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Reduction of Toxic Cr6+ Ions Using Fluidized Bed of Iron Particles

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Abstract

The kinetics of the cementation of chromium ions from potassium dichromate solution onto fluidized bed of iron particles were investigated in a stirred tank reactor. Variables studied were physical properties of the solution, stirring speed (rpm) and temperature. The rate of cementation was found to increase with increasing rpm and concentration. The rate of cementation was expressed in terms of the liquid–solid mass transfer coefficient (k). The data were correlated by the equation:

$$Sh = 0.52\ Sc^{0.33} Re^{0.4957}$$

The high rates of mass transfer obtained in this work and the high area per unit volume of fluidized bed of iron qualify them for building high space time reactors suitable for purification of hydrometallurgical leach liquors and removal of heavy metal from waste water by cementation.

Keywords: Chromium ions; Fluidized bed; Heavy metal; Waste water; Biometallic; Electroplating

Introduction

Hexavalent and trivalent chromium are the stable form of presence of chromium in water. Cr(IV) is known to be carcinogenic and toxic; thus causing health problems e.g., vomiting, severe diarrhea, pulmonary congestions and liver damage. Whereas Cr (III) is less toxic [1,2] Cr(III) is essential in human nutrition (especially in glucose metabolism) [3-6]. Chromium ions are non-degradable and can accumulate in living tissue. Although some heavy metals in low dosage are essential micronutrients for plants and animals, in higher doses they can detrimentally affect the health of most living organisms [7-9].

From economical aspect, the advantages of chromium applications in different industries [10,11], such as the production of stainless steel, in electroplating, refractory industry, tanning of leather, pigment and chemical industry, etc., contrast with its negative external effects as a hazardous pollutant. Numerous soils, waste sites, groundwater, and surface waters are contaminated with anthropogenic Cr(VI) [12-14].

In general, chromium (VI) is removed from waste water by various methods such as adsorption [15-32] biometallic as high efficiency removing method [33], Coagulation precipitation [34], Electrocoagulation [35-38], membrane [39-45], sorption [46-56], Step-by-step deposition and extraction technique [57], reduction [58-60].

Cementation is one of the oldest and simplest hydrometallurgical processes, which has been used as a means of extracting metals from solution. Only in the past 20 years, considerable attention has been paid to two main industrial applications of cementation. The first involves the recovery of metals from leach solution [57-59] and the second is concerned with the purification of electrolyte solutions to remove metals which are more electropositive than the metal to be deposited, e.g., Cu, Co, Ni, Cd from $ZnSO_4$ electrolyte [61-64].

Experimental Part

Materials and methods

All chemical reagents [$K_2Cr_2O_7$, H_2SO_4] were in analytical reagent grade. Stock solutions of 0.001- 0.002- 0.003 and 0.004 M of $K_2Cr_2O_7$ were prepared by dissolving AR grade chemicals in distilled water. Iron particles were etched in dilute HCl to remove the oxide layer, washed with distilled water and dried before each run. The size of iron particles was between 1.0 and 0.8 mm ($\cong$0.9 mm).

Apparatus: Figure 1 shows the experimental setup used in the present study. It consisted mainly baffled cylindrical container of volume 3/4 liter. The container is stirred with 4 Blade 45° pitched blade metal turbine coated with epoxy. The dimensions of the cylinder are as follows: J (baffles thickness)=1 cm, W (blade width)=1 cm, L (blade length)=1.25 cm, D_a (Impeller diameter)=5 cm and E (Impeller height)=3 cm.

Procedure: Before each run 0.75 L of acidified potassium dichromate solution were introduced to the container. The rate of cementation of Cr6+ on the iron particles was determined by measuring the change in Cr6+ concentration with time. The time dependence of chromium concentration was monitored during cementation by withdrawing a sample of 5 cm^3 at different time intervals for analysis by titration against standard ferrous ammonium sulfate (0.01N) in presence of sodium diphenylamine sulfonate as an indicator.

The solution viscosity and density needed for data correlation were determined experimentally by an Ostwald viscometer and a density bottle respectively [65], while the diffusivity of acidified potassium dichromate was obtained from the literature [66,67].
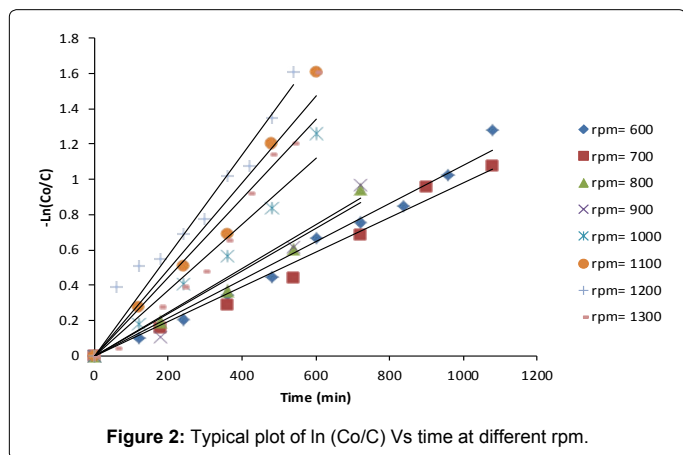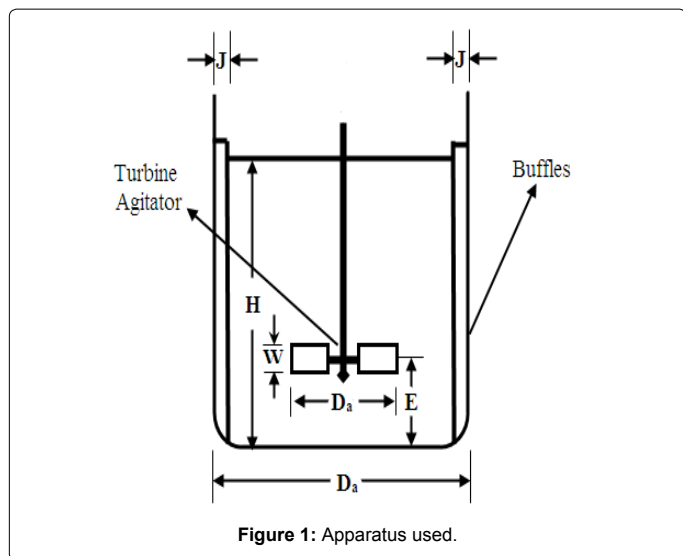
Results and Discussion

The mass transfer coefficient of the diffusion controlled cementation of chromium on zinc particles was obtained under different conditions from the potassium dichromate concentration-time data. Figure 2 show that the data fit the equation: $-V_s \dfrac{dC}{dt} = KAC$ which upon integration

Figure 1: Apparatus used.

Figure 2: Typical plot of ln (Co/C) Vs time at different rpm.

yields; $\ln\dfrac{C_o}{C} = \dfrac{KA}{V_s}t$ where C_o is the initial concentration of potassium dichromate, C is the concentration of potassium dichromate at time (t), V_s is the solution volume, A is the surface area of the iron particles in the bed, which was calculated in terms of particle diameter from the equation: $A = \dfrac{6m}{\tilde{n}d_p}$ where: m=mass of iron particles; ρ=density of iron; d_p=particle diameter. The mass transfer coefficient (K) was calculated from the slope of the straight line obtained by plotting $\ln(C_o/C)$ versus time typical figure is shown in Figure 2.

To correlate the present mass transfer data, the method of dimensional analysis was used. The present data could be correlated by the functional equation:

$K=f(\rho, \mu, D, V, d_i, d_p)$ Where: K=mass transfer coefficient; ρ=density of the solution; μ=viscosity of the solution; D=diffusivity of chromium ions; V=impeller linear velocity, d_p=iron particle diameter, d_i=impeller diameter.

Dimensional analysis leads to writing of the previous equation in the form of $\dfrac{Kd_p}{D} = a\left(\dfrac{\mu}{\rho D}\right)^{\alpha}\left(\dfrac{\rho Nd_i^2}{\mu}\right)^{\beta}$
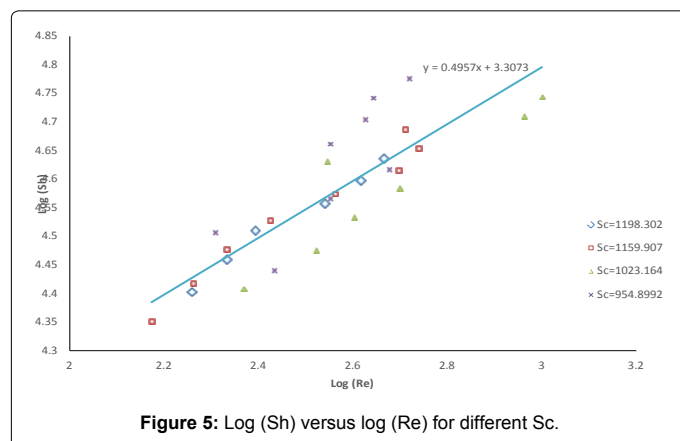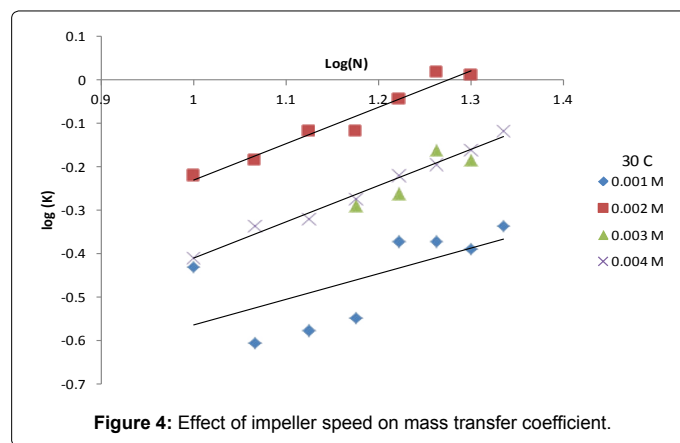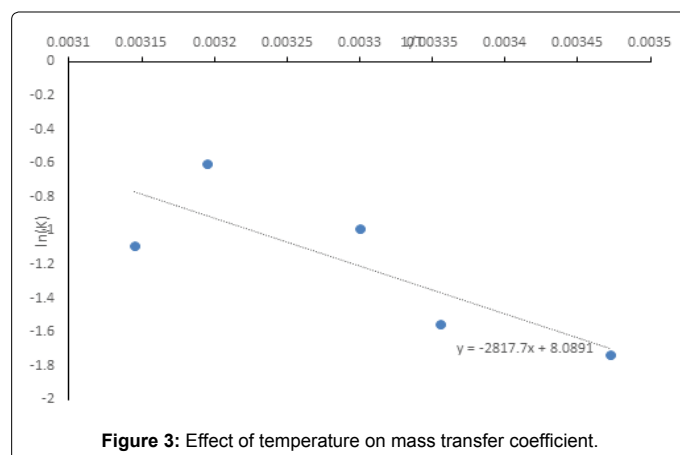
The exponent β and the constant (a) were determined using the experimental data. Following previous theoretical and experimental

studies in mass transfer [68,69], the exponent 0.33 was used for α. Figure 4 Shows the effect of impeller speed on the mass transfer coefficient, Figure 5 shows the effect of Re on Sh at different Sc and the equation).

Figure 5 shows the present data for the conditions: $954.899 < Sc < 1198.3024$; $2.16 \times 10^4 < Re < 5.97 \times 10^4$ fit the equation:

$Sh=0.52 \, Sc^{0.33}Re^{0.4957}$

The increase in the mass transfer coefficient of Cr⁶⁺ cementation on iron particles with increasing impeller rotation speed confirms the diffusion controlled nature of cementation reaction [70,71]. Figure 3 also shows that the activation energy is 4.5 kcal/mole <5 kcal/mole thus insuring the diffusion effect. The increase in the rate of mass

Figure 3: Effect of temperature on mass transfer coefficient.

Figure 4: Effect of impeller speed on mass transfer coefficient.

Figure 5: Log (Sh) versus log (Re) for different Sc.

transfer with increasing impeller speed is attributed to the increase in the intensity of turbulence in the agitated vessel which reduces the liquid phase diffusion layer thickness around the iron particles with a consequent increase in the mass transfer coefficient, which is related to the diffusion layer thickness (δ) by the equation [68,69]

$$K = \frac{D}{\ddot{a}}$$

Conclusion

The use of fluidized bed of iron to reduce Cr^{6+} to Cr^{3+} which is non-toxic found to be diffusion controlled. The using of the powder increase the surface area and thus the rate of reduction i.e., it offers high space time yield cementation reactor suitable for reduction of Cr^{6+}. The present mass transfer equation can be used for fluidized (suspended) bed reactor.

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