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Mass transfer characteristics of reciprocating screen stack electrochemical reactor in relation to heavy metal removal from dilute solutions

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Abstract

Rates of mass transfer were measured for copper deposition from dilute acidified copper sulphate solution on reciprocating arrays of separated and closely packed screens by the limiting current technique under different conditions of amplitude, frequency of oscillation and copper ion concentration. The mass transfer data for the diffusion controlled copper deposition at the limiting current from a solution of constant concentration were correlated by the equations:

$$j_D = 0.732 Re_v^{-0.35}$$

for the closely packed screen array, and

$$j_D = 0.98 Re_v^{-0.38}$$

for the separated screen array.

A mathematical model based on the surface renewal theory was found to agree fairly with the above equations. Study of the removal of copper by constant current electrolysis at the limiting current using an insoluble lead anode has shown that the reactor is capable of reducing copper ion concentration below the maximum permissible value in a time which depends on the operating conditions.

The potential of using the present reactor for processing sparingly soluble reactants such as immiscible organic liquids, organic solids and gases which need to be dispersed prior to reacting at the electrode was highlighted. Also the possibility of using oscillating screen array as a catalytic reactor suitable for conducting liquid–solid diffusion controlled catalytic reactions such as removal of organic pollutants from industrial effluents by wet oxidation was noted.

Keywords: Mass transfer; Copper deposition; Electrochemical reactor; Vibration; Water pollution

1. Introduction

Increasing awareness of the risks associated with hazardous chemical waste disposal is causing governments to implement stricter environmental legislation to prevent pollution and environmental damage by industrial waste. Industrial waste water containing toxic ions represents a challenging case owing to the difficulty of removing these ions by biodegradation. Furthermore, some heavy metals such as Pb, Cu, Hg and Cr inhibit or prevent the oxidation of organic waste by bacteria [1]. Pollution by toxic metals including Cd, Cu, Cr, Pb, Hg and Zn is generated by a wide range of manufacturing industries such as mining, metal finishing, printed circuit fabrication and metallurgical industries. Recently, with the advent of high space-time yield electrochemical reactors, the electrochemical technique has proved to be a very powerful tool for removing heavy metals from waste solutions. In many cases the technique was found to be superior to other techniques such as chemical precipitation, ion exchange and cementation [2–4]. The technique is gaining a growing acceptance by industry in view of the fact that it does not only diminish the toxic ion concentration to the safe level but also it allows recovery of precious

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Nomenclature

a	amplitude of oscillation
$\acute{a}$	constant
A	cathode area
C	concentration of Cu^{2+}
C_b	bulk concentration of Cu^{2+}
C_i	interfacial concentration of Cu^{2+}
C_0	initial concentration of Cu^{2+}
d	cylinder diameter
d_h	hydraulic diameter of the screen
d_w	screen wire diameter
D	diffusivity of Cu^{2+}
f	frequency of oscillation
F	Faraday's constant
i_L	limiting current density
I_L	limiting current
j_D	mass transfer factor ($St \cdot Sc^{0.67}$)
K	mass transfer coefficient
K_0	mass transfer coefficient without vibrationt
K_c	mass transfer coefficient obtained from the constant current electrolysis
L	vertical plate height
N	rate of copper deposition
Q	volume of the solution in the reactor
t	time
t_r	contact time
u	velocity component parallel to the mass transfer surface
V	solution velocity past a stationary cylinder or screen
V_r	instantaneous relative velocity between a sinusoidal vibrating plate and solution
V_v	vibrational velocity ($V_v = 2\pi fa$)
x	distance parallel to the mass transfer surface
y	distance perpendicular to the mass transfer surface
Re	Reynolds number for stationary cylinders and screens in cross flow ($\rho Vd/\mu$)
Re_v	vibrational Reynolds number ($\rho V_v d_h/\mu$)
$Re_{v,w}$	vibrational Reynolds number based on wire diameter ($\rho V_v d_w/\mu$)
Sc	Schmidt number ($\mu/\rho D$)
Sh	Sherwood number ($K d_w/D$)
St	Stanton number (K/V_v)
Greek letters	
α, β	proportionality constants
μ	solution absolute viscosity
ρ	solution density
ω	angular velocity ($2\pi f$)

metals such as Ag, Au and Cu. For the usually small concentrations of metal ions in waste waters, cathodic deposition of metals such as Cu, Ag, Zn, Pb and Cd is diffusion controlled [2–6], and hence, the rate of metal deposition, N, is given by [7,8]:

$$N = \frac{I_L}{ZF} = KAC \tag{1}$$

The above equation shows that to obtain a high rate of metal removal from such a dilute solution the electrochemical reactor should have a high mass transfer coefficient or a high surface area or both. Some electrochemical reactors satisfying the above criteria have been developed and used successfully in industry for waste water treatment. These reactors include three-dimensional electrodes such as the fluidized bed electrode and the fixed bed electrode, and two-dimensional electrodes such as the rotating cylinder electrode [2–6].

In view of the high specific area and the high turbulence promoting ability of woven screens, the present work aims at exploring the possibility of using oscillating horizontal arrays of separated and closely packed screens electrochemical reactors in removing and recovering heavy metals from dilute solutions such as industrial effluents and leach liquors resulting from leaching low grade ores. The present study was carried out using copper deposition in view of its industrial importance. The performance of the suggested reactor was evaluated by determining (i) the reactor mass transfer behaviour using the well-known limiting current technique [7], and (ii) the extent to which the reactor can reduce Cu^{2+} concentration by constant current electrolysis under different operating conditions. In earlier reports [9,10], the mass transfer behaviour of oscillating horizontal single screen and array of screens was studied by measuring the limiting current of the cathodic reduction of $K_3Fe(CN)_6$. The authors correlated their data for single screen by an equation which shows that the mass transfer coefficient increases with the 0.33 power of the vibrational velocity. For vibrating screen array, the deviation from the single screen behaviour was presented without data correlation. The authors used an amplitude ranging from 0.25 to 1.5 cm while the frequency range was limited to 0.75–5 Hz. The results of the present study are expected to differ from the early study on vibrating horizontal screens [9,10] not only because of the difference in the range of experimental conditions but also because the metal depositing system used in the present work may induce surface roughness and significant natural convection compared to the ferri-ferrocyanide system used in the earlier study.

Apart from metal deposition, the present reactor is also suitable for processing systems involving sparingly soluble reactants such as electro-organic synthesis using immiscible liquid organic reactants or sparingly soluble solid particle reactants. In this case the oscillating screen array would efficiently disperse the reactant in the aqueous phase beside acting as an electrode [11,12]. The reactor is also suitable for electrochemical processing of gaseous reactants, e.g., flue gas desulphurisation where SO_2 is first absorbed in aqueous solution and then anodically oxidized to H_2SO_4 [13]. In this case the oscillating screen array would enhance the gas–liquid mass transfer [14] and the liquid–solid mass transfer simultaneously.

Previous studies on the use of screens in building electrochemical reactors of high space-time yield include gas sparged screens [15,16], rotating horizontal single and array of circular screens (discs) [17], and horizontal and vertical screens stirred by single and two phase flow [18,19]. Previous studies on the use of vibrations to enhance the rate of liquid–solid mass transfer was limited to simple geometries with limited specific area such as flat plates, cylinders and spheres [20–28]. Little has been done to study the rate of mass transfer at vibrating surfaces of high specific area such as fixed beds. El-Shazly et al. [29] studied the liquid–solid mass transfer behaviour of an oscillating bed of copper Raschig rings in acidified $K_2Cr_2O_7$ solution, and the data were correlated by the equation:

$$Sh = 0.76 Sc^{0.33} Re_{\mathrm{v}}^{0.75} \left(\frac{d_{\mathrm{c}}}{L}\right)^{0.35} \tag{2}$$

where d_{c} is the reactor diameter and L is the bed height. Raschig ring diameter was used as the characteristic length in calculating Sh and Re_{v}.

2. Theory

Theoretical studies on the effect of vibration on the rate of mass transfer have lead to the development of four models which can be outlined as follows:

(i) The *stretched film model* which was advanced by Lemlich and Levy [30] assumes that the rate of mass transfer increases by vibration owing to the formation of an effective film area equal to the total area swept by the vibrating surface during each cycle. For a vibrating flat plate this model leads to [25]:

$$\frac{K}{K_0} = I + \alpha Re_{\mathrm{v}} \left(\frac{a}{L}\right)^2 \tag{3}$$

Plate length L is used as characteristic length for Re_{v}. This model applies when high frequency low amplitude vibrations are used.

(ii) The *quasi-steady state model* assumes that at any instant the rate of mass transfer is determined by the instantaneous relative velocity, V_{r}, given by the equation (assuming sinusoidal vibration)

$$V_{\mathrm{r}} = a\omega \cos \omega t \tag{4}$$

where ω is the angular velocity ($2\pi f$, f being the frequency of oscillation).

For a given geometry the mass transfer coefficient can be estimated from the steady flow (forced convection) mass transfer equation by replacing the steady flow solution velocity by the instantaneous relative velocity, i.e., Eq. (4). For a vibrating flat plate, this model leads to the equation [20,23]:

$$Sh = 0.506 Sc^{0.33} Re_{\mathrm{v}}^{0.5} \tag{5}$$

Plate length, L, is used as the characteristic length in Sh and Re_{v}. This model is suitable for very low frequencies.

(iii) The *analogy model* assumes that vibration affects the diffusion layer in a manner similar to its effect on the hydrodynamic boundary layer. Based on the assumption, mathematical treatment leads to the following equation for a vibrating flat plate [20,23]:

$$Sh = \beta Re_{\mathrm{v}}^{0.5} \left(\frac{L}{a}\right)^{0.5} \tag{6}$$

Plate length, L, is used as the characteristic length in Sh and Re_{v}.

(iv) In the *combined model*, the steady state material balance equation:

$$u\frac{\mathrm{d}C}{\mathrm{d}x} = D\frac{\mathrm{d}^2C}{\mathrm{d}y^2} \tag{7}$$

was solved for the vibrating surface by using the velocity distribution results obtained by Schlichting [31] for vibrating surfaces. Using this model, Jameson [27] obtained the following equation for vibrating horizontal cylinders:

$$Sh = 0.746 Sc^{0.33} Re_{\mathrm{v}}^{0.5} \left(\frac{a}{r}\right)^{1/6} \tag{8}$$

cylinder radius, r, being the characteristic length in calculating Sh and Re_{v}. A similar equation was obtained for vibrating flat plate but with a coefficient of 0.665 instead of 0.746 and with plate length, L, as the characteristic length instead of the cylinder radius, r [20,23,32]. Experimental verification of the above models has shown that these models have limited applicability, and this leaves a room for other models to be tested.

The present work explores the possibility of applying the surface renewal theory [33] to vibrating screens. Assuming that the solution is stagnant, vibrating screen wires in their journey up and down past different locations are subjected repeatedly to a fresh solution. The residence time of the wire at each location is t_{r}, and during this time unsteady state diffusion takes place between the wire and the solution before the wire travels to the next location where the wire again meets a fresh solution. This situation can be treated with Fick's second law of diffusion:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = D\frac{\mathrm{d}^2C}{\mathrm{d}y^2} \tag{9}$$

with the boundary conditions:

$$C = C_{\mathrm{i}}, \quad \text{for } y = 0 \quad \text{at } t > 0 \tag{10}$$

$$C = C_{\mathrm{b}}, \quad \text{for } y \to \infty \quad \text{at } t > 0 \tag{11}$$

$$C = C_{\mathrm{b}}, \quad \text{for } y = 0 \quad \text{at } t = 0 \tag{12}$$

Integrating Eq. (9) using the above boundary conditions leads to

$$\frac{C_{\mathrm{b}} - C}{C_{\mathrm{b}} - C_{\mathrm{i}}} = \operatorname{erfc}\left[\frac{y}{(Dt)^{0.5}}\right] \tag{13}$$

The flux of the reactant crossing the $y=0$ plane towards the wire surface is expressed by

$$N = -D\left(\frac{\mathrm{d}C}{\mathrm{d}y}\right)_{y=0} = C_{\mathrm{b}} - C_{\mathrm{i}}\left(\frac{D}{\pi t}\right)^{0.5} \tag{14}$$

The mean value of the flux over the time interval t_r is

$$N = \frac{1}{t_r}\int_0^{t_r} N\,\mathrm{d}t = 2(C_b - C_i)\left(\frac{D}{\pi t_r}\right)^{0.5} \tag{15}$$

since

$$N = K(C_b - C_i) \tag{16}$$

From Eqs. (15) and (16) it follows that

$$K = 2\left(\frac{D}{\pi t_r}\right)^{0.5} \tag{17}$$

The contact time for t_r of the wire with a certain location in the solution is given by

$$t_r = \frac{d_w}{V_v} \tag{18}$$

substituting for t_r in Eq. (17) we get:

$$K = 2\left(\frac{DV_v}{\pi d_w}\right)^{0.5} \tag{19}$$

i.e.,

$$K = \frac{2}{\pi^{0.5}} D^{0.5} V_v^{0.5} d_w^{-0.5} \tag{20}$$

Multiplying both sides by d_w/D

$$\frac{Kd_w}{D} = \frac{2}{\pi^{0.5}} D^{-0.5} V_v^{0.5} d_w^{0.5} \tag{21}$$

The above equation can be converted to a dimensionless equation by multiplying the right hand side of the equation by $(\mu\rho/\rho\mu)^{0.5}$ and rearranging

$$\frac{Kd_w}{D} = \frac{2}{\pi^{0.5}}\left(\frac{\mu}{D\rho}\right)^{0.5}\left(\frac{\rho V_v d_w}{\mu}\right)^{0.5} \tag{22}$$

i.e.,

$$Sh = 1.129 Sc^{0.5} Re_{v,w}^{0.5} \tag{23}$$

Dividing both sides of the above equation by $Sc \cdot Re_{v,w}$.

$$St = 1.129 Sc^{-0.5} Re_{v,w}^{-0.5} \tag{24}$$

$$St \cdot Sc^{0.5} = 1.129 Re_{v,w}^{-0.5} \tag{25}$$

The prediction of the above model that $Sh \propto Re_{v,w}^{0.5}$ agrees with other models such as the quasi-steady model, the analogy model and the combined model [20–23].

3. Experimental technique

The apparatus (Fig. 1) consisted of the cell, the electrical circuit and the vibrating system. The cell was made of a cylindrical plexiglass container of 15.5 cm diameter and 30 cm height. The cathode was either an array of 5 closely packed horizontal stainless steel screens or an array of 5 separated screens, screen separation was fixed at 1 cm in view of an earlier study which showed that the mass transfer coefficient increases slightly with increasing screen separation and then remains constant for separation ≥1 cm [9].

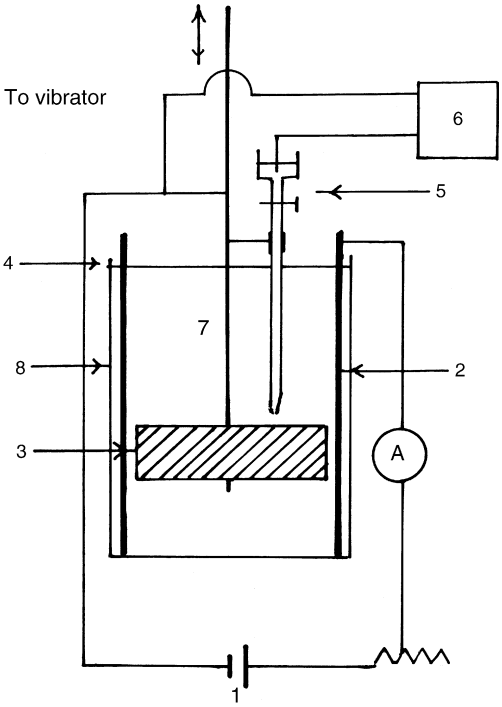

Fig. 1. The Apparatus. 1, 10 V dc power supply; 2, cylindrical copper anode; 3, closely packed array of screens cathode; 4, electrolyte level; 5, Luggin tube with a copper reference electrode; 6, potentiometer; 7, stainless steel holder; 8, cylindrical plexiglass container.

Each screen had a diameter of 10 cm, mesh number of 6 wire/inch, wire diameter of 0.089 cm, hydraulic diameter d_h of 0.375 cm and screen porosity of 0.808. The number of screens/bed was limited to 5 in view of an earlier study using the ferricyanide system which showed that the mass transfer coefficient is not affected by the number of screens higher than five [9]. Two different anodes were used in the present work. A cylindrical copper sheet anode (soluble anode) of 15 cm diameter and 30 cm height was used to study the effect of cathode oscillation on the limiting current and the mass transfer coefficient of copper deposition on the screen stack cathode, the soluble copper anode keeping the bulk concentration of Cu^{2+} constant during measurements. An insoluble lead anode similar to the copper anode in its dimensions was used to study the rate of Cu^{2+} removal from dilute solutions at the oscillating screen stack by constant current electrolysis. The screen stack cathode was held in the center of the cell by a vertical 2 mm diameter stainless steel wire which penetrated the horizontal screen stack at its center. The immersed part of the stainless steel wire which acted as cathode holder and current feeder was isolated with epoxy except at the contact with the screens. The oscillating system was similar to that described in earlier reports [9,10], and consisted of a vertical Teflon oscillating shaft coupled at one end to an eccentric rotating disk (disk crank) by means of a connecting rod. The disk was driven by a variable speed motor through V belt drive. The disk crank had holes at different radii permitting variation of amplitude of oscillation. Frequency was varied by controlling the rotational speed of the motor by means of a variac. The reciprocating vertical Teflon shaft was connected at its other end to the stainless steel cathode holder. The electrical circuit consisted of 12 V dc power supply with a voltage regulator and a multirange ammeter connected in series with the cell. Before each run the cell was filled with acidified $CuSO_4$ solution and the frequency and amplitude of cathode oscillation were adjusted to the required values. The limiting current of Cu deposition was determined by increasing the current stepwise and measuring the corresponding cathode potential until the limiting current plateau at which the current became independent of cathode potential was obtained. Cathode potential was measured against a reference copper electrode placed in the cup of a Luggin tube by means of a high impedance voltmeter. The Luggin tube was filled with a solution identical in composition to the cell solution, and the tip of the Luggin tube was placed 1–2 mm from the cathode surface. The Luggin tube was clamped to the oscillating cathode holder. The $CuSO_4$ solutions used in the present study were 0.001, 0.005 and 0.01 M. In all cases 0.5 M H_2SO_4 was used as a supporting electrolyte. All solutions were prepared with A.R. chemicals and distilled water. The physical properties of the solutions (ρ, μ and D) needed for data correlation were taken from the literature [34]. To study of the rate of copper removal by constant current electrolysis in a cell with lead anode, the current was fixed at the limiting current of the initial Cu^{2+} concentration and the particular vibration intensity. The change of Cu^{2+} with time was measured with atomic absorption spectrophotometer. Temperature was 25 ± 1 °C. The area of the screen bed (A) needed to determine the mass transfer coefficient was calculated in terms of screen geometrical parameters as mentioned elsewhere [17].

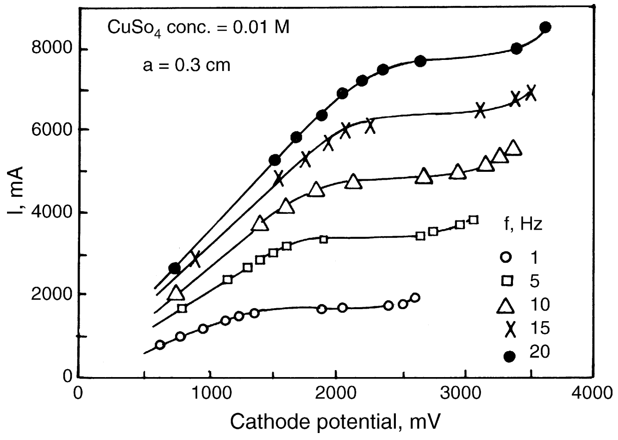

Fig. 2. Typical polarization curves at different oscillation frequency of closely packed array of screens.

4. Results and discussion

4.1. Mass transfer study by measuring the limiting current

To study the mass transfer behaviour of the reactor, the limiting current of copper deposition was measured under different conditions using a copper anode to maintain the bulk concentration of Cu^{2+} constant. Polarization curves with well-defined limiting current plateau were obtained under different conditions (Fig. 2), the limiting current obtained from these curves was used to calculate the mass transfer coefficient according to Eq. (1). Fig. 3a and b show the effect of oscillation frequency on the mass transfer coefficient of copper deposition at different amplitudes and different copper sulphate concentrations at closely packed and separated screen array, respectively. The mass transfer coefficient increases with increasing frequency and amplitude of bed oscillation. The same result is shown in Fig. 4a and b where the mass transfer coefficient is plotted against the vibrational velocity for the closely packed and separated arrays, respectively. Fig. 4a and b show that for a given vibrational intensity, the mass transfer coefficient increases with decreasing $CuSO_4$ concentration probably because of the increase in the effective diffusivity of Cu^{2+} ions and decrease in Sc with decreasing $CuSO_4$ concentration [7]. The closely packed array mass transfer data were correlated (Fig. 5) for the conditions $Sc = 1830$ and $3 < Re_v < 818$ by the equation:

$$j_D = 0.732 Re_v^{0.65} \tag{26}$$

with an average deviation of ±15%. Eq. (26) can be written also in the form:

$$Sh = 0.732 Sc^{0.33} Re_v^{0.65} \tag{27}$$

For the present equations to be comparable with earlier studies [9,10] on vibrating screens, screen hydraulic diameter d_h rather than wire diameter d_w was used as a characteristic length in calculating Re_v. The separated screen array data were correlated (Fig. 6) for the condition $Sc = 1830$ and $3 < Re_v < 818$ by the equation

$$j_D = 0.98 Re_v^{-0.38} \tag{28}$$

with an average deviation of ±9%. Eq. (28) can be also written in the form

$$Sh = 0.98 Sc^{0.33} Re_v^{0.62} \tag{29}$$

The mass transfer enhancement at vibrating screen arrays (separated and closely packed) ranges from 1.5 to 28 times the natural convection value.

Fig. 7 shows a comparison between the model prediction (Eq. (25)) and the experimental data (Eqs. (27) and (29)). To compare Eq. (25) with Eqs. (27) and (29), both sides of Eq. (25) were multiplied by $Sc^{0.167}$ which is equal to 3.326 for the present Sc; also the right hand side of Eq. (25) was multiplied by a correction factor (0.487) to convert $Re_{v,w}$ which uses the wire diameter as a characteristic length to Re_v which uses the hydraulic diameter of the screen as a characteristic length. Accordingly Eq. (25) takes the form

$$j_D = 1.829 Re_v^{-0.5} \tag{30}$$

Fig. 7 shows that Eq. (30) is in a fair agreement with Eqs. (27) and (29) which represent the present experimental data. The fact that model prediction lies below experimental data may be attributed to the role of the flow conditions induced by screen vibration which was ignored in developing the model. These flow conditions involve three consecutive processes [35]. Firstly,

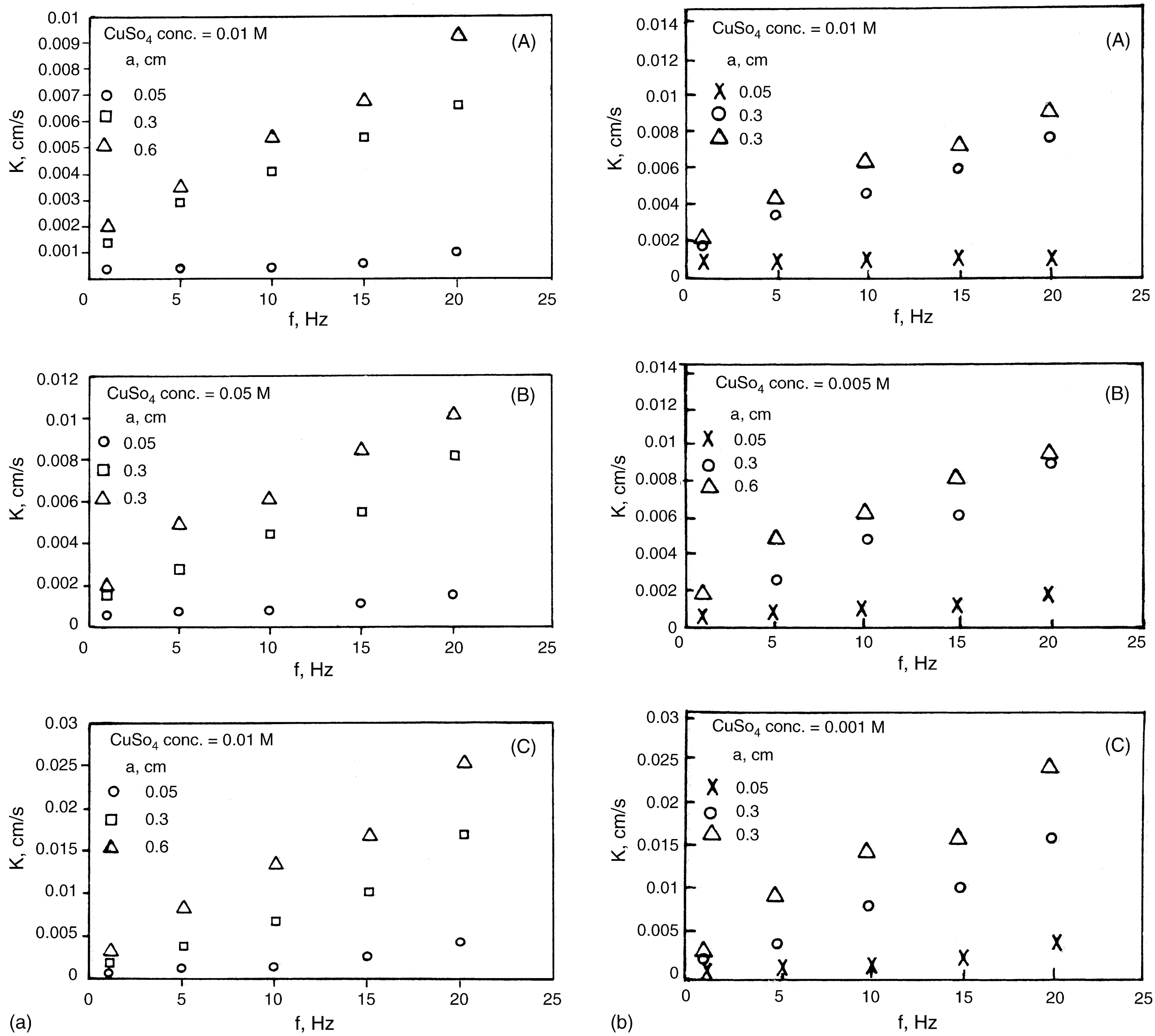

Fig. 3. Effect of frequency of oscillation on the mass transfer coefficient at different amplitudes. (a) Closely packed array of screens and (b) separated screen array.

there is the generation of quasi-steady jet flow very close to each grid bar. Secondly, the jets interact and break down to give turbulence which is advected by the jets. Finally, this turbulence decays with distance away from the grid. Kuhn [36], who studied heat transfer rates behind oscillating grids, argued that both small scale turbulence formed behind the screen and induced bulk flow contribute to enhancing the rate of transfer at the oscillating grid.

Fig. 7 shows that for a given Re_v, the separated screen array produces higher rate of mass transfer than the closely packed array. This may be attributed to: (i) loss of some active area at the points of contact between the packed screens, (ii) eddy damping by friction with the screen wires inside the closely packed array is faster than in case of the separated array, and (iii) replenishment of the depleted solution inside the closely packed array from outside the array by convective diffusion is not fast enough to compensate for the copper ions deposited on the array.

It would be instructive to discuss the discrepancy between the present results and the early results of Zaki et al. [9] who used the ferricyanide system to study the mass transfer behaviour of oscillating screens at low frequencies (0.75–5 Hz). The authors found that Sh increases with the 0.33 power of Re_v. This value is at variance with all the theoretical models including the present one which predicts an exponent of 0.5 for the dependance of Sh on Re_v. The value 0.33 is also much lower than the present experimental exponents which were obtained for a wider frequency range (1–20 Hz). In view of the fact that all the available theoretical models cannot explain the exponent 0.33 obtained for vibrating screens at the low frequency range and the exponents 0.62 and 0.65 of the high frequency range, it would be useful to recall the mechanism presented by Zaki et al. [9] to explain mass transfer at vibrating screens. The authors have found that the mass transfer mechanism at oscillating screens is similar to the mass transfer at stationary screens and cylinders in cross flow at relatively low Re where Sh is related to Re by the equation

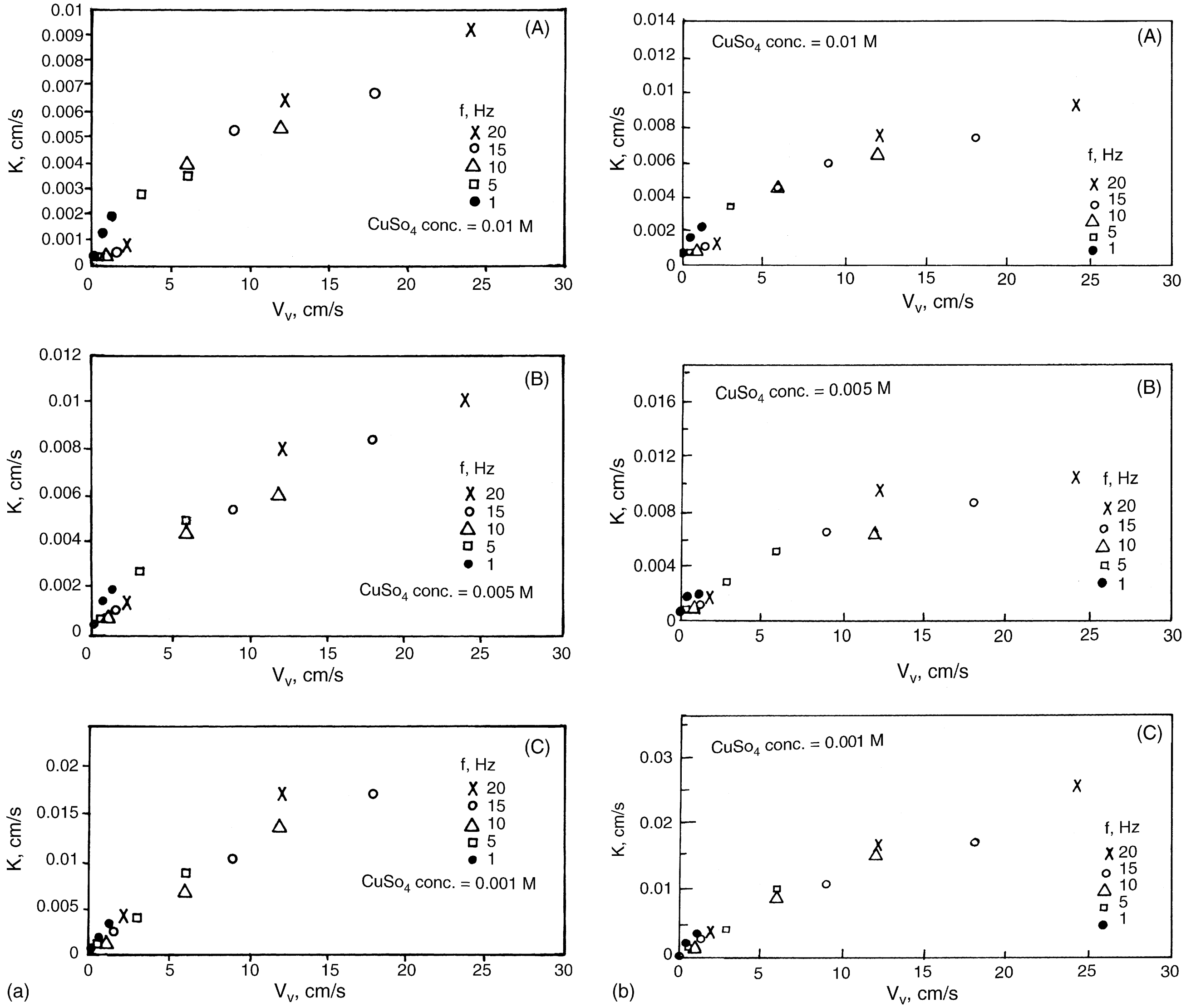

Fig. 4. Effect of vibration intensity on the mass transfer coefficient at different oscillation frequencies. (a) Closely packed array of screens and (b) separated screen array.

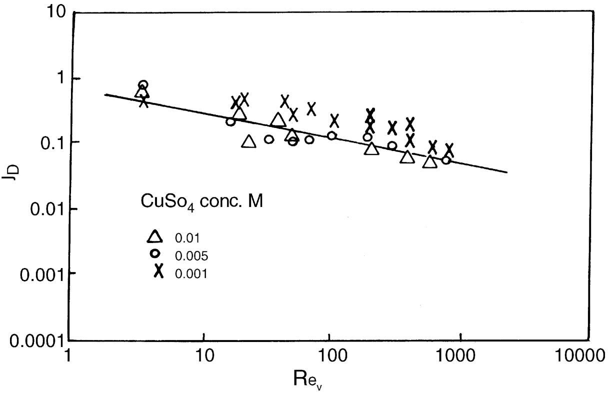

Fig. 5. Overall mass transfer correlation at oscillating array of closely packed screens.

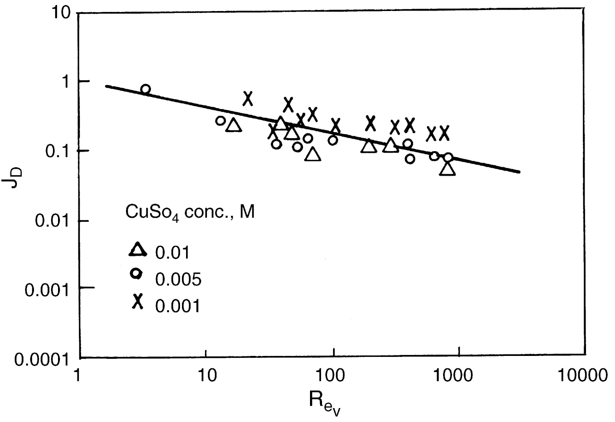

Fig. 6. Overall mass transfer correlation at oscillating array of separated screens.

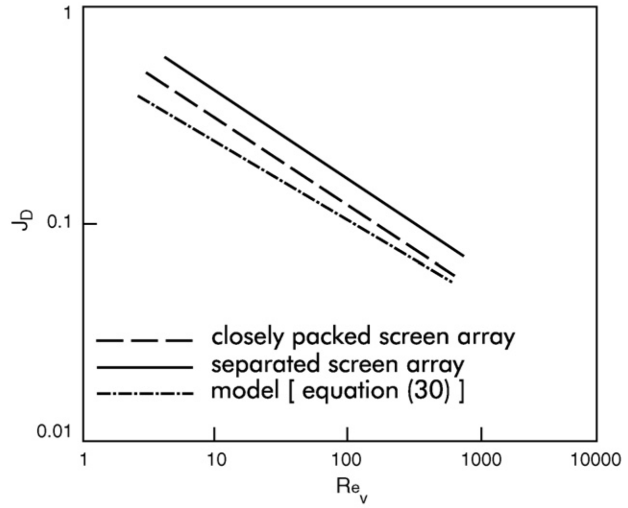

Fig. 7. Comparison between the overall mass transfer correlations of closely packed array and separated screen array.

[37–40]:

$$Sh = \acute{a}Re^{0.33} \tag{31}$$

The above equation is dictated by a laminar boundary layer around the screen wires or cylinders and a turbulent wake resulting from boundary layer separation [9,37]. Previous studies on mass transfer at cylinders in cross flow have shown that increasing the level of turbulence by increasing Reynolds number leads to increasing the *Re* exponent in Eq. (31) to a value ranging from 0.33 to 0.805 depending on the range of Reynolds number [37]. It seems that a similar situation exists in case of oscillating screens; in the present work frequencies ranging from 1 to 20 Hz were used while in the study of Zaki et al. The range was limited to a maximum of 5 Hz. Accordingly, the intensity of turbulence generated under the present conditions as a result of the relative motion between the oscillating screen wires and the solution is much higher than that generated under the conditions used by Zaki et al. [9]. The difference in the intensity of turbulence generated in the oscillating hydrodynamic boundary layer of the present work and the work of Zaki et al. [9] accounts for the difference in the Re_v exponents obtained by the two studies.

The present Re_v exponents [Eqs. (27) and (29)] agree with the value 0.62 obtained by Rao et al. [24] who used the ferricyanide limiting current technique to measure the rate of mass transfer at a cylinder subjected to horizontal transverse vibrations using amplitudes ranging from 0.24 to 3.7 cm and frequencies ranging from 1.67 to 15 cycles per second. The authors correlated their data by the equation:

$$Sh = 0.41 Sc^{0.33} Re_\mathrm{v}^{0.62} \tag{32}$$

The present Re_v exponents, 0.65 and 0.62, also agrees with the value obtained by Sugano and Ratkowsky [25] who studied the effect of transverse vibration on the rate of mass transfer from horizontal naphthalene cylinders to air in the range $5 < Re_\mathrm{v} < 2000$. The authors correlated their data by the equation:

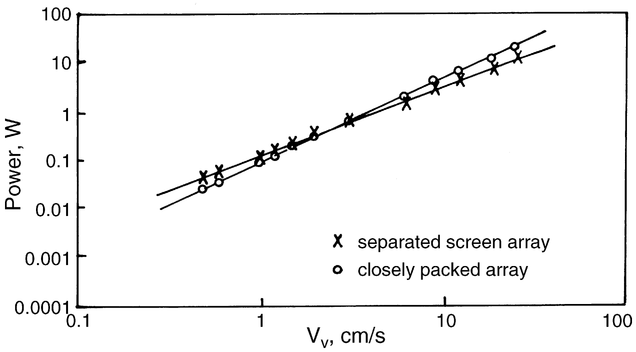

Fig. 8. Effect of vibration velocity on mechanical power consumed in oscillating closely packed array and separated screen array.

$$Sh = 0.237 Sc^{0.33} Re_\mathrm{v}^{0.653} \left(\frac{2a}{d}\right)^{0.243} \tag{33}$$

Takahashi et al. [28], who used the electrochemical technique to study rates of mass transfer at vibrating horizontal cylinders, correlated their data for the range $20 < Re_\mathrm{v} < 800$ by the equation:

$$Sh = 0.384 Sc^{0.33} Re_\mathrm{v}^{0.63} \tag{34}$$

To assist in the economic evaluation of the present reactor in comparison with other reactors, mechanical power consumed in oscillating the screen array was measured as mentioned elsewhere [41]. Fig. 8 shows that within the present range of conditions, separated array consumes more energy at low vibrational velocities than the closely packed array, and this trend is reversed at high vibrational intensities.

4.2. Study of the removal of Cu^{2+} from dilute solutions by constant current electrolysis

In order to test the extent to which the oscillating bed of horizontal screens electrochemical reactor can reduce Cu^{2+} concentration from a synthetic waste solution, the cylindrical copper anode used in studying the mass transfer behaviour of the reactor was replaced by an insoluble cylindrical lead anode. Fig. 9 shows that constant current electrolysis at the limiting current of the initial Cu^{2+} concentration at different vibrational velocities decreases the Cu^{2+} content with time to a value depending on the vibrational velocity. At vibrational velocities higher than 12 cm/s the reactor could reduce Cu^{2+} concentration to a value below the maximum permissible value (0.5 ppm) [2]. It would be of interest to compare the mass transfer coefficient of copper removal from a solution whose concentration decreases with time with the value predicted from Eq. (27). Since copper is being deposited in the present study at the limiting current, i.e., under diffusion control, it follows that the rate of copper deposition in the batch reactor is given by the following first order rate Eq. [5]

$$-Q\frac{\mathrm{d}C}{\mathrm{d}t} = K_\mathrm{c} A C \tag{35}$$

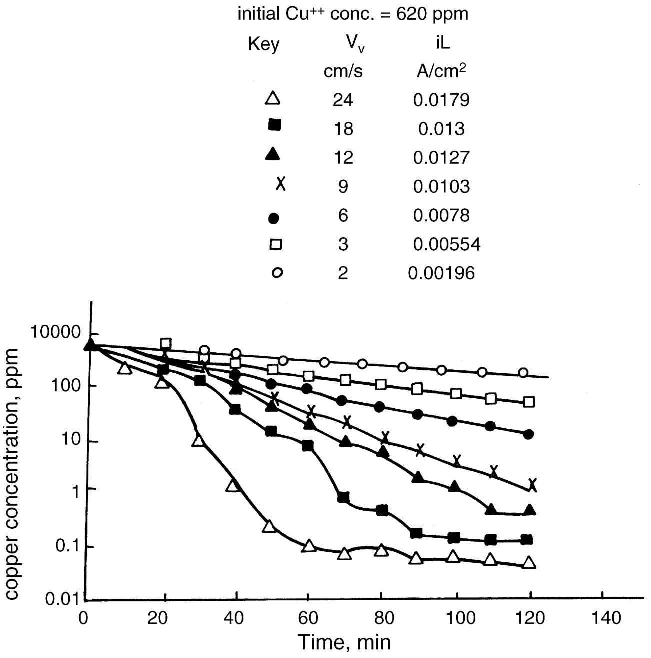

Fig. 9. Change of Cu^{2+} concentration with time of electrolysis at different vibrational velocities.

which integrates to

$$Q \ln \frac{C_0}{C} = K_c A t \tag{36}$$

Table 1

Comparison between the mass transfer coefficient obtained from Eq. (27) and the value determined from the data of copper removal by constant current electrolysis (K_c)

f (Hz)	a (cm)	V_v (cm/s)	Re_v	K (cm/s)	K_c (cm/s)
20	0.6	24	818	0.00929	0.0138
15	0.6	18	613	0.00676	0.00945
20	0.3	12	409	0.00659	0.009055
15	0.3	9	307	0.00532	0.007018
10	0.3	6	204	0.00405	0.00464
5	0.3	3	102	0.00287	0.00328
20	0.05	2	68	0.00101	0.001698

Initial Cu^{2+} concentration = 0.01 M (620 ppm).

Fig. 10 shows that the present Cu^{2+} concentration–time data fit Eq. (36). Figs. 9 and 10 show that at high vibrational intensities such as 18 and 24 cm/s, residual copper ion concentration remains almost constant after a certain time. A similar finding was observed with other reactors used for heavy metal removal at high degrees of stirring [4]. This may be attributed to the fact that as the Cu^{2+} concentration decreases, its deposition potential is shifted to a more negative value. At extremely low Cu^{2+} concentrations, the deposition potential becomes so negative that competing reactions such as dissolved oxygen reduction and H_2 evolution from the highly acidic solution become dominant [5]. The mass transfer coefficient of copper removal in the reactor using an insoluble lead anode was calculated from the slope of the plot in C_0/C versus t. Table 1 shows a comparison between the mass transfer coefficient of copper removal by electrolysis at a constant current from a cell using insoluble lead anode and the values obtained from Eq. (27) at different vibrational intensities. The data show that the mass transfer coefficient of copper removal is on the average some what higher than that predicted from Eq. (27), i.e., Eq. (27) is a conservative equation which can be used safely in the design and operation of reactors where concentration decreases with time. The higher mass transfer coefficient obtained during copper removal from a cell with insoluble lead anode may be attributed to the following effects which come into play especially at high vibrational intensities: (i) prolonged copper deposition at the limiting current inside the screen array induces surface roughness to the screen wires [5]. Surface roughness enhances the rate of mass transfer through increasing the diffusional area and promoting the generation of turbulent eddies [5,42], (ii) as mentioned above, as the concentration of Cu^{2+} decreases, simultaneous H_2 evolution at the cathode is likely to take place [5]. Evolution of H_2 bubbles enhances the rate of mass transfer of copper deposition at the cathode surface as a result of bubble induced flow during bubble growth, bubble detachment from the cathode surface and bubble motion in the solution [43–45], and (iii) increase of the effective diffusion coefficient with time as a result of the decrease in Cu^{2+} concentration in the solution [7].

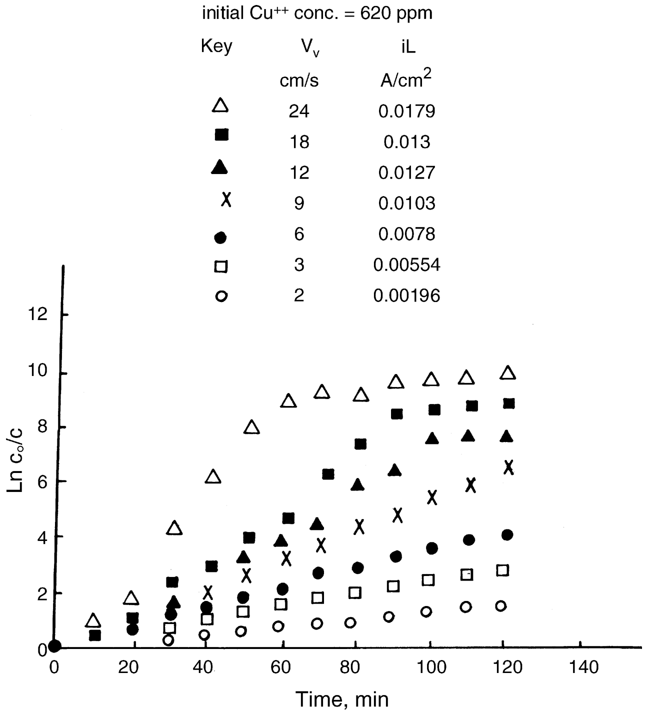

Fig. 10. $\ln C_0/C$ vs. time of electrolysis at different vibrational velocities.

5. Conclusions

The present preliminary study leads to the following conclusions:

1. High rates of mass transfer and high rates of copper electrodeposition were obtained at oscillating horizontal array of screens cathode. Within the present range of vibration

intensities used in the present work the mass transfer coefficient of copper deposition increased with 0.65 power of the vibrational intensity; the rate of diffusion controlled copper deposition increased by a factor ranging from 1.5 to 28 compared to the natural convection value. Separated array produces higher rates of mass transfer than closely packed arrays. However, in deciding between separated and closely packed screen arrays other parameters should be considered such as area per unit volume and current distribution. A closely packed screen arrays have higher area per unit volume but its current distribution is less uniform than a separated screen array owing to the high resistivity inside the closely packed array.
2. Constant current electrolysis of acidified dilute solutions of $CuSO_4$ at the limiting current using oscillating array of screens could reduce Cu^{2+} concentration below the maximum permissible value in a time which depends mainly on the vibration intensity. Surface roughness induced by prolonged copper deposition and simultaneous hydrogen evolution during constant current electrolysis contributed along with the bed oscillation to enhancing the rate of mass transfer and the rate of copper deposition especially at high oscillation frequencies. Accordingly, the use of Eqs. (27) and (29) in the design and operation of heavy metal removal reactors is approximate. These equations are better suited for reactors used to conduct diffusion controlled reactions free from interfering effects such as surface roughness and gas evolution.
3. Apart from heavy metal removal from industrial effluents, the high specific area and the high mass transfer rates produced by the oscillating screen array suggest its use in conducting the following processes: (i) liquid–solid diffusion controlled catalytic reactions (non-electrochemical) such as wet oxidation of organic pollutants from industrial effluents [46,47] and (ii) the favourable performance of oscillating horizontal screen array in building absorption columns [14] qualifies the present reactor for processing gaseous reactants such as flue gas desulphurisation where SO_2 is simultaneously absorbed and anodically oxidized to H_2SO_4 [13]. Also the favourable performance of vibratory agitators [11,12] in dispersing solid particles qualifies the present reactor for conducting electroorganic synthesis involving sparingly soluble solid or immiscible liquid reactants. The reactor can be operated continuously or batchwise. In case of continuous operation, a high degree of conversion per pass can be obtained at low feed rates in view of the high area/unit volume, high mass transfer coefficient and high residence time. To design such reactor, further studies are needed on the effect of variables such as the effect of superimposed solution flow and the presence of sparingly soluble reactants (liquids, solids and gases) on the rate of mass transfer.
4. Theoretical models such as the surface renewal model as well as other models such as the quasi-steady model, the analogy model and the combined model are limited in their ability to explain the mass transfer behaviour of vibrating screens over a wide range of frequencies. The similarity in mass transfer behaviour between vibrating screens and mass transfer at stationary screens and horizontal cylinders in cross flow offers a more plausible qualitative mechanism.

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