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Reduction of hexavalent chromium using zerovalent iron spheres packed in a rotating basket reactor: kinetic and mass transfer study

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ABSTRACT

Kinetics of hexavalent chromium reduction to trivalent chromium onto iron spheres, packed in a rotating basket reactor was investigated under different conditions, such as H_2SO_4 acid concentration, basket rotational speed, sphere diameter, and solution temperature. The rate of Cr(VI) reduction was found to increase with increasing basket rotational speed, H^+ ions concentration, and temperature. On the other hand the rate decreases with increasing the diameter of iron spheres. The activation energy was found to be 4.9 kcal/mol which confirm the diffusion controlled nature of the reaction. The thermodynamic parameters for the present study were calculated at 25°C and was found to be 17.99 kJ mol^{-1}, 278.98 J mol^{-1} K^{-1}, and 103.6 kJ mol^{-1} for ΔH, $-\Delta S$, and ΔG, respectively. Rate of Cr(VI) reduction expressed in terms of the rate of mass transfer was correlated to the controlling parameters by the dimensionless equation

$$\mathrm{Sh} = 0.3463\ \mathrm{Re}^{0.55}\ \mathrm{Sc}^{0.33}$$

The present mass transfer data was found to agree with the surface renewal theory.

Keywords: Hexavalent chromium; Reduction; Packed basket; Iron spheres; Kinetics; Mass transfer; Thermodynamic; Rotating reactor

1. Introduction

Heavy metals are considered as non-biodegradable toxic pollutants which may be released in the environment by various activities. Hexavalent chromium is one of the most dangerous industrial pollutants which exists in effluents discharged by industries, such as: electroplating, metal finishing, printed circuit and plastic etching, pigments, metallurgy, textile, dying, wood preservation, from blow down of cooling towers, organic, and pharmaceutical industries, where it is used as oxidizing agent. Usually large quantities of hexavalent chromium are released into environment via leakage, poor storage, or improper disposal practices [1–4]. Hexavalent chromium exists as oxy-anions such as chromate ($Cr_2O_7^{2-}$), bichromate ($HCrO_4^-$), and dichromate ($Cr_2O_7^{2-}$), it is highly soluble, mobile, acutely toxic, mutagenic, teratogenic, and carcinogenic [5–7]. In contrast, trivalent chromium has a low solubility in water and readily precipitates as $Cr(OH)_3$ or Cr(III) complexes with organic ligands, it can also precipitated or absorbed onto the surface of clay minerals. The compounds of Cr(III) are reported to be 10–100 times less toxic than those of Cr(VI) compounds [8–10]. Thus, reduction of Cr(VI) to Cr(III) serves both to immobilize Cr and reduce its toxicity.

Much research has focused on the remediation of Cr(VI) and many treatment processes have been developed. Physico-chemical adsorption has been researched for a long time [11–15], but the cost is high and Cr(VI) is just transferred instead of being reduced. Bioremediation by strains of bacteria can effectively degrade Cr(VI) and is economically favorable [16–18], but the presence of bacterial toxicants at many waste sites would limit their growth and effectiveness. Electrochemical techniques [19–22] and electro-coagulation process [23–25] have been used for Cr (VI) reduction. Chemical reduction of Cr(VI) to Cr(III) followed by precipitation of reduced chromium with alkali is the most commonly used method [26,27]. The reducing agent is generally sulfur dioxide, sulfite, bisulfate, or ferrous sulfate, but this process is usually accompanied with secondary wastes and high volume of sludge production.

Recently there has been a great interest in using zerovalent state metals such as metallic iron scrape for *in situ* reduction of hexavalent chromium [1,4,28–35]. It is well known from literature that the reaction between Cr(VI) and metallic iron occurs easily and spontaneously in acidic solution owing to the large difference in their reduction potentials [19,30,33–38], according to the reaction:

$$2HCrO_4^- + 3Fe + 14H^+ \rightarrow 2Cr^{+++} + 3Fe^{+++} + 8H_2O \qquad (1)$$

Despite the work done on Cr(VI) reduction by metallic iron, there is still a room for developing new more efficient reactors. The aim of the present study is to examine the performance of a new reactor, namely a rotating perforated basket packed with iron spheres in Cr(VI) reduction.

The performance of the new reactor was investigated over a wide range of conditions, such as basket rotational speed, sulfuric acid concentration, diameter of iron spheres, and temperature. A special attention was given to solutions containing large excess of H_2SO_4 and Cr^{6+} concentrations to simulate effluents arising from organic oxidation and plastic etching prior to metallization.

2. Experimental part

2.1. Materials

All chemical reagents, such as $K_2Cr_2O_7$ (CAS number 7778-50-9), H_2SO_4, and HCl (CAS number 7664-93-9), were in analytical reagent grade. Stock solution of acidified dichromate (0.03 M $K_2Cr_2O_7$ with H_2SO_4 concentration ranging from 0.5, 1 and 2 M) were prepared by weighting the purified grade chemicals and dissolving it in distilled water. The iron (23/3 solid steel) spheres ranged from 0.65 to 0.4 cm were purchased from Ezz El-Dekhela company, Alexandria, Egypt. The iron spheres were washed (etched) in dilute HCl to remove the oxide layer then washed with distilled water and dried, which created fresh sites for oxidation and made the surface more active.

2.2. Batch experiments

The experimental setup used in the present study is shown in Figs. 1(a) and 1(b). It consists of plexi-glass container of 15 cm diameter and 25 cm height, fitted with four rectangular baffles fixed to the container wall 90° from one another. The iron spheres were packed in a perforated plexi-glass basket of length 8 cm, width 3 cm, and thickness of 2.2 cm as shown in Fig. 1(b). It was fitted at the center to an isolated stainless steel shaft which was connected to a variable speed motor. The perforated packed basket rotational speed was varied within the range 75–375 rpm. Three liters of acidified potassium dichromate solution were used in each experiment. A typical experiment runs lasted 21 min, where samples of 5 ml were taken from reaction solution every 3 min and analyzed for Cr(VI). Cr(VI) concentration was determined spectrophotometrically with diphenylcarbazide at 540 nm using UV spectrophotometer (Shimadzu Model: UV 1601) [39]. Temperature of solution was controlled by using a thermo stated water bath and ranged from 25 to 55°C. Physical properties of the solution such as viscosity and density were measured using viscometer and density bottle while diffusivity

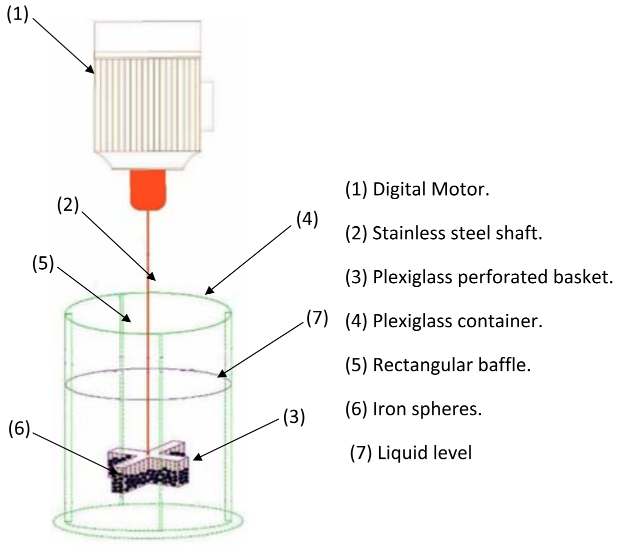

Fig. 1(a). Experimental setup.

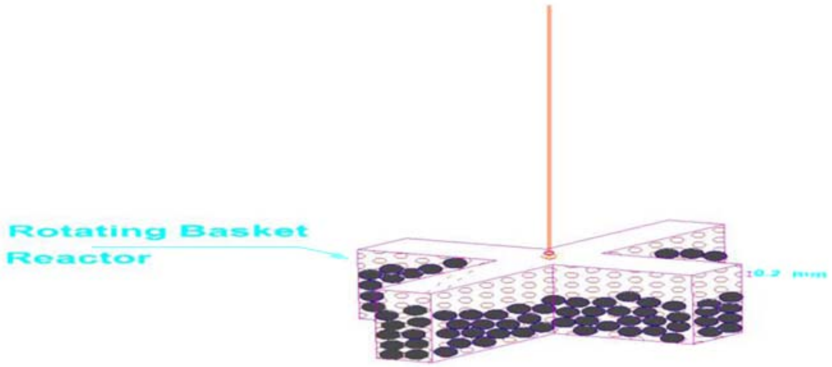

Fig. 1(b). Rotating basket reactor packed with some iron spheres.

was taken from the literature [40,41] and was corrected for the change in temperature using the Stokes–Einstein equation [40,41].

3. Results and discussion

3.1. Kinetic study

Reduction of acidified chromate by iron spheres is a heterogeneous reaction which involves the following step: (i) diffusion of chromate ion from the solution bulk to iron surface, (ii) reduction of chromate ions at iron surface according to Eq. (1), and (iii) diffusion of Fe^{++} ions along with Cr^{+++} from interface to bulk of the solution.

It has been reported that Cr(VI) reduction on Fe metal in acidic media follows first-order kinetics according to the following equation [1,8,29,33,34]:

$$-Q\ dC/dt = KAC \tag{2}$$

which integrates to

$$\text{Ln}\ (C_0/C) = KAt/Q \tag{3}$$

where C_0 and C are the initial concentration and the concentration at any time (t) of acidified potassium dichromate solution, respectively, K is the mass transfer coefficient cm/min, Q is the solution volume, and A is the area of iron spheres (cm^2).

A linear plot of ln C_0/C vs. t is a verification that the Cr(VI) reduction rate at different operating conditions is a first-order kinetics with respect to Cr(VI) ions as shown in Fig. 2. The solid–liquid mass transfer coefficient, K, was obtained from the slope (KA/Q).

3.2. Effect of basket rotational speed

Fig. 3 shows the effect of rotational speed of packed basket on mass transfer coefficient at different H_2SO_4 concentrations. The data are shown to fit the relation:

$$K\ \alpha\ \omega^{0.55} \tag{4}$$

It is clear that the rate of Cr(VI) reduction increases by the increase in the basket rotational

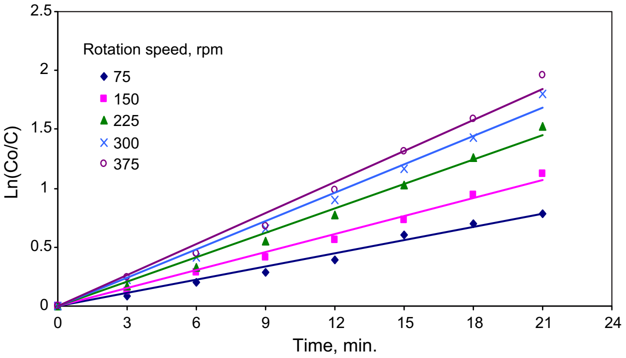

Fig. 2. Typical plot of Ln(C_0/C) vs. time at different basket rotational speed (Cr^{6+} conc. = 0.03 M, H_2SO_4 conc. = 1 M, sphere diameter = 6.4 mm, temp. = 25℃).

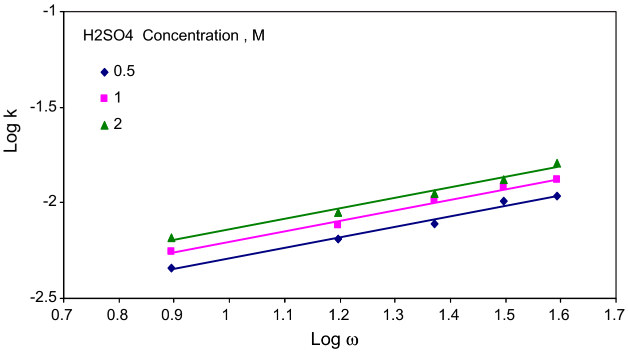

Fig. 3. Effect of basket rotational speed on mass transfer coefficient at different H_2SO_4 concentration (sphere diameter = 6.4 mm, temp. = 25℃, Cr^{6+} conc. = 0.03 M).

speed. The increase in mass transfer coefficient, *K*, by the increase in the basket rotational speed is due to the decrease in diffusion layer thickness on iron spheres as rpm increases. This enhancing effect can be also explained in the light of the approximate flow pattern observed in the present work. During basket rotation, the iron spheres move past the solution. A developing hydrodynamic boundary layer and a diffusion layer is formed around each sphere, in the rear of each sphere the developing hydrodynamic boundary layer breaks down with the formation of a turbulent wake. The relatively thin developing hydrodynamic boundary layer and diffusion layer along with the formation of a turbulent wake in the rear of each sphere enhances the rate of mass transfer with a consequent increase in the rate of diffusion controlled reduction of hexavalent chromium. Besides, since any rotational motion induced within, a vessel tends to produce a secondary flow in the vertical direction by virtue of continuity [42], it is also probable that this secondary flow contributes to enhancing the rate of mass transfer when it percolates through the basket. In this case, a developing hydrodynamic boundary layer and diffusion layer will be built at each sphere with the formation of a turbulent wake in the rear of each sphere. The successive build up and decay of the hydrodynamic boundary layer and diffusion layer enhances the rate of mass transfer.

3.3. Effect of increasing the solution acidity

Fig. 3 shows that for a given set of conditions the mass transfer coefficient of hexavalent chromium reduction increases with increasing H_2SO_4 concentration from 0.5 to 1.5 M (initial pH range of the solution 3–2.1), this may be attributed to the increase in Schmidt number (Sc) of the solution ($\mu/\rho\ D$). According to the hydrodynamic boundary layer theory for a given relative velocity between the solution and the transfer zinc surface the diffusion layer thickness decreases with increasing Sc [43]. This is also in accord with the stoichiometry of this reaction (Eq. (1)), which requires 7 mol of hydrogen ions for each mol of Cr(VI) and is highly dependent on H^+ ion concentration.

3.4. Effect of sphere diameter

The diameter of iron spheres has an effect on rate of Cr(VI) reduction as shown in Fig. 4. As the diameter of iron sphere increases the mass transfer coefficient decreases.

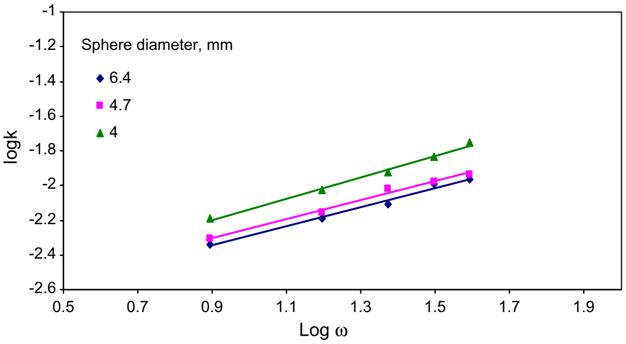

Fig. 4. Relation between mass transfer coefficient and basket rotational speed at different iron sphere diameter (H_2SO_4 conc. = 0.5 M, Cr^{6+} conc. = 0.03 M, temp. = 25°C).

This may be attributed to the fact that as each sphere in the rotating basket rotates in the solution, a hydrodynamic boundary layer and a diffusion layer are built on its surface. As the size of the ring increases, the average thickness of the boundary layer increases with a consequent increase in the diffusion layer thickness, accordingly the mass transfer coefficient decreases [44,45]. Besides, as the particle size of the packing increase, the porosity of the basket increases and the interstitial solution velocity inside the rotating basket decreases with a consequent decrease in the rate of mass transfer and the rate of Cr(VI) reduction.

3.5. Mass transfer study

From the above result, it is obvious that the mass transfer coefficient, *K*, depends on the basket rotational speed, Sc, temperature of solution, and on the diameter of packing material (iron spheres). The following dimensionless mass transfer equation was found to correlate the mass transfer coefficient to these variables.

$$\mathrm{Sh} = \alpha\,\mathrm{Sc}^{0.33}\,\mathrm{Re}^{\beta} \qquad (5)$$

where Sh is the Sherwood number, $\mathrm{Sh} = Kd_s/D$; Sc is the Schmidt number, $\mathrm{Sc} = \mu/\rho\ D$; Re is the Reynolds number, $\mathrm{Re} = \rho V d/\mu$, α and β are constants; d_s is the diameter of iron sphere (cm); V is the basket linear velocity, $\omega\ d/2$, ω is the angular velocity (rad s^{-1}), d is the basket characteristic length (cm), ρ is the density of solution (g cm^{-3}); μ is the viscosity of the solution (g cm^{-2} s^{-1}); D is the diffusion coefficient (cm^2 s^{-1}); and K is the mass transfer coefficient (cm s^{-1}).

The exponent of Sc was fixed at 0.33 following previous theoretical and experimental studies in mass transfer [45]. Fig. 5 shows that plotting of log Sh vs.

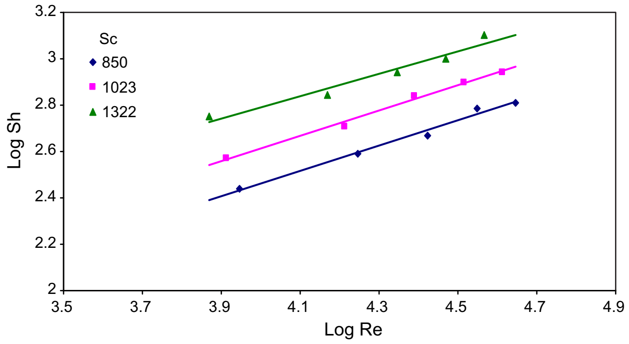

Fig. 5. Log Sh vs. Log Re at different H_2SO_4 concentration (sphere diameter = 6.4 mm, temp. = 25˚C, Cr^{6+} conc. = 0.03 M).

log Re, obtain slope of 0.55. Fig. 6 shows that for the conditions $850 < Sc < 1322$, $8.8 \times 10^3 < Re < 3.7 \times 10^4$, the present data fit the following equation:

$$\mathrm{Sh} = 0.3463\,\mathrm{Re}^{0.55}\,\mathrm{Sc}^{0.33} \tag{6}$$

With standard deviation 10.9 ± %, the above equation can be used in the design and operation of the suggested packed rotating basket reactor.

The 0.55 exponent of the linear velocity (V) of the rotating packed basket indicated by Eq. (6) is in a fair agreement with the prediction of the surface renewal mass transfer theory which seems to be applicable to the present situation. Each sphere in the basket is exposed repeatedly to fresh solution as it moves from location to location during basket rotation; the contact time spent by ring at each location is t^{-}. During the contact time of each particle with the fresh solution at every location, an unsteady state diffusion takes place from the solution to the ring according to Fick's law of diffusion, which is as follows:

$$\mathrm{d}C/\mathrm{d}t = D\mathrm{d}^2C/\mathrm{d}y^2 \tag{7}$$

Integrating the above equation as reported elsewhere [46]

$$K = 2(D/\pi t^{-})^{0.15} \tag{8}$$

The contact time (t^{-}) between each sphere and fresh solution at different locations can be expressed by the equation:

$$t = d_s/V \tag{9}$$

Substituting t^{-} in Eq. (8) we get:

$$K = 2(DV/\pi d_s)^{0.5} \tag{10}$$

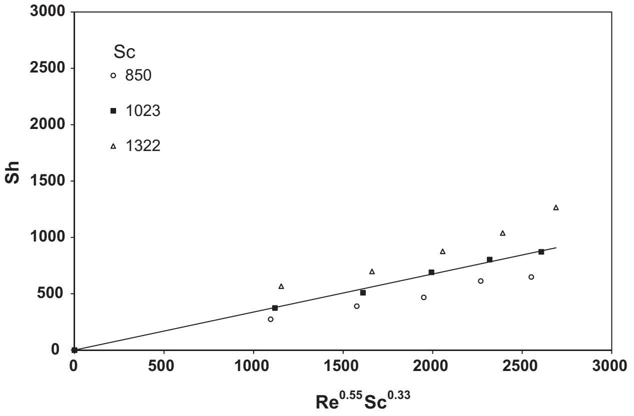

Fig. 6. Overall mass transfer correlation.

Eq. (10) follows the following relation:

$$K\,\alpha\,V^{0.5} \tag{11}$$

which agree fairly with the present experimental exponent of 0.55.

3.6. Thermodynamic study

To confirm the diffusion-controlled mechanism of the reaction, the effect of temperature on reaction rate was examined. An Arrhenius plot (Fig. 7) shows that the data fit Arrhenius equation:

$$K = A\,e^{-(E_a/RT)} \tag{12}$$

The activation energy for Cr(VI) reduction on packed iron sphere in basket reactor was found to be equal to 4.9 kcal/mol for temperature ranging 25–55˚C, the value tend to support the diffusion-controlled nature of the reaction [47].

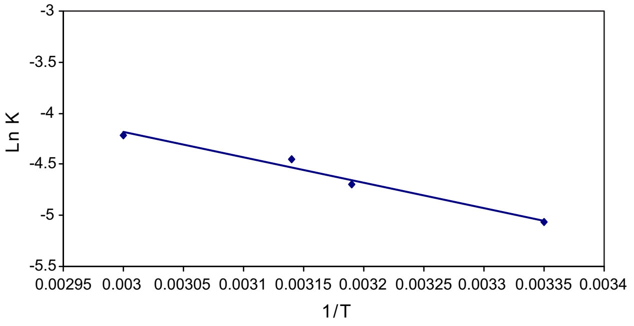

Fig. 7. Linear plot of Arrhenius equation (sphere diameter = 6.4 mm, basket rotational speed = 150 rpm, Cr^{6+} conc. = 0.03 M, H_2SO_4 conc. = 0.5 M).

The thermodynamic activation parameters, namely enthalpy change ΔH, entropy change ΔS, and free energy change ΔG, were calculated from the equations:

$$\Delta H = E_a - RT \tag{13}$$

$$\Delta S/R = \ln A - \ln BeT/h \tag{14}$$

$$\Delta G = \Delta H - T\Delta S \tag{15}$$

where A is the frequency factor, B is the Boltzmann's constant, e is 2.7183, h is the Plank's constant, and T is the absolute temperature. The values of the thermodynamic parameter for the present study were found to be $17.99\,\text{KJ mol}^{-1}$, $278.98\,\text{J mol}^{-1}\text{K}^{-1}$, and $103.6\,\text{KJ mol}^{-1}$ for ΔH, $-\Delta S$, and ΔG (25℃), respectively.

4. Conclusions

Reduction of Cr(VI) by iron spheres packed in a rotating basket reactor was shown to be an efficient process which achieves a high degree of Cr(VI) reduction. The reduction kinetics was investigated under different conditions of H_2SO_4 concentration, basket rotational speed, temperature, and iron sphere diameter. It was found that the mass transfer coefficient and the rate of reduction reaction increased by the increase in H_2SO_4 concentration, temperature, and basket rotational speed. The rate of reduction was found to decrease by increasing in sphere diameter. The diffusion controlled nature of the reduction reaction was ensured by calculating the activation energy of the reaction which was found to be equal to 4.9 kcal/mol. The experimental data are well correlated in terms of a dimensionless mass transfer correlation, which is useful for the design and operation of the reactor used for reduction of toxic Cr^{6+} ions from wastewater to a less toxic and precipitated form (Cr(III)) by the present technique.

The mass transfer study for the present work agrees fairly with surface renewal theory of mass transfer. The present study found that Cr^{6+} reduction by Fe in a highly acidic solutions containing relatively high Cr^{6+} concentration is a diffusion controlled reaction which is consistent with the finding of Gregory and Riddiford who used copper instead of iron in the same acidified solution [48].

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