

Cathodic Deposition of Cadmium from Diluted Solutions onto Stainless Steel Rotating Disc Electrode

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Abstract- The mass transport properties of a stainless steel electrode were characterized based on the electrodeposition of cadmium from diluted solutions containing Cd (II) ions. The study was performed in a three-electrode configuration using 0.5 M of sodium sulfate as the supporting electrolyte with Cd (II) concentration ranging from 50 to 200 mg/L. From the current potential curves under conditions of the experiment, the limiting currents were determined at potential of -1.0 V against a saturated calomel electrode, and were used to calculate the diffusion coefficients, the diffusion and hydrodynamic layer thicknesses and the mass transfer coefficients for Cd (II). Dimensionless Sherwood, Reynolds and Schmidt numbers were fitted to final empirical correlation: $Sh = 0.664Re^{0.528}Sc^{1/3}$ For $25101 < Re < 52726$ and $449 < Sc < 787$.

Keywords- Electrochemical Deposition; Cadmium; Rotating Disk Electrode; Stainless Steel Cathode

NOMECLATURE

A	=	Electrode surface area, m ²
C	=	Concentration, mol L ⁻¹ or mg L ⁻¹ or ppm
c_b	=	Bulk concentration, mol L ⁻¹ or mg L ⁻¹ or ppm
D	=	Diffusion coefficient, m ² s ⁻¹
E	=	Electrode potential (vs. SCE), V
F	=	Faraday constant=96500, Coulomb mol ⁻¹
i_L	=	Limiting current, A
k_m	=	Mass transfer coefficient, m s ⁻¹
n	=	Charge number of electrode reaction
r	=	Disc radius (a characteristic dimension), m
RDE	=	Rotating disc electrode
RE	=	Reference electrode
Re	=	Reynolds number = $r^2\omega/\nu$
s	=	Slope of Livich equation
SCE	=	Saturated calomel electrode
Sc	=	Schmidt number = ν/D
Sh	=	Sherwood number = $k r/D$

Greek Symbols:

δ	=	Diffusion layer thickness, m
δ_H	=	Hydrodynamic layer thickness, m
μ	=	Fluid viscosity, kg m ⁻¹ s ⁻¹
ν	=	Kinematic viscosity, m ² s ⁻¹
ω	=	Rotation speed, rpm or m s ⁻¹

I. INTRODUCTION

The rotating disc electrode has been used for investigating the hydrodynamic, kinetics and mechanism of electrochemical reaction. The hydrodynamic and the mass-transfer characteristic are well-understood and current density on the disc electrode is supposed to be uniform. However, the current distribution is uniform only at the limiting current where the concentration of the reactant is zero at the electrode surface [1]. Rotating disc electrodes (RDE) represent very practical systems for current-potential curve determination and the RDE, with precise limiting current behavior, probably is the most promising of all solid electrode systems. The rotating disc electrode solves many problems connected with the use of solid electrodes both from the

experimental and theoretical point of view. It is one of the few convective electrode systems for which the hydrodynamic equations and the convective-diffusion equation have been solved rigorously for the steady state. The RDE consists of a disc of metal embedded in a cylindrical insulator holder; it is rotated about its center, the bottom end of the metal disc is exposed to the solution [2].

Electrochemical techniques, in particular mass-transfer measurements by limiting-current method, provide convenient and accurate means for the determination of local and average transport rates. Applying analogies between momentum, heat, and mass transport, electrochemical measurements provide insight into the fundamental aspects of transport which are convenient for obtaining transport-rate correlation. These are useful for design purposes in electrochemical system such as electrowinning and electrochemical treatment of waste water [3]. The limiting-current technique is based on driving an electrochemical reaction to its maximum possible rate where it is limited by mass transport. The limit is indicated by a current plateau "the limiting current" on a current-versus-potential plot. To calculate the limiting current i_L , Levich [4] has obtained the solution of the convective-diffusion equation for the rotating disc electrode by applying Von Karman's hydrodynamic theory assuming that within the diffusion layer, there is no convection, an approximation which means that the variations in the velocity components must occur within distance much greater than the diffusion layer thickness by at least a factor of 10. This assumption should be verified for any hydrodynamic system under study. The solution of the convective-diffusion equation expressed in terms of limiting current is:

$$i_L = 0.62nFAD^{2/3}\nu^{-1/6}\omega^{1/2}C_b \quad (1)$$

Equation (1) is called Levich equation in which the limiting current is proportioned to the square root of angular velocity (ω). Diffusion coefficient (D) is determined by the slope of the curve of limiting current and $\omega^{1/2}$.

The mass transfer coefficient (k_m) is determined by the limiting current according to the following relation [5]:

$$K_m = \frac{i_L}{nFAC_b} \quad (2)$$

The diffusion layer thickness (δ) is calculated according to the following equation [1]:

$$i_L = \frac{nFADC_b}{\delta} \quad (3)$$

For the purpose of comparison of different systems it is usual to apply dimensionless numbers such as the Sherwood number, Reynolds number and Schmidt number instead of mass transfer coefficient and superficial solution velocity. For rotating disc electrode, these dimensionless numbers are defined as follows:

$$Sh = \frac{K_m d}{D} \quad Re = \frac{r^2 \omega}{\nu} \quad Sc = \frac{\mu}{\rho D}$$

Accordingly, mass transport data are correlated experimentally using the following dimensionless relationship valid for a great variety of electrolytic reactor designs:

$$Sh = cRe^m Sc^{0.33} \quad (4)$$

Cadmium has been electrochemically studied for some time, and the literatures are quite broad. Most of the research work has been accomplished by using either mercury or mercury amalgam working electrodes and applying different techniques such as ac polarography, potential step, current step, faradic impedance, and others [6, 7]. In these kinds of electrodes the cadmium deposition process started from either perchlorate or sulfate baths. For the cathodic deposition of Cd on solid electrodes many works have been published using either fixed bed or rotating cylinder electrodes [7-32]. In this case, the cadmium deposition process was studied by electrochemical techniques such as current step, faradic impedance, and others. The kinetics and diffusion coefficient of cadmium are almost investigated in these works, however, no mass transfer correlations were established using stainless steel as RDE.

Cadmium electrodeposition has been tried also in organic solvents and ionic liquids [33-37], however, the electrochemical reduction of Cd (II) in these media is diffusion not mass transfer control.

The aim of present work is to study the cathodic deposition of cadmium on stainless steel electrode in sulfate medium and determining the mass transfer correlation presented by Equation (4) for this system.

II. EXPERIMENTAL

The experiments were carried out in a conventional three-electrode cell with separated compartments for each electrode. A stainless steel disc electrode as working electrode, a large-surface area platinum counter electrode, and a saturated calomel reference electrode (SCE) within a luggin capillary were used. The hydrodynamic voltammetric experiments were carried out using a model 273A potentiostat/galvanostat system from EG and G Princeton Applied Research Corporation. The stainless steel electrode was polished to mirror-like surface, using 1.0 and 0.3 and 0.04 μm alumina slurries, consecutively, on polishing clothes. The current-voltage curves were obtained for several rotations (800, 1000, 1200, 1600 rpm) by linear sweep of cathodic potential from 0 to -1.4 V with scan rate 20 mV/s. Distilled and de-ionized water was used to prepare solutions. The

testing solutions, which contain metallic ions, were prepared from CdSO_4 using 0.5 mole/L of sodium sulfate as the supporting electrolyte with Cd (II) concentration ranging from 50 to 200 mg/L. The resulting solution was presented at pH of 4.8.

III. RESULT AND DISCUSSION

A series of voltammograms were obtained from the rotating disc electrode in the hydrodynamic voltammetric mode. The potential was swept on stainless steel rotating disc electrode, using four different rotation rates, (800, 1000, 1200, 1600 rpm) and three different initial concentrations of Cd(II) solutions, (50, 100, 200ppm). Figure 1 shows the polarization curves at different rotation rates for different initial concentrations of Cd (II) solutions and without cadmium. Application of the Levich equation is an appropriate test to verify whether an electrode process is conducted under mass-transfer controlled condition. The limiting currents measured at the midpoint of the plateaus are plotted as a function of the square roots of rotation rates (i_L vs. $\omega^{1/2}$) for different initial concentrations of Cd (II) as shown in Figure 2. During Cd (II) reduction, hydrogen evolution is always a competitive process.

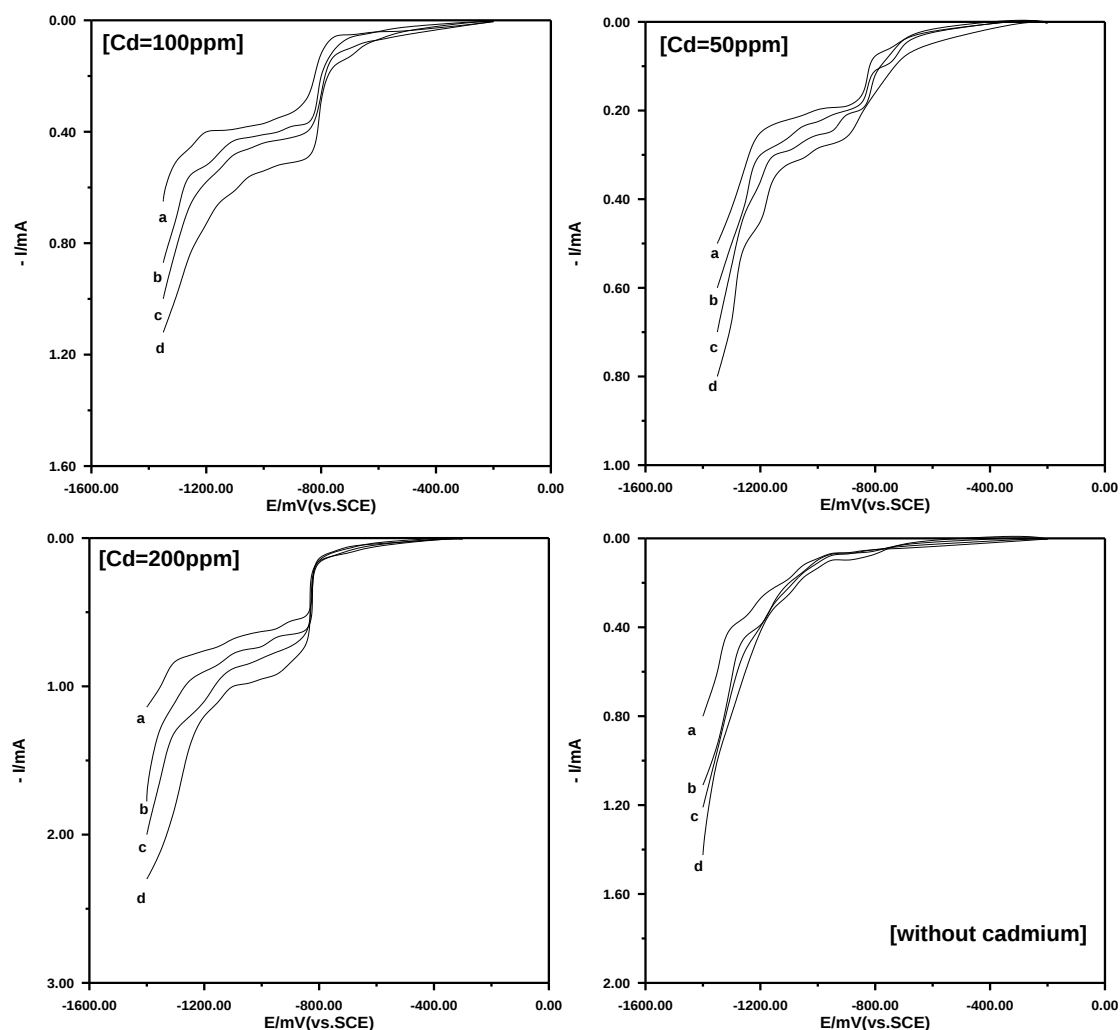


Fig. 1 Cathodic polarization curves on stainless steel RDE for different Cd (II) concentrations and without cadmium:
a) 800 rpm, b) 1000 rpm, c) 1200 rpm, d) 1600 rpm

In the range of potential in which the reduction becomes mass transfer controlled, the reduction of oxygen and of chloride also contributes to the recorded current. All these reduction processes amplify the response apparently without changing its shape, taking this fact into account, a series of background voltammograms are recorded under the same conditions using the support electrolyte without cadmium as shown in Figure 1. These values of background currents are subtracted from total current for the same value of ($\omega^{1/2}$) such that the resulting values are exclusive for cadmium reduction current. As predicted by the Levich equation, the plots are linear, confirming the fact that under the conditions of this study, cadmium deposition becomes mass-transport controlled at potential -1.0 V vs. SCE. Data from the curves in Figure 2 were used for the estimation of the diffusion coefficient (D) of Cd (II) in the chosen medium, provided the slope(s) in Levich's plot can be expressed as:

$$s = 0.62nAFD^{2/3}v^{-1/6}C_{Cd}$$

$$\text{Where } s = \frac{i_L}{\omega^{1/2}}$$

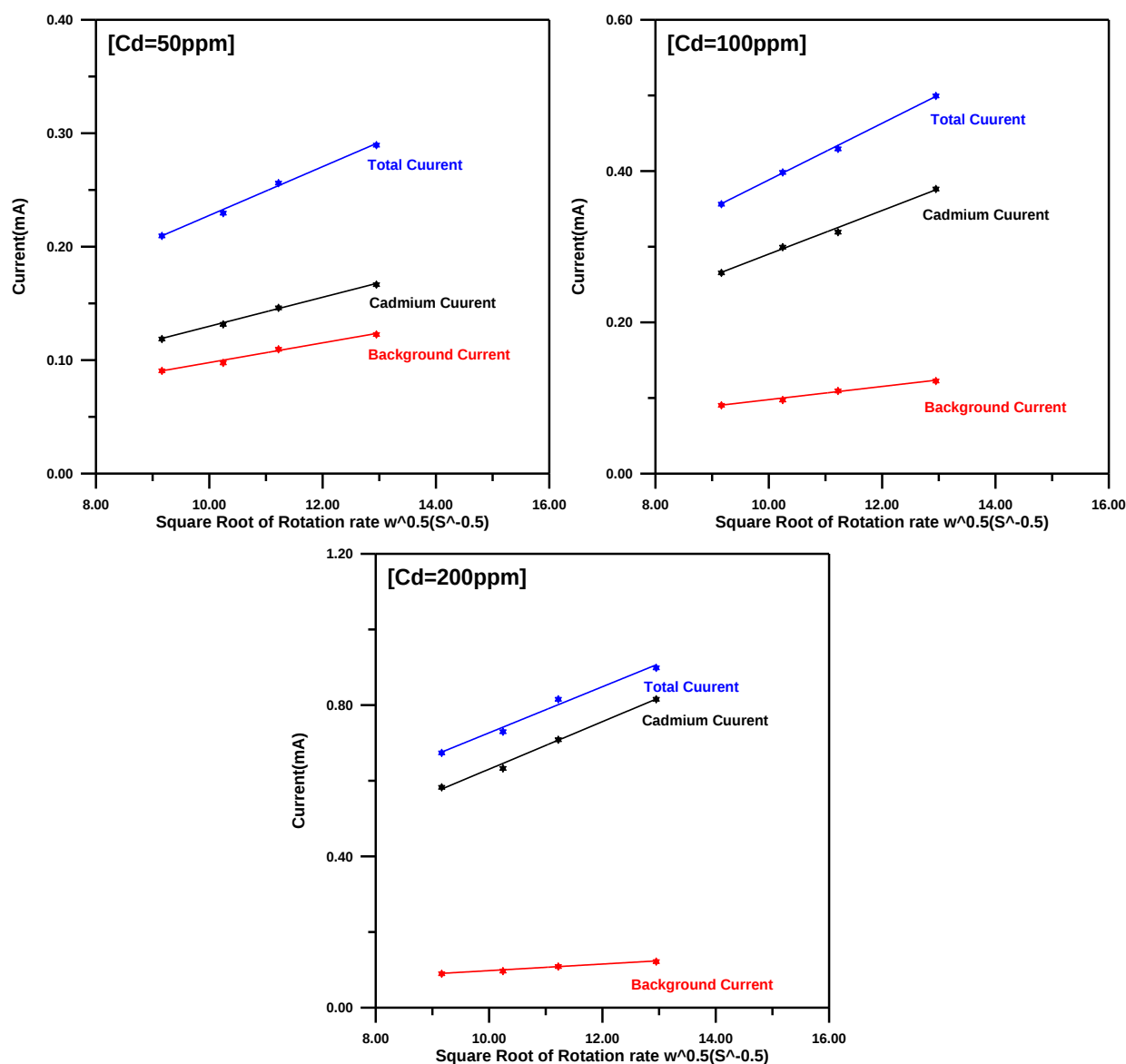


Fig. 2 Levich plots for limiting currents taken at potential of -1.0 V vs. SCE. for different Cd (II) concentrations in 0.5 M of sodium sulfate

Diffusion coefficients are tabulated against bulk concentration of Cd (II) as shown in Table 1. It can be seen from Table 1 that the diffusion coefficient decreases with increasing the bulk concentration of Cd (II). Mayer [38], Cohen et al. [39], and Weischedel [40] found that the diffusion coefficients of cadmium in mercury electrode are: 1.81×10^{-5} , 1.52×10^{-5} , and $1.53 \times 10^{-5} \text{ cm}^2/\text{s}$ respectively in sulfate medium, while Braunstein et al. [41] reported diffusion coefficient of $1.51 \times 10^{-5} \text{ cm}^2/\text{s}$ in nitrate medium.

TABLE 1 DIFFUSION COEFFICIENT FOR CD (II) IN AQUEOUS MEDIA AT 298K

Cd(II) (ppm)	$10^2 v$ ($\text{cm}^2 \text{ s}^{-1}$)	$10^5 D$ ($\text{cm}^2 \text{ s}^{-1}$)
50	0.715	1.592
100	0.724	1.287
200	0.731	1.127

On cadmium electrode using sulfate medium, Montiel et al. [13] calculated diffusion coefficient to be $4.53 \times 10^{-5} \text{ cm}^2/\text{s}$ while on glassy carbon electrode, Tramontina et al. [14] found the diffusion coefficient to be $0.71 \times 10^{-5} \text{ cm}^2/\text{s}$. In present work, the average value of diffusion coefficient on stainless steel electrode is $1.34 \times 10^{-5} \text{ cm}^2/\text{s}$ which is in agreement with data in literature for sulfate medium using mercury electrode.

Figure 3 shows the diffusion layer thickness (δ) versus the limiting current calculated according to Equation (3). It is cleared that the limiting current increases in inverse proportion to the diffusion layer thickness. Equation (3) illustrates that i_L can be enhanced by increased stirring because δ decreases, and since the limiting current is proportional to concentration, the

diffusion layer thickness decreases with increasing the concentration. The overall problem of removal of metals from dilute solution is to select the way of causing convection influence the thickness of diffusion layer and bring the bulk solution to the diffusion layer by physical flow, utilizing flow conditions that at the same time will minimize the diffusion layer thickness [2].

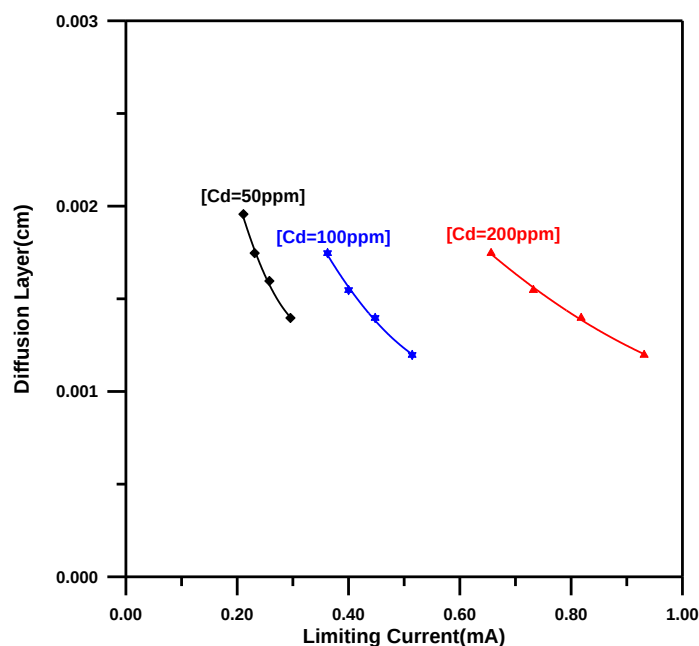


Fig. 3 Variation of diffusion layer thickness with limiting current at different Cd (II) concentrations

Figure 4 shows the variation in the hydrodynamic layer thickness (δ_H) with the rotation velocity of cathode electrode. Hydrodynamic layer thickness is calculated from the following equation [1]:

$$\delta \approx \left(\frac{D}{v}\right)^{1/3} \delta_H \quad (5)$$

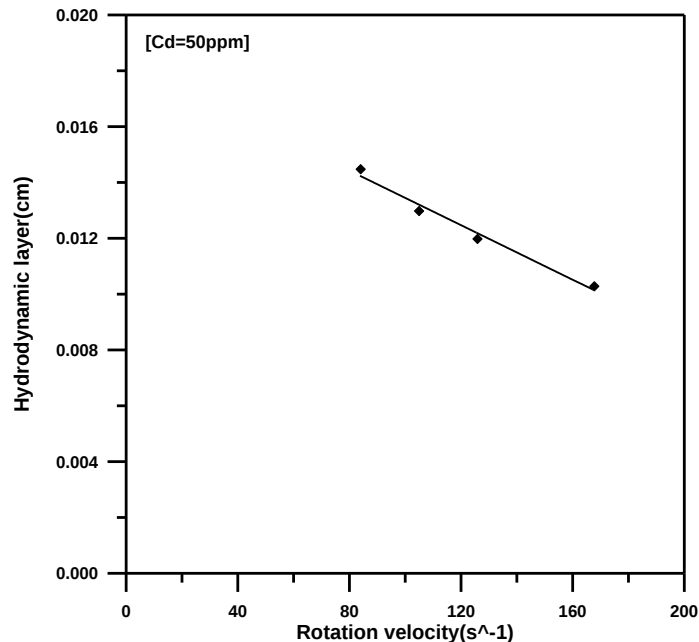


Fig. 4 Variation of hydrodynamic layer thickness with rotation velocity at Cd(II) concentration 50 ppm

It can be seen that δ_H decreases when the rotation velocity increases and physically, δ_H can be pictured as the approximate thickness of the liquid layer dragged by the rotating disc [2]. This agrees well with literature; as demonstrated by rearrangement of Equation (5) to be:

$$\frac{\delta}{\delta_H} \approx \left(\frac{v}{D}\right)^{-1/3}$$

In aqueous solutions containing 200 ppm Cd (II): $D = 1.127 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ and $v = 0.731 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$

$$\frac{\delta}{\delta_H} \approx \left(\frac{0.731 \times 10^{-2}}{1.127 \times 10^{-5}} \right)^{\frac{1}{3}} \approx \frac{1}{10}$$

Which means that δ is only about 10% that of δ_H . Since the large concentration changes occur within a distance of 10^{-3} cm from the electrode, whereas the viscous fluid flow effects extend out for a few tenths to 1 mm away, depending on rotation velocity, it is reasonable to suppose that there is no convection within the diffusion layer [1].

Mass transfer coefficients (k_m) with the rotating disc electrode were calculated from the limiting currents (i_L) using Equation (2) then plotted against the square root of rotation velocity ($\omega^{1/2}$) as shown in Figure 5. It can be seen that higher rotation velocities enhance the mass transfer coefficient, hence increasing the reduction rate of Cd (II).

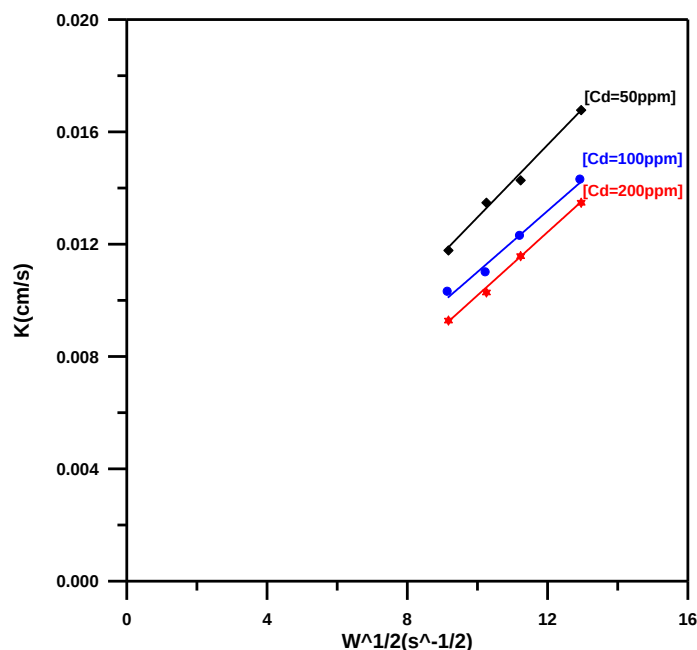
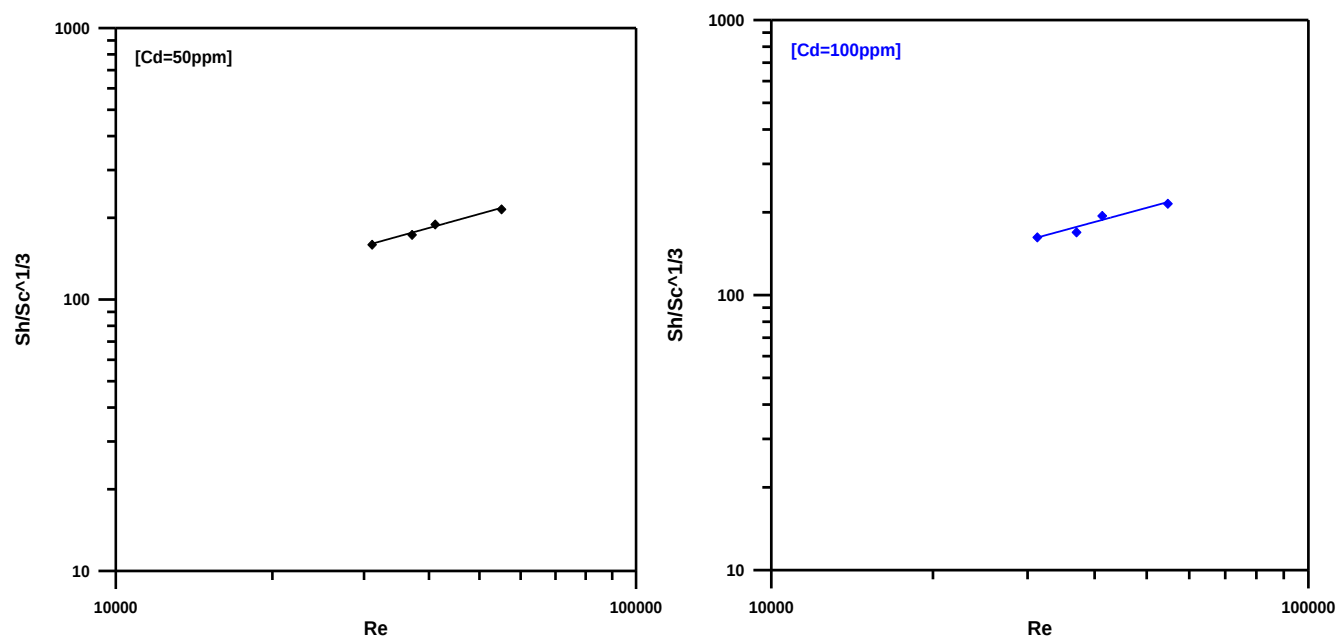


Fig. 5 Variation of K_m with square root of rotation velocity

Figure 6 summarizes all the experimental results and the data for all three initial concentrations of Cd (II) solutions (50, 100, 200 ppm) which have been fitted to find the following empirical correlation: $Sh = 0.664 Re^{0.528} Sc^{1/3}$ for $25101 < Re < 52726$ and $449 < Sc < 787$.



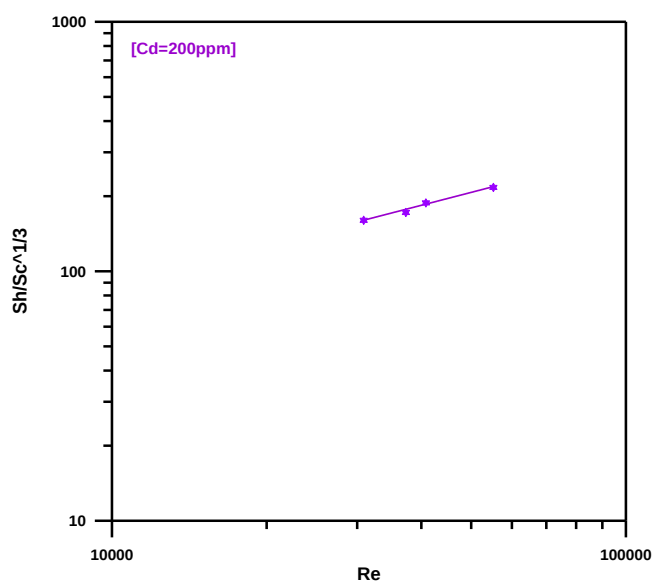


Fig. 6 Sherwood-Reynolds correlations for stainless steel rotating disc electrode at different initial concentration of Cd (II)

IV. CONCLUSIONS

This work shows, in a very convincing way, the suitability of the rotating disc technique to study the mass transfer properties of cadmium on stainless steel electrode. The cathodic deposition of cadmium becomes mass transfer control at cathode potential more negative than -1.0 V vs. SCE. The diffusion coefficient of cadmium on stainless steel electrode is closer to that obtained from the literatures using mercury and glassy carbon as cathode electrodes, while differ from that obtained using cadmium electrode which reflects the effect of structure and morphology of the cathode surface on the electrochemical reduction process. The diffusion layer thickness (δ) is approximately 10% hydrodynamic layer thickness (δ_H), therefore, application of Levich equation is suitable for determining the limiting currents for reduction of cadmium. The mass transfer was correlated to be $Sh = 0.664Re^{0.528}Sc^{1/3}$ as a unique correlation that describes the cathodic deposition of cadmium on stainless steel cathode.

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