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Production of copper powder from synthetic wastewaters by cementation on a longitudinal finned rotating zinc cylinder

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ABSTRACT

This study aims to the enhancement of Cu^{2+} ions removal from wastewaters and recovery of the metal value by cementation on a longitudinal finned rotating zinc cylinder. The effect of different parameters such as cylinder rotational speed (rpm), initial Cu^{2+} ions concentration and the effect of the fin height to cylinder diameter (e/d) on the rate of Cu^{2+} ions cementation was investigated. In addition, the effect of drag reducing polymer on the rate of Cu^{2+} cementation was examined. The rate of cementation was expressed in terms of the mass transfer coefficient. The results revealed that the mass transfer coefficient increases with increasing rpm, initial Cu^{2+} concentration and e/d ratio. The present results show that finned rotating cylinder enhances rate of cementation compared to smooth rotating cylinder by percentage ranges from 28.79 to 134.85 depending on the operating conditions. On the other hand, the presence of drag reducing polymer retards the rate of cementation. The present data fit the following dimensionless equations: For smooth cylinder: $Sh = 0.74\ Re^{0.69}\ Sc^{0.33}$. For finned rotating cylinder: $Sh = 0.38\ Re^{0.9}\ Sc^{0.33}\ (e/d)^{0.25}$. The importance of the above correlations in the design and operation of industrial-scale rotating cylinders cementation reactors was pointed out.

Keywords: Cementation; Removal of heavy metal; Rotating cylinder; Recovery of metals; Wastewater treatment

1. Introduction

Environmentalists' concern over the presence of toxic heavy metal ions in the aquatic environment stems from the fact that these metal ions are non-biodegradable and can accumulate in living tissues. Furthermore, the presence of heavy metal ions in wastewater inhibits biodegradation of organic pollutants, which might be present in the wastewater. There are many technologies which have been developed over past years to remove heavy metal ions. The most important of such technologies are chemical precipitation, adsorption, ion exchange and membrane processes. However, all of them have their drawbacks. Chemical precipitation requires extremely long settling time and produces a large amount of sludge; ion exchange and adsorption are expensive and require frequent regeneration. On the other hand, membrane processes possess operational problems due to fouling

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of membranes [1]. Cementation is one of the most effective and economic techniques used for the removal and recovery of toxic and valuable metals from industrial wastewater. Cementation is used as a general term to describe the process whereby an electronegative metal ion is precipitated from a solution from its salts by another electropositive metal.

The cementation reactions are considered as heterogeneous process which may be limited by diffusion through the mass boundary layer. Within the literature, different methods have been applied to enhance the rate of cementation reactions such as the increase in active surface area using fixed bed [2,3] and fluidized bed [4,5] or the generation of high degree of turbulence through the use of vibrational motion [6], gas sparging [7], mechanical agitation [8,9] and jet impingements [10]. Rotating cylinder electrode is characterized by high mass transfer coefficient [11–13] due to the high turbulence conditions which prevail even for low rotational speed. However, the active area of the rotating cylinder electrode is limited by its diameter and active height.

Thus, the aim of this study was to investigate the performance of longitudinal finned rotating zinc cylinder on the rate of copper ions cementation. Fins could enhance the rate of cementation by dual effects, first fins increase active surface area. Second fins act as turbulence promoters. To this end, the following parameters have been investigated: Initial Cu^{2+} ion concentrations, rotational speed of finned rotating cylinder (rpm) and the effect of fin height to cylinder diameter ratio (e/d). An attempt to correlate the present mass transfer data has been envisaged using dimensional analysis to obtain overall mass transfer correlations of the finned and smooth rotating cylinder.

In addition, the present work aims at investigating the effect of the presence of drag reducing polymers on the rate of copper ions cementation. Since the addition of a minute amount of a drag reducing polymers to a turbulent Newtonian flow can result in a large decrease in frictional drag. These polymers have the potential of being used in agitated vessels to reduce power consumption by virtue of the ability of polymer molecules to damp the small-scale high-frequency eddies which prevail in the hydrodynamic boundary layer at the impeller, shaft and the wall of the agitated vessel [14].

2. Materials and methods

Fig. 1 shows a schematic diagram of the experimental set-up. It consisted mainly of a 15-cm-diameter plexiglass vessel and a 2 cm diameter rotating zinc cylinder. The zinc cylinder was placed in the centre of the vessel at a distance of 4 cm from the vessel bottom. A length of 9 cm of zinc cylinder was immersed in solution. The zinc rotating cylinder was connected to a multispeed digital motor. Precaution was taken during run to avoid vibration and eccentric motion. Solutions of different Cu^{2+} ions concentrations were prepared using distilled water and analytical reagent grade chemicals. Longitudinal fins were machined in the zinc cylinder, fin heights were 0.5, 1, 1.5 and 2 mm. Before each run, zinc cylinder was pickled in 10% HCl to remove any oxide layer, washed with distilled water and dried. Before each run, 2.5 L of the copper sulphate solution was placed in the vessel. The required cylinder rotation speed was adjusted by the variac, rotation speed was measured automatically by a digital tachometer. Kinetics of the Cu^{2+} ions cementation was followed by withdrawing 5 mL sample every 5 min during the course of run under different conditions. The samples were analysed for copper ions concentration by iodometry [15] using fresh starch as indicator. Initial solution pH was kept constant at 4 and all runs were carried out at temperature of 25 ± 2˚C. Density and viscosity of all solutions were measured using density bottle and Ostwald viscometer, respectively [16]. The diffusivity of Cu^{2+} ions was obtained from the literature [17].

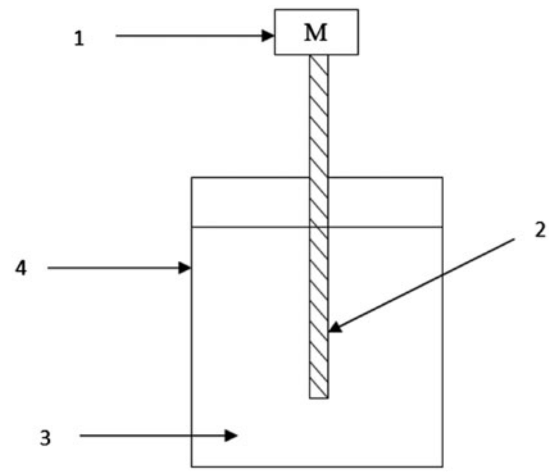

Fig. 1. Schematic diagram of the experimental setup.
Notes: (1) Digital Motor, (2) Finned rotating zinc cylinder, (3) $CuSO_4$ solution, and (4) Plexiglass container.

In order to study the effect of drag reducing polymer, a certain amount of polymer (polyethylene oxide a product of union carbide) was added to the solution in the form of a powder.

3. Ressults and discussion

Cementation of copper on zinc can be represented by the following overall reaction [18]:

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+} \quad (1)$$

The rate of Cu^{2+} cementation in the present batch reactor is given by:

$$-V_s(\mathrm{d}C/\mathrm{d}t) = kAC \quad (2)$$

Which upon integration for the conditions at $t = 0$, $C = C_0$ and at any time t, $C = C$ yields:

$$V_s \ln(C_0/C) = kAt \quad (3)$$

where V_s is solution volume, C_0 and C are initial Cu^{2+} concentration and the concentration at any time t, respectively, A is the active projected surface area of the zinc cylinder, t is the time and k is the mass transfer coefficient.

Fig. 2 shows a typical plot of $\ln(C_0/C)$ vs. time at different speed of rotation. It is well obvious that a linear relationship is obtained which indicates a first-order reaction kinetic. This finding is consistent with previous studies using other geometries [10].

3.1. Effect of cylinder rotational speed (rpm)

Figs. 3 and 4 show the effect of cylinder rotational speed (rpm) on the mass transfer coefficient at different initial Cu^{2+} concentrations for smooth and finned rotating cylinders, respectively. The data fit the following equations:

For smooth rotating cylinder:

$$k \propto (\mathrm{rpm})^{0.69} \quad (4)$$

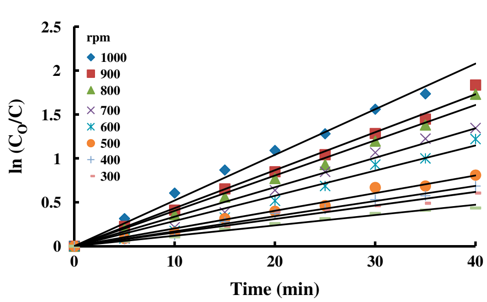

Fig. 2. Typical plot of $\ln(C_0/C)$ vs. time at different rpm (Cu^{2+} initial concentrations, ppm = 1,500, e/d = 0.025).

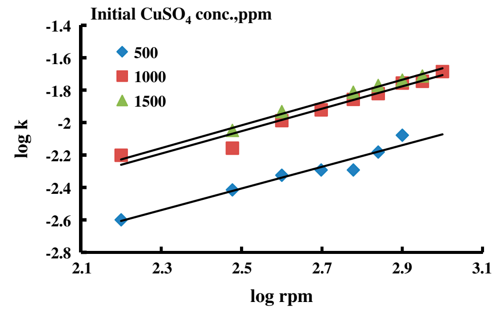

Fig. 3. Plot of $\log k$ vs. log rpm at different initial Cu^{2+} concentrations (smooth cylinder).

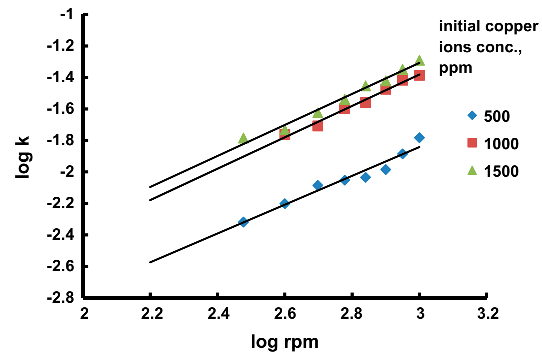

Fig. 4. Plot of $\log k$ vs. log rpm at different initial Cu^{2+} concentrations (e/d = 0.1).

For finned rotating cylinder:

$$k \propto (\mathrm{rpm})^{0.9} \quad (5)$$

It is obvious that the exponent of rpm varies between 0.69 and 0.9. This range is consistent with previous mass transfer studies on rotating cylinder [19]. The increase in mass transfer coefficient with the increase in rpm may be attributed to that as rotational speed increases the thickness of the hydrodynamic boundary layer and diffusion boundary layer decrease with a consequent increase in the rate of mass transfer.

The higher exponent (0.9) in case of finned cylinder compared to smooth cylinder can be explained as follows: (i) fins increase the rate of cementation by the increase in surface area of the cylinder, (ii) fins also act as a turbulence promoters due to vortex formation in the space between fins which has been reported by many authors [20,21].

3.2. Effect of (e/d) ratio

Fig. 5 shows the relation between log k vs. log (e/d) at different rpm. The mass transfer coefficient can be related to (e/d) ratio as follows:

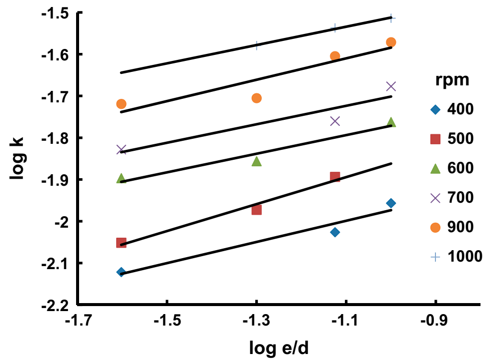

Fig. 5. log k vs. log (e/d) at different rpm (Cu^{2+} concentrations, ppm = 1,500).

$$k \; \alpha \; (e/d)^{0.25} \tag{6}$$

The data show that the mass transfer coefficient increases as (e/d) increases due to the increase in eddies formation in the space between fins as stated previously. The enhancement ratio (γ) defined by the equation:

$$\gamma = \left(\frac{k_f - k}{k}\right) \times 100 \tag{7}$$

where $k_{f,}$ and k are mass transfer coefficient for finned and smooth cylinder respectively.

Table 1 shows the values of enhancement ratios for different initial Cu^{2+} concentrations, different rpm and different (e/d) ratios. The values of (γ) range from 28.79 to 134.85 depending on different operating conditions.

Table 1
Enhancement efficiency at different rpm, e/d ratios and initial Cu^{2+} conc

	ppm					
	(e/d = 0.05)		(e/d = 0.75)		(e/d = 0.1)	
rpm	1,000	1,500	1,000	1,500	1,000	1,500
200	28.79	50.48	18.06	32.72	112.28	94.37
300	34.8	23.98	47.74	18.12	122.15	85.98
400	39.29	10.35	35.64	36.65	70.65	60.39
500	32.03	43.7	50.8	72.32	65.82	91.41
600	66.6	53.51	66.07	61.8	83.86	90.55
700	58.51	44.3	76.9	73.96	85.84	110.7
800	43.7	67.03	74.08	91.24	93.75	110.12
900	43.5	72.56	97.31	117.44	115.6	134.85
1,000	40.6	101.38	91.83	122	102	134.16

3.3. Correlation of the present mass transfer data

An overall mass transfer correlation was envisaged using the dimensionless groups; Sh, Re and Sc which are often used to correlate mass transfer data. The exponent of Sc was fixed at the established value of 0.33 according to previous studies [22].

Fig. 6 shows that the mass transfer data for smooth rotating cylinder fit the following correlation:

$$Sh = 0.74\,Re^{0.69}\,Sc^{0.33} \tag{8}$$

For the conditions Sc = 2,103 and 3,126 < Re < 18,176.

With average standard deviation = 2.66%.

Fig. 7 shows that the mass transfer data for finned rotating cylinder fit the correlation:

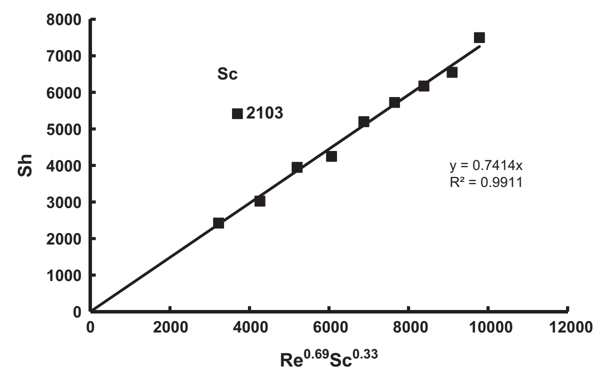

Fig. 6. Overall mass transfer correlation for copper ions cementation on smooth zinc rotating cylinder.

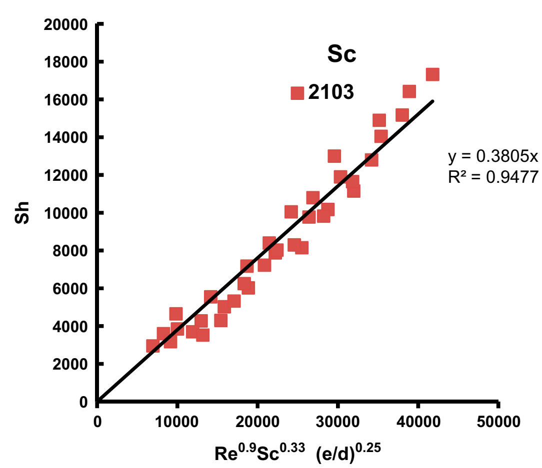

Fig. 7. Overall mass transfer correlation for copper ions cementation on finned zinc rotating cylinder.

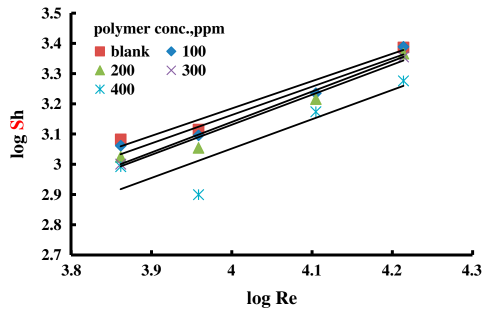

Fig. 8. log Sh vs. log Re at different drag reducing polymer concentrations (Sc = 1,288, smooth cylinder).

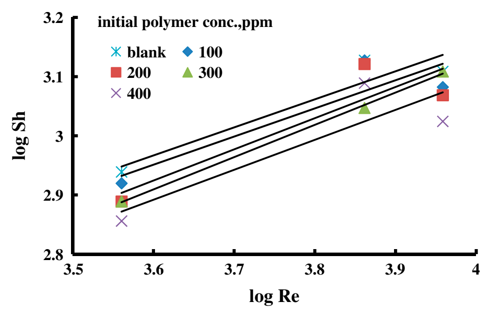

Fig. 9. log Sh vs. log Re at different drag reducing polymer concentrations (Sc = 1,288, $(e/d) = 0.025$).

$$Sh = 0.38\,Re^{0.9}\,Sc^{0.33}\,(e/d)^{0.25} \quad (9)$$

For the conditions $Sc = 2{,}103$, $0.025 < (e/d) < 0.1$ and $3{,}126 < Re < 18{,}176$.

With average standard deviation = 10.3%.

Poulson [22] studied mass transfer at rough surface for four different geometries using three different experimental techniques. He found that for each geometry Sherwood number is linearly related to Re number which is in a fair agreement of the present results. The present Re exponent 0.9 is consistent with the value 0.92 obtained by Holland [23] who used a rotating cylinder covered with electrodeposited Cu powder to recover Cu^{++} from $CuSO_4$ solutions.

3.4. The effect of the presence of drag reducing polymer

Figs. 8 and 9 depict the relation between log Sh vs. log Re at different concentrations of drag reducing polymer for finned and smooth rotating cylinder respectively. In general, the presence of drag reducing polymer retards the rate of mass transfer.

The present decrease in the rate of mass transfer in polymer containing solution is consistent with the results of previous studies on the effect of polymers on the rate of mass transfer coefficient at packed beds [24], rotating discs [25], and tube wall [26]. This decrease in the mass transfer rate may be attributed to the increase in the diffusion layer thickness as a result of eddy damping by the polymer molecules [27].

4. Conclusions

The performance of a finned rotating zinc cylinder in the removal of Cu^{2+} from synthetic wastewater and recovery of metal value by cementation has been investigated in relation to different parameters. The following conclusions have been withdrawn

(1) The rate of Cu^{2+} removal from synthetic wastewater was found to increase, with increasing rpm, e/d ratio, and initial Cu^{2+} concentration.
(2) The fins enhance the rate of Cu^{2+} cementation by an amount which ranges from 28.79 to 134.85% depending on the operating conditions.
(3) The mass transfer data were correlated with dimensionless analysis. The obtained mass transfer correlations can be used for the design and operation of finned rotating reactors used to conduct Cu^{2+} removal by cementation.
(4) Drag reducing polymer was found to decrease the rate of cementation, so before using them, their benefits of energy saving should be weighed against their adverse effects on the rate of cementation.

List of symbols

A — active projected area of the rotating cylinder (cm^2)
C — final concentration of the solution (M)
C_0 — initial concentration of the solution (M)
d — cylinder diameter
e — fin height
k — mass transfer coefficient of smooth rotating cylinder (cm/s)
k_f — mass transfer coefficient of finned rotating cylinder (cm/s)
t — time of cementation (s)
V — volume of solution (L)

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