

# RECOVERY AND REUSE OF HEXAVALENT CHROMIUM FROM AQUEOUS SOLUTIONS BY A HYBRID TECHNIQUE OF ELECTRODIALYSIS AND ION EXCHANGE

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**Abstract** - The chrome plating industry is one of the highly polluting industries whose effluent mainly consists of chromium(VI). This compound is highly toxic to aquatic life and human health. The rinse water constituents reflect the chrome plating bath characteristics; generally dead tank wash water contains about 1% of the plating bath concentration. Other metals and metal compounds usually considered as toxic can be precipitated out by suitably adjusting the pH of the wastewaters. However, Cr(VI) is soluble in almost all pH ranges and therefore an efficient treatment is required for the removal and recovery of chromium, and also for the reuse of wastewaters. The present study aims to recover the chromium by a hybrid technique of electrodialysis and ion exchange for the removal and concentration of chromate ions from the effluent. The different modes of operation like batch recirculation process, batch recirculation process with continuous dipping and continuous process were carried out to remove and recover the chromium from the effluent and the percentage reductions of chromium were found to be 98.69%, 99.18% and 100%, respectively.

**Keywords:** Chromium(VI); Electrodialysis; Ion exchange; Anionic exchange resin (AXR); Anionic exchange membrane (AXM).

## INTRODUCTION

Chromium and its salts find extensive use in photography, chromium plating, textile manufacture, tanning of leather, manufacturing green varnishes, paints, inks and glasses for porcelain, etc. in which more and more chromium enters the wastewater, ground water or soil. It is very well known that chromium exists either in the Cr (VI) or trivalent Cr (III) form. Due to its toxicity and mobility, Cr (VI) is a contaminant and a monitoring process in situ in the environment must be immediately developed. The hexavalent form is more hazardous to living organisms than the trivalent form, since the

international agency for research on cancer has determined that hexavalent chromium is carcinogenic to humans (Boddu et al., 2003).

The acidic chromium-bearing waste can be treated by simple neutralization to some extent, but largely to reduce the corrosiveness of the usually acidic solution (Jenkins and Watson 1974). Neutralized chromium wastes may be disposed of directly or some form of solid-liquid separation (sedimentation, filtration, etc.) may be employed. The processes involving the reduction of chromium to the trivalent form and the subsequent precipitation of the reduced chromium with alkali are often used to dispose of chromium bearing waste. This general

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process is employed extensively by intermediate and large plating plants for treatment of chromium wastewaters (Garrett et al., 1958; Haribabu and Upadhyay, 1992; Kramer, 1967; Patnaik and Das, 1995; Watson and Kenneth, 1953). The use of alkaline reagents such as  $\text{Ca}(\text{OH})_2$  and  $\text{NaOH}$  for removing copper and chromium ions was evaluated. Separation of heavy metals such as chromium compounds from petrochemical industries' cooling water wastes was achieved by conversion of hexavalent chromium to trivalent chromium. The maximum conversion occurred in the pH range of 2.0 - 2.3, adjusted by ferrous sulfate and sulfuric acid (Mirbagheri and Hosseini, 2004).

Electrochemical techniques have also been utilized with different degrees of success. A typical electrochemical process consists of the reduction of chromate at the cathode of a cell to chromium (III) ions, which are precipitated and removed as highly insoluble species, normally  $\text{Cr}(\text{OH})_3$ , at a later stage. Since this precipitate is capable of blocking the cathode surface, different approaches have been devised for its removal, either by chemical dissolution or by electrochemical means through potential inversion so as to re-oxidize it to soluble chromate and produce more concentrated  $\text{Cr}(\text{VI})$  solution for reuse (Abda et al., 1991; Golub and Oren, 1989; Vilar et al., 2003).

The viability of ion exchange as an alternative process for treatment of rinse water was investigated by determining the efficacy of two ion exchange systems, system 1: "strong" cationic resin – "strong" anionic resin and system 2: "strong" cationic resin – "weak" anionic resin (Tenorio and Espinosa, 2001). The simultaneous recovery of  $\text{Cr}(\text{VI})$  and  $\text{Cr}(\text{III})$  ions through charged ion exchange membranes by using three detachable cells was tested at different current densities (Ali Tor et al., 2004).

Ion exchange has been used for decades in water and wastewater purification processes: undesired ions contained in the waters are exchanged by preferred ions from the fixed matrix of the ion exchanger (Barros et al., 2003). However, regeneration of ion exchange resin is carried out using concentrated solutions, and the liquids produced by the necessary operation give rise to secondary pollution issues. A promising alternative process was suggested by coupling ion exchange to electrodialysis (Glueckauf 1959; Ganzi et al. 1987; Ganzi et al. 1997). The hybrid technique combines the advantages of the separate methods; in particular, the technique is fully continuous, contrary to ion exchange. Its current industrial application is the production of ultrapure water by removal of all ions.

Practically the hybrid system consists of percolating the electrolyte solution through an ion exchange bed between two ion-selective membranes

that divide the cell into three compartments. For its main application, ultrapure water production, mixed beds of cation-and anion-exchange resins are used (Thate et al., 1999). Water electrolysis occurs at the electrodes of the two external chambers and  $\text{H}^+$  and  $\text{OH}^-$  formed are transferred to the resin bed. Another configuration uses a cation exchange only and two cation exchange membranes for metal removal from the rinsing waters of plating industries, as investigated for  $\text{Ni}^{2+}$  removal or for the case of cupric ions (Mahmoud et al., 2003; Spoor et al., 2001a; Spoor et al., 2001b).

The efficiency of hybrid technique processes is usually presented in terms of continuous regeneration of the sorbent upon continuous supply of  $\text{H}^+/\text{OH}^-$  by electrodes and simultaneous migration of the ions to be removed to the electrode compartments. In addition, the presence of the resin greatly enhances the electrical conductivity of the two-phase medium, in particular for very dilute waters (Helfferich 1962). Therefore, a hybrid system can perform purification of media that can not be treated by continuous electrodialysis.

The hybrid system involves a number of phenomena, namely ion exchange, ion transport in the conducting porous bed, mass transport through the membranes, and ion transport to the electrodes. All of them are strongly coupled to each other. In this present investigation, an attempt is made to study the hybrid technique of electrodialysis and ion exchange for the removal and concentration of chromate ions from the effluent via different modes of operation like batch recirculation process, batch recirculation process with continuous dipping and continuous process.

## MATERIALS AND METHODS

### Materials

All the chemicals used were of analytical grade. Chromium solution was prepared by dissolving potassium chromate ( $\text{K}_2\text{CrO}_4$ ) in double distilled water. Ruthenium dioxide coated titanium metal ( $\text{RuO}_2/\text{Ti}$ ) was used as anode and stainless steel plate as cathode. Wastewater was pumped into the electrochemical cells, and anolyte and catholyte were recirculated at a controlled rate with the help of peristaltic pumps. The trade name of the anion exchange resin (AXR) used in the present investigation is Ceralite IRA 400. The various properties of Ceralite IRA 400 are given in Table 1. Ceralite IRA 400 is a  $\text{Cl}^-$  form strongly basic AXR. Ceralite IRA 400 was treated with sodium hydroxide solution to obtain the  $\text{OH}^-$  form AXR before its use.

**Table 1: Properties of the ion exchange resin Ceralite IRA 400**

S. No	Parameter	Ceralite IRA 400
1	Manufacturer/supplier	CDH, New Delhi
2	Ionic group	Cl <sup>-</sup> form strongly basic AXR
3	Particle size	0.4–0.6 (effective size) mm
4	Physical form beads	Brown resinous spherical beads
5	Density	0.694 g/ml
6	Exchange capacity (fresh)	3–3.5mequiv./g
7	Moisture content	42–48 wt%
8	Maximum Temperature	150 °C
9	pH range	0–14
10	Cross-linking	8% DVB
11	Porosity	0.42
12	Nominal diameter	0.5mm

### Experimental Setup

The experimental setup consists of a specially designed hybrid reactor that had an effective membrane area of  $7 \times 7 \text{ cm}^2$ . The hybrid device is a plate-and-frame cell provided with three compartments - an anode, a process stream, and a cathode. The geometric dimensions of each of the compartments were  $7 \times 7 \times 1.5 \text{ cm}^3$ . The stainless steel sheet (of dimensions  $7 \times 7 \times 0.2 \text{ cm}^3$ ) of area  $49 \text{ cm}^2$  was used as a cathode, and noble metal oxides ( $\text{TiO}_2$  and  $\text{RuO}_2$ ) coated on expanded Ti mesh of area  $40 \text{ cm}^2$  were used as an anode. The middle compartment is separated from the anodic and cathodic compartments with the help of two carboxylic anionic exchange membranes. The middle compartment and cathodic compartment were filled with anionic exchange resin (AXR).

A plating rinsewater reservoir of 5 L capacity was used. The rinsewater from the reservoir was passed from the reservoir to the top of the middle compartment with the help of a peristaltic pump. 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 purposes and then returned to the hybrid reactor). In the anodic compartment, an anolyte reservoir of 500 mL capacity was used and 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, it will be returned to the plating tank itself as makeup solution. Fresh rinsewater will be taken in the anolyte reservoir for further operation. For the cathodic compartment, a catholyte reservoir of 500 mL capacity was used and 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). Fresh process water will be taken in the reservoir of catholyte for further operation. The electrical circuit part consisted of a multioutput DC regulated power supply (0-2 A, 0-30 V, Aplab Model) together with ammeter and voltmeter connected to the hybrid reactor (which is a plate-and-frame cell) provided with three compartments - an anode, a cathode, and a process streams.

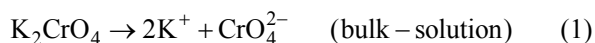
### EXPERIMENTAL PROCEDURE

The process presented here consists of a multipurpose plate and frame electrochemical cell with three compartments; an anode, a cathode and a process stream. The PVC compartment frames were separated by anion exchange membranes and filled with ion-exchange resin and bolted together with PVC and steel end plates. The process compartment is separated from the anodic and cathodic compartments with the help of two carboxylic anionic exchange membranes. The process and cathodic compartments were filled with the required quantity of anionic exchange resin. The purpose of the resin is twofold: to enhance the electrical conductivity and increase the residence time of the chromate in the reactor. Anolyte and catholyte recycle streams were pumped up-flow to remove hydrolytically produced gases which could effect current distribution if allowed to accumulate. The preliminary experiments were carried out by varying the cell voltage from 2.5 to 12.5 V. As the cell voltage increases, the efficiency of the treatment decreases due to the higher current. At higher

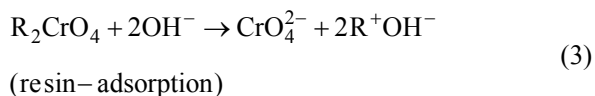
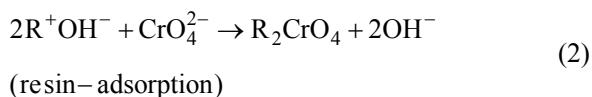
current, the solution heated up and the treatment did not occur efficiently. Thus, the process is dependent on applied voltage and only at a low voltage of about 5 volts is high efficiency obtained; we have therefore taken the cell voltage as 5V for all the experimental studies. The synthetic effluent was prepared with potassium chromate at a single concentration (312.39 mg/L) and experiments were carried out at 5 volts by using a direct current power supply with a flow rate of 10 mL/min. During the electrolysis, the samples were collected periodically and were analyzed for total chromium by using a Spectroquant NOVA 60 spectrophotometer. The pH measurements were done by using a pH meter. The chromate ions are removed from the feed solution by the anionic exchange resin in the process compartment. The adsorbed chromate ions then migrate towards the anodic compartment through an anionic exchange membrane under the influence of the electric field. The chromate ions were concentrated in the anodic compartment for return to the plating bath. The hydroxide ions were electrochemically generated at the cathode, then migrated continuously to regenerate the process stream anionic exchange resin. Hydronium ions produced at the anode are excluded by the anionic membrane from entering the process stream and serve to balance the charge with incoming chromate ions to produce purified chromic acid. The following reactions were carried out in the hybrid system.

### In the Process Stream

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 the chromate anion. The reaction taking place in the bulk can be represented as

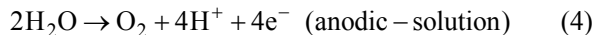


Anionic resin adsorbs chromate ion. The following reactions take place:

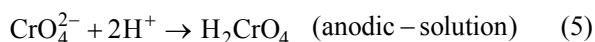


### In the Anode Compartment

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

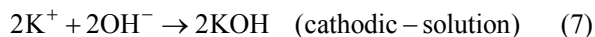


Under the electric field, chromate ion and hydroxide ion, due to their affinity toward the anode, pass through the anion exchange membrane and the concentration of chromic acid becomes enriched. In the bulk of the anode compartment, the following reaction takes place to produce chromic acid:



### In the Cathode Compartment

At the cathode, the following reactions take place:



## MODES OF OPERATION

### Batch Recirculation Process

The diagram of the batch recirculation process is shown in Fig. 1. In the batch recirculation process, rinsewater (synthetic effluent) of concentration 312.39 mg/L was prepared using potassium chromate and used as an 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 500 mL each, as described earlier. The flow rate of 10 mL/min was maintained for all fluid flows. Using a direct current regulated power supply, the required cell voltage (5 volts) was maintained and the experiments were carried out. Every hour, the samples of all reservoirs were collected and analyzed for total chromium using the Merck Spectroquant NOVA 60, barcode-based spectrophotometer, with diphenyl carbazide as indicator. The pH measurements were done using a pH meter. The experiments were continued until the minimum concentration of chromium was reached.

### Batch Recirculation Process with Continuous Dipping

The diagram of the batch recirculation process with continuous dipping is shown in Fig. 2. The plated metal article from the electroplating bath was taken out and washed in four rinse water tanks of the same volume; the first wash tank water is called dead tank wash. The article was rinsed 5 seconds in each wash water tank. In the batch recirculation process, the hybrid reactor was placed in the dead tank wash of the chromium electroplating line; the inlet process stream of the hybrid reactor was the dead tank wash. The outlet from the process stream was recycled to the wash water tank with the help of a peristaltic pump. The anolyte and catholyte solutions were recycled with the help of peristaltic pumps as shown in the Fig. The process was carried out at 5 volts and the flow rate of the each stream was same at 10 mL/min. Every hour the samples of all reservoirs were collected and analyzed for total chromium using the Merck Spectroquant NOVA 60, barcode-

based spectrophotometer, with diphenyl carbazide as indicator. The pH measurements were done using a pH meter.

### Continuous Process

An experimental study carried out to determine the break-even point of the hybrid reactor is shown in Fig. 3. It is very 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 compartment and the test solution containing 312.39 mg/L of Cr (VI) was made to run in the cell. This experiment was carried at 5 volts and with the flow rate of 10 mL/min. The anolyte and catholyte solutions were recycled separately with the help of peristaltic pumps. The chromate solution (rinsewater) was continuously passed through the central compartment and the output was collected in a separate container. The outlet samples were taken periodically and analyzed for chromate and pH.

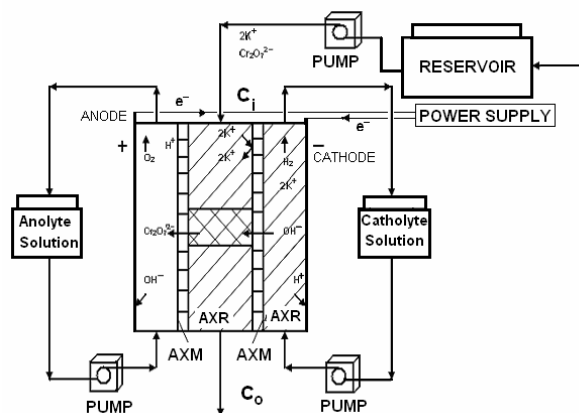


Figure 1: Batch recirculation process

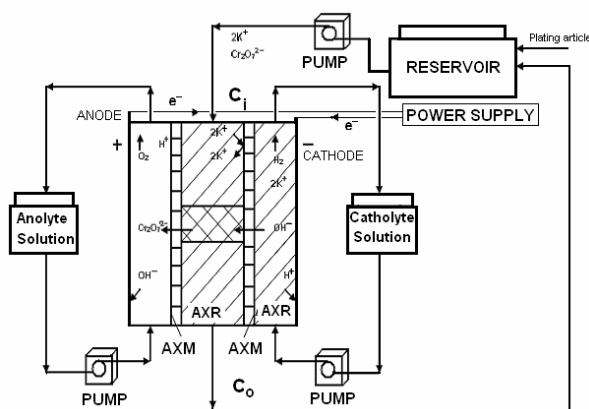


Figure 2: Batch recirculation process with continuous dipping

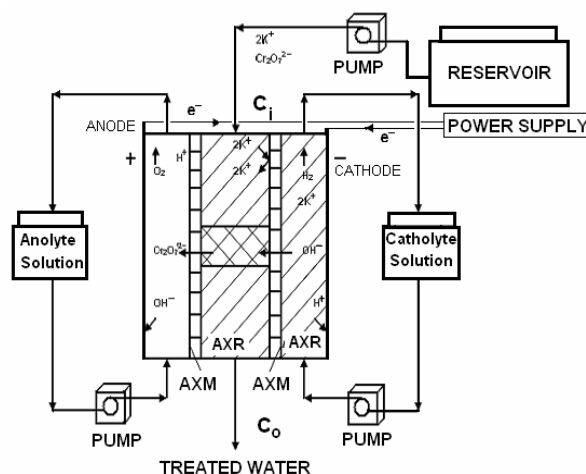


Figure 3: Continuous Process

## RESULTS AND DISCUSSION

### Batch Recirculation Process

The experiment was carried out for the initial concentration of 312.39 mg/L of wastewater with the flow rate of 10 mL/min and at 5 volts. Fig. 4 and Fig. 5 show the temporal decrease of the output concentration of the chromium (or the temporal increase of the % reduction of the chromium) from the initial concentration of 312.39 mg/L, until it reaches the equilibrium point. The maximum removal and recovery of chromium were obtained from the batch recirculation process at 35 hours of operation, indicating that the equilibrium concentration was reached at 35 hours.

### Batch Recirculation Process with Continuous Dipping

The experiment was carried out for varying initial concentrations of wastewater while dipping the plating article into the rinse water reservoir with the flow rate of 10 mL/min and at 5 volts. Fig. 6 shows the number of dips increases from 1-70 dips with the increase in concentration of chromium developed in the rinse water reservoir. The maximum number of dips used here is 70 dips and the respective initial concentration was analyzed as 2177.62 mg/L. After 70 hours of operation the final concentration achieved was 120.14 mg/L and the percentage reduction of Cr(VI) was found to be 94.48%. Fig. 7 shows that the output concentration decreases with

time until it reaches the equilibrium; after that, the output concentration increases with time. Fig. 8 shows that the anolyte concentration increases with time and finally reached 59.33 mg/L. Fig. 9 shows that the percentage reduction of chromium increases with time. After 50 h of operation, the percentage reduction of chromium starts to decrease with time. This indicates that the middle compartment resin bed was exhausted with chromium ions due to the increasing alkali content in the cathodic compartment. To avoid this situation, the solution in the cathodic compartment should be replaced.

### Continuous Process

The experiment was carried out for the initial concentration of 312.39 mg/L of wastewater with the flow rate of 10 mL/min and at 5 volts. Fig. 10 and 11 show that the chromate ion concentration decreases with time in the outlet of the middle compartment; after reaching saturation, the outlet concentration increases with time. The concentration in the anodic compartment increased with time, whereas the rate of increase was fairly constant in the cathodic solution. The result shows that the final concentration in the anodic compartment was three-fold higher than the inlet concentration of chromate ions. Fig. 12 shows that the percentage reduction of chromium is maintained at 100% up to the operation time of 120 h. After 120 h of operation, it starts to decrease because of bed exhaustion and alkali production in the cathodic compartment.

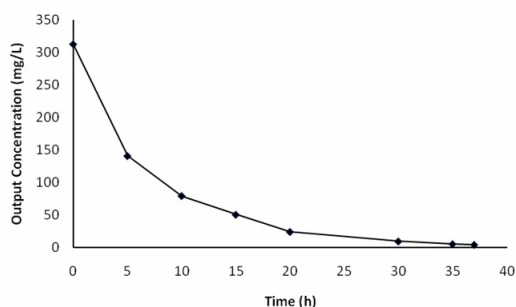


Figure 4: Output Concentration Vs Time

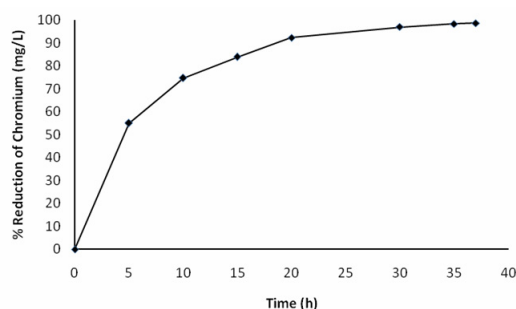


Figure 5: %Reduction of Chromium Vs Time

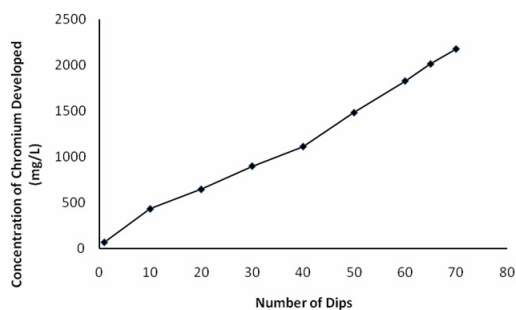


Figure 6: Effect of Number of dips

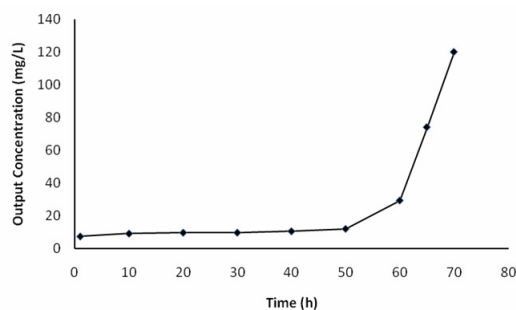
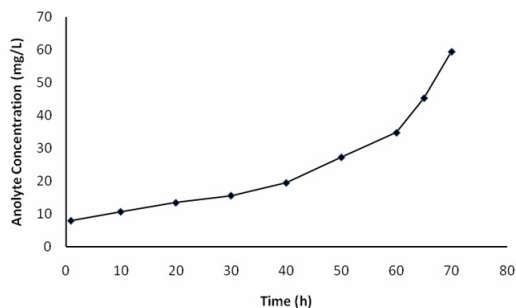
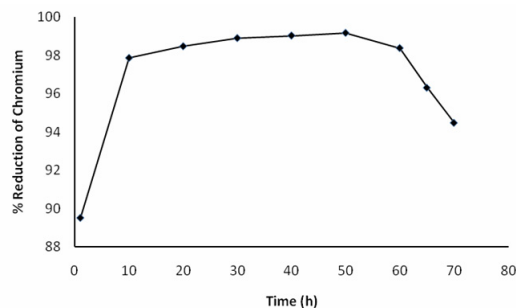


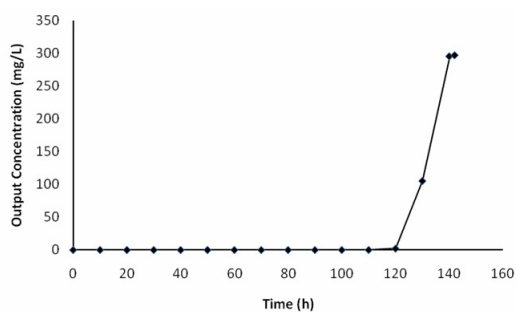
Figure 7: Output Concentration Vs Time



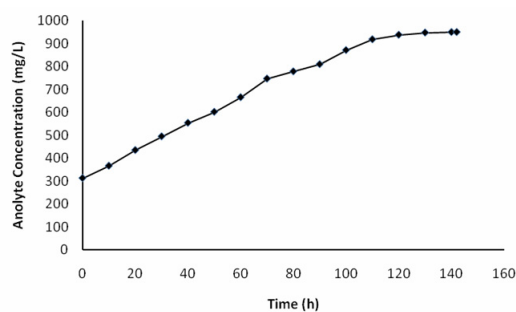
**Figure 8:** Anolyte Concentration Vs Time



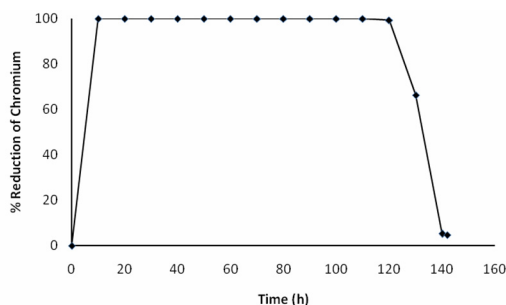
**Figure 9:** % Reduction of Chromium Vs Time



**Figure 10:** Break Through Curve Analysis



**Figure 11:** Anolyte Concentration Vs Time



**Figure 12:** % Reduction of Chromium Vs Time

## CONCLUSION

The present investigation reports on concentrating chromate ions from chrome plating rinse water in the anodic compartment of a hybrid reactor and on removing chromate ion continuously from the central compartment of rinse water by recycling the water; consequently, 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. The different modes of operation like a batch recirculation process, batch recirculation process with continuous dipping and continuous process were carried out successfully and the percentage reductions of chromium were found be

98.69, 99.18 and 100% respectively, at 5 volts and with a flow rate of 10 mL/min.

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