Effect of electrode pulsation on the rate of simultaneous electrochemical recovery of copper and regeneration of ferric salts from dilute solutions

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ABSTRACT

The effect of vertical plate electrode pulsation on the rate of cathodic copper deposition and anodic oxidation of ferrous sulphate was studied in a divided cell. Electrode oscillation was found to enhance the rate of diffusion controlled copper deposition and ferrous sulphate anodic oxidation by a factor ranging from 1.9 to 7.8 compared to the natural convection value depending on the vibration velocity. Electrode pulsation was found to increase the current efficiency of copper deposition from 52% to 98%, while the current efficiency of anodic oxidation of $FeSO_4$ increased from 35% to 92% depending on the vibration velocity.

Also, electrode vibration was found to decrease electrical energy consumption of copper deposition from 4 to 1.56 kWh/kg; for anodic oxidation of $FeSO_4$ electrode vibration reduces energy consumption from 3.35 to 1.25 kWh/kg depending on vibration velocity. The importance of the present results for treating dilute solutions containing copper and ferrous ions such as printed circuit etching solution, pickling waste solutions, chemical machining waste solution, mine drainage water, leaching liquor obtained by leaching low grade copper sulphide ore by ferric salts was highlighted. The present technique has the advantage of recovering a precious metal and recycling a valuable chemical in one step, this satisfies the policy of zero discharge industry.

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1. Introduction

Dilute solutions containing Cu^{2+} and Fe^{2+} ions are discharged as effluents from the following industrial processes: (i) printed circuit by ferric salts [1], (ii) pickling of Cu and Cu alloys by acidified ferric sulphate [2–4], (iii) chemical machining of Cu and Cu alloys by ferric salts [5], (iv) chalcopyrite [$FeCuS_2$] mines drainage solution [6], (v) hydrometallurgical leaching of low grade copper sulphide ores by acidified ferric sulphate [7–9], (vi) electrowinning of copper from leaching solutions containing iron [10,11]. Effluents containing Cu^{2+} and Fe^{2+} pose an environmental threat and their treatment is mandatory to remove at least toxic Cu^{2+} in order to meet the stringent environmental standards imposed by governments. According to the American Standards Cu^{2+} should not exceed 0.5 ppm in the discharged waste [12]. Previous studies have concentrated on Cu^{2+} removal by different techniques such as cementation [13,14], ion exchange [15], membrane processes such as electrodialysis and reverse osmosis [16], adsorption [17], electrocoagulation [18], and electrodeposition using different elec-

trodes such as the rotating cylinder electrode and the fixed bed electrode [19,20]. The electrochemical technique has the advantage that it recovers Cu^{2+} as a valuable metal without producing a sludge or using chemicals which may complicate the pollution problem.

The aim of the present work is to explore the possibility of simultaneous copper deposition and ferric salt regeneration from dilute solution containing both Cu^{2+} and Fe^{2+} ions in a divided electrolytic cell with two oscillating vertical plate electrodes. Simultaneous Cu recovery and ferric salt regeneration would improve the energy efficiency of both processes while the use of oscillating electrodes would enhance the rate of cathodic Cu deposition and anodic oxidation of $FeSO_4$ because both processes are diffusion controlled [21,22]. The use of vibroagitation to enhance the rate of diffusion controlled processes has been receiving a growing interest [23–31] in view of the fact that it is more economic than rotary agitation [31]. The oxidized ferric salt can be recycled back e.g. in case of pickling of copper and copper alloys or in case of leaching of low grade copper sulphide ores, recycling of the ferric salt would decrease the operating costs of such processes. In case of chalcopyrite mine waste solution, $Fe_2(SO_4)_3$ remaining after copper removal can be treated with limestone to precipitate $Fe(OH)_3$ at pH 3. In contrast, the neutralization of ferrous sulphate cannot be carried out with

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Nomenclature

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a	amplitude of oscillation
a_1–a_4	constant
A	cathode area
C	concentration
C_o	initial concentration
D	diffusivity
E	total cell voltage
f	frequency of oscillation
F	Faraday's constant.
g	acceleration due to gravity
i_L	limiting current density
i	current density
K	mass transfer coefficient
K_o	natural convection mass transfer coefficient
L	cathode height
t	time of electrolysis
Q	volume of the solution in the reactor
V	vibration velocity ($V = a(2\pi f)$)
R_e	vibrational Reynolds number ($\rho V d / \mu$)
Sc	Schmidt number ($\rho V d / \mu$)
Gr	Grashof number $\left((gL^3/\gamma^2)(\Delta\rho/\rho)\right)$
Sh	Sherwood number (KL/D)
μ	solution viscosity
ρ	solution density
$\Delta\rho$	density difference
γ	kinematic viscosity

Fig. 1. Cell and electrical circuit used for constant current electrolysis. (1) Power supply; (2) multirange ammeter; (3) voltmeter; (4) cathode; (5) anode; (6) porous diaphragm; (7) Plexiglas cell; (8) electrolyte level; (9) plastic holder; (10) To vibrator.

limestone since precipitation of ferrous hydroxide requires a pH of 9–10 [32].

2. Experimental technique

Fig. 1 shows the cell and electrical circuit used in the present work. The cell was a rectangular Plexiglas container of the dimensions 10 cm × 10 cm for the base and 25 cm height. The cell was composed of two halves combined together by bolts and nuts through side and bottom flanges. A tight porous diaphragm made of synthetic fabric was inserted between the two halves to separate the two cell compartments, the edges of the porous diaphragm were held firmly by placing them between two rubber gaskets bonded to the cell flanges to prevent solution leakage. The cell cathode was a rectangular copper plate of 8 cm width and 24 cm height. A Pb/PbO$_2$ electrode was prepared before runs by electrolyzing 0.5 M H$_2$SO$_4$ between a lead anode and a lead cathode at a current density of 0.1 A/cm^2 for 5 min. The upper 16 cm of each electrode as well as the back of each electrode were isolated with epoxy resin i.e. the active height of each electrode was 8 cm. The two electrodes were bolted to a plastic holder which was connected to a vibrator. The details of the vibrator were described in an earlier work [30]. The electrical circuit consisted of 15 V d.c power supply with a voltage regulator and a multirange ammeter connected in series with the cell. A voltmeter was connected in parallel with the cell to measure its voltage.

Two series of experiments were carried out; in the first series the limiting current of copper deposition from acidified CuSO$_4$ solution was determined at different vibration velocity using a single compartment cell and a copper anode. In the second series of experiments electrolysis was conducted at a constant current equal to the limiting current corresponding to the operating vibration velocity where cathodic Cu deposition and anodic FeSO$_4$ oxidation take place simultaneously in the aforementioned divided cell using a copper cathode and Pb/PbO$_2$ anode.
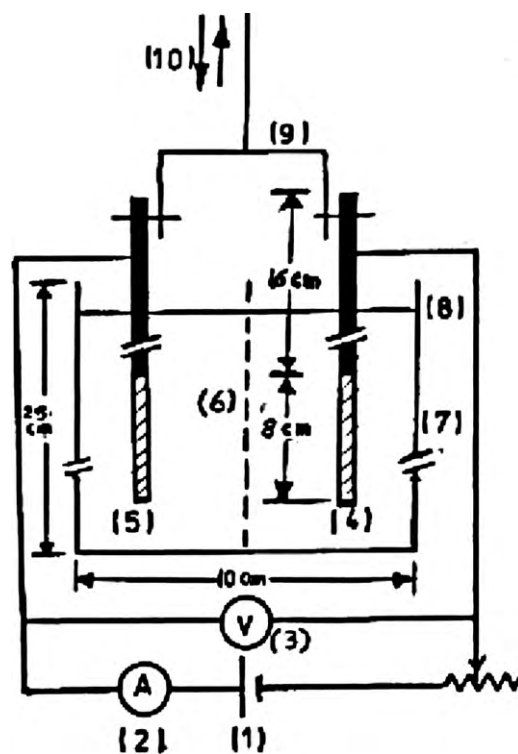
The limiting current of Cu deposition at different vibration velocity was determined in the aforementioned cell but without diaphragm using a copper anode instead of the lead anode, the backs of the copper anode and copper cathode were isolated with epoxy. Polarization curves from which the limiting current was determined were plotted by increasing the current stepwise and measuring the corresponding steady state cathode potential against a reference copper electrode placed in the cup of a Luggin tube filled with the cell solution, the tip of the Luggin tube was placed 1–2 mm from the vibrating cathode surface (Fig. 2) [33,34]. Limiting current at different vibration velocity was determined using a solution composed of 0.1 M CuSO$_4$ + 0.5 M H$_2$SO$_4$.

Constant current electrolysis experiments were carried out at different vibration velocities using a divided cell, current was fixed at the limiting current corresponding to the particular vibration velocity. The cathode compartment was filled with 1150 cm^3 solution composed of 0.1 M CuSO$_4$ + 0.5 M H$_2$SO$_4$ while the anode compartment was filled with 1150 cm^3 solution composed of 0.2 M FeSO$_4$ + 0.5 M H$_2$SO$_4$. During electrolysis a sample of 2 cm^3 was taken from both the catholyte and the anolyte for analysis of copper and iron respectively every 3 min. Analysis was carried out by atomic absorption. The solubility of Fe$_2$(SO$_4$)$_3$ in 0.5 M H$_2$SO$_4$ is high enough (about 55 g/100 g H$_2$O) to obviate any interference with analysis. All solutions were prepared using A.R. Chemicals and distilled water. Frequency of electrode vibration ranged from 1.33 to 2 Hz while amplitude ranged from 0.5 to 2 cm; vibration velocity ranged from 4.2 to 25 cm/s. Temperature was ±25 °C.

3. Results and discussion

The constant current electrolysis experiments were conducted at a current equal to the limiting current of the initial Cu^{++} concentration and the applied vibration velocity. The limiting current was determined from polarization curves. Fig. 3 shows typical
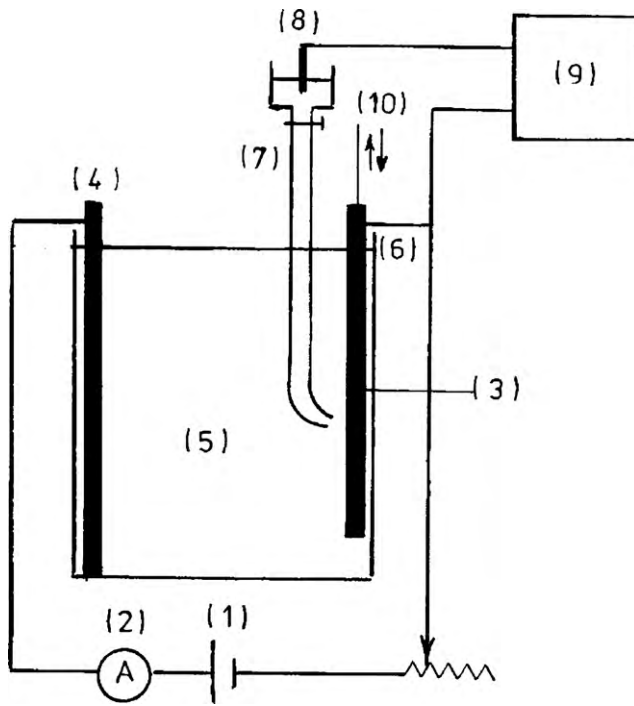
Fig. 2. Cell and electrical circuit used for limiting current measurement. (1) Power supply; (2) multirange ammeter; (3) copper cathode; (4) copper anode; (5) Plexiglas cell; (6) electrolyte level; (7) Luggin tube; (8) reference electrode; (9) high impedance voltmeter; (10) To vibrator.
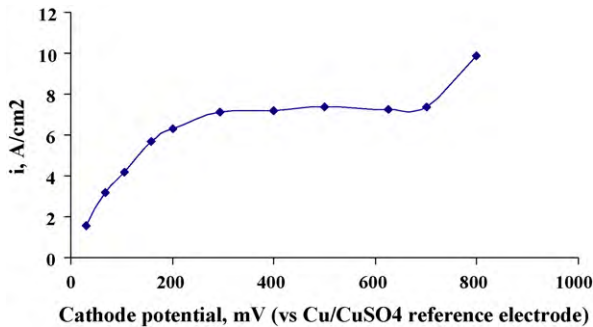

Fig. 3. Typical polarization curve for the deposition of copper under natural convection from 0.1 M CuSO$_4$ in 0.5 M H$_2$SO$_4$.

polarization curve with a well defined limiting current plateau obtained under natural convection, limiting current at different vibration velocity was obtained potentiostatically by fixing the cathode potential at 500 mV and measuring the corresponding steady state current. Fig. 4 shows the effect of vibration velocity on
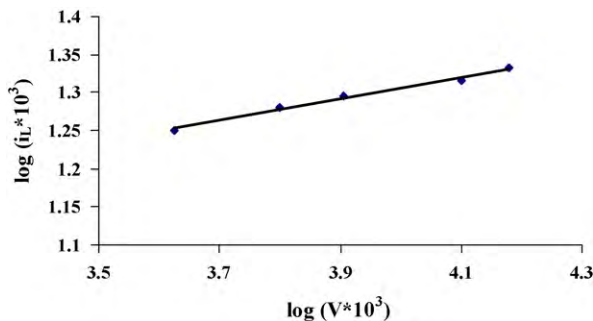

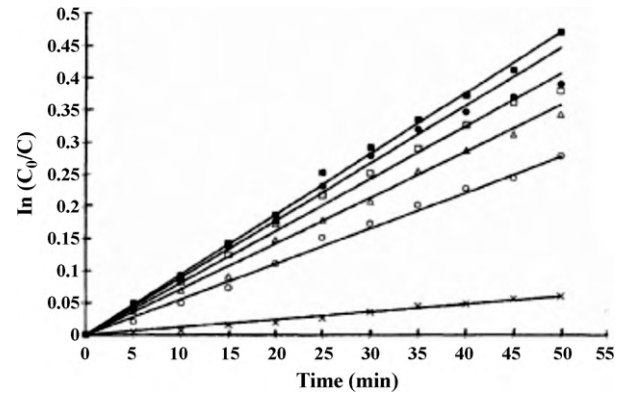**Fig. 4.** Effect of vibration velocity on the limiting current density of copper deposition.

Fig. 5. ln C_o/C vs. t for copper deposition during constant current electrolysis. Vibration velocity, cm/s: (X) — 0 (natural convection); (○) — 4.2; (△) — 6.3; (□) — 8.4; (●) — 12.6; (■) — 16.8.

the limiting current of copper deposition. The data fit the equation.

$$i_L = a_1 V^{0.14} \tag{1}$$

The vibration velocity V was calculated from the equation

$$V = a(2\pi f) \tag{2}$$

The natural convection limiting current (at $V = 0$) obtained in the present work is in a fair agreement with the value predicted from the natural convection mass equation [33]

$$Sh = 0.67(ScGr)^{0.25} \tag{3}$$

The physical properties used to calculate ScGr was taken from the literature [25–27].

The vibration velocity exponent 0.14 of Eq. (1) is at variance with the value 0.5 obtained by previous studies for pulsating plate electrodes under conditions where pulsating flow overshadows the effect of natural convection [17,18]. The criterion for the predominance of the pulsating flow over natural convection flow was established by Acrivos as follows [36].

$$Gr/Re^2Sc^{0.33} < 0.1 \tag{4}$$

For the present range of conditions $Gr/Re^2Sc^{0.33}$ is higher than 0.1, accordingly in the present case both natural convection and pulsating flow contribute to enhancing the rate of mass transfer.

Attempts to obtain a limiting current for the anodic oxidation of FeSO$_4$ on Pb/PbO$_2$ failed to give a well defined limiting current plateau despite the diffusion controlled nature of the reaction [22,34] probably because of the interference of oxygen evolution at the Pb/PbO$_2$ anode.

Figs. 5 and 6 show that the constant current electrolysis concentration–time data for the simultaneous cathodic deposition of copper and anodic oxidation of FeSO$_4$ fit the batch reactor equation [21]

$$Q\frac{dC}{dt} = KAC \tag{5}$$

which integrates to

$$\ln\frac{C_o}{C} = \frac{KAt}{Q} \tag{6}$$

The mass transfer coefficient K was obtained from the slope (KA/Q) of the plot ln C_o/C vs. t.

It is noteworthy that Fig. 6 was plotted in terms of ln C_o/C of Fe$_2$(SO$_4$) vs. t, the initial concentration of Fe$_2$(SO$_4$)$_3$ at zero time of electrolysis was found to have a definite value because of the chemical oxidation of FeSO$_4$ by PbO$_2$ previously formed on the Pb anode.
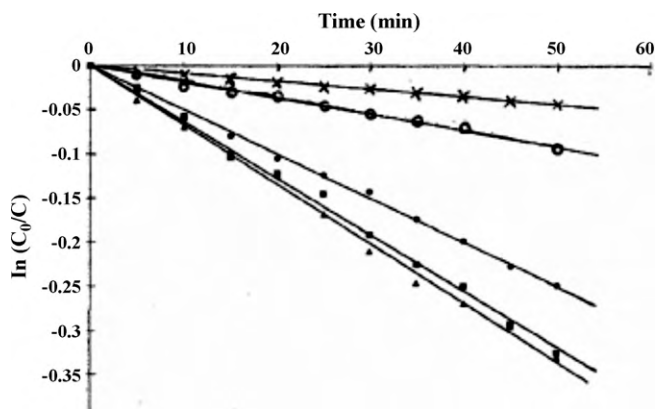
Fig. 6. ln C_o/C vs. t for the anodic oxidation of FeSO$_4$. Vibration velocity, cm/s: (X) — 0 (natural convection); (◯) — 4.2; (●) — 12.6; (■) — 16.75; (▲) — 25.2.
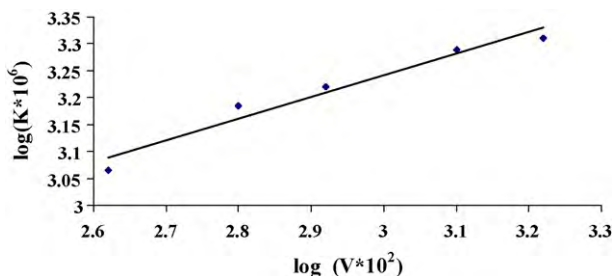

Fig. 7. Effect of vibration velocity on the mass transfer coefficient of copper deposition during constant current electrolysis.

Fig. 7 shows that the mass transfer coefficient of copper deposition increases with increasing vibration velocity according to the equation

$$K = a_2 V^{0.4} \tag{7}$$

The exponent 0.4 reflects the outcome of the interaction between natural convection, pulsating flow and surface roughness induced by the copper powder deposited at the limiting current [37]. Besides increasing the diffusional area, surface roughness potentiates the combined effect of pulsating flow and natural convection via turbulence generation [38] when the flow crosses protrusions of large peak to valley height, the generated turbulence penetrate the diffusion layer and renews the solution at the cathode surface [37,38].
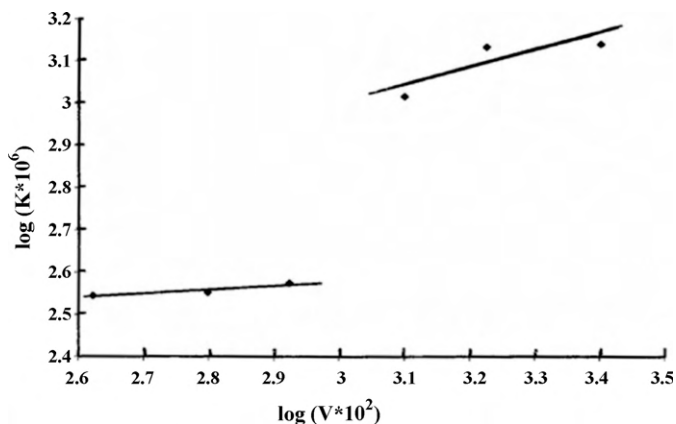

Fig. 8. Effect of vibration velocity on the mass transfer coefficient of FeSO$_4$ anodic oxidation during constant current electrolysis.

Fig. 8 shows the effect of vibration velocity on the mass transfer coefficient of the anodic oxidation of FeSO$_4$, the data show two distinct regions, at low vibration velocities ($V < 8.4$ cm/s) the mass transfer coefficient increases slightly with the vibration velocity according to the equation.

$$K = a_3 V^{0.11} \tag{8}$$

while at relatively high values of vibration velocities, the data fit the equation

$$K = a_4 V^{0.4} \tag{9}$$

The low effect of vibration velocity on the mass transfer coefficient of the anodic oxidation of FeSO$_4$ at vibration velocities <8.4 cm/s may be ascribed to the powerful stirring effect of O$_2$ bubbles which evolve simultaneously with FeSO$_4$ oxidation at the anode during electrolysis. Evolving O$_2$ bubbles enhance the mass transfer coefficient of FeSO$_4$ anodic oxidation via micro- and macro-convection. Micro-convection arises when the bubble leaves the electrode surface as soon as the bubble buoyancy force exceeds the surface tension force holding the bubble to the electrode surface, fresh solution rushes to fill the void left by the bubble at the electrode surface thus enhancing the rate of mass transfer through a surface renewal mechanism [39]. Macro-convection is induced by the rising bubble swarm; the rising gas–liquid dispersion reduces the diffusion layer thickness according to the hydrodynamic boundary layer theory [40]. As the vibration velocity increase beyond 8.4 cm/s it seems that pulsating flow becomes strong enough to detach O$_2$ bubbles prematurely from the anode surface by virtue of the high shear stress exercised by the pulsating flow on the electrode surface. The prematurely detached small sized bubbles contribute to enhancing the rate of mass transfer along with pulsating flow. Pulsating flow not only increase the rate of mass transfer through decreasing the diffusion layer thickness but also increases the available active electrode area by decreasing the blanketing effect of O$_2$ bubbles adhering to the anode surface by their early removal [41,42] and subsequent rise in the diffusion layer by virtue of their small size. According to Whitney and Tobias [43] who studied the mechanism of mass transfer at vertical surfaces by curtains of rising gas bubbles, small sized bubbles rising inside the diffusion layer enhances the rate of mass transfer at the vertical surface by surface renewal mechanism while bubbles rises outside the diffusion layer enhances the rate of mass transfer by macro-convection in a manner similar to natural convection. It is noteworthy that the exponent 0.4 of Eqs. (7) and (9) agree fairly with the value 0.5 predicted from the surface renewal model [23,39]. This suggests that mass transfer takes place under the present conditions at the cathode and anode by a complex mechanism to which surface renewal contributes a great deal.

Fig. 9 shows that the mass transfer coefficient of copper deposition increases by a factor ranging from 4.6 to 7.8 by pulsation compared to the natural convection value while Fig. 10 shows that the enhancement ratio for FeSO$_4$ oxidation ranges from 1.9 to 7.5 depending on the vibration velocity.

To assist in the economic evaluation of the present technique in comparison with other techniques, the effect of electrode pulsation on electrical energy consumption was determined; to calculate the electrical energy consumption, the effect of vibration velocity on the current efficiency was determined first. Fig. 11 shows that the average current efficiency during constant current copper deposition increases with increasing vibration velocity i.e. simultaneous H$_2$ evolution with copper deposition decreases with increasing vibration velocity. In case of FeSO$_4$ oxidation Fig. 12 shows that the current efficiency starts to increase with vibration velocity at $V > 6$ cm/s at the expense of O$_2$ evolution.
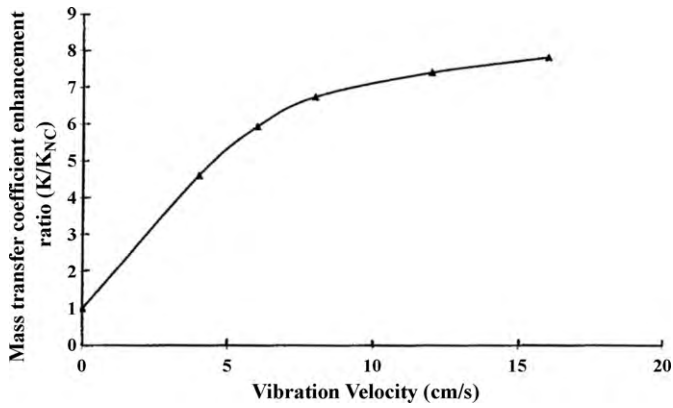
Fig. 9. Mass transfer enhancement ratio for copper deposition at different vibration velocity.
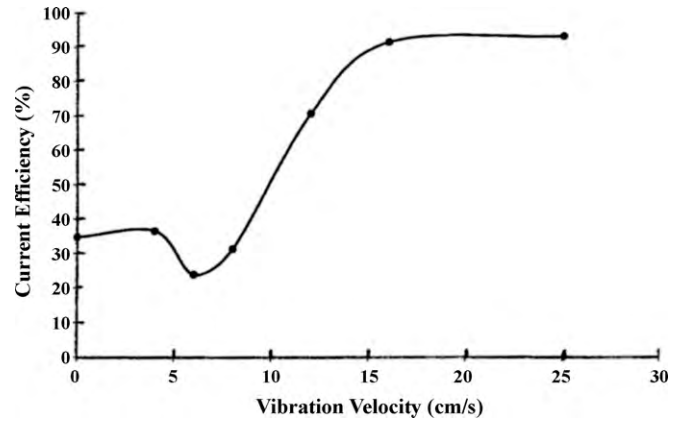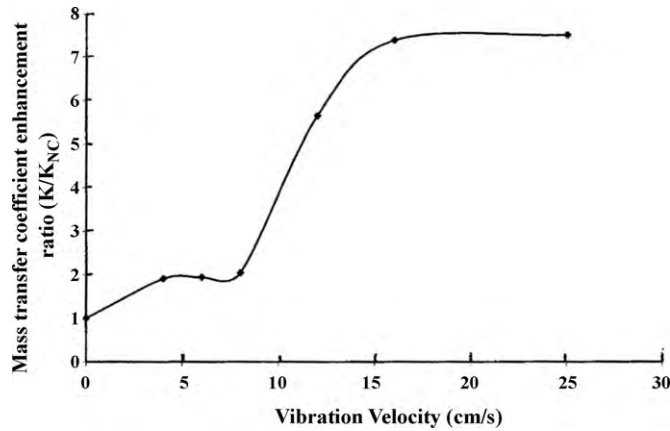

Fig. 10. Mass transfer enhancement ratio for the anodic oxidation of $FeSO_4$ at different vibration velocity.

Fig. 12. Effect of vibration velocity on the current efficiency of $FeSO_4$ anodic oxidation.
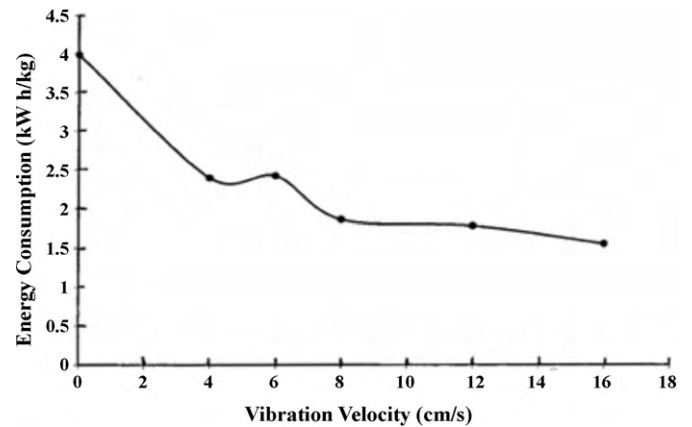

Fig. 13. Effect of vibration velocity on the energy consumption of copper deposition.

Electrical energy consumption (E.C) in kWh/kg was calculated from the equation

$$E.C = \frac{I \times E}{1000 \times m} \tag{10}$$

where m is the amount of copper or $Fe_2(SO_4)_3$ produced in kg/h, m was calculated from Faraday's law and the current efficiency.

Fig. 13 shows that the energy consumption for copper deposition decreases with increasing vibration velocity down to 1.56 kWh/kg which is less than the value 2 kWh/kg reported in the literature for electrowinning of copper [10,11].

Fig. 14 shows that vibration velocity beyond 6.6 cm/s reduces energy consumption for $FeSO_4$ oxidation down to 1.25 kWh/kg of $Fe_2(SO_4)_3$ compared to the value 1.9 kWh/kg reported in the literature [22] for the production of $Fe_2(SO_4)_3$ by electrolysis at the limiting current using a divided cell. The decrease in energy consumption with increasing vibration velocity may be attributed to: (i) increase in the limiting current and current efficiency as a result of mass transfer enhancement; (ii) electrode vibration tends to decrease the total cell voltage as shown in Table 1; the decrease in cell voltage may be ascribed to the early removal of the bubble layer by electrode oscillation, the bubble layer adhering to the
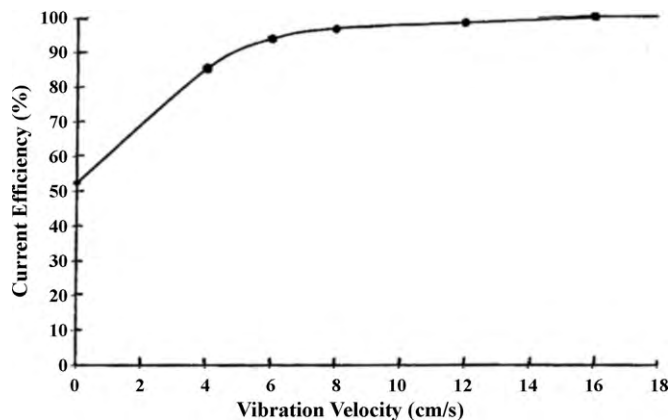

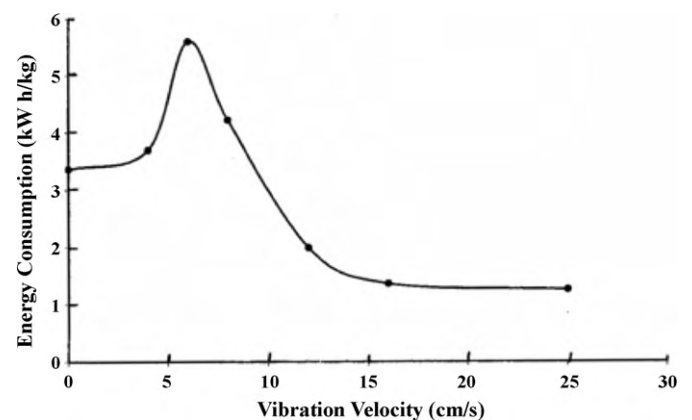**Fig. 11.** Effect of vibration velocity on the current efficiency of copper deposition.

Fig. 14. Effect of vibration velocity on the energy consumption of $FeSO_4$ oxidation.

Table 1
Effect of vibration on the total cell voltage during constant current electrolysis.

Vibration velocity, cm/s	Current density, A/cm^2	Cell voltage, V
0 (natural convection)	0.0078	2.44
4 .2	0.0179	2.823
6 .3	0.019	2.787
8 .4	0.02	2.755
12 .6	0.021	2.646
16 .8	0.0215	2.596

electrode surface considerably increases the cell resistance and the ohmic drop (IR) which constitutes a sizable component of the total cell voltage [39,44].

4. Conclusion

The present study has shown that simultaneous copper deposition and $Fe_2(SO_4)_3$ regeneration in a divided electrochemical reactor with pulsating plate electrodes is a promising technique for managing dilute solutions containing Cu^{++} and Fe^{++} which are discharged from many technical processes. Electrode pulsation increases the rate of production of copper and $Fe_2(SO_4)_3$ by a factor ranging from 1.9 to 7.8 depending on vibration velocity. Electrode pulsation also increases the current efficiency of copper deposition and $FeSO_4$ oxidation with a consequent decrease in electrical energy consumption. The present work contributes to the current trend of zero discharge of effluents by recovering a precious metal and recycling a valuable chemical. Work is underway to further improve the process using 3 dimensional electrodes, namely a vibrating vertical stack of closely packed screens. The high specific area and the high rate of mass transfer of such electrode would increase substantially the productivity of the reactor.

Under the present conditions where electrode vibration is accompanied by gas evolution and the development of surface roughness, mass is transferred at the electrodes by a complex mechanism where pulsating flow, natural convection, bubble induced micro- and macro-convection and turbulence generated by surface roughness contribute to enhancing the rate of mass transfer. The vibration velocity exponent 0.4 of Eqs. (7) and (9) suggested that surface renewal plays an important role in the present mass transfer mechanism.

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