A comparison of the electrochemical recovery of palladium using a parallel flat plate flow-by reactor and a rotating cylinder electrode reactor

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ABSTRACT

The production of catalytic converters generates large amounts of waste water containing Pd 2+, Rh 3+ and Nd 3+ ions. The electrochemical treatment of these solutions offers an economic and effective alternative to recover the precious metals in comparison with other traditional metal recovery technologies. The separation of palladium from this mixture of metal ions by catalytic deposition was carried out using a rotating cylinder electrode reactor (RCER) and a parallel plate reactor (FM01-LC) with the same cathode area (64 cm²) and electrolyte volume (300 cm³). The study was carried out at mean linear flow velocities of 1.27 < v < 11.36 cm s⁻¹ (120 < Re = vD/ν < 1080) for the FM01-LC reactor and 20 < v < 140 cm s⁻¹ (7390 < Re = vD/ν < 51,700) for the RCER. The morphology of the palladium deposits at the entrance and at the exit of the electrolyte compartment of the FM01-LC reactor showed the effect of the manifold distributors during the electrolysis; the manifolds generate micro turbulences, increasing the mass transport coefficient in these areas and favouring rapid recovery of palladium ions. More uniform high purity palladium deposits were obtained on the surface of the RCER. The cumulative current efficiency to recover 99% of Pd 2+ ions in the parallel plate electrode reactor was 35% while the recovery of 97% of Pd 2+ in the RCER was 62%. The volumetric energy consumption during the electrolysis was 0.56 kW h m⁻³ and 2.1 kW h m⁻³ for the RCER and the FM01-LC reactors, respectively. Using a three-dimensional stainless steel electrode in the FM01-LC laboratory reactor, 99% of palladium ions were recovered after 30 min of electrolysis while in the RCER, 120 min were necessary.

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1. Introduction

The high catalytic activity and corrosion resistance of palladium metal together with the physicochemical properties of its alloys makes it a very important material for industrial and research applications. The widespread use of such applications has contributed to raising the cost of palladium over the last decade [1]. The increasing environmental and technical difficulties to obtain palladium and other platinum group metals (PGM) from natural sources have emphasized the need to search for new and effective recovery methods. PGM can be recovered from the spent catalysts used in different industrial process [2]. One of these processes, the oxidation of the unburned hydrocarbons to carbon dioxide and water in the presence of oxygen taking place within the catalytic converters of modern automobiles, uses most of the palladium produced worldwide [3]. The process on the PGM alloys supported on an inert monolithic substrate based on zeolites, operates as a three-way catalytic reaction carrying out the oxidation of hydrocarbons and CO to CO₂ as well as the reduction of NOₓ to N₂, as indicated in the following reactions:

\[ 4C_\text{m}H_m + (m + 4n)O_2 \rightarrow 2mH_2O + 4nCO \] (1)
\[ 4C_\text{m}H_m + (m + 2n)O_2 \rightarrow 2mH_2O + 4nCO \] (2)
\[ 4nCO + 4O_2 \rightarrow 4nCO_2 \] (3)
\[ 2NO_2 + N_2 + xO_2 \] (4)

During the fabrication process of the catalytic converters, high concentrated solutions, typically between 150 and 200 g dm⁻³ of palladium and 100 and 150 g dm⁻³ of rhodium in concentrated HNO₃, HCl or citric acids, are used. Other metallic ions such as neodymium are used as dispersants to help to impregnate the ceramic zeolite substrate. At the end of the impregnation process the wasted solutions still contain substantial amounts of palladium and rhodium with higher concentrations of neodymium, which is not impregnated on the ceramic substrate and remains in solution. The increasing concentration of neodymium over time after
several impregnation processes, compared with the concentrations of palladium and rhodium, makes the impregnation efficiency low and eventually a point is reached when the concentration of neodymium is too high that the solution cannot longer be used with new substrates. In order to reuse the remaining palladium and rhodium ions, a separation process from the neodymium ions is necessary. The main general characteristic of these solutions is that they are highly acidic, i.e., 1–5 mol dm⁻³ HNO₃ or HCl, which limits the type of recovery process. The processes implemented to recover Pd²⁺ from acid media in the presence of other metallic ions or from solutions containing palladium only, include: extraction with organic solvents [4–6], ionic exchange resins [7,8], adsorbing on activated carbon [9,10] and the use of supported liquid membranes [11]. The majority of these processes use a number of chemical reactants that require more than one unit operation using sophisticated equipment. These processes result in an increase of the operational cost to remove palladium and might not be suitable with the extremely acidic conditions.

Electrochemical reactors used for metal recovery have seen continuous improvement in design and performance over the last three decades [12–14] and they represent a viable option to selectively recover pure metals in its most valuable metallic form. The recovery of palladium from effluents discharged by the catalytic converters manufacturers can be carried out using a filter-press cell or a rotating cylinder electrode cell. These systems are easy to construct and the operational variables can be accurately controlled [15]. Both types of reactor have been widely used for metal recovery from synthetic and industrial solutions with high current densities and good energy efficiencies [16–20]. The different hydrodynamic and mass transport characteristics involved in the design of these two reactors are important during the metal recovery. The present work aims to compare the efficiencies and the volumetric energy consumption during the recovery of palladium ions using a parallel plate filter-press reactor and the rotating cylinder electrode reactor. The design of both types of reactors favours large mass transport regimes.

2. Experimental

2.1. Electrochemical cell

A typical three-electrode glass cell of 50 cm³ capacity for the working electrode compartment was used to study the electrochemical characteristics of the spent solutions containing rhodium, palladium and neodymium ions before the use of the parallel and rotating cylinder reactors. The working electrode was a stainless steel plate 303 (AI304) grade of 0.07 cm². The counter and reference electrodes were a platinum wire and Ag/AgCl(sat), respectively. The working electrode was polished with silicon carbide sand paper grade 600 and 1200 consecutively followed by polishing with microcloth felt (Buehler®) with decreasing particle size of powder alumina (1.0, 0.3 and 0.05 µm). The electrode was finally rinsed with deionised water and left in an ultrasonic bath for 5 min. Linear sweep voltammetry and constant potential electrolysis were applied via a potentiostat–galvanostat EcoChemie Autolab (PGSTAT20) coupled to a PC fitted with a General Purpose, Electrochemical Software (GPES) Version 4.5.

2.2. Reactants and procedure

The electrolyte solution was a mixture of Rh(NO₃)₃ and Pd(NO₃)₂·2H₂O standards (Johnson Matthey) and Nd₂O₃ (Rho dia Electronics & Catalysis) at concentrations of 100, 500 and 1200 mg dm⁻³, respectively, in 1 mol dm⁻³ HNO₃ supporting electrolyte at 298 K temperature. The solutions were deoxygenated with nitrogen for 10 min before each experiment. The volume of electrolyte treated in each electrochemical reactor was 300 cm³ and the working electrode area in each case was 64 cm², maintaining the same ratio electrode area to solution volume at 0.213 cm² cm⁻³ in the two reactors. During the electrolysis at constant potential the electrode was maintained at −0.10 V vs. Ag/AgCl. The cell voltage was measured with a high impedance digital voltmeter. All the experiments were carried out in duplicate and the electrolysis time was 2 h. An aliquot of 1 cm⁻³ was taken from the electrolyte every 10 min to analyse the concentration of the dissolved metal ions. The concentrations were determined by ion plasma (±5% accuracy) coupled to a mass spectrometer detector (ICP-MS) using a model 7500 Agilent.

2.2.1. Electrolysis in the FM01-LC reactor

The parallel plate cell reactor FM01-LC is very versatile and can be used in divided or undivided configuration with an interelectrode gap that can be varied between zero, using lantern blade electrodes, and 0.5 cm to allow space for turbulence promoters or a three-dimensional electrode. The geometric characteristics and full description of this cell has already been given by several authors [15–17]. Fig. 1a and b shows the electrical and electrolytic circuit and an expanded view of the undivided reactor, respectively. A
PTFE turbulence promoter type D, described in Ref. [16], was used in the electrolyte compartment. Two cathodes were used: a flat plate stainless steel and a three-dimensional electrode formed with cross linked stainless steel fibres of approximately 1 mm diameter. In both cases a graphite anode plate was used. The projected area of each electrode was 64 cm² (16 cm × 4 cm) and the interelectrode distance was 0.55 cm for the planar cathode and 0.4 cm for the three-dimensional electrode. The study was carried out at mean linear flow velocities between 1.3 and 11.4 cm s⁻¹, which represent Reynolds number between 120 < Re < 1080. The Reynolds numbers were calculated according to the following relationships:

\[ Re = \frac{\nu d_e}{\nu} \]  \hspace{1cm} \text{parallel plates}  \hspace{1cm} (5)  
\[ Re = \frac{\nu d}{\nu} \]  \hspace{1cm} \text{rotating cylinder}  \hspace{1cm} (6)  

where \( \nu \) is the mean linear velocity (cm s⁻¹); \( d_e \) is the hydraulic diameter of the cell, \( d_e = 2BS/(B+S) \); \( B \) (cm) is the height of the electrodes and \( S \) (cm) their separation; \( \nu \) is the kinematic viscosity (cm² s⁻¹). For the RCER, \( \nu \) is the peripheral velocity (cm s⁻¹), \( \nu = rd_f \); \( d \) is the diameter of the rotating cylinder electrode (cm), and \( f \) is the rotation frequency (rev s⁻¹).

2.2.2. Electrolysis in the rotating cylinder electrode reactor (RCER)

This electrochemical reactor consisted of a stainless steel cathode of 3.8 cm external diameter and 6.1 cm height giving a projected area of 64 cm² and four interconnected graphite plates of 12.5 cm × 4.8 cm × 0.7 cm symmetrically distributed at 1.2 cm distance from the cathode. The electrode was rotated at 100, 300 and 700 rev min⁻¹ using a Silverson L4RT motor of 4/5 HP fitted with variable speed control. The rotating cylinder was polished in sequence with two silicon carbide abrasives (800 and 1200 grade) and then with a felt cloth (Buehler®) using decreasing alumina wet powder of 1.0, 0.3 and 0.05 μm size. The electrode was thoroughly rinsed with distilled water before each experiment. Fig. 2a and b shows the electrical and electrolyte circuits and an upper view of the distribution of the electrodes within the reactor, respectively.

3. Results and discussion

3.1. Diffusion coefficient

Fig. 3 shows the current vs. potential curves of a solution of 1 mol dm⁻³ HNO₃ containing Rh³⁺, Pd²⁺ and Nd³⁺ at 100, 500 and 1200 mg dm⁻³ concentration, respectively using a stainless steel rotating disc electrode (0.07 cm²). The figure also shows the current potential curve for the background electrolyte, which shows that no significant electrochemical activity was observed within the range of 0.3 V to −0.250 V vs. Ag/AgCl. The current potential curves in the presence of the three ions mentioned above start at the open circuit potential (OCP) of 0.31 V vs. Ag/AgCl and the potential at which the current is significant depends on the rotation rate; at 100 rpm, the current started at 0.02 V vs. Ag/AgCl whereas at 1200 rpm the current starts earlier at 0.1 V vs. Ag/AgCl. A steep plateau, characteristic of a mass transport controlled deposition reaction, was observed between −0.02 V and −0.2 V vs. Ag/AgCl. The reaction corresponds to the electrodeposition of palladium [21,22], possibly accompanied by the reduction of hydrogen protons:

\[
[Pd(NO_3)_2(H_2O)_3]^+ + 2e^- \rightarrow Pd + NO_3^- + 2H_2O, \hspace{1cm} E^0 = 0.912 \text{ V vs. SHE} \hspace{1cm} (7)
\]
\[
2H^+ + 2e^- \rightarrow H_2, \hspace{1cm} E^0 = 0.0 \text{ V vs. SHE} \hspace{1cm} (8)
\]

The inset of Fig. 3 shows the Levich plot \( j_l \) vs. \( \omega^{1/2} \), where the linear trend confirms that the reduction is a mass transport controlled process. The limiting currents measured at −0.1V vs. Ag/AgCl were used to plot the Levich equation. The mean diffusion coefficient \( D_1 \) calculated from the slope of the curve was 11.7 ± 0.5 × 10⁻⁶ cm² s⁻¹. This value

Fig. 3. Polarization curves of the synthetic mixture of Rh³⁺, Pd²⁺ and Nd³⁺ at 100, 500 and 1200 mg dm⁻³ in 1 mol dm⁻³ HNO₃, respectively, using a stainless steel electrode disc (0.196 cm²) at different rotation rates: (a) 100, (b) 300, (c) 500, (d) 700, (e) 900 and (f) 1200 at a scan sweep rate of 5 mV s⁻¹. Inset: Levich plot of limiting current density for Pd²⁺ reduction vs. square root of rotation speed at the RDE. The limiting current values were taken at −0.1V vs. Ag/AgCl.
is comparable with other diffusion coefficients values found for palladium ions in different electrolytic media; for example in hydrochloric acid at pH 1 was \(8.96 \times 10^{-6}\) cm\(^2\) s\(^{-1}\) [23], in \(5 \times 10^{-3}\) mol dm\(^{-3}\) perchloric acid + \(5 \times 10^{-2}\) mol dm\(^{-3}\) sodium perchlorate + 7.5 \(\times\) \(10^{-4}\) mol dm\(^{-3}\) palladium chloride the coefficient was 6.7 \(\times\) \(10^{-5}\) cm\(^2\) s\(^{-1}\) [24] and in a solution containing 9.5 \(\times\) \(10^{-4}\) mol dm\(^{-3}\) PdCl\(_2\) + 0.1 mol dm\(^{-3}\) Na\(_2\)SO\(_4\), the coefficient was 9 \(\times\) \(10^{-6}\) cm\(^2\) s\(^{-1}\) [25]. Some authors have reported rather low diffusion coefficient of 2.35 \(\times\) \(10^{-8}\) cm\(^2\) s\(^{-1}\) in a solution containing 0.1 mol dm\(^{-3}\) nitric acid and 20 \(\times\) \(10^{-3}\) mol dm\(^{-3}\) of palladium nitrate [22]. This value is two orders of magnitude smaller despite the fact that the concentration of palladium ions was four times larger. The authors do not provide any reason for this and neither do they compare their value with other works reported in the literature.

3.2. Electrolysis in the parallel plate reactor FM01-LC

Fig. 4 shows the normalised concentration of palladium ions vs. time at different mean linear flow velocities using three configurations of the electrodes: a flat plate, a flat plate electrode with turbulence promoter “D” [16] and a three-dimensional cathode. The electrolysis was carried out at –0.10 V vs. Ag/AgCl. The curves show that on the flat plate in the absence of a turbulence promoter, the fastest depletion of palladium occurs at number of Reynolds of 1080 (11.4 cm s\(^{-1}\)). The figure also shows the comparison at a fixed Reynolds number of 840 (9 cm s\(^{-1}\)) for the three configurations. In the flat plate electrode with an empty channel at Re 840 (9 cm s\(^{-1}\)), 98% of Pd\(^{2+}\) ions were removed in 100 min of electrolysis while in the presence of a turbulence promoter and with the three dimensional electrodes, 99% of palladium ions were removed in 80 and 30 min of electrolysis, respectively. In all cases the selectivity of the process was high: the chemical analysis of the solution shows that Rh\(^{3+}\) and Nd\(^{3+}\) ions remained in solution during this time.

The images of Fig. 5 show the qualitative amount of palladium deposited (darker areas) on the flat plate electrode at different controlled mean linear electrolyte velocities. The accumulation of palladium metal at the entrance of the cell increased with the mean linear flow velocity and the effects of the entrance manifolds that distribute the flow are more noticeable at the highest Re number of 1080 (11.4 cm s\(^{-1}\)). This experimental observation agrees with the theoretical prediction that the formation of the microturbulences increases the mass transport coefficient during the first 3 cm of the reactor inlet and in the width of the electrolyte channel, i.e. along the z-axes [26,27].

The electrochemically recovered palladium was highly pure; the metal was carefully removed from the surface of the stainless steel flat plate electrode and dissolved in nitric acid. The analysis of this solution by ICP shows that 99 wt.% of the deposit is palladium and 1% rhodium and neodymium that were adsorbed on the porous of the deposit. This small percentage suggests that neither Rh\(^{3+}\) nor Nd\(^{3+}\) have electrochemical activity in this electrolyte [28].

3.2.1. Analysis of the electrodeposits after the electrolysis

Some authors have characterized the mass transport of commercial reactors such as the FM01-LC using different methods namely, flow visualization inside the flow channel by dye injection [29,30], laser-induced fluorescence [31], cooper electrodes of known dimensions inside the channel [16] or with mathematical models using a commercial computational fluid dynamics (CFD) packages [26,27]. In this work, the palladium deposits (known as black palladium) on the flat plate electrode at the end of the electrolysis is shown in well defined areas on the electrode surface and can be a quantitative indication of the mass transport in the electrolyte channel. Fig. 5 shows the image of the electrolyte surface at different Reynolds numbers between 120 < Re < 1080 (1.3 < v < 11.4 cm s\(^{-1}\)). The darker areas at the entrance and at the exit of the electrolyte channel indicate that more palladium was deposited on these regions and that the mass transport coefficient was larger in these areas than at the centre of the channel. The less darker areas near the exit indicate lower mass transport than near the entrance of the channel. The reason for this could be the less turbulent regime in the regions that do not coincide with the flow jets of the exit manifold and due to the gradual decrease of the

![Fig. 4](image-url)  Normalised concentration of Pd\(^{2+}\) vs. time during the electrolysis of 500 mg dm\(^{-3}\) Pd\(^{2+}\), 100 mg dm\(^{-3}\) Rh\(^{3+}\) and 1200 mg dm\(^{-3}\) Nd\(^{3+}\) in 1 mol dm\(^{-3}\) HNO\(_3\) at different mean linear flow velocities in three different electrodes using the parallel plate electrode reactor FM01-LC. Flat plate: (a) (●) 1.3 cm s\(^{-1}\); (b) (○) 3.8 cm s\(^{-1}\); (c) (○) 6.3 cm s\(^{-1}\); (d) (□) 9.0 cm s\(^{-1}\); and (e) (□) 11.4 cm s\(^{-1}\). At 3 cm s\(^{-1}\) mean linear electrolyte velocity with (f) (○) turbulence promoter and (g) (●) three dimensional electrode.

![Fig. 5](image-url)  Images of the stainless steel flat plate electrode after the electrolysis of a solution containing Rh\(^{3+}\), Pd\(^{2+}\) and Nd\(^{3+}\) at 100, 500 and 1200 mg dm\(^{-3}\) in 1 mol dm\(^{-3}\) HNO\(_3\), respectively, at different mean linear flow velocities: (a) 1.3 cm s\(^{-1}\); (b) 3.8 cm s\(^{-1}\); (c) 6.3 cm s\(^{-1}\); (d) 9.0 cm s\(^{-1}\); and (e) 11.4 cm s\(^{-1}\).
concentration of palladium ions along the electrolyte channel towards the exit.

At Reynolds numbers between 120 < Re < 1080 (Fig. 5a–d) the “entrance effect” due to the manifold [26,27,32] causes higher local mass transport coefficients than those in the middle of the channel, around 4–15 cm from the inlet of the electrolyte, when the flow has developed. The effect of the exit manifold can also be observed at the end of the reactor channel where the amount of palladium increases with the mass transport Fig. 5d and e. As the Reynolds number increases, the amount of palladium accumulated at the end of the electrolyte channel is larger as the local mass transport is again larger than in the centre of the channel.

It can be seen that in the range 120 < Re < 840, the accumulation of palladium at the entrance reaches up to 4 cm approximately and at the end of the channel after 15 cm. This leaves a region between 4 cm and 15 cm were the flow develops into a laminar flow. This behaviour was also observed by Vázquez et al. [26,27] who used the data for the redox couple Cu2+/Cu+ from Brown et al. [16]. They predicted the velocity profiles and the local mass transport coefficients along the electrolyte channel in the same electrolytic cell using CFD methods and compared these values with the k_m values obtained from the empirical equation proposed for Pickett [33] and the k_m values obtained from current limiting current values by Brown et al. [16].

Vázquez et al. [26,27] found that a fully developed flow in this cell occurred in 70% of the electrolyte channel between 4 and 15 cm after the inlet of the electrolyte at Re numbers between 197 and 787 (2.4–9.7 cm s⁻¹). In the same range of mean electrolyte flow velocities, Brown et al. [16] measured the currents generated along the channel and found that the areas with larger currents were at the entrance (0–4 cm) and at the exit (15–16 cm) which agrees with the findings proposed by Vázquez et al. [26,27]. In fact the comparison of the mass transport coefficients obtained by CFD and the experimental values from Brown et al. [16], a relative error of 4.5% and 28.6% at Reynolds numbers of 197 (2.4 cm s⁻¹) and 533 (6.5 cm s⁻¹), respectively, was reported. At a Re number of 1080 (11.4 cm s⁻¹) Fig. 5e shows that this behaviour is slightly different since the accumulation of palladium metallic occurs mainly at 6 and 9 cm from the channel entrance and at 3 and 4 cm in the y-axes. Our observation is qualitative based on the intensity of the darkness of the deposit, which gives only a rough indication. The microturbulences or recirculations increases at high flow velocities causing higher rates of metal removal [30]. This can be explained because the relative error found by Vázquez et al. [26,27] was considerably larger (41%) when the values of the mass transport coefficient k_m, calculated by CFD and experimentally were compared at a Reynolds number of 918 (11.0 cm s⁻¹), which is a similar mean linear flow velocity to the one used in this paper.

### 3.3. Electrolysis in the rotating cylinder electrode (RCER)

The rate of palladium removal from a solution of 1 mol dm⁻³ HNO₃ containing Rh⁴⁺, Pd⁰²⁺ and Nd³⁺ at concentrations of 100, 500 and 1200 mg dm⁻³, respectively was determined using the rotating cylinder electrode reactor. Fig. 6 shows the decay of the normalised concentration of palladium vs. time when a potential of −0.10 V vs. Ag/AgCl was applied to the cylinder electrode. At low Re numbers of 7390 (20 cm s⁻¹) and 22,167 (60 cm s⁻¹) the rate of recovery depends on the mass transport velocity of the electrolyte but the concentration decay appears to be linear. At the two higher Re numbers, 37,000 (100 cm s⁻¹) and 51,700 (140 cm s⁻¹) the concentration decay is exponential and very similar and does not increase with the increase of the Reynolds number. It was found that redissolution of palladium metallic, back into the solution occurs at Re number higher than 51,700 (140 cm s⁻¹). The reason of this dissolution is not clear but we assume that is due to the very high shear velocity occurring at more than 100 cm s⁻¹ peripheral velocity on the surface of the cylinder electrode, which is able to detach the newly formed metallic palladium.

Fig. 6 shows that at Reynolds number of 37,000 (100 cm s⁻¹) and 51,700 (140 cm s⁻¹), 97% and 98% of the palladium ions have been removed after 120 min on the RCER. If compared with the rate of palladium recovery using the FM01-LC parallel plate electrode reactor with an empty channel, Fig. 4 shows that 98% of palladium ions have been removed in 100 min at Re number of 840 (9 cm s⁻¹). Using a turbulence promoter and a three dimensional electrode in this reactor, the recovery of 99% palladium ions occurred at 80 and 30 min, respectively. This indicates the advantages of the turbulence promoters and the 3D electrodes as well as the role of the jets flow distributor in the manifold of the FM01-LC that favour mass transport and makes the recovery process faster than that on the rotating cylinder electrode reactor.

### 3.4. Figures of merit

The comparison of the two types of electrochemical reactors during the recovery of palladium ions was obtained through the calculation of several performance parameters such as: the product of the mass transport coefficient and the electrode area per unit volume, k_mA_e for parallel plate and k_mA_e for three dimensional electrode, the current efficiency, φ and the volumetric energy consumption, E_v, using the following expressions [15]:

\[
\ln \left( \frac{C(0)}{C(t)} \right) = -k_mA_e t, \quad \text{flat plate electrode, channel flow} \tag{9}
\]

\[
\ln \left( \frac{C(0)}{C(t)} \right) = -k_mA_e t \frac{V_e}{V_R}, \quad \text{three-dimensional electrodes} \tag{10}
\]

where A_e is A/V_e and A/V_e for the flat plate and three-dimensional electrodes, respectively.

\[
\%\phi = 100 \times \left( \frac{2FE_{cell} \Delta c}{MRT} \right) \tag{11}
\]

\[
E_v = \frac{2FE_{cell} \Delta c}{3.6 \times 10^4 \mu M} \tag{12}
\]
Table 1: Performance measurements during the highest recovery of Pd$^{2+}$ ions taken after of electrolysis. Electrolyte: 1 mol dm$^{-3}$ HNO$_3$ containing Rb$^+$, Pd$^{2+}$ and Nd$^{3+}$ at concentrations of 100, 500 and 1200 mg dm$^{-3}$, respectively: (a) parallel plate electrode reactors. TP is turbulence promoter D [16] and (b) rotating cylinder.

<table>
<thead>
<tr>
<th>Reynolds number (mean linear flow rate, v$_i$ (cm s$^{-1}$))</th>
<th>Electrolysis time (min)</th>
<th>Metal recovered (%)</th>
<th>Mass transport area, $10^4 	imes k_m A_e$ (s$^{-1}$)</th>
<th>Current efficiency, $\phi$ (%)</th>
<th>$E_t$ (kWh m$^{-3}$)</th>
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<tbody>
<tr>
<td>(a) FM01-LC</td>
<td></td>
<td></td>
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<tr>
<td>120 (1.3)</td>
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<tr>
<td>1080 (11.4)</td>
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<td>(b) RCER</td>
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</table>

where $z$ is the number of electrons, $F$ is the Faraday constant, $M$ is the molar mass of metal, $l$ the applied current, $V_{cell}$ the cell voltage, $\Delta C$ the concentration difference, $C_i$ and $C_o$ the concentration at time zero and $t$ of the electrolysis, respectively. $A$ the electrode area, $q$ the average electrical charge during the electrolysis time and $V_{el}$ the volume of electrolyte within the reactor and $V_e$ the electrode volume.

Table 1 shows the values of $k_m A_e$, $\phi$ and $E_t$ for the highest palladium recovery after electrolysis for each reactor. The first noticeable effect is that the global mass transport coefficient associated with the electrode area is larger as the mean linear velocity increases in the two reactors. In the parallel plate electrolyte reactor without turbulence promoter the microturbulences at the inlet and outlet of the channel increase the product of the global mass transport coefficient associated with the electrode area per unit volume, $k_m A_e$. This results in more palladium metal deposited and an increase of the electrode area as shown in Fig. 5 by the darker zones where more palladium is deposited near the inlet and the exit of the channel. When comparing the value of $k_m A_e$ without $3.25–5.25 \times 10^{-4}$ s$^{-1}$ and with $7.60 \times 10^{-4}$ s$^{-1}$ turbulence promoter at Re of 840 (9 cm s$^{-1}$). Table 1 shows that the global mass transport increases by 1.4 times despite the fact that some areas of the electrode are blocked by the contact with the turbulence promoter. When a three dimensional stainless steel electrode was used the increase of the $k_m A_e$ value respect to the empty channel was 4.2 times at the same mean flow velocity, however this increase is mostly due to the high surface electrode area of this electrode. The values of the $k_m A_e$ product obtained in the RCER are lower compared with the FM01-LC reactor even under the consideration that in this reactor the highest mean linear flow velocity provide a very good mixing of the electrolyte and the Reynolds numbers used were always higher. The mass transport coefficients associated to the area for other systems are within the same order of magnitude as those presented in Table 1. For example using stainless steel rotating cylinder electrodes Rivera et al. [34] found $k_m A_e$ values of $3.25–5.25 \times 10^{-4}$ s$^{-1}$ during the recovery of 922 mg dm$^{-3}$ of copper ions from a chromium-plating industry and Grau and Bisang [35] found $k_m A_e = 0.83 \times 10^{-4}$ s$^{-1}$ for the recovery of cadmium from a 500 mg dm$^{-3}$ solution of its ions.

Comparing the current efficiencies of the recovery process in the two reactors, the value was higher for the RCER than in the FM01-LC reactor. This could be due to the fact that palladium metal deposits are more homogeneous on the cylinder electrode surface, resulting in more uniform current and potential distributions. The current efficiency in the RCER decreases as the Reynolds number increases due to the re-dissolution of Pd metallic back into the solution. In the FM01-LC the experimental and theoretical evidence shows that palladium metal deposition occurs mainly at the entrance and exit of the electrolyte channel suggesting slightly uneven current and potential distributions. Table 1 also shows the values of the volumetric energy for the two systems. In general, the volumetric energy required by the parallel plate electrode reactor FM01-LC is higher than for the RCER, especially when the three dimensional electrode was used. This could be compensated by the fact that only 30 min were required to extract 99% of the palladium ions in the 3D electrode. The volumetric energy consumptions using the RCER are always lower than 1 kWh m$^{-3}$, which agrees with the higher current efficiency observed in this system. These values are lower when compared with the volumetric energy efficiency in other electrochemical recovery systems using cylindrical electrodes, for example: copper recovery in a RCE (4–7 kWh m$^{-3}$) [34], tin recovery on cylindrical graphite bars (2–10 kWh m$^{-3}$) [36] and cadmium on an undivided RCE reactor (1–2.5 kWh m$^{-3}$) [35].

3.5. Mass transport

The mass transport coefficient associated to the electrode area $k_m A_e$ was calculated for the parallel plate electrode reactor containing a three dimensional electrode. The values of $k_m A_e$ as a function of the mean linear velocity of the electrolyte were adjusted to the equation:

$$k_m A_e = p v^q$$  \( (13) \)

where $q$ is associated to the hydrodynamic regime [37,38]. Fig. 7 shows the log $k_m A_e$ vs. log $v$ for an empty channel and for a channel containing the stainless steel 3D electrode during the recovery of Pd$^{2+}$ ions. The curves were obtained from the limiting current values taken from the polarization curves when the potential was sweep from the OCP at 0.31 V to $-0.25 V$ vs. Ag/AgCl at 3 mV s$^{-1}$ potential sweep rate and mean linear flow velocities within the range $1.26 \leq v \leq 12.62$ cm s$^{-1}$ ($120 \leq Re \leq 1080$). The limiting currents were taken at $-0.1 V$ vs. Ag/AgCl. In both cases, the q values (Eq. (13)) are within the same order of magnitude: 0.60 for the empty channel and 0.52 for the three dimensional electrode. This shows that despite been within the limits of a laminar flow ($120 \leq Re \leq 1080$) the flow, developed inside the cell appears to be as turbulent as $q$ is larger than 0.30, characteristic of a laminar flow [27,33]. The slightly lower $q$ value for the three dimensional electrode could be due to a flow laminization similar to the one observed by Brown et al. [17] for nickel three-dimensional electrodes and Bengoa et al. [29] where the flow pattern is uniform along the channel due to the better axial dispersion when metallic foams and turbulent promoters inside the channel of the FM01-LC reactor were used. In their work the authors report q values around 0.41 and 0.51 for electrodes with similar geometry, indicating that in the three-dimensional electrodes the flow tends to
be laminar. For comparison, Fig. 7 also shows this effect on the $q$ value for the curves obtained when a solution of ferricyanide and copper sulphate were used with nickel and copper flat plate electrodes, respectively. The $q$ values obtained for the ferricyanide and the copper systems are similar, 0.70 and 0.71, respectively, and like the $q$ value displayed in this work (0.60), they denote clear turbulent flow behaviour.

### 4. Conclusions

Palladium ions could be selectively recovered up to 99% purity from a synthetic mixture and from a solution obtained from a catalytic converter manufacturer containing Pd$^{2+}$, Rh$^{3+}$ and Nd$^{3+}$ in 1 mol dm$^{-3}$ HNO$_3$. The microturbulences, due to the jets stream of the manifolds in the FM01-LC reactor at the inlet and at the exit of the electrolyte channel, favours high mass transport and help to decrease the electrolysis time (<100 min) to recover palladium ions, in comparison with the RCR (~120 min). As a result the deposition of palladium in the FM01-LC was localised at the entrance and near the exit of the electrolyte channel. In contrast, the rotating cylinder electrode reactor shows homogeneous and even metal deposition on the surface but more electrolysis time was needed to recover the same amount of palladium ions.

The current efficiency in the FM01-LC reactor varies between 24% and 35% while in the RCR is 40–84%. The decrease of the current efficiencies as the Reynolds number increases in the RCR is due to the re-dissolution of palladium metallic into the solution. The FM01-LC reactor requires more energy per volume (1.08–2.86 kW h m$^{-3}$) than the rotating cylinder electrode (0.56–0.88 kW h m$^{-3}$) for the electrochemical recovery of 96–99 wt.% of palladium ions from spent solutions used to manufacture catalytic converters.

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### References


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**Fig. 7.** Log $k_A/v_A$ vs. log $v$ for three different solutions: 100 mg dm$^{-3}$ (0.97 x 10$^{-3}$ mol dm$^{-3}$) Rh$^{3+}$, 500 mg dm$^{-3}$ (5 x 10$^{-3}$ mol dm$^{-3}$) Pd$^{2+}$ and 1200 mg dm$^{-3}$ (8.32 x 10$^{-3}$ mol dm$^{-3}$) Nd$^{3+}$ in HNO$_3$. 1 mol dm$^{-3}$; with empty channel (●) and for a channel containing a stainless steel three dimensional electrode (□); and for a channel containing a stainless steel three dimensional electrode (○); 7 x 10$^{-3}$ mol dm$^{-3}$ potassium ferricyanide plus 12.5 x 10$^{-3}$ potassium ferrocyanide in 1 mol dm$^{-3}$ potassium hydroxide, nickel electrode with empty channel (■)[17]. 7 x 10$^{-3}$ CuSO$_4$ in 1.5 mol dm$^{-3}$ H$_2$SO$_4$, empty channel with a flat plate copper electrode (▲)[16,26].