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Removal and recovery of copper via a galvanic cementation system
Part I: Single-pass reactor

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Abstract

A galvanic system for the removal of copper from aqueous solutions using a divided flow-through cell is proposed. The present study looks into the feasibility of removing copper from dilute electroplating rinse water and recovering it in metallic form by a galvanic cementation process. This process does not require an external supply of energy due to the spontaneous chemical reaction between the copper/iron couple. Therefore, this operation is attractive in reducing operating costs, especially when dealing with low ion concentrations and serves as an alternative to current wastewater treatments available. The performance of the proposed system was evaluated as a function of cathode potential, catholyte flow rates, initial copper(II) concentration and types of electrode materials used. Results have shown that the galvanic flow system can remove copper effectively below the maximum permissible level from simulated copper(II) solutions. For a sample of copper bearing rinse water with relatively low conductivity containing 74.2 mg L^{-1} copper, 81.2% removal of the copper was achieved using a reticulated vitreous carbon as cathode.

List of symbols

A_e	specific surface area (m^{-1})
C_{inlet}	inlet copper(II) concentration (mol L^{-1})
C_{outlet}	outlet copper(II) concentration (mol L^{-1})
D	diffusion coefficient ($m^2\ s^{-1}$)
E°	standard potential (V)
F	Faraday constant (96 485 A s mol^{-1})
I_L	limiting current (mA)
k_m	mass transfer coefficient (m s^{-1})
n	charge of the electrodeposited metal ion
Q	volumetric flow rate (L s^{-1})
Re	Reynolds number, $uv^{-1}A_e^{-1}$
Sc	Schmidt number, vD^{-1}
Sh	Sherwood number, $k_m \varepsilon A_e^{-1} D^{-1}$
ε	porosity
u	superficial velocity (m s^{-1})
v	kinematic viscosity ($m^2\ s^{-1}$)

1. Introduction

Primary sources of copper in industrial waste streams are metal finishing operations, which include electroplating, electroless plating and printed circuit board (PCB) manufacturing [1]. Copper is also widely used in the production of wire, brass, pipes, cooking utensils etc. Therefore, copper is frequently found in water and wastewater in significant quantities. USEPA requires 1.3 mg L^{-1} in drinking water as the copper concentration action level [2]. Apart from that, the value of copper metal frequently makes recovery processes important. Current treatment approaches on copper-bearing wastewater include precipitation, coagulation or flocculation, ion exchange, liquid ion exchange or liquid–liquid extraction, cementation, membrane separation, evaporation or distillation, adsorption, electrolysis, catalysed reduction, electrodialysis, electrowinning, microfiltration and reverse osmosis [3–5]. Treatment technologies that involve hydroxide precipitation with pH adjustment have economic limitations due to the high cost of sludge disposal in landfills. Besides the high capital costs involved in using ion exchange resins, strong acid and alkaline solutions are needed to regenerate the resins and the resulting solution needs to be disposed of [6]. The reverse osmosis technique also suffers from technical and economic limitations such as difficulty in membrane selection due to the high pressure applied. Both of these techniques involve high capital and operating costs.

The electrochemical methods of treatment have the ability to recover metals in pure and saleable metallic form via redox reaction without any addition of chemicals [7–9]. A number of cell technologies for the removal of heavy metals are commercially available such as Chemelec Cell, Eco-Cell, Porocell and others

[10–12]. All these treatment technologies are categorized as electrolytic cells, which need power consumption. Dilute solutions with low metal ion concentrations have very low electrical conductivities and have kinetic as well as thermodynamic limitations [13], therefore requiring a high electrical power input to produce high recoveries using electrodialysis and electrowinning techniques. Hence, dilute solutions like rinse water will impart additional operating costs resulting in the electrochemical technique to be less economical.

The ideal solution to this problem would be a system, which recovers and recycles both the metal and the water without any need of an external supply of energy because it is based on a spontaneous chemical reaction. For this reason, the galvanic process (an electrogenerative mode process) will turn out to be a new alternative to the conventional electrochemical method. This system has been investigated over the past three decades [14–20]. Surprisingly, the studies have received little attention. Despite its advantages, the stationary batch galvanic system which depends only on a slow process of free diffusion, exhibits mass transfer limitation. Recent work has discussed the importance of forced convection to improve the efficiency of electrochemical methods for dilute wastewater treatment by providing intimate contact between the flowing stream and the electrode surface [16, 21, 22].

In this paper, we present a galvanic flow-through system with three-dimensional porous electrodes which was designed for the removal of copper. The galvanic reaction of copper/iron may be represented by the equations:

$$\text{Anode:}\quad \mathrm{Fe} \rightleftharpoons \mathrm{Fe}^{2+} + 2\,\mathrm{e}^- \quad E^\circ = 0.44\,\mathrm{V} \tag{1}$$

$$\text{Cathode:}\quad \mathrm{Cu}^{2+} + 2\,\mathrm{e}^- \rightleftharpoons \mathrm{Cu} \quad E^\circ = 0.34\,\mathrm{V} \tag{2}$$

$$\text{Overall:}\quad \mathrm{Cu}^{2+} + \mathrm{Fe} \rightleftharpoons \mathrm{Cu} + \mathrm{Fe}^{2+} \quad E^\circ = 0.78\,\mathrm{V} \tag{3}$$

The application of high-surface area three-dimensional porous electrodes has also been suggested for the recovery of several metal pollutants from dilute solutions [23–25]. The aim of the present study is to investigate the feasibility of removing copper from dilute solutions with the single-pass system designed. This system allows the flow of wastewater through the reactor once-only for treatment and is well suited to high removal rates at minimum pumping speed. This system has been proven to be efficient by Yiu [26] in removing hexavalent chromium from electroplating wastewater to below the maximum permissible level.

The performance of the system in the treatment of simulated dilute acid copper wastes with concentrations less than 500 mg L^{-1} was evaluated using graphite and reticulated vitreous carbon. A real effluent sample from the rinse water tank of a copper plating industrial plant was also treated with the current system.

2. Experimental details

The schematic diagram of the galvanic flow cell is shown in Figure 1. The cell had two electrolyte compartments of dimensions 5 cm × 2 cm × 1 cm separated by an anion exchange membrane R4030 (The Electrosynthesis Co.). In the cathode compartment, there were two calming zones at the electrolyte inlet and outlet filled with glass wool. The cell can be represented as follows:

$$\mathrm{Fe}|\mathrm{Fe}^{2+}\|\mathrm{Cu}^{2+},\mathrm{Cu}|\mathrm{C}$$

The reference electrode was a saturated calomel electrode. A copper sheet was used as a cathode current collector while the anode current collector was a stainless steel sheet. Parafilm (American National $\mathrm{Can}_{\mathrm{TM}}$) and I-C wafer dicing mounting tape (Pokico Packaging System) were placed between the compartments as gaskets. The galvanic components were sandwiched together with six screws. Two types of porous cathode were used: porous graphite sheet (SG-132) (The Electrosynthesis Co.) and reticulated vitreous carbon (80 ppi) (The Electrosynthesis Co.). Both cathodes were 1 cm thick. Steel wool weighing 3.0 g was used as the anode. The experimental setup consisted of a laboratory-scale galvanic flow cell, two peristaltic pumps Minipuls 2 (Gilson), anolyte and catholyte reservoirs and sample collection tanks (Figure 2(a)). The electrolyte solutions were pumped into the cell through the inlet opening at the bottom by a peristaltic pump and flowed out of the cell from the outlet at the top of the cell. The electrochemical cell was operated as a single-pass reactor where the electrolyte solutions were passed through the cell only once. The anolyte flow rate was fixed at 2.0 mL min^{-1} throughout the experiments.

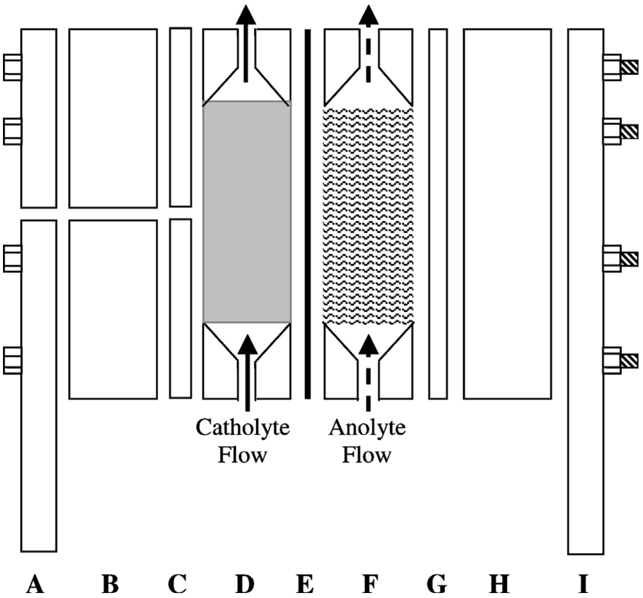

Fig. 1. Schematic diagram of flow cell (side view): (A, B, H and I) stainless steel support; (C) copper sheet current collector; (D) Teflon for cathode compartment; (E) anion exchange membrane; (F) Teflon for anode compartment; (G) stainless steel current collector.

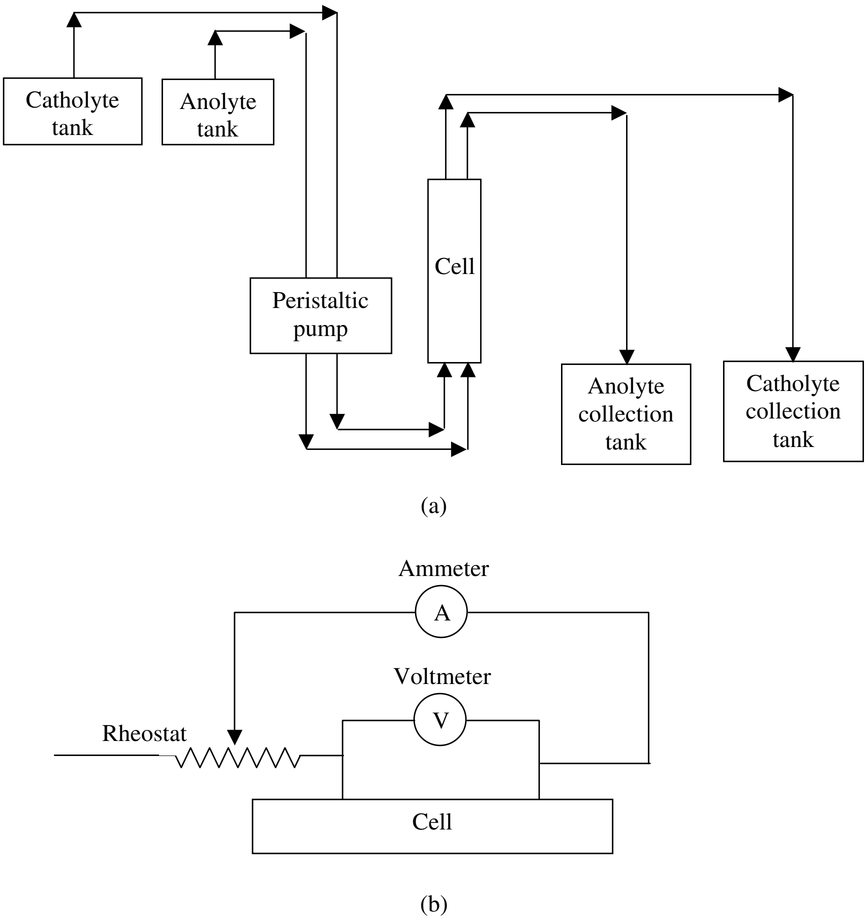

Fig. 2. Experimental set-up (a) and electrical circuit (b).

Experiments were carried out by varying the concentrations of copper(II) ions ranging from 10 to 500 mg L^{-1} in 0.5 M sulfuric acid as the catholyte and 1.00 M sodium chloride as the anolyte. All solutions were prepared from analytical grade chemicals using deionized and distilled water. All experiments were carried out at room temperature, 27 °C. The concentration of the influent and effluent of the system were determined by an Instrumentation Laboratory IL357 atomic absorption spectrophotometer. The output current and potential of the system were measured with a Fluke 77 Series II multimeter. The electrical circuit is shown in Figure 2(b). After each experiment, the cell was disassembled and washed thoroughly with deionized water. The electrodes were stripped of any deposits by soaking in 1:1 aqueous nitric acid. In all experiments, 60 min were required to reach steady-state conditions. The electrolyte solutions leaving the cell were sampled, and the remaining copper(II) concentrations quantified by an atomic absorption spectrophotometer were used to monitor the performance of the system in percentage of copper removal.

3. Results and discussions

As a test of reproducibility, a particular experimental run was performed three times. The maximum deviation from the average of any of these experimental values over the three runs was 5%. The system using 3.0 g of steel wool as anode, shows a constant percentage of copper removal over six hours of operation in the treatment of 100 mg L^{-1} of copper(II) at a flow rate of 2.0 mL min^{-1}. Thus, it is unlikely that anode passivation would take place throughout the studies.

3.1. *Cathodic polarization curves*

The system was initially loaded with maximum resistance which was gradually decreased until it was short-circuited. In all experiments, 15 min were required to reach a steady state after each change of cathodic potential. At the end of the predetermined interval, cathode potential and current readings were recorded.

Figures 3 and 4 show plots of the cathodic potential against current density, for systems utilizing electrode SG-132 and RVC 80 ppi at various flow rates. It has been shown that cell polarization decreases with increase in catholyte flow rate. Work with other electrolytic cells [23, 25, 27] have shown that the polarization curves are similar for the range of flow rates studied except for an increase in limiting current with increase in flow rates. The decrease becomes less pronounced at high catholyte flow rates (e.g., 20.1 mL min^{-1}) probably because the higher catholyte flow rate enhances the rate of mass

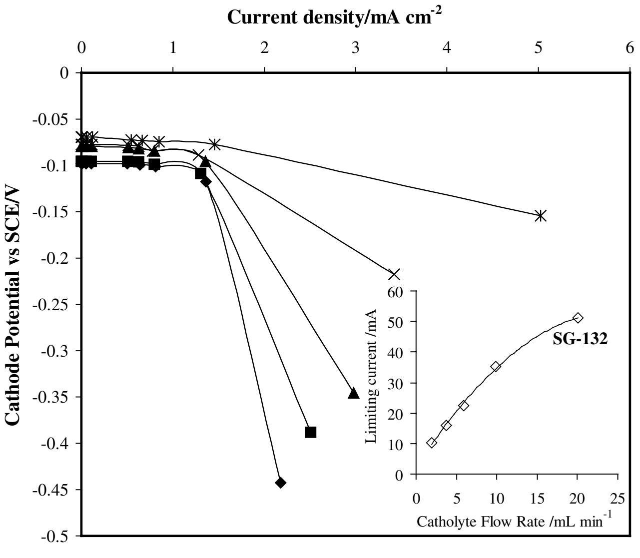

Fig. 3. Polarization curve for system utilizing electrode SG-132 for catholyte flow rate of 2.0 (◆), 3.8 (■), 5.9 (▲), 9.9 (×) and 20.1 mL min^{-1} (*) at a constant copper(II) concentration of 100 mg L^{-1} in 0.5 M H_2SO_4. Inset shows variation of limiting current with catholyte flow rate for the system.

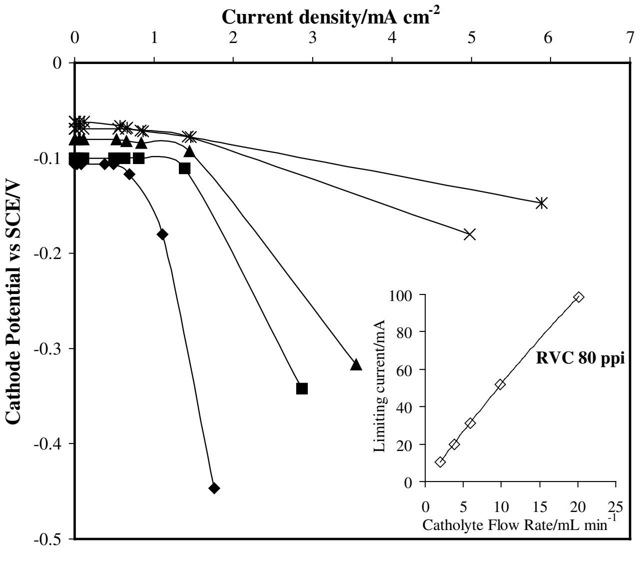

Fig. 4. Polarization curve for system utilizing electrode RVC 80 ppi for catholyte flow rate of 2.0 (◆), 3.8 (■), 5.9 (▲), 9.9 (×) and 20.1 mL min^{-1} (*) at a constant copper(II) concentration of 100 mg L^{-1} in 0.5 M H_2SO_4. Inset shows variation of limiting current with catholyte flow rate for the system.

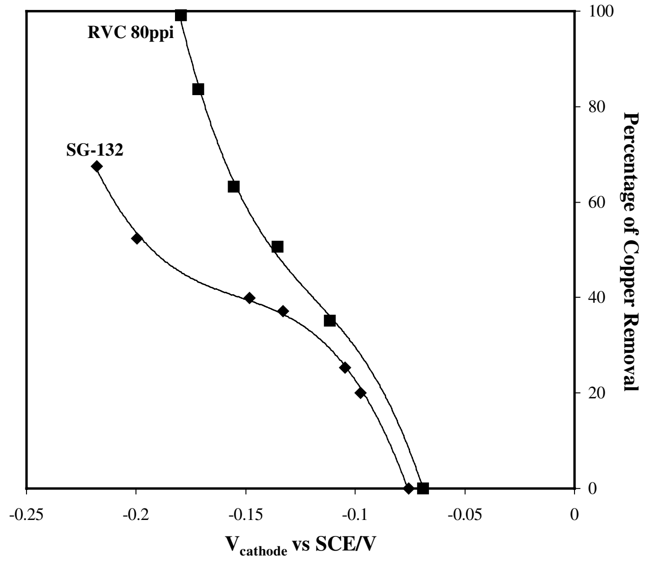

Fig. 5. Effect of varying the cathode potential (vs SCE) at a constant copper(II) concentration of 100 mg L^{-1} in 0.5 M H_2SO_4 and at fixed catholyte flow rate of 9.9 mL min^{-1} for systems utilizing electrode SG-132 and RVC 80 ppi.

transfer of the reactants and products to and from the electrode surface, respectively, with a consequent decrease in concentration polarization. It must be noted that both systems, though utilizing different types of electrodes, behave similarly (Figures 3 and 4). At low currents, no significant polarization occurs. This may be attributed to the low percentage of copper removal, as observed in Figure 5. As a result the concentration gradient from the bulk electrolyte to the cathode surface was also less. Moreover, increase in catholyte flow rates increases the limiting current that is obtained from the material balance equation as follows:

$$I_L = nF(QC_{\text{inlet}} - QC_{\text{outlet}}) \qquad (4)$$

This is shown in the insets of Figures 3 and 4. Apparently, at high flow rates, side reactions such as hydrogen evolution tend to occur more rapidly [28]. This reaction is also contributing to the total current density. Such phenomenon also occurs in electrolytic cells [29, 30].

3.2. *Effect of cathode potential*

The effect of cathode potential on the percentage of copper removal is shown in Figure 5. The higher the resistance loaded, the lower was the system performance as the cathode potential shifted to more positive values. This is due to the limitation in kinetics and transport at catalytic sites where a slow electron-transfer electrode reaction occurs at high resistance. The percentage removal increased as the potential shifted to more negative values. Therefore, it can be concluded that the optimum conditions for the system could be achieved by operating it in a short-circuit manner.

3.3. *Effect of catholyte flow rates*

The dependence of percentage copper removal on catholyte flow rate is plotted in Figure 6. For both systems using porous graphite sheet and reticulated vitreous carbon, operating at flow rates 2.0 mL min^{-1} or below and 3.8 mL min^{-1}, respectively, nearly 100% of copper(II) ions was reduced to copper metal. As the flow rate was increased, the percentage removal of copper dropped for the system using porous graphite sheet.

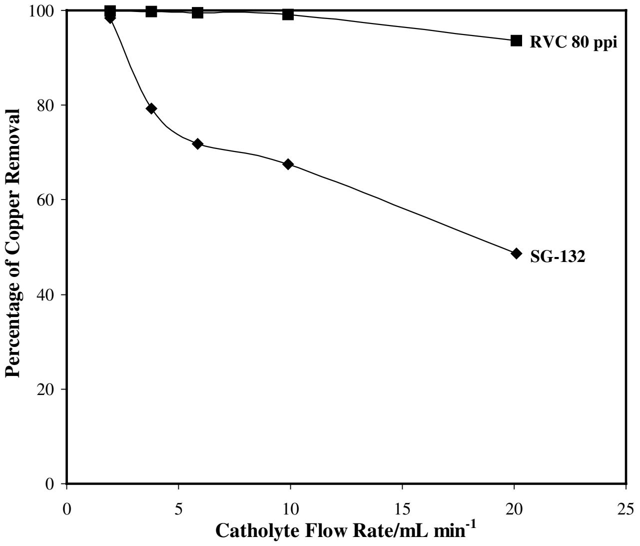

Fig. 6. Effect of varying the catholyte flow rates at a constant copper(II) concentration of 100 mg L^{-1} in 0.5 M H_2SO_4 for systems utilizing electrode SG-132 and RVC 80 ppi.

However, for the system using reticulated vitreous carbon, this was only significant at 20 mL min^{-1}. High flow rates reduce the mass-transfer resistance by increasing the convection in the cathode pores [23]. This increases the diffusive transport of reacting species to the surface of electrode surface once they have entered the pores. Nevertheless, the effect of decrease in residence time of copper ions at the porous cathode is more pronounced compared to the increase in the mass transfer coefficients at higher flow rates, and, therefore the conversion efficiency is lower [23, 28]. This is shown in Table 1. The concentration of effluent from the single-pass reactor decreases almost exponentially with residence time, as depicted in Figure 7, for both types of electrode.

3.4. *Effects of initial copper(II) ion concentration*

The performance of the system was further evaluated as a function of copper(II) concentration at a fixed catholyte flow rate using both types of electrode. The initial concentration was varied between 10 and 500 mg L^{-1}. It is clearly shown in Figure 8 that the performance of the system generally dropped with increasing initial copper(II) concentration for porous graphite sheet. In the case of the system utilizing reticulated vitreous carbon, the percentage of copper removal dropped significantly only at 500 mg L^{-1} of copper(II). This showed that the removal of copper(II) from the catholyte is highly concentration dependent. This may be attributed to the large number of reacting species at high copper(II) concentrations corresponding to slow charge transfer rate.

Table 1. Effect of flow rate on the removal of copper and values of k_m for system utilizing electrode RVC 80 ppi

Catholyte flow rate /mL min^{-1}	Flow velocity /m s^{-1}	Residence time /min	C_{inlet}/C_{outlet}	k_m /m s^{-1}
2.0	1.63×10^{-4}	5.13	1000.0	4.25×10^{-6}
3.8	3.15×10^{-4}	2.65	500.0	7.39×10^{-6}
5.9	4.88×10^{-4}	1.71	200.0	9.76×10^{-6}
9. 9	8.25×10^{-4}	1.01	111.1	1.47×10^{-5}
20.1	1.68×10^{-3}	0.5	15.9	1.75×10^{-5}

Initial copper(II) concentration of 100 mg L^{-1} in 0.5 M H_2SO_4.

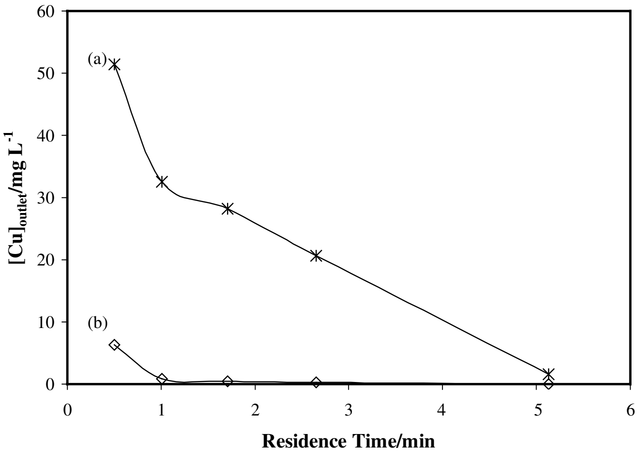

Fig. 7. Effect of varying the residence time of the electroactive species in the electrode at a constant copper(II) concentration of 100 mg L^{-1} in 0.5 M H_2SO_4 for systems utilizing electrode (a) SG-132 (b) RVC 80 ppi.

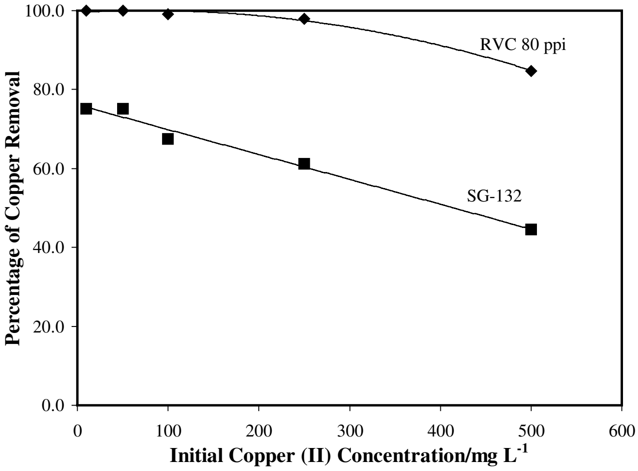

Fig. 8. Effect of varying the initial copper(II) concentration at a constant catholyte flow rate of 9.9 mL min^{-1}.

3.5. *Choice of electrodes*

The influence of electrode types on cell performance is depicted in Figures 5, 6 and 8. All the improvements observed in the cell performance were attributed to the available specific surface area for reaction. Table 2 shows that reticulated vitreous carbon is a more suitable electrode material compared to porous graphite sheet due to its high porosity and relatively high specific surface area [21, 31, 32].

Table 2. Physical properties of electrode porous graphite sheet, SG-132 and reticulated vitreous carbon, RVC 80 ppi. (The Electrosynthesis Co.)

Type of electrode	Form	ε	BET surface area /m^2 g^{-1}	A_e /m^2 m^{-3}
SG-132	Sheet	50%	0.3	Not given
RVC	Sheet 80 ppi	97%	1	5300

3.6. *Mass transfer study*

The data from Table 1 were used to calculate the dimensionless Sherwood and Reynolds numbers. From the mass transfer data obtained in this work, the correlation $Sh = 0.94\,Re^{0.63}Sc^{0.33}$ was obtained. The results of this work as well as some of the results cited in the literature [30, 33–35] are compared in Table 3. The exponent of *Re* obtained here is close to those values obtained by the other authors.

3.7. *Application on industrial wastewater*

A sample of wastewater was obtained from the rinse water tank of a copper plating plant and its characteristics are given in Table 4. Applying the results obtained for simulated effluent, this rinse water sample was treated using an 80 ppi reticulated vitreous carbon cathode at various flow rates ranging from 2.0 to 20.1 mL min^{-1}. The initial copper concentration of 74.2 mg L^{-1} dropped to 19.8% from the initial value at flow rate of 2.0 mL min^{-1} as shown in Figure 9. In this case, the percentage conversion to copper metal was rather low compared to the studies using simulated effluent in a single-pass. This showed that the effluent needs to go through further treatment (e.g., recirculating the effluent through the reactor several times) before achieving the maximum permissible discharge level for copper. This may be due to the low electrolyte conductivity of the rinse water sample. The rinse water sample had lower conductivity in comparison with the simulated copper waste solution, which caused an increase in the *iR*-drop within the cell. The simulated effluent had a conductivity of 199.3 mS cm^{-1}, which is approximately 200 times greater than the conductivity of the rinse water sample. The results also showed that increasing catholyte flow rates decreased the percentage of copper removal. To meet the legislation, a batch recycle mode operation involving recirculation of copper waste solution is needed.

Table 4. Characteristics of copper plating rinse water sample

Parameter	
Conductivity /mS cm^{-1}	1.2
pH	2.3
Turbidity/FAU	32
Total dissolved solids/mg L^{-1}	19
Trace elements/mg L^{-1}:	
copper	74.2
iron	9.2
nickel	ND
cadmium	ND
zinc	ND
chromium	ND
aluminium	ND

ND – Below detection limit.

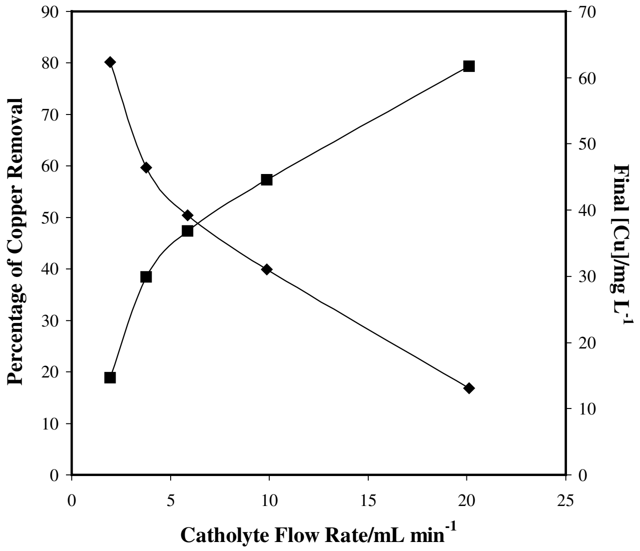

Fig. 9. Performance of the system for the rinse water sample at various flow rates: Percentage of copper removal (◆) and final copper(II) concentration (■).

4. Conclusions

It has been demonstrated that it is feasible to treat both simulated and real acid copper waste solution with the galvanic cementation process. A flow-by reticulated

Table 3. The exponent of the Reynolds numbers in various systems

Type of cell	Cathode material	ε (grade in ppi)	A_e /m^{-1}	Exponent of *Re*	Reference
Electrolytic	RVC	0.97 (45)	2710	0.69	[30]
Electrolytic	RVC	0.97 (100)	6700	0.48	[33]
Galvanic	RVC	0.97 (80)	5300	0.63	This work
Electrolytic	Packed-bed	0.46	–	0.72	[34]
Electrolytic	Carbon felt	0.86 or 0.90	11000 or 8800	0.61 or 0.72	[35]

vitreous carbon electrode has been utilized for effective removal of copper ions below 1.0 mg L^{-1} from dilute solutions. Initial success on the use of the galvanic system for dilute copper waste treatment provides room for further development. Consequently, there is a need to design and fabricate such economical treatment technology towards rinse water reuse and recycling in metal finishing operations. Besides eliminating waste water, recovering the copper in metallic form helps to minimize or totally eliminate waste generated and subsequently moving towards zero emission industry.

In Part II of this work, a batch recycle-mode galvanic system will be discussed. The efficiency of the single pass reactor and the recirculation system will be evaluated on both simulated and real effluent of acid copper solution. With the recycle mode operation, it is shown that copper ion levels may be reduced below 1.0 mg L^{-1} with good efficiency.

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