REMOVAL OF CUPRIC IONS FROM WASTEWATER BY CEMENTATION ON A GAS SPARGED FIXED BED OF ZINC CYLINDERS

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ABSTRACT

The cementation of cupric ions from a simulated wastewater effluent consisting of copper sulphate solution using a gas sparged fixed bed of zinc cylinders was investigated as a possible technique for the removal of small amounts of cupric ions present in waste streams. Variables studied were initial copper sulphate concentration, bed height, and N_2 flow rate. The values of the volumetric mass transfer coefficient were found to decrease with increasing bed height and initial copper sulphate concentration. The percentage recovery of cupric ions from solution decrease with increasing initial copper sulphate concentration. More than 65 % of the total copper in solution was deposited in less than 10 min. for an initial concentration of 3.15 g Cu^{++} L^{-1} and superficial N_2 velocity of 3.157×10^{-2} $cm.s^{-1}$.

Keywords: Cementation, Heavy metals, Fixed bed, Volumetric mass transfer coefficient, Zinc cylinders

INTRODUCTION

Heavy metals such as copper, nickel, chromium, lead, mercury, cadmium,...etc are present in many industrial wastewaters and must be removed prior to discharge. The presence of these toxic ions in the wastewater effluents cause severe pollution problems. Various treatment processes have been developed to remove heavy metals from waste-water (Peter et al. 1985). The cementation processes has been used in industry for a long time, not only in hydrometallurgy (Biswas and Davenport 1890) but also in the purification of process streams and wastewater (Strickland and Lawson 1973; Gould et al. 1984; Hendrickson et al, 1984; Mackinnon et al. 1971; Mackinnon and Ingrahm 1971)). The cementation reaction is an electrochemical process by which a more noble metal is precipitated from solution and is replaced in solution by a metal higher in the electromotive series. The removal of heavy metals such as copper and lead by cementation has been studied by a number of researchers. (Agelidis et al 1988) studied the lead removal from wastewater by cementation using a fixed bed of iron spheres. (El-Tawil 1987) studied the cementation of copper from dilute copper sulphate solution on a fixed bed of iron powder. Agelidis et al and El-Tawil used single phase flow as a mode of stirring, while in the present work a gas sparging was used as a mode of stirring. Also the surface geometry used was a zinc cylinders.

Previous studies have shown that cementation reactions are diffusion controlled (Ku and Chen 1992; Nadkarni et al. 1967; Nadkarni and Wadsworth 1967; Rickard and Fuerstenau 1968; Strickland and Lawson 1973; Agelidis et al. 1985; Jiong and Ritchie 1986). The advantages of the cementation process include its relative simplicity, ease of control, low energy consumption, and recovery of valuable or toxic metals.

The objective of the present work is to study the removal of cupric ions from simulated wastewater effluent by cementation technique using gas sparged fixed bed of zinc cylinders.

EXPERIMENTAL

The experimental set up used in the experiments is shown in Figure (1). It consisted of a nitrogen cylinder, a rotameter, and a plexiglass column. Inside diameter of the cylindrical column is 5.5 cm and is 120 cm high. The column was fitted at its bottom with a G4 sintered glass distributor of 5 cm diameter and is 0.5 cm thick. The average diameter of the pores of sintered distributor was 5-10 microns. Zinc cylinders 0.7 cm diameter and 0.7 cm height were compacted at random in the column resting on the sparger. Bed height was changed, the heights employed were 1.9, 2.4 and 2.9 cm. Before each run, the system was first cleaned and new zinc cylinders were used as a fixed bed. Following that, 1.75 liter of fresh copper sulphate ($CuSO_4.5H_2O$) solution were introduced carefully in the column in order to avoid mixing as far as possible before nitrogen stirring. In the mean time nitrogen gas was allowed to pass through the column. The nitrogen flow rate was controlled by a regulator and measured by a calibrated rotameter Three cm^3 samples were withdrawn at 1 min intervals for copper sulphate analysis by titrating against 0.02 N sodium thiosulphate using starch as indicator (Vogel 1961).

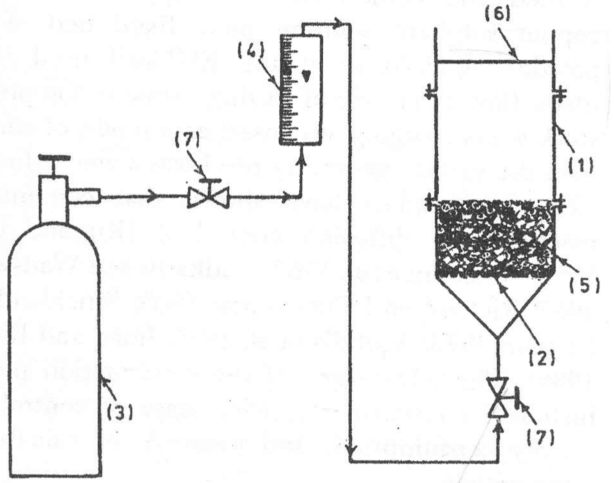

Figure 1• Experimental apparatus for gas sparging

1- Cylindrical column
2- Sintered glass for gas distribution
3- Nitrogen cylinder
4- Rotameter
5- Fixed bed
6- Electrolyte level
7- Control valves

Figure 1. Experimental apparatus for gas sparging.

The cementation experiments were carried out at room temperature (22 $\pm$ 1°C) and each experiment was conducted only for 10 min. The volumetric mass transfer coefficient was calculated from Cu^{++} concentration-time data. Nitrogen superficial velocities ranged from 1.226 x 10^{-2} to 3.508 x 10^{-2} $m.s^{-1}$. The concentration of the copper sulphate solutions employed ranged from 0.05 to 0.35 M. All solutions were prepared using A.R grade chemicals and distilled water.

RESULTS AND DISCUSSION

The cementation reaction

$$Cu^{++} + Zn = Cu + Zn^{++} \qquad (1)$$

is a diffusion controlled reaction whose rate in a batch reactor can be represented by the equation:

$$-V\frac{dc}{dt} = KAC \qquad (2)$$

which integrates to

$$Ln\left(\frac{C_o}{C}\right) = \frac{KAt}{V} \qquad (3)$$

where A is the surface area of the particles (m^2), C the concentration at time t (mol/L), C_o the initial concentration (mol/L), K is the mass transfer coefficient (m/s), t the time and V the reaction volume (L). Equation (3) was used to calculate the volumetric mass transfer coefficient of copper cementation on zinc cylinders under different conditions.

Figure (2) represents a typical plot of ln C_o/C vs.t at different nitrogen superficial velocities, the volumetric mass transfer coefficient was obtained from the slope of ln C_o/C vs.t.

Figure (3) shows the effect of the N_2 superficial velocity on the volumetric mass transfer coefficient at different bed heights. It is noticed that from this figure, the magnitude of the volumetric mass transfer coefficient decreased with increasing bed height. By plotting the percentage recovery as a function of initial copper sulphate concentration at different bed heights, it was found that, the percentage recovery decreased with increasing bed height (cf. Figure (4)).

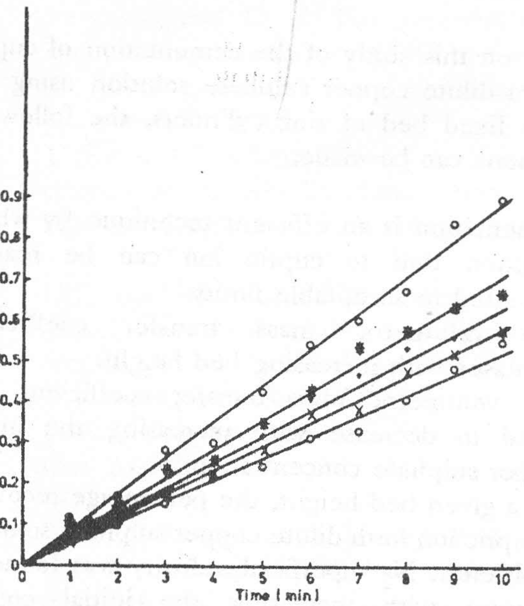

Figure 2. Ln C_o/C vs t initial concentration of $CuSO_4$. $5H_2$ O=0 05 M bed height = 2.9 cm supervicial gas velocity V, cm/s.
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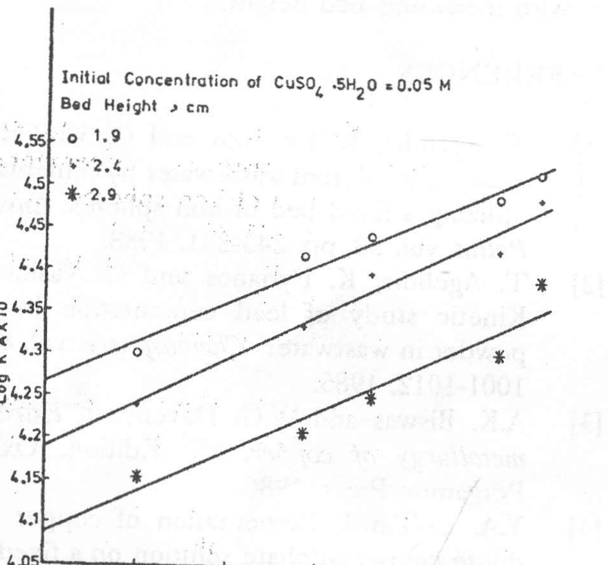

Figure 3. Effect of superficial gas velocity on the volumetric mass transfer coefficient at different bed heights.

The observed decrease in volumetric mass transfer coefficient with bed height may be attributed to the fact that, as the gas-liquid dispersion progresses through the bed, the local copper sulphate concentration decreases along the bed with a consequent decrease in the rate of mass transfer. This agrees with the finding of El-Tawil 1987) who studied the cementation of cupric ions from dilute copper sulphate solution using fixed bed of iron particles.

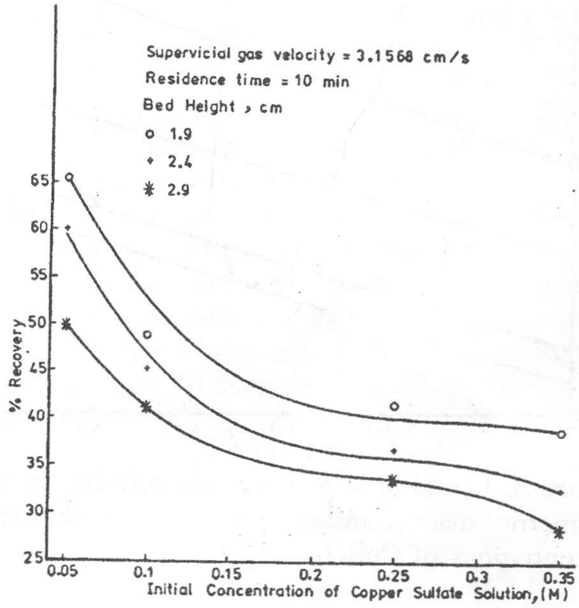

Figure 4. Effect of initial concentration of $CuSO_4$. $5H_2O$ on the % recovery of cupric ion from solution at different bed heights.

Figure (5) shows the effect of nitrogen superficial velocity on the volumetric mass transfer coefficient at different initial copper sulphate concentrations. It was found that at constant bed height, the volumetric mass transfer coefficient decreases with increasing concentration.

By plotting the percentage recovery as a function of initial copper sulphate concentration at different superficial N_2 velocity, it was found that, the percentage recovery decreases with increasing the concentration of copper sulphate (cf. Figure 6). This may be attributed to the fact that, low initial Cu^{++} concentration, the precipitated copper would form a thin layer which will not slow the precipitation reaction, whereas doubling the concentration will lead to denser precipitate which would lead to additional resistance to mass transfer. Therefore, slowing down the precipitation reaction with a consequent decrease in the percentage recovery and the rate of mass transfer decreases.

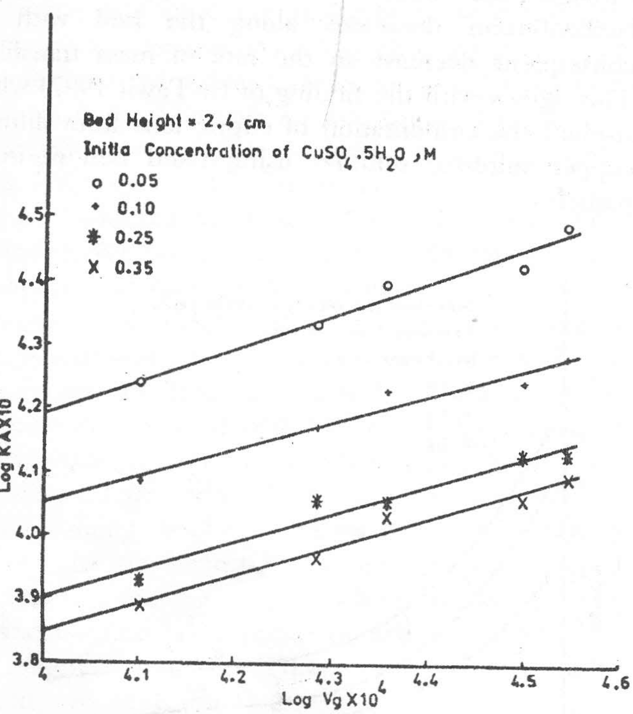

Figure 5. Effect of superficial gas velocity on the volumetric mass transfer coefficient at different concentrations of $CuSO_4$. $5H_2O$.

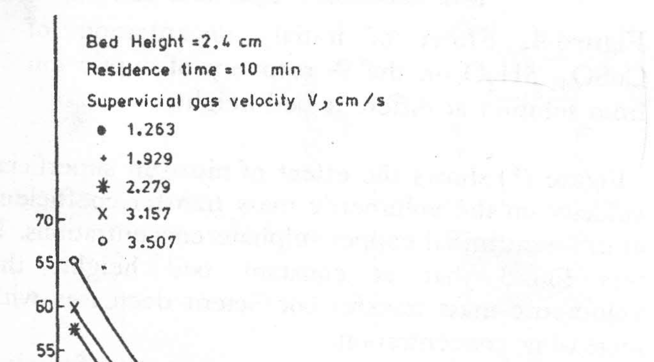

Figure 6. Effect of initial concentration of $CuSO_4$. $5H_2O$ on the % recovery of cupric ion from solution at different superficial gas velocities

CONCLUSIONS

Based on this study of the cementation of cupric ion from dilute copper sulphate solution using gas sparged fixed bed of zinc cylinders, the following conclusions can be made:

1. Cementation is an efficient technique by which pollution due to cupric ion can be readily decreased to acceptable limits.
2. The volumetric mass transfer coefficient decreases with increasing bed height.
3. The volumetric mass transfer coefficient was found to decrease with increasing the initial copper sulphate concentration.
4. For a given bed height, the percentage recovery of cupric ion form dilute copper sulphate solution at different N_2 superficial velocity was found to decrease with increasing the initial copper sulphate concentration.
5. For a given superficial N_2 velocity, the percentage recovery of cupric ion from dilute copper sulphate solution was found to decrease with increasing bed height.

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