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Rates of Mass Transfer Controlled Electrochemical and Catalytic Reactions Conducted in a Fixed Bed Reactor Built of Lessing Rings

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The mass transfer behaviour of a fixed bed of Lessing rings was studied using a technique which involves the diffusion controlled dissolution of copper in acidified dichromate. Variables studied were ring diameter, solution velocity and physical properties of the solution. The mass transfer coefficient was found to increase with increasing solution velocity and decreasing the ring diameter. The mass transfer data were correlated by the following dimensionless equation

$$Sh=1.076\ Sc^{0.33}\ Re^{0.625}$$

The above equation was found to predict mass transfer coefficients higher than those obtained by the electrochemical technique under the same conditions because of the non-uniform current distribution inside and outside the rings. Also, the present study has revealed that Lessing rings produce higher rates of mass transfer than Raschig rings under the same conditions. Implications of the above equation for the design and operation of catalytic and heterogeneous reactors used to conduct diffusion controlled liquid-solid reactions were highlighted.

Keywords: mass transfer; fixed bed electrochemical reactor; catalytic reactor; lessing rings; diffusion controlled reactions.

1. INTRODUCTION

Despite the much work that has been done on fixed bed reactors, recent studies show that there is still a room for improving the performance of such reactors and diversifying their applications [1-14]. In view of their high space-time yield resulting from their high specific area and high mass transfer coefficient, fixed beds are used widely in building electrochemical and catalytic reactors used

to conduct diffusion controlled reactions . Examples of such reactions include electrochemical removal of heavy metals and organic pollutants from industrial waste solutions, electroorganic and electroinorganic synthesis, catalytic reactions include removal of organic pollutants by wet oxidation, immobilized enzyme catalyzed biochemical reactions and photocatalytic reactions. Fixed bed reactors are also used for removing heavy metal by cementation on a less noble metal or by ion exchange resins.

Fixed beds can be built using either small particles or large particles. Although beds of small particles size have large area per unit volume, they suffer from some drawbacks such as the high pressure drop and the high pumping power beside the fact that these beds may be clogged easily during operation especially if the process involves metal deposition. To avoid these problems fixed beds using large particles such as Raschig rings, Lessing rings, spheres and cylinders are used. Raschig rings and Lessing rings have the advantage over spheres and cylinders that the bed porosity is high and the pressure drop is relatively low. Lessing rings are similar in structure to Raschig rings except for the fact that Lessing rings contain an internal rectangular baffle which bisects the ring longitudinally into two halves. Although some work has been done on the mass transfer behaviour of fixed beds of Raschig rings, little has been done on the mass transfer behaviour of fixed beds of Lessing rings. Hassan et al [1] using an electrochemical technique which involves measuring the limiting current of the cathodic reduction of $K_3Fe(CN)_6$ studied the mass transfer behaviour of a fixed bed of Lessing rings using a flow by fixed bed reactor where the current flow is perpendicular to solution flow . Although the results of Hassan et al can be used in designing electrochemical reactors , these results cannot be used in designing non electrochemical reactors such as catalytic and heterogeneous liquid-solid reactors in view of the fact that the electrochemical technique suffers from the problem of current distribution inside and outside the rings forming the bed [15]. Current density is high at the outer ring surface while inside the ring surface the current density is low especially for vertical and inclined rings , accordingly the reaction rate is not uniform all over the ring surface .

The aim of the present work is to study the mass transfer behaviour of a fixed bed of Lessing rings under forced convection using a technique which doesn't suffer from the problem of current distribution namely the mass transfer controlled dissolution of copper in acidified potassium dichromate [16, 17]. The technique has been widely used to study mass transfer at different geometries owing to its high degree of accuracy and simplicity where no expensive equipments are needed [18-21].

2. EXPERIMENTAL TECHNIQUE

The apparatus (fig.1) consists of the fixed bed reactor, 30 liter plexiglass storage tank and plastic centrifugal pump (0.5 horsepower). The reactor was made of a plexiglass cylindrical column of 40 cm height and 10 cm inner diameter; it was divided into three sections. The inlet section which had a height of 25 cm was packed with glass spheres to ensure a fully developed calm flow in the next working section. The working section which had a height of 10 cm was randomly packed with copper Lessing or Raschig rings. Three ring sizes with an aspect ratio (l/d) =1 were used, ring diameters were

0.9, 1.25 and 1.6 cm. The outlet section (5 cm height) was fitted with an over flow weir from which the solution was recycled to the plastic storage tank.

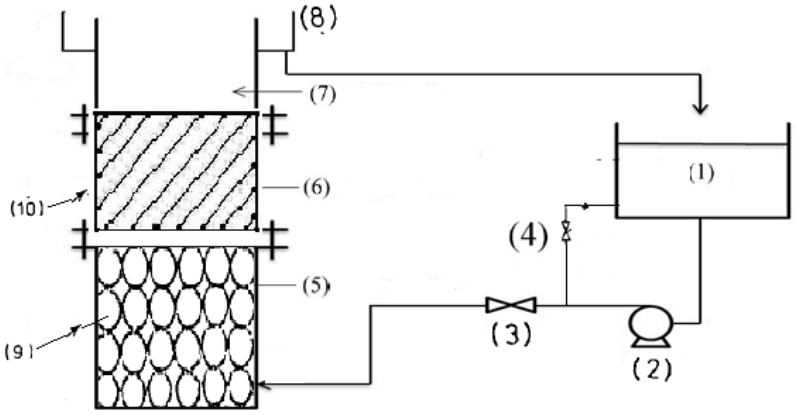


Figure 1 . Experimental setup. (1) Plastic storage tank , (2) Plastic centrifugal pump , (3) Control valve , (4) bypass plastic valve , (5) Inlet section , (6) Working section , (7) outlet section , (8) Overflow weir , (9) Glass spheres , (10) Copper Lessing rings or copper Raschig rings

Before each run 25 liter of fresh acidified dichromate solution were placed in the storage tank, the solution was circulated between the storage tank and the reactor by the plastic pump. Solution velocity was controlled using a bypass with two plastic valves and was measured volumetrically by a graduated cylinder and a stopwatch. The rate of reaction was followed by withdrawing 5 cm^3 of the solution every 2 minutes for chromate analysis by titration against standard ferrous ammonium sulphate solution using sodium diphenylamine as indicator [22].

Three solution compositions were used, namely: 0.003 M $K_2Cr_2O_7$ + 0.5 M H_2SO_4 , 0.003 M $K_2Cr_2O_7$ + 1 M H_2SO_4 and 0.003 M $K_2Cr_2O_7$ + 1.5 M H_2SO_4 . All solutions were prepared from A.R grade chemicals and distilled water. Temperature was 25 ± 2^oC during runs. Solution density and viscosity needed for data correlation were determined at the run temperature using a density bottle and an Ostwald viscometer respectively [23]. The diffusion coefficient of $K_2Cr_2O_7$ was taken from the literature [17] and was corrected for the change in temperature using the Stokes –Einstein equation. Table 1 shows the physical properties of the solutions used at 25 ^oC.

Table 1 . Physical properties of the solutions used at 25^oC

Solution composition	Density (ρ;g/cm^3)	Viscosity (μ;Poise)	Diffusivity ($D\times10^6$;cm^2/s)	Schmidt number(Sc)
0.003 M $K_2Cr_2O_7$ + 0.5 M H_2SO_4	1.026	0.0096	10.147	922
0.003 M $K_2Cr_2O_7$ + 1 M H_2SO_4	1.06	0.0105	8.945	1107
0.003 M $K_2Cr_2O_7$ + 1.5 M H_2SO_4	1.117	0.0126	7.662	1472

3. RESULTS AND DISCUSSION

For the present batch recirculating reactor the rate of the diffusion controlled liquid-solid reaction is given by the equation [24, 25]

$$-Q\frac{dC}{dt} = K\,A\,C \qquad (1)$$

which integrates to

$$\ln\left(\frac{Co}{C}\right) = \frac{K\,A}{Q}\,t \qquad (2)$$

where K is the mass transfer coefficient; A is the bed area (number of rings forming the bed * ring area); Q is the solution volume; C_o and C are the initial chromate concentration and the concentration at time t respectively.

The mass transfer coefficient was calculated from the slope $(\frac{KA}{Q})$ of the plot $\ln(\frac{Co}{C})$ Vs. t . Fig.2 shows a typical $\ln(\frac{Co}{C})$Vs. t at different superficial fluid velocity. Fig.3 shows the effect of superficial fluid velocity on the mass transfer coefficient at different ring size and different Sc where the data fit the equation

$$K = a\,V^{0.625} \qquad (3)$$

where V is the superficial fluid velocity.

The high mass transfer coefficient of the fixed bed is attributed to the repeated build up and breakdown of developing hydrodynamic boundary layer around each ring as the solution progresses inside the bed , in addition , boundary layer separation at the rear of each particle generates turbulence which enhances the rate of mass transfer at the rings [26] .

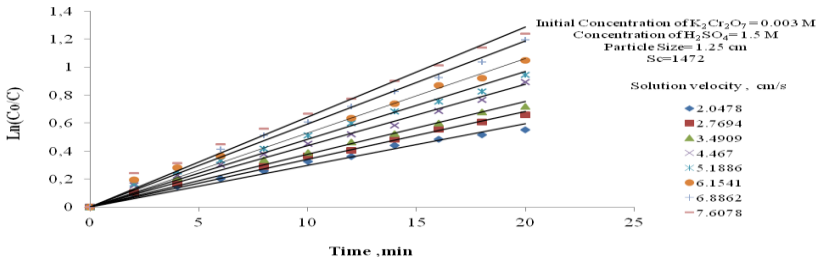
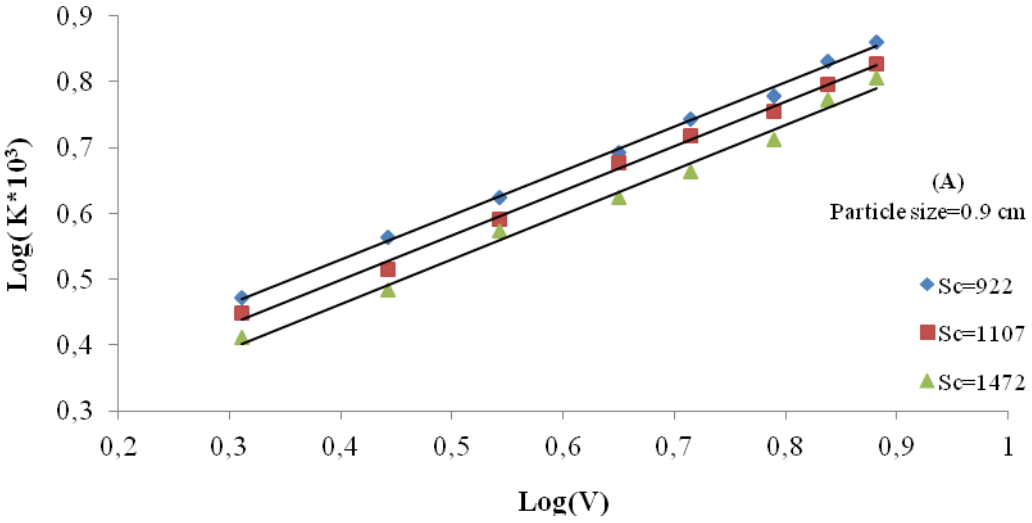


Figure 2 . Typical $\ln(C_o/C)$ Vs. t plot



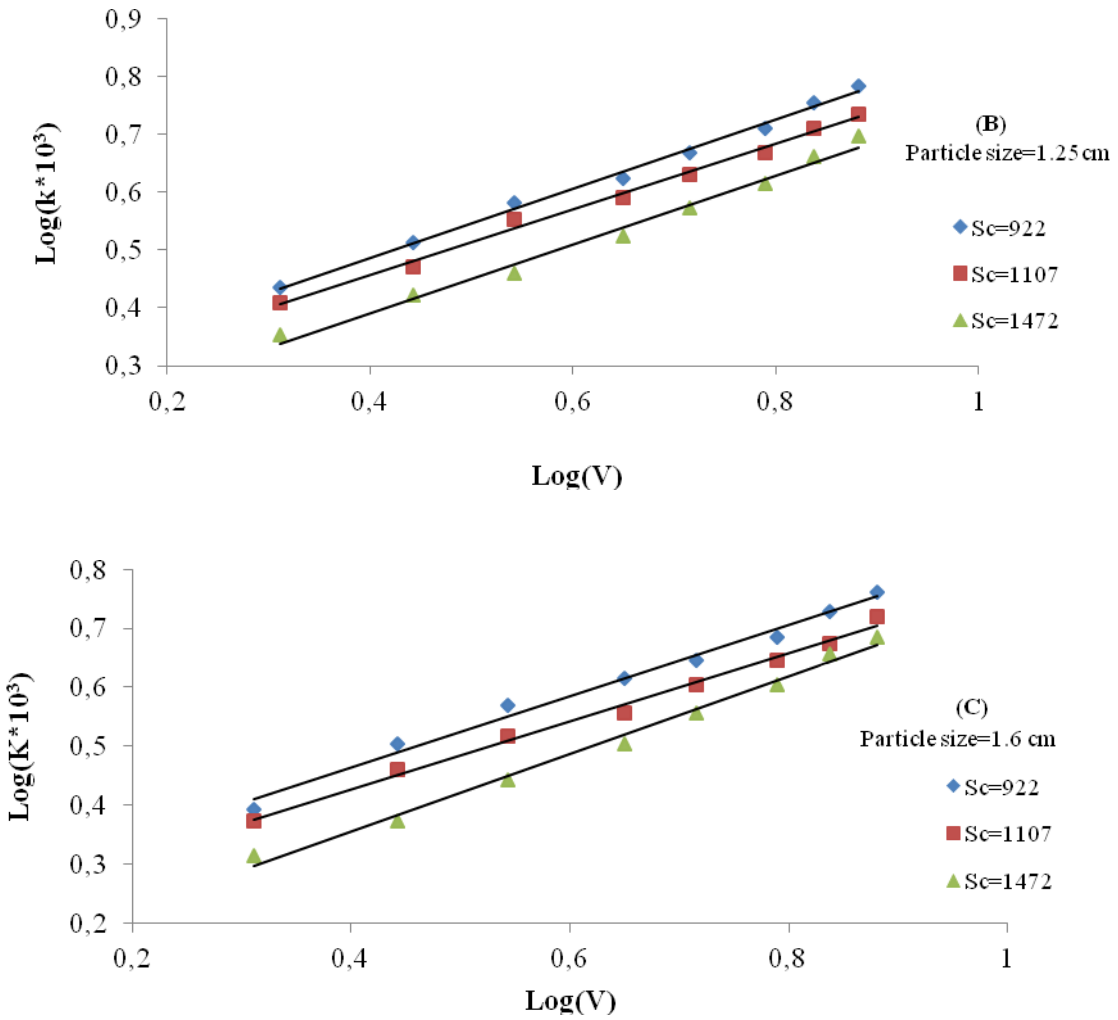


Figure 3 . Effect of superficial fluid velocity on the mass transfer coefficient for different Sc at different ring diameter

An overall mass transfer coefficient was envisaged in terms of the dimensionless groups Sh , Sc and Re which are usually used in correlating forced convection mass transfer data .Fig.4 shows that the present data for the conditions 922 <Sc<1472, 163 < Re < 1229 fit the equation

$$Sh=1.076\ Sc^{0.33}\ Re^{0.625} \qquad (4)$$

where Sh is Sherwood number ($\frac{K\,d}{D}$); Sc is Schmidt number ($\frac{\mu}{\rho\,D}$); Re is Reynolds number ($\frac{\rho V d}{\mu}$).

With an average deviation of ±3.6 %. In obtaining the above equation, the exponent of Sc was fixed at 0.33 following previous theoretical and experimental studies in mass transfer [24-26]. The Re exponent 0.625 is in a fair agreement with the value obtained by different authors who used different particle geometry. The comprehensive review of Colquhoun and Stepanek [27] shows that Re exponent obtained by different authors who studied mass transfer at fixed beds ranged from 0.5 to 0.66 depending on particle geometry and the range of Re. More recently, Zaki et al [28] obtained a Re exponent of 0.5 for a fixed bed of cylinders using the present technique .

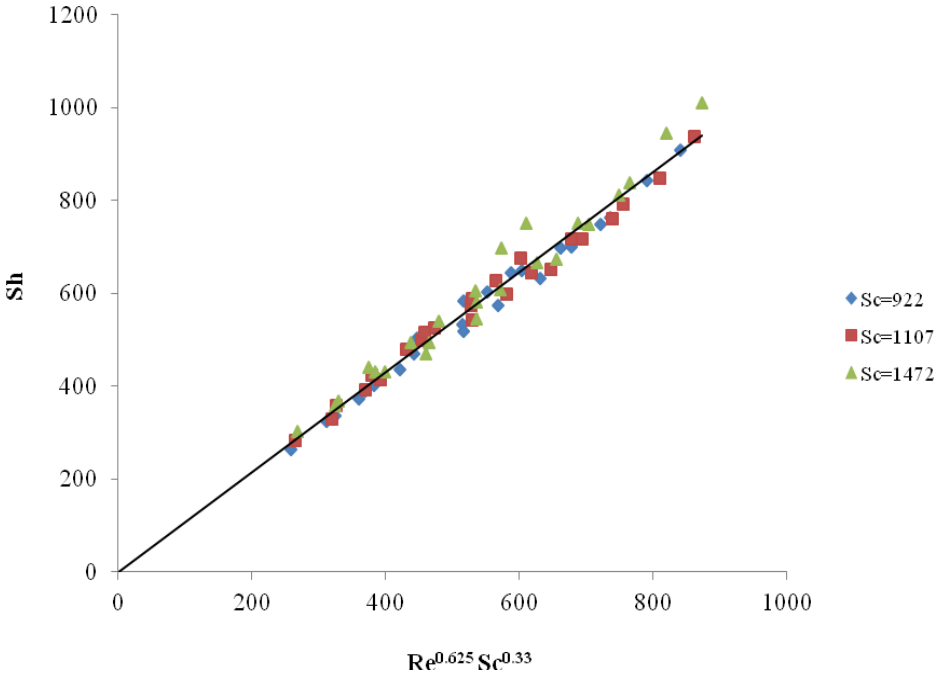


Figure 4 . Overall mass transfer correlation at a fixed bed of Lessing rings

It would be of interest to compare between the present mass transfer coefficients with those predicted from the equation obtained by Hassan et al [1] using the electrochemical technique , namely ;

$$Sh=1.57\ Sc^{0.33}\ Re^{0.46} \quad (5)$$

Fig.5 shows that for a given set of conditions the present data lie above the data of Hassan et al as expected in view of the fact that as opposed to the electrochemical technique used by Hassan et al, the present technique allows the reaction to take place on different parts of the rings including the internal surface of vertical and inclined rings. In case of the electrochemical technique such surfaces are inaccessible to the current and hence to the reaction because of the shielding effect of the ring wall.

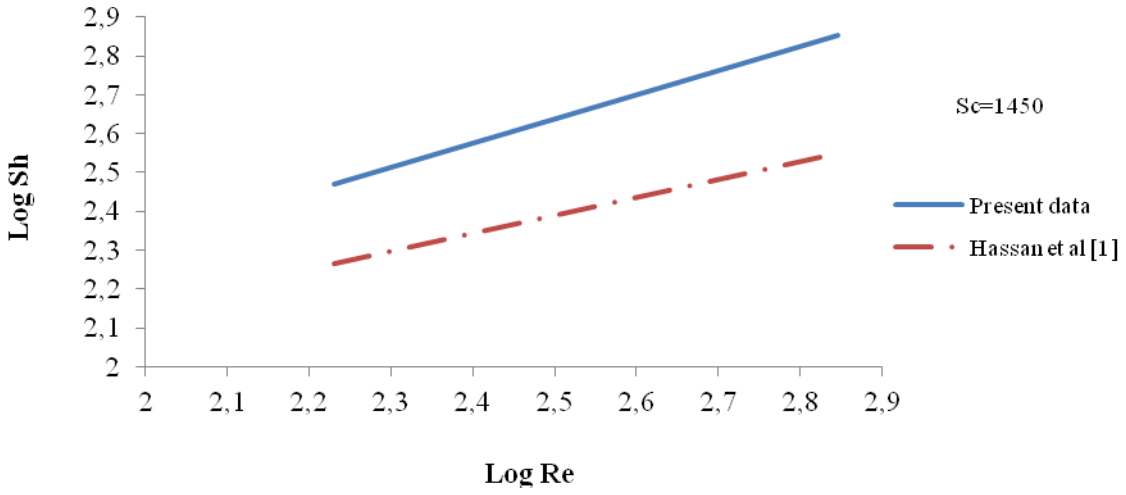
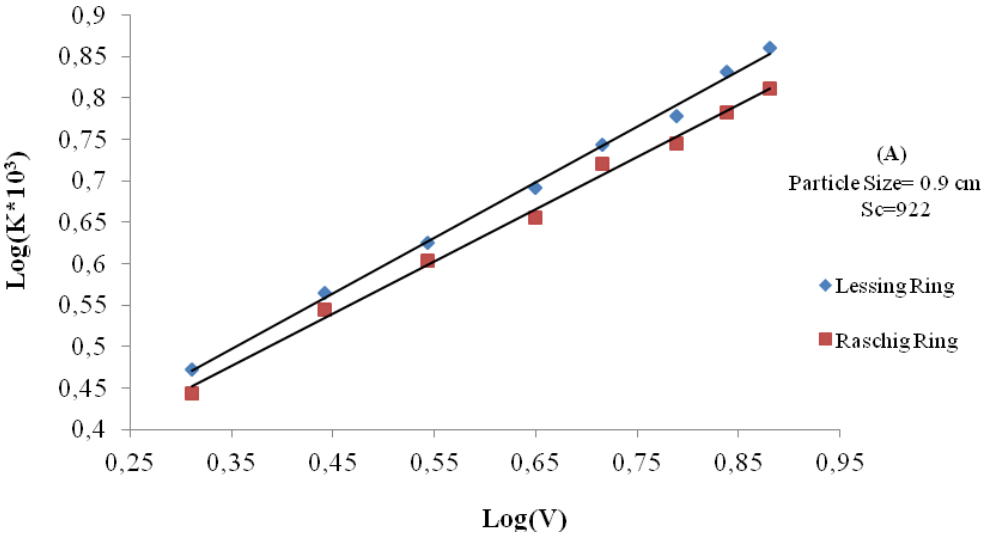
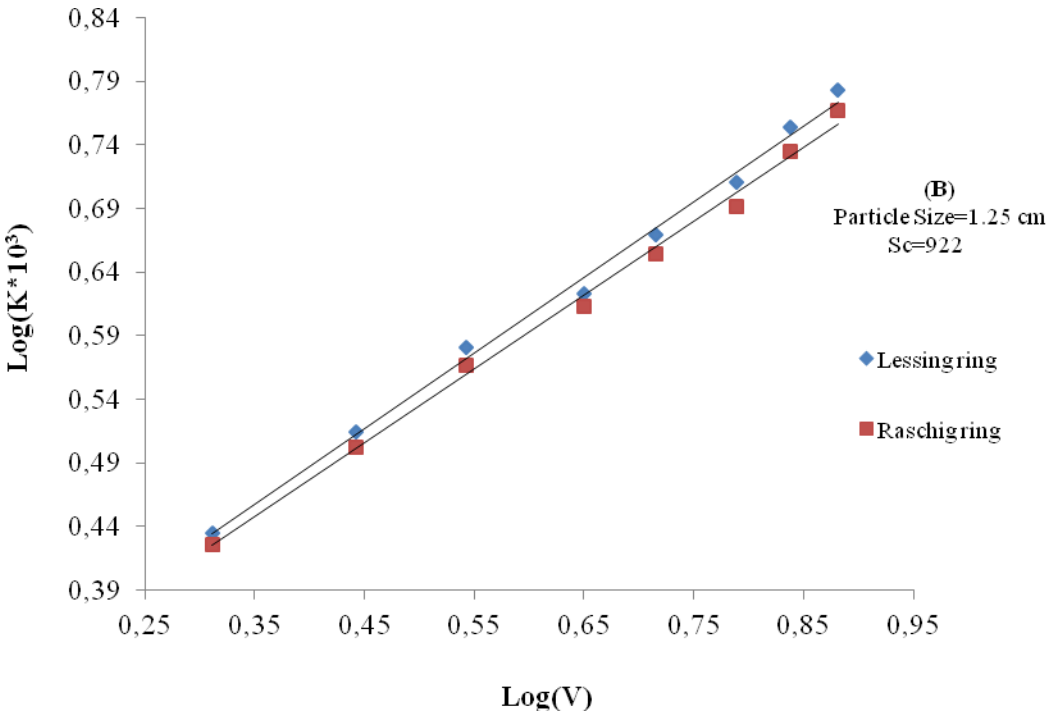


Figure 5 . Comparison between the present mass transfer data for Lessing rings and the data obtained by the electrochemical technique

In an attempt to throw some light on the difference in behaviour between Raschig rings and Lessing rings and the role of internal baffle in case of Lessing ring , a series of experiments were conducted on a fixed bed of Raschig rings under the same conditions used for Lessing rings. Fig.6 shows a comparison between the mass transfer behaviour of beds of Raschig rings and beds of Lessing rings, the data show that for a given set of conditions Lessing rings produce higher rates of mass transfer , this may be attributed to the enhancing effect of the baffle especially in vertically oriented rings where boundary layer separation takes place downstream of the baffle with turbulence generation which enhances the rate of mass transfer at the neighboring rings [29, 30] . If the larger area of Lessing rings is considered beside the higher mass transfer coefficient this would result in a higher volumetric mass transfer coefficient (KA) for Lessing rings and hence higher productivity than Raschig rings under the same conditions.





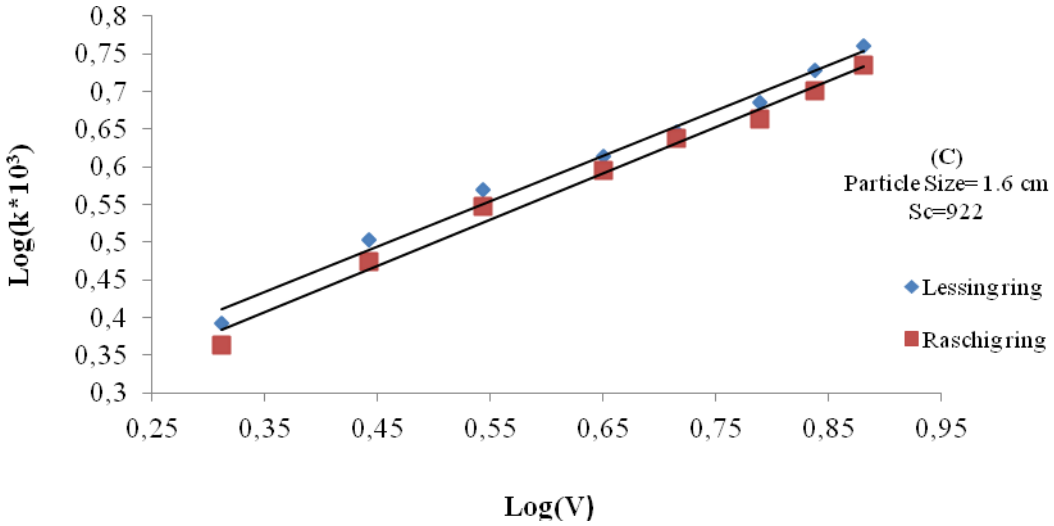


Figure 6 . Comparison between the mass transfer behaviour of beds of Lessing rings and beds of Raschig rings

4. CONCLUSIONS

(1) The high mass transfer coefficient of fixed beds of Lessing rings qualifies these beds for building high space- time yield catalytic and heterogeneous reactors suitable for conducting diffusion controlled liquid-solid reactions . Examples of catalytic liquid-solid reactions include photocatalytic reactions, immobilized enzyme catalyzed biochemical reactions and removal of organic pollutants from wastewater by catalytic wet oxidation. Examples of liquid-solid non catalytic heterogeneous reactions include removal of heavy metals from wastewater by cementation on a less noble metal and removal of Cr^{6+} and nitrates from wastewater by reduction on iron scrap.

(2) The technique involving the diffusion controlled dissolution of copper in acidified dichromate is more suitable for studying mass transfer at fixed beds of perforated particles such as Lessing rings and Raschig rings than the traditional electrochemical technique which gives reduced mass transfer coefficient as a result of the inaccessibility of the ring inner surface to electrical current owing to the shielding effect of the ring wall especially in case of vertical and inclined rings. Mass transfer equations obtained by the electrochemical technique such as equation (5) are suitable only for the design and operation of electrochemical reactors but underestimate the rate of mass transfer in case of non-electrochemical reactors such as catalytic and liquid-solid heterogeneous reactors , the present mass transfer correlation is more suitable for such reactors .

(3) Fixed bed reactors employing Lessing rings have a higher productivity than those which employ Raschig rings under the same conditions because of the higher volumetric mass transfer coefficient of Lessing rings (KA) .

LIST OF SYMBOLS:

A bed area (total surface area of the rings forming the bed)

a constant

C chromate concentration at time t
C_o initial chromate concentration
d ring diameter (particle size)
l ring length
D diffusivity of dichromate
K mass transfer coefficient
Q solution volume
Re Reynolds number $(\frac{\rho V d}{\mu})$
Sc Schmidt number $(\frac{\mu}{\rho D})$
Sh Sherwood number $(\frac{K d}{D})$
t time
V superficial fluid velocity
ρ solution density
μ solution viscosity

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