

REMOVAL OF Cr^{6+} IONS FROM WASTEWATER IN PRESENCE OF QUATERNARY AMMONIUM SALTS

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ABSTRACT

The rate of reduction of Cr^{6+} to Cr^{3+} reaction in $K_2Cr_2O_7$ has been studied and it is found to be first order. The rate of reaction at 0.05 mole of $K_2Cr_2O_7$ have been measured in absence of quaternary ammonium salts as CTAB (Cetyl trimethyl ammonium bromide) and CPYB (Cetyl trimethyl pyridinium bromide). The rates of reaction are also measured in presence of CTAB and CPYB at four different temperatures (25, 30, 35 and 40°C). Effects of rotations are also studied. The rate of reaction was decreased by addition of salts. Thermodynamic parameters ΔG^* , ΔH^* and ΔS^* are given.

1. INTRODUCTION

Chromium VI, the dangerous forms, is (Dickinson, 1974) used in metal finishing (chrome plating) chromium chemical production, chromium pigments of paints and textiles and some wood preservatives. It is also used in cooling towers to prevent corrosion in the cooling loops.

Solid waste containing chromium VI can become a hazard when disposed in land fills because this forms of chromium is very mobile in ground water whereas chromium III is not.

Electroplating operations, leather tanneries, and textile manufacturing are the largest sources of water releases.

1.1. Health effects

Chromium III is required for health, and all ordinary exposures are considered to be safe. Chromium VI can produce liver and kidney damage, internal hemorrhage, dermatitis, respiratory damages and lung cancer.

1.2. Environmental effects

Chromium occurs in liquid wastes in two forms, trivalent and hexavalent. Hexavalent chromium is toxic and known to be carcinogenic substance. It is responsible for lung cancer, chrome ulcer, perforation of nasal septum and kidney damage. According to IS: 2490 and IS: 2296, (Jenkins, 1978) the threshold-limiting value for hexavalent chromium is 0.1 mg/L. the limit of liquid wastes discharged into the sea is 1 ppm. For trivalent chromium, it is a practice to keep the concentration below 4 ppm.

Cementation is used as a general term to describe the process whereby a metal is precipitated from a solution of its salts by another more electropositive metal. Such reactions have been and are being, used extensively in the mineral industry, both for the recovery of values (e.g. the extraction of copper from leach streams with iron (Rickard and Fuerstenau, 1968) or gold recovery from cyanide leach solution (Nicol, *et al.*, 1979) also for copper recovery from cyanide liquors

(Hsu, *et al.*, 1998; Kakovskii, *et al.*, 1967) and for purification of process streams (e.g. the removal and recovery of copper and cadmium from zinc sulphate electrolyte with metallic zinc). The metal used need not to be of highest purity. On the other hand, when metals such as copper are treated they are converted into essentially pure metal powders so that cementation is one of the most effective and economic techniques for recovering toxic and/or valuable metals from industrial waste solution (Shcherbakov and Kakovskii, 1967; Lo, and Yu., 1992, Guerra and Dreisinger, 1999). All authors have reported diffusion controlled mechanism at room temperature (Ravindea, and Milton 1967; Strickland, and Lawson, 1970, Maklufi, *et al.*, 1997; Makhloufi, *et al.*, 1998; Mishra and Paramguru, 1999; Shaltout 1999; Joon, *et al.*, 2000; Nosier and Sallam, 2000; Ismail, *et al.*, 2001).

The most important source of chromium pollution is dusterial. Industries that use large amount of chromium as chromate or dichromate are the textile, leather tannins and metal finishing for corrosion protection. Hexavalent chromium compounds causes dermatitis (Ismail, *et al.*, 2001), perforation of nasal septum and inflammation of larynx and liver. Skin lesions and kidney damage could be produced as a result of occupational exposure to hexavalent chromium compound is probably a carcinogen and the lung is principle site of action (Katat, 2000).

The object of the present work is to study the kinetics of the reduction of Cr^{+6} to Cr^{3+} on rotating iron cylinder in presence of some cationic SAS as CTAB (Cetyl trimethyl ammonium bromide) and CPYB (Cetyl trimethyl pyridinium bromide).

2. MATERIALS AND METHODS

2.1. Chemicals

Surfactants used in the present work were cationic sas, BDH Analar (Cetyl trimethyl ammonium bromide CTAB and cetyl trimethyl pyridinium bromide CTYB). The

concentration of surfactant was ranged from 5×10^{-5} to 1×10^{-3} mol/L.

The apparatus used in the reduction of (Cr^{+6}) from the solution, consisted of an immersed iron cylinder in a 600 ml glass beaker containing 500 mL of experimental solution. The iron cylinder used in each run had 7cm length and 1.4 cm diameter, only the peripheral surface of the cylinder was exposed to the solution. The cylinder was rotated by means of variable speed motor whose speed was controlled by avaviac. The frequency of rotation recorded as revolution per second was counted by an optical tachometer.

Analar potassium dichromate and redistilled water containing 1.5 mol/L sulfuric acid (98% w/w) were used in the preparation of blank solution (0.05 mol/L) and in the presence of five different concentrations of ammonium salts. The rate of reaction was determined at different temperature (25, 30, 35 and 40°C) as well as at different cylinder rotation speeds 125, 250, 375and 500 r.p.m. The determination of hexavalent (Cr^{+6}) concentration was carried out at 365 nm using UV-160A spectrophotometer.

2.2. Reduction precipitation

The reduction precipitation (Katat, 2000) method finds wide applications in the treatment of chromium. It is economical and the removal efficiency is high (98-99 per cent). However, there are three steps involved in this methods:

1. PH adjustement
2. Reduction
3. Precipitation.

PH adjustement is achieved with the use of sulphuric acid whereby the pH is reduced to 2-3. At this level, the reduction of Cr^{+6} to Cr^{+3} can be achieved very efficiently. The equalization technique where acidic waste from some other plant is mixed with the liquid waste can also be used, thereby reducing the cost of treatment.

3. RESULTS AND DISCUSSION

Reduction of Cr^{+6} by iron cylinder takes place according to equation:

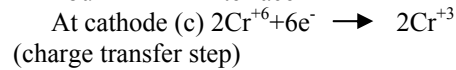
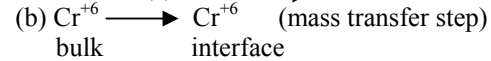
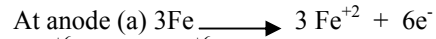
$$dC/dt = -K A^* C/V' \quad (1)$$

The rate controlling step was the diffusion of hexavalent chromium ions (Cr^{+6}) to the iron surface.

Assuming that (Cr^{+6}) concentration is negligible at iron solution interface, C is (Cr^{+6}) concentration represented in (mol l^{-1}) at time t (sec), K is the mass transfer coefficient which depends upon fluid flow and temperature (cm/sec), A^* is the exposed area of the iron cylinder (cm^2) and V' represents the volume of the solution (cm^3).

Accordingly, the rate of hexavalent chromium reduction is proportional to its concentration and the exposed iron area and

the mechanism of the reaction seems to be electrochemical in nature i.e it takes place through a galvanic cell where k act as a cell anode while Cr^{+6} reduction takes place at cathodic sites as follow



Integrating equation (1) leads to

$$\ln C_0/C = KA^* /V' \quad (2)$$

Where, C_0 is (Cr^{+6}) concentrations at zero time. Figs. 2 and 3 show the relation between $\log C_0/C$ against time for the blank solution and different concentrations of CTAB at 250 rpm. Tables (1, 2) and figures (1, 2) indicated that, the reaction is a first order reaction.

Table (1): First order rate constants ($k \cdot 10^3 \text{ sec}^{-1}$) for cementation on zinc metal in presence of CPYB at different temperatures and 250 rpm.

Conc. of CTAB x 10^{-5} M	10	20	30	50	100
Temp. ° C					
25	3.77	2.86	2.33	2.05	1.45
30	4.58	3.60	2.82	2.80	1.85
35	5.85	5.30	3.60	3.20	2.31
40	7.90	5.89	5.11	4.80	3.31

Table (2): First order rate constants ($k \cdot 10^3 \text{ sec}^{-1}$) for cementation on zinc metal in presence of CTAB at different temperatures and 250 rpm.

Conc. of CPYB x 10^{-5} M	10	20	30	50	100
Temp. ° C					
25	3.20	2.6	2.15	1.96	1.40
30	3.89	3.40	2.80	2.66	1.70
35	5.52	4.80	3.18	3.11	2.20
40	6.90	5.46	4.88	4.62	2.80

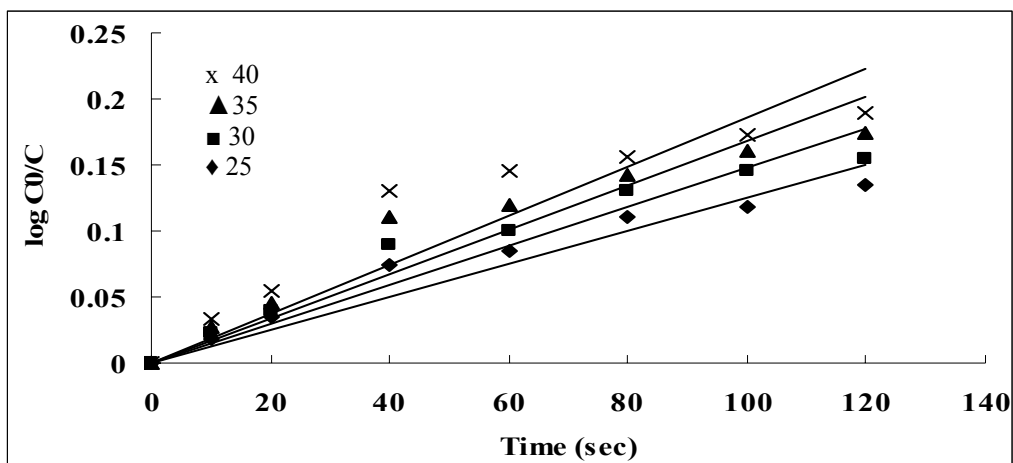


Fig. (1): The relation between $\log C_0/C$ & t for blank solution at 25° C and 250 rpm at different temperatures.

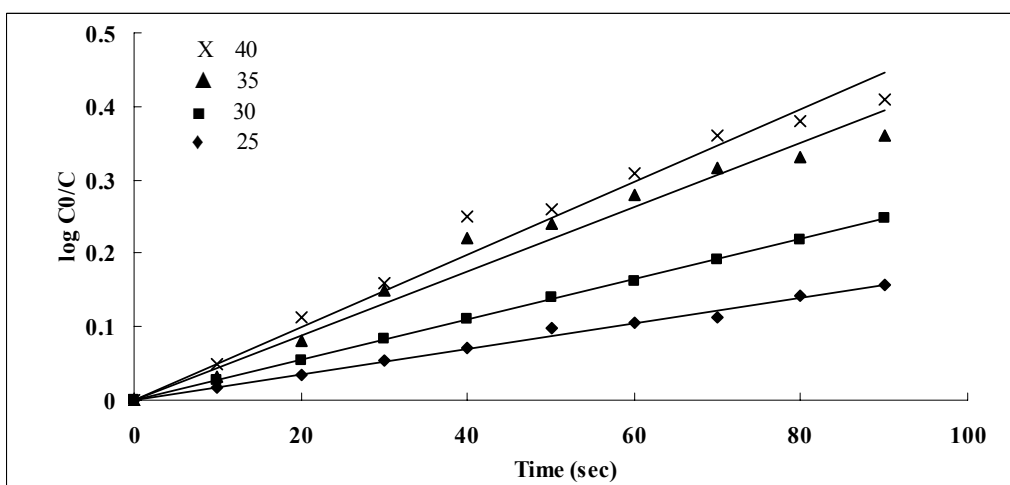


Fig. (2): The relation between $\log C_0/C$ & t for CTAB at 25° C and 250 rpm at different temperatures.

3.2 Effect of stirring on the reaction

Figure (3) gives the variation of $\log C_0/C$ with time at different speeds of rotation (rpm) of iron cylinder at 25°C for acidified 0.05 mol/L potassium dichromate solution as a blank solution and in the presence of SAS. The effect of rotational speed on the mass transfer coefficient (K) can also be used to determine whether a reaction is diffusion or chemically controlled. Table (2) confirm the fact that the reaction is diffusion controlled (Donmez *et al.*, 1999; Darweesh, 2004). The plots pass through origin, which prove that the cementation reaction is still a first order in presence of additives. The rate constant of reaction for different surfactant composition were calculated from the slopes of $\ln C_0/C$ Vs time lines. Tables (3) give the relation between % inhibition of SAS and concentration at 250 rpm and 25° at different temperatures. The cementation process is inhibited by addition of SAS. The percentage of inhibition for cementation reaction is calculated from the following relation:

$$\% \text{ inhibition} = \frac{k - k'}{k} 100 \quad (3)$$

where k is reaction rate constant in blank solution [250 rpm].

k' = rate constant of the reaction in presence of SAS. Table (3) gives the relation between the percentages of inhibition of the rate of cementation and SAS concentration at 25°C. The % inhibition depends on the types of SAS and its concentration. The order of cementation inhibition is blank < CPYB > CTAB.

The decrease in the rate of cementation in the presence of SAS may be attributed to:

(i) SAS may form a thin adsorbed film on the iron metal which leads to decrease the rate of reduction reaction; also adsorption of SAS on the surface depends mainly on the structure. CPYB which has aromatic ring which are adsorbed on the surface of the

metal more than CTAB which is aliphatic (Darweesh, 2004).

(ii) The decrease in the diffusion coefficient (D) of Cr^{+3} in solutions containing SAS is due to the increase in the interfacial viscosity η in accordance to Stokes-Einstein equation [Ismail *et al.*, 2001].

$$\eta \frac{D}{T} = \text{constant} \quad (4)$$

Where T is the absolute temperature. The increase in the interfacial viscosity is caused by the adsorption of SAS molecules on the iron surface. CPYB is more inhibitor than CTAB because it has more than one functional group.

The surfactants used in practical applications are usually mixture of surface-active components due to:

- i- The very high costs of pure substances production.
- ii-The surfactants mixture in many practical applications has much better properties than those of their individual components.

The values of rate of cementation k for mixed surfactants. Table (4) illustrated that the rate of reduction of Cr^{6+} on rotating zinc cylinder decreases on addition one surfactants to other due to synergism⁽¹⁸⁾. The values of synergism parameter S_1 were calculated by using the relationship given by Aramaki and Hackerman⁽¹⁹⁾

$$S_1 = \frac{I_{\text{mix}} - I}{I - I} \quad (5)$$

where I_{mix} is the rate of reduction in presence of mixed surfactants, I' is rate of reduction in presence of single surfactant and I is rate of reduction of blank.

Thermodynamic treatment of the reaction

From the integrated form of Arrhenius equation

$$\ln(1) = \frac{-E}{RT} + \ln(A) \quad (6)$$

where R is the gas constant, E is the activation energy and A is the frequency factor. The values of E are given in table (5).

The values for enthalpy of activation, ΔH^* , entropy of activation ΔS^* , and free energy of activation ΔG^* , can be obtained by using the following equations:

$$\Delta H^* = E - RT \quad (7)$$

$$\frac{\Delta S^*}{R} = \ln(A) - \ln\left(\frac{\alpha T e}{h}\right) \quad (8)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (9)$$

where α is the Boltzman constant, e is 2.7183 and h is Plank's constant.

Although the change in the free energy of activation, ΔG^* , with the SAS concentration for all used SAS is only small values, (Table

5), and variations occur in the enthalpy of activation values ΔH^* and the entropy of activation ΔS^* , with SAS concentration where in all these cases ΔH^* and ΔS^* compensate each other to produce little changes in ΔG^* .

However all the values of ΔS^* are highly negative values, indicating a more ordered system and non-random distribution of the SAS on the electrode. These values are independent of the type of SAS and the number of the substituent present in each SAS.

In general, the values of E and ΔH^* decreases as the SAS concentration decreases Table(5), which may be attributed to that; the SAS increases the local solution viscosity at the Fe surface with a consequent decrease in the diffusivity of Cr^{6+} ion. The SAS molecules decreases the natural convection flow arising from the density difference between the bulk solution and the solution at the electrode surface due to the repulsion force between the Fe and the NH_4^+ group of the SAS, leading to decrease the rate of oxidation.

Table (3): The relation between the percentage inhibition of SAS and concentration at 250 rpm and 25°C.

Conc. x 10 ⁻⁵ M	10	20	30	50	100
CTAB	29.7	46.2	56.20	61.47	72.70
CPYB	40.186	51.4	58.81	63.40	73.70

Table (4): The effect of mixed SAS on the rate of removal of Cr⁶⁺ at 25 °C.

$C_{\text{CPYB}} \cdot 10^5$ M	$C_{\text{CTAB}} \cdot 10^5$ M	$K_{\text{blank}} \times 10^3$ Sec ⁻¹	K in presence of mixed SAS Sec ⁻¹	% reduction
10	10	5.35	1.65	70.28
	20		1.56	70.9
	30		1.48	72.38
	50		1.42	73.50
	100		1.38	74.25
20	10	5.35	1.43	73.32
	20		1.39	74.06
	30		1.30	75.74
	50		1.18	78.00
	100		1.10	79.50
30	10	5.35	1.40	73.58
	20		1.31	76.00
	30		1.20	77.61
	50		1.11	79.29
	100		1.08	79.85
50	10	5.35	1.32	74.76
	20		1.23	77.0
	30		1.16	78.31
	50		1.10	79.4
	100		0.95	82.24
$C_{\text{CTAB}} \cdot 10^5$ M	$C_{\text{Triton-x-100}} \cdot 10^5$ M	$K_{\text{blank}} \times 10^3$ Sec ⁻¹	K in presence of mixed SAS Sec ⁻¹	% reduction
10	10	5.35	1.98	63.6
	20		1.89	65.65
	30		1.74	67.53
	50		1.68	68.65
	100		1.60	70.14
20	10	5.35	1.82	66.0
	20		1.70	68.28
	30		1.65	69.21
	50		1.54	71.26
	100		1.48	72.35
30	10	5.35	1.72	67.91
	20		1.68	68.65
	30		1.60	70.14
	50		1.51	71.81
	100		1.41	73.6
50	10	5.35	1.60	70.9
	20		1.52	71.58
	30		1.43	73.23
	50		1.32	75.33
	100		1.21	77.3

Table (5): Thermodynamic parameters of different SAS at 25°C.

C. 10 ⁵ mol/L	ΔG^* KJ mol/L	ΔH^* KJ mol/L	ΔS^* J K ⁻¹ mol/L
CTAB			
1	96.137±3.8	24.02±0.66	242±2.19
5	105.6±10.2	35.841±2.16	235±9.5
10	105.06±8.12	36.52±1.21	230±1.67
50	97.69±6.12	24.981±4.0	244±1.15
CPYB			
1	95.952±1.66	22.92±0.66	235±2.12
5	99.652±3.65	31.118±1.86	230±3.12
10	103.57±2.89	36.521±2.52	225±2.16
50	96.441±5.3	24.921±4.20	240±3.15
Blank			
1	92.73±6.72	37.42±3.4	185.53±11.1
5	93.2±9.6	35.34±4.8	194±15.96
10	93.85±9.2	36.27±4.66	193±15
50	93.92±6.85	42.75±3.47	171±11.3

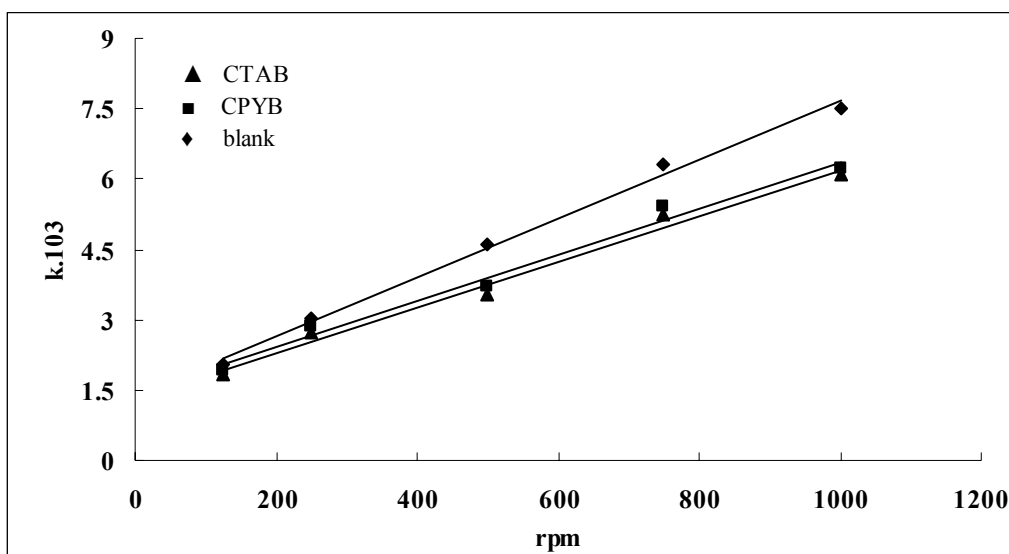


Fig. (3): The relation between rate constant and rpm at 25°C

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