Cementation of Cd Ions on Zinc Using a Rotating Fixed Bed Impeller Basket Reactor

Yousra Hamdy Farid[1*]

[1]*Basic Science Department, Alexandria Higher Institute for Engineering & Technology (AIET), Alexandria, Egypt*

Author's contribution

The sole author designed, analyzed, interpreted and prepared the manuscript.

Original Research Article

ABSTRACT

Cementation or metal displacement reaction is one of the most effective techniques for removing toxic metals from industrial waste solutions.

Aims: The main purpose of this work is to study the rate of cementation of cadmium by using a rotating bed of Zn Raschig rings packed in a perforated impeller basket for the investigation of the removal of Cd $^{2+}$ from waste solution.

Study Design: The reactor was tested for Cd^{2+} concentration removed, the diameter of Zinc Raschig rings, and the rotational speed of the basket.

Methodology: The results indicate that there are two rates of cementation for Cd-Zn system, a high rate at the beginning, followed by a lower rate after the initial period. The results also show that percentage removal of Cd^{2+} ions from solution increases by increasing the speed of basket rotation, and as the diameter of Zn Raschig ring packed in the basket reactor, increases the removal of Cd^{2+} decreases. The cadmium deposits on zinc as powder.

Results: The removal of Cd^{2+} is optimum for ring diameter of 0.5 cm, initial concentration of 100 ppm, and basket rotation speed of 500 rpm. The experimental data fit the following equation: $Sh = 0.041\, Sc^{0.33} Re^{0.40}$.

This equation can be used for the design scale-up and operation of reactors used to remove Cd^{2+} from wastewater by cementation.

Conclusion: Rates of cementation were expressed in terms of the rate of mass transfer, the mass transfer coefficient increases as the rotational speed of the basket increases.

Corresponding author: Email: dr.yousra.hamdy@aiet.edu.eg;

NOMENCLATURES

A : Area of zinc Raschig rings (cm^2)
C_o : Initial concentration of cadmium ion (ppm)
C_e : Concentration of cadmium ion at equilibrium (ppm)
C : Concentration of cadmium ion at any time (ppm)
D : Characteristic length (basket diameter) (cm)
D : Diffusivity (cm^2 /s)
K : Mass transfer coefficient (dimensionless)
N : Rotation speed (rps)
Q : Volume of the solution (cm3)
q_e : Equilibrium mass adsorbed heavy metal per unit mass (mg/g)
Re : Reynold number = $\rho N d^2/\mu$ (dimensionless)
Sh : Sherwood number = Kd/D (dimensionless)
Sc : Schmidt number = $\mu\rho/D$ (dimensionless)
T : Time (min)
      Greek
P : Density of the solution (g/cm3)
μ : Viscosity of the solution (g /cm.S)
δ : The diffusion layer thickness (cm)

1. INTRODUCTION

Heavy metals are the metals with exceptionally high atomic weights withinside the variety of 63.5–200.6 g mol^{-1} and the densities greater than5 gr/cm^3 [1]. Heavy metals solutions were broadly utilized in steel finishing, electroplating, painting, floor remedy industry, and revealed circuit board manufacture [2]. Natural waters are infected with numerous heavy metals precipitating from mining waters and commercial discharges. The heavy metals are of unique situation as they are non-degradable and persistent. Commonly encountered metals of situation consist of Pb^{2+}, Cd^{2+}, and Zn^{2+}. Cadmium has a long biological half-life (more than 20 years) and it is index ed with the aid of using the US-EPA as one of the 126 precedence contaminants and as a recognized carcinogen. Many techniques may be used to dispose of cadmium ions from wastewaters which include chemical precipitation, ion trade, opposite osmosis, adsorption, cementation and electro dialysis [3]. Previous research on the usage of ion exchange for heavy metal elimination used both fluidized beds and fixed beds of the resin. Both techniques are afflicted by drawbacks which include the high-pressure drop-in case of fixed beds and the low slip velocity in case of fluidized beds. The low slip velocity results in a low charge of mass switch among the solution and the resin particles with a consequent low charge of heavy steel elimination [4].

The removal rate of copper ions from an industrial waste solution by cementation in an air sparged bed of zinc powder was studied [5]. The removal of lead ions from aqueous solution by iron oxide nanomaterials with cobalt and nickel doping was studied [6].

The selective removal and recovery of Cd ions from electroplating bath wastewater (containing high amounts of Cd, medium amounts of Zn, Cu, Fe and small amounts of Ni, Co, Mn), were studied and the precipitation-based separation scheme was developed [7].

Several studies have shown that synthetic hydroxyapatite (HA) have potential for remediation because it can immobilize a great number of heavy metals from aqueous media by forming low soluble phosphate minerals, which have potential to immobilize Pb in Pb-contaminated soils and wastes due to low solubility of lead orthophosphates [8]. Phosphate rocks (PR), which are considered low-cost materials, have been proposed and tested for heavy metal removal from contaminated waste and soils [9,10]. Several studies showed that (PR) was very effective in retaining Pb and less effective in the removal of Cd from aqueous solutions [11,12]. A comparison of the ability of rock phosphate (RP), hydroxyapatite (HA) and compost materials to remove lead and cadmium from synthetic single aqueous solutions were studied [13].

The ability of using some agriculture wastes, released in the nature, has been tested for this purpose. Soy bean hulls, cotton seed hulls, rice straw and sugarcane bagasse, as examples of agricultural adsorbents, have been used to remove Co^{2+}, Cr^{3+}, Ni^{2+} and Zn^{2+} from aqueous solutions [14]. Also, canola meal was used to remove Cd^{2+}, Zn^{2+} and Ni^{2+} from aqueous solutions [15]. The feasibility of using various agricultural sugarcane bagasse, Waste tea leaves, egg shell, rice husk, activated carbon, zeolites, olive stones, wood saw dust, maize corn cob and Jatropha oil cake, to remove cadmium ions from aqueous solution under different experimental conditions was studied [16-19].

The investigation of the removal of Cd^{2+}, Cr^{6+}, Pb^{2+} and Cu^{2+} from simulated wastewater was studied by many techniques like Chemically Modified Agricultural Waste Material [20], the electrodialysis technique [21], zinc column test [22], and a rotating fixed bed of ion exchange resin [23].

The removal Cd^{2+} by ion-exchange resin Amberjet 1200H and the adsorption characteristics were described by Freundlich isotherms [24]. Also synthesize of two porous adsorbents of zeolite-imidazolate frameworks" ZIF-8 and ZIF-67" were investigated for the removal of Cu^{2+} from wastewater [25].

Cementation or metal displacement reaction is one of the most effective and economic techniques for removing toxic and/or valuable metals from industrial waste solutions. It has been demonstrated to be a feasible technique because of its relative simplicity, ease of control, low energy consumption and recovery of valuable or toxic metals.

The Cementation of cadmium by the zinc column test also was a feasible treatment process which can achieve a high degree of cadmium removal within a fairly reasonable contact time [26,27].

The aim of the present work is to explore the possibility of using a rotating bed of Zn Raschig rings packed in a perforated impeller basket for removing Cd^{2+} from waste solution. Basket rotation would enhance the rate of mass transfer of the Cd^{2+} ions to the zinc particles by virtue of the flow induced inside the bed by the centrifugal force [28].

2. EXPERIMENTAL DETAILS

2.1 Apparatus

The experimental set-up used in this study is shown in Fig. 1. It consisted mainly of a Plexiglas container of 15 cm diameter and 30 cm height, fitted with 4 rectangular baffles fixed to the container wall 90° from one another.

A Plexiglas screen basket impeller (mesh no. 10) was used, each basket is of height= 6cm, width= 2.7cm, and length=4 cm [29].

The basket was attached to a shaft which was connected to a variable speed dc motor of 0.5 hp. Motor rotation speed was controlled by means of a variac and was measured by an optical tachometer. The basket rotational speed was varied within the range (*100 to 500* rpm).

2.2 Procedure

Before every run, the cylindrical Plexiglas container and the stainless-steel basket Fig. (1) Were washed with tap water, distilled water and dried. Before every run, the Zn rings have been etched with the aid of using dilute HCl to dispose of the oxide layer, washed with distilled water and dried. Solutions with concentration of 100, and 200 mg/l of Cd^{2+} ions have been organized with the aid of using dissolving AR grade chemical compounds in distilled water. Two litters of $CdCl_2$ solution were fed into the container. The basket was packed with Zn Raschig rings of 0.4, 0.9 and 1.6 cm diameter. The rotational speed used was 100, 200, 300, 400, & 500 rpm.

A test runs lasted 60 min, where samples of 0.1 ml were taken from the reaction solution at distinct time durations for analysis.

The samples had been analyzed for its cadmium ions content using a *Perkin-Elemer 2380* atomic spectrophotometer (Cd wavelength, λ= 228.8 nm). The solution pH was adjusted to be (5.2).

All experiments had been achieved at 25°C. Density and viscosity of the solution used had been measured by using density bottle and an Ostwald viscometer respectively [30]. The diffusivity of cadmium ion in solution was obtained from the literature and was corrected for the change in temperature using the Stokes-

Einstein correlation [31,32] and Diffusion Mass Transfer in Fluid Systems [31,33].

The reproducibility of the results is valid through following the above method used to obtain the data.

2.3 Preparation of the Solution

a. 100 ppm solution is prepared by dissolving 0.41 grams of $CdCl_2$ in two litres of distilled water.

b. 200 ppm solution is prepared by dissolving 0.82 grams of $CdCl_2$ in two litres of distilled water.

3. RESULTS AND DISCUSSION

The following parameters were studied and their effect on the percentage removal of Cd^{2+} ions.

3.1 Effect of Zinc Raschig Rings Diameter

Fig. 2 (a, b,c,d,e,and f) represent the effect of basket rotational speed on the percentage removal of Cd^{2+} ions at exceptional time periods using (100 and 200 mg/l) Cd^{2+} initial

concentration for diameters of Raschig rings of (0.5 , 1, and 1.6 cm).

As the diameter of Zn Raschig ring packed inside the basket reactor increases the percentage removal of Cd^{2+} decreases. Maximum removal of Cd^{2+} was obtained for ring diameter of 0.5 cm. This can be attributed to the fact that when every ring inside the bed rotates in the solution, the hydrodynamic boundary layer and diffusion layer are constructed on its surface. When the ring size increases the average thickness of the hydrodynamic boundary layer increases with a consequent growth in the diffusion layer thickness, as a consequence to that the mass transfer coefficient decreases [34].

3.2 Effect of Contact Time and Initial Concentration

The results in Fig. 2 show the impact of initial concentrations on the percentage removal of Cd^{2+}, the data show that the percentage removal of Cd^{2+} decreases because the initial Cd^{2+} concentration will increase from 100 to 200 ppm. The removal of Cd^{2+} is optimum for initial concentration of 100 ppm. It was observed that cadmium removal by cementation can be described by the first-order reversible kinetics [35].
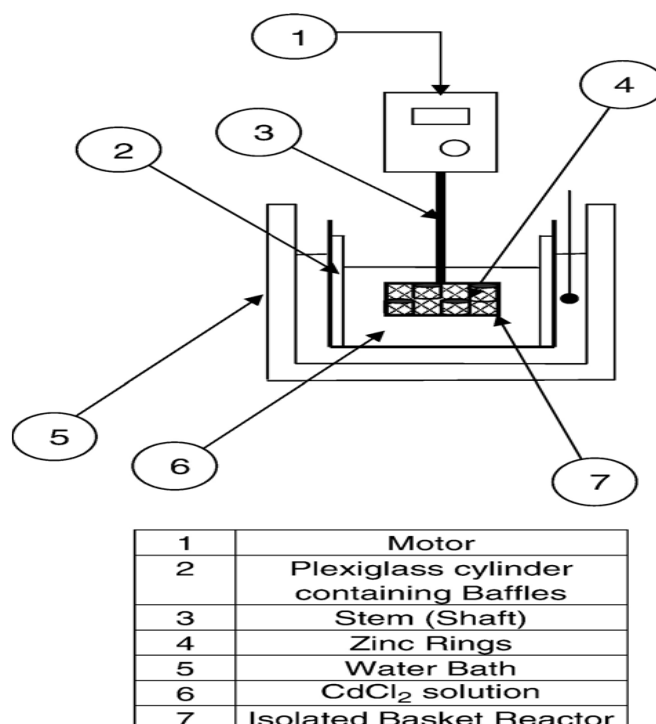

1	Motor
2	Plexiglass cylinder containing Baffles
3	Stem (Shaft)
4	Zinc Rings
5	Water Bath
6	$CdCl_2$ solution
7	Isolated Basket Reactor

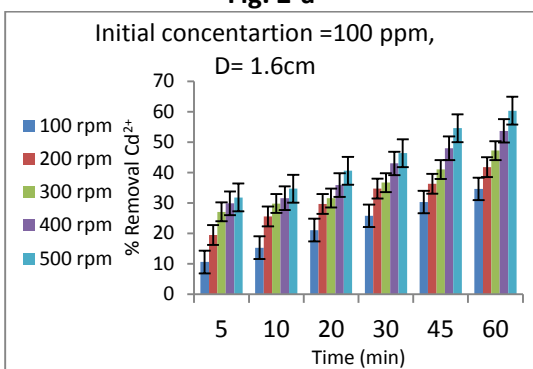**Fig. 1. Schematic diagram of the batch experimental setup**
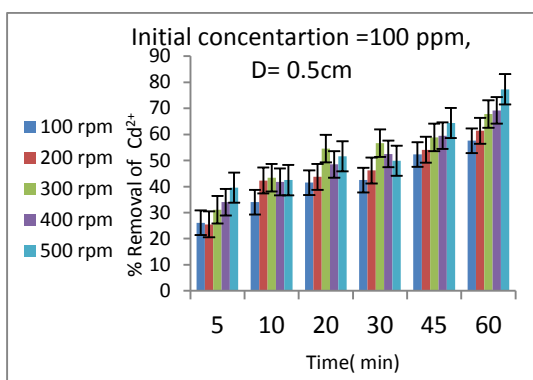
Fig. 2-a
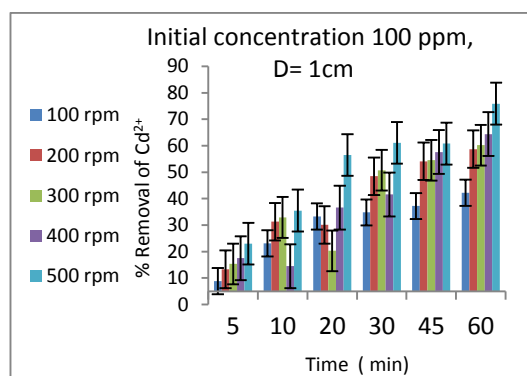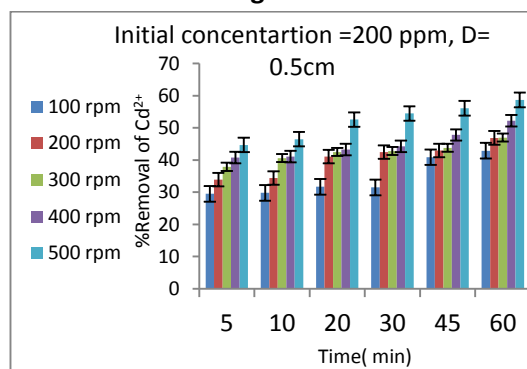

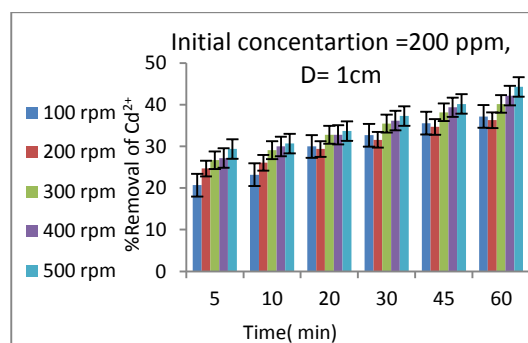**Fig. 2-b**

Fig.2-c

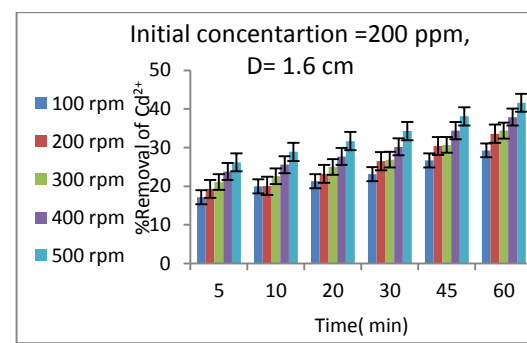**Fig. 2-d**

Fig.2-e

Fig. 2-f

Fig. 2. Effect of basket rotational speed on % removal of Cd²⁺ using (100 and 200 mg/l) Cd²⁺ concentration for diameters of Raschig rings (0.5, 1, and 1.6 cm) on the percentage removal of Cd²⁺ ions

The percentage removal of Cd^{2+} will increase with growth touch time. These results show that there are two stages of rates of cementation for the Cd-Zn system. First stage is a higher rate at the beginning (attributed to the instantaneous utilization of the most readily available active sites on the bed surface known as "bulk diffusion"), followed by the second stage which is lower rate after the initial period, and essentially an equilibrium stage [36].

3.3 Effect of Basket rotational Speed on Rate of Cementation

a. The increase in the mass transfer coefficient K with increasing bed rotation speed can be explained in terms of the flow pattern at the rotating fixed beds [37]. When the solution inside the bed moves radially through the centrifugal force, it is changed by fresh solution which moves axially towards the bed as shown in Fig. 3. As the solution moves radially and axially beyond precipitation of particles a diffusion layer

of thickness δ is constructed around every particle, the thickness of which decreases with increasing rpm with a consequent increase in K according to the equation:

$$K = D/\delta. \tag{1}$$

b. A linear plot of ln (C_o /C) vs. t is verification that the cementation rate is first order with respect to Cd^{+2} ions as shown in Fig.4 where ln (C_o/C) is plotted against time at different basket rotational speeds. That figure shows that for a given set of condition there are two rates of cementation, a high rate at the beginning followed by a lower rate after the initial period.
This phenomenon is attributed to the fact that cementation of cadmium on zinc Raschig rings in rotating basket reactor takes place through two mechanisms:

i.   At the beginning of every test the only resistance to the rate of diffusion-controlled cementation is the liquid phase diffusion layer surrounding each ring
ii. With growing the time of cementation, the zinc rings become coated with a porous layer of cadmium powder which increases the resistance to the rate of mass transfer of Cd^{2+} from the solution bulk to the surface of the zinc rings.
iii. The overall resistance to the rate of mass transfer of Cd^{2+} ions from the solution bulk to the zinc surface consists of the liquid phase diffusion layer outside the zinc metal and porous cadmium powder layer surrounding the zinc rings as shown in Fig. 5. The increase in the rate of Cd^{2+} removal with increasing the degree of stirring shows that the liquid phase diffusion of Cd^{2+} throughout the diffusion layer

surrounding each particle is the rate determining step given the fact that intraparticle diffusion is not sensitive to stirring [38].

3.4 Data Correlation

$$\ln (C_o/C) = (KA/Q) \, t. \tag{2}$$

The mass transfer coefficient, K, for Cd^{2+} cementation on the rotating fixed bed of Raschig rings was correlated to other parameters by the dimensionless equation:

$$Sh = \alpha \; Sc \; \gamma \; Re\beta. \tag{3}$$

Where Sh is The Sherwood number (Kd_r/D), Sc is the Schmidt number ($\mu/(\rho D)$), and Re is Reynold number ($\rho Nd^2/\mu$).

The constants α, β and γ are obtained experimentally as follow: the exponent of Sc was fixed at 0.33 as previous studies on theoretical and experimental mass transfer [29, 39].

Fig. 6   for plotting of log Sh vs. log Re, gives slope of 0.40, which is the constant β.

Fig. 7 shows that the overall mass transfer correlation, and obtain slope 0.041, which is the constant number α. The present data fit the following equation:

$$Sh = 0.041 \; Sc^{0.33} Re^{0.40}. \tag{4}$$

The present mass transfer data was found to agree with Amin et. al which had a dimensionless equation: $Sh = 0.046 \; Sc^{0.33} Re^{0.45}$. [39]
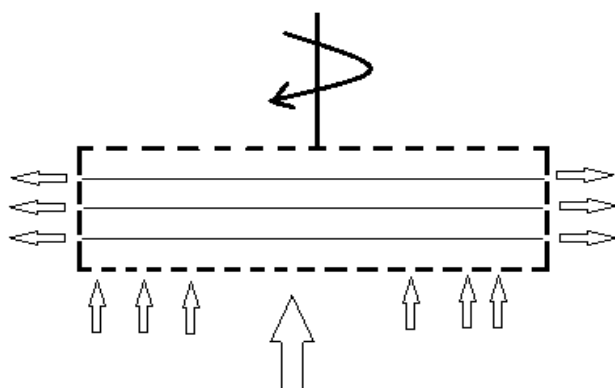

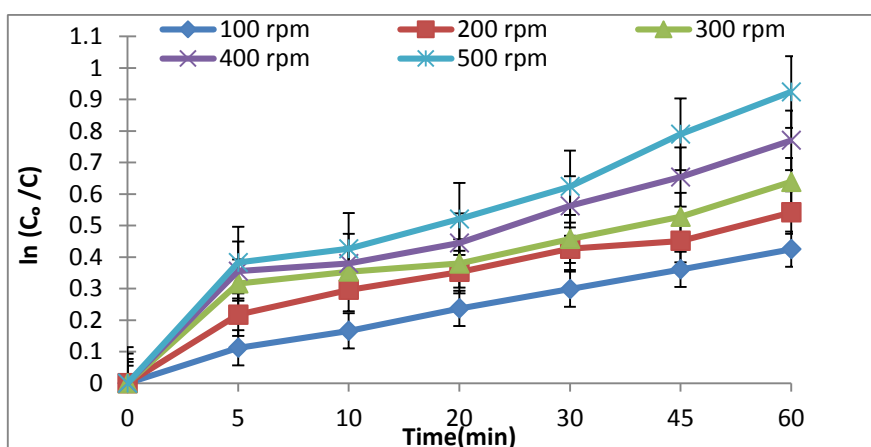**Fig. 3. Approximate flow pattern at the rotating basket**

Fig. 4. Typical plot of ln (C$_o$/C) vs. time at different basket rotational speed using 100 mg/l CdCl$_2$ concentration and diameter of zinc ring= 1.6 cm
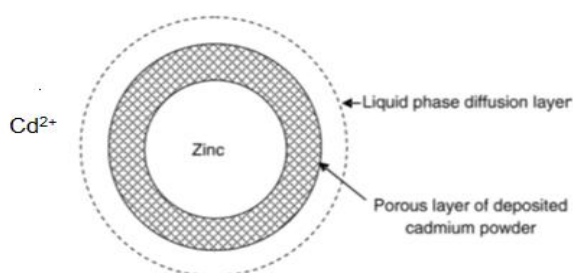

Fig. 5. Illustration of the two mass transfer resistances around zinc ring during cementation
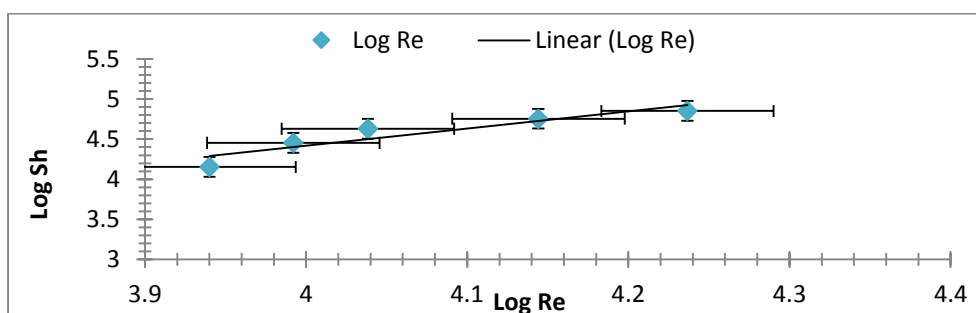

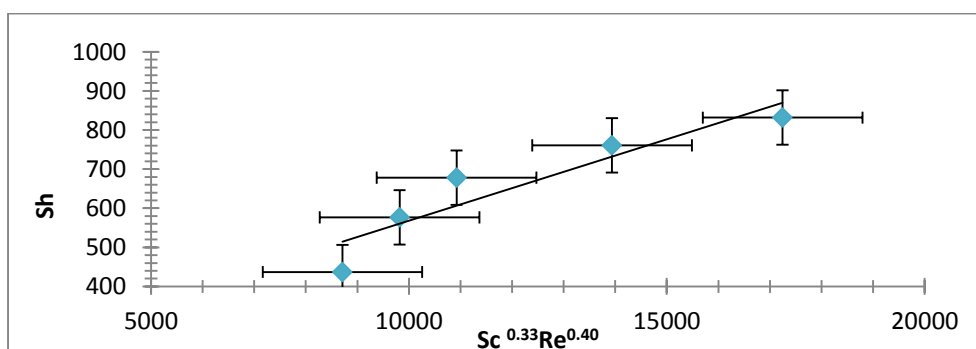**Fig. 6. Log Sh versus Log Re at diameter of zinc ring=1.6 cm**

Fig. 7. Overall mass transfer correlation for cementation of cadmium On Zinc Raching Ring in rotating basket reactor

4. CONCLUSION

- Cementation of cadmium by zinc rings in a rotating basket reactor was proven to be an effective process which achieves a high degree of cadmium removal from waste solution.
- cadmium powder produced may be accumulated through scraping the cylindrical partitions of the reactor with a knife.
- Within the existing variety of situations Cd^{2+}removalthrough the rotating basket reactor became discovered to happen thru diffusion controlled first order reaction.
- The present study shows that for the Cd-Zn cementation system there are two rates of cementation, first is high rate at the beginning, then a lower rate after the initial period.
- The results obtained from this study show that by increasing the basket rotation speed, the rate of cementation or percentage of Cd^{+2} ions removal from solution increases.
- As the diameter of Zn Raschig ring packed in the basket reactor increases the per-centage removal of Cd^{2+} decreases.
- The percentage removal of Cd^{2+} is optimum for ring diameter of 0.5 cm, initial concentration of 100 ppm and basket rotation speed of 500 rpm. Which may reach about 80 % removal.
- A dimensionless equation representing the data was obtained.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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