The use of a rotating cylinder electrode to recover zinc from rinse water generated by the electroplating industry

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ABSTRACT

This work concerns the application of a laboratory scale rotating cylinder electrode (RCE) to recover zinc from rinse water generated by the electrolytic zinc process (initially 1,300, 4,400, 50, 20 mg L^{-1} of Zn(II), Fe(III), Ag(I) and Cr(VI), respectively, at pH 2), although it is also applicable to other electroplating industries. Experimental results demonstrated the convenience of the removal of ferric ions, as (Fe(OH)$_{3(s)}$) by a pH adjustment to 4, before zinc electro recovery on the RCE. The generation of smooth zinc deposits on the RCE was obtained at Reynolds numbers within the range of $15,000 \leq \text{Re} \leq 124,000$ and limiting current densities (J_L) in the interval of -4.8 to -13 mA cm^{-2}. The zinc recovery reached a conversion of 67% in 90 min of electrolysis for Re = 124,000 and $J = -13$ mA cm^{-2}, 21% current efficiency, and energy consumption of 9.5 kWh m^{-3}. The treated solution can be recycled back through the same rinsing process.

Key words | electroplating industry, metal ions removal, rinse water, rotating cylinder electrode, zinc deposition

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INTRODUCTION

The metallic zinc-plating industry generates large amounts of aqueous effluents, which contain heavy metals, originating from the rinses of metal-coated items (Walsh 2001). The removal of these metals is traditionally carried out by physicochemical methods, where different metals are precipitated as hydroxides, generating great amounts of sludge that must be subsequently confined. Even with this treatment, solubility limits for heavy metal hydroxides in many instances exceed those allowed by the environmental legislation (Rivera et al. 2008).

Electrochemical technologies have attracted attention, because they recover metals in their most valuable form: a zero-valence state, without requiring the addition of chemicals, which generate byproducts and would later require treatment or confinement (Fornari & Abbruzzese 1999; Ragnini et al. 2000; Walsh 2001; Rivera et al. 2008). Moreover, electrorecovered metals and water, treated with these electrochemical methods, can be reutilized in the same process. The latter avoids economic loss due to required treatment, and reduces water consumption and environmental impact.

In a previous paper by our group, the convenience of using a rotating cylinder electrode (RCE) for the recovery of copper from an effluent, generated by the plastics chromium-plating industry, was demonstrated on a laboratory scale (Rivera et al. 2008). Moreover, this reactor has been used for recycling zinc from solutions obtained in mining processes (St-Pierre et al. 1996), for tin and cadmium recovery (Bazan & Bisang 2004; Grau & Bisang 2007), for photo silver recovery (Wang et al. 2000), for the removal of copper contained in effluents (Masse et al. 1995), and for selective palladium recovery from acid solutions (Terrazas-Rodríguez et al. 2011).

The formation of metal deposits under mass-transport-limited conditions is achieved by applying a limiting current density to the RCE and by rotating the cylinder under turbulent flow conditions (Gabe & Walsh 1984; Rivera & Nava 2007). Recently, our group characterized the mass transport for a laboratory scale RCE during zinc deposition from synthetic dilute solution, in the Reynolds interval comprising between $15,000 < \text{Re} < 125,000$, and established this correlation (Recéndiz et al. 2011), for the same cell employed here:

$$\text{Sh} = 0.65 \, \text{Re}^{0.48} \, \text{Sc}^{0.356} \qquad (1)$$

The value of the coefficient, 0.65, is associated with shape and cell dimensions, whereas the exponent of

Reynolds number (Re), 0.48, is attributed to the hydrodynamic conditions at the deposit-RCE interface. The difference between this correlation and those obtained by other authors is discussed in detail in a previous publication (Recéndiz *et al*. 2011). The Sherwood number (Sh) is related to mass transport by forced convection:

$$Sh = \frac{k_m d}{D} \qquad (2)$$

The Re is associated with hydrodynamics originated by inner cylinder rotation:

$$Re = \frac{ud}{v} \qquad (3)$$

And the Schmidt number relates to the electrolyte properties:

$$Sc = \frac{v}{D} \qquad (4)$$

where k_m is the mass transport coefficient in cm s^{-1}, d is the rotating cylinder electrode diameter in cm, D is the diffusion coefficient of the electroactive specie in cm^2 s^{-1}, u is the peripheral velocity imposed by the rotation of cylindrical electrode in cm s^{-1}, and v is the kinematic viscosity of the electrolyte in cm^2 s^{-1}.

Thus, the limiting current density (J_L), Equation (6), is obtained by combining Equations (1), (2), and (5):

$$k_m = \frac{J_L}{zFC_o} \qquad (5)$$

$$J_L = 0.65 \frac{zFDC_o}{d} Re^{0.48} Sc^{0.356} \qquad (6)$$

where z is the number of electrons exchanged in the electrochemical reaction, F is the Faraday constant (96,485 mol^{-1}), and C_o is the electroactive species concentration in the bulk in mol cm^{-3}. In Equation (6) J_L is observed to depend on the velocity applied to the RCE and the electrolyte properties.

This paper concerns the zinc recovery from rinse water generated by the electroplating industry using a laboratory scale RCE, particularly from the electrolytic zinc process. The recovery of zinc as deposit on RCE was carried out by applying a limiting current density to the RCE at different Reynolds numbers.

METHODS

Experimental details

The waste rinse water used herein was generated by a zinc electrolytic process (Table 1). Analytical grade reactants and deionized water (Milli-Q™) were also employed.

Equipment

For the electrolyses, a potentiostat-galvanostat EG&G model PAR 273, with M270 software, was employed. Metal ions concentration was determined with a 220FS Spectra AA Varian Atomic Absorption Spectrometer.

Figure 1(a) shows the diagram of a device fabricated for the laboratory studies (Rivera *et al*. 2008; Recéndiz *et al*. 2011), consisting of a 500-cm^3 glass reactor with a temperature controlled bath. A 316 stainless steel cylinder with a 3.8 cm diameter and a length of 11 cm was used as the cathode. Six RuO$_2$/TiO$_2$ dimensional stable anodes (DSA) plates, supplied by De Nora™, 13 cm long, 2 cm wide and 0.3 cm thick, interconnected and attached to the reactor wall

Table 1 | Typical analysis of rinse water, initial value and after iron precipitation. Metal ions concentration was determined by atomic absorption analysis

Element	Initial conc.[a]/mg L^{-1}	Conc. after iron precipitation[b]/mg L^{-1}
Zn	1,300	1,220
Fe	4,400	35
Ag	50	20
Cr	20	3

[a]The typical pH value of rinse water was 2.
[b]The resulting pH 4 was adjusted to precipitate iron.
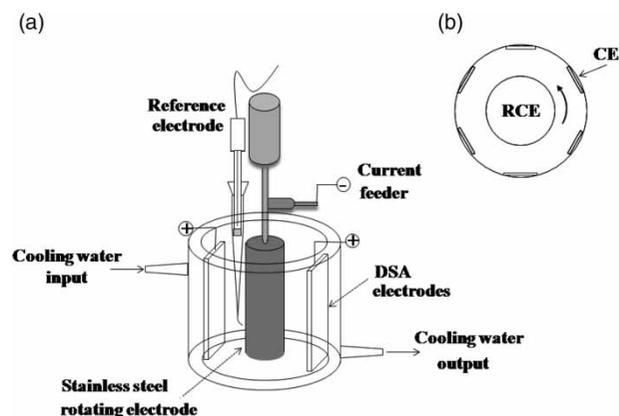

Figure 1 | (a) Rotating cylinder electrode scheme, (b) device employing six plates as the counter electrode.

(Figure 1(b)), were used as anodes. The six-plate device employed as the counter electrode prevents vortex formation. Table 2 shows the parameters of the RCE cell used in this work and its electrolyte transport properties. An electric motor of variable velocity (Caframo™, model BDC 3030) was used to rotate the inner cylinder. It is important to point out that the RCE used in this work is similar to that reported by Rivera *et al.* (2008) and Recéndiz *et al.* (2011).

Methodology

Pretreatment of the waste rinse water (iron precipitation)

The presence of iron during electrolysis experiments (not shown herein) obstructed the removal of zinc, maintaining constant its concentration versus time. In addition, considering that iron provokes loss in current efficiency, it was removed from the waste rinse water through precipitation. Iron precipitation consisted in the complete oxidation of ferrous to ferric ions by adding hydrogen peroxide (30%), followed by a pH adjustment to 4, with caustic soda, to precipitate ferric ions as ferric hydroxides ($Fe(OH)_{3(s)}$). It is important to point out that silver, chromium, and zinc at pH 4 remain soluble in the solution.

Electrolyses at RCE

Table 3 shows the limiting current density values (J_L), estimated by Equation (6), as a function of Re. The J_L values become more quantitative with Re, because the Nernst diffusion layer is comprised of convection, enhancing the rate of the electrochemical process under mass-transport-limited conditions. These currents were used for the cathodic

Table 2 | RCE reactor parameters and electrolyte properties

Reaction volume, V_R	350 cm^3
RCE diameter, d	3.8 cm
RCE length, L	11 cm
RCE area, A_{RCE} (in contact with electrolyte)	80 cm^2
Distance of RCE to the bottom	0.03 cm
Length and width of the plates used as anodes (attached to the reactor walls)	13 cm × 2 cm
Anode and cathode gap	1.75 cm
Counter electrode area, A_C, (six plates, in contact with the solution)	84 cm^2
Diffusion coefficient, D (Recéndiz *et al.* 2011)	2.92×10^{-6} cm^2 s^{-1}
Kinematic viscosity, ν (Recéndiz *et al.* 2011)	0.01 cm^2 s^{-1}

Table 3 | Limiting current densities applied to RCE as a function of Reynolds values (determined by Equation (6) and electrolyte properties reported in Table 2)

Re	J_L/mA cm^{-2}
15,000	−4.8
62,000	−9.4
124,000	−13

removal of Zn(II) from the waste rinse water after iron precipitation. The sampling time for the analyses of Zn(II) was every 2 min at the beginning of electrolysis, $t \leq 10$ min, in order to observe the nucleation process at stainless steel; then this sampling time was increased from 5 to 20 min, where massive deposition of zinc onto the zinc coating occurs (Recéndiz *et al.* 2007). The J_L values were determined on the basis of the parameters and electrolyte properties reported in Table 2. The cylinder surface was polished with 240 grit silicon carbide paper and rinsed with distilled water before each experiment. It is important to mention that at these turbulent conditions, $15,000 \leq Re \leq 124,000$, the convection originating from the rotation of the inner cylinder predominates over the convection induced by the gas (oxygen) generated at the counter electrode, which is quickly removed from the counter electrode and electrolyte (Rivera & Nava 2007). All the electrolyses were performed at $T = 298$ K.

RESULTS AND DISCUSSION

Pretreatment of the waste rinse water (iron precipitation)

The composition of the solution resulting from the pretreatment considered here is compared with the initial composition and given in Table 1. It is clearly observed that iron removal is almost complete (from 4,400 to 35 mg L^{-1}) and the zinc concentration remains practically constant (from 1,300 to 1,220 mg L^{-1}). The 60 and 85% removal of silver and chromium, respectively, after preconditioning the solution, can be associated with the precipitation process of these metal ions with the iron hydroxide.

Zinc recovery using RCE

Considering that iron provokes a current efficiency loss during zinc electrorecovery, the rinse water was employed after iron precipitation. The metal ion concentrations obtained at the end of the three electrolyses performed on

the RCE, at three different Reynolds numbers (15,000, 62,000 and 124,000), are compared with the initial concentrations, and shown in Table 4. This table also shows pH values after the electrolysis.

Analysis of Table 4 reveals that zinc removal was successful for the three different Re. The iron concentration diminished slightly, while the removal of silver and chromium was complete at the end of the three electrolyses. On the other hand, pH suffered a slight decrease at the end of electrolysis due to increase of proton concentration during water anodic oxidation at the anode.

The silver removal is due to its deposition on the RCE interface, as the deposition potential of Ag(I)/Ag(0) is 1,200 mV more positive than that of Zn(II)/Zn(0) (Pourbaix 1974). The removal of iron and chromium can be associated with their precipitation as $Fe(OH)_{3(s)}$ and $Cr(OH)_{3(s)}$ at the RCE interface, due to hydrogen evolution, which usually occurs during zinc deposition (Recéndiz et al. 2007), producing an elevated local pH. It is important to mention that the reduction potential of H^{+}/H_2 is 800 mV more positive than that of Zn(II)/Zn (Pourbaix 1974). The quality of recovered zinc was estimated at a value of 94% for the three electrolyses shown in Table 4.

Figure 2 shows the normalized decay of the Zn(II) concentration as a function of the electrolysis time at three different Reynolds (15,000, 62,000 and 124,000). The initial part of the electrolysis, $t < 20$ min, is apparently independent of Re, and at longer times these curves show dependence on Re. For the curve corresponding to a Re of 15,000, between 25 and 50 min, the depletion of Zn(II) remains constant; afterwards, the concentration decreases linearly with time. For the electrolysis performed at Re of 62,000, the zinc ions decrease linearly during the electrolysis time. The behaviour observed for the electrolysis at Re of 124,000 is quite different, showing two plateaus at $30 <$
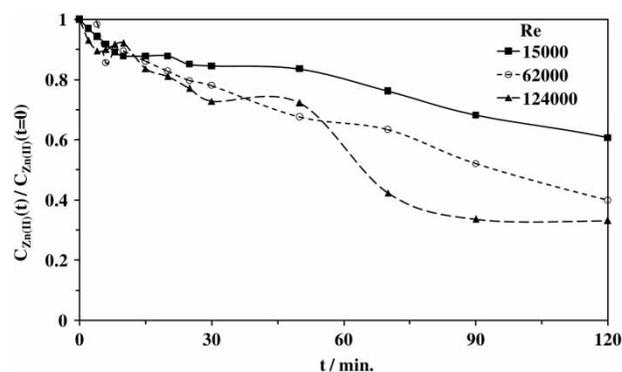
Table 4 | Metal ion concentration in rinse water

	Initial conc.	Conc. at the end of electrolysis (120 min)		
		Re 15,000[a]	Re 62,000[b]	Re 124,000[c]
$C_{Zn(II)}$/mg L^{-1}	1,220	740	480	400
$C_{Fe(III)}$/mg L^{-1}	35	25	10	10
$C_{Ag(I)}$/mg L^{-1}	20	0	0	0
$C_{Cr(VI)}$/mg L^{-1}	3	0	0	0
pH	4	3.5	3.5	3.5

J_L was taken from Table 3.
[a]$J_L = -4.8$ mA cm^{-2},
[b]$J_L = -9.4$ mA cm^{-2},
[c]$J_L = -13$ mA cm^{-2}.

Figure 2 | Normalized decay of the Zn(II) concentration during electrolysis of the rinse water in the RCE at Reynolds numbers of: 15,000 (-4.8 mA cm^{-2}), 62,000 (-9.4 mA cm^{-2}), and 124,000 (-13 mA cm^{-2}). $A_{RCE} = 80$ cm^{-2}, $V_R = 350$ cm^3, $T = 298$ K.

$t < 50$ min and at $90 < t < 120$ min. The curves shown in Figure 2 did not present an exponential decay of the normalized zinc concentration as expected.

The independence, with respect to the Re, of the zinc depletion at short electrolysis times, $t < 20$ min, can be attributed to the formation of the first nuclei of zinc on the stainless steel surface, which is random and has a varying degree and distribution of protuberances. This last is in agreement with that previously reported during the electro winning of zinc from concentrated solutions in sulfuric acid medium (Recéndiz et al. 2007) and during the deposition of zinc from dilute solutions (Recéndiz et al. 2011).

The linear depletion of zinc at $t > 20$ min, for the electrolyses performed at Reynolds of 15,000 and 62,000, can be determined by the hydrogen evolution (Recéndiz et al. 2007, 2011). With respect to the electrolyses at Re of 124,000, the apparition of two plateaus at $30 < t < 50$ min and at $90 < t < 120$ min may be due to the more quantitative reduction of protons from the medium and the subsequent modification of the interfacial pH, probably giving rise to the formation of surface Zn hydroxides. It is important to remark that, at Re of 124,000, normalized zinc concentration decreases to 0.33 (400 mg L^{-1}), which represents 67% zinc recovery, in 120 min. The recoveries of zinc obtained here were less than those obtained by St-Pierre et al. in 1996, who obtained 96% zinc recovery from synthetic solutions (initially 5,000 mg L^{-1} Zn(II) in 1 M H_2SO_4; finally 200 mg L^{-1} Zn(II)), at 295 K, using a RCE, under limiting current conditions. The best zinc recovery obtained by St-Pierre and coworkers is mainly attributed to the initial concentration of zinc ion, which was four times greater than that employed herein. On the other hand, the treated solution here can be recycled back through the same rinsing process owing to the rinsing water, in

practice, having similar quality to that obtained at the end of the electrolysis (120 min) (Table 4).

Figure 3 shows current efficiencies of the Zn(II)/Zn process at the RCE for the three electrolyses shown in Figure 2. These were obtained using Equation (7) (Rivera *et al.* 2008):

$$\varphi = \frac{zF\Delta C_{Zn(II)}V_R}{Q} \times 100 \tag{7}$$

where φ is the current efficiency (dimensionless) $\Delta C_{Zn(II)} = (C_{Zn(II)}(t=0) - C_{Zn(II)}(t))$ in $mol\,cm^{-3}$, V_R is the solution volume in cm^3, and Q is the total charge employed in the electrolysis in coulombs.

Analysis of Figure 3 reveals the dependence of current efficiencies on the percentage of zinc recovered; however, these efficiencies do not show a marked dependence on convection. Particularly, in zinc recoveries above 20%, the efficiency drastically decreases (approx. 20%) for the three Reynolds studied. These low current efficiencies are attributed to zinc deposits formed at fixed limiting current densities, which were calculated based on the initial concentration of zinc. The hydrogen evolution partial current increases as the zinc concentration decreases (partial current due to zinc reduction decreases), as the total current density is fixed. Thus zinc recovery efficiency decreases with the percentage of zinc recovered.

Current efficiencies obtained here are similar to those reported by other authors during removal of zinc with a RCE from a solution, originating from mining residues, which initially has $6,800\,mg\,L^{-1}$ (St-Pierre *et al.* 1996). These authors obtained low current efficiencies, at holding limiting current conditions, due to the parasitic hydrogen evolution reaction. Recently Nava and coworkers reported 95% current efficiency during Cu(II) removal (from 922 to
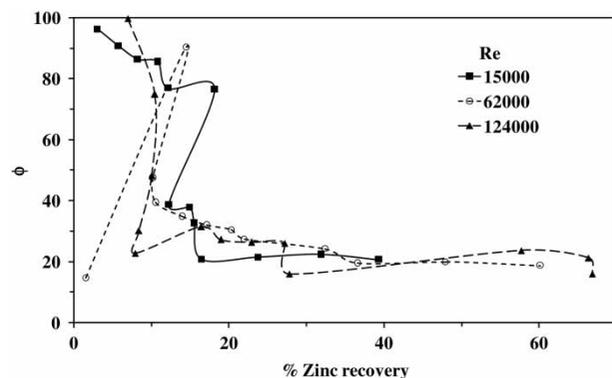
Figure 4 | Energy consumption (Equation (8)) during zinc removal from rinse water in the RCE, evaluated from the electrolyses similar to those in Figure 2.

$43\,mg\,L^{-1}$, at J_L of $25\,mA\,cm^{-2}$), coming from a rinse water from the electrolytic copper process (Rivera *et al.* 2008).

Figure 4 shows energy consumption (E_{cons}) of the Zn(II)/Zn process at the RCE for the three electrolyses shown in Figure 2, using Equation (8) (Rivera *et al.* 2008):

$$E_{cons} = \frac{zFE_{cell}\Delta C_{Zn(II)}}{\varphi 3.6} \times 100 \tag{8}$$

where E_{cell} is the cell potential in volts, and 3.6 is a factor that converts to $kWh\,m^{-3}$ units.

The analysis of Figure 4, for the three Re studied (15,000, 62,000 and 124,000), shows that energy consumption increases as a function of the percentage of zinc recovery to achieve values between $0.5 < E_{cons} < 10.4\,kWh\,m^{-3}$.

The electrochemical treatment applied to rinse water at RCE, through removal of Zn(II), permits, on one hand, this treated water to be recycled back through the same rinsing process, and, on the other hand, the metallic zinc recovered can be reutilized in the same electroplating industry. The results shown here indicate that this process can be successfully applied achieving a 67% zinc recovery at 90 min of electrolysis, with $9.5\,kWh\,m^{-3}$ energy consumption at Re = 124,000 and $J = -13\,mA\,cm^{-2}$.

CONCLUSIONS

It has been demonstrated that quantitative zinc electrorecovery with a RCE from rinse water generated by the electroplating industry (initially 1,300, 4,400, 50, 20 mg L^{-1}

Figure 3 | Integral current efficiencies (evaluated from Equation (7)) during zinc removal from the rinse water in the RCE, evaluated from electrolyses similar to those in Figure 2.
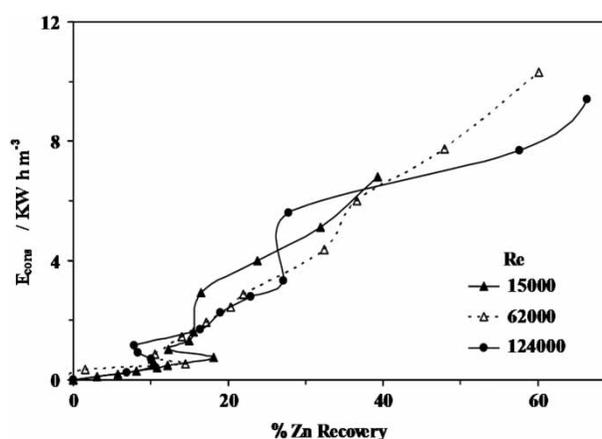
of Zn(II), Fe(III), Ag(I) and Cr(VI), respectively, at pH 2) is possible if iron has been previously removed from the solution as $(Fe(OH)_{3(s)})$ by a pH adjustment to 4. The electrochemical removal of Zn(II) from rinse water using a RCE allows this treated water to be recycled back through the same rinsing process. In addition, the metallic zinc recovered can be reutilized in the same electroplating industry.

The electrolytic removal of Zn(II) at the RCE was achieved at Reynolds numbers between $15,000 \le Re \le 124,000$ and limiting current densities between $-13 \le J_L \le -4.8$ mA cm^{-2}. The zinc recovery reached a conversion of 67% with 9.5 kWh m^{-3} energy consumption at Re = 124,000 and J = -13 mA cm^{-2}.

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