

# METAL RECOVERY FROM WASTEWATER WITH AN ELECTROCHEMICAL METHOD

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**T**raditional undergraduate chemical engineering laboratory courses place emphasis on familiarizing students with the equipment of unit operations, chemical reaction engineering, and process control. Few environmentally oriented experiments, such as wastewater treatment, are available to students. The experimental project described in this paper is concerned with the application of electrochemical engineering principles to wastewater treatment. Wastewater containing toxic heavy metal ions is generated in large quantities from the microelectronics, metal finishing, mining, and photographic industries. Metal Waste sources and their characteristics are listed in several publication.<sup>[1,2]</sup>

Wastewater may be freed of toxic metal ions by electrodepositing them in metallic form. An example of this was the use of a silver tower electrolyzer<sup>[3]</sup> to recover silver from spent photographic fixing solutions. Zhou and Chin<sup>[4,5]</sup> described an electrolytic process for simultaneously recovering heavy metal ions from wastewater at the cathode and destruction of cyanide ions at the anode. Khristoskova and Lazavou<sup>[6]</sup> studied an electrolytic process to remove hexavalent chromium from wastewater. Shifrin, *et al.*,<sup>[7]</sup> discussed the advantage of adding RuO<sub>2</sub> to a TiO<sub>2</sub> anode to treat wastewater. Hertwig, *et al.*,<sup>[8]</sup> and Tison<sup>[9]</sup> used a rotary drum electrode to recover copper. Fleishmann, *et al.*,<sup>[10]</sup> used a fluidized bed as the cathode to plate copper onto metal particles. Bennion and Newman<sup>[11]</sup> used a flow-through porous-electrode to remove copper ions from dilute solutions. Robertson and Dossenbach<sup>[12]</sup> developed a gas-sparging cell to improve mass transfer in an electrolytic cell for wastewater treatment. A general review of electrochemical removal of metals from aqueous solutions was given by Kuhn,<sup>[13]</sup> and a review of electrochemical cell design for metal recovery was given by Robertson, *et al.*<sup>[14]</sup> The basic electrochemistry and engineering principles were discussed by Weininger,<sup>[15]</sup> and the environmental and economic factors of the electrolytic metal recovery process were discussed by O'Keefe and Ettel.<sup>[16]</sup>

## OBJECTIVES

The objectives of this project in a chemical engineering laboratory course are

- To demonstrate to students that toxic heavy metal ions in wastewater can be reduced by electrodeposition of the metals at a porous cathode
- To enhance students' experience of chemical reaction engineering by determining the reaction rate constant of the electrodeposition reaction, its activation energy, and the effect of mass transfer on the rate constant
- To improve students' economic consciousness by evaluating the current efficiency and energy consumption of the process

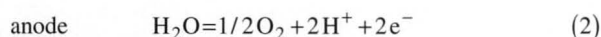
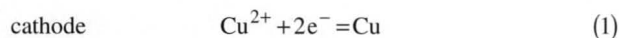
Students perform the electrolysis experiment to reduce toxic metal ions from an initial concentration of 50-250 parts per million (ppm) to a low level acceptable for discharge as required by the U.S. Environmental Protection Agency's (EPA) regulations. By measuring the concentration changes of the metal ion at various controlled anode-to-cathode cell voltages, temperatures, and water recirculation rates, students determine the reaction rate constant, its activation energy, and the effect of mass transport of metal ions on the rate of electrodeposition reaction. By measuring the amount of metal recovered and the total electric charges used in the electrolysis, students calculate the current efficiency and energy requirement of the process and compare the results to those reported in the literature.

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## ELECTROLYTIC SYSTEM AND DATA ANALYSIS

In this project, a flow-through electrochemical cell operating in a recirculation mode in a solution tank is used for recovering copper from wastewater containing 50-250 ppm of cupric ( $\text{Cu}^{2+}$ ) ion and 0.05 M  $\text{Na}_2\text{SO}_4$ . The cathodic and anodic reactions in the cell are



The cupric ion concentration in the wastewater is to be reduced by electrodepositing copper on a porous carbon cathode to less than 1.0 ppm to satisfy EPA regulations for discharging copper ions to waste streams.<sup>[17]</sup>

The copper electrodeposition reaction is a first-order reaction with respect to cupric ion concentration in the wastewater. By assuming a uniform concentration throughout the solution tank and electrolytic cell, the concentration change of cupric ion at a given set of controlled anode-to-cathode cell voltage, temperature, and wastewater recirculation rate, can be described by

$$\frac{C}{C_0} = \exp(-kat) \quad \text{with } a = \frac{A}{V_{\text{sol}}} \quad (3)$$

where  $C$  is the concentration of cupric ion in wastewater at time  $t$ ;  $C_0$  is the initial concentration of cupric ion;  $k$  is a first-order reaction rate constant for the deposition of cupric ion at the cathode;  $A$  is the total cathode area; and  $V_{\text{sol}}$  is the volume of wastewater in the solution tank.

Since the total surface area of the porous cathode is not easy to determine, one may consider the product,  $ka$ , as the effective volumetric reaction rate constant of the copper electrodeposition reaction. According to Eq. (3), a plot of  $\ln C$  vs.  $t$  would yield a straight line, and the value of  $ka$  can be evaluated from the slope of the straight line. The values of  $ka$  depend on the wastewater temperature, the electrode potential of the cathode, and the water recirculation rate. The cathode potential can be changed by varying the anode-to-cathode cell voltage in the experiment.

The activation energy,  $E_{\text{act}}$  is evaluated by measuring the volumetric reaction rate constant,  $ka$ , at various solution temperatures at a constant cell voltage and a wastewater recirculation rate according to the Arrhenius equation

$$ka = ka_{\infty} \exp\left(-\frac{E_{\text{act}}}{RT}\right) \quad (4)$$

where  $T$  is the absolute temperature,  $R$  is the universal gas constant, and  $ka_{\infty}$  is the frequency factor. According to Eq. (4), a plot of the logarithm of volumetric reaction rate constant,  $ka$ , versus the reciprocal of absolute temperature ( $1/T$ ) would result in a straight line, and the activation energy can be evaluated from the slope of the straight line.

The instantaneous current efficiency of copper electrodeposition reaction at a given electrolysis time can be evaluated by calculating the rate of change of cupric ion concentration,  $dC/dt$ , from the experimental  $C$  vs.  $t$  curve and by comparing the value to the cell current,  $I$ , at the same electrolysis time, according to Faraday's law

$$\text{Current Efficiency (\%)} = \frac{V_{\text{sol}} \frac{dC}{dt}}{I} \times 100 \quad (5)$$

where  $F$  is the Faraday constant (96,500 C/equiv) and  $n$  is the number of electrons transferred in the cathode deposition reaction (2 equiv/mol). The average current efficiency is obtained by comparing the mass of copper recovered at the end of a run to the total charge passed during the run according to

$$\text{Average Current Efficiency (\%)} = \frac{W}{\frac{M}{nF} \int_0^{\theta} I dt} \times 100 \quad (6)$$

where  $\theta$  is the total electrolysis time in seconds,  $W$  is the mass of copper deposited at the cathode, and  $M$  is the atomic mass of copper (63.5 g/mol).

The energy consumption per kilogram of copper removed from wastewater is calculated by integrating the experimental cell current and voltage curve with respect to the time according to

$$\text{Energy (kWh/kg-metal)} = \frac{\int_0^{\theta} I E_{\text{cell}} dt}{3600 \times 1000 W} \quad (7)$$

where  $E_{\text{cell}}$  is the anode-to-cathode voltage and  $W$  is the mass of copper recovered in kilograms.

## EXPERIMENTAL METHOD

**Apparatus** • The experimental apparatus is shown schematically in Figure 1. It consists of a solution tank, and electrolytic cell, a recirculation pump, a control valve, a rotameter, a connecting pipe, a direct current (DC) power supply, an immersion heater, and a glass thermistor probe. The solution tank is a 16-gallon rectangular polypropylene container with quarter-inch wall thickness. It is equipped with a spigot at the bottom of the front wall for draining wastewater at the end of the experiment. The electrolytic cell is a commercial electrochemical reactor in the form of two concentric cylinders, as shown in Figure 2. The inner cylinder is a ruthenium oxide-coated titanium mesh anode (commercially called "dimensionally stable anode," or DSA) of 2 13/16" outside diameter, 12" long, and 1/16" thick. The outer cylinder is a porous carbon felt cathode that was pre-coated with a thin layer of copper. The cathode dimensions are 4 3/4" outside diameter, 3/8" thick, and 10 3/4" long.

The anode and cathode are placed in a cylindrical polyvinyl chloride (PVC) casing of 12 1/2" in length and 5 1/2" outside diameter, as shown in Figure 3. Wastewater containing heavy metal ions is pumped by the recirculation pump to one end of the electrolytic cell and flows through the annular space between the anode and the cathode where the heavy metal ions are recovered by electrodeposition at the porous cathode surface. The wastewater exits at the other end of the concentric cell and is continuously recirculated by the pump between the solution tank and the electrolytic cell through a 3/4" PVC pipe, as shown in Figure 1.

The solution flow rate through the electrolytic cell is read on the rotameter and can be adjusted at the control valve to a maximum of 15 gallons per minute. Two insulated electric cables connect the anode and the cathode to the DC power supply. During the electrolysis, the anode-to-cathode cell voltage is set at the power supply, and the cell current is read on a built-in ammeter of the power supply. The immersion heater is an electric heater encased in a stainless steel sheath and Teflon coating. A power controller is used to adjust the heater output from 0 to 1.0 kW. The heater and the glass thermister probe are connected to a temperature controller that maintains the wastewater temperature at a constant value for the runs above the room temperature. Due to the stability of the construction materials, the maximum wastewater temperature that could be operated on this equipment was 50°C.

**Experimental Procedures** • 1. *Calibration of Copper Ion Selective Electrode* • The concentration of cupric ion in wastewater during the run is measured with a cupric ion selective electrode. The potential of this electrode with respect to a built-in reference electrode is first calibrated with the following standard solutions: 1000 ppm  $\text{Cu}^{2+}$  + 0.05 M  $\text{Na}_2\text{SO}_4$ ; 100 ppm  $\text{Cu}^{2+}$  + 0.05 M  $\text{Na}_2\text{SO}_4$ ; 10 ppm  $\text{Cu}^{2+}$  + 0.05 M  $\text{Na}_2\text{SO}_4$ ; 1 ppm  $\text{Cu}^{2+}$  + 0.05 M  $\text{Na}_2\text{SO}_4$ ; 0.1 ppm  $\text{Cu}^{2+}$  + 0.05 M  $\text{Na}_2\text{SO}_4$ . The calibration procedures involve insertion of the cupric ion selective electrode in 50 mL of a standard solution, addition of 1 mL of an ionic strength adjuster (5 M  $\text{NaNO}_3$ ), and reading the electrode potentials with a digital pH/mV meter. A sample calibration curve showing the potential of cupric ion selective electrode as a function of cupric ion concentration at 25°C is shown in Figure 4.

2. *Wastewater Treatment Experiment* • A simulated wastewater containing 50-250 ppm  $\text{Cu}^{2+}$  and 0.05 M  $\text{Na}_2\text{SO}_4$  is prepared in the solution tank by adding an appropriate amount of cupric sulfate and sodium sulfate salts into 53 L of tap water. The recirculation pump is turned on for 10 to 15 minutes, until the solution is well mixed. The initial cupric ion concentration and solution pH is measured with the cupric ion selective electrode and a combination pH electrode on the pH/mV meter. The wastewater flow rate (10-60 L/min) through the electrolytic cell is adjusted at the control valve to a desired level, and a constant water temperature (25-50°C) is set at the temperature controller. Electrolysis is started by applying a constant anode-to-cathode cell voltage (3-6 V) from the DC power supply. The cell

current, cupric ion concentration, and solution pH are measured at specified time intervals. The run continues until the cupric ion concentration in the wastewater drops to less than 1.0 ppm to permit discharge of wastewater into the drain system. Electric power to the DC power supply, the recirculation pump, and the immersion heater are then turned off. The solution tank is cleaned and rinsed with fresh tap water. The electrolytic cell is removed from the solution tank and disassembled for visual inspection of the cell components.

**System Cost** • The costs of the electrolytic cell, the equipment, and the construction materials are listed in Table 1. The total capital cost (excluding the labor for assembly and testing) of the experimental system was \$6,340 in 1998 U.S. dollars. The system cost could be reduced to less than \$4,000 if a spare pH/mV meter, a pH electrode, and a temperature controller were available in the laboratory. The material cost to run an experiment is estimated to be \$18.63, as shown in

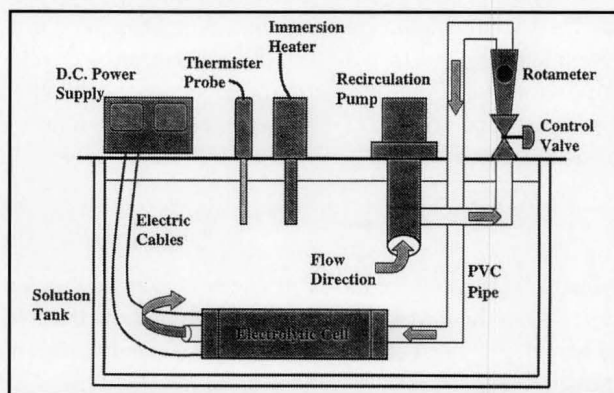


Figure 1. Schematic arrangement of solution tank, electrolytic cell, recirculation pump, control valve, rotameter, DC power supply, immersion heater, thermister probe, pipe connection, and direction of solution flow.

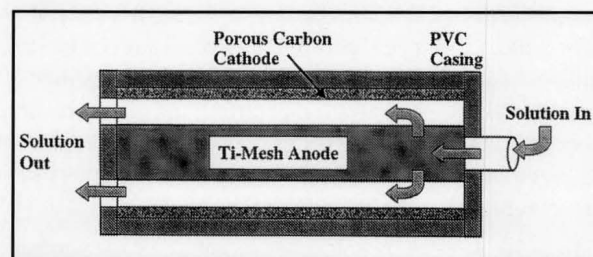


Figure 2. Schematic of electrolytic cell.

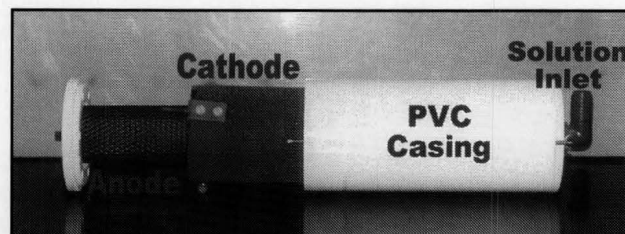
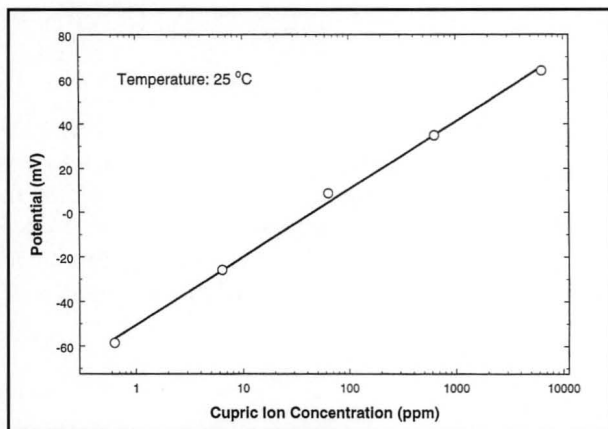


Figure 3. Photo of the electrolytic cell showing the arrangement of Ti-mesh anode, Cu-precoated porous cathode, and PVC casing prior to assembly.

Table 1. The replacement cylindrical cathode can be reused in several experimental runs. With proper cleaning and rinsing after each experiment, we used a single cathode cartridge six to ten times without affecting the quality of data collection.



**Figure 4.** Calibration curve showing potential versus cupric ion concentration of a cupric ion selective electrode at 25°C.

**TABLE 1**  
Capital Cost of Experimental System  
and the Materials Cost for One Experimental Run  
in 1998 U.S. Dollars

<i>Item</i>	<i>Cost</i>
<b>Capital Cost of System</b>	
• Electrolytic cell with 3 replacement cathode cartridges and DC power supply	\$2,000
• 16-gallon polypropylene solution tank with cover	160
• Polypropylene recirculation pump with motor	360
• Rotameter	70
• Teflon-coated immersion heater, power controller, thermister probe, and temperature controller	1,600
• Combination copper ion selective electrode with filling solution kit	450
• pH/mV meter and combination pH electrode with filling solution kit and electrode holder	1,200
• Other construction materials (plastics, hardware, connecting pipies, pipe fittings, etc.)	500
<b>TOTAL</b>	<b>\$6,340</b>
<b>Cost of Materials</b>	
• Replacement cathode cartridge (\$55 per cartridge, pro-rated for approximate useful life of six experimental runs)	\$ 9.17
• 0.025 kg of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (technical grade, \$189.06 per 3-kg bottle)	1.58
• 0.4 kg of anhydrous $\text{Na}_2\text{SO}_4$ (technical grade, \$52.38 per 3-kg bottle)	6.98
• 20 mL of 5M $\text{NaNO}_3$ solution (\$45 per 1000-mL bottle)	0.90
<b>TOTAL</b>	<b>\$ 18.63</b>

## IMPLEMENTATION IN LAB COURSE

The project has been a part of a senior-level chemical engineering undergraduate laboratory course at Clarkson University since 1998. The course consists of a weekly lab period of 6 hours, and the project was assigned to a group of 3 to 4 students as a three-week mini-thesis project. Each student group was able to complete one experimental run in one 6-hour lab period. Prior to the first-week lab period, the students were asked to submit a preliminary lab report describing the equipment setup, experimental procedures, theoretical background for data analysis, and safety precautions. The instructor then held a pre-lab meeting with the students and assigned specific objectives to the group. Since each group was able to carry out only three experimental runs during the three-week period, the objectives were confined to one of the following scenarios:

- To examine the effect of anode-to-cathode cell voltage on the reaction rate constant,  $k_a$ , by conducting the experiment at three cell voltages while holding wastewater temperature and recirculation rate constant
- To determine the activation energy of the copper electrodeposition reaction by conducting the experiment at three temperatures while holding the cell voltage and wastewater recirculation rate constant
- To examine the effect of mass transfer on the reaction rate constant,  $k_a$ , by conducting the experiment at three flow rates while holding the cell voltage and solution temperature constant

In the subsequent two weeks, the student group was asked to make an oral report to the instructor prior to the second and third lab period. The oral report consisted of presenting the previous week's experimental results, data analysis, comparison with known literature results, discussion of the difficulties encountered in the previous lab period, and modification of experimental procedures, if necessary. The safety precautions were also reviewed in the oral report. One week after completion of the third week's experiment, the group submitted a final project report to the instructor, summarizing all experimental results, theory, and data analysis

## EXPERIMENTAL RESULTS

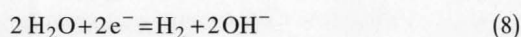
This section presents the typical experimental results collected by the students. Figure 5 shows a Ti-mesh anode, an unused cathode, and a cathode after the electrolysis experiment. The black ruthenium oxide coated Ti-anode was inert and stable in the present electrolytic system, and the electrolysis did not change its color. The unused porous carbon cathode was dark in color, although it was pre-coated with a thin-layer Cu from the commercial supplier (the dark color was caused by oxidation of the thin copper coating by air during storage and shipping). After the experiment, the color of the porous cathode changed to bright metallic copper, indicating that a significant quantity of copper was recovered from the wastewater by electrolysis.

Figure 6 is a semi-logarithmic plot of cupric ion concentration versus electrolysis time for three controlled anode-to-cathode cell voltages of 3.5 V, 4.5 V, and 5.5 V at 28°C and a wastewater recirculation rate of 38 L/min. In all the runs, the students were able to reduce the cupric ion concentration in the wastewater from an initial value of 60-250 ppm to less than 0.5 ppm, permitting discharge of the wastewater to the waste stream at the end of each experimental run. The concentration of cupric ion decreased logarithmically with the time as described by Eq. (3), and the rate of concentration change increased with increasing cell voltage. Using regression analysis, the effective volumetric reaction rate constant,  $k_a$ , could be calculated from the slope of the linear lines.

**Reaction Rate Constant** • Figure 7 is a plot of  $k_a$  versus cell voltage for a series of runs at 28°C and 38 L/min of wastewater recirculation rate. The value of  $k_a$  varied linearly with the cell voltage from 0.0003 s<sup>-1</sup> at 3 V to 0.0006 s<sup>-1</sup> at 6 V, as described by Ohm's law. This indicates that ohmic resistance of the wastewater played an important role in the copper electrodeposition reaction.

The pH of the wastewater decreased from an initial value of 6-7 to a final value around 3 at the end of the run. This increase in acidity was caused by the anode reaction in Eq. (2), where H<sub>2</sub>O molecules were decomposed to O<sub>2</sub> gas and H<sup>+</sup> ions. The rate of pH decrease was fast at the beginning of an experimental run and slowed down with increasing electrolysis time.

**Current Efficiency and Energy Requirement** • The main side reaction at the cathode was the reduction of H<sub>2</sub>O molecules to H<sub>2</sub> gas and OH<sup>-</sup> ions.



The OH<sup>-</sup> ions generated from the above reaction neutralized the H<sup>+</sup> ions produced at the anode, and thus decreased the rate of pH change at large electrolysis time. Figure 8 shows the instantaneous cathode current efficiency for the copper electrodeposition reaction as a function of electrolysis time for two controlled cell voltages at 28°C and 38 L/min of wastewater recirculation rate. The instantaneous current efficiency was calculated from the rate of cupric ion concentration change in the wastewater using Eq. (5). The rate of copper electrodeposition

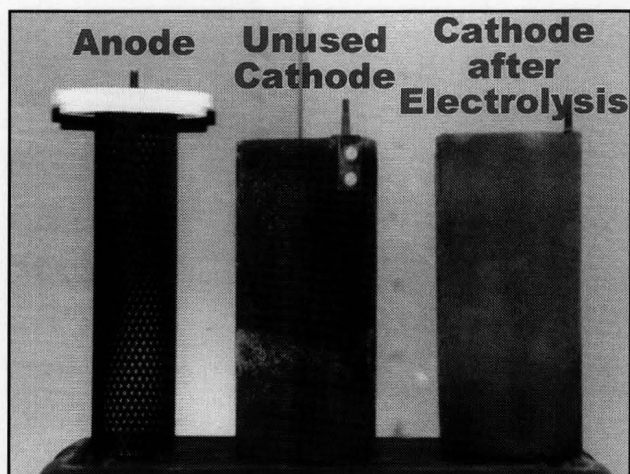


Figure 5. Photograph showing a Ti-mesh anode, an unused cathode, and a bright metallic copper-colored cathode after the electrolysis experiment.

decreased with decreasing concentration of cupric ions. At the beginning of the electrolysis, the cupric ion concentration in the wastewater was high (50-250 ppm) and the current efficiency was nearly 100%. As the electrolysis proceeded, the cupric ion concentration was reduced, and the current efficiency for the copper deposition reaction decreased logarithmically with increasing electrolysis time. At the end of an experimental run, the instantaneous current efficiency was typically less than 1%.

The average current efficiency can be calculated by integrating the instantaneous current efficiency curve in Figure 8 with respect to the time and dividing the result with the total electrolysis time of an experimental run. It can also be calculated using Eq. (6) from the total amount of copper removed from the wastewater

$$W = V_{\text{sol}}(C_o - C_{\text{final}}) \quad (9)$$

where  $V_{\text{sol}}$  is the volume of wastewater in the solution

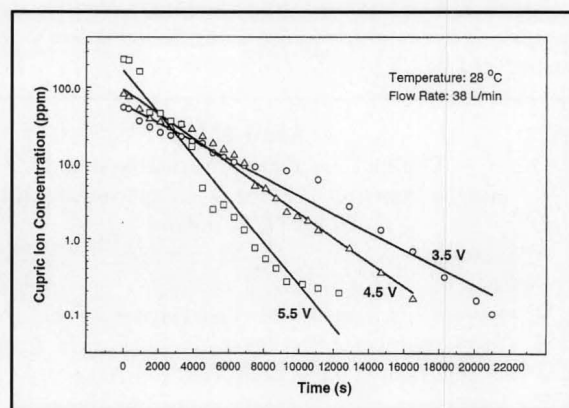


Figure 6. Cupric ion concentration versus electrolysis time for three controlled anode-to-cathode cell voltages at 28°C and 38 L/min of wastewater recirculation rate.

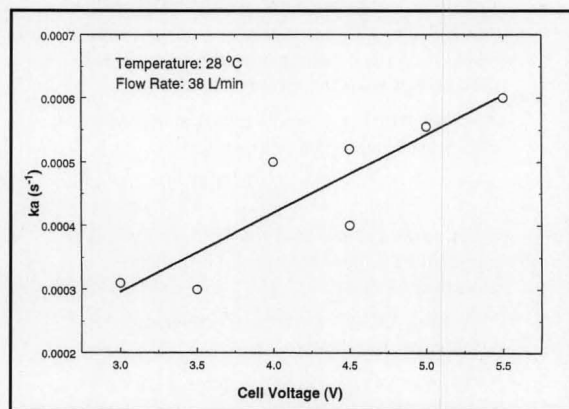


Figure 7. Effective volumetric reaction rate constant,  $k_a$ , of copper electrodeposition reaction versus cell voltage at 28°C and a solution flow rate of 38 L/min.

tank and  $C_o$  and  $C_{final}$  are the initial and final cupric ion concentrations in the experimental run. The two methods provided an opportunity for the students to check the accuracy of mass balance in their experimental measurement. The cell current increased with increasing the controlled cell voltage. For a given experimental run, the current was nearly constant. It typically exhibited a 2-5% decrease throughout the entire run. Consequently, the product of average current and experimental duration was used as the total charge in Eq. (6) for calculation of the average cathode current efficiency.

Table 2 summarizes the results of average current efficiency for three-controlled cell voltages of 3 V, 4 V, and 5 V at 28°C and 38 L/min of solution recirculation rate. The table also lists the average cell current and the initial and final cupric ion concentrations in each run. All the experiments were able to reduce cupric ion concentration from 210-220 ppm to less than 0.5 ppm in the wastewater. Although Fig-

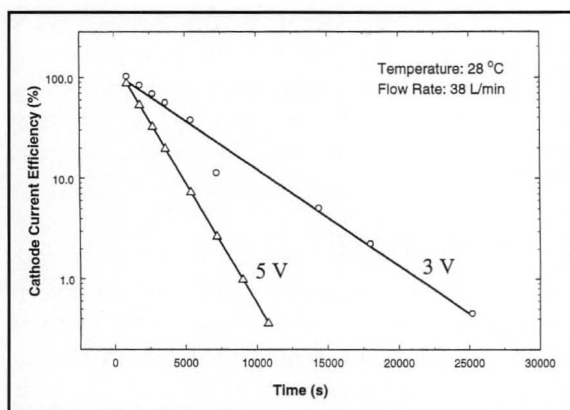
ure 8 seems to show that the instantaneous current efficiency for copper electrodeposition decreased with increasing cell voltage, the average current efficiency remained approximately constant at around 25%. This is because the cell current was larger and the total electrolysis time was shorter at a higher cell voltage.

The consumption of electric energy per kilogram of copper recovered from the wastewater by electrolysis was calculated by integrating the product of cell current and cell voltage with respect to the time, as shown in Eq. (7). The results are listed in the last column of Table 2 for the three controlled cell-voltage runs at 28°C and 38 L/min of wastewater recirculation rate. Although the average current efficiency for copper electrodeposition was independent of the cell voltage, the electric energy consumption increased with increasing cell voltage. The electric energy per kilogram of copper recovered varied from 11 kWh at 3 V to 17 kWh at 5 V. These values agreed with the work of Zhou and Chin,<sup>[4]</sup> who reported a value of 13-30 kWh/kg-Cu for the electrolytic treatment of a wastewater using a rotating barrel plater.

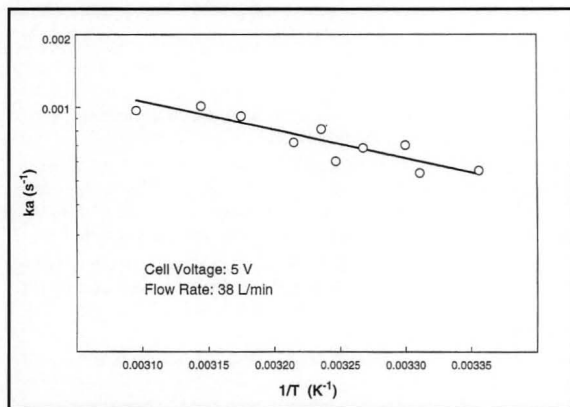
**Activation Energy** • Some groups carried out the electrolytic wastewater treatment at several temperatures with constant cell voltage and solution recirculation rate. Figure 9 is an Arrhenius plot of  $k_a$  versus reciprocal of absolute temperature ( $1/T$ ) for ten experimental runs over the temperature range of 28-50°C at a constant cell voltage of 5 V and 38 L/min recirculation rate. The data exhibited a linear relationship between  $\ln(k_a)$  and  $1/T$ , as suggested by Eq. (4). The activation energy,  $E_{act}$ , as calculated from the slope of the straight line, was 22 kJ/mol.

**Mass Transfer Aspects of Electrodeposition Reaction** • For electrodeposition of metal from a dilute solution, the rate-controlling step is generally the transport of metal ions from the bulk solution to the cathode surface. Increasing the solution velocity near the cathode enhances the mass transfer rate. Figure 10 shows the values of  $k_a$  over a range of water recirculation rate of 10-60 L/min at a common cell voltage of 5.5 V and a temperature of 33°C. The results indicate that  $k_a$  increased with increasing recirculation rate, and thus the velocity of wastewater passing the porous cathode. The linear relationship between  $k_a$  and the recirculation rate of the log-log plot implies a strong mass transfer influence on the rate of copper electrodeposition reaction in the present system. But if the copper electrodeposition reaction was completely controlled by mass transfer, the reaction rate constant would be expected to be independent of the anode-to-cathode cell voltage. The fact that  $k_a$

Continued on page 155.



**Figure 8.** Instantaneous cathode current efficiency for copper electrodeposition reaction for two controlled cell-voltages at 28°C and 38 L/min of solution recirculation rate.



**Figure 9.** Semi-logarithmic Arrhenius plot of  $k_a$  versus  $1/T$  for copper electrode deposition reaction at the porous cathode.

Controlled Cell Volt (V)	Average Cell Current (A)	Initial Cu <sup>2+</sup> Concen. (ppm)	Final Cu <sup>2+</sup> Concen. (ppm)	Average Current Efficiency (%)	Electric Energy (kWh.kg-Cu)
3	6.1	214	0.2	23	11.3
4	10.8	217	0.3	26	13.2
5	13.6	223	0.5	24	17.7

## Metal Recovery from Wastewater

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increased with increasing both cell voltage and water-flow rate suggests that the copper electrodeposition reaction in the present dilute electrolytic system was under a mixed control of mass transfer and ohmic resistance of the wastewater. Increasing temperature increased the diffusivity of cupric ion and electric conductivity of wastewater, and thus the rate of electrodeposition of copper at the cathode.

### SAFETY AND VERSATILITY OF THE PROJECT

This experimental project is relatively safe. No toxic or harmful chemicals are used, and it is carried out at the ambient temperature to 50°C. Wastewater in this temperature range would not scorch the operators in the event of accidental contact. Although the electrolysis releases O<sub>2</sub> and H<sub>2</sub> gases from the solution tank, their quantities are small and do not pose a fire hazard. The equipment should be placed in a well-vented area, however, and students are advised not to light any matches near the experimental area. To avoid electric shocks, students are advised to dry their hands before operating power switches. They should also wear safety goggles to protect against accident spill of wastewater samples or standard solutions during the measurement of cupric ion concentration.

Although the present experiment was assigned to students as a three-week mini-thesis project, it can also be used as a short experimental project to be completed in one 6-hour lab period. In this case, the experimental objectives will be confined to a determination of the reaction rate constant for a given set of cell voltage, water recirculation rate, and temperature. To enhance students' economic consciousness, they should also perform the current efficiency and energy requirement calculations and compare the results with the literature values.

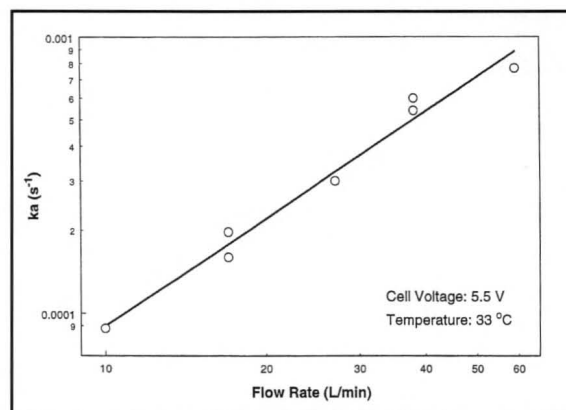
### CONCLUSIONS

An experimental project to enhance students' experience in electrochemical reaction engineering and wastewater treatment has been developed for use in a senior-level undergraduate chemical engineering laboratory course. The project involves electrolysis experiments to reduce cupric ions in wastewater by electrodepositing them in metallic form at a porous cathode. By measuring the concentration changes of cupric ion as a function of electrolysis time at various controlled cell voltages, temperatures, and water-flow rates, students determine the reaction rate constant, its activation energy, and the role of mass transfer in the electrodeposition reaction. They also calculate the current efficiency and energy requirement for recovery of copper from the wastewater. The project is also suitable for use as a short experiment in a single lab period, or it can be assigned to students as a mini-thesis project to be completed in a period of three to four weeks.

### ACKNOWLEDGMENT

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**Figure 10.** Log-log plot of the effective volumetric reaction rate constant,  $k_a$ , as a function of wastewater flow rate through the electrolytic cell at a cell voltage of 5.5 V and 33°C.

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