.67
240	0.049	4.33	0.117	4.33	0.111	3.00	0.210	4.17

$$K = -\frac{V_e k_m A_e}{V_r} \quad (2)$$

where V_e is the cathode volume, A_e is the specific surface area (the active area/unit volume of cathode), V_r is the total volume of catholyte and k_m is the mass transfer coefficient.

Since V_e/V_r is a constant, the values of $k_m A_e$, taken from the slopes of $\ln C(t)/C(0)$ against time plots, presented in the Table 3, give an indication of cell efficiency for each operating condition. The results shown in Table 3 were calculated using Equations 1 and 2. Considering that V_e/V_r is 0.027 for the cell configuration used in this study and taking into account the approximate electrode areas taken from the RVC manufacturer's literature, it is possible to calculate the mass transport coefficient, k_m , also presented in Table 3. The cell configuration that showed the most Pb(II) removal (80 ppi) presented a k_m value of $4.17 \times 10^{-3} \text{ cm s}^{-1}$ that is apparently flow rate dependent. But also it is interesting to note that the k_m values do not increase much with the RVC porosity, at least for 60 and 240 dm³ h⁻¹ data. This is in agreement with previous results [17] where it is noted that RVC foam appears to be a poor turbulence promoter, and most of the improvement in performance comes from the increase in A_e .

The current efficiency for the configuration using an 80 ppi cathode and flow rate of 240 dm³ h⁻¹ was 14% for the removal of 99% of the metal ion, which meant a reduction in the Pb(II) concentration from 43.3 to 0.43 mg dm⁻³ in 13.4 min. Although the literature reports higher current efficiency than we found for 90% lead removal [17], the equipment used in this study has shown very satisfactory performance. In the experiments reported here the electrolysis was never terminated before the Pb(II) concentration reached 0.1 mg dm⁻³ or less. As shown in Fig. 3,

reduction to 0.1 mg dm⁻³ occurred in 20 min of electrolysis for the 80 ppi cathode and a flow rate of 240 dm³ h⁻¹.

4. Conclusions

The cell used in this study showed a good performance in removing lead from simulated effluents. The inclusion of a flow spreading mesh mounted on the RVC cathode avoided the development of preferential flow channels, as confirmed by the uniform colour change in the cathode after each experiment.

Hydrodynamic voltammetry was adequate for studying the Pb(II) reduction reaction under mass transport control. The limiting current plateaux in the resulting voltammograms showed the range of potential over which the Pb(II) reduction reaction is mass transfer controlled.

Using these potentials, the concentration of Pb(II) was reduced to 0.1 ppm during recirculation times ranging from 20 min to 2 h, depending on the RVC porosity and the flow rate and using $V_e/V_r = 0.027$. Best rates of lead removal were obtained at the higher cathode porosities and flow rates.

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