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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 $\text{K}_2\text{Cr}_2\text{O}_7$ has been studied and it is found to be first order. The rate of reaction at 0.05 mole of $\text{K}_2\text{O}_2\text{O}_7$ have been measured in absence of quaternary Ammonium salts as CTAB and CPYB. The rates of reaction are also measured in presence of CTAB and CPYB at four different temperatures. Effects of rotations are also studied. The rate of reaction was decreased by addition of salts. Thermodynamic parameters ΔG^* , ΔH^* and ΔS^* are given.

INTRODUCTION

Chromium VI, the dangerous forms, is⁽²⁾ 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.

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.

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.

The threshold-limiting value for hexavalent chromium is 0.1 mg/1. 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.

Chromic acid and its salts are used as oxidizing agents in the manufacture of organic chemicals. They are also widely used in electroplating industries for the deposition of chromium metal. As much as 431 ppm of chromium is present in the rinse for a 20 l/min drag out (S.H.Jenkins,1987).

In fertilizer-industry waste, hexavalent chromium is between 20 and 30 ppm and must be removed before biological treatment. It finds its way into the liquid effluent through the blow-down of the cooling tower. Chromates and dichromate are present in the cooling water as scale and corrosion inhibitors. Blow-down is done when the total amount of dissolved solids in the water increases to around 700 ppm from an initial value of 100 ppm.

Chromium has been associated with soil infertility only *in* a few places because of high concentration. Chromium in the form of chromate chemicals is toxic to plant. Chromium VI is toxic to aquatic life. Chromium water concentration should not exceed 10 ppm for protection of aquatic species.

So removal of chromium VI or its conversion to chromium III is a substantial to protect our health and environment. Cementation is one way to fulfill this purpose. It is one of the oldest and simplest hydrometallurgical processes, which has been used as a means of extracting metals from solution. Only in the past 20 years, considerable attention has been paid to two main industrial applications of cementation.

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The first involves the recovery of metals from leach solution and the second is concerned with the purification of electrolyte solutions to remove metals which are more electropositive than the metal to be deposited, e.g. Cu, Co, Ni, Cd from ZnSO₄ electrolyte (E.C. Lec *et al.* 1978 & G. Power *et al.* 1987).

Many applications have been reported in industry [7-11] for the recovery of metals and purification of electrolyte solution. Almost all the authors have reported that electrochemistry of the reaction at room temperature is diffusion-controlled (Gehan M.El. Subburuiti *et al.* 1995)

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 (A.M. Esmail *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 (Tanaka 1976).

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 CTAES and CPYB.

MATERIALS AND METHODS

Experimental Technique

Chemicals

Surfactants used in the present work were cationic, BDH Analar (acetyl trimethyl ammonium bromide and acetyl trimethyl pyridinium bromide). The composition of surfactant was ranged from 5 x 10⁻⁵ to 1 x 10⁻³ mol l⁻¹.

Figure (1) is a block diagram of the apparatus used in the reduction of (Cr⁰) from the solution. The apparatus 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⁻¹ sulfuric acid (98% w/w) were used in the preparation of blank solution (0.05 mol l⁻¹) as well as 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 500, 375, 250 and 125 r.p.m. The determination of hexavalent (Cr⁺⁶) concentration was carried out at 365 nm using UV-I60A spectrophotometer through the equation(7).

Reduction precipitation

The reduction precipitation⁽¹⁴⁾ 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 adjustment
2. Reduction
3. Precipitation.

pH adjustment 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.

The order of the reaction

Reduction of Cr⁺⁶ by iron cylinder take place according to reaction:

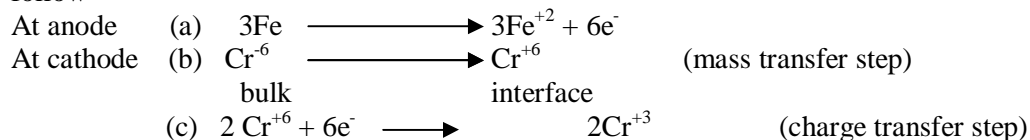
$$dC/dt = -KA*C/V \quad (1)$$

The kinetics of this reaction have been studied extensively⁽¹⁷⁾ where, the rate controlling step was found to be the diffusion of hexavalent chromium ions (Cr⁺⁶) to the iron surface. In such case, The rate of

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change of hexavalent chromium ions (Cr^{+6}) concentration in the solution is given by equation (1). 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 now and temperature (cm^2/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, the mechanism of the reaction seems to be electrochemical in nature i.e it take place through a galvanic cell where k act as a cell anode while Cr^{+6} reduction take place at cathodic sites as follow



Integrating equation (1) leads to

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

Where, C is (Cr^{+6}) concentrations at zero time.

Figure (2) and (3) shows the relation between $\log C_0/C$ against time for the blank solution as well as in the presence of different concentrations of CTAB at 250 rpm. Table (1. 2) and figures (2, 3) indicated that, the reaction is a first order reaction. Fig (2) shows the relation between $\log C_0/C$ against time blank solution while Fig (3) demonstrate the same relation at different concentration of CTAB at 250 rpm. 3.4 Effect of stirring on the reaction

Figure (4) give the variation of $\log C_0/C$ with time at different speed of rotation (rpm) of iron cylinder at 25°C for acidified 0.05 mol l⁻¹ potassium dichromate solution as a blank solution as well as 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, if the mass transfer coefficient increases with increasing stirring speed, then the reaction is diffusion controlled, if the mass transfer coefficient (K) is independent on stirring speed, then the reaction is chemically controlled. The data shown in table (2) confirm the fact that the reaction is diffusion controlled^(16 and 17).

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. Table (3) summarizes the obtained results at different temperatures. It is found that cementation process is inhibited by addition of SAS. The percentage of inhibition for cementation reaction is calculated from the following relation:

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

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

\bar{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. It was found that the % inhibition depending 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.

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CPYB which has aromatic ring which are adsorbed on the surface of the metal more than CTAB which is aliphatic⁽²⁰⁾.

(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

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

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 effect of binary mixture of surface active compounds or surfactants has been studied in several cases. In many industrial applications, surfactants are invariably mixtures as they are produced from feedstock containing mixed hydrocarbon chain length. It not only exhibits superior properties as compared to only singular surfactant but also can be produced at a relatively lower cost.

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

- i. The very high costs of pure substances production.
- ii. The fact that 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 are given in table (4). It is found that the rate of reduction of Cr⁶⁺ on rotating zinc cylinder decreases on addition one surfactants to other due to synergism⁽¹⁸⁾. The values of synergism parameter S_i was calculated by using the relationship given by Aramaki and Hackerman⁽⁹⁾

$$S_i = \frac{I_{\max} - I}{I' - I} \quad (5)$$

where I_{max} 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

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

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:

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

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

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

where a 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, (Table 5), and variations occur in the enthalpy of activation 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^* .

It is noticed that all values of ΔS^* are highly negative values, indicating a more ordered system and non-

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random distribution of the SAS on the electrode. These values are found to be independent of the type of SAS and the number of the substituent present in each SAS.

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

Conc. of CTAB $\times 10^{-5}$	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 temperature and 250 rpm.

Conc. of CTAB $\times 10^{-5}$	10	20	30	50	100
Temp. ° C					
25	3.20	2.6	2.15	1.96	1.40
30	3.89	4.80	2.80	2.66	1.70
35	5.52	5.46	3.18	3.11	2.20
40	6.9	5.46	4.88	4.62	20.80

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

Conc. of CTAB $\times 10^{-5}$	10	20	30	50	100
CTAB	29.7	46.2	56.20	61.47	72.70
CTAB	40.186	51.4	58.81	63.40	73.70

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

C _{CPYB} -10 ⁵ Mol l ⁻¹	C _{CTAB} -10 ⁵ Mol l ⁻¹	K _{blank} × 10 ³	K in presence of mixed SAS	% 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 20 30 50 100	5.35	1.43	73.32
			1.39	74.06
			1.30	75.74
			1.18	78.00
			1.10	79.50
30	10 20 30 50 100	5.35	1.40	73.58
			1.31	76.00
			1.20	77.61
			1.11	79.29
			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

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

C _{CTAB} - 10 ⁵ Mol l ⁻¹	C _{Triton-x-100} ·10 ⁵ Mol l ⁻¹	K _{blank} × 10 ³	K in presence of mixed SAS	% 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	69.23
	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

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

$C \cdot 10^5 \text{ mol l}^{-1}$	$\Delta G^* \text{ KJ mol l}^{-1}$	$\Delta H^* \text{ KJ mol l}^{-1}$	$\Delta S^* \text{ JK}^{-1} \text{ mol l}^{-1}$
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	96.44±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

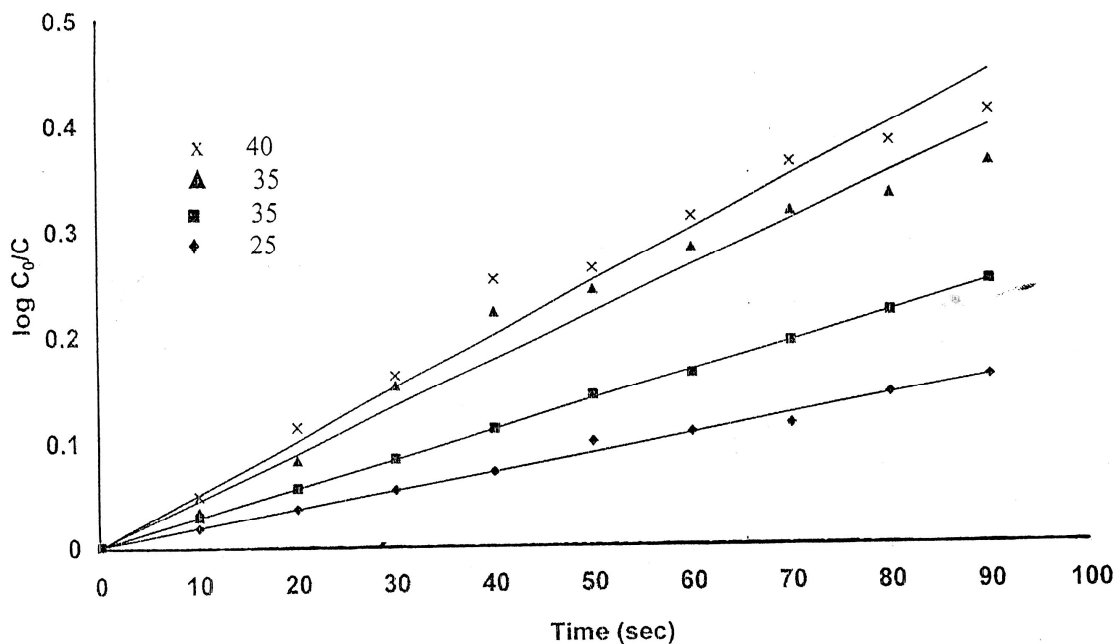


Figure (1): The relation between $\log C_0 / C$ & Time in (sec) for CTAB At 25°C And 250 rpm at different temperature.

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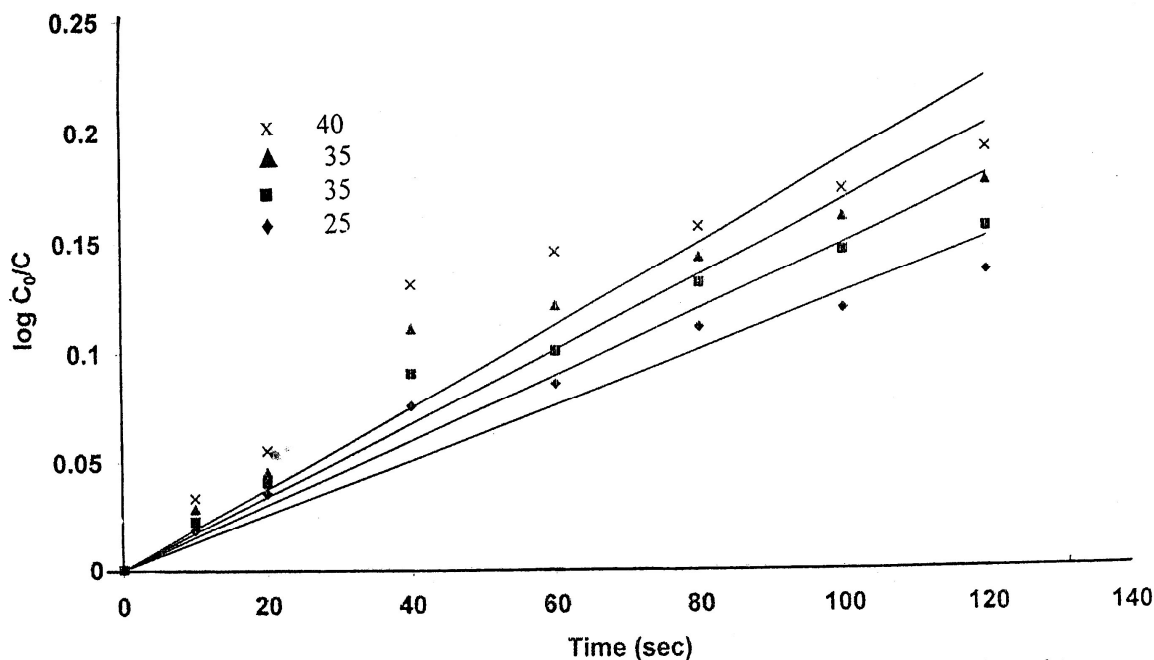


Figure (2): The relation between $\log C_0/C$ & Time in (sec) for blank solution At 25° C And 250 rpm at different temperature.

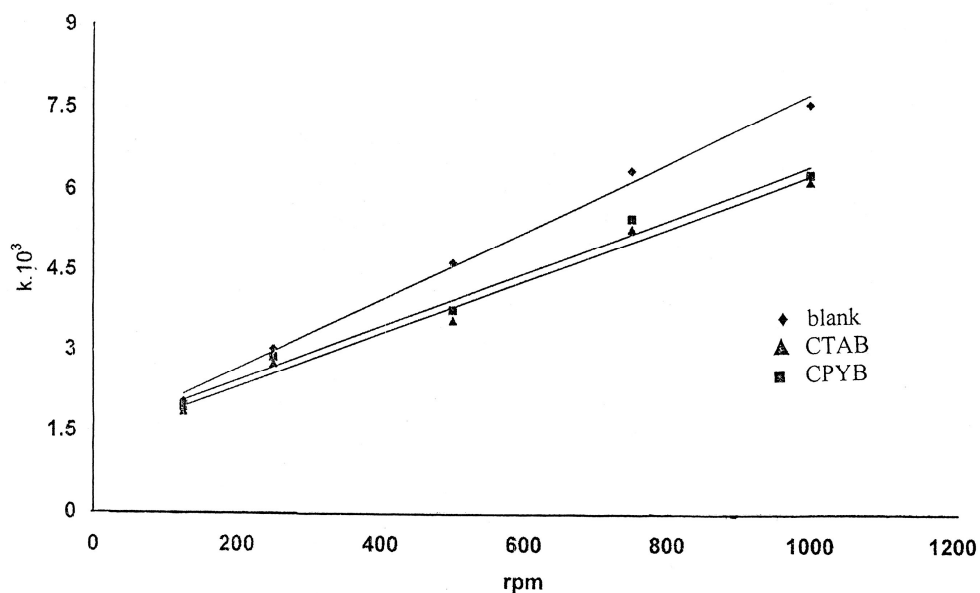


Figure (3): The relation between Rate Constant and rpm at 25° C

In general, it is found that the values of E and AH^* decreases as the SAS concentration decreases as shown in Table (5), which may be attributed to that; the SAS increase the local solution viscosity at the Fe surface with a consequent decrease in the diffusivity of Cr^{6+} ion, and, also, 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 in the rate of oxidation.

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