MINIMIZATION OF CHLORIDE AND SULPHATE IONS CONCENTRATIONS IN THE EFFLUENTS FROM AN ELECTROPLATING PLANT

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Abstract

The present research deals with the study of the minimization of chloride and sulphate ion concentrations in the effluents from an electroplating plant. Material balance was performed to find the maximum allowable effluents (i.e. hexavalent chromium and cyanide) concentrations.

Cyanide oxidation and chromate reductions were simulated using potentiometeric titration at constant current with two polarized electrodes (platinum). Effects of current, temperatures, hydrogen ion concentration, initial concentration and quality of wastewater on the titration processes were studied, and it was found that the optimum potentiometeric titration endpoints (set points) are:

Process	Voltage (V) Current (µA) 2	5	10
Chromate Reduction	0.301	0.374	0.479
Cyanide Oxidation	0.721	0.874	1.119
Cyanate Oxidation	0.312	0.375	0.487

Introduction

In most parts of the world the authorities set acceptance standards for the discharge of industrial-effluents into sewers and watercourses, therefore effluent treatment is necessary. Chemical methods are still used widely and effectively for the treatment of effluents from electroplating processes (1).

Cyanide is oxidized in the, alkaline stream by sodium hypochlorite at pH = 11-11.5 in two stages, where the cyanide is oxidized to cyanate which in term oxidized to bicarbonate (2,3). Chromates are reduced in the acid stream by sodium bisulphite at pH= 2.5 (4,5). The two flows are brought together in the neutralizing section of the plant. Sulphuric acid or caustic soda is added at the neutralizing stage to adjust pH to the optimum value (8-8.5) for the precipitation of the heavy metals as hydroxides (1), which are then settled out as sludge. The sludge is drawn off for dewatering and disposed off as semi-solid cake (6).

Cyanide oxidation and chromate reductions are controlled by redox sensors, which are operating, by the mechanism of potentiometric titration at constant current with two polarized electrodes (7,8).

Sulphate and chloride ions are the final products of the above mentioned treatment reactions (9,10) Therefore, the concentrations of these ions are controlled by:

A. The concentrations of the effluents (i.e. hexavalent chromium and cyanide). The maximum allowable concentrations can be calculated by making a material balance.

B. The amounts of agents added. Optimum amounts of the oxidizing and reducing agents can be achieved using the redox sensors.

Experimental

A. Material Balance:

Material balance was performed in order to see the maximum effluent concentrations (i.e. chromate and cyanide) that may be allowed to enter the effluent treatment plant without producing sulphate and chloride ion concentrations higher than the permissible levels. The calculation was made on the bases of trial and error, where in each trial the effluent concentrations were changed to see the effect on the sulphate and chloride concentrations.

B. Apparatus

The apparatus for potentiometric titration study are shown schematically in Figs. (1 and 2). The electric circuit consist of:

D.C. power supply type Farnell with fine adjustment. Voltmeter type 3467. A logging multi-meter. Galvanometer (10 A) type W.G. PYE. Digital Ammeter type PM 2552-Philips. And two identical platinum electrodes (0.6x0.6) cm supplied by Cambridge Institute Company.

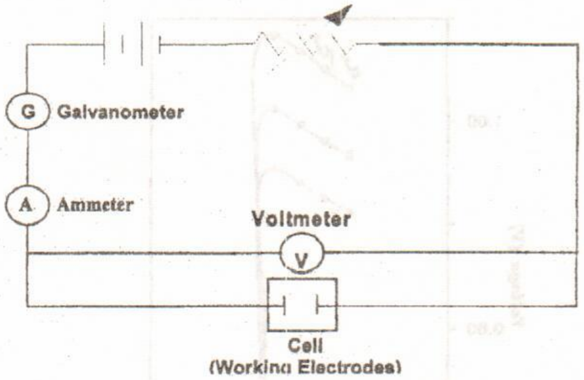

Fig. (1) The Electrical Circuit (The Potentiometer).

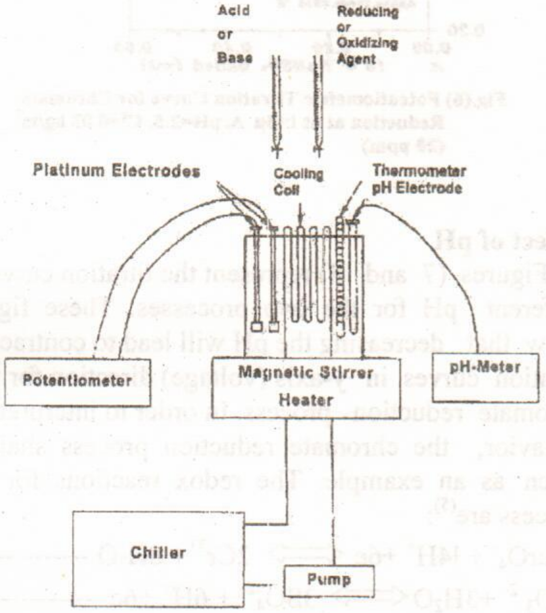

Fig. (2) Laboratory Apparatus for Potentiometric Titration Study

C. Experimental Procedure:

In each experiment, one liter of the model wastewater (prepared in the laboratory) is taken. Dissolved oxygen is purged from the model chromate solution by bubbling nitrogen gas. Whilst, industrial wastewater (provided from the plant) was used directly without any pretreatment. Temperature and pH are adjusted to the specific values and the current is allowed to pass at the specific value. Temperature, pH and current are observed during the experiments for readjustment.

After reaching a stable reading, the voltage is recorded. Small equal increments of the oxidizing and reducing agents is added. The voltage is recorded after each addition until a significant change in the voltage is observed indicating the endpoint.

Results and Discussion

Figures (3 and 4) show the titration curves for the two processes (i.e. cyanide oxidation and chromate reduction) as a potentiometric titration curves at constant current with two polarized electrodes. It is quite obvious that the case is a titration of irreversible system by reversible one for the two processes(7, 8).

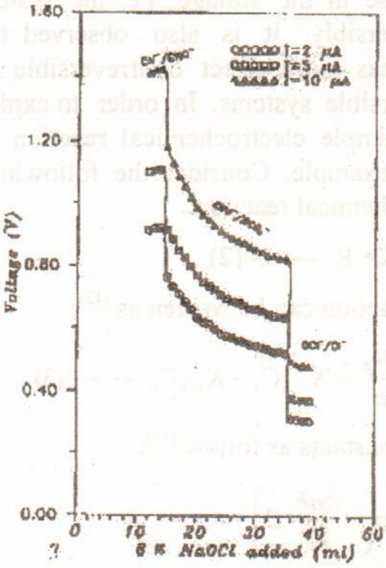

Fig.(3) Potentiometric Titration Curve for Cynaide Oxidation of Temperature=298 K, pH=11.5, C^o=0.3 kg/m³ (300ppm).

Effect of Current

Figures (3 and 4) represent the titration curves at different current, as the applied current is increased, the voltage is also increased. This agrees, as expected, with the argument of the equation which represents the relationship between voltage and current for the potentiometric titration at constant current with two polarized electrodes (11, 12):

$$V = 2\left(\frac{dE}{di}\right)_{i=0} i_c \text{ --------- } (1)$$

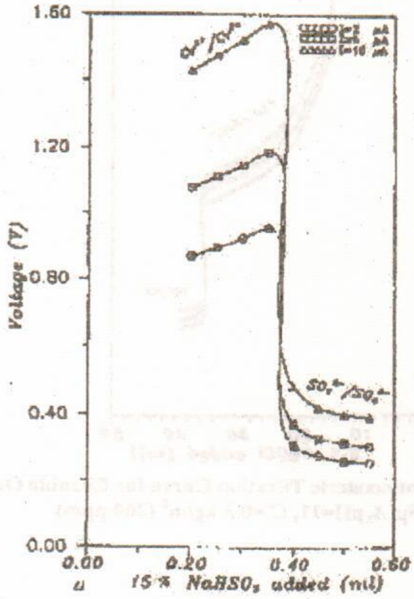

Fig.(4) Potentiometeric Titration Curve for Chromate Reduction at Temperature =298 K, pH=2.0, C^o= kg/m³ (20ppm).

Effect of Temperature

Titration curves at different temperatures are shown in Figs. (5 and 6) for the two processes. These figures show that increasing the temperature will lead to a decrease in the voltage, i.e. the system will behave irreversibly. It is also observed that the temperature has more effect on irreversible systems than on reversible systems. In order to explain this behavior, a simple electrochemical reaction will be taken as an example. Consider the following first-order electrochemical reaction:

$$O + ne \Longleftrightarrow R \text{ --------(2)}$$

The rate of reaction can be written as [13]:

$$r = -\frac{dN_o}{dt} = \frac{dN_R}{dt} = K_{F,h}C_o - K_{B,h}C_R \text{ ----(3)}$$

and the rate constants as follow [14]:

$$K_{F,h} = K^o_{F,h}\exp\left(-\frac{\alpha nF}{RT}E\right) \text{------(4)}$$

$$K_{B,h} = K^o_{B,h}\exp\left(-\frac{(1-\alpha)nF}{RT}E\right) \text{------(5)}$$

According to Equations (4 and 5), as the temperature increases the difference between forward and backward rate constants ($K_{F,h}$ and $K_{B,h}$) will decrease and the rate of the reaction will decrease consequently, indicating the approaching to reversibility condition.

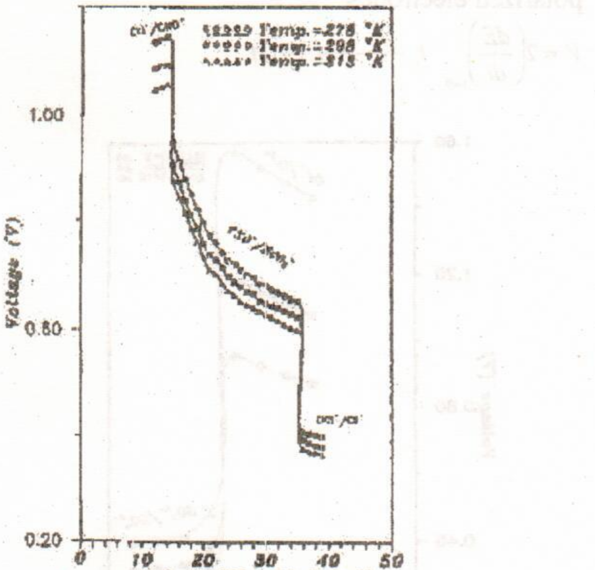

Fig.(5) Potentiometeric Titration Curve for Cyanide Oxidation at I=5μ A, pH=11, C°=0.3 kg/m³ (300 ppm)

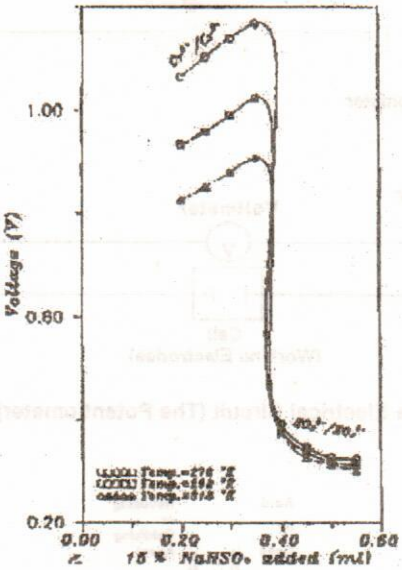

Fig.(6) Potentiometric Titration Curve for Chromate Reduction at at I=5μ A, pH=2.5, C°=0.02 kg/m³ (20 ppm)

Effect of pH

Figures (7 and 8) represent the titration curves at different pH for the two processes. These figures show that decreasing the pH will lead to contract the titration curves in y-axis (voltage) direction for the -chromate reduction process. In order to interpret this behavior, the chromate reduction process shall be taken as an example. The redox reactions for this process are[5]:

$$2HcrO_4^- + 14H^+ + 6e \Longleftrightarrow 2Cr^{3+} + 8H_2O \text{ ----------(6)}$$

$$3SO_3^{\ 2-} + 3H_2O \Longleftrightarrow 3SO_4^{2-} + 6H^+ + 6e \text{ ------------(7)}$$

The rates of reactions can be written as:

$$-\frac{dN_{HCrO_4^-}}{dt} = K_{F,h1}\left[HCrO_4^-\right]^{S_1}\left[H^+\right]^{S_2} - K_{B,h1}\left[Cr^{3+}\right]^{S_3} \text{ -----(8)}$$

$$-\frac{dN_{SO_3^{2-}}}{dt} = K_{F,h2}\left[SO_3^{2-}\right]^{S_4} - K_{B,h2}\left[SO_3^{2-}\right]^{S_5}\left[H^+\right]^{S_6} \text{ -----(9)}$$

Equations (8 and 9) show that as the pH decrease, the rate of chromate reduction will increase (i.e. the irreversibility will increase) and the voltage will increase. Whilst, the rate of sulphite oxidation will decrease and the voltage will increase.

Figure (7) also indicates that the pH variation has larger effect on the chromate reduction process than that on sulphite oxidation. This was interpreted as that $S_2 \gg S_6$.

The above reasoning can also be used for the cyanide oxidation process.

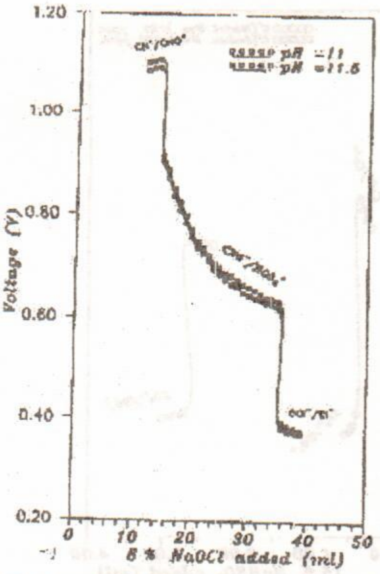

Fig.(7) Potentiometric Titration Curve for Cyanide Oxidation at Temperature=298 K, I=5 μ A pH=11, C^o=0.3 kg/m^3 (300 ppm)

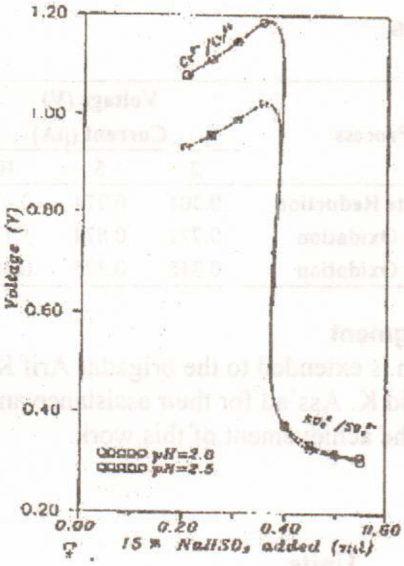

Fig.(8) Potentiometric Titration Curve for Chromat Reduction at Temperature=298 K, I=5 μ A C^o=0.02 kg/m^3 (20 ppm)

Effect of Initial Concentration:

Figures (9 and 10) show the titration curves at different initial concentrations for the two processes. These figures show that the change of initial concentration has no important effect on the titration curve except that it will change the amount of the titrant needed for completion of the reaction.

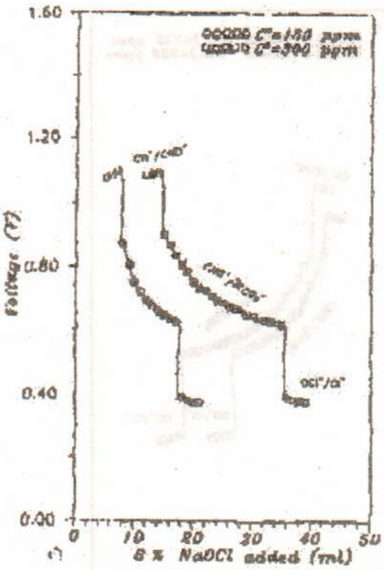

Fig.(9) Potentiometric Titration Curve for Cyanide Oxidation at Temperature=298 K, I=5 μ A pH=11.

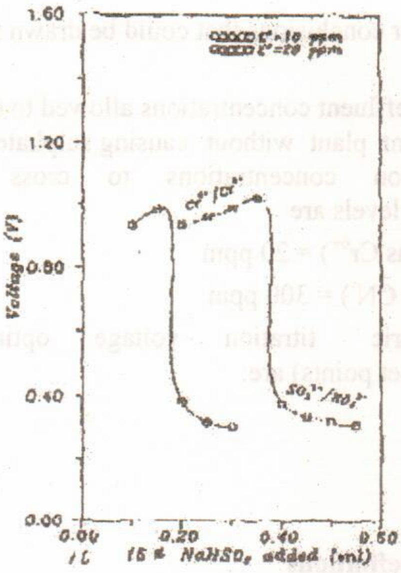

Fig.(10) Potentiometric Titration Curve for Chromate Reduction at Temperature=298 K, I=5 μ A pH=2.5, C^o=0.3 kg/m^3

Effect of Wastewater Quality:

Figures (11 and 12) represent a comparison between the titration curves of the model and industrial wastewater for the two processes. The major differences are observed in the titration substance sections of the titration curves. This behavior can be interpreted as that there are other oxidizable or reducible compounds in the industrial wastewater interfering in the process (mixed potential effect $^{(15, 16)}$)

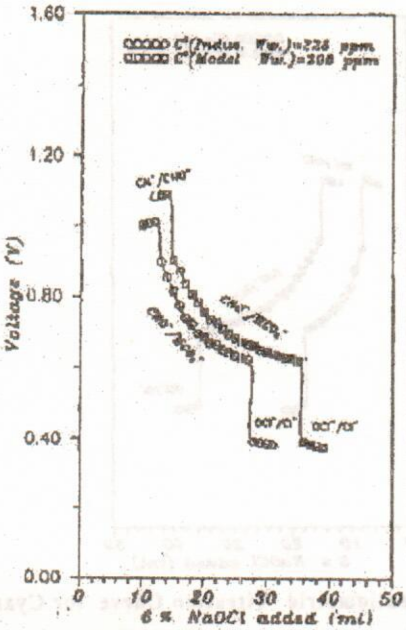

Fig.(11) Potentiometric Titration Curve for Cyanide Oxidation at Temperature=298 K, pH=11, I=5 μ A

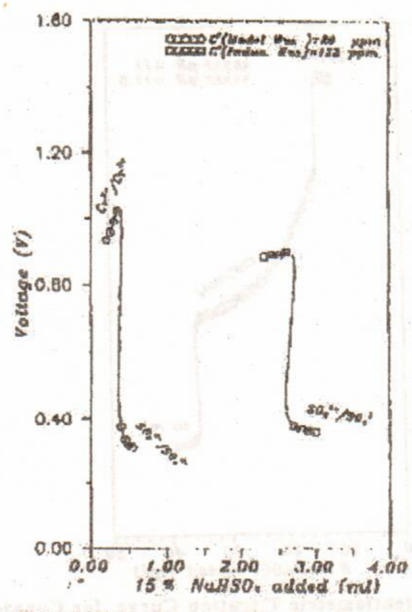

Fig.(12) Potentiometric Titration Curve for Chromate Reduction at Temperature=298 K, I=5 μ A

The two major conclusions that could be drawn from this work are,

1. Maximum effluent concentrations allowed to enter the treatment plant without causing sulphate and chloride ion concentrations to cross the permissible levels are

   Chromate (as Cr^{6+}) = 20 ppm

   Cyanide (as CN^-) = 300 ppm
2. Potentiometric titration voltage optimum endpoints (set points) are:

Conclusions

Process	Voltage (V)		
	Current (μA)		
	2	5	10
Chromate Reduction	0.301	0.374	0.479
Cyanide Oxidation	0.721	0.874	1.119
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Acknowledgment

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Nomenclature

Symbol	Definitions	Units
A	Ampere	A
CI	Concentration of Species (i)	gmol/cm3
Cio	Initial Concentration of Species (i)	gmol/cm3
e	Electron	-
E	Electrode Potential	V
F	Faraday's Constant (96487 coulomb/g.equivalent)	
I	Current	A
k	Electrochemical Rate Constant Electrochemical Rate Constant at Zero Potential	
N	Number of Electrons	
Ni	Number of Moles of Species	gmol
OI	Oxidized State of Species (i)	-
r	Rate of Reaction	gmol/cm2.s
R	Gas Constant	J/gmol.K
RI	Reduced State of Species (i)	-
Si	Reaction Order with Respect to Species (i)	-
t	Time	S
T	Temperature	K
V	Voltage	V

Subscripts and Creek Letters

B	Backward
C	Cathodic
F	Forward
H	Heterogeneous Process
i	Species
0	Oxidized State
R	Reduced State
α	Transfer Coefficient of an Electrochemical Process

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