Reduction of Toxic Cr^{6+} Ions in Presence of Non Toxic Acid

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Abstract: Chromium VI is a toxic and carcinogenic element; it could be detected in waste water getting out from many industries as tannery, textile and electroplating of metals. Oxidation reduction process is the most economic and simple way of removing Cr^{6+} by conversion into Cr^{3+} (non hazard). The rate of reduction reaction of Cr^{6+} to Cr^{3+} in $K_2Cr_2O_7$ has been studied in absence of nontoxic acids and it is found to be first order reaction. Different acids as acetic acid, formic, glycinecitric acids were also tested at different temperatures and reactions. The rate of the reaction in each case was measured. Thermodynamic parameters ΔG*, ΔH* and ΔS* are estimated from the experimental measurements.

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1. Introduction

Environmental preservation is nowadays matter of deep concern; that is why much work has been done on this subject in the last years. The word "pollution" has no many presences in our lives, due to the great development in the industrial field. Pollution can be identified as very contaminants that could change the nature balance due to human levels (1). Water is essential for life, since it is required for various purposes in community life such as cocking, drinking, washing, warring gardens, etc. but as the community developed and with concentration of pollution in cities, the demand of water increases. Also, with the rapid industerlization-take place, a vast amount of water is required to run industries. Subsequently, amount of industrial wastes discharged into water resources increased, and the demand for industrial water treatment, particularly containing heavy metals, in necessary.

Heavy metals release in waste waters is one of the most worrying pollution causes. As it affects on life may particularly serious, referring to plants and animals (mainly fishes), or to man, reached indirectly by the toxics through food chain.

The removal of heavy metals from waste is a topic with great industrial importance, as there are a great number of large industries, which must spend millions of dollars each year to deal with this issue. The most common heavy metals to be removed are: cadmium, chromium, cobalt, copper, lead, manganeses, mercury, vanadium and zinc.

There are many industries where process operations results in large quantities of the pollutants in the effluents being discharged, e.g., refineries, gas, gas undertakings, alloys, electroplating rinse solution, metal finishing industries and reach and effluent solutions from the manufacture of chemicals.

Processes of metal removal from waste water effluents must be selected to remove the metal either in this existing form, or converted to a form suitable for the removal processes. In general, metals must either be precipitated or else attached to an insoluble species, e.g. through adsorption or ion exchange (2).

Chromium:

Chromium is steel-grey, lustrous, hard, metallic, and takes a high polish. Its compounds are toxic. It is found as chromites ore. Siberian red lead (crocoites $PbCrO_4$) is a chromium ore prized as a red pigment for oil paints (3).

Chromium exists in several valence states, ranging from chromium (III) to chromium (VI). However, the three major forms of chromium that commonly exist in the environment are chromium (0), chromium (III) and chromium (VI). Only trivalent and hexavalent are biologically significant (4). Hexavalent chromium compound appear to be 10 to 100 times more toxic than their Cr^{3+} counterparts when both are administers the oral route (5). Metallic chromium (0) is relatively non toxic.

1.3 Hexavalent chromium

Hexavalent chromium compounds are chromium trioxide, chromium anhydride, chromium acid and dichromate salts.

Cr^{6+}, a know carcinogen, forms relatively soluble precipitates, and dose not absorb readily. Cr^{6+} is carcinogenic because it is highly reactive interacting with the body's chemistry and functions (6-9).

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 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.

Cementation 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. The first involves the recovery of metals from leach solution (10-12) 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 $ZnSO_4$ electrolyte (13-15).

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 (20).

The most important source of chromium pollution is dusterial. Hexavalent chromium compounds causes dermatitis (21), 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 (22).

Aim of work

The objective of the present work is devoted to study the kinetics of the reduction of Cr^{+6} to Cr^{3+} on rotating iron cylinder in presence of some non toxic organic acids at different concentrations and different rpm to remove as much as possible the Cr^{+6} from waste water.

2. Experimental work

Figure (1) is a block diagram of the apparatus used in recovery of (Cr^{+6}) from the solution which permits the rotation of an immersed iron cylinder in a 600ml glass beaker containing 499ml of experimental solution. The iron cylinder used in each run is of 7cm length and 1.4cm diameter, only the peripheral surface of pure iron was exposed to the solution. The cylinder was rotated in experimental solution with variable speed motor. The frequency of rotation recorded as revolution per second was counted by an optical tachometer.

Kinetic measurement

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 acid. The rate of reaction was determined at different temperature 25, 30, 35 and 40°C as well as at different rotations 650, 500, 375, 250 and 125 r.p.m. Analar 4 non toxic acids were used.

Through the proceeding reaction, at different time intervals 10, 20, 30 minutes, 1ml sample was taken from reaction solution and diluted to 10ml by redistilled water. The determination of hexavalent (Cr^{+6}) concentration was carried out at 365 nm using UV-160A spectrophotometer through the equation (7).

3. Results and Discussion

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 (environmental protection agency 1985) 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.

Chromic acid and its salts are used in tanning industries and as oxidizing agents in the manufacture of organic chemicals. They are also widely used in electroplating industries for the deposition of chromium metal (16).

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 dichromates 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.

Reduction precipitation

The reduction precipitation (7, 9) 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.

3.3 The order of the reaction

In our work, oxidation-reduction reaction between potassium dichromate and iron takes place to produce trivalent chromium ions (Cr^{+3}). The kinetics of this reaction have been studied extensively (23-25) where, the rate controlling step was found to be the diffusion of hexavalent chromium ions (Cr^{+6}) to iron surface. In such case, the rate of change of hexavalent chromium ions (Cr^{+6}) concentration in the solution is followed as in equation (1)

$$\frac{dc}{dt} = -KA^* \frac{C}{V} \qquad (1)$$

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 flow and temperature conditions (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 decreasing the hexavalent chromium ions (Cr^{+6}) concentration is proportional to its concentration and the exposed iron area, the mechanism of the reaction seems to be electrochemical in nature i.e. it takes place through a galvanic cell where Fe act as the cell anode where Cr^{6+} reduction take place at cathode site as follows

Reaction at the anode (a) $3Fe \longrightarrow Fe^{+2} + 6e^-$ (dissolution of metal in acidic medium)

Reaction at the cathode (b) $\underset{\text{bulk}}{Cr^{+6}} \longrightarrow \underset{\text{interface}}{Cr^{+6}}$ (mass transfer step)

(c) $Cr^{+6} + 6e^- \longrightarrow Cr^{+3}$ (charge transfer step)

This reaction is diffusion controlled whose rate in a batch reactor can be represented by integration equation (2)

$$\ln C_o/C = KA^* /V' \qquad (2)$$

This equation may be represented as a straight line where, C_o is (Cr^{+6}) concentrations at zero time and the other symbols have the definition mentioned above. Figure (2) shows the relation between log C_0/C against time for the blank solution while figure (3) demonstrate the relation between log C_0/C against time at different concentrations of acetic acid at 250 rpm. Table (1) and figures (2,3) show that, the reaction is a first order reaction in according to equation (1) and (2).

The rate constant of reaction for different acetic acid derivatives composition were calculated from the slopes of $\ln C_0/C$ Vs time lines. Table (1) summarizes the obtained results at different temperatures. It is found that Cr^{+6} reduction process is inhibited by addition of acids. The percentage of inhibition for Cr^{+6} reduction is calculated from the following relation:

$$\% \text{ inhibition} = \frac{k - \bar{k}}{k} 100 \qquad (4)$$

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

$\bar{k}$ = rate constant of the reaction in presence of organic acid. Table (3) gives the relation between the percentages of inhibition of the rate of Cr^{+6} reduction and organic acid concentration at 25° C. It was found that the % inhibition depending on the types of organic acid and its concentration. The order of Cr^{+6} reduction inhibition is

citric >glycine> Acetic acid > formic

The decrease in the rate of Cr^{+6} reduction in the presence of acid may be attributed to:

Organic acid may form a thin adsorbed film on the iron metal which leads to decrease the rate of reduction reaction, also adsorption of organic acid on the surface depends mainly on the structure. Citric, glycine have more than one functional group which are adsorbed on the surface of the metal more than acetic acid which has one functional group (25, 26).

(i) The decrease in the diffusion coefficient (D); of Cr^{+3} in solutions containing acids is due to the increase in the interfacial viscosity η in accordance to Stokes-Einstein equation (9, 10)

$$\eta \frac{D}{T} = \text{constant} \qquad (5)$$

Where T is the absolute temperature. The increase in the interfacial viscosity is caused by the adsorption of acids molecules on the iron surface.

Trichloro acetic acid is more inhibitors than other because it has more than one functional group. From table (3) it is obvious that the order of decreasing the rate of reduction as follows:

Formic <Acetic <glycine< Citric

3.4 Effect of stirring on the reaction

Figures (4,5) give the variation of log C_0/C with time at different speed of rotation (rpm) of iron cylinder at 25^0C for acidified 0.05 mol l^{-1} potassium dichromate solution as a blank solution as well as in the presence of formic acid. The effect of rotational speed on the mass transfer coefficient (K) can also be used to determine whether the 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 (3) represent that the reaction is diffusion controlled (16 and 17).

Adsorption isotherm

The degree of surface coverage θ was calculated by the relation

$$\theta = \frac{K - \overline{K}}{K} \qquad (6)$$

$\overline{K}$ = rate of the reaction for blank solution

K = rate of the reaction in presence of additive

The adsorption of surfactant on Zn electrode is found to obey Langmuir isotherm equation (7)

$$\frac{\theta}{1-\theta} = Ac\left[\exp\frac{\Delta G}{RT}\right] \qquad (7)$$

where A = constant

C = concentration of organic substances

ΔG = energy of adsorption

R = Gas constant, [8.314 $J.mol^{-1}.l^{-1}$]

Fig. (4) and table (4) represents a typical plot of log (θ/1-θ) vs. log c which would give straight line. The slopes of the curves are nearly equal to unity and are reasonably linear in accordance with Langmuir isotherm equation (7).

It has been postulated on the derivation of Langmuir isotherm that adsorbed molecules do not interact with each other (15). Interaction of adsorbed species by mutual repulsion or attraction would make the slope of the plot deviate from unity.

Thermodynamic treatment of the reaction

From the integrated form of Arrhenius equation

$$\ln K = \frac{-E}{RT} + \ln(A) \qquad (2)$$

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 (6).

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:

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

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

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

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 acids concentration for all used acids is only small, (Tables 6), and variations occur in the enthalpy of activation ΔH* and the entropy of activation ΔS*, with acids 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-random distribution of the acids on the electrode. These values are found to be independent of the type of acids and the number of the substituent present in each acid, where these acids compounds affect the process by dissolution of copper metal.

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

Table (1) The values of rate constants ($k.10^3$) for solution of different concentration of acids at 25°C and 250 rpm.

Acid	Conc. 10^4 mol l^{-1}					
	0.0	0.5	1	5	10	50
	k. 10^3 sec^{-1}					
Acetic	7.6	5.7	4.4	3.3	2.7	2.0
Monochloro Acetic	7.6	5.00	3.85	3.1	2.65	1.90
Dichloro Acetic	7.6	4.6	3.53	2.90	2.60	1.82
Trichloro Acetic	7.6	4.4	3.40	2.81	2.51	1.71

The values of the rate constants k. 10^3 at different temperatures for all acids and at 250 rpm c = 1x 10^{-4} mol. l^{-1}

Table (2a) The values of rate constant for blank solution at different rpm and 25˚C.

Acid	Temperature			
	25	30	35	40
Acetic Acid	4.3	5.14	6.12	7.18
Formic Acid	3.85	4.55	5.55	6.53
Glyceric Acid	3.53	4.28	5.23	6.34
Citric Acid	3.4	4.2	5.01	6.10

Table (2b) The values of rate constant for solutions in presence of $5x10^{-5}$ mol l^{-1} CH_3COOH.

rpm	**k. 10^3**
125	2.13
250	3.11
375	4.70
500	7.60

rpm	**k. 10^3**
125	1.22
250	1.75
375	3.10
500	4.7

Table (3) :The values of percentage inhibition for all acids at 25˚C and 250 rpm.

Acids	Conc. 10^4				
	0.5	1	5	10	50
Formic Acid	25	39.3	56.57	64.5	73.7
Acetic Acid	34.2	49.3	59.21	65.5	75.0
Glyceric Acid	39.47	53.55	61.85	66	76.1
Citric Acid	42.1	55.26	63.0	67	77.5

Table (4):The values of the rate constants k.10^3 for solution in presence of different concentration of acids at different temperatures and 250 rpm.

C.10^4 mol l^{-1} T˚C	0.0	0.5	1.0	2.0	3.0	4.0	5.0
a) Formic acid							
25	7.7	5.7	4.4	3.3	2.66	2.2	2.0
30	8.5	6.6	5.2	3.7	3.2	2.63	2.37
35	9.86	7.91	6.15	4.75	3.7	3.3	3.1
40	11.11	9.1	7.3	5.61	4.7	4.0	3.7
b) Acetic acid							
25	7.6	5.70	3.85	2.95	2.30	2.0	1.63
30	8.5	6.0	4.6	3.55	2.70	4.33	2.1
35	9.86	7.20	5.65	4.30	3.43	3.2	2.7
40	11.11	8.50	6.8	5.25	4.21	3.8	3.3
C)glycineacid							
25	7.6	4.6	3.6	2.6	2.1	1.7	1.3
30	8.5	5.6	4.3	3.15	2.15	2.15	1.7
35	9.86	6.8	5.3	3.8	3.1	2.7	2.10
40	11.11	8.10	6.4	4.7	3.8	3.31	2.7
c) Citric acid							
25	7.6	4.4	3.4	3.01	2.9	2.7	2.6
30	8.5	5.2	4.0	3.3	3.2	3.1	2.5
35	9.86	6.3	5.4	5.2	4.8	4.5	4.2
40	11.11	8.0	6.2	5.4	5.1	4.8	4.7

Table (5): The relation between the degree of coverage and concentration of acid

Acids	$C.10^4$ Mol. l^{-1}	θ	$1-\theta$	$\frac{\theta}{1-\theta}$	$\log\frac{\theta}{1-\theta}$	log C
Acetic Acid	0.5	0.342	0.658	0.519	-1.715	-5.30
	1	0.493	0.507	0.972	-1.9878	-5.0
	5	0.592	0.408	1.45	0.1616	-4.30
	10	0.655	0.345	1.898	0.278	-4.00
	50	0.75	0.25	3.0	0.477	-3.20
Formic Acid	0.5	0.25	0.75	0.333	-0.477	-5.30
	1	0.343	0.607	0.647	-0.188	-5.0
	5	0.566	0.454	1.246	0.096	-4.30
	10	0.645	0.455	1.417	0.1513	-4.00
	50	0.737	0.263	2.802	0.448	-3.20
Glyceric Acid	0.5	0.395	0.605	0.6528	-0.185	-5.30
	1	0.536	0.464	1.155	0.063	-5.0
	5	0.619	0.38	1.628	0.212	-4.30
	10	0.66	0.34	1.941	0.288	-4.00
	50	0.755	0.25	3.00	0.477	-3.20
Citric Acid	0.5	0.421	0.589	0.721	-0.14	-5.30
	1	0.553	0.447	1.237	0.092	-5.0
	5	0.63	0.37	1.70	0.230	-4.30
	10	0.67	0.33	2.030	0.31	-4.00
	50	0.775	0.225	3.444	0.537	-3.20

Table (6): Thermodynamic parameters for all acid used

Acid	**Parameter**	**C x 10^4 (mol / l^{-1})**						
		0	**0.5**	**1.0**	**2.0**	**3.0**	**4.0**	**5.0**
Acetic Acid	E	19.986	26.20	29.683	29.817	31.518	34.4	36.9
	ΔH	17.507	23.70	27.207	27.338	29.04	32.11	34.3
	-ΔS	226.8	210.5	199.95	201.7	198.11	188	183
	ΔG	85.13	86.00	86.819	87.500	88.1	88.6	88.9
Formic Acid	E	19.986	24.603	26.188	28.568	28.71	31.36	32.891
	ΔH	17.507	22.125	23.709	26.09	26.262	28.881	30.30
	-ΔS	226.8	213.7	210.5	205	206.2	194.0	195
	ΔG	85.13	85.84	86.479	87.25	87.742	88.215	85.461
Glyceric Acid	E	19.986	29.382	21.35	30.56	33.21	34.6	37.3
	ΔH	17.507	26.90	18.875	28.00	30.73	32.1	34.9
	-ΔS	226.8	199.0	228	200.5	193	190	183
	ΔG	85.13	85.357	86.895	87.79	88.9	88.8	89.50
Citric Acid	E	19.986	19.04	32.655	34.31	32.6	32.62	33.8
	ΔH	17.507	16.67	30.1	31.833	30.13	30.1	31.3
	-ΔS	226.8	234.1	191	186.6	192	193	189.4
	ΔG	85.13	86.4	87.14	87.50	87.57	87.5	87.9

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