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ORIGINAL ARTICLE

Improving the rate of Cu^{+2} recovery from industrial wastewater using a vertical array of reciprocating perforated zinc discs

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Abstract This work investigates the possibility of improving the rate of Cu^{+2} recovery and/or removal from industrial wastewater by cementation technique using an array of pulsating horizontal perforated zinc discs. The results show that the rate of cementation was found to increase by increasing frequency and amplitude of oscillation (vibrating velocity); disc diameter; copper ion concentration and solution temperature while decreasing by increasing the disc separation. Under certain conditions using pulsating array of perforated zinc discs was found to increase the rate of mass transfer by a factor of 17 times the stagnant discs. The activation energy of the reaction was found to be 8.948 kcal/mol which indicates that under the present conditions cementation takes place under mixed control, i.e. the reaction is partially diffusion control. As such no overall mass transfer correlation could be obtained.

1. Introduction

Cementation out of the conventional methods of recovery of metals such as, electro-winning from aqueous or fused salt baths, gaseous reduction chemical precipitation of metal compounds has been proved for its advantage of its suitability for recovery of value from very dilute solutions. Cementation relies on the theory that a more electropositive metal ion in solution, when brought into contact with positive metal, is displaced from the solution and cemented on the latter method to the following equation:

$$mN^{+n} + nM_{(s)} = nM^{+m} + mN$$

where N and M represent the noble metal the reductant one respectively; n and m are its valences respectively. It is importance in the recovery of metal values from metallurgical wastes and/or ores were discussed in many researches [1–5]. Copper ions, as a pollutant, do not accumulate in body in massive amounts, though copper can cause illness or even death. Many attempts have been made for improving the rate of cementation and reducing both time and power consumption, some

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Nomenclature

A_m	amplitude of oscillation (cm)	k	rate of mass transfer (cm/s)
A	active surface area of the perforated zinc disc (cm^2)	R	gas constant (J/mol K)
A_o	constant at Arrhenius equation	t	time (s)
C	$CuSO_4$ concentration at any time t (mol/l)	T	absolute temperature (K)
C_o	initial $CuSO_4$ concentration (mol/l)	Vi	vibrating velocity (cm/s)
D	Cu^{+2} diffusivity (cm^2/s)	V_s	solution volume in the reactor (cm^3)
f	frequency of oscillation (s^{-1})	μ	solution viscosity (g/cm s)

studied the effect of certain surfactants [1,2], gas sparging [3] and ultrasound [6] to reduce process time. This work investigates the possibility of enhancing the performance of a batch reactor used for the removal and/or recovery of copper ions from industrial effluents using an array of pulsating perforated zinc discs. Recently surface vibration (oscillation) has received a great attention as a tool for enhancing the rate of mass transfer in diffusion controlled processes. Tojo et al. [7] who studied the effect of vibratory agitation on the rate of mass transfer using a reciprocating perforated disc came to the conclusion that vibratory agitation needs less energy than rotary agitation for the same degree of mixing. Kalantary et al. [8] studied the effect of vibratory agitation on the rate of metal deposition during electroplating in a cylindrical cell using perforated disc, the authors reported that vibratory agitation increases the rate of metal deposition by a factor ranging from 3 to 20 depending on the operating conditions. Mubarak et al. [9] found that disc reciprocation has increased the rate of cementation of copper on reciprocating horizontal perforated zinc disc by a factor ranging from 2.8 to 5.5 compared to cementation on stagnant disc. Elshazly [10,11] in his investigations for the rate of copper recovery from industrial wastewater by cementation using pulsating zinc cylinders and pulsating vertical parallel plates, found that pulsation has increased the rate of cementation by a factor ranging from 2.5 to 5 and from 2.75 to 4.8, compared to stagnant cylinders and stagnant plates respectively. The present work seeks to test the performance of oscillating perforated zinc disc in removing copper ions by cementation from a synthetic solution which simulates industrial waste solutions such as electroplating rinsing solutions and printed circuits industries. The study covered a wide range of conditions which include the effect of initial copper ions concentration, frequency and amplitude of pulsation, disc separation, disc diameter and solution temperature.

2. Experimental part

Fig. 1 shows the experimental setup used in the present study. It consisted of the vibrating system and the reactor which consisted of a multilayer of reciprocating perforated zinc discs. Different disc diameters ranging from 6 to 12 cm and different disc separations ranging from 1 to 2.5 cm were used, and the amplitude of oscillation was changed from 1 to 4 cm. The oscillation intensity was expressed by the vibration intensity (Vi) where $Vi = 2A_m f$. The number of zinc discs, disc perforation diameter and its thickness were kept constant at 4, 0.5 mm and 1 mm respectively. For finding out the nature of cementation reaction under the above mentioned conditions the effect of solution temperature was investigated in the range from 25 to 40 °C and hence the activation energy was determined using Arrhenius equation. The multilayer perforated zinc discs were placed in a Plexiglas column of 20 cm diameter and 40 cm height. The layers were held inside the column by insulated stainless steel stem of 3 mm diameter which penetrated the discs at its centres. The stem was fixed to the top (vibrating system). The upper end of the stem was connected to the vibrator through a Teflon sleeve. Vertical oscillation was induced to the zinc layers by means of a mechanical vibrator connected to the upper end of the stem. The mechanical vibrator was described by the author in previous investigations [9–12]. The rate of cementation of copper on zinc was followed by measuring the change in concentration of Cu^{+2} with time. Before each run, 4 l of fresh $CuSO_4$ solution was placed in the column, in the mean time the solution was subjected to oscillation at the required vibration intensity. Samples of the solution (5 ml) were withdrawn at regular time intervals. The intervals ranged from 2 to 3 min at high and low vibration intensities respectively. The samples were analysed by spectrophotometric analysis. The mass transfer coefficient was calculated from the concentration time data as shown in Fig. 2. Four different $CuSO_4$ concentrations were used ranging from 0.02 to 0.3 M. All solutions were prepared using AR chemicals and distilled water. A digital portable pH meter was used to measure the

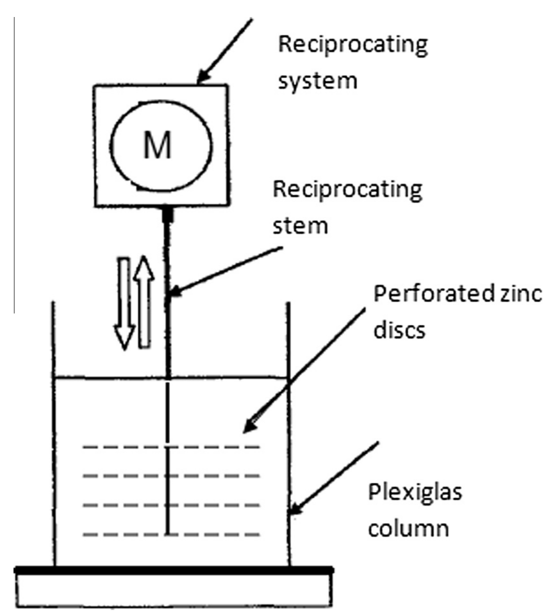

Figure 1 Experimental setup.

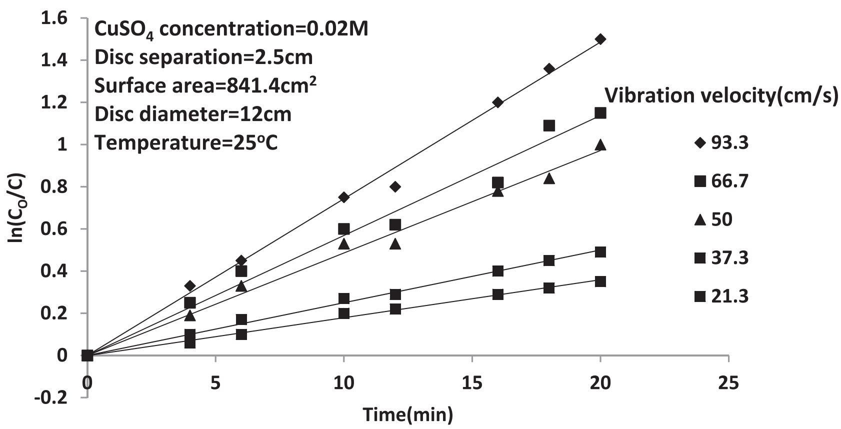

Figure 2 $\ln(C_o/C)$ vs. time at different vibration intensity.

solution pH and NaOH and/or H_2SO_4 were used for adjusting the solution pH at 5.

3. Results and discussion

The present study was conducted in a simple batch reactor. For simple batch reactor the mass transfer coefficient can be calculated by the following equation [13,14]:

$$-V_s dC/dt = kAC \quad (1)$$

Which upon integration yields

$$V_s \ln(C_o/C) = kA\ t \quad (2)$$

where V_s is the solution volume; C_o and C are initial concentration of $CuSO_4$ and the concentration at any time t; A is the active area of the oscillating multilayer perforated discs; t is the time of reaction. The mass transfer coefficient was obtained under different conditions by plotting $\ln(C_o/C)$ vs. time, the slope of the resulting straight line gives (kA/V_s) from which k was obtained.

3.1. Effect of initial $CuSO_4$ concentration

Fig. 3 shows that the mass transfer coefficient has been increased by increasing the initial $CuSO_4$ concentration within the range from 0.02 to 0.3 M. These results may be attributed to fact that increasing the initial $CuSO_4$ concentration will increase the available Cu^{+2} in the solution and that may increase the thickness and/or the area of deposited layer on the zinc disc surface accordingly the surface roughness on the zinc surface will actually increase. Increasing the surface roughness was proved to increase the rate of mass transfer [15]. In addition increasing the initial concentration to certain range will probably increase the Cu^{+2} diffusivity which also increases the rate of mass transfer.

3.2. Effect of solution temperature

As shown in Fig. 4 it is clear that at a given vibration velocity increasing the solution temperature has increased the mass transfer coefficient which may be ascribed to the reduction in solution viscosity and that increase the diffusivity and reduce the diffusion layer thickness according to Stokes–Einstein equation [13]:

$$D\mu/T = \text{constant} \quad (3)$$

and hence increasing the mass transfer coefficient according to the equation ($k = D/\delta$), where D is the diffusion coefficient, and δ is the boundary layer thickness.

The activation energy of the reaction was determined using Arrhenius equation [13]:

$$k = A_o e^{-E/RT} \quad (4)$$

As shown in Fig. 5 the activation energy E was found to be 8.948 kcal/mol which indicates a mixed control mechanism, i.e. both diffusion and chemical reaction steps contributed to determining the rate of the reaction, the reaction under the present conditions is partially diffusion controlled. The discrepancy between the present finding and the other cementation studies which conclude that cementation of Cu^{+2} on Zn is diffusion controlled [9–12] may be attributed to the strong enhancing effect of the new system of pulsating array of perforated zinc discs compared to other enhancing means such as mechanical stirring and gas sparging. It seems that the turbulences generated by perforated disc pulsation eliminate a considerable part of the mass transfer resistance to the extent that the rate of mass transfer approaches in magnitude the rate of the chemical step. In case of using stirring or gas sparging to enhance the rate of cementation the rate of mass transfer is still slow compared to the chemical step, hence the cementation reaction is described in these cases as diffusion controlled.

3.3. Effect of zinc perforated disc separation

Fig. 6 shows the relation between the mass transfer coefficient and the vibration intensity at different perforated disc separation ranging from 1 to 2.5 cm. The fact that the mass transfer coefficient increases with decreasing the disc separation may be ascribed to short distance travelled by the jets generated from disc perforations before collision in the free space with the jets generated from the consequent disc. The short distance caused the generated turbulences due to jets collision to be strong which reduce the hydrodynamic boundary layer thickness and hence the diffusion layer and that increase the rate of mass transfer and cementation rate. In addition reducing the

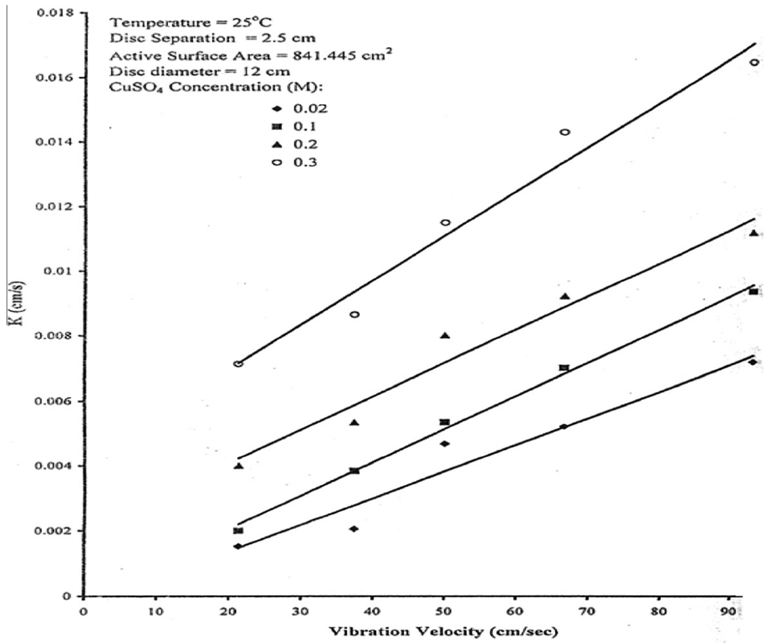

Figure 3 Mass transfer coefficient vs. vibration velocity at different initial $CuSO_4$ concentrations.

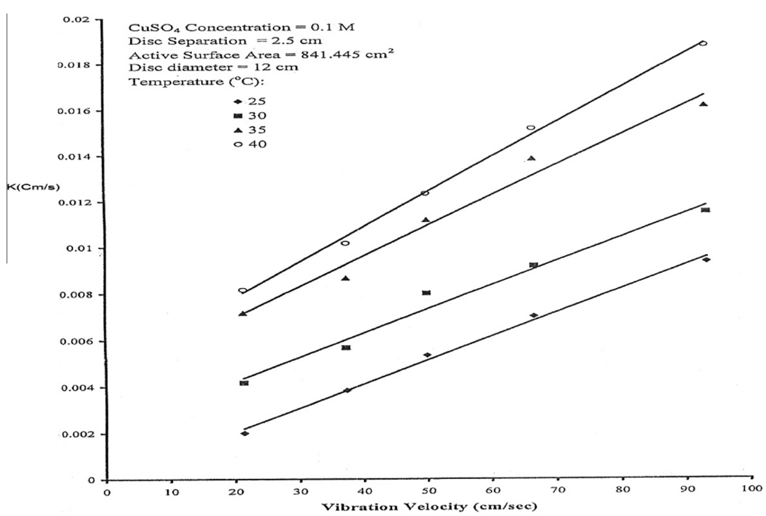

Figure 4 Mass transfer coefficient vs. vibrating velocity at different solution temperature.

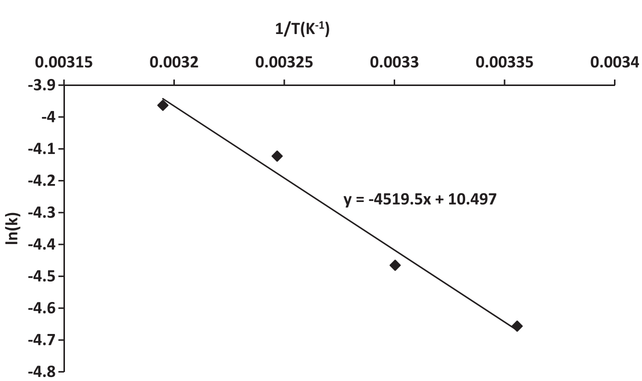

Figure 5 $\ln k$ vs. $1/T$.

distance between discs will decrease the free area between discs and that induced secondary flow resulting from disc oscillation inside these free regions to increase with a consequent decrease in the thickness of the hydrodynamic boundary layer and the diffusion layer in the vertical direction, this also increases the rate of mass transfer and the cementation rate.

3.4. Effect of frequency and amplitude of oscillation

Figs. 7 and 8 show the relation between the mass transfer coefficient and the vibrating intensity at different amplitudes ranging from 1 to 4 cm and the relation between $\log V$ and $\log k$ at different $CuSO_4$ concentrations respectively. It is clear that by increasing the frequency and amplitude of oscillation the value

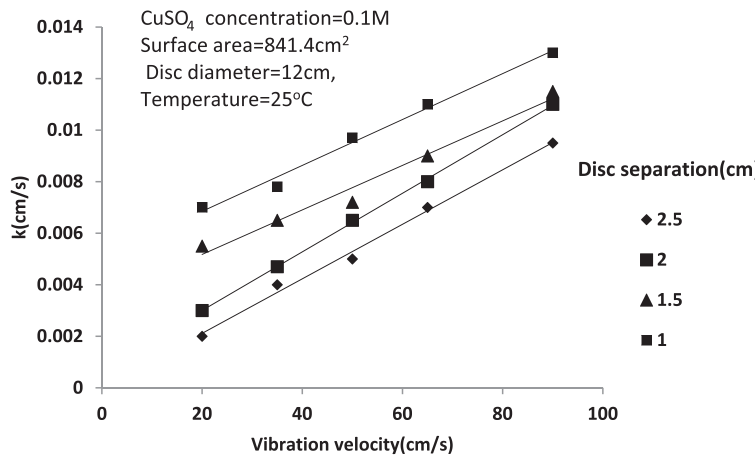

Figure 6 Mass transfer coefficient vs. vibrating velocity at different perforated disc separation.

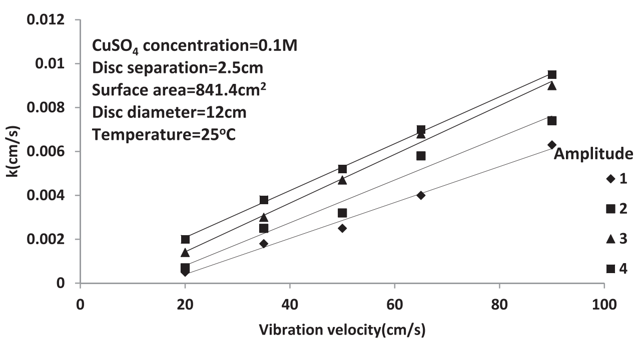

Figure 7 Mass transfer coefficient vs. vibration velocity at different amplitude.

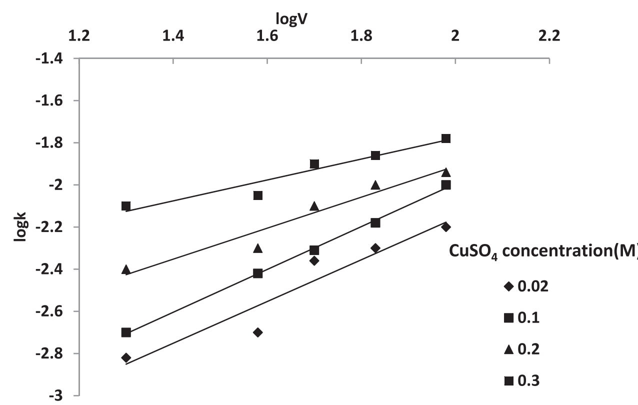

Figure 8 $\log k$ vs. $\log V$ at different $CuSO_4$ concentration.

of the mass transfer coefficient increases according to the following equation:

$$k = \alpha V^{0.877}$$

where α is constant; Vi is the vibrating velocity ($V = 2fA_{\rm m}$), f = frequency; $A_{\rm m}$ = amplitude this increase may be attributed to disc oscillation which gives rise to oscillatory flow that reduces the diffusion layer at the disc surface [16]. In addition as the perforated discs oscillate a jetting effect takes place throughout the disc holes according to Thompson and Turner [17] these jets disintegrate into turbulent eddies which decrease the diffusion layer thickness at the disc surface and increase the mass transfer coefficient.

3.5. Effect of disc diameter on the mass transfer coefficient

As shown in Fig. 9, it is clear that the rate of mass transfer increased by increasing the disc diameter, which seems to be related to the turbulence generated at the disc surface due to disc perforations and mechanical oscillation. These turbulences reduce the thickness of the diffusion layer at the disc surface and improve cementation process. The decrease in the rate of mass transfer with decreasing the disc diameter may be ascribed to the fact that decreasing the disc diameter will increase the annular space between pulsating perforated discs and the reactor wall, accordingly an axial flow through this area will take place instead of the jetting flow through the disc perforations which may damp the eddies generated from the disc perforations and that build boundary layer on the disc surface and reduce the rate of mass transfer and cementation rate.

4. Conclusions

The present results have shown that using an array of pulsating horizontal perforated zinc discs for removing and/or recovering Cu^{+2} from wastewater by cementation is very effective compared to other methods of enhancing the rate of cementation such as mechanical stirring or gas sparging. The rate of cementation was found to increase by increasing frequency and amplitude of oscillation (vibrating velocity); disc diameter; copper ion concentration and solution temperature while decreasing by increasing the disc separation. The results show that under certain conditions using pulsating array of perforated zinc discs were found to increase the rate of mass transfer by a factor of 17 times the stagnant discs. The activation energy of the reaction was found to be 8.948 kcal/mol which

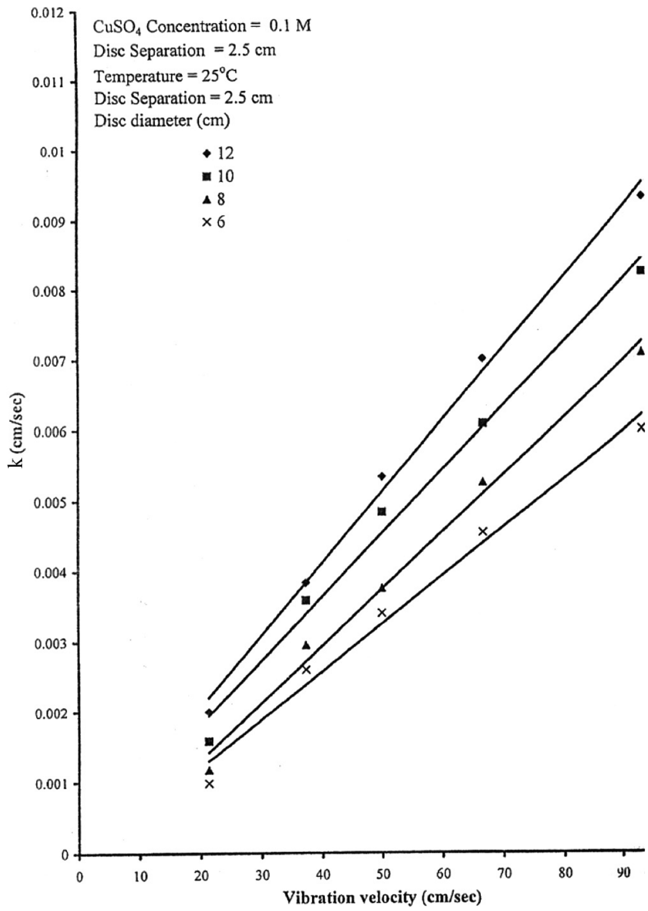

Figure 9 Mass transfer coefficient vs. vibration velocity at different disc diameter.

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