

Removal of Cadmium Ions from Industrial Wastewater by Cementation

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Electroplating waste solutions constitute a major source for environmental pollution with heavy metal ions such as Cu^{++} , Cd^{++} , Pb^{++} , and Cr^{6+} . These ions are lethal to man and aquatic life as well, therefore should be removed from wastewater before disposal of waste. The present work is concerned with the removal of Cd^{++} from waste solutions by cementation on zinc in a batch stirred tank reactor lined with a cylindrical zinc sheet. The rate of Cd^{++} removal was studied under different conditions of impeller rotation speed, initial Cd^{++} concentration, temperature, and time of cementation. It was found that the rate of Cd^{++} removal increases with increasing impeller rotation speed, temperature, initial concentration and residence time. Mechanistic study of the reaction through activation energy ($35.98 \text{ kJ mol}^{-1}$) determination showed that cementation of Cd^{++} on zinc is a diffusion controlled reaction. Visual observations showed that cadmium deposits on zinc are in the form of powder. Cadmium powder is a valuable salable product which can improve the economy of the process

Rates of cementation were expressed in terms of the rate of mass transfer. The experimental data for the conditions:

$$8444 < Re < 56768 \text{ and } 707 < Sc < 1567$$

fit the following equation:

$$Sh = 0.394 Re^{0.438} \cdot Sc^{0.33} - 17.208$$

Addition of polyox WSR- 301 drag reducing polymer was found to reduce the rate of cementation by an amount depending on polymer concentration.

Keywords:

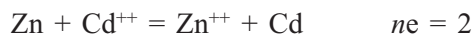
Cementation, heavy metals, mass transfer coefficient, zinc cylinder, drag reducing polymer.

Introduction

The presence of heavy metals in aquatic environments is known to cause severe damage to aquatic life beside the fact that these metals kill microorganisms during biological treatment of wastewater with a consequent delay of the process of water purification.^{1,2} Most of the heavy metal salts are soluble in water and form aqueous solutions, and consequently cannot be separated by ordinary physical means of separation.³ Cadmium is considered highly toxic and therefore its allowable fraction in water resources is limited to 5–10 ppb. Recently, cadmium has become a major environmental concern due to its introduction to natural water reservoirs. Fully developed cadmium poisoning among industrial workers show two main effects; renal dysfunction and emphysema. Exposure is usually by the oral route and the kidney is the critical organ.^{4,5} The major sources for cadmium contamination are: (i) Ni/Cd battery production which may deliver both Cd^{++} and Ni^{++} to ground water in untreated aqueous wastes or through uncontrolled disposal of used batteries, (ii) cadmium plating, which also introduces cyanide used as a strong

complexing agent; and (iii) cadmium is introduced directly to the ground and from there to ground water resources in cultivated area where cadmium-rich phosphate based fertilizers are used. Also non-ferrous metal mines represent a major source of cadmium release to the aquatic environment.^{4,6} Contamination can arise from mine drainage water, wastewater from the processing of ores, overflow from the tailing pond, and rainwater run-off from the mine area. The smelting of non-ferrous metal ores has been estimated to be the largest human source of cadmium release to the aquatic environment.⁴ Among treatment techniques for wastewater containing cadmium are: ion exchange on zeolites, adsorption on activated carbon, binding by immobilized algae, adsorption on hydroxyapatite powder, liquid membranes, cathodic reduction and chemical precipitation.^{7,8} All of these methods have drawbacks, e.g. chemical precipitation requires extremely long settling times and leaves the waste solution with several ppm of Cd^{++} ; ion exchange, adsorption and liquid membrane are very expensive and may require frequent regeneration for adequate performance. Electrochemical recovery of Cd^{++} from wastewater is an energy intensive process.

Cementation represents one of the most powerful techniques for removing heavy metals from wastewater. It consists in displacing the toxic metal ions from the waste solution by a more active non-toxic metal, for instance, Cd^{++} can be removed from wastewater by cementation on zinc according to the reaction:



Most of the previous studies were carried out on the removal of Cu^{++} , Pb^{++} and Ag^+ from wastewater,⁹ scant attention was given to the removal of Cd^{++} by the cementation technique. These studies have shown that in most of the cases cementation is a diffusion controlled reaction and hence need to be accelerated by stirring.^{10–14} Different authors used different stirring methods to enhance the rate of cementation such as cementation on a rotating cylinder,¹⁰ rotating disc,¹¹ fixed bed and fluidized bed,¹⁴ Nosier¹⁵ and Zarraa¹⁶ used gas sparging to promote the rate of cementation.

The present work is aimed to study the removal of Cd^{++} from simulated wastewater by cementation on zinc using mechanical stirring as a mean of enhancing the rate of the process. Hence, an agitated vessel lined with a cylindrical Zn sheet was used.

Experimental Technique

The experimental set-up used in the experiments is shown in Fig. 1, it consisted of 3 dm³ cylindrical glass container lined with a cylindrical zinc sheet. The container was fitted with a variable speed motor. The zinc sheet had 0.14 m diameter, and 0.1 m height. The back surface of the zinc sheet facing the container wall was isolated with epoxy resin. The impeller was made of pyrex glass with 2 blade propeller of 0.04 m diameter. The impeller was mounted centrally on a 0.3 m glass shaft at a distance of 0.02 m from the vessel bottom. The impeller was connected to a variable speed motor

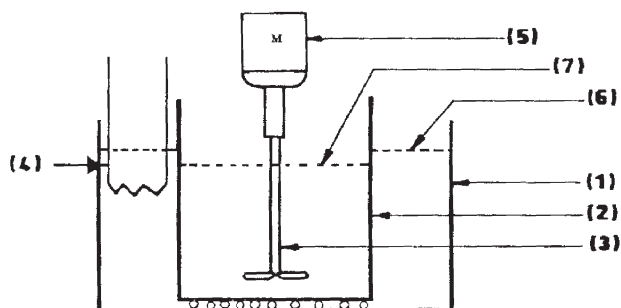


Fig. 1 – Experimental apparatus; 1 – Rectangular water bath, 2 – Cylindrical glass container, 3 – Agitator, 4 – Thermostat, 5 – Variable speed motor, 6 – Water level, 7 – Electrolyte level

shaft. The rotational speed of the stirrer was adjusted by the variac and measured by an optical tachometer. The cylindrical glass container and its contents were immersed in a rectangular water bath to control the temperature. Before each run, the zinc sheet was degreased with trichloroethylene, etched in diluted HCl to remove oxides, washed with distilled water and dried. 2 dm³ of fresh $\text{Cd}(\text{SO}_4)$ solution were introduced into the cylindrical vessel, provided that the zinc sheet is completely immersed in the solution at the various speed of rotation. Two ml of samples were withdrawn at 5 min intervals, for Cd^{++} analysis was carried out using a Perkin Elmer 2380 atomic absorption spectrophotometer. The experiments were carried out at temperature ranging from 22.5 to 40 °C. The cadmium-bearing solution was prepared using A.R grade cadmium sulphate and distilled water. The solution pH value was 5.2. The initial Cd^{++} fraction used in the present study were 100 and 200 ppm respectively. The angular speed of rotation ranged from 31.42 to 146.61 rad s⁻¹.

The viscosity and density of the solution needed for data correlation were measured by an Ostwald viscometer and a density bottle respectively. The diffusivity of CdSO_4 solution was obtained from the literature,¹⁷ and was corrected for the temperature change using the Stokes-Einstein equation.

An attempt was made to assess the effect of drag reducing polymer on the rate of Cd^{++} removal; drag reducing polymers have the potential of being used in agitated vessels to reduce the power required to rotate the agitator.¹⁸ Different fraction of polyox WSR-301 drag reducer in the range from 20 to 120 ppm, were used.

Results and discussion

Before testing the effect of different variables on the rate of cementation of Cd^{++} on Zn, it would be of interest to determine thermodynamically the extent to which the reaction: $\text{Zn} + \text{Cd}^{++} = \text{Zn}^{++} + \text{Cd}$ can proceed in the indicated direction to make sure that this technique can reduce Cd^{++} concentration to extremely low values. Applying the Vant-Hoff isotherm to the above reaction.¹⁹

$$\Delta G = \Delta G^0 + \frac{RT}{zF} \ln \frac{[\text{Zn}^{++}]}{[\text{Cd}^{++}]} \quad (1)$$

At equilibrium $\Delta G = 0$ and $[\text{Zn}^{++}]/[\text{Cd}^{++}] = K$

$$\text{Therefore } \Delta G^0 = - \frac{RT}{zF} \ln K$$

Since $\Delta G^0 = -zE^0F$, where E^0 is the standard e.m.f of the galvanic cell through which the cemen-

tation reaction takes place according to the modern electrochemical theory of cementation.²⁰ The galvanic cell made of Zn with Cd electrodes has $E^0 = 0.36$ volt, therefore $0.36 = \frac{0.059}{2} \log K$, from which the equilibrium constant $= 2.5 \cdot 10^{12}$ which is the final ratio between Zn^{++} and Cd^{++} , i.e cementation of Cd^{++} on Zn would proceed almost to completion under favourable kinetic conditions.

The rate of cementation of Cd on Zn in a batch reactor can be represented by the equation:

$$-V \left(\frac{dy}{dt} \right) = k_d A \gamma \quad (2)$$

Fig. 2, represents a typical plot of $\ln(\gamma_0/\gamma)$ against time at different angular speed of rotation. The mass transfer coefficient, k_d was obtained from the slope of $\ln(\gamma_0/\gamma)$ versus t . Fig. 3, shows the effect of angular speed of rotation on the mass transfer coefficient under different initial mass concentrations of Cd^{++} . The data fit the equation:

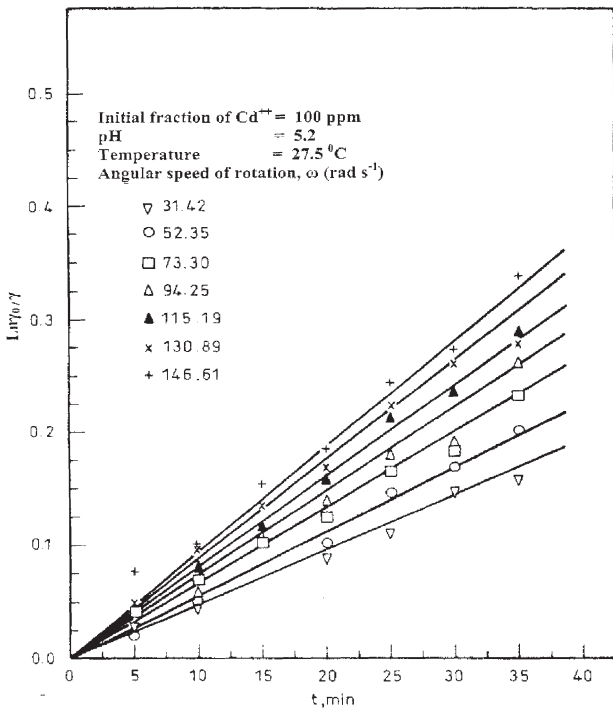


Fig. 2 - $\ln \gamma_0/\gamma$ versus t plot at different angular speed of rotation

$$k_d = a_1 \omega^{0.512} \quad (3)$$

Where ω is the angular speed of rotation. The increase in (k_d) with increasing the initial fraction of Cd^{++} may suggests that the reaction is diffusion controlled. The diffusion - controlled nature of the reaction was confirmed by the fact that the mass transfer coefficient increases systematically with in-

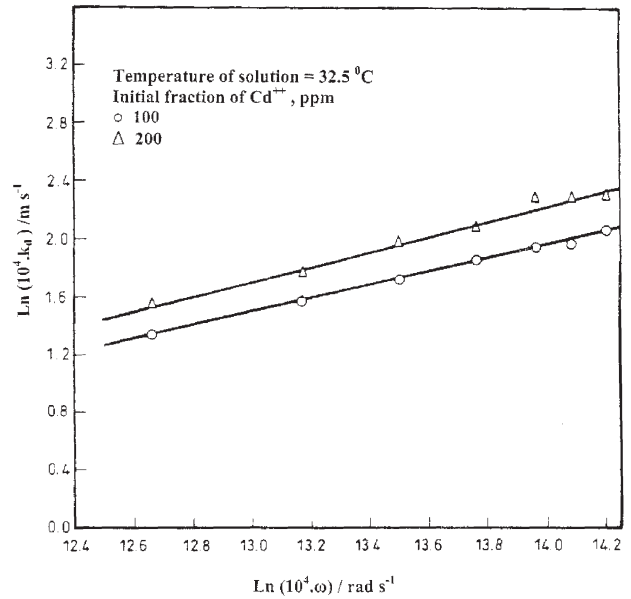


Fig. 3 - Effect of angular speed of rotation on the mass transfer coefficient at different initial Cd^{++} fraction

creasing angular speed of rotation, as shown in Fig. 3.

Increasing angular speed of rotation reduces the diffusion layer thickness (δ) across which Cd^{++} has to diffuse to reach the zinc surface (Cf. Fig. 4) with a consequent increase in the rate of Cd^{++} deposition. Impeller rotation generates three types of fluid motion in the agitated vessel, namely, axial flow, radial flow, and swirl flow.²¹ Axial flow and radial flow are more effective in enhancing the rate of Cd^{++} diffusion to the container wall than swirl flow. In the absence of baffles in the agitated vessel, as in the present work, the less effective type of flow, namely swirl flow, predominates.²¹

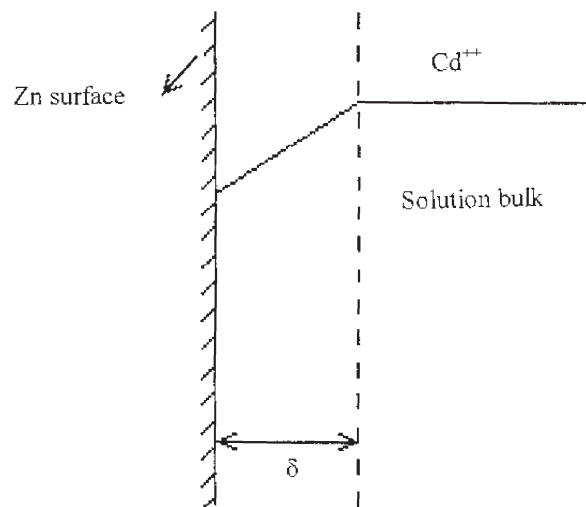


Fig. 4 - Diffusion layer through which Cd^{++} diffuse from the solution bulk to the Zn surface

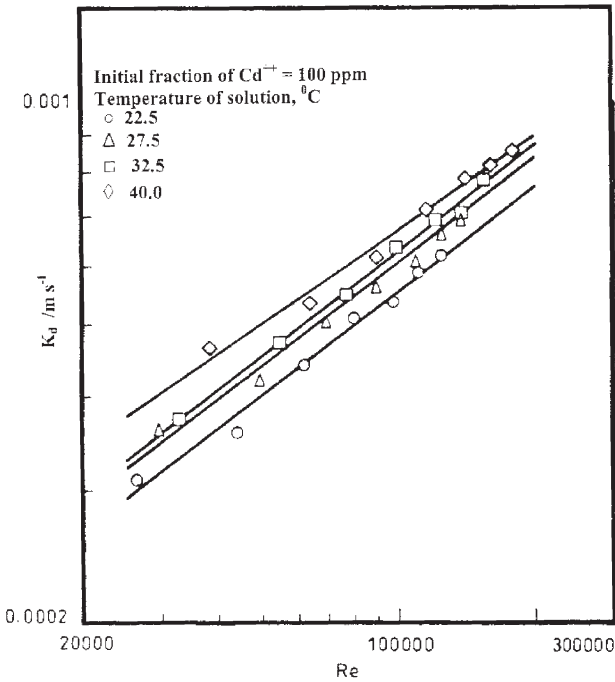


Fig. 5 – k_d versus Re for different temperature

Fig. 5, represents a typical plot of (k_d) versus (Re) at different temperatures of solution. The data fit the equation:

$$k_d = a_2 Re^{0.46} \quad (4)$$

The exponent 0.46 agrees with the value obtained in mass transfer studies in agitated vessel.²² Fig. 6, shows that increasing solution temperature increases the rate of Cd^{++} removal probably because the increase of temperature reduces solution viscosity with a consequent increase in Cd^{++} diffusivity (D) according to the Stokes-Einstein equation.²³

$$D\mu/T = \text{constant} \quad (5)$$

To lend support to the diffusion-controlled mechanism of the present reaction, the activation energy of the reaction was determined by plotting $\ln(k_d)$ versus $\ln(1/T)$ (Fig. 7) according to Arrhenius equation.²⁴

$$k_d = B e^{-E_a/RT} \quad (6)$$

The value of the activation energy (35.98 kJ mol^{-1}) shows that the cementation process is diffusion-controlled. This result is consistent with the fact that the rate of cementation increases with increasing the angular speed of rotation (Fig. 3).

An overall mass transfer correlation was envisaged using the dimensionless groups; Sh , Re and Sc which are often used to correlate mass transfer data

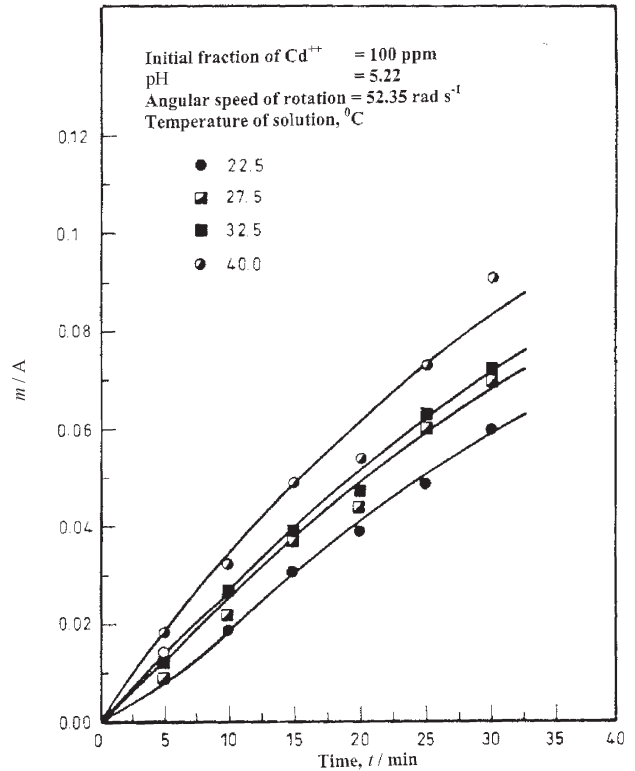


Fig. 6 – Amount of cadmium deposited per unit surface area versus time at different temperature

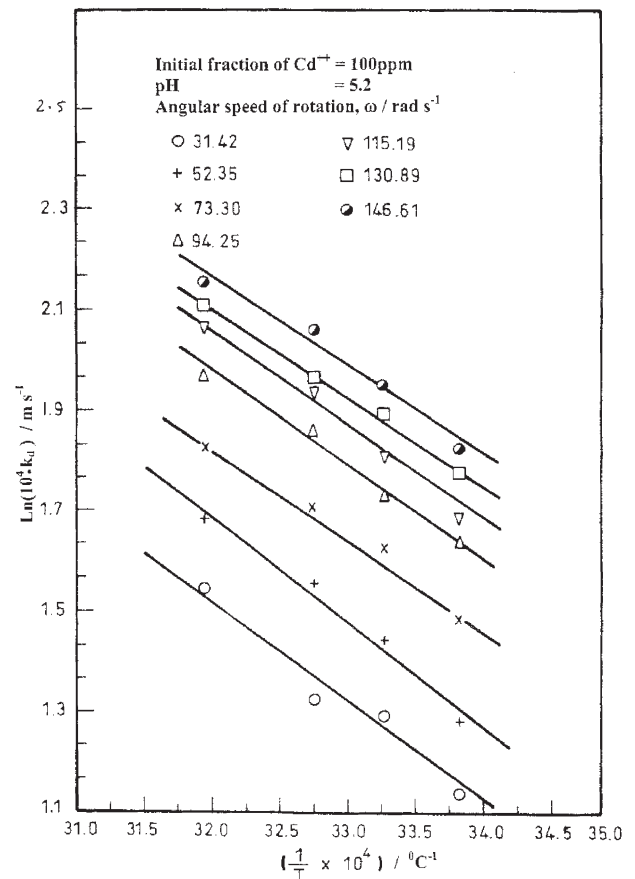


Fig. 7 – Arrhenius plot of the experimental result

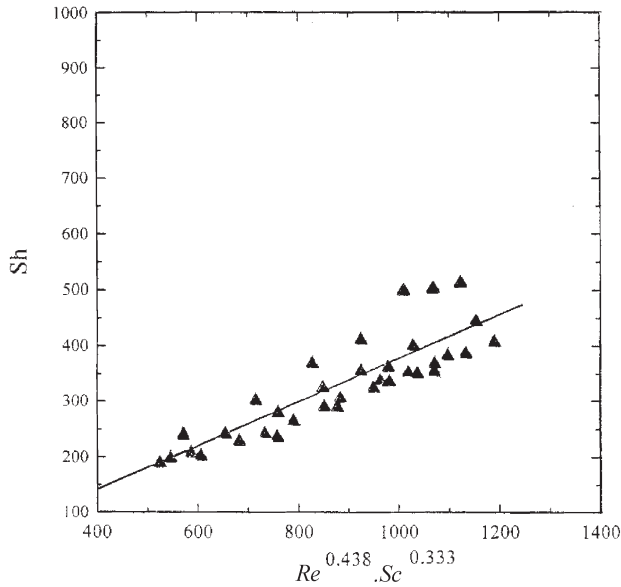


Fig. 8 – Overall mass transfer correlation

in agitated systems. The impeller diameter was used as the characteristic length in calculating, both, (*Re*) and (*Sh*) numbers. Fig. 8, shows that the present data for the conditions:

$$8444 < Re < 56768 \text{ and } 707 < Sc < 1567$$

fits the following equation with an average deviation of $\pm 8.51\%$.

$$Sh = 0.394 Re^{0.438} \cdot Sc^{0.33} - 17.208 \quad (7)$$

In obtaining the above equation the exponent of *Sc* was fixed at the established value of 0.33.

Drag reducing polymers have the potential of being used in agitated vessels to reduce energy consumed in rotating the impeller by virtue of their ability to damp small scale high frequency eddies which prevail in the impeller zone.²⁵ Eddy damping may lead to a reduction in the rate of mass transfer. This section deals with the effect of polyox WSR-301 drag reducing polymer on the rate of Cd⁺⁺ cementation on Zn. The addition of polyox WSR-301 polymer to the solution reduces the rate of cementation by an amount of 36.6 % (Fig. 9). The % reduction in the mass transfer coefficient increases with increasing polymer concentration. 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 tube wall,^{26,27} rotating discs,²⁸ rotating cylinder,^{29,30} and packed beds.³¹ This decrease in the mass transfer coefficient may be attributed to the increase in the diffusion layer thickness as a result of eddy damping by the polymer molecules.

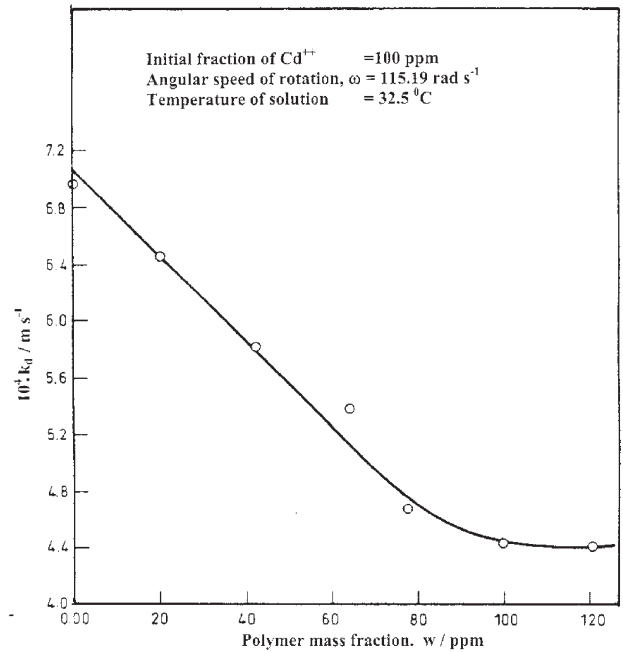


Fig. 9 – Effect of polyox WSR-301 fraction on the mass transfer coefficient

Conclusion

1 – In view of the present results, the use of agitated vessels in conducting cementation reactions can be highly recommended in practice. The reactor is simple in design and operation, it can be operated batch wise or continuously (continuous stirred tank reactor). The salable product (metal powder) can be collected easily by scraping the cylindrical walls of the reactor with a doctor knife.

2 – The rate of Cd⁺⁺ removal from synthetic wastewater was found to increase with increasing degree of agitation, temperature and initial Cd⁺⁺ concentration.

3 – Mechanistic study of the present cementation process revealed that the process is diffusion – controlled.

4 – A dimensionless equation representing the data was obtained. This equation can be used for the design scale up and operation of reactors used to remove Cd⁺⁺ from wastewater by cementation.

5 – Polyox WSR-301 polymer reduces the rate of cementation by an amount of 36.6 % (Cf. Fig. 9)

List of symbols

- A – Cylindrical sheet surface area, m²
- a₁, a₂ – Proportionality constants
- B – Pre-Exponential Factor, m³ mol⁻¹
- D – Diffusion coefficient, m² s⁻¹

- d – Impeller diameter, m
 E_a – Reaction Activation Energy, kJ mol^{-1}
 E^0 – Standard e.m.f. of the galvanic cell through which cementation takes place
 F – Faraday's constant
 K – Equilibrium constant
 k_d – Mass transfer coefficient, m s^{-1}
 n – Rotation per second of the impeller, rps.
 ne – Number of electrons involved in the reaction
 R – Gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
 T – Temperature, K
 t – Time, s
 V – Volume of the solution in the reactor, m^3
 z – Charge number
 w – Mass fraction, ppm
 Re – Reynolds number ($\rho n d^2 / \mu$)
 Sc – Schmidt number ($\mu / \rho D$)
 Sh – Sherwood number ($k_d d / D$)
 ΔG – Free energy of the reaction
 ΔG^0 – Standard free energy of the reaction
 ρ – Solution density, kg m^{-3}
 μ – Solution viscosity, $\text{kg m}^{-1} \text{s}^{-1}$
 δ – Layer thickness
 γ – mass concentration, kg dm^{-3}
 γ_0 – initial mass concentration, kg dm^{-3}

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