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An oblique rotating barrel electrochemical reactor for removal of copper ions from wastewater

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Abstract

An experimental study was performed using an oblique rotating barrel cathode to recover copper from a simulated wastewater, which initially contained 100 parts per million (ppm) of cupric ions. The barrel was a perforated cylindrical polypropylene basket having several axial and circumferential fins on its exterior surface. It was partially filled with copper Raschig rings and was partially submerged in the wastewater at a tilted angle from the horizontal position. During the operation, the barrel was slowly rotating about its axis and the copper rings were made as the cathode by connecting them to a d.c. power supply through a dangler contact. The movement of exterior fins and tumbling motion of copper rings provided a high mass transfer rate and a large cathode area for copper electrodeposition reaction. The cupric ion concentration in the wastewater was reduced to less than 1.0 ppm, permitting discharge of the treated wastewater to the drain system. With an operating cell voltage of 2.5–5.0 V, the overall cathode current efficiency was 53–20%, and the electric energy requirement was 4 to 21 kWh per kilogram of copper recovered from the wastewater. An apparent first order reaction rate constant for copper electrodeposition reaction on the Raschig rings was measured as a function of process variables including cell voltage, barrel rotational speed, percentage barrel loading, barrel tilt angle and percent barrel immersion.

List of symbols

A	total copper particle surface area (m^2)
C	cupric ion concentration (ppm)
C_0	initial cupric ion concentration (ppm)
D	diffusivity of the cupric ion in water ($m^2\ s^{-1}$)
d_p	copper particle diameter (m)
d_b	barrel diameter (m)
E	anode-to-cathode cell voltage (V)
F	faradaic constant (96 500 C mol^{-1})
g	gravitational acceleration (9.8 m s^{-2})
Gr	Grashof number defined as $g(\rho_p - \rho_l)\rho_l d_p^3/\mu^2$ (dimensionless)
I	cell current (A)
M	atomic mass of copper (63.5 g mol^{-1})
n	number of electrons transferred in a half-cell reaction ($n = 2$ for copper electrodeposition reaction)
k	apparent reaction rate constant (m s^{-1})
k_m	mass transfer coefficient (m s^{-1})
Re	Reynolds number defined as $d_p(d_b\Omega)\rho_l/\mu$ (dimensionless)
Sc	Schmidt number defined as $\mu/(\rho_l D)$ (dimensionless)
Sh	Sherwood number defined as $k_m d_p/D$ (dimensionless)
t	electrolysis time (s)
V_{sol}	solution volume (m^3)
W	mass of copper recovered by electrodeposition (g or kg)

Greek symbols

α	empirical coefficient in Equation 8 (dimensionless)
ε	energy consumption per kg of copper removed (kWh per kg (Cu))
θ	total electrolysis time (s)
η_{au}	average current efficiency (%)
Ω	barrel rotational speed (rad s^{-1})
ρ_l	solution density (kg m^{-3})
ρ_p	copper particle density (kg m^{-3})
μ	solution viscosity (kg $m^{-1}\ s^{-1}$)
ω	rotation rate (rpm)

1. Introduction

Wastewater containing toxic metal ions, such as cadmium, chromium, copper, gold, lead, nickel, silver, tin and zinc, is generated in large quantities during electroplating, manufacturing of microelectronic parts, mining, and processing of photographic films [1]. These toxic metals should be removed from wastewater before discharge for environmental and economic reasons. Although many separation technologies, such as membrane processes and chemical precipitation, are used to remove toxic metal ions, the electrolytic process is attractive because of its ability to remove the contaminants at low operating costs. The electrolytic process does not generate sludge [2], which needs further disposal by landfill. In addition, the metals in wastewater are recovered for reuse.

A variety of electrolytic cells have been designed using porous plate, packed-bed and fluidized-bed electrodes [3–6]. These electrodes have large surface area and high reaction rate per unit volume. The rotating barrel electrode has been recently studied for removal of heavy metal ions [7–10] from wastewater. This electrode consists of metal particles in a perforated horizontal cylindrical barrel. During the electrolysis, the barrel is partially submerged in the electrolyte, and rotates slowly about its axis. The barrel rotation produces a tumbling motion of the metal particles and offers a high mass transfer rate and a large surface area for electrodeposition. Tison and Howie [7, 8] studied the effectiveness of a horizontal rotating barrel electrode for wastewater treatment. Zhou and Chin [2, 9, 10] reported a batch and a continuous electrochemical process consisting of a horizontal rotating barrel cathode and a packed-bed anode to simultaneously recover copper and destroy cyanide in a waste copper cyanide solution. They studied the mass transfer and particle motion in a plating barrel at different rotation speeds [9, 11].

The oblique barrel electrode, which is a perforated cylindrical basket rotating in the electrolyte with an inclination from the horizontal, has not been widely reported in the literature. In small process plants, the oblique rotating barrel offers the advantages of simple setup, easy maintenance and good solution flow [12]. Schab and Hein [13] used an oblique rotating barrel to recover silver from waste photographic fixing solutions.

In the present work, an oblique rotating barrel was used to recover copper from a wastewater initially containing 100 parts per million (ppm) of Cu^{2+} and 0.05 M Na_2SO_4. The rotating barrel was partially filled with copper Raschig rings as the cathode, and the cupric ions in the wastewater were removed by electrodeposition on the copper rings:

$$Cu^{2+} + 2\,e^- = Cu(s) \tag{1}$$

This reaction is first order with respect to cupric ion concentration [6], and the apparent reaction rate constant can be determined by measuring the cupric ion concentration in the wastewater as a function of the electrolysis time. The purpose of this work is examine the performance of the oblique rotating barrel electrode by determining the apparent reaction rate constant as a function of various operating parameters, including the cell voltage, rotation speed, barrel tilt angle, percentage loading and percentage immersion. The average current efficiency for the copper electrodeposition reaction and the electric energy consumption per kilogram of copper recovered from the wastewater were compared to those of the packed-bed and porous electrodes.

2. Experimental set-up

The experimental setup consisted of an oblique rotating barrel, a solution tank, a direct current (d.c.) power supply, and an ammeter. The solution tank was a 20 L rectangular Plexiglas container as shown in Figure 1. It functioned as the electrolytic cell and was filled with 14 L of a simulated wastewater initially containing 100 ppm Cu^{2+} ions and 0.05 M Na_2SO_4 with an initial pH of 5–6. The cathode was a rotating cylindrical barrel that could be inserted into the solution tank at different tilt angles. The barrel was a perforated polypropylene

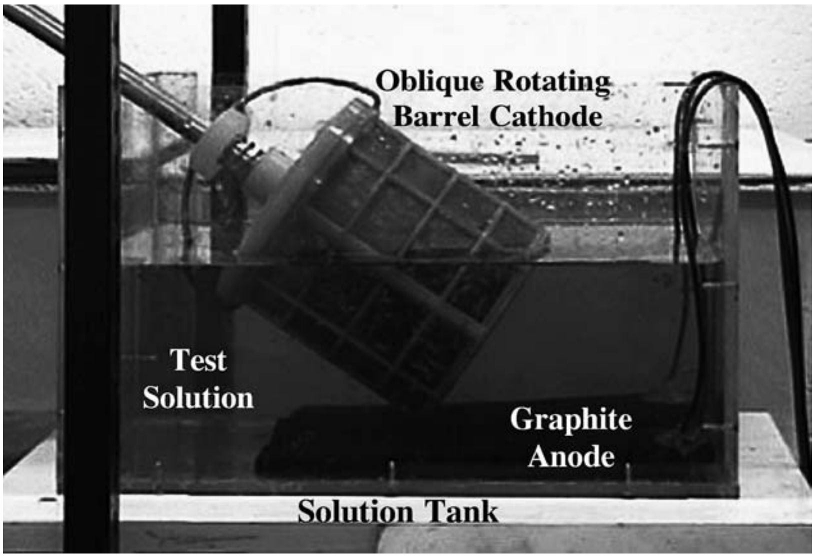

Fig. 1. Photograph of electrolytic cell consisting of a solution tank, an oblique rotating barrel cathode and a graphite anode.

basket of 150 mm in diameter and 150 mm in height. The screened basket wall was 24-mesh in size with 0.7 mm openings. It had 4 fins along the circumferential direction and 8 fins along the axial direction on its exterior surface. The barrel cathode was partially filled with copper Raschig rings of 10 mm in height, 6.35 mm in outer diameter, and 0.76 mm in wall thickness. The total cathode surface area varied from 0.18 m^2 at 15% of barrel loading (i.e., the percentage volume of barrel occupied by copper rings) to 0.84 m^2 at 70% loading. A stainless steel dangler ball of 15 mm in diameter provided the electric contact to the copper rings. The barrel was driven by a variable speed electric motor that had a speed range of 0–20 revolutions per minute (rpm). Three graphite plates located at the cell bottom as shown in Figure 1 were used as the anode. The total exposed area the anode was 0.135 m^2. This anode area was found to be large enough to allow the overall cell process to be controlled by the cathode reaction. The anode and the cathode were connected to a d.c. power supply. A built-in voltmeter in the d.c. power supply was used to measure the anode-to-cathode cell voltage. An external ammeter was used to measure the electric current to the cell. During the experiment, a solution sample was taken every 15 min and the cupric ion concentration was measured with a copper ion selective electrode connected to a pH/mV meter. All experiments were made at a room temperature of 25 ± 1 °C.

3. Results and discussion

Figure 2 shows the typical plots of cupric ion concentration in wastewater versus the electrolysis time. In this particular set of experiments, the cell voltage varied from 2.5 to 5.0 V while the other operating parameters were held constant at 20 rpm of barrel rotating speed, 50% of barrel loading, 45° of barrel tilt angle (from the horizontal position), and 50% of barrel immersion (i.e., the percent barrel volume immersed in the water). It can be noted that a higher cell voltage resulted in a higher rate of copper ion electrodeposition reaction. The semi-logarithmic plots show a linear behaviour that agreed with the first order kinetics for copper ion electrodeposition reaction [6]. The cupric ion concentration versus time relation can be obtained by modelling the cell as a batch reactor with the first order kinetics:

$$\ln C = \ln C_0 - \frac{kA}{V_{\text{sol}}} t \tag{2}$$

where C is the cupric ion concentration at a given electrolysis time t, A is the total cathode surface area, V_{sol} is the wastewater volume, C_0 is the initial cupric ion concentration, and k is an apparent first order reaction rate constant for electrodeposition of copper ion at the cathode. The total cathode surface area A was estimated by multiplying the exposed area of each copper Raschig ring with the total number of copper rings inside the barrel. The process of copper electrodeposition consists of two consecutive steps. Initially, the cupric ions diffuse to the cathode surface, and subsequently they undergo the electrodeposition reaction of Equation 1. The apparent reaction rate constant is the resultant of the convective mass transfer coefficient of the cupric ions and the intrinsic kinetic reaction rate constant. In addition, the total exposed particle area A, which is used in the computation of k in Equation 2, is likely to be different from the true active area available for copper electrodeposition reaction on the tumbling particles. The term of an 'apparent' reaction rate constant is used here to include the influence of mass transfer and effective cathode area on the rate of electrodeposition process. The apparent reaction rate constant was calculated from the slope of each semi-logarithmic plot of cupric ion concentration versus time by regressing experimental data using Equation 2.

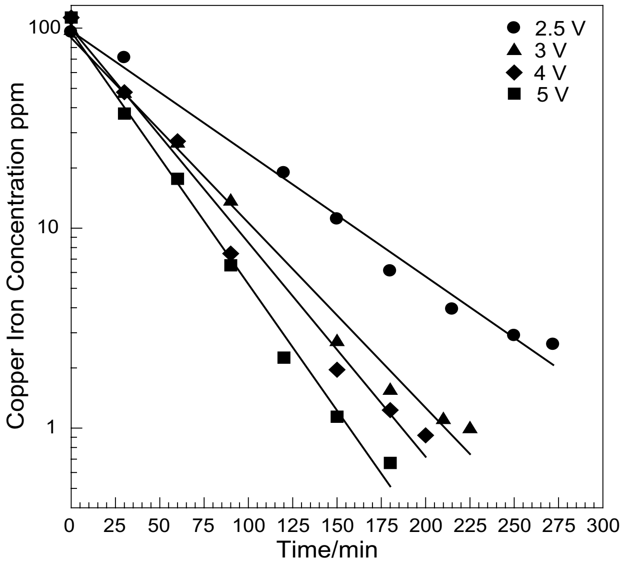

Fig. 2. Plot of cupric ion concentration versus electrolysis time for four cell voltages at 50% barrel loading, 50% barrel immersion, 45° barrel tilt angle, and 20 rpm barrel rotation speed. In all the runs, the total cathode area was 0.59 m^2 and the cell contained 14 L of a simulated wastewater at 25 °C.

3.1. *Effect of cell voltage*

The apparent reaction rate constants are plotted against cell voltage in Figure 3 for a set of experimental runs at 50% of barrel loading, $\omega = 20$ rpm (rotation speed), 45° tilt and 50% barrel immersion. The reaction rate constant increased with increasing cell voltage and reached a maximum value of 1.15×10^{-5} m s^{-1} at 5.5 V of cell voltage. The increase in the reaction rate constant was due to the improved kinetics at high cell voltages. At the applied cell voltage greater than 5.0 V, surface passivation was observed, which reduced the rate of copper electrodeposition process. This cathode passivation was caused by the side reaction of hydrogen

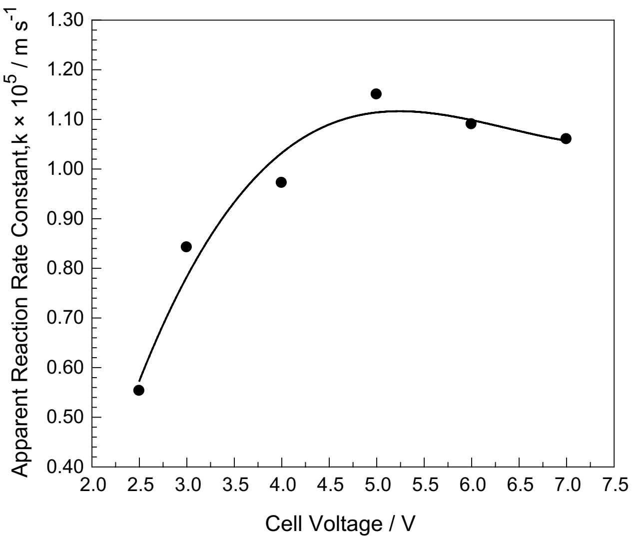

Fig. 3. Apparent reaction rate constant versus cell voltage at 50% barrel load, 50% barrel immersion, 45° barrel tilt angle and 20 rpm barrel rotational speed.

evolution, which produced a high concentration of OH^- ions at the cathode surface:

$$2\,H_2O + 2\,e^- \longrightarrow H_2 + 2\,OH^- \tag{3}$$

The OH^- ions generated reacted with Cu^{2+} ions and formed a black layer of $Cu(OH)_2$ on the copper particles. That is,

$$Cu^{2+} + 2\,OH^- \rightarrow Cu(OH)_2(s) \tag{4}$$

The anode reaction in the present cell was the decomposition of water molecules to oxygen gas:

$$2\,H_2O + 4\,e^- \rightarrow O_2(g) + 4\,H^+ \tag{5}$$

The above reaction increased the acidity of the waste solution, and the solution pH decreased from an initial value of 5–6 to a final value around 3.1. The pH decrease was fast at the beginning of the electrolysis and slowed down with increasing electrolysis time. This behavior was caused by the shifting of current efficiency at the cathode. At the beginning of the electrolysis, the instantaneous cathode current efficiency for copper electrodeposition reaction was nearly 100%. However, the cathode current efficiency decreased logarithmically with increasing time due to the decreasing cupric ion concentration in the wastewater. At the cupric ion concentrations less than 10 ppm, the current efficiency became very low and the electric current at the cathode was mainly consumed by the hydrogen evolution side Reaction 3. This side reaction generated the OH^- ions, which neutralized the H^+ ions produced at the anode, and slowed down the pH change in the waste solution.

The percentage average current efficiency (η_{av}) was obtained by comparing the mass of copper recovered from wastewater at the end of a run to the total charge passed according to Faraday's law:

$$\eta_{av} = \frac{W}{\frac{M}{2F}\int_0^\theta I\,dt} \tag{6}$$

where W is the mass of copper (g) recovered at the cathode, θ the total electrolysis time (s), M the atomic mass of Cu (63.5 g mol^{-1}), I the cell current, and F the faradaic constant (96 500 C mol^{-1}). The mass of copper recovered was calculated from the solution volume, V_{sol}, the initial concentration, C_0, and the final concentration, C_{final}, of cupric ions by $W = V_{sol}(C_0 - C_{final})$. Table 1 summarizes the average current efficiency, the average current density, and the initial and final cupric ion concentrations for four experimental runs at the cell voltages below the onset of cathode passivation. The average current efficiency decreased from 50% at a cell voltage of 2.5 to 20% at 5.0 V. These current efficiency values compare favourably with those of the other electrode configurations. Zhou and Chin [2] used a flow-through packed-bed cathode; they obtained a 29% to 39% current efficiency to recover copper from a wastewater initially containing 6000 ppm of cupric ions. Chin [6] used a flow-by porous cathode to treat a wastewater initially containing 100 ppm of cupric ions and obtained a 23% to 26% current efficiency. The average cell current in Table 1 was calculated by integrating the instantaneous cell current with respect to the time and then dividing the integration by the total electrolysis time. In general, the cell current was nearly constant for a given controlled cell voltage; it exhibited only 1 to 6% decrease throughout an experimental run.

The energy consumption per kilogram of copper recovered from wastewater, ε, was calculated by inter-

Table 1. Cathode current efficiency and energy consumption at different cell voltages with 14 L of wastewater at 25 °C, 50% barrel load, 45° barrel tilt angle, 50% barrel immersion, 20 rpm, and 0.59 m^2 total cathode area

Cell voltage /V	Average cell current /A	Total electrolysis time /min	Initial Cu^{2+} concentration /ppm	Final Cu^{2+} concentration /ppm	Average current efficiency /%	Electric energy consumption /kWh per kg (Cu)
2.5	0.55	175	95	2.6	53.0	4.0
3	0.85	225	97	1	35.7	7.1
4	1.45	200	113	0.9	27.6	13.3
5	1.84	180	113	0.7	20.0	21.4

grating the product of experimental cell current, I, and cell voltage, E_{cell}, with respect to the time according to

$$\varepsilon = \frac{\int_0^{\theta} I E_{\text{cell}} \mathrm{d}t}{3600\, W} \tag{7}$$

This quantity is listed in the last column of Table 1. The electric energy consumption increased with increasing cell voltage, from 4.0 kWh per kg(Cu) at 2.5 V to 20.7 kWh per kg(Cu) at 5 V. These results were comparable to the values of 14 to 34 kWh per kg(Cu) for the flow-through packed-bed electrode [2] and 11 to 18 kWh per kg(Cu) using the flow-by porous carbon cathode [6].

3.2. *Effect of barrel rotating speed*

Figure 4 shows the plots of apparent reaction rate constant versus barrel rotating speed at two cell voltages of 3.5 and 4.5 V, while the other operating parameters were held constant at 45° tilt angle 50% loading and 50% immersion. The apparent reaction rate constant increased from 5.5×10^{-6} to 1.2×10^{-5} m s^{-1} when the rotation speed rose from 4 to 20 rpm at 3.5 V. The linear relation of k versus ω in the log–log plots implies that the increase in apparent reaction rate constant is due to improved mass transfer with increasing rotation speed. The mass transfer coefficient, k_{m}, in an oblique plating barrel is related to the Reynolds (Re), Schmidt (Sc) and Grashof (Gr) numbers by [11]:

$$Sh = \frac{k_{\text{m}} d_{\text{p}}}{D} = \alpha Re^{0.32} (Sc\ Gr)^{0.5} \tag{8}$$

$$Re = \frac{d_{\text{p}} (d_{\text{b}} \Omega) \rho_l}{\mu} \tag{9}$$

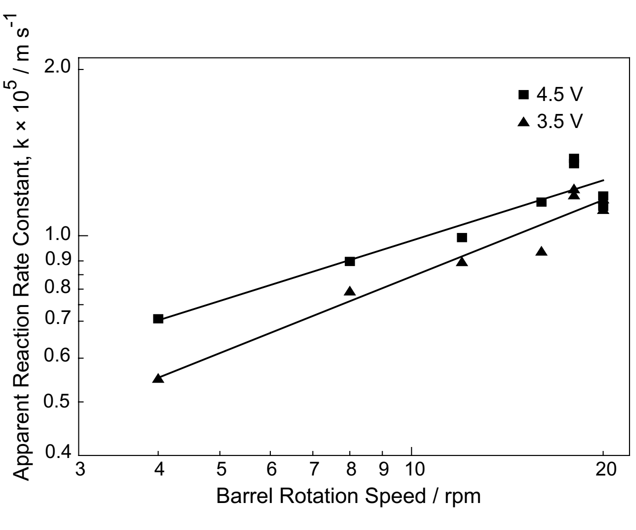

Fig. 4. Log-log plot of the apparent reaction rate constant versus barrel rotating speed at 3.5 V and 4.5 V cell voltage. The other operating conditions were kept constant at 50% barrel load, 50% barrel immersion, and 45° barrel tilt angle.

$$Sc\ Gr = \frac{g(\rho_{\text{p}} - \rho_{\text{l}}) d_{\text{p}}^3}{\mu D} \tag{10}$$

where d_{p} is the equivalent particle diameter (i.e., the diameter of a spherical particle that has the same volume as the nonspherical particle), d_{b} is the diameter of the rotating barrel, D is the diffusion coefficient of an active diffusing species, Ω is the rotational speed in rad s^{-1}, ρ_{p} is the density of the particles, and ρ_{l} and μ are the solution density and viscosity, respectively. In the above equations, the particle equivalent diameter d_{p} is used as the characteristic length, and the product of barrel diameter and rotational speed, $d_{\text{b}}\Omega$, is used as the characteristic velocity. The Reynolds number, which is the ratio of the inertial force to viscous fore of the fluid, represents the effect of barrel rotational speed on mass transfer. The Grashof number, which is defined as $g(\rho_{\text{p}} - \rho_{\text{l}})\rho_{\text{l}} d_{\text{p}}^3/\mu^2$, represents the influence on mass transfer by the fluid buoyant force exerting on the copper particles. The quantity α in Equation 8 is an empirical coefficient depending on the tilt angle, percentage loading, and percentage immersion. The values of α are tabulated in the work of Zhou and Chin [11]. At a 45° barrel tilt angle, 50% barrel load and 50% barrel immersion, the value of α is 8.9×10^{-5}.

In the present work, the diffusivity of cupric ion, D, was taken to be 7.2×10^{-10} m^2 s^{-1} [14]; the solution viscosity μ was taken as 9.0×10^{-4} kg m^{-1} s^{-1} at 25 °C; the barrel diameter d_{b} was 0.15 m; the copper particle density ρ_{p} was 8954 kg m^{-3}; and the solution density ρ_{l} was 1000 kg m^{-3}. The copper particle was in the shape of Raschig ring of 10 mm in height, 6.35 mm in outer diameter, and 0.76 mm in wall thickness. The equivalent diameter, as calculated from the following equation, was 6.30 mm:

$$d_p = \left(\frac{6\ V_{\text{particle}}}{\pi} \right)^{1/3} = \left(\frac{6 \times 133.5\,\text{mm}^3}{\pi} \right)^{1/3} = 6.30\,\text{mm}$$

Table 2 shows a comparison between the calculated mass transfer coefficients and apparent reaction rate constants at 4.5 V cell voltage, 50% barrel loading, 45° barrel tilt angle, and 50% barrel immersion. The apparent reaction rate constant was smaller than the mass transfer coefficient. The ratio of k/k_{m} varied from 0.52 to 0.7 with an average of 0.59 as shown in the table. These results imply that the copper electrodeposition in the present cell was mass transfer and kinetically controlled.

3.3. *Effect of percentage barrel loading*

The apparent reaction constant is plotted against percent barrel loading (i.e., the percentage barrel volume occupied by copper rings) for three cell voltages in Figure 5. In these experiments, the loading changed from 15% (with a cathode area of 0.18 m^2) to 70%

Table 2. Comparison between the apparent reaction rate constant and calculated mass transfer coefficient at different barrel rotating speeds, 4.5 V cell voltage, 50% barrel load, 45° barrel tilt angle, and 50% barrel immersion

Barrel rotating speed, ω rpm	Apparent reaction rate constant, k /m s^{-1}	Mass transfer coefficient, k_m /m s^{-1}	k/k_m
20	1.1×10^{-5}	2.1×10^{-5}	0.52
18	1.4×10^{-5}	2.0×10^{-5}	0.70
16	1.2×10^{-5}	1.9×10^{-5}	0.63
12	9.9×10^{-6}	1.8×10^{-5}	0.55
8	9.0×10^{-6}	1.6×10^{-5}	0.56
4	7.1×10^{-6}	1.2×10^{-5}	0.59
	Average		0.59

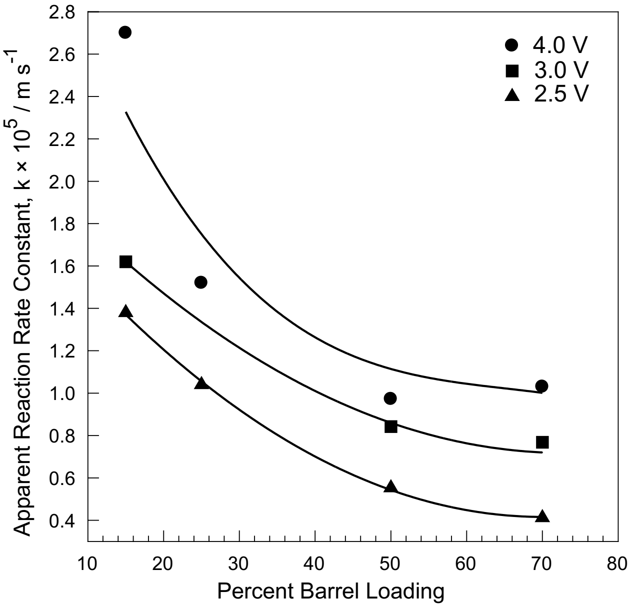

Fig. 5. Effect of percent barrel loading on the apparent reaction rate constant at three cell voltages, 45° barrel tilt angle, 50% barrel immersion and 20 rpm barrel rotational speed.

(with a cathode area of 0.84 m^2) while the tilt angle, immersion and rotational speed were kept constant at 45°, 50% and 20 rpm, respectively. For a given cell voltage, the apparent reaction rate constant initially decreased with increasing loading and reached a constant value at 50% to 70%. This decrease was partially due to the deterioration of mass transfer with increased loading [11]. As the percent loading increased, the tumbling motion of the Raschig rings became more restricted, resulting in poor solution circulation and lower values of mass transfer coefficient and apparent reaction rate constant. In addition, the total particle area was used in calculating the apparent reaction rate constant. Although the total particle area increased with increasing loading, the fraction of true effective area for copper electrode deposition reaction was likely to decrease with increasing loading due to the current penetration problem. This factor again caused a decrease in the apparent reaction rate with increasing barrel loading.

3.4. *Effect of barrel tilt angle*

In Figure 6, the apparent reaction rate constants are plotted against barrel tilt angle from the horizontal position for a set of runs at 4.5 V cell voltage, 50% loading, 50% barrel immersion and 18 rpm of rotating speed. The apparent reaction constant decreased with increasing tilt angle. The highest reaction constant occurred at 15°. At this position, there was good tumbling motion of copper rings, which improved solution agitation inside the barrel and enhanced mass transfer rate of copper ions to the copper rings. At a vertical position of 90°, the copper rings rotated as a rigid body and there was no tumbling motion. This resulted in a lower mass transfer rate, a lower current penetration into the particle bed, and thus a smaller reaction rate constant.

3.5. *Effect of percentage barrel immersion*

The effect of percent barrel immersion (i.e., the percent barrel volume inside the wastewater, which was achieved

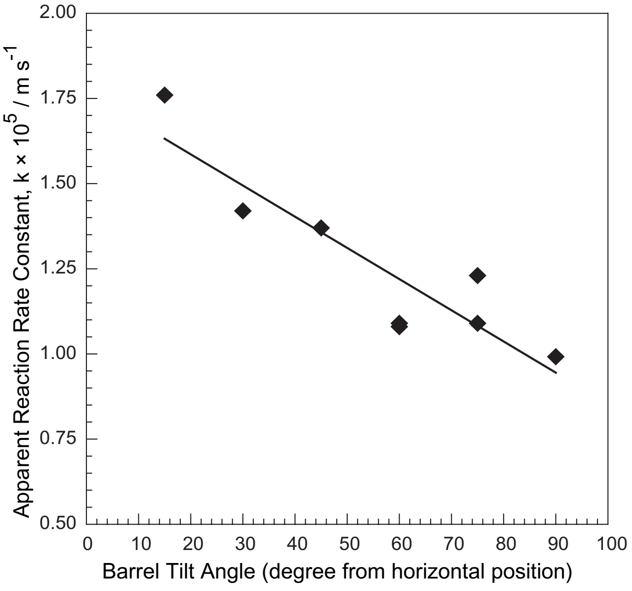

Fig. 6. Effect of barrel tilt angle on the apparent reaction rate constant at 4.5 V cell voltate, 50% barrel load, 50% barrel immersion, and 18 rpm barrel rotational speed.

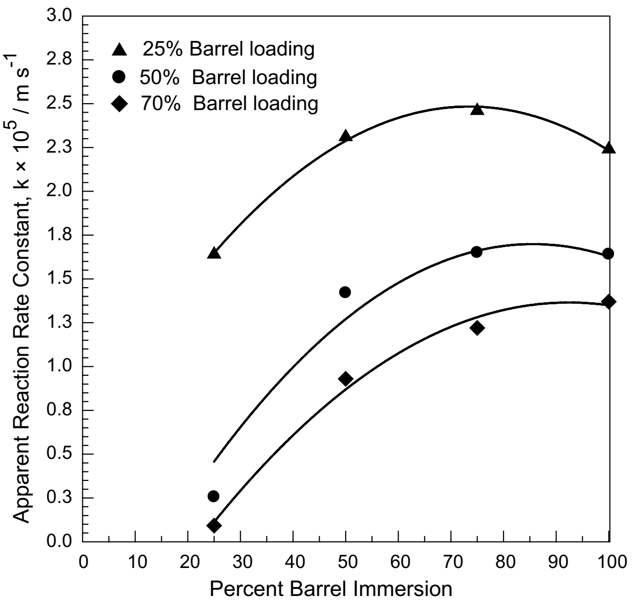

Fig. 7. Effect of barrel immersion on the apparent reaction rate constant at three barrel loadings, 4.5 V cell voltage, 30° barrel tilt angle, and 18 rpm barrel rotation speed.

by changing the water levels in the experiment) on the apparent reaction rate constant at three barrel loadings is shown in Figure 7 for a set of runs at 4.5 V cell voltage, 30° barrel tilt angle and 18 rpm of rotating speed. The apparent rate constant increased when the barrel immersion increased from 25% to 75% of its volume. This was due to improved solution transfer by the exterior fins when the barrel was rotating at a sufficient depth inside the water. The apparent reaction rate constant reached a maximum value in the barrel immersion range 75% to 100% of its volume. Good solution transfer occurred only at the barrel top and middle regimes immediately below the liquid surface, where the bulk solution in the cell was scooped up by the exterior revolving fins, and then flowed by gravity through the meshed wall to the interior of the barrel. This liquid pumping action was weak in the oblique barrel bottom-apex regime deep in the water. When the loading was low as shown by the data at 25% and 50% of barrel volume, most copper Raschig rings were located in the apex regime, and the apparent reaction rate constant decreased when the barrel was fully immersed at 100% of its volume.

4. Conclusions

This study has demonstrated that an oblique rotating plating barrel loaded with copper Raschig rings, was a simple and efficient device for the recover of copper from wastewater initially containing 100 ppm of cupric ions. The revolving movement of the exterior fins and the tumbling motion of copper rings inside the barrel provided a high mass transfer rate and a large cathode area for copper electrodeposition reaction. The cupric ion concentration in the wastewater was reduced to less than 1.0 ppm, permitting discharge of the treated wastewater to the drain system. The average cathode current efficiency ranged from 20% at 5 V of cell voltage to 53% at 2.5 V of cell voltage. Depending upon the values of controlled cell voltage, the electric energy consumption varied from 4 to 21 kWh per kg of copper recovered. An apparent first order reaction rate constant for copper electrodeposition reaction on the Raschig rings was examined as a function of various process variables. The reaction rate constant generally increased with increasing cell voltage, barrel rotational speed and percent immersion in the wastewater, and decreased with increasing percent loading and tilt angle from the horizontal position. Cathode passivation was observed at high cell voltages with the formation of black $Cu(OH)_2$ coatings that reduced the apparent reaction rate constants on copper rings.

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