Article

Galvanostatic Removal of Pb²⁺ Ions from Diluted Solutions by the Use of a Membrane-Less Flow-Through Cell with Stainless Steel Wool Electrodes

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A remoção de íons Pb²⁺ a partir de soluções diluídas foi estudada, em condições galvanostáticas, usando uma célula de fluxo sem membrana com eletrodos de esponja de aço inoxidável (SSW). A metodologia de superfície de resposta (variáveis independentes: corrente elétrica e vazão) foi usada para obter as condições ótimas para a remoção de Pb²⁺ a partir de 2 L de uma solução de Pb(NO₃)₂ 50 mg L⁻¹ em NaNO₃ 0,10 mol L⁻¹ + H₃BO₃ 0,10 mol L⁻¹ (pH 4,8). A partir das superfícies de respostas, concluiu-se que a vazão (59-341 L h⁻¹) não influencia significativamente no processo de remoção de Pb²⁺. Por outro lado, o aumento da corrente elétrica leva a uma maior remoção de Pb²⁺, com valores significantemente melhores de consumo de energia específica e eficiência de corrente quando comparados àqueles relatados na literatura. Para um experimento realizado na região de condições ótimas (70 mA e 200 L h⁻¹), uma conversão de Pb²⁺ de 99,6% foi atingida depois de 90 min de eletrólise. A utilização da célula de fluxo sem membrana com eletrodos de SSW, além de ser energeticamente mais eficiente, levou à remoção de Pb²⁺ em ambos os eletrodos, mais predominantemente no anodo, sobre o qual 95% dos íons Pb²⁺ foram convertidos a PbO₂.

The removal of Pb²⁺ ions from dilute solutions was investigated under galvanostatic conditions using a membrane-less flow-through cell with stainless steel wool (SSW) electrodes. The response surface methodology (independent variables: electric current and volumetric flow rate) was used to find the optimal conditions for Pb²⁺ removal from 2 L of an aqueous solution of 50 mg L⁻¹ Pb(NO₃)₂ in 0.10 mol L⁻¹ NaNO₃ + 0.10 mol L⁻¹ H₃BO₃ (pH 4.8). The obtained response surfaces revealed that the volumetric flow rate (59-341 L h⁻¹) does not substantially affect the Pb²⁺ removal process. On the other hand, the electric current increase led to higher Pb²⁺ removal, with significantly improved values of specific energy consumption and current efficiency when compared with those reported in the literature. For an experiment carried out in the optimum-condition region (70 mA and 200 L h⁻¹), a Pb²⁺ conversion of 99.6% was attained after 90 min of electrolysis. The use of the membrane-less flow-through cell with SSW electrodes, besides being significantly more energy efficient, led to Pb²⁺ removal on both electrodes, but predominantly in the SSW anode, on which more than 95% of the Pb²⁺ ions were converted to PbO₂.

Keywords: electrolytic removal of Pb²⁺ ions, electrochemical treatment, Pb²⁺ wastewater, simultaneous cathodic/anodic Pb²⁺ removal, factorial design, response surface methodology

Introduction

Nowadays, environmental agencies of many countries require the treatment of aqueous effluents containing toxic metallic ions, such as Cd^{2+}, Cr^{6+} and Pb^{2+}, to decrease their concentrations to lower values than those permitted for discharge into sewers (few mg L⁻¹ down to zero, depending on the country). The treatment of these effluents is usually done adjusting their pH or adding a suitable counter-ion to form precipitates. The resultant solid sludge may then be sent to a licensed landfill. Despite the efficiency of this methodology, the possible mobility of those metallic ions may lead to contamination of watercourses.

Electrochemical techniques have been extensively used for the treatment of aqueous effluents because they offer an environmentally and friendly way of removing toxic metallic ions[1-15] and/or organic species[16-22] via redox reactions. The environmental compatibility is the main advantage of electrochemical methods, as the reagent, the electron, is a "clean reagent".[23,24] However, the removal of

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metallic ions from dilute aqueous solutions is hindered by slow mass-transfer kinetics. Therefore, the use of conventional plane electrodes is ineffective because of low current efficiencies and high energy consumptions.[25] This limitation can be overcome by the use of three-dimensional porous electrodes,[26] which lead to an enhancement of the mass-transfer rate and allow the use of low current densities, but with a relatively high electric current *per* unit cell volume.[27]

Specifically for Pb^{2+} ions, several works on their removal from aqueous solutions using three-dimensional electrodes were reported in the literature. De Leon and Pletcher[1] investigated the influence of different anions at pH 2 (perchlorate, nitrate, tetrafluoroborate, sulfate and chloride) on the kinetics and current efficiency for Pb^{2+} reduction at a reticulated vitreous carbon (RVC) cathode. The reaction was under mass-transport control only in chloride media, and with other anions in solution the reaction exhibited slower kinetics. For perchlorate, nitrate and tetrafluoroborate, the anion effect was attributed to slow steps in the nucleation and/or early growth of the lead deposition on the carbon surface. In sulfate media, it was attributed to surface poisons and formation of a passivating layer. RVC cathodes of 20, 45, 60 and 80 pores *per* inch were also employed by Bertazzoli and co-workers[2,3] for Pb^{2+} reduction from a simulated effluent (50 mg L^{-1} $Pb(NO_3)_2$ + 0.5 mol L^{-1} H_3BO_3 + 0.05 mol L^{-1} $NaNO_3$, pH 4), at a constant potential under mass-transport control. According to these authors, the flow-through cell used was able to reduce the Pb^{2+} concentration from *ca.* 50 to 0.1 mg L^{-1} during recirculation times ranging from 20 to 40 min, depending on the RVC porosity and flow rate, and higher degrees of Pb^{2+} reduction were attained at higher cathode porosities and flow rates. Using cyclic voltammetry and atomic force microscopy, Carreño *et al.*[4] also investigated anion effects on Pb^{2+} removal from aqueous solutions using a RVC electrode. Higher removal efficiencies were achieved in chloride media, and lowest efficiencies were achieved in sulfate media, which were also attributed to the formation of a passivating surface film.

A three-dimensional cathode formed by a stack of copper screens was used by El-Dead *et al.*[5] for Pb^{2+} removal from a flowing alkaline solution (3 mol L^{-1} NaOH). As expected, the limiting electric current for Pb^{2+} electrodeposition increased with Pb^{2+} concentration, electrolyte flow rate, screen mesh size, and/or cathode thickness. Ragnini *et al.*[6] proposed the removal of Pb^{2+} from aqueous solutions (50 mg L^{-1} $Pb(NO_3)_2$ + 0.5 mol L^{-1} H_3BO_3 + 0.05 mol L^{-1} $NaNO_3$, pH 4.8) using a flow-trough cell with a recycled niobium felt. These were obtained by pressing niobium tips resulting from machining

of electron-beam refined niobium ingots. Operating at constant potential (−0.95 V *vs.* SCE), the Pb^{2+} concentration was reduced to 0.5 mg L^{-1} during recirculation times from 94 to 150 min, depending on the flow rate. As expected, higher degrees of Pb^{2+} removal were attained for higher flow rates. Kelsall and co-workers[7,8] reported results of experiments and modeling of simultaneous recovery of Pb and PbO_2 in aqueous effluents from lead-acid battery recycling plants. From an electrolyte containing 1 mmol L^{-1} Pb^{2+} at pH 12, the Pb^{2+} concentration was depleted to less than 0.06 mg L^{-1} in a batch recycle reactor system with graphite felt anodes and graphite or titanium felt cathodes. Simultaneous cathodic Pb and anodic PbO_2 electrodeposition resulted in more rapid Pb^{2+} depletion than for either reaction separately. Experimental electric current density-potential and charge efficiency-potential relationships were in broad agreement with model predictions, with near unity current efficiencies for mass-transport controlled PbO_2 deposition from the electrolyte.

As reviewed above, none of the cited works reports the use of stainless steel wool (SSW) as electrode material for removing Pb^{2+} from aqueous effluents. However, Paidar *et al.*[9] reported the use of SSW and graphite felt to simultaneously remove Cu^{2+} and Zn^{2+} from diluted solutions, and concluded that SSW was a promising alternative material to graphite felt for the construction of three-dimensional electrodes. Moreover, SSW offers the advantage of simple electrode regeneration by anodic polarization. Using mild-steel wool and a stainless-steel mesh coil for gold electrowinning, Barbosa *et al.*[10] observed that electrolyte recirculation enhanced gold recovery from diluted liquors. Elsherief[11] designed a flow-by cell with a spiral wound steel electrode for Cd^{2+} electrowinning. Using 250 mL of solution and optimized operating conditions, the Cd^{2+} concentration was reduced from 500 to less than 5 mg L^{-1} in 90 min.

In previous works, we reported on the prospects of a membrane-compartmentalized flow-through cell with a SSW cathode for Pb^{2+} removal from diluted solutions, under potentiostatic[12] or galvanostatic[13] conditions. In the first condition, the cell performance was evaluated for three cathode potentials: −0.70, −0.80 and −0.90 V *vs.* SCE. At −0.90 V *vs.* SCE and a volumetric flow rate (Q) of 250 L h^{-1}, the Pb^{2+} concentration was reduced from 50 to 1 mg L^{-1} (98% conversion) in a 90 min electrolysis.[12] Using the same electrochemical flow-through cell under galvanostatic conditions, the response surface methodology (RSM) was employed to find the optimum conditions for Pb^{2+} removal from diluted solutions.[13] From the obtained response surfaces for Pb^{2+} removal efficiency and current efficiency as a function of the electric current (I) and

Q, it was concluded that the region around –0.25 A and 250 L h⁻¹ (optimized condition) was the best one for Pb^{2+} removal, with values of Pb^{2+} removal efficiency and electric current efficiency of 93 and 22%, respectively, after a 30 min electrolysis. Furthermore, a value of Pb^{2+} removal efficiency of almost 99% was achieved after only 40 min of electrolysis.

In this work, the removal of Pb^{2+} ions from diluted solutions was also investigated under galvanostatic conditions, but now using a flow-through cell with both the cathodes and the anode made of SSW. This cell is similar to the flow-through cell used in previous works,[12,13] but with two important changes: the cationic membranes were removed and the two stainless steel plate (SSP) electrodes were covered with SSW and used as cathodes (the SSW electrode previously used as the cathode is now used as the anode). The benefits of such changes promptly became evident on the values of Pb^{2+} fractional conversion ($X_{Pb^{2+}}$), current efficiency (Φ^e) and specific energy consumption (w). Thus, in order to determine the optimal conditions for the electrolytic removal of Pb^{2+} ions, I and Q were simultaneously investigated as independent variables through a factorial design and also by RSM.[28,29]

Experimental

Chemicals

The diluted solution containing Pb^{2+} ions was prepared using analytical-grade chemicals and distilled and deionized water (Milli-Q® system, Millipore). Lead nitrate (Aldrich), sodium nitrate (Merck) and boric acid (Merck)

were used to prepare this solution with the following composition: 50 mg L⁻¹ $Pb(NO_3)_2$ in 0.1 mol L⁻¹ $NaNO_3$ + 0.10 mol L⁻¹ H_3BO_3 (pH 4.8). Atomic absorption standard solutions used in the analyses were prepared using a Titrisol standard solution (Merck).

Central composite rotatable design

A central composite rotatable design (CCRD)[30] with two independent variables (I and Q) was employed to find the optimum conditions for Pb^{2+} removal. Five levels of each independent variable were chosen and three replications were carried out at the central point, totaling 11 experiments (see Table 1). Based on preliminary results, the ranges of the independent variables were: I from 44 to 86 mA and Q from 59 to 341 L h⁻¹. The independent variables were coded according to the following equation:[28]

$$x_i = \frac{X_i - X_{i0}}{\Delta X_i} \tag{1}$$

where x_i, X_i, X_{i0} and ΔX_i are the coded level of the ith independent variable, the real value of the ith independent variable, the real value of the ith independent variable in the central point, and the half of the difference between the upper and lower values of the ith independent variable, respectively.

The correlations between the independent variables and the responses were obtained by using second-order models (least-squares method):

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i=1}^{k} \sum_{i \neq j=1}^{k} \beta_{ij} x_i x_j + \varepsilon \tag{2}$$

Table 1. Coded/real values and obtained responses (calculated according to equations 4, 5 and 6) for the central composite rotatable design (CCRD) corresponding to the Pb^{2+} fractional conversion ($X_{Pb^{2+}}$), electric-current efficiency (Φ^e), and energy consumption (w), for a 30 min electrolysis

Run	Coded levels		Real values*		Responses		
	x_1	x_2	X_1	X_2	$100\, X_{Pb^{2+}}$	$100\, \Phi^e$	$w\,/\,(kW\ h\ kg^{-1})$
1	−1	−1	0.050	100	90.5	47.8	1.00
2	−1	+1	0.050	300	89.0	47.2	1.27
3	+1	−1	0.080	100	97.9	31.5	1.71
4	+1	+1	0.080	300	99.0	32.5	1.63
5	−1.41	0	0.044	200	80.7	47.1	0.97
6	+1.41	0	0.086	200	90.6	29.9	1.81
7	0	−1.41	0.065	59	95.6	37.4	1.37
8	0	+1.41	0.065	341	98.0	38.2	1.32
9	0	0	0.065	200	96.0	36.1	1.43
10	0	0	0.065	200	98.9	36.8	1.41
11	0	0	0.065	200	97.8	37.4	1.39

*X_1 = electric current, I (in A); X_2 = flow rate, Q (in L h⁻¹).

where Y is the response, β_0 a constant coefficient, β_i, β_{ii} and β_{ij} the coefficients for the linear, quadratic and interaction effects, respectively, x_i and x_j the coded levels for the independent variables, k the number of independent variables and ε the random error.[28] In the present case, the mathematical relationships between the coded levels of the independent variables ($I \equiv x_1$ and $Q \equiv x_2$) and the responses ($X_{Pb^{2+}}$, Φ^e and w) were approximated by a second-order polynomial equation:

$$Y = b_0 + b_1 x_1 + b_2 x_2 + b_{11} x_1^2 + b_{22} x_2^2 + b_{12} x_1 x_2 \qquad (3)$$

where Y is the predicted response, b_0 a constant, b_1 and b_2 the linear coefficients, b_{11} and b_{22} the quadratic coefficients and b_{12} the interaction coefficient.

Experiments in the central point were performed in order to estimate the pure error. All the experiments were randomly carried out in order to minimize the effect of unexplained variability on the observed responses due to systematic errors.[23] Finally, the results were analyzed by the least-squares method and response surfaces[28,29] were generated in order to determine the best conditions for Pb^{2+} removal.

Electrolytic system and procedure for Pb^{2+} removal

The whole system for Pb^{2+} removal (Figure 1) consisted of a membrane-less flow-through electrochemical cell (diameter of 150 mm and length of 80 mm), a PVC reservoir, a magnetic recirculation pump, and a flowmeter to control the solution flow rate. The flow-through electrochemical cell (Figure 2) was mounted, in a
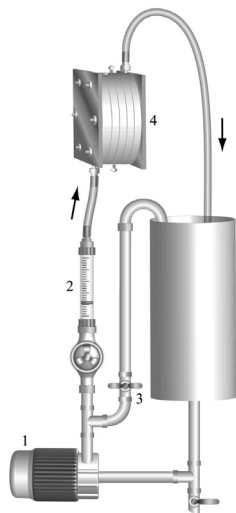
Figure 1. Schematic representation of the continuous flow-through system: (1) pump, (2) flowmeter, (3) bypass and (4) membrane-less flow-through cell (diameter of 150 mm and length of 80 mm).
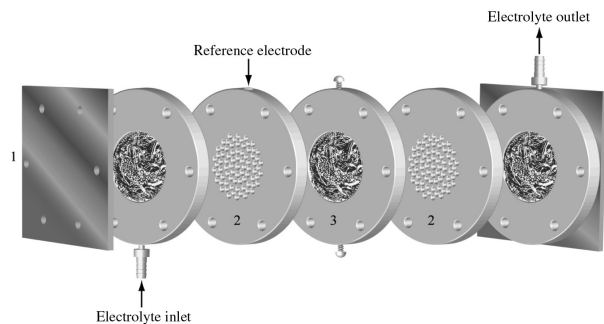
Figure 2. Expanded view of the membrane-less flow-through cell with stainless steel wool (SSW) cathodes and anode: (1) SSW fixed on stainless steel plates as cathodes, (2) turbulence promoters and (3) SSW anode.

"sandwich" form, using five PVC circular plates with the following dimensions: inner and outer diameters of 70 and 150 mm, respectively, and thickness of 12 mm. Each cell end contained a cathode made of Amway® SSW (70 mm of diameter and 6 mm of thickness, *ca.* 9 g) pressed against an SSP (150 mm × 150 mm × 5 mm). In order to prevent leakage, silicone gaskets, with format identical to that of the PVC plates but thickness of 2 mm, were used between these plates. Two of the PVC plates acted as turbulence promoters, allowing a uniform electrolyte flow distribution and standardization of the mass transport within the cell.[6] In the central PVC plate, an Amway® SSW anode (70 mm of diameter and 12 mm of thickness, *ca.* 18 g) was fixed by pressing against an SSP ring. The distance between each cathode and the anode was 22 mm. As described in detail elsewhere,[13] their surface areas *per* unit volume were 2.7×10^3 and 1.4×10^3 m^{-1}, respectively.

The assembled system was loaded with 2 L of the diluted Pb^{2+} solution and the performance of the cell evaluated by CCRD. All experiments on the galvanostatic removal of Pb^{2+} ions were conducted in the recirculation mode, using a PAR 273A potentiostat/galvanostat controlled by the Echem software. The electrolytic solution was periodically sampled and its Pb^{2+} content analyzed by a Varian SpectrAA 200 spectrophotometer with an air/acetylene flame.

Data analysis

In this work, as pointed out above, three parameters were used to evaluate the performance of the electrochemical system in each CCRD point: $X_{Pb^{2+}}$, Φ^e and w. The value of $X_{Pb^{2+}}$ was calculated as:

$$X_{Pb^{2+}} = \frac{(C_0 - C)}{C_0} \qquad (4)$$

where C_0 is the initial Pb^{2+} concentration and C the Pb^{2+} concentration after a given electrolysis time. The value of Φ^e was calculated as:

$$\Phi^e = \frac{nFV(C_0 - C)}{\int_0^t I(t)\,dt} \qquad (5)$$

where n is the stoichiometric number of electrons for the global reaction of Pb²⁺ conversion, F the Faraday constant and V the volume of electrolytic solution used in each test. Finally, the value of w (in W h kg⁻¹) was calculated as:

$$w = \frac{U_{cell}\,nF}{3600M\,\Phi^e} \qquad (6)$$

where U_{cell} is the cell voltage, M the molar mass of lead and 3600 the conversion factor from second to hour.

Results and Discussion

Optimization of Pb²⁺ removal

Initially, a 2³-full-factorial design with three independent variables and two levels for each variable was adopted to evaluate the influence of I, Q and surface area of the cathodes (only SSP or SSW fixed on SSP) on the Pb²⁺ electrolytic conversion (data not shown). From the results thus obtained, it became clear that lower values of w were obtained for the membrane-less flow-through cell operating with the cathodes of higher surface area (SSW fixed on SSP). Thus, with these cathodes, a set of experiments using a CCRD with only two independent variables (I and Q, Table 1) was conducted in order to obtain the optimum conditions for Pb²⁺ removal. Then, using the obtained responses (see Table 1), a multiple linear-regression analysis (least-squares method) was employed to generate three second-order models,[31] describing the dependence of $X_{Pb^{2+}}$, Φ^e and w on the two independent variables. The obtained equations for the three adjusted models containing only the statistically significant coefficients (at 95% confidence level) are:

$$X_{Pb^{2+}} = 0.9758 + (5.96 \times 10^{-2})\,x_1 - (4.41 \times 10^{-2})\,x_1^2 \qquad (7)$$

$$\Phi^e = 0.3643 - (6.91 \times 10^{-2})\,x_1 + (1.40 \times 10^{-2})\,x_1^2 + (1.08 \times 10^{-2})\,x_2^2 \qquad (8)$$

$$w\,/\,(W\ h\ kg^{-1}) = 1410.00 + 283.80\,x_1 - 86.23\,x_1 x_2 \qquad (9)$$

where x_1 and x_2 correspond to the coded levels for I and Q, respectively.

The response surface generated by equation 7 (Figure 3a) shows that, up to a certain point, the increase of the electric current positively influences the Pb²⁺ conversion process, leading to $X_{Pb^{2+}}$ values higher than 0.98 after a 30 min electrolysis, which is a significant improvement
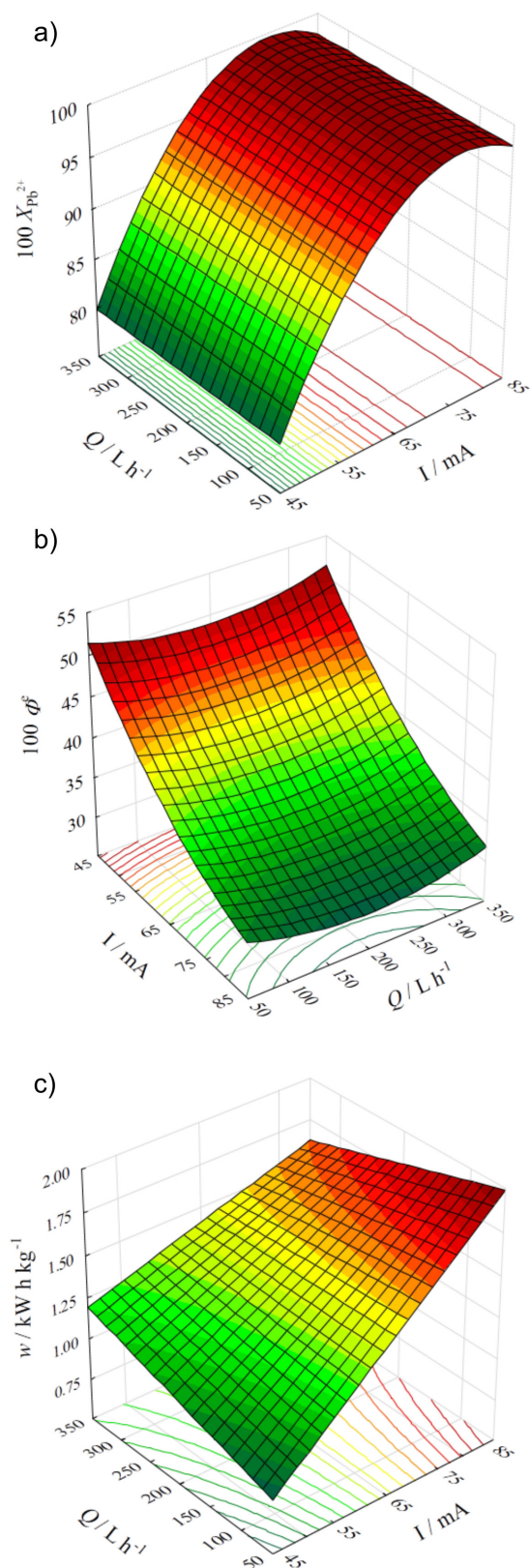
Figure 3. Response surfaces generated from the CCRD method using equations 7, 8 and 9, for a 30 min electrolysis under galvanostatic conditions: (a) Pb²⁺ fractional conversion ($X_{Pb^{2+}}$), (b) current efficiency (Φ^e) and (c) specific energy consumption (w).

when compared with those obtained in previous works.[12,13] It is worthwhile to point out that two simultaneous processes contribute for Pb^{2+} removal during electrolyses using the membrane-less flow-through cell: $Pb^{2+} + 2e^- \rightarrow Pb$ on the cathodes and $Pb^{2+} + 2H_2O \rightarrow PbO_2 + 4H^+ + 2e^-$ on the anode.

On the other hand, as one would expect, the corresponding values of Φ^e decrease as I is increased, as illustrated in Figure 3b. This occurs because competitive parallel reactions, such as the oxygen, water and nitrate reduction reactions ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$, $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ and $NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$, respectively), and the water oxidation reaction ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$), become important as I is increased.

As one would also expect, increases in I led to higher values of w (Figure 3c), although the highest obtained value is significantly lower than those reported in the literature for Pb^{2+} removal.[1,4,7,12,13] The value of w depends on the cell voltage, which can be expressed as:[24]

$$U_{cell} = U^o_{cell} + \Sigma|\eta| + \Sigma IR \qquad (10)$$

where U^o_{cell} is the thermodynamic equilibrium cell voltage, $\Sigma|\eta|$ the sum of the overpotentials at each electrode and ΣIR the sum of all ohmic drops in the cell due to the flow of I through resistances (R). At this point, it is worthwhile to remember that the cationic membranes were removed in the flow-through cell used in the present work. Therefore, the contribution from ΣIR was strongly minimized, thus remaining only the contributions from ohmic drops associated to the electrolyte, the distance between the electrodes and the magnitude of the electric current. It is clear from equation 7, that Q has no significant influence on $X_{Pb^{2+}}$ (see also Figure 3a), although several other studies showed that the rate of electrochemical reactions under mass transport conditions is dependent on Q.[2,3,6,12] According to Koene and Janssen,[32] increases in Q enhance the electrochemical-reaction rate as a consequence of the diffuse layer becoming thinner. In the present case, lower Q values possibly promoted insignificant changes in the mass transport coefficient, while higher ones led to the formation of preferential streaming channels and/or dead zones.[33] Similarly for Φ^e (Figure 3b), the influence of Q is practically insignificant. However, in the case of w (Figure 3c) there is a dependence on Q: for low I values, w increases with Q, while the opposite occurs for high I values. Such behavior is quite complex, being determined by the interplay between U_{cell} and Q.

The use of RSM also allows to find the region of optimum conditions for Pb^{2+} removal within the experimental ranges. Thus, taking Figure 3a into account

and considering that Q affects the value of w, an optimized experiment was carried out by fixing I and Q at 70 mA and 200 L h^{-1}, respectively. At these conditions, after a 30 min electrolysis the obtained values of $X_{Pb^{2+}}$ and w were equal to 0.98 and 1.5 kW h kg^{-1}, respectively, while the value of Φ^e was 0.35. Additionally, as it can be seen in Figure 4, after a 90 min electrolysis, the Pb^{2+} concentration dropped to 0.21 mg L^{-1} ($X_{Pb^{2+}} = 0.996$). Furthermore, by measuring the mass of the SSW electrodes (anode and cathodes) before and after the experiments, it became clear that more than 95% of the Pb^{2+} ions in solution were removed as PbO_2 deposited on the SSW anode.
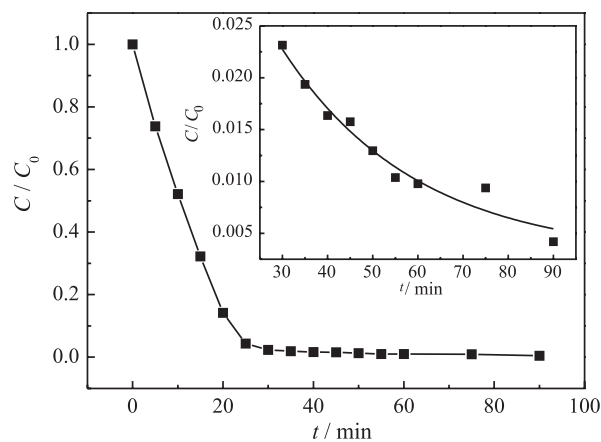
Figure 4. Normalized Pb^{2+} concentration (C/C_0) *vs.* time for Pb^{2+} removal at 70 mA and 200 L h^{-1} in the membrane-less flow-through cell with SSW electrodes. Insert: expanded view of results beyond 30 min of electrolysis.

Figure 4 shows that the decrease of the normalized Pb^{2+} concentration [C/C_0] as a function of time is not exponential, as one would expect for a mass-controlled reaction.[13] Nevertheless, the values of $X_{Pb^{2+}}$ and Φ^e are significantly higher than those reported in the literature[1,3,7,12,13] for the experimental parameter range used in the present study. By comparing the results obtained in the present work with those that we previously reported for a membrane-compartmentalized flow-through cell with a SSW cathode for Pb^{2+} removal[12,13] (see Table 2), one can clearly see that

Table 2. Comparison of the results for Pb^{2+} removal from diluted solutions using a flow-through cell with stainless steel wool (SSW) as cathodes and anode (membrane-less cell, this work) or a flow-through cell with SSW only as cathode, for a 30 min electrolysis

Method	U_{cell} / V	$100\ X_{Pb^{2+}}$	$100\ \Phi^e$	w / (kW h kg^{-1})
Galvanostatic [this work]	2.05	35	98	1.5
Galvanostatic[a,13]	3.30	22	93	4.1
Potentiostatic[b,12]	3.50	17	81	5.3

[a]At –0.25 A and 250 L h^{-1} by using a factorial design; [b]at –0.90 V *vs.* SCE and 250 L h^{-1}.

Table 3. Summary of the ANOVA with the data obtained using the CCRD (Table 1) for the Pb²⁺ fractional conversion ($X_{Pb^{2+}}$), for a 30 min electrolysis

| Source of variation	Sum of squares	Degrees of freedom	Mean square (MS)	F_{ratio} (model significance, MS)
Regression (R)	313.80	5	62.76	$MS_R/MS_r = 19.56$[a]
Residual (r)	16.04	5	3.21	
Lack of fit (Lof)	11.59	3	3.86	$MS_{Lof}/MS_{Pe} = 1.74$[b]
Pure error (Pe)	4.45	2	2.23	
Total	329.84	10	—	

Determination coefficient: 0.951; [a]$F_{5,5} = 5.05$; [b]$F_{3,2} = 19.16$ (at 95% confidence level).

the membrane-less flow-through cell with SSW cathodes and anode here reported is much more efficient.

Validation of the quadratic models developed

Analysis of variance (ANOVA)[31] was applied to numerically validate the three quadratic models ($X_{Pb^{2+}}$, Φ^e, and w) here developed (Table 3 exemplifies the ANOVA for the $X_{Pb^{2+}}$ model; the data for the Φ^e and w models can be seen in Tables S1 and S2 in the Supplementary Information, SI). The F-test (Fisher's distribution) was also used in order to evaluate the model that best fits the population from which the data were sampled. This statistical test is based on the ratio of two scaled sums of squares reflecting different sources of variability.[30,31] With the aid of ANOVA and the F-test, it was found that the regressions for the three models were statistically significant, since the calculated F-ratio for the regressions (19.56 for $X_{Pb^{2+}}$, 38.46 for Φ^e and 48.23 for w) were greater than the values of the critical F-value (5.05 at 95% confidence level). For all models, the calculated values of the F-ratio for lack of fit (1.74 for $X_{Pb^{2+}}$, 9.21 for Φ^e and 7.23 for w) were smaller than the critical ones (19.16 at 95% confidence level), thus indicating that the data are well adjusted to the models. The use of an F-test presupposes that the residuals have a normal distribution.[30,31] Figure 5 illustrates a typical plot of the residuals *versus* the predicted values for the $X_{Pb^{2+}}$ model; similar plots for the Φ^e and w models can be seen in the SI (Figure S1). The fact that these plots present no systematic errors (all the residuals are randomly distributed around the mean) confirms the good agreement for the models.[31] The determination coefficients (R^2) for the models, which are additional parameters for assessing the fitting quality of the models, were close to unity (0.951 for $X_{Pb^{2+}}$, 0.975 for Φ^e and 0.980 for w), indicating that the models were statistically significant.[30] Finally, probability plots were also obtained to evaluate the statistical significance of the coefficients for the three developed models ($X_{Pb^{2+}}$, Φ^e and w). Figure 6 illustrates this plot for the $X_{Pb^{2+}}$ model; as it can be seen, the terms different from zero were statistically significant. Similar results were obtained in the probability

plots for the Φ^e and w models, as can be seen in Figure S2 in the SI.
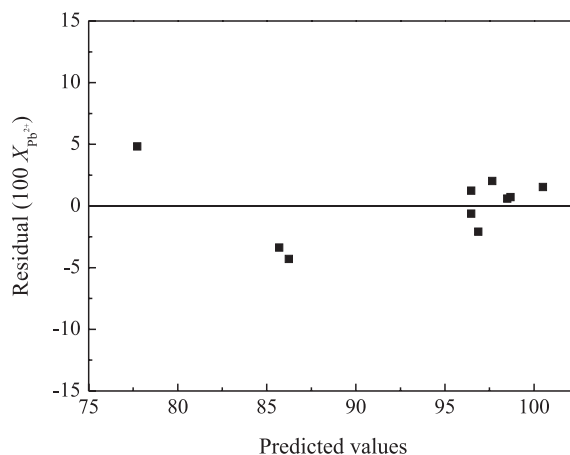
Figure 5. Residual plot for the model of Pb²⁺ fractional conversion ($X_{Pb^{2+}}$) for a 30 min electrolysis under galvanostatic condition, using the flow-through cell with SSW cathodes and anode.
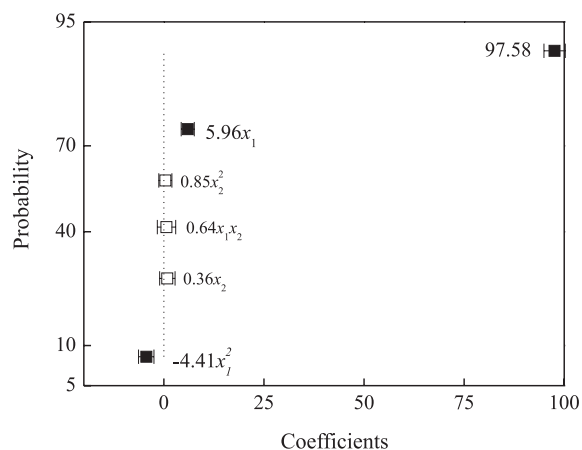
Figure 6. Normal probability plot for the model of Pb²⁺ fractional conversion ($X_{Pb^{2+}}$) for a 30 min electrolysis under galvanostatic condition, using the flow-through cell with SSW cathodes and anode.

Conclusions

The results here reported for the removal of Pb²⁺ ions from diluted solutions allow to conclude that a

membrane-less flow-through cell with stainless steel wool (SSW) as cathodes and anode is significantly more efficient and economical than a previously used flow-through cell with SSW only as cathode.

The use of factorial design along with RSM was useful for the optimization of the electrolytic removal process in a relatively small number of experiments; the conditions predicted by the developed models are in good agreement with the experimental results, as confirmed by variance analysis. The obtained response surfaces from the developed models revealed that Q (in the range 59-341 L h^{-1}) did not substantially affect the Pb^{2+} removal process. On the other hand, the increase of I led to higher values of Pb^{2+} conversion, at reasonable values of current efficiency and specific energy consumption, especially when compared with those reported in the literature. An experiment carried out within the optimum-conditions region (using 70 mA and 200 L h^{-1}, [Pb^{2+}] = 50 mg L^{-1}, 2 L of solution) yielded a Pb^{2+} conversion of about 99.6%, after 90 min of electrolysis.

Finally, it should be emphasized that the use of a membrane-less flow-through cell with SSW as cathodes and anode, besides being significantly more energy efficient, led to Pb^{2+} removal in both electrodes, but predominantly in the anode. In the experiment mentioned above, more than 95% of the removed Pb^{2+} ions were converted to PbO$_2$ on the SSW anode.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as a PDF file.

Acknowledgments

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Supplementary Information

Galvanostatic Removal of Pb²⁺ Ions from Diluted Solutions by the Use of a Membrane-Less Flow-Through Cell with Stainless Steel Wool Electrodes

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Table S1. Summary of the ANOVA with the data obtained using the CCRD (Table 1) for the current efficiency (Φ^e), for a 30 min electrolysis

| Source of variation	Sum of squares	Degrees of freedom	Mean square (MS)	F_{ratio} (model significance, MS)
Regression (R)	411.99	5	82.40	$MS_R/MS_r = 34.50^a$
Residual (r)	11.49	5	2.39	
Lack of fit (Lof)	11.42	3	3.81	$MS_{Lof}/MS_{Pe} = 14.63^b$
Pure error (Pe)	0.52	2	0.26	
Total	423.93	10	–	

Determination coefficient: 0.972; $^aF_{5,5} = 5.05$; $^bF_{3,2} = 19.16$ (at 95% confidence level).

Table S2. Summary of the ANOVA with the data obtained using the CCRD (Table 1) for the specific electric energy consumption (w) after a 30 min electrolysis

Source of variation	Sum of squares	Degrees of freedom	Mean square (MS)	F_{ratio} (model significance, MS)
Regression (R)	788611.95	5	157722.39	$MS_R/MS_r = 35.12^a$
Residual (r)	22452.50	5	4490.50	
Lack of fit (Lof)	19392.36	3	6464.12	$MS_{Lof}/MS_{Pe} = 4.22^b$
Pure error (Pe)	3060.15	2	1530.07	
Total	811064.45	10	–	

Determination coefficient: 0.973; $^aF_{5,5} = 5.05$; $^bF_{3,2} = 19.16$ (at 95% confidence level).

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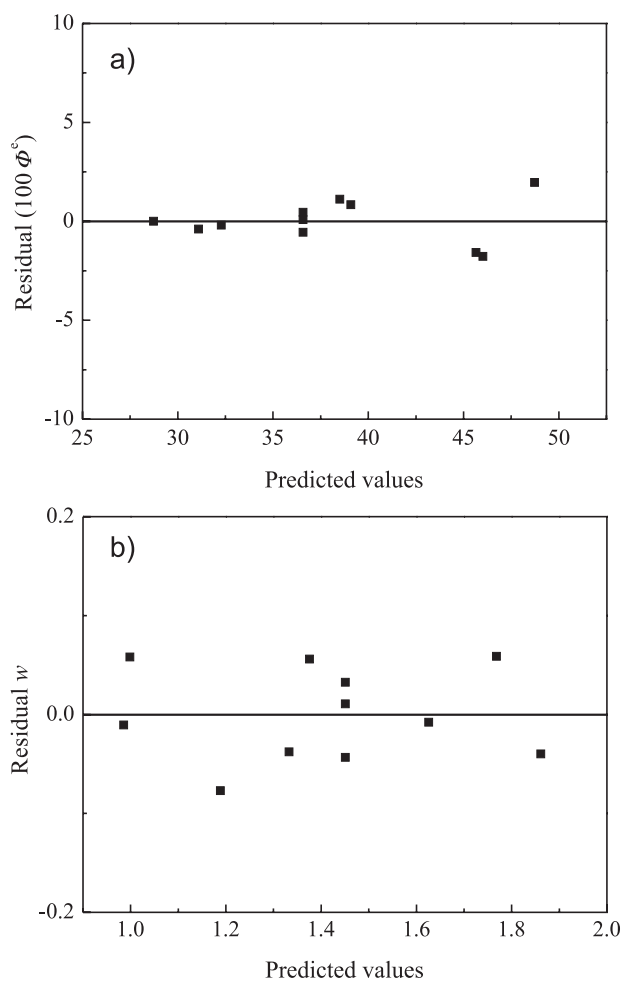
Figure S1. Residual plots for the models of (a) current efficiency (Φ^e) and (b) specific energy consumption (w) for a 30 min of electrolysis under galvanostatic condition, using the flow-through cell with SSW cathodes and anode.
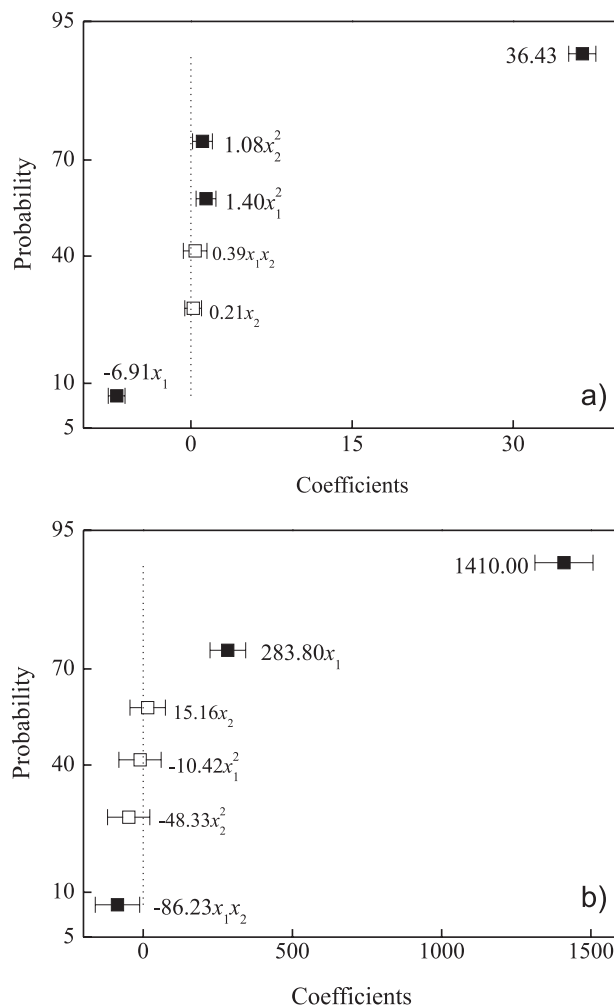
Figure S2. Normal probability plots for the models of (a) current efficiency (Φ^e) and (b) specific energy consumption (w) for 30 min of electrolysis under galvanostatic condition, using the flow-through cell with SSW cathodes and anode.