



Trade Science Inc.

Environmental Science

An Indian Journal

Current Research Paper

ESAIJ, 2(1), 2007 [75-82]

Reduction Of Toxic Cr⁶⁺ Ions In Presence Of Acetic Acid Derivatives



Corresponding Author

Howaida M.El-Kashlan
Faculty of Education, Physics and chemistry
Department, Alexandria University,
Alexandria, (EGYPT)
Email: helkashlan@hotmail.com



Co-Author

Dalia M.S.A.Salem
National Institute of Oceanography and Fishening, Kayet-Bey,
Alexandria, (EGYPT)

Received: 6th December, 2006Accepted: 21st December, 2006Web Publication Date: 27th December, 2006

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 Cr⁶⁺ by conversion into Cr³⁺ (non hazard). The rate of reduction reaction of Cr⁶⁺ to Cr³⁺ in K₂Cr₂O₇ has been studied in absence of nontoxic acids and it is found to be first order reaction. Different acids as acetic acid, mono, di and trichloro acetic acid were also tested at different temperature and reaction. The rate of the reaction in each case was measured. Thermodynamic parameters ΔG*, ΔH* and ΔS* are given. © 2007 Trade Science Inc. - INDIA

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 cooking,

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 industrialization taking 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

Current Research Paper

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, manganese, 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].

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 industrial. 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.

EXPERIMENTAL

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.

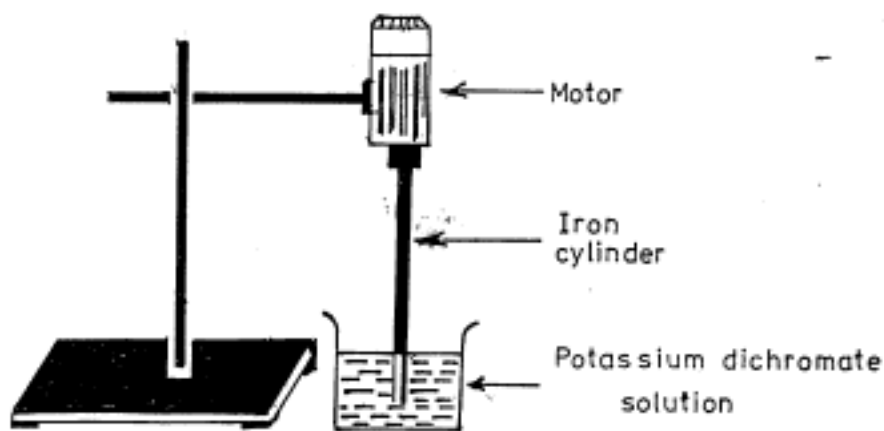


Figure 1: Diagram of apparatus

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 method:

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

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)

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

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 electrochemi-

Current Research Paper

cal in nature i.e. it takes place through a galvanic cell where Fe act as the cell anode where Cr⁶⁺ reduction take place at cathode site as follows

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

At cathode (b) $\text{Cr}^{6+} \xrightarrow{\text{bulk}} \text{Cr}^{+6} \xrightarrow{\text{interfac}} \text{Cr}^{+6}$ (mass transfer step)

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

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

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

This equation may be represented as a straight line where, C_0 is (Cr⁶⁺) 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 and 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 Cr⁶⁺ reduction process is inhibited by addition of acids. The percentage of inhibition for Cr⁶⁺ reduction is calculated from the following relation:

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

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

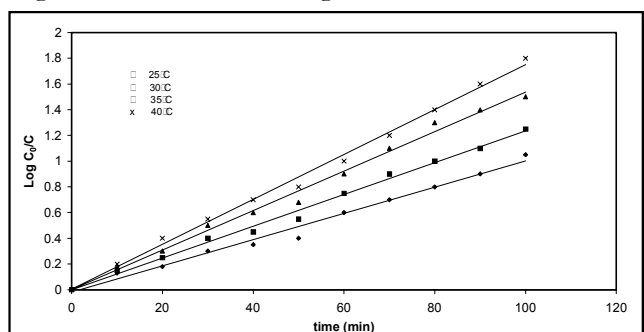


Figure 2: The relation between $\log C_0/C$ and time for blank solution at different temperature

TABLE 1: The values of rate constants ($k \cdot 10^3$) 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
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

TABLE 2: The values of percentage inhibition for all acids at 25°C and 250 rpm.

Acids	Conc. 10^4				
	0.5	1	5	10	50
Acetic	25	39.3	56.57	64.5	73.7
Monochloro acetic	34.2	49.3	59.21	65.5	75.0
Dichloro acetic	39.47	53.55	61.85	66	76.1
Trichloro acetic	42.1	55.26	63.0	67	77.5

the percentages of inhibition of the rate of Cr⁶⁺ 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 Cr⁶⁺ reduction inhibition is

Trichloro > Dichloro > chloro > Acetic acid

The decrease in the rate of Cr⁶⁺ 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. Trichloroacetic acid, dichloroacetic acid, chloroacetic acid and acetic acid have more than one functional group which is adsorbed on the surface of the metal more than acetic acid which has one functional group^[25,26].

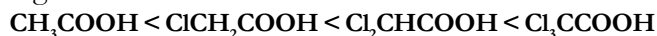
The decrease in the diffusion coefficient (D); of Cr³⁺ in solutions containing acids is due to the increase in the interfacial viscosity η in accordance to Stokes-Einstein equation^[9, 10]

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

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

Current Research Paper

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:



Effect of stirring on the reaction

Figure 3 gives 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 acetic 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, 17].

Adsorption isotherm

The degree of surface coverage θ was calculated by the relation

$$\theta = \frac{\bar{k} - k}{\bar{k}} \quad (5)$$

\bar{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 (6)

$$\frac{\theta}{1-\theta} = Ac \left[\exp \frac{\Delta G}{RT} \right] \quad (6)$$

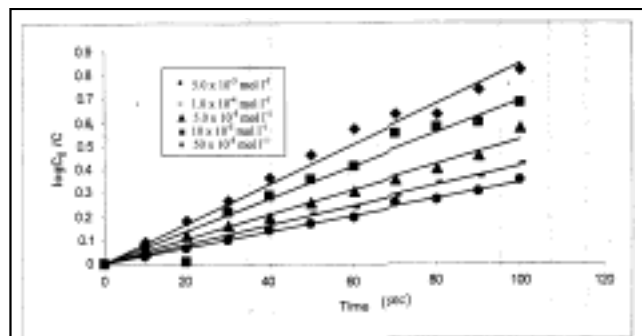


Figure 3: The relation between $\log C/C_0$ & t for different concentration of acetic acid at 25°C and 250 rpm

TABLE 3: The values of rate constant for blank solution and acids at different rpm and 25°C

Rpm	Acids				
	Blank	Acetic	Monochloro acetic	Dichloro acetic	Trichloro acetic
125	2.13	1.22	1.1	1.08	1.05
250	3.11	1.75	1.55	1.45	1.35
375	4.70	4.5	4.30	4.1	3.9
500	7.60	6.2	5.6	5.1	4.4
650	9.5	8.0	7.1	6.3	5.5

where A = constant

C = concentration of organic substances

ΔG = energy of adsorption

R = Gas constant, [8.314 J.mol⁻¹.l⁻¹]

Figure 4 and TABLE 4 represents a typical plot of $\log (\theta/1-\theta)$ 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 (6).

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

$$\ln K = \frac{-E}{RT} + \ln(A) \quad (7)$$

where R is the gas constant, E is the activation energy and A is the frequency factor. The values of E are calculated from 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:

$$\Delta H^* = E - RT \quad (8)$$

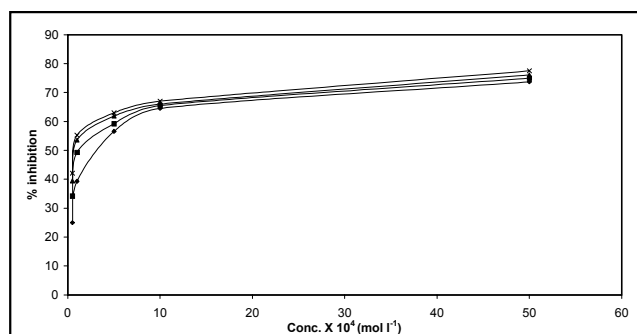


Figure 4: The relation between % inhibition and concentration of all acids at 25°C and 250 rpm

Current Research Paper

TABLE 4: The relation between the degree of coverage and concentration of acid

Acids	C.10 ⁴ Mol. l ⁻¹	θ	1-θ	$\frac{\theta}{1-\theta}$	$\log \frac{\theta}{1-\theta}$	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
Monochloro acetic	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
Dichloro acetic	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
Trichloro acetic	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 5: The values of the rate constants k.10³ for solution in presence of different concentration of acids at different temperatures and 250 rpm.

C.10 ⁴ mol l ⁻¹	0.0	0.5	1.0	2.0	3.0	4.0	5.0
T°C							
a) Acetic acid							
25	7.6	5.7	3.85	2.95	2.30	2.0	1.63
30	8.5	6.2	4.6	3.55	2.70	4.33	2.1
35	9.86	7.2	5.65	4.30	3.43	3.2	2.7
40	11.11	8.5	6.8	5.25	4.21	3.8	3.3
b) Monochloro acetic acid							
25	7.6	5.70	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	7.13	5.61	4.7	4.0	3.7
c) Dichloro acetic acid							
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	6.6	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) Trichloro acetic 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

$$\frac{\Delta S^*}{R} = \ln(A) - \ln\left(\frac{\alpha T e}{h}\right) \quad (9)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (10)$$

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 Cr⁶⁺ 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.

Current Research Paper

TABLE 6: Thermodynamic parameters for all acid used

Acid	Parameter	$C \times 10^4 \text{ (mol / l}^{-1}\text{)}$						
		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
	$-\Delta S$	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
Monochloro acetic 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
	$-\Delta S$	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
Dichloro acetic 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
	$-\Delta S$	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
Trichloro acetic 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
	$-\Delta S$	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

TABLE 7: The values of the rate constants k. 10^3 at different temperatures for all acids and at 250 rpm $c = 1 \times 10^{-4} \text{ mol.l}^{-1}$

Acids	Conc. 10^4				
	0.5	1	5	10	50
Acetic acid	25	39.3	56.57	64.5	73.7
Monochloro acetic	34.2	49.3	59.21	65.5	75.0
Dichloro acetic	39.47	53.55	61.85	66	76.1
Trichloro acetic	42.1	55.26	63.0	67	77.5

REFERENCES

- [1] B.J.Alloway, D.C.Ayres; 'Chemical Principles of Environmental Pollution', Blackie Academic and Professional, London, 1st Ed., 5 (1993).
- [2] C.Metcalf, A.Eddy; 'Water Resources and Environmental Engineering', McGraw-Hill Book Company, New York, (1972).
- [3] A.M.Ahmed, M.A.AKatat; Kinetic Study of Removal of (Cr^{+6}) on Rotating Iron Cylinder in Presence of Sulfur Compounds, M.Sc., Alexandria University, Egypt, (2000).
- [4] L.M.Mayer, L.L.Schick; Environ.Sci.Technol., **15**, 1482 (1981).
- [5] S.A.Katz, H.Salem; J.Appl.Toxicol., **13**, 217 (1993).
- [6] D.B.Singh, D.C.Rupainwar, G.Prasad; J.Chem.Tech. Biotechnol., **53**, 127-131 (1992).
- [7] D.Gang, S.K.Banerji, T.E.Clevenger; Proceeding of the Conference on Hazardous Waste Research, Columbia, Missouri, 64-67 (2002).
- [8] V.B.Vouk; 'Hand Book on The Toxicology of Metals', Amsterdam, New York, Oxford, Elsevier Science publishers, (1979).
- [9] F.M.M.Morel, J.G.Hering; 'Principles And Applications of Aquatic Chemistry', Wiley press, New York, N.Y, (1993).
- [10] 'A Guide to Everyday Pollution Hazards', by John Harte, Cheryl Holdren, Richard Schneider, and Christine Shirtey, Printed in the United States of America Copyright by the Regents of the University of California (1991).
- [11] A.K.Biswas, W.G.Daven; 'Extractive Metallurgy of Copper', Pergamon Press, New York, (1979).
- [12] V.Ettel; 'Comprehensive Treatise in Electrochemistry', **2**, Ed J O'M Bockris, Plenum, New York, (1981).
- [13] P.Bro, K.C.Lang; Environ.Sci.Technol., **8**, 925 (1974).
- [14] G.Genon, P.Parti; Gaglia Chim.Ind.(Milan), **65**, 79 (1983).
- [15] D.J.Hendrickson, M.M.Benjamin, J.F.Ferguson, L.Goebel; J.Water Pollution Control Federation, **5**, 468, (1984).
- [16] J.P.Gould, M.Y.Masingale, Miller; J.Water Pollution Control Federation, **3**, 280, (1984).
- [17] Y.Ku, C.Chen; Sep.Sci.Tech, **27**, 1259 (1992).
- [18] D.J.Mackinnon, T.R.Ingraham; Can.Metall.Q., **10**, 197 (1971).
- [19] D.J.Mackinnon, T.R.Ingraham, R.Kerby; Can.Metall. Q., **10**, 165 (1971).
- [20] R.M.Nadakarni, C.E.Jelden, K.C.Bowles, H.E. Flanders, M.W.Wadsworth; Trans.Metall.Soc. AIME, **239**, 581 (1980).
- [21] R.M.Nadakarni, M.W.Wadsworth; Trans.Metall.Soc.

Current Research Paper

- AIME, **239**, 1066 (1967).
- [22] Environmental Health Criteria 61, 'Chromium' World Health Organization, Geneva, (1988).
- [23] P.Bigaliev, A.Montaldi, E.Majone; Carcinogenesis, **3**, 1333 (1982).
- [24] G.M.El Subruiti, A.M.Ahmed; Alex Eng.J., **33**, 69 (1995).
- [25] Environmental Protection Agency, Health Assessment Document for Chromium. Final report. EPA 600/8-83-014F, D.C.Washington, (1985).
- [26] E.F.Saad, E.A.Hamed, A.A.El-Bardan, A.M.Ahmed; Bull. of Electrochemistry, **7**, 87 (1991).
- [27] National Research Council Chromium, D.C.Washington, Committee on Biologic effects of Atmospheric Pollutants, National Academy of Science, (1974).