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Removal and recovery of copper via a galvanic cementation system part II: batch-recycle reactor

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Abstract

This paper describes a batch-recycle galvanic reactor, operated in the flow-by configuration, for the removal of copper from dilute industrial effluents. A three-dimensional cathode, 80 ppi reticulated vitreous carbon, was used for this purpose. Mass transfer studies show that the average mass transfer coefficient was proportional to the Reynolds number, Re^{f}, where $f = 0.68$, which was independent of the concentration of reactant species under the experimental conditions. A comparison of the performance between a single-pass and a batch-recycle reactor was also conducted with an initial copper concentration of 10 mg l^{-1}, 100 mg l^{-1} and 500 mg l^{-1}. A 500 ml feed of 74.2 mg l^{-1} of copper in electroplating rinse water with a low conductivity of 1.2 mS cm^{-1} was reduced to less than 1.0 mg l^{-1} in 150 min at a flow rate of 500 ml min^{-1}.

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};
C_0	copper (II) concentration at treatment time = 0, mol l^{-1};
C_t	copper (II) concentration at treatment time t, mol l^{-1};
D	diffusion coefficient, $m^2\ s^{-1}$;
k_m	mass transfer coefficient, m s^{-1};
L	electrode length, m;
Re	Reynolds number, $uv^{-1}A_e^{-1}$;
Sc	Schmidt number, vD^{-1};
Sh	Sherwood number, $k_m\varepsilon A_e^{-1}D^{-1}$;
u	superficial velocity (volumetric flow rate/electrode cross sectional area), m s^{-1};
V_e	cathode volume, cm^3;
V_T	total volume of catholyte (cell + reservoir), cm^3;
ε	porosity;
ν	kinematic viscosity, $m^2\ s^{-1}$

1. Introduction

Electrochemical techniques offer an efficient means for the prevention and remedy of pollution problems particularly in the plating, metal finishing and electronic industries [1, 2]. Besides being a clean and versatile approach, recovering and recycling both the metal and the water provide great economic benefits. For dilute metal-bearing waste waters, porous three-dimensional electrodes in the form of carbon [3], metallic felt or foams [4, 5], reticulated vitreous carbon (RVC) [6–8], carbon felt [9–10] and stainless steel wool [11] are often considered to provide high specific surface area and overall mass transfer rates. In recent years, several papers have been published concerning the use of electrochemical reactors for the removal of heavy metals in a continuous single-pass mode and batch recirculation mode [12–15]. However, no specific publication focuses on the difference between the two approaches.

In the previous paper, removal and recovery of copper utilizing a single-pass galvanic cementation system was described [16]. It was confirmed that a single-pass system allows efficient copper removal below the maximum permissible level for simulated solutions. However, an outlet copper concentration below 1.0 mg l^{-1} was not achieved under any conditions when treating industrial wastewater. Hence, for solutions with very low electrical conductivities, another mode of operation, the batch-recycle system needs to be used for higher efficiency copper removal.

In this work, a batch-recycle galvanic system is studied along with its mass transfer characteristics. Furthermore, comparative studies between single-pass and batch-recycle reactors are made based on the influence of flow rates and initial copper concentrations.

2. Experimental details

Details of the galvanic flow cell used were described in part I of this series [16]. The cell was divided into two compartments by an anion exchange membrane R4030 (The Electrosynthesis Co.) This Cu/Fe system, which utilized 80 ppi RVC as cathode and steel wool as sacrificial anode, was operated in a batch-recycle mode. The hydraulic flow circuit, driven by a peristaltic pump Minipuls 2 (Gilson) for flow rates ranging from 3.8 to 20.1 ml min^{-1} and Masterflex pump (Cole-Palmer) for flow rates ranging from 50 to 500 ml min^{-1}, provided a continuous supply of reacting species to the electrodes, as shown in Figure 1. In this system, the electrolytes flow separately and simultaneously in a closed circuit through the catholyte and anolyte compartments and return to their respective reservoirs of volume 500 ml. Successive sampling and measurements using a Perkin Elmer 3100 Model Atomic Absorption Spectrophotometer were carried out to determine the copper concentrations in the catholyte reservoir. Various initial copper concentrations 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 were used. Application of this system was also performed on industrial wastewater.

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%.

3.1. *Performance of a batch-recycle reactor*

Figure 2 depicts the plot of normalized copper concentration as a function of time for different flow rates at an initial copper (II) concentration of 10 mg l^{-1}. All the curves have the same profile in which the copper (II) concentration dropped exponentially with time. Such a trend is evidence of a mass transport controlled process [13]. A linear relationship with ln (C_t/C_0) is observed in the insets from Figure 2 over the treatment time for all the flow rates examined. The plots exhibit best fit lines with linear correlation coefficients of 0.99 and above. However, a slight deviation of ln (C_t/C_0) against time from linearity occurs for higher flow rates. This is especially true for an initial copper concentration of 500 mg l^{-1}; the data for a flow rate 500 ml min^{-1} is more

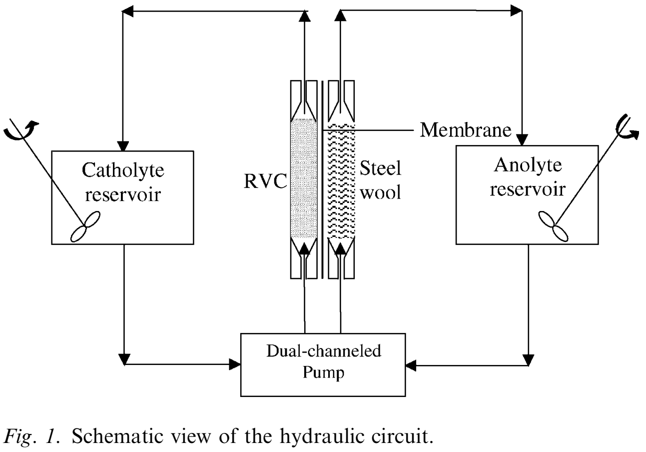

Fig. 1. Schematic view of the hydraulic circuit.

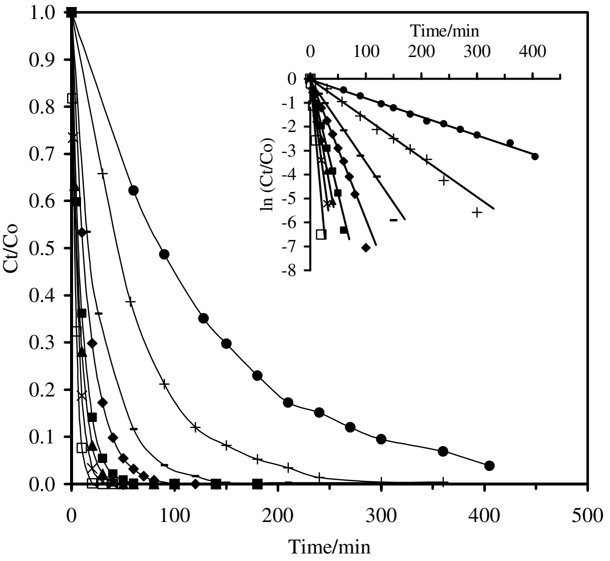

Fig. 2. Normalised concentration [C_t/C_0] vs. time for copper removal experiment obtained at a constant copper (II) concentration of 10 mg l^{-1} in 0.5 M H_2SO_4 for catholyte flow rate of 3.8 ml min^{-1} (●), 9.9 ml min^{-1} (+), 20.1 ml min^{-1} (–), 50 ml min^{-1} (◆), 100 ml min^{-1} (■), 150 ml min^{-1} (▲), 300 ml min^{-1} (×) and 500 ml min^{-1} (□). Inset: Plots of ln[C_t/C_0] against time for the data shown.

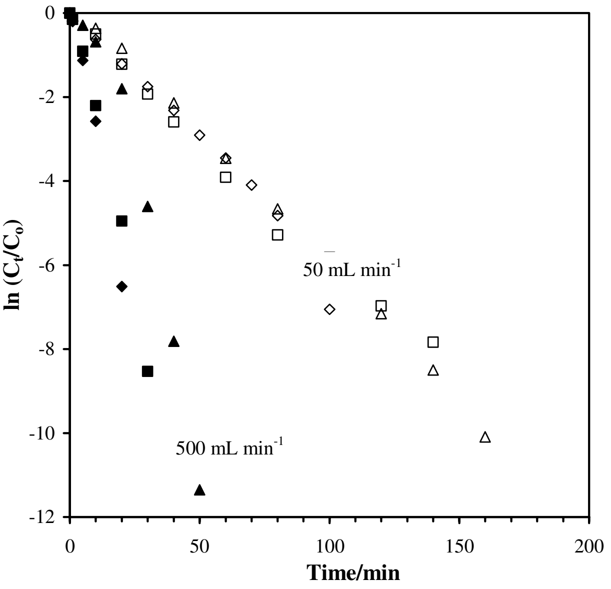

Fig. 3. Logarithm of normalized copper concentration against time for 10 mg l^{-1} (◇), 100 mg l^{-1} (□) and 500 mg l^{-1} (△) at flow rate 50 ml min^{-1}. The solid points correspond to various concentrations at flow rate 500 ml min^{-1}.

dispersed with a linear correlation coefficient of 0.94. As is evident from Figure 3, the linearity for the ln (C_t/C_0) against time plot was confirmed only for the first 10 min of treatment times at 500 ml min^{-1} as compared to the first 100 min of treatment times at 50 ml min^{-1}. This may explained by the fact that an increase in flow rate increases the copper removal rate and therefore leads to the dramatic fall of the remaining copper concentration in the reservoir. This tends to cause the loss of current efficiency in the cell [17]. On the other hand, the initial concentration had no significant influence on the copper removal rate as illustrated in Figure 3.

The current system may be approximately modeled as [13, 17, 18]:

$$\ln(C_t/C_0) = -\frac{V_e k_m A_e}{V_T} t \tag{1}$$

From the slopes of ln (C_t/C_0) against time plots, the values of $k_m A_e$ could be calculated since V_e/V_T is a constant and they are presented in Table 1. The data show that the value of $k_m A_e$ is flow rate dependent. From these results, it can be seen that the system performs better at higher flow rates for all the initial copper concentrations examined.

From the experimental results, it was found that$A_e k_m$ may be correlated with u by the empirical expression:

$$A_e k_m = 1.18u^{0.68} \tag{2}$$

This expression holds for the different flow rates and initial copper concentrations mentioned previously.

Table 1. Values of $k_m A_e$ taken from the slopes of the $\ln(C_t/C_0)$ against time plots

C_0 (mg l^{-1})	Flow rate (ml min^{-1})	Superficial velocity (10^2 m s^{-1})	% Removal after 60 min	$k_m A_e$ (10^2 s^{-1})
10	3.8	0.03	37.8	0.7
	9.9	0.08	62.1	1.4
	20.1	0.17	88.4	2.8
	50	0.42	96.8	4.9
	100	0.83	99.8	7.9
	150	1.25	> 99.9	10.6
	300	2.50	> 99.9	14.3
	500	4.17	> 99.9	21.5
100	3.8	0.03	36.5	0.7
	9.9	0.08	67.7	1.5
	20.1	0.17	91	3.4
	50	0.42	98	4.8
	100	0.83	99.9	8.1
	150	1.25	99.9	10.0
	300	2.50	> 99.9	14.8
	500	4.17	> 99.9	20.8
500	3.8	0.03	39.4	0.6
	9.9	0.08	66.2	1.5
	20.1	0.17	77.3	2.5
	50	0.42	96.8	5.3
	100	0.83	98.5	5.9
	150	1.25	99.7	7.2
	300	2.50	> 99.9	11.0
	500	4.17	> 99.9	18.2

Further, mass transport data were correlated using the dimensionless relationship in the form [19]:

$$Sh = \mathrm{m}\, Sc^{\mathrm{b}} Re^{\mathrm{f}} \tag{3}$$

For flow systems, the Schmidt number usually appears to the power 1/3 [9]. Figure 4 shows the logarithmic plots of *Sh* against *Re* for the removal of copper. Statistical analysis of the data in Figure 4 yields the best-fit line:

$$Sh = 0.22 Sc^{0.33} Re^{0.68} \tag{4}$$

This correlation is compared graphically with those obtained by other authors [7, 9, 13, 21]. The correlation constant for our results is somewhat lower than for the electrolytic systems. However, it should be pointed out that the power dependence of *Re* in the present work on a galvanic reactor is as high as or even higher than those presented in Table 2.

3.2. *Comparison between single-pass and batch-recycle reactors*

A set of experimental runs was conducted to compare the performance of a single-pass reactor with a batch-recycle reactor in treating dilute solutions. Initially, a single-pass system was used to treat 500 ml of different initial copper concentration viz., 10, 100 and 500 mg l^{-1} at a fixed flow rate. This single-pass reactor was a plug flow reactor as modeled below:

$$\ln(C_{\text{inlet}}/C_{\text{outlet}}) = -\frac{k_m A_e l}{u} \tag{5}$$

The remaining copper concentrations in the catholyte solutions leaving the cell were determined. The percentage of copper removal in a single-pass and the amount of time used in the treatment of 500 ml of solutions at a particular flow rate was also recorded. This duration of

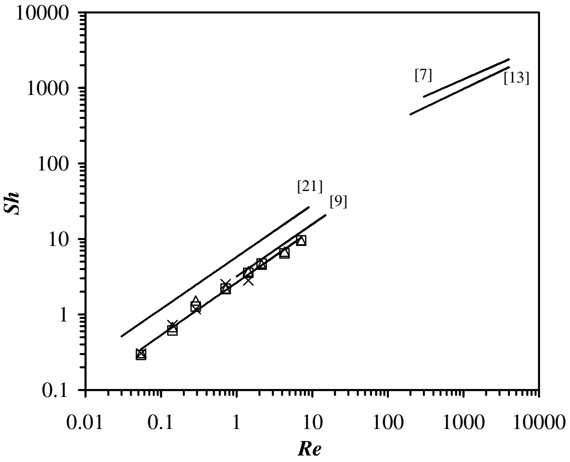

Fig. 4. Dimensionless mass transfer (*Sh*) and flow rate (*Re*) correlation determined from copper removal data. Inlet copper concentrations: 10 mg l^{-1} (□), 100 mg l^{-1} (△) and 500 mg l^{-1} (×). (———) Best-fit line. Correlations by other authors are shown together with the corresponding reference number.

Table 2. Comparison of the value of power dependence of *Re* with some literature data

Type of cell	Cathode material	Porosity, ε (grade in ppi)	Specific surface area, A_e (m^{-1})	Power dependence of *Re*	Reference
Electrolytic	RVC	0.97 (10, 60, 100)	1300–6700	0.44	[7]
Electrolytic	Carbon felt	0.94	21 818	0.69	[9]
Electrolytic	RVC	0.97 (10, 30, 60, 100)	1300–6700	0.48	[13]
Electrolytic	RVC	0.97 (45)	2710	0.69	[21]
Galvanic	RVC	0.97 (80)	5300	0.67	This work

time (Table 3) was then set as the time for sampling in a batch-recycle system. A catholyte sample was withdrawn and the remaining copper concentration was determined by an atomic absorption spectrophotometer. The experiments were performed at flow rates ranging from 20.1 to 500 ml min^{-1}. The basis of comparison used in this work is the percentage of copper removal achieved in both systems at the time taken for treating 500 ml of solution in a single-pass mode.

As a comparison, Figure 5 shows the percentage of copper removal for both single-pass and batch-recycle galvanic reactors in treating 500 ml of solutions at three flow rates: 20.1 ml min^{-1} (Figure 5a), 100 ml min^{-1} (Figure 5b) and 500 ml min^{-1} (Figure 5c). Generally, it can be said that for 10 and 100 mg l^{-1} of initial copper (II) concentration, the percentage of copper removal are significantly higher (at 95% confidence level in *t*-test) in a single-pass reactor at a lower range of flow rates (20.1–100 ml min^{-1}). In contrast, a higher copper removal was obtained for higher initial copper concentrations of 500 mg l^{-1} at a higher range of flow rates (100 to 500 ml min^{-1}) in a batch-recycle reactor. This is again verified by the space–time yield presented in Table 4. Hence, it can be deduced that a batch-recycle reactor should be chosen when treating a given sample at a set flow rate if its percentage of removal in a single-pass reactor was less than 30% (valid only for initial copper concentration of 10 to 500 mg l^{-1} in 0.5 M H_2SO_4). In other words, a single-pass reactor is a more suitable mode of operation when treating low initial copper concentration solutions where high removal can be obtained per pass. In the cases where high initial copper concentration solutions are involved, a batch-recycle reactor would give a more satisfactory result at high flow rates because there is an increase in mass transport.

3.3. *Application on industrial wastewater*

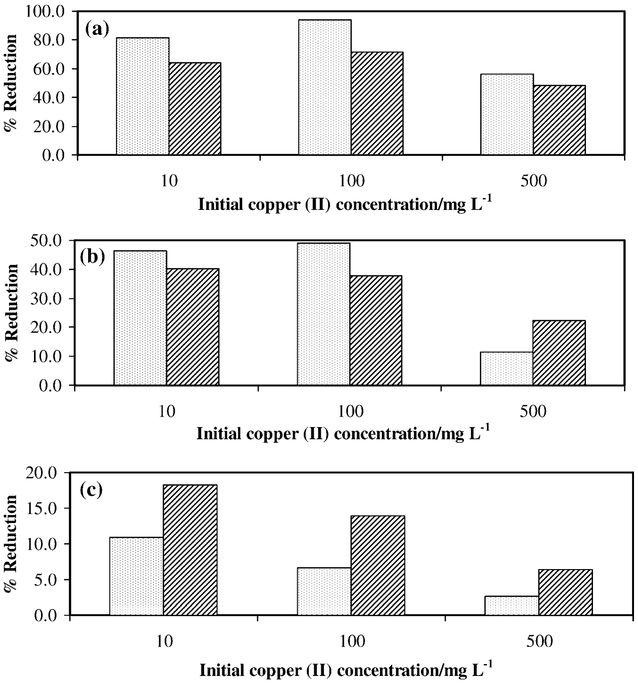

Fig. 5. Percentage of copper removal for both single-pass (▒) and batch-recycle reactors (▨) at the treatment time of 500 ml of solutions in a single pass at flow rates: (a) 20.1 ml min^{-1}, (b) 100 ml min^{-1} and (c) 500 ml min^{-1}.

Based on the results obtained using simulated solutions, studies on rinse water from a copper plating plant were conducted with the existing system. The characteristics of this sample of wastewater were reported in the previous paper [16]. A batch-recycle reactor operating at 500 ml min^{-1} successfully reduced the copper concentration in 500 ml of sample from an initial copper (II) concentration of 74.2 mg l^{-1} to less than 1.0 mg l^{-1} after 150 min. However, only 84.2% of copper was removed

Table 3. Duration of time needed in the treatment of 500 ml of solutions in a single-pass mode at various flow rates

Flow rates (ml min^{-1})	Time (min)
20.1	26.0 ± 0.2
100	5.0 ± 0.1
500	1.0 ± 0.1

Table 4. Space–time yield for the treatment of 500 ml of solutions in a single pass and a batch-recycle reactor at various flow rates

Flow rate (ml min^{-1})	Initial copper (II) concentration (mg l^{-1})	Space–time yield (g l^{-1} h^{-1})	
		Single-pass	Batch-recycle
20.1	10	0.954	0.817
100		2.79	2.41
500		3.27	5.50
20.1	100	11.1	8.48
100		29.3	22.6
500		20.0	42.1
20.1	500	33.4	28.8
100		34.6	67.4
500		40.0	96.1

in a single-pass system operating at 1.7 ml min^{-1} consuming approximately twice the duration time needed for a batch-recycle system. This clearly demonstrates that the treatment of industrial wastewater with very low electrical conductivities using a single-pass system is not economically viable on the basis of time consumption comparison.

4. Conclusions

The batch-recycle galvanic reactor used in this study showed satisfactory performance for the removal of copper from dilute simulated solutions and industrial wastewater. Mass transfer studies have revealed that the dependence of the average mass transfer coefficients with flow rate in this work correspond well with the literature data reported elsewhere [21]. The mass transfer rate in the electrode is high and can be estimated for different operating conditions by means of the correlation $Sh = 0.22Re^{0.68}Sc^{0.33}$. The use of a batch-recycle system proves to be more suitable compared to a single-pass system in treating low conductivity wastewater and this has allowed us to look further for improvement and possible scale-up of this system. Apart from that, preconditioning of industrial effluents and enhancing the surface area of electrodes are among other alternatives to be studied.

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References

1. D. Pletcher, Industrial Electrochemistry (Chapman and Hall Ltd., New York, 1984), pp. 325.
2. J.D. Genders and N.L. Weinberg, Electrochemistry for A Cleaner Environment (Electrosynthesis Co., East Amherst, New York, 1992), pp. 422.
3. D.N. Bennion and J. Newman, *J. Appl. Electrochem.* **2** (1972) 113.
4. J.M. Marracino, F. Coeuret and S. Langlois, *Electrochim. Acta* **32** (1987) 1303.
5. S. Langlois and F. Coeuret, *J. Appl. Electrochem.* **19** (1989) 43.
6. J. Wang and H.D. Dewald, *J. Electrochem. Soc.* **130** (1983) 1814.
7. C. Ponce De Leon and D. Pletcher, *Electrochim. Acta* **41** (1996) 533.
8. R. Bertazzoli, R.C. Widner, M.R.V. Lanza, R.A. Di Iglia and M.F.B. Sousa, *J. Braz. Chem. Soc.* **8** (1997) 487.
9. R. Carta, S. Palmas, A.M. Polcaro and G. Tola, *J. Appl. Electrochem.* **21** (1991) 793.
10. K. Kinoshita and S.C. Leach, *J. Electrochem. Soc.* **129** (1982) 1993.
11. M. Paidar, K. Bouzek, M. Laurich and J. Thonstad, *Water Environ. Res.* **72** (2000) 618.
12. A.K.P. Chu, M. Fleischmann and G.J. Hills, *J. Appl. Electrochem.* **4** (1974) 323.
13. D. Pletcher, I. Whyte, F.C. Walsh and J.P. Millington, *J. Appl. Electrochem.* **21** (1991) 659.
14. D. Pletcher, I. Whyte, F.C. Walsh and J.P. Millington, *J. Appl. Electrochem.* **21** (1991) 667.
15. D. Pletcher, I. Whyte, F.C. Walsh and J.P. Millington, *J. Appl. Electrochem.* **23** (1993) 82.
16. Y.P. Hor and N. Mohamed, *J. Appl. Electrochem.* **33** (2003) 279.
17. R.C. Widner, M.F.B. Sousa and R. Bertazzoli, *J. Appl Electrochem.* **28** (1998) 201.
18. C. Ponce De Leon and D. Pletcher, *J. Appl. Electrochem.* **25** (1995) 307.
19. E. Heitz and G. Kreysa, Principles of Electrochemical Engineering Extended version of a DECHEMA Experimental Course (VCH Verlagsgesellschaft, Federal Republic of Germany, Weinheim, 1986), pp. 294.
20. J.C. Card (1987) PhD dissertation University of Wisconsin-Madison.
21. J. Podlaha and J.M. Fenton, *J. Appl. Electrochem.* **25** (1995) 299.