Management of Chromium Plating Rinsewater Using Electrochemical Ion Exchange

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The chrome plating industry effluent mainly contains chromium(VI) in dragout and rinsewater whose constituents reflect the plating bath characteristics. Normally dragout/dead tank wash water contains about 1% of the plating bath concentration. As chromium(VI) is soluble in all pH ranges, an efficient treatment is required for recovery of chromium for the reuse of treated water. The present study endeavors to recover the chromium by an electrochemical ion exchange (EIX) method. This combines ion exchange (IX) and electrodialysis (ED) for the removal and concentration of chromate ions from the effluent and recycles the treated water for conservation of water. The maximum chromium removal achieved is 98.82% in the batch recirculation mode of operation of EIX at voltage 12.5 V.

Introduction

Wastewaters containing toxic metal ions such as cadmium, copper, gold, lead, nickel, silver, and zinc are generated in large quantities in the mining, metal finishing, microelectronic fabrication, and photographic film processing industries. Chromium and its salts find extensive use in photography, chromium plating, textile manufacture, tanning of leather, manufacturing green varnishes, paints, inks, glasses for porcelain, etc. The toxic effects of chromium are well-known.[1,2] Cr(VI) has been reported to be responsible for lung cancer, chrome ulcers, nasal septum perforation, brain damage, and kidney damage. Chromium(VI) normally exists in anionic forms ($Cr_2O_7^{2-}$, $HCrO_4^{-}$, CrO_4^{2-}) in water depending on pH and concentration.[2] In highly acidic media (pH <1) the Cr(VI) ion exists mostly as $HCrO_4^{-}$ ($pK_1 = 6.51$ and $pK_2 = 5.65$). At pH between 2 and 6 there is equilibrium between $Cr_2O_7^{2-}$ and $HCrO_4^{-}$ ions. Under alkaline conditions (pH >8) it exists predominantly as chromate anion. The equilibrium between chromate and dichromate ions in water can be shown as the following equation: $Cr_2O_7^{2-} + 2OH^{-} \leftrightarrow CrO_4^{2-} + H_2O$.

Intermediate and large plating plants for treatment of chromium wastewater employ a process involving the reduction of chromium(VI) to the trivalent form and the subsequent precipitation of the reduced chromium with alkali to dispose of chromium-bearing waste. Chromium(VI) could be removed by activated carbon[3] or by its reduction to trivalent chromium in Soya cake[4] and biological methods.[5] A mixed plating rinse wastewater containing zinc, chromium(VI), chromium(III), and cyanide was treated by ion exchange (IX) columns.[6–9] Electrochemical techniques were exploited for the removal of chromium(VI) from wastewater either by combined electrocoagulation–electroflotation[10,11] or through reduction of chromate[12] at the cathode or using a bipolar electrochemical

precipitation process.[13] Using electrodialysis (ED), the recoveries of chromium and other heavy metals[14,15] from spent metal plating baths were studied. The application of ED for removal of ionic species[16] from wastewater treatment seems to be efficient in eliminating ionic species from wastes without a sludge problem. Electrodialysis is not an economical process for treating diluted solutions because of its high electrical resistance and the development of concentration polarization phenomena. To overcome these problems, ion exchange resins were introduced into the ion-depleting compartments of an electrodialysis stack. The EIX process[17–28] is a combination of electrodialysis (ED) and conventional ion exchange (IX). Another configuration uses a cation exchange only and two cation exchange membranes for heavy metal removal from the rinsing waters of plating industries, as investigated by Spoor et al.[20] for Ni^{2+} removal, or by Mahmud et al.[22] for the case of cupric ions.

The present study endeavors to treat the chrome plating rinsewater by the electrochemical ion exchange (EIX) method which combines ion exchange (IX) and electrodialysis (ED), for the removal and concentration of chromate ions from rinsewater and recycle the treated water for rinsing so that the conservation of water can be achieved.

Materials and Methods

Materials. All the chemicals used were of analytical grade. Based on the practical data collected from different plating industries, the synthetic rinsewater concentration for Cr(VI) ion was fixed at around 300 ± 20 mg L^{-1}. The synthetic rinsewater of Cr(VI) concentration of 312.39 mg L^{-1} was prepared using standard potassium chromate solution. K_2CrO_4 used is not a primary standard substance; hence it was standardized using standard ferrous ammonium sulfate (which was standardized against standard $K_2Cr_2O_7$ solution). Similarly CrO_3 is also a secondary standard chemical, and its solution was also standardized in the same manner as above. The ion-selective membranes NEOSEPTA AMX anion exchange membranes (Tokuyama Corp., Japan) and a strong base anion resin, Amberlite-IRA400, were used for the EIX experiments.

Experimental Setup. The diagram of the experimental setup is shown in Figure 1, which consists of a specially designed

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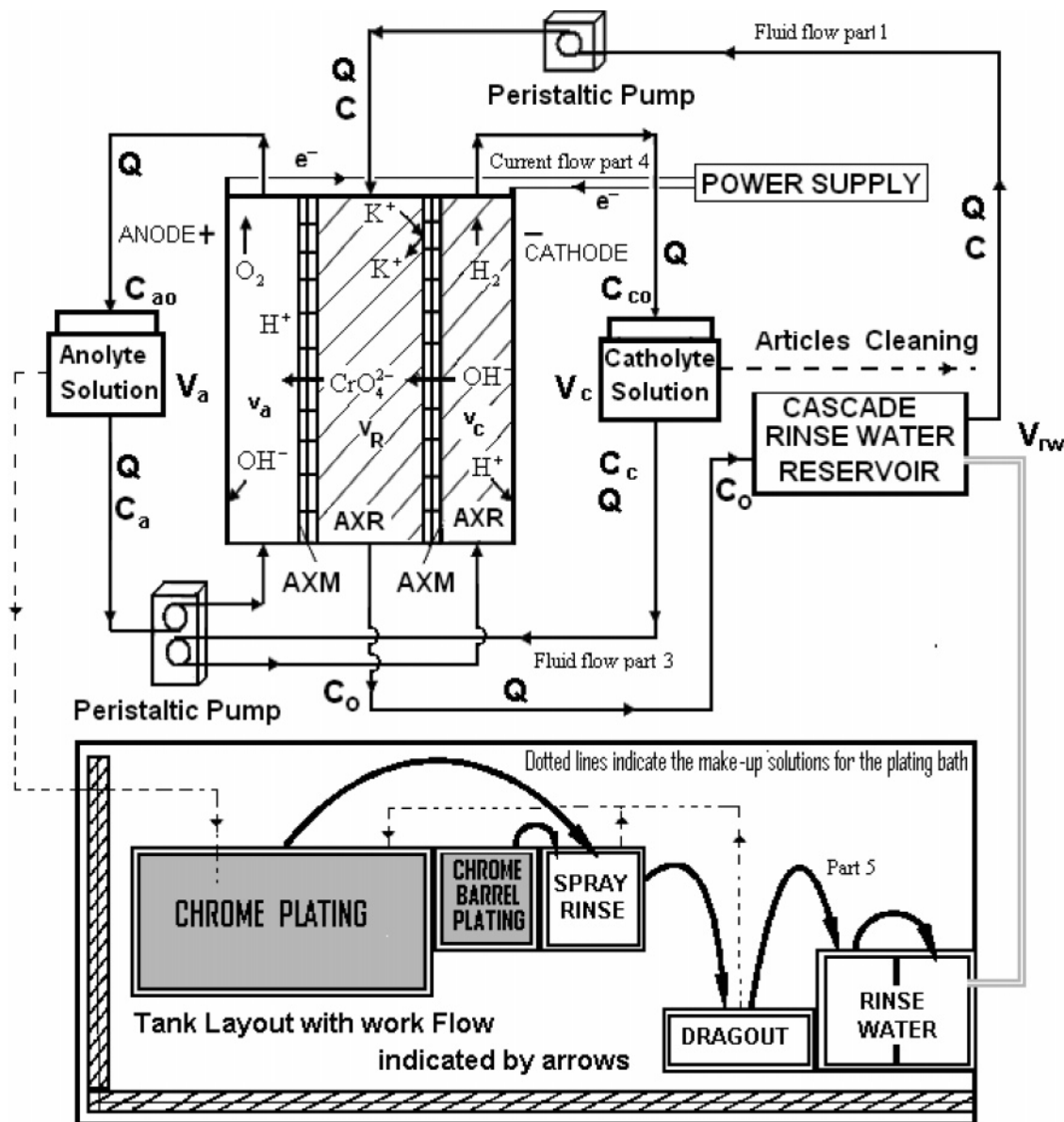‖ SASTRA-Deemed University.
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Figure 1. Schematic diagram of the experimental setup.

EIX unit that had an effective membrane area of 7×7 cm^2. The EIX device is a plate-and-frame cell provided with three compartments—an anode, a process stream, and a cathode—as shown in Figure 1. The geometric dimensions of each of the compartments were $7 \times 7 \times 1.5$ cm^3. The stainless steel sheet (of dimensions $7 \times 7 \times 0.2$ cm^3) was used as a cathode, and noble metal oxides (TiO$_2$ and RuO$_2$) coated on expanded Ti mesh of area 40 cm^2 was used as an anode. The middle compartment is separated from the anodic and cathodic compartments with the help of two anionic exchange membranes (see Figure 1). The middle compartment and cathodic compartment were filled with anionic exchange resin (AXR). Further, the setup includes three solution flow parts, current flow part 4, and plating tank layout with work flow as shown in Figure 1.

Fluid Flow Part 1. This part comprises of a middle compartment of EIX, the plating rinsewater reservoir of 1 L capacity, and a peristaltic pump. The rinsewater from the reservoir was passed from the reservoir to the top of the middle compartment. The effluent from the outlet provided at the bottom of the middle compartment is again allowed to enter

the reservoir in case of recirculation (otherwise this stream will be taken for rinsing purpose and then returned to EIX).

Fluid Flow Part 2. This part includes an anodic compartment, an anolyte reservoir of capacity 300 mL, and a peristaltic pump. It is operated always in batch recirculation mode. Plating rinsewater will be taken as the anolyte. It is to be recirculated from the bottom of the anolyte compartment to the top, and once the concentration builds up above 1000 mg L^{-1}, it will be returned to the plating tank itself as makeup solution which is shown as a dotted line in Figure 1. Fresh rinsewater will be taken in the anolyte reservoir for further operation.

Fluid Flow Part 3. This part consists of a cathodic compartment, a catholyte reservoir of capacity 300 mL, and a peristaltic pump. It is operated always in batch recirculation mode with process water, which is the catholyte, and is recirculated from the bottom of the cathodic compartment to the top. Once the concentration attains sufficient strength in the catholyte reservoir, it will be taken out and used for cleaning of the work piece (pretreatment) which is shown as a dotted line in the Figure 1.

Fresh process water will be taken in the reservoir of catholyte for further operation.

Current Flow Part 4. This is the electrical circuit part, consisting of a multioutput dc regulated power supply (0−2 A, 0−30 V, Aplab Model) together with ammeter and voltmeter connected to the EIX device (which is a plate-and-frame cell) provided with three compartments—an anode, a cathode, and a process stream—as shown in Figure 1.

Experimental Procedures

Batch Recirculation Process. The synthetic effluent, rinsewater of concentration 312.39 mg L^{-1}, was prepared using potassium chromate and used as effluent in the process stream as well as for anolyte whereas fresh process water was taken as the catholyte. The reservoir volume of the effluent is 1 L, while those of anolyte and catholyte are 300 mL each as described earlier. The flow rate of 10.7 mL min^{-1} was maintained in all fluid flows. Using a direct current regulated power supply, the required cell voltage was maintained and the experiments were carried out. At every hour the samples of all reservoirs were collected and analyzed for total chromium using the Merck Spectroquant NOVA 60, barcode-based spectrophotometer, using diphenyl carbazide as indicator,[29] and verified using an atomic absorption spectrophotometer, Varian Model SpectraA 220.

The pH measurements were done using a pH meter. The experiments were continued until the minimum concentration of chromium was reached. The experiments were repeated at different cell voltages such as 5, 7.5, 10, and 12.5 V.

Generation of Rinsewater. One liter of plating chrome bath was prepared having the composition of 200 g L^{-1} CrO$_3$ and 1 g L^{-1} sulfuric acid. In the plating operation the acid acts as a catalyst. About 20 mild steel sheets were taken, each of size 7 × 5 × 0.1 cm^3, and they were first pretreated and chrome plated one by one in the bath solution to get a good finishing. Then they were washed one by one in a series of four wash tanks containing 300 mL of water, equipped for the rinsing operation. Normally the first washing tank is called the dead tank or dragout tank (together with spray rinse) and the other tanks are called rinsewater tanks. Generated rinsewater and synthetic effluent were used for the study.

Breakthrough Point of EIX. An experimental study was carried out to understand the breakthrough point of the electrochemical ion exchange reactor. It is very much important to study the operational capacity of the resin and the process. A known weight of the resin was packed inside the middle and cathodic compartments, and the test solution containing 312.39 mg L^{-1} Cr(VI) was made to run in the cell. The experiments were conducted at two different voltages such as 12.5 and 15 V at a constant flow rate of 10.7 mL min^{-1}. The anolyte and catholyte solutions were recycled separately at the same flow rate of process stream. The chromate solution (rinsewater) was continuously passed through the central compartment; the output was collected in a separate container and at the outlet samples were taken periodically, analyzed for chromate and pH. With the same weight of the resin packed inside the middle compartment, the experiment was repeated in the cell without electrodes.

Performance of EIX. Synthetic effluent was prepared with potassium chromate of varying concentrations (1000, 500, and 100 mg L^{-1}), and experiments were carried out under different applied voltages (5, 7.5, 10, 12.5, and 15 V) using a dc regulated power supply at various flow rates. The anolyte and catholyte solutions were recycled separately at desired convenient flow
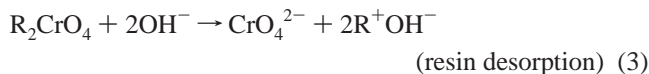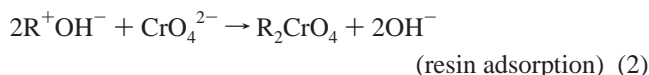
rates. The chromate solution was continuously passed through the central compartment; the output was collected in a separate container and at the outlet samples were taken periodically and analyzed for chromate and pH.

Theoretical Development

Reaction Mechanism. In the central processing compartment, the rinsewater containing dilute potassium chromate enters and becomes ionized. Under alkaline conditions (pH >8) potassium chromate exists predominantly as chromate anion. The reaction taking place in the bulk can be represented as
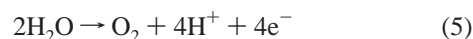
$$K_2CrO_4 \rightarrow 2K^+ + CrO_4^{2-} \tag{1}$$

Anionic resin adsorbs chromate ion. The following reactions take place.

$$2R^+OH^- + CrO_4^{2-} \rightarrow R_2CrO_4 + 2OH^-$$
$$\text{(resin adsorption)} \tag{2}$$

$$R_2CrO_4 + 2OH^- \rightarrow CrO_4^{2-} + 2R^+OH^-$$
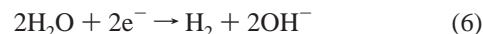$$\text{(resin desorption)} \tag{3}$$

Under field, chromate ion and hydroxyl ion, due to their affinity toward the anode, pass through the anion exchange membrane and the concentration of chromic acid becomes enriched. In the bulk of the anode compartment the following reaction takes place to produce chromic acid.

$$CrO_4^{2-} + 2H^+ \rightarrow H_2CrO_4 \tag{4}$$

At the anode, the pH is around 2; the following reaction takes place at the anode, which results in the liberation of oxygen.

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{5}$$

At the cathode, the following reaction takes place.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{6}$$

Chromate ions are removed from the flowing solution by the anion exchange resin in the process compartment. The adsorbed ions then migrate under the influence of an electric field through an anion membrane and into the anode compartment, where they could be concentrated and returned to the plating bath. The decontaminated wastewater may then be further recycled for rinsing. Hydroxyl ions electrochemically produced at the cathode migrate continuously to regenerate the process stream anion exchange resin. Hydronium ions produced at the anode are excluded by the anion membrane from entering the process stream and serve to balance the charge with incoming chromate ions to produce purified chromic acid.

Process Modeling. One possible mode of operation of EIX is that which involves the continuous recirculation of the effluent. Due to this, there is a gradual depletion of the concentration of Cr(VI) ion in the process stream with the gradual production of hydroxyl ion in the cathodic chamber and chromic acid in anodic chamber takes place. The mode of operation is depicted in Figure 1.

In order to design the plant for EIX processes, development of the models is essential which explains the variation of the concentration of Cr(VI) ions with time in the reservoirs. The basic assumptions involved in the ensuing derivation may be outlined as follows.

Table 1. List of the Parameters

parameter	symbol
specific electrode area [$6(1 - \epsilon)/d_p$] of AXR, cm^{-1}	a
area of AXM	A_m
specific surface area (A_m/v_R) of AXM, cm^{-1}	a_m
initial concentration of chromate in the reservoir, mg L^{-1}	C^o
concentration Cr(VI) ion leaving the anodic compartment, mg L^{-1}	C_{ao}
concentration of Cr(VI) entering the anodic compartment, mg L^{-1}	C_a
concentration Cr(VI) ion leaving the middle compartment, mg L^{-1}	C_o
concentration of Cr(VI) entering the middle compartment, mg L^{-1}	C
concentration at the particle−film interface, mg L^{-1}	C_o*
diffusion coefficient of chromate ion	D
particle diameter of AXR	d_p
specific energy consumption for EIX operation, kW h kg^{-1}	E
Faraday's constant 96 500 C mol^{-1} or A s mol^{-1}	F
current intensity, A	I
mass transfer coefficient to the particle surface, cm s^{-1}	k_p
migration mass transfer coefficient, cm s^{-1}	k_m
electrons exchanged	z
volumetric flow rate of process stream, anolyte, and catholyte, mL min^{-1}	Q
volumetric flow rate of anolyte (with respect to Table 3), mL min^{-1}	Q_a
regression coefficient	R^2
time, h	t
superficial velocity, m s^{-1}	U
applied voltage, V	V
volume of middle compartment, mL	v_R
volume of rinsewater reservoir tank, mL	V_{rw}
volume of anode compartment, mL	v_a
volume of anolyte reservoir, mL	V_a
extent of chromate ions removal, ($C^o - C$)/C^o	$X(t)$
extent of chromate ions buildup, ($C_a - C^o$)/C^o	$Y(t)$
migration coefficient, cm s^{-1} A^{-1}	α
bed porosity	ϵ
fluid density, kg m^{-3}	ρ
residence time of Cr(VI) ion in middle compartment (v_R/Q), s	τ_R
residence time of Cr(VI) ion in effluent tank (V_{rw}/Q), s	τ

Back-mix flow exists in the central compartment, the anodic compartment, and the cathodic compartment in the present reactor system; that was arrived at based on a tracer experiment. Hence the concentration of reactive species is the same throughout the compartment and equal to the exit concentration. An approximate model which represents the given EIX is developed based on a continuous stirred tank flow reactor in which the reactions and physical phenomena take place. A dynamic material balance to each of component or species of every compartment can be written as

[rate of change mass in the system] =
  [rate of mass input] − [rate of mass output] ∓
  $\sum$ [rate of mass disappeared or generated due to
      physicochemical phenomena] (7)

All the reservoirs are perfectly back-mix systems. The parameters for all the equations are given in Table 1 separately.

Model for Cr(VI) Ion Depletion in Rinsewater Reservoir.
The concentration variation of Cr(VI) ion in the process stream (central compartment) of EIX (fluid flow part 1) is written as

$$\epsilon v_R\left(\frac{dC_o}{dt}\right) = QC - QC_o - [6(1 - \epsilon)v_R(k_p/d_p)C_o + \alpha I A_m C_o] \quad (8)$$

The left-hand side (LHS) represents the rate of change of mass of Cr(VI) in the pore volume of the central compartment, where

v_R is the volume of the central compartment, ϵ is the bed porosity, and C_o is the concentration of Cr(VI) ion leaving the middle compartment. The first two terms of the right-hand side (RHS) are the rate of mass of Cr(VI) ion entering and leaving the central compartment where Q is the volumetric flow rate of the process stream and C is the concentration of Cr(VI) entering the process compartment. The next two terms present inside the square brackets represent the rate of disappearance of mass of chromate ions in the solution in which the first term is due to sorption of chromate ions in the resin phase and the second term accounts for diffusion through the membrane due to ionic migration. As a matter of fact, for dilute solutions, sorption of chromate ion in resins is usually diffusion-controlled and it is generally admitted that external transfer is the rate-controlling process.[28] The driving force is the concentration difference through the diffusion film, and the expression should be [$6(1 - \epsilon)/d_p]v_R k_p(C_o - C_o*)$, where k_p is the mass transfer coefficient to the particle surface, d_p is the particle diameter, and C_o* is the concentration at the particle−film interface. Owing to the high exchange capacity of the resin, to the weak concentration in solution, and to the relatively long duration of the experiments, the amount of chromate anion on the resin is always of little significance. Moreover, the resin has a high preference for the ions of high valence and therefore acts as well for chromate anions. Thus, the concentration near the resin surface remains zero during the experiments. Assuming phase equilibrium, the concentration in the solution near the interface, C_o*, is zero, which leads to [$6(1 - \epsilon)/d_p]v_R k_p C_o$.

The next dominant transport process is ionic migration, which accounts for the transfer of chromate ion through liquid toward the interface of membrane that passes through the AXM to the liquid bulk in the anode compartment. The migration flux of chromate anion is defined on the basis of the local concentration of chromate anions in the central compartment, and the potential gradient is governed by the Nernst−Einstein relation as ($D/RT)zFC_o$ grad Φ, where D represents the diffusion coefficient of chromate ion. For the sake of simplicity the overall parameter α can be used to express the migration rate as $\alpha I C_o A_m$ in which α was assumed to vary linearly with the current, where α is the migration coefficient, I is the current intensity, and A_m is the area of AXM.

The reservoir (rinsewater tank) is always a perfectly back-mix system. Hence the mass balance equation for the rinsewater reservoir tank is

$$V_{rw}\left(\frac{dC}{dt}\right) = QC_o - QC \quad (9)$$

where V_{rw} is the volume of the rinsewater reservoir tank.

Since there is no accumulation of the chromate ion in the liquid phase of the middle compartment, the reactor is assumed to be under steady-state conditions as $dC_o/dt = 0$, and eq 8 is rewritten as

$$\frac{C_o}{C} = \cfrac{1}{1 + \cfrac{[6(1 - \epsilon)/d_p]v_R k_p}{Q} + \cfrac{\alpha I A_m}{Q}} = \cfrac{1}{1 + (k_p a + k_m a_m)\tau_R} \quad (10)$$

where a is the specific surface area [$6(1 - \epsilon)/d_p$] of the ion exchange resin, a_m is the specific area (A_m/v_R) of the ion exchange membrane, k_m is the migration mass transfer coefficient, and τ_R is the residence time of chromate ion (v_R/Q) in

the middle compartment. The mass balance eq 9 is solved after substitution of the expression for C_o from eq 10, knowing the initial concentration of chromate ion, $C = C^o$ at $t = 0$ in the reservoir. Then the following resultant equation gives the variation of concentration of Cr(VI) in the effluent reservoir.

$$\frac{C}{C_o} = \exp\left[-\frac{t}{\tau}\left(\frac{(k_p a + k_m a_m)\tau_R}{1 + (k_p a + k_m a_m)\tau_R}\right)\right] \quad (11)$$

where C^o is the initial concentration of chromate and τ is the residence time of chromate ion (V_{rw}/Q) in the effluent reservoir, respectively.

It should be noted that the extent of chromate ion removal is defined as $X(t) = (C^o - C)/C^o$. The extent of chromate ions remaining in the reservoir is $(1 - X)$, which is C/C^o, decreases exponentially with time. In accordance with eq 11, the slope of the plot of $\ln(C/C^o)$ versus t or $\ln(1 - X)$ versus t is $(1/\tau)\{[(k_p a + k_m a_m)\tau_R]/[1 + (k_p a + k_m a_m)\tau_R]\}$, from which the value of $(k_p a + k_m a_m)$, the total transfer coefficient is computed.

Model for Buildup of Cr(VI) Ion in Anolyte Reservoir during Batch Recirculation Middle Compartment. The mass balance of Cr(VI) ion in the anodic compartment of EIX is as follows:

$$v_a\left(\frac{dC_{ao}}{dt}\right) = QC_a - QC_{ao} + \alpha I A_m C_o \quad (12)$$

The LHS represents the rate of change of Cr(VI) in the anodic compartment, where v_a is the volume of the anode compartment and C_{ao} is the concentration of Cr(VI) ion leaving the anodic compartment. The first two terms of the RHS are the rate of the mass of Cr(VI) ion entering and leaving the anodic compartment, where C_a is the concentration of Cr(VI) entering the anodic compartment. The third term accounts for the rate of diffusion of Cr(VI) ion into the anodic compartment through the membrane due to migration. The mass balance for the analytic reservoir is given as

$$V_a\left(\frac{dC_a}{dt}\right) = QC_{ao} - QC_a \quad (13)$$

Since there is no accumulation of the chromate ion in the anode compartment of the EIX reactor, the anode compartment is assumed to be under steady-state conditions as $dC_a/dt = 0$, and eq 12 is rewritten as

$$C_{ao} = C_a + (\alpha I A_m/Q)C_o = C_a + k_m a_m \tau_R C_o \quad (14)$$

The expressions for C_{ao} in eq 14 and C_o from eq 10 are substituted in the dynamic mass balance eq 13 and is solved to get the concentration of chromate ion buildup in the anolyte reservoir knowing the initial concentration of chromate ion ($C = C^o$ at $t = 0$). Thus, the expression for C_a is written as follows:

$$C_a = C^o + \left(\frac{\tau}{\tau_a}\right)\left(\frac{k_m a_m}{k_p a + k_m a_m}\right)(C^o - C) \quad (15)$$

Then the extent of the concentration of chromate ion buildup (defined as $Y(t) = (C_a - C^o)/C^o$) in the anolyte reservoir is rewritten as

$$Y(t) = \left(\frac{\tau}{\tau_a}\right)\left(\frac{k_m a_m}{k_p a + k_m a_m}\right)X(t) \quad (16)$$

The value of $(k_p a/k_m a_m)$, the ratio of the transfer coefficients, is computed from the slope, $(\tau/\tau_a)[k_m a_m/(k_p a + k_m a_m)]$, of the

plot of $X(t)$ versus $Y(t)$ versus t. From sum and ratio values the individual transfer coefficients can be calculated.

Model for Buildup of Cr(VI) Ion in Anolyte Reservoir during Continuous Operation of Middle Compartment. Since there is no accumulation of the chromate ion in the liquid phase of the middle compartment of the EIX reactor, it can also be assumed that the reactor is under steady-state conditions as $dC_o/dt = 0$ and eq 10 is rewritten as

$$C_o = \frac{C^o}{[1 + (k_p a + k_m a_m)\tau_R]} \quad (17)$$

The dynamic mass balance eq 13 is solved by combining eqs 14 and 17, to get the concentration of chromate ion buildup in the anolyte reservoir knowing the initial concentration of chromate ion, ($C = C^o$ at $t = 0$), when the central compartment is operating in continuous mode. Thus, the expression for C_a is shown as follows:

$$C_a = \left(\frac{1}{\tau_a}\right)\left(\frac{k_m a_m \tau_R}{1 + (k_p a + k_m a_m)\tau_R}\right)C^o t + C^o \quad (18)$$

or

$$Y(t) = \left(\frac{1}{\tau_a}\right)\left(\frac{k_m a_m \tau_R}{1 + (k_p a + k_m a_m)\tau_R}\right)t \quad (19)$$

The slope of the plot of t versus $Y(t)$ gives the value $(1/\tau_a)\{k_m a_m \tau_R/[1 + (k_p a + k_m a_m)\tau_R]\}$. The individual transfer coefficients can be calculated from the slopes of the plots of $\ln(1 - X)$ vs t of eq 11 and $Y(t)$ vs t of eq 19.

Results and Discussion

Batch Recirculation Process. The effects of applied voltage to EIX on depletion of chromium ion (in the effluent reservoir) and the specific power consumption were investigated when EIX was operated under batch continuous recirculation mode. The results are presented in Figure 2 and Table 2. It is observed that, as the time increases, the rate removal of the chromium continuously decreases until it reaches the minimum concentration of chromium in the reservoir. Table 2 presents the specific power consumption and percent chromium removal for various cell voltages. By comparison of the results of different voltages, it was noted that, at higher voltage of operation, the minimum concentration in the effluent reservoir attains in shorter time. The specific energy consumption or power consumption for operation, E, kW h kg^{-1}, is computed using the expression $[VIt/10^3]/[(C^o - C)V_{rw}/10^6]$, where the numerator represents the power input in kilowatt hours, V is the applied cell voltage in volts, I is the measured averaged current in amperes in the circuit, and t is the duration of electrolysis in hours for bringing the initial concentration, C^o, mg L^{-1}, of effluent to final concentration C, mg L^{-1}, in the volume of the reservoir, V_{rw} liters. More than 98% chromium removal is achieved for various cell voltages of operation, but the specific energy consumption is more at higher cell voltage, which may be due to electrode reactions taking place at the anode at faster rate. Since more than 98% chromium removal is achieved for various applied voltages, the treated water can be recycled for rinsing purposes.

The slope of the plot of $\ln(C/C^o)$ versus t is $(1/\tau)\{(k_p a + k_m a_m)\tau_R/[1 + (k_p a + k_m a_m)\tau_R]\}$, which was obtained from eq 11 by linear regression. The values of $(k_p a + k_m a_m)$, the total transfer coefficient, was computed and are presented in Table 2 along with the linear regression coefficient R^2. The goodness
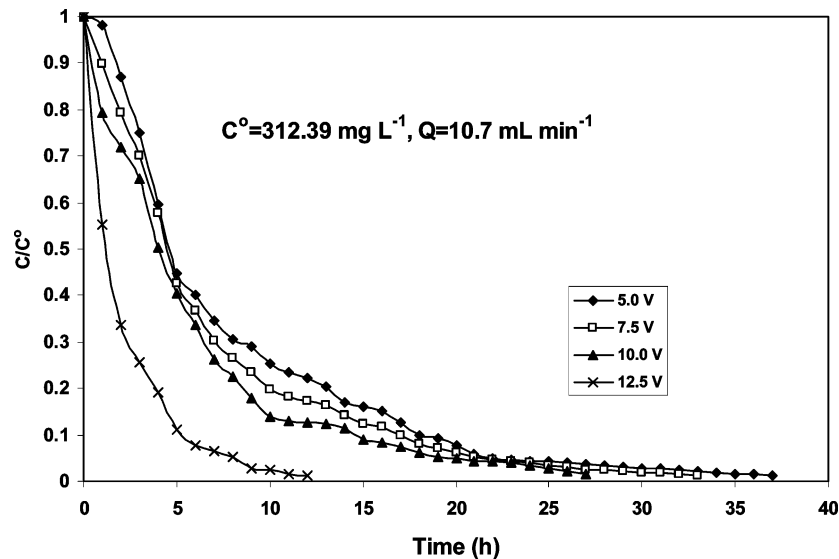
Figure 2. Effect of applied voltage on the variation of C/C^o with electrolysis time.

Table 2. Effect of Applied Voltage on Chromium Removal and Energy Consumption

no.	appl voltage, V	measd average current, A	final concn Cr(VI) in effluent, mg L^{-1}	% removal Cr(VI)	power consumption, kWh kg^{-1}	$k_pa + k_ma_m$, s$^{-1} \times 10^3$	R^2
1	5.0	0.06	4.09	98.69	36.0	0.331 456	0.989 43
2	7.5	0.089	4.09	98.69	71.4	0.379 096	0.994 13
3	10.0	0.119	4.0	98.71	104.2	0.442 039	0.989 43
4	12.5	0.149	3.67	98.82	72.4	2.156 392	0.992 46

of fit is more than 0.98, which is the evidence for the model to fit well. The values of ($k_pa + k_ma_m$), the total transfer coefficient at different voltages, indicates that at lower applied voltage the adsorption process might be dominating.

Generation of Rinsewater. The buildup of concentration of Cr(VI) due to rinsing in three tanks as the number of plated metal sheets is presented in Figure 3. For each and every washing of sheets, the increase of concentration in each of the tanks gives the relation between the numbers of sheets plated or plated area and the corresponding concentration rise in each tank. That is, it can be seen from these figures that the Cr(VI) concentration of the dead tank is considerably high compared to the concentration in the other tanks. That is why the solutions of the dragout tank are generally used for making up of the plating bath to avoid the loss of proprietary chemicals such as brighteners used normally by plating shops. Moreover, the
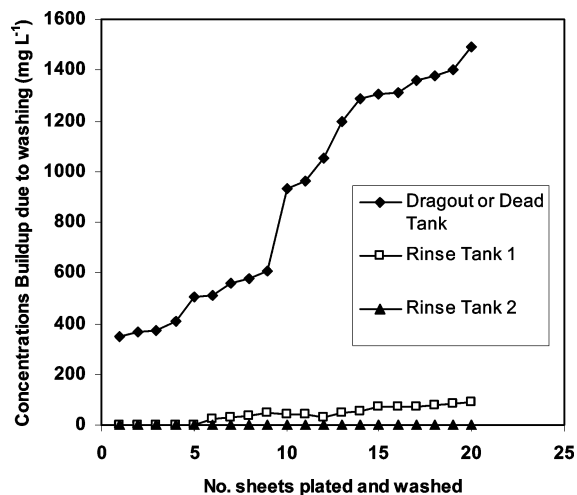
concentration built up in the solution depends upon the area of the metal plate and configuration of the article.

Breakthrough Point of EIX. The pH of chromate solution when entering the central compartment is 6 and its concentration is 312.39 mg L^{-1}; when the solution leaves the compartment, the pH increases to 11 whereas the Cr(VI) concentration reduces to zero until the breakthrough point. The outlet concentration of Cr(VI) from the central compartment with respect to the discharged volume (in liters) for two different voltages beyond the breakthrough point is presented in Figure 4. The breakthrough curve shows that at the outlet the concentration of Cr(VI) is zero up to a certain point of discharge of volume collected and then the concentration of chromate ion in the effluent increases and reaches its initial value as if the bed has attained saturation. When the EIX is operated at 15.0 V, it is observed (from Figure 4) that the concentration of chromate ion is approximately zero up to the discharge of 7 L of effluent from the middle compartment and afterward the concentration
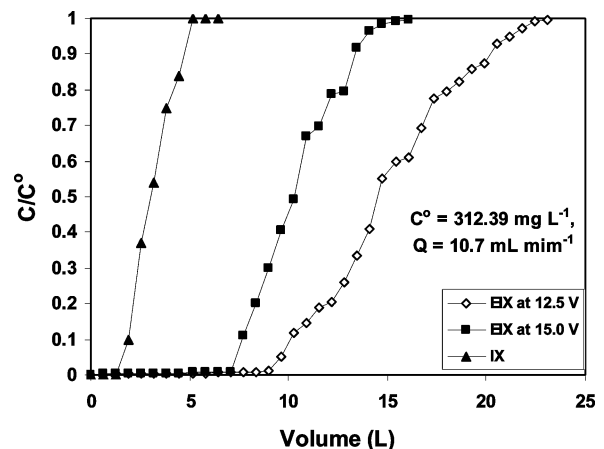

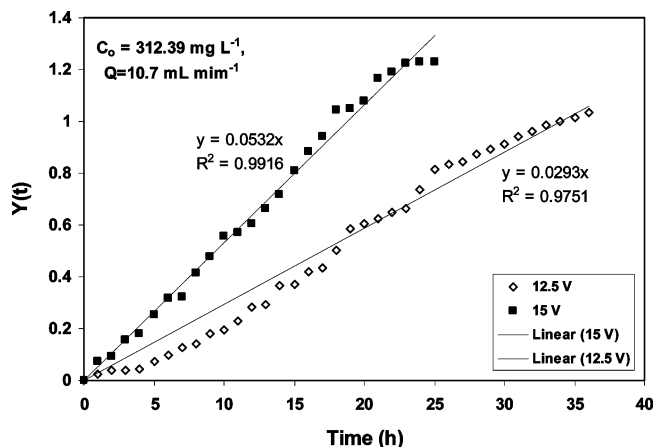**Figure 3.** Number of plated mild steel sheets vs chromate ion concentration buildup in a series of rinse tanks.

Figure 4. Breakthrough curve analysis.

Figure 5. Effect of applied voltage on the extent of anolyte concentration buildup.

$$k_p a_p = \frac{10.9 U (1-\epsilon)}{d_p}\left(\frac{UD}{d_p}\right)^{0.51}\left(\frac{D\rho}{\mu}\right)^{0.16} \quad (20)$$

where U is the superficial velocity (volumetric flow rate of fluid per unit area of the bed cross section), D is the fluid-phase diffusivity, ρ is density; and μ is viscosity, in consistent units. With the above relationship, the obtained value of $k_p a_p$ is $2.152\,059 \times 10^{-1}$ s^{-1}; this is around 100 times higher than the experimental value.

The difference probably indicates that the treatment process functions not via the whole bed but through a small length of it, an "absorption front". Initially, this front concerns the initial input region, and with time this region is inactive and the adsorption front proceeds toward the output region. Probably the applied potential affects the length of this front and the increase of $(k_p a + k_m a_m)$; with the increase of applied potential is an index of the increasing length of the absorption front. The comparison of the obtained values of $k_p a$ and $k_m a_m$ (0.048 969 $\times 10^{-3}$ s^{-1} and 2.107 422 $\times 10^{-3}$ s^{-1}) confirms the experimental results of the breakthrough point; i.e., the absorbed flow of CrO_4^{2-} is higher respect to the flow of CrO_4^{2-} that leaves the ion exchange bed. That is, the bed accumulates CrO_4^{2-}, and its final value is very close to the saturation value The concentration of OH ion keeps increasing in the catholyte reservoir because of water electrolysis. As the large amount of OH continues to enter the central compartment, at breakthrough the OH concentration builds up to such an extent that the chromate ions are not able to reach the surface of ion exchange resin. Hence, without any adsorption the entire Cr(VI) coming from the concentration of chromate ions in the output reaches the initial value as if the bed has reached saturation. At this moment, breakthrough is avoided by replacing the catholyte reservoir solution by fresh water.

Performance of EIX. The results of experiments carried out at different sets of conditions by varying parameters such as the initial concentration of the test solution (1000, 500, and 100 mg L^{-1} Cr(VI)) and applied voltage (5, 7.5, 10, 12.5, and 15 V) using a dc power supply and various flow rates are presented in Table 3. The maximum removal rate of Cr(VI) could be achieved in the process stream invariably at lower applied voltages in all experiments. It was also observed from the results that increase of applied voltages decreases the removal efficiency of Cr(VI) in the process stream but increases the energy consumption. The pH of the central compartment is around 11, and that of the anodic compartment is 2.

of the chromate ion in effluent increases and reaches the initial value. On the other hand, when the bed is operated at 12.5 V, it seems to discharge 9 L of effluent up to the breakthrough point. With the same weight of the resin packed inside the middle compartment, the result of the experiment without electrodes is well presented in Figure 4, which shows that this system is able to discharge 1.3 L of chromate-free effluent.

The effect of voltages on the concentration profile of Cr(VI) in the anolyte reservoir with respect to time is presented in Figure 5 when the middle compartment is operated continuously (effluent of the middle compartment is not recirculated). At higher voltage, the rate of accumulation is higher. The trend of accumulation of the concentration in the anodic reservoir is linear with respect to time, and the regression coefficients are 0.98 and 0.99. As per the model developed, eqs 18 and 19 represent the expressions for buildup of the concentration which is also linear; hence this confirms the validity of the model.

From the slope of the plot of t versus $Y(t)$ the value of $k_m a_m$ is computed knowing the value of the sum of the transfer coefficients, obtained from the batch recirculation mode experiments. In other words, when EIX is operated at 12.5 V, in the case of the batch recirculation process, the sum of transfer coefficients $(k_p a + k_m a_m)$ from Table 2 is 2.156 392 $\times 10^{-3}$ s^{-1} and from Figure 5 the slope is 0.0293 h^{-1}; from these two values, the individual transfer coefficients, $k_m a_m$ and $k_p a$, are 0.048 969 $\times 10^{-3}$ s^{-1} and 2.107 422 $\times 10^{-3}$ s^{-1}, respectively.

The coefficient $k_p a_p$ can be estimated using the available dimensional relationship,[30] between the dimensionless numbers.

Table 3. Effects of Operating Parameters Such as Applied Voltage, Initial Rinsewater Concentration, Volumetric Flow Rate of Anolyte, and Process Stream on Percent Removal of Cr(VI); Energy Consumption in Single-Pass Experiment

initial concn C^o, mg L^{-1}	appl voltage, V	flow rate, mL min^{-1}		concn Cr(VI), mg L^{-1}		pH		energy consumption, kW h kg^{-1}
		Q	Q_a	C_o	C_{ao}	middle	anolyte	
1000	5.0	2.0	6.0	190	2230	11.87	2.08	3.09
	7.5	2.0	4.0	350	2210	12.53	2.33	8.56
	10.0	1.6	2.8	383	2130	11.09	2.23	20.10
	12.5	2.0	4.0	450	2240	12.42	2.08	28.22
	15.0	0.8	7.0	520	2190	12.20	2.21	111.68
500	5.0	2.0	7.6	2	1090	11.47	2.27	5.02
	7.5	1.0	8.0	2	1110	11.49	2.69	22.33
	10.0	1.2	4.4	27	1130	11.47	2.27	34.94
	12.5	2.0	4.8	50	1240	11.15	2.06	34.49
	15.0	2.4	3.3	84	1230	11.48	2.08	44.82
100	5.0	2.4	6.4	1	224	10.65	2.89	21.26
	7.5	2.0	5.4	1	222	10.97	3.13	56.18
	10.0	3.2	6.4	2	220	10.75	3.14	62.60
	12.5	2.2	6.4	14	265	11.39	2.94	164.07
	15.0	2.0	4.0	25	270	11.26	2.26	298.33

Conclusion

The present investigation reports on concentrating chromate ions in the anodic compartment of an EIX from the electroplating rinsewater and on removing chromate ion continuously from the central compartment of rinsewater to recycle the water so that the same water can be used for rinsing and water conservation can be achieved. The alkali generated in the cathodic compartment can be used for pretreatment of work pieces to be plated. In batch continuous recirculation process of EIX the maximum chromium removal achieved is 98.82%, which is obtained at voltage 12.5 V. Specific power consumption obtained for the effluent is 72.39 kW h kg^{-1}. The order of the concentration buildup in the dragout and resin tanks with respect to the total area of the plated sheets to be cleaned for a given capacity of the wash tank has been indicated.

Acknowledgment

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