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Effect of operating conditions on the Cu^{2+} removal from wastewater by cementation on a fixed bed of zinc cylinders

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ABSTRACT

This work investigates the effect of operating conditions on the rate of Cu^{2+} removal from synthetic waste of copper sulphate solution by cementation on a fixed bed of zinc cylinders under different conditions of solution flow rate, initial copper sulphate concentration, bed height, cylinder diameter and solution temperature. The values of the mass transfer coefficient was found to increase with increasing solution flow rate and temperature, while it decreased with increasing bed height, cylinders diameter and initial copper sulphate concentration. The value of the activation energy of the reaction ranged from 2.5 to 4.60 kCal/mol with lower and higher solution flow rates, respectively, which show that the reaction is diffusion controlled. The mass transfer correlation was deduced by dimensional analysis and was found to be in the form that: $Sh = 2.1\ Re^{0.867}\ Sc^{0.33}\ (d/h)^{-1.02}$. In addition, another correlation was deduced for the effect of entrance region by removing the calming section which was found to be in the form that: $Sh = 2.30\ Re^{0.870}\ Sc^{0.33}\ (d/h)^{-0.96}$. The obtained results can help in the design of a continuous flow reactor that may be used for the removal of heavy metals from wastewater.

Keywords: Wastewater treatment; Cementation; Fixed bed; Hydrodynamics; Heavy metal removal

1. Introduction

The presence of toxic heavy metals ions, such as Cu^{2+}, Cd^{2+}, Pb^{2+}, in the wastewater effluents causes severe pollution problems, so these toxic elements must be removed prior to discharge[1]. Various methods are available for removal including neutralization, precipitation, sorption and ion-exchange [1–3]. Cementation reaction is an electrochemical reaction (process) by which a more noble ion is precipitated from solution and is replaced in solution by a metal higher in the electromotive series [2]. Cementation proved to be one of the most effective economic techniques for recovering toxic valuable metals

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from industrial waste solutions [3–5]. Cementation has also been used in purifying leach liquor prior to electro-winning of metals from solution and plating some metals with silver or copper. The advantages of the cementation process include its relative simplicity, ease of control and the possible recovery of valuable metals. However, the consumption of scarifying metals and redox potential of scarifying metals limit the application of this process [6]. Cementation reactions had been studied extensively. It is now accepted that the rate-controlling step in these reactions is the diffusion of the electroactive ion to the reaction surface [3–5]. In cementation processes, the nature of the deposited metals surface highly influences the reaction rate. It was reported that the rate increases once a porous deposit is formed. This was attributed to the increase in surface area and to the generation of small eddies in the laminar boundary layer by the deposit protrusions. When a coherent deposit is formed, the rate was found to decrease with increasing deposit mass and tends to fall to zero [7]. The efficiencies are determined by rate factors, so that the reaction kinetics is essentially influenced by factors such as the geometry of the less noble metal surface, temperature, concentration of the metal ions, stirring mode and velocity. Direct observation of the morphology of the precipitate by various optical methods reveals that it can grow in different forms, ranging from the compact and fine-grained, coherent structures of low porosity to coarse-grained dendritic structures, characterized by a much larger porosity[8]. Since copper metal is insoluble, the most copper enters the water system by copper salts. Such copper salts are used in electroplating industry, engraving and photography, while wastes from rinses tanks and filter cleanouts usually discharge into the sanitary system. Copper ions, as pollutants, do not accumulate in the human body in massive amounts, though copper can cause illness or even death. So, copper and heavy metals which may be present in industrial wastewater must be removed [9,10].

The objective of the present work is to study the effect of hydrodynamic conditions on the rate of cupric ion removal from industrial waste solutions using fixed bed of zinc cylinders; the fixed bed has the advantage that it gives high interfacial area of contact which increases the rate of mass transfer, but has the problem of increasing the pressure drop over the column, which in turn increases the pumping power loss [11]. The main objective of this research is to study the effect of operating conditions on the rate of Cu^{2+} cementation on a fixed bed of zinc cylinders.

2. Experimental part

2.1. Experimental set-up

Fig. 1 shows the experimental set-up used in the present study; it contains a plexiglass column reactor (D) of 10 cm inside diameter and 100 cm height, a fixed bed of zinc cylinders (aspect ratio = 1) packed randomly in a stainless-steel wire screen basket coated with epoxy (F) and a calming section of glass spheres (E) with 50 cm height which was used to eliminate the entrance effect; the column was fitted with 2.0 cm diameter inlet tube at its bottom and an overflow weir (G) at the top; the overflow weir (G) was fitted with an outlet tube of 2.0 cm diameter. Copper sulphate solution flows from storage tank (A) via ¼ hp plastic head centrifugal pump (B) to enter the bottom of the reactor through perforated plastic screen (H). The flow can be regulated via discharge and recycle two-inch plastic valves. Samples were withdrawn from the top of the overflow weir (G). The mass transfer coefficient between the zinc cylinders and the copper sulphate solution was determined by measuring the change in copper sulphate concentration with time. For a batch operation, 16 L of fresh copper sulphate solution was circulated at the beginning of each run; the zinc cylinders fixed bed was stacked randomly in a plexiglass column; then, the solution was pumped to circulate through the system

2.2. Procedure

At the beginning of each run, zinc cylinders were abraded and washed well with very dilute hydrochloric acid and then washed with distilled water for few minutes, and then stacked randomly at stainless steel wire

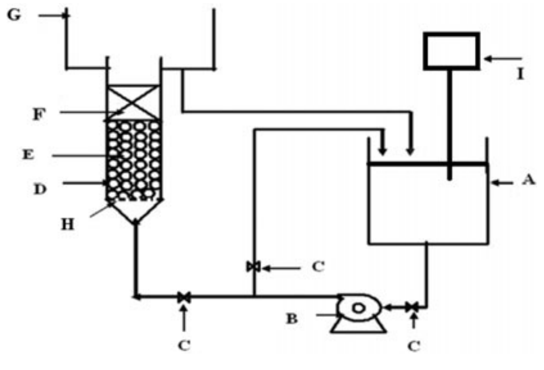

Fig. 1. Experimental set-up with calming section.
Notes: A—storage tank; B—centrifugal pump; C—plastic ball valves; D—plexiglass reactor; E—calming section; F—fixed bed of zinc cylinders; G—overflow weir; H—perforated plastic screen; I—thermostat coil heater.

screen basket coated with epoxy and held at the top of the calming section (Fig. 1) or directly held at the bottom of the column; meanwhile, 16 L of copper sulphate solution was achieved using ¼ hp plastic head centrifugal pump. To follow the change in copper sulphate concentration with time, samples of the solution (5 ml) were withdrawn at regular time intervals range from 3 to 5 min at different solution velocities. The samples were titrated against standard (0.01 N) sodium thiosulphate solution using potassium iodide and starch solution as indicators [12]. The titration itself is an indirect operation; 5 ml of the sample was treated with 5 ml H_2SO_4 and excess amount of KI (25 ml) was added to the solution with agitation till brown colour changes to pale yellow; hence, a starch solution was added with agitation where the colour turns blue. Titrate against 0.01 N sodium thiosulphate until the dark blue colour of starch–iodine complex disappears. Four different initial concentrations were used in the present work: 0.025, 0.05, 0.075 and 0.1 M. All experiments were carried out using A.R. Chemicals and distilled water at temperatures ranging from 25 to 40˚C adjusted using thermostat coil heater (I) and at a solution pH of (3.8 ± 0.2) which was adjusted using portable pH meter, diluted HCl and NaOH solutions.

3. Results and discussions

The present study was conducted in a simple batch reactor. For simple batch reactors, the rate of the reaction is given by [13,14]:

$$-V_s \frac{dC}{dt} = KAC \tag{1}$$

which upon integration yields

$$-V_s \int_{C_0}^{C} \frac{1}{C} dC = KA \int_{0}^{t} dt \tag{2}$$

$$V_s \ln \frac{C_0}{C} = KAt \tag{3}$$

where V_s is the solution volume in the reactor; C_0, C are the initial $CuSO_4$ concentration and the concentration at any time t, respectively; A is the active surface area of the zinc cylinders; t is the time; and K is the mass transfer coefficient. As shown in Fig. 2, the mass transfer coefficient was obtained under different conditions by plotting ln (C_0/C) vs. time; the slope of the resulting straight line gives (KA/V_s) from which K was calculated.

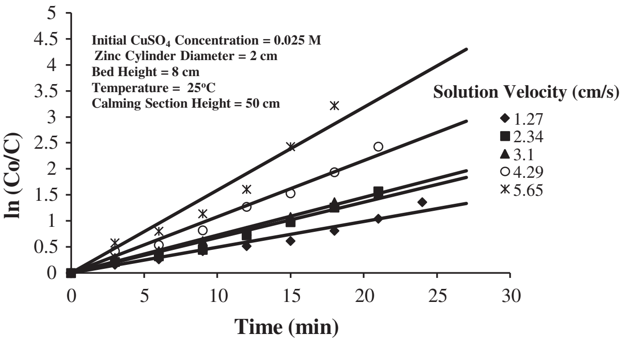

Fig. 2. ln (C_0/C) vs. time for different solution velocity.

3.1. Effect of solution flow rate (solution velocity)

Fig. 2 shows that the mass transfer coefficient increased with increasing solution flow rate. This may be attributed to the fact that increasing solution velocity increases the possibilities of eddies formation near the solid surface of zinc cylinders; this increases the degree of turbulence, thus lower the boundary and diffusion layers thicknesses, consequently, faster rates of mass transfer are obtained, that is, faster cementation rates. Fig. 3 shows that increasing the solution velocity from 1.27 to 5.65 has increased the mass transfer coefficient by approximately 10% of its value at lower velocity.

3.2. Effect of initial copper sulphate concentration

As shown in Fig. 3, within the range of 0.025 to 0.1 M $CuSO_4$, it is clear that by increasing the initial concentration at a given solution velocity, the mass

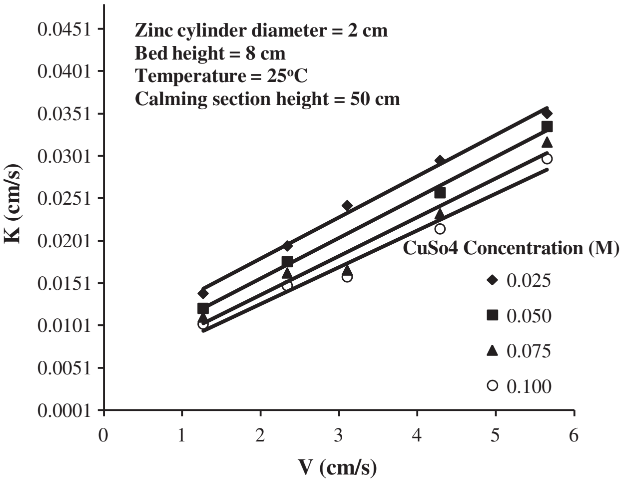

Fig. 3. Mass transfer coefficient vs. solution velocity at different $CuSO_4$ concentrations.

transfer coefficient decreased. This may be attributed to the fact that by increasing the initial copper sulphate concentration, the interionic attraction increases and the diffusion coefficient decreases, which causes the mass transfer rates to decrease [15].

3.3. Effect of bed height

Fig. 4 shows the relation between the mass transfer coefficient and the solution velocity at different bed heights ranging from 2 to 8 cm. It is clear that by increasing the bed height, the value of the mass transfer coefficient decreases. This may possibly be attributed to the increase in the resistance to solution flow through the bed layers, thus, damps the eddies which may be formed and increases the boundary layer and diffusion layers thickness, which decreases the rate of mass transfer and cementation rate.

3.4. Effect of zinc cylinder diameter

From Fig. 5, it is clear that the mass transfer coefficient decreased by increasing the zinc cylinder diameter. This may be ascribed to the fact that by increasing zinc cylinder diameter, the possibility for building up the hydrodynamic boundary layer increases and hence the diffusion layer thickness increases on the cylinder surface, and consequently, the rate of cementation decreases.

3.5. Effect of solution temperature

Fig. 6 shows the effect of solution temperatures within the range from 25 to 40°C. It is clear that increase in temperature, at a given solution velocity, increases the value of the mass transfer coefficient. This is probably because increasing temperature decreases the solution viscosity with a consequent increase in the diffusivity according to the Stokes–Einstein equation:

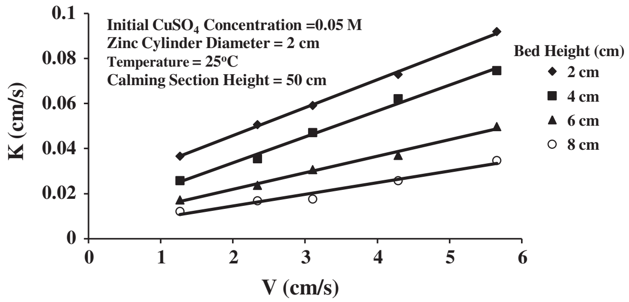

Fig. 4. Mass transfer coefficient vs. solution velocity for different bed heights.

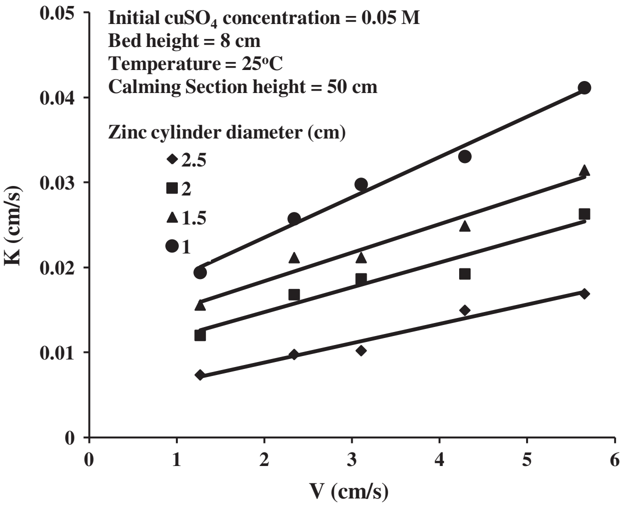

Fig. 5. Mass transfer coefficient vs. solution velocity for different zinc cylinder diameters.

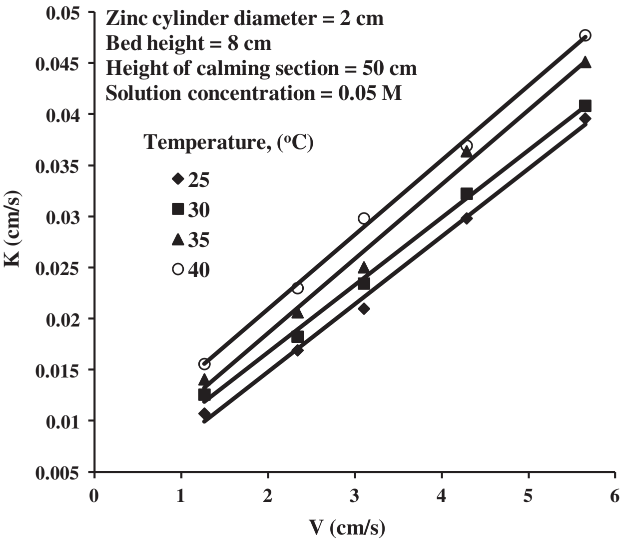

Fig. 6. Mass transfer coefficient vs. solution velocity at different solution temperatures.

$$\mu D/T = \text{const} \tag{4}$$

The increase in the diffusivity with temperatures increases also the mass transfer coefficient ($K = D/\delta$) and the rate of cementation. Fig. 7 shows that the effect of temperature on the rate of cementation fits the Arrhenius equation:

$$K = A_0 e^{-E/RT} \tag{5}$$

with an activation energy (*E*) of 3.04–6.0 kCal/mol with respect to the solution velocity. This value confirms the diffusion-controlled mechanism of cementation of copper on zinc [16,17].

3.6. Overall correlation with calming section

In all previous investigations, a calming section of 50 cm in the entrance region of the fixed bed unit was used. Dimensional analysis was used to correlate the present data aided by the aforementioned experimental results. The mass transfer coefficient can be related to other variables by the functional equation:

$$\mathrm{Sh} = a\,\mathrm{Sc}^{\alpha}\,\mathrm{Re}^{\beta}(\mathrm{d/h})^{\gamma} \tag{6}$$

According to the previous theoretical and experimental studies in mass transfer, the value of constant α was fixed at 0.33 [18]. Fig. 8 shows the relation between log Sh vs. log Re which shows that the value of constant β in the present study is 0.867, while Fig. 9 shows the relation between log Sh vs. log d/h which shows that the value of constant γ in the present study is –1.02.

Fig. 10 shows the overall correlation for cementation of copper on a fixed bed of zinc cylinders which shows that the value of constant *a* in the present study is 2.1. Thus, the overall mass transfer correlation becomes:

$$\mathrm{Sh} = 2.1\,\mathrm{Re}^{0.867}\,\mathrm{Sc}^{0.33}(\mathrm{d/h})^{-1.02} \tag{7}$$

Under the range of conditions that: $261 < \mathrm{Re} < 1{,}164$, $1{,}539 < \mathrm{Sc} < 1{,}704$, $0.25 < \mathrm{d/h} < 1$.

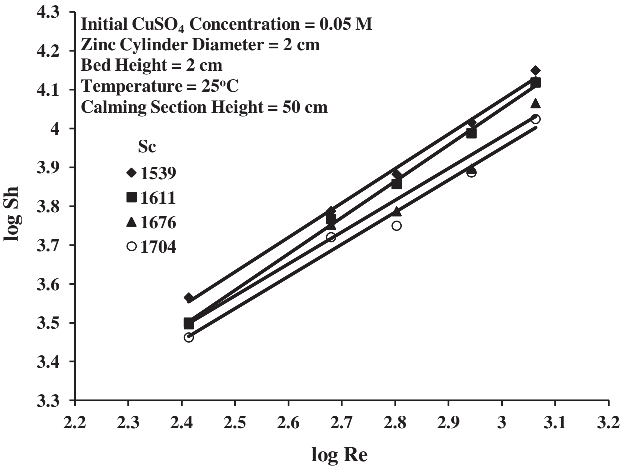

Fig. 8. log Sh vs. log Re for different Sc.

3.7. Effect of flow in entrance region

The presence of calming section is essential for uniform fluid flow through the working section, as it eliminates the turbulences that may be formed due to the entrance region. The removal of calming section (Fig. 1 without part E) results in non-uniformity of flow and generation of eddy turbulence which increases the rate of mass transfer. The system was investigated under different conditions of initial $CuSO_4$ concentration and bed height; again the rate of mass transfer decreased by increasing both bed height and initial solution concentration. Same figures (not presented here) were found for the exponent of Re and (d/h) to be 0.87 and –0.96, respectively, and Fig. 11 represents the overall correlation for cementation of copper on a fixed bed of zinc cylinders without calming section which shows that the value of the overall constant in the present study is 2.3. Thus, the overall mass transfer correlation becomes:

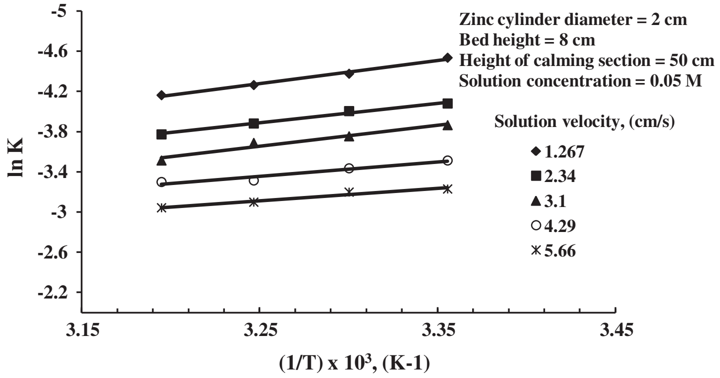

Fig. 7. ln *K* vs. 1/*T* for different solution velocities.

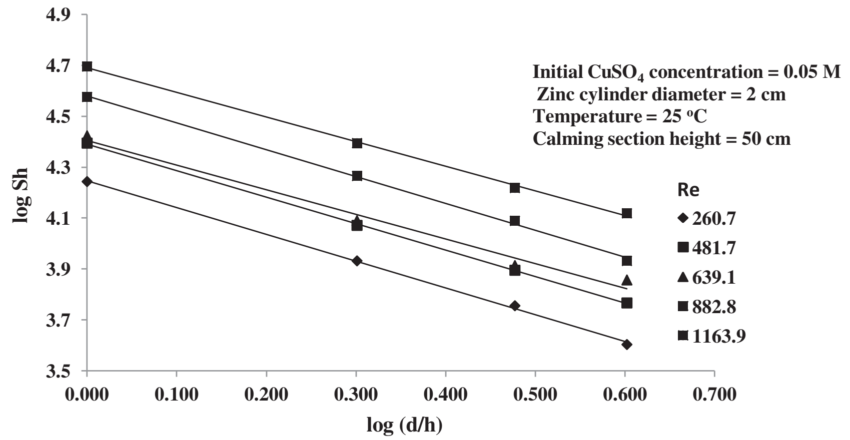

Fig. 9. log Sh vs. log (d/h) for different Re.

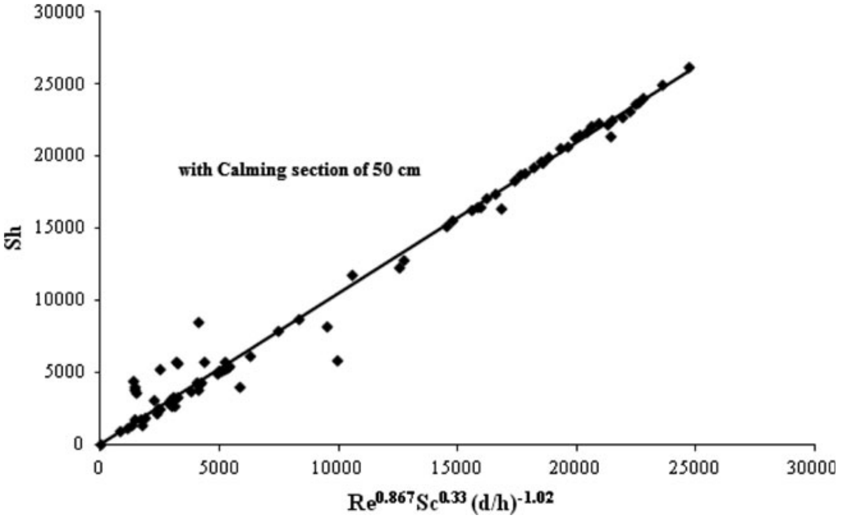

Fig. 10. Overall mass transfer correlation for cementation of copper on a fixed bed of zinc cylinders.

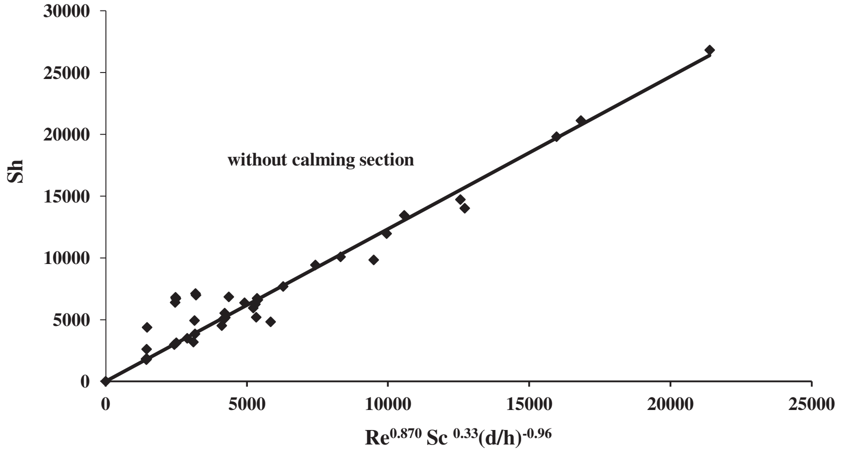

Fig. 11. Overall mass transfer correlation for cementation of copper on a fixed bed of zinc cylinders without calming.

$$\mathrm{Sh} = 2.3\,\mathrm{Re}^{0.87}\,\mathrm{Sc}^{0.33}\,(\mathrm{d}/\mathrm{h})^{-0.96} \tag{8}$$

Under the range of conditions that: $261 < \mathrm{Re} < 1{,}164$, $1{,}539 < \mathrm{Sc} < 1{,}704$, $0.25 < \mathrm{d}/\mathrm{h} < 1$.

The obtained results indicate that removing the calming section has increased the rate of mass transfer. These results may be contradicting with the finding of Sedahmed et al. [19]. The enhancements effects of removing the calming section may be attributed to the turbulences generated at the entrance region which generates eddies, reduces the diffusion boundary layer thickness and improves the rate of mass transfer.

4. Conclusion

This work investigated the effect of hydrodynamic conditions on the rate of Cu^{2+} removal from synthetic waste of copper sulphate solution by cementation on a fixed bed of zinc cylinders under different conditions. Solution flow rate and temperature were found to improve the rate of mass transfer, while bed height, cylinders diameter and initial copper sulphate concentration were found to decrease it. The value of the activation energy of the reaction was found to be in the range from 2.5 to 4.60 KCal/mol with lower and higher solution flow rates, respectively, which show that the reaction is a diffusion-controlled one. A mass transfer correlation was deduced by dimensional analysis and was found to be in the form that: $\mathrm{Sh} = 2.1\ \mathrm{Re}^{0.867}\ \mathrm{Sc}^{0.33}\ (\mathrm{d}/\mathrm{h})^{-1.02}$. In addition, another correlation was deduced for the effect of entrance region by removing the calming section which was found to be in the form that: $\mathrm{Sh} = 2.30\ \mathrm{Re}^{0.870}\ \mathrm{Sc}^{0.33}\ (\mathrm{d}/\mathrm{h})^{-0.96}$. The obtained results can help in the design of a continuous flow reactor that may be used for the removal of heavy metals from wastewater.

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