



CHROMIUM REMOVAL BY A BIPOLAR ELECTRO-CHEMICAL PRECIPITATION PROCESS

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ABSTRACT

This research was conducted in laboratory to investigate an alternative for Cr removal from an electroplating wastewater using the electro-chemical precipitation (ECP) process. The ECP unit, operated in the bipolar mode, had six steel plates including the anode and cathode and was supplied with DC power. The electroplating wastewater used in the experiments contained Cr concentrations in the range of 570-2100 mg/l. The Cr removal efficiencies in the bipolar ECP units were higher than 99% and the Cr concentrations in the treated effluent were less than 0.5 mg/l. The acceptable conditions of the bipolar ECP unit treating the electroplating wastewater were found to be: $I - 1.0$ amp (or $i - 6.70$ amp/m²) and initial pH (pH_i) of 4.5. At these acceptable conditions, the electric power and steel electrode plate consumptions were 20.0 kWh/m³ and 1.1-2.8 kg-Fe/kg Cr removed, respectively. X-ray fluorescence and X-ray diffractometric analysis performed on the precipitated sludge revealed the main compounds to be maghemite (Fe₂O₃) and chromite (FeCr₂O₄). The percent Fe₂O₃ and FeCr₂O₄ contents of the dried ECP sludge were 68% and 25%, respectively. From the mass balance analysis, the percent of Cr removal by precipitation in the ECP unit and adsorption on the ECP sludge were 85.1 and 14.8%, respectively.

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KEYWORDS

Electroplating wastewater, chromium, electrochemical precipitation, heavy metal removal, sludge.

LIST OF ABBREVIATIONS

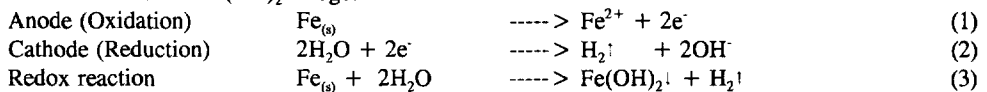
AC	Alternative current
C _e	Effluent Cr concentration (mg/l)
C _o	Initial Cr concentration (mg/l)
DC	Direct current
E	Electrical potential (volt)
ECP	Electro-chemical precipitation
h	hour
I	Electrical current (amp)
i	Current density (amp/m ²)
min	minute

Min OT	Minimum operation time (min)
OT	Operation time (min)
P _c	Power consumption (kWh/m ³)
pH _i	Initial pH
S	Siemen, conductivity unit
SVI	Sludge volume index

INTRODUCTION

The presence of heavy metals in electroplating wastewaters can cause serious damage to the environment when discharged directly without proper treatment. The most toxic contaminants found in electroplating wastewaters are acid cyanide and heavy metals such as chromium (Cr), nickel (Ni), copper (Cu) and mercury (Hg). Methods to remove heavy metals from the wastewaters are: chemical precipitation, ion exchange, electrodialysis and electro-chemical precipitation. Precipitation of heavy metals as hydroxides through the addition of lime is a well-established technology, but it generates large volume of relatively low density sludge which could pose problems in the sludge disposal.

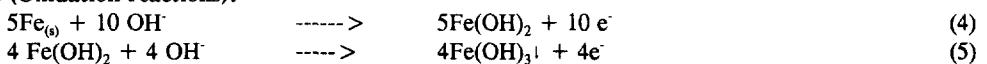
Electro-chemical precipitation (ECP) is based on the same principle as an electrolytic cell in which at least two electrode plates are installed as anode and cathode. The DC power source supplies electric current to the ECP unit filled with an electrolyte solution. In the ECP unit, the electrode dissolves from the anode (Eq. 1) and hydrogen gas (H₂) is generated at the cathode (Eq.2)(Peter *et al.*, 1974). The overall redox reaction (Eq. 3) results in the formation Fe(OH)₂ sludge.



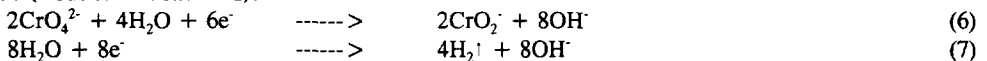
Pickett (1979) proposed the use of a multiple ECP cell arrangements which can be monopolar electrode with cells in series, monopolar electrode with cell in parallel, or bipolar electrode with multiple cells in series. Due to its lower power consumption and operation time requirement, the bipolar ECP unit was found to be superior to the monopolar ECP unit for Cr ions removal from an electroplating wastewater (Kongsricharoern, 1994).

The ECP process has been found effective in removing heavy metals from a variety of industrial wastewaters (Dennis and Diebold, 1984; Farrell, 1991; Beck *et al.*, 1974 and Lin and Peng, 1994) and in treating potable water (Vik *et al.*, 1984). These researchers reported the heavy metal removal mechanisms to be precipitation and adsorption, but theoretical and analytical studies were not undertaken in details. The research reported herein has emphasized the removal of Cr from an electroplating wastewater using the ECP process. The chemical reactions responsible for the removal of Cr compounds were hypothesized to be as follows:

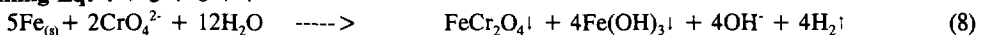
Anode (Oxidation reactions):



Cathode (Reduction reactions):



Combining Eq. 4 + 5 + 6 + 7



The overall reaction (Eq. 8) indicates the production of chromite (FeCr₂O₄) sludge which is a proposed mechanism of Cr removal. In addition, part of the Cr could adsorb to the Fe(OH)₃ sludge and be removed by sedimentation. Based on the above hypothesis, the specific objectives of this study were:

- to determine acceptable conditions of the bipolar ECP unit in removing Cr from an electroplating

wastewater, and

- to verify the mechanism of Cr removal in the bipolar ECP unit as proposed in Eq. 8.

MATERIALS AND METHODS

The ECP experiments were conducted at the Ambient Laboratory of the Environmental Engineering Program, the Asian Institute of Technology (AIT), in which the ambient temperatures were 28-33 °C. The electroplating factory where the Cr wastewater was collected for study is located in Bangkok city, Thailand. It employs a non-cyanide based, chrome plating processes. The Cr wastewater, collected separately from the chrome rinsing bath, was kept at 5°C until use. The Cr concentrations and pH values were 215-3860 mg/l and 1.5-5.5, respectively.

Experimental Set-up

The ECP unit, made of acrylic plate with a size of 5 x 30 x 10 cm³ (width x length x depth), had an effective volume of 1.5 l. The unit had six steel electrode plates. The size and area of each steel electrode plate was 0.3 x 10 x 30 cm³ (thickness x width x length) and 300 cm², respectively. The steel electrode plates were prepared by etching the steel plates with concentrated HCl, steel brushing to remove scale, rinsing with tap water, drying at 150 °C for 1 h, they were cooled in a desiccator and weighed. The distance between these electrode plates was fixed at 1 cm apart. The electrical potential (E) supplied to the ECP unit was controlled by a variable voltage transformer. The experimental set-up of the ECP unit, as shown in Fig. 1, was based on Pickett (1979).

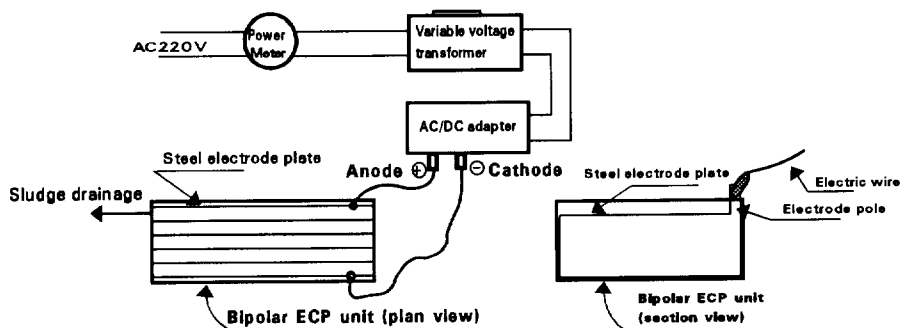


Fig.1. Experimental set-up of the ECP unit - schematic diagram

Experimental Procedures

Determination of acceptable ECP conditions. The acceptable conditions of the ECP unit were selected based on the ECP operating conditions that would result in the Cr concentrations remaining in the effluent of less than 0.5 mg/l (which is the effluent standard of the Ministry of Industry, Thailand) and requiring the least power consumption (P_c).

At the beginning of each batch experiment, the ECP unit was filled with 1.5 l of the Cr wastewater. The experimental conditions used in this research are shown in Table 1. The mixed liquor or precipitated sludge samples were periodically collected from the ECP unit as shown in Table 1. The remaining total Cr

concentrations were measured in the filtrate of these samples.

TABLE 1 PARAMETERS VARIATION DURING THE ECP EXPERIMENTS

Parameters	Values
Initial Cr concentration, C_o (mg/l)	500, 1100, 2000, 3000
Operation time, OT (min)	0, 2, 4, 6, 8, 10, 13, 15, 18, 20, 25, 30, 35, 40, 45, 50
Initial pH, pH_i	1.5, 3.0, 4.5, 6.0, 7.5
Electrical current, I (amp)	0.5, 1.0, 1.5, 2.0, 5.0

The initial Cr concentration (C_o) values were varied by diluting the concentrated Cr wastewater with tap water to the desired Cr concentrations. The pH of the Cr wastewater was adjusted by adding H_2SO_4 or NaOH to obtain the desired pH_i values; the conductivity value of the Cr wastewater at each of these pH_i values was adjusted by adding 1N KCl solution to obtain the same conductivity of 1.45 mS/cm. The I values applied to the ECP unit were adjusted with a variable voltage transformer, while the temperatures of the ECP mixed liquor were adjusted with a manually operated water cooling unit to be in the optimum range of 25-45°C (Kongsricharoern, 1994).

At each OT, about 20 ml of the mixed liquor was sampled from the middle part of the ECP unit by a 25-ml plastic syringe. The mixed liquor sample was filtered immediately through a 0.45 μ m glass filter, and the filtrate sample analyzed for the remaining Cr concentration using an atomic absorption spectrophotometer. The solids retaining on the filter paper were dried at 103 °C for 2 h, cooled in a desiccator and weighed for determination of the TSS production in the ECP unit.

Verification of Cr removal mechanism in the ECP unit. The mechanism of Cr removal in the ECP unit, as proposed in Eq.8, was verified by studying the percent content of Cr and type of Cr compounds present in the precipitated sludge. About 1.5 l of the Cr wastewater was directly fed to the ECP unit operating at the acceptable conditions found earlier. The precipitated sludge was then collected, dried at 103 °C for 24 h and cooled in a desiccator. The percent contents of the various compounds present in the precipitated sludge were determined by X-ray fluorescence spectrometry (model JEOL EDXRF XR 200), while the forms of Cr contained in the ECP sludge were determined by X-ray diffractometry (model JEOL JDX-8030).

Other chemical and physical analysis were conducted according to the methods described in "Standard Methods" (APHA, AWWA, WPCF, 1989).

EXPERIMENTAL RESULTS

Acceptable ECP Conditions for Cr Removal

Effects of pH_i . During the batch ECP experiments, pH of the mixed liquor were found to increase during the first few minutes of the operation time, and remained rather stable afterwards up to the 60 min operation time (OT). The pH increase at the beginning could be due to the production of OH^- ions dissociated from water, as shown in Eq. 6 and 7. After that all the pH values became relatively stable in the range of 10.5-11.5, probably due to the formation of $Fe(OH)_3$ compounds (Eq. 4 and 5).

A preliminary study found pH_i to have an effect on the final mixed liquor pH. At the pH_i of 1.5, the mixed liquor pH was increased to about 7. However, at the pH_i range of 3.0-7.5, because of lower concentration of H^+ ions available to react with the produced OH^- ions (Eq.8), the mixed liquor pH was increased to values between 10.5-11.5. Therefore, because Fe(II) and Fe(III) ions normally precipitate under basic conditions, the pH_i of the wastewater to be fed to the ECP unit should be adjusted above 3 so as to create sufficient OH^- ions to precipitate the Fe(II) and Fe(III) ions.

Fig. 2 shows the effects of pH_i on the Cr removal efficiencies in the ECP unit. As the pH_i value of 1.5 caused the mixed liquor pH to be only about 7 which was not suitable for Fe(II) and Fe(III) precipitation (Eq.8) (Eckenfelder, 1989), hence less Cr removal during the 0-10 min OT; in addition, some Fe compounds were found to precipitate further in the mixed liquor filtrate sample after only about 5 min of storage. The OT required to reach Cr concentrations of less than 0.5 mg/l in the mixed liquor is shortest for pH_i of 4.5 and longest for pH_i of 7.5. To achieve the Cr concentrations in the mixed liquor filtrate of less than 0.5 mg/l, the data of Fig. 2 suggest that the pH_i be maintained at 4.5.

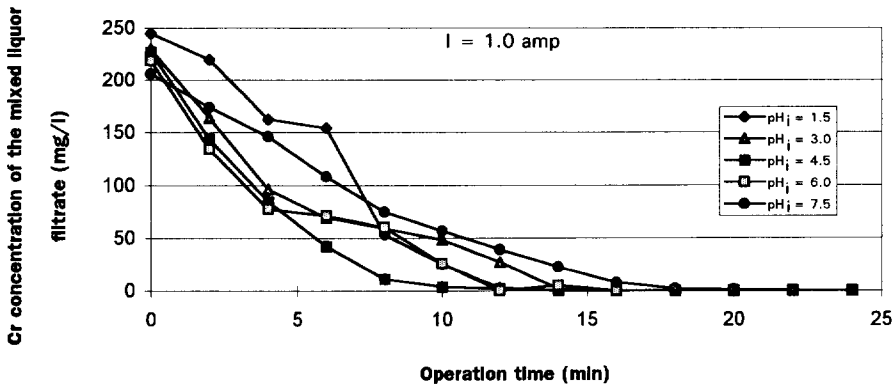


Fig. 2. Effects of pH_i on Cr removal efficiencies in the ECP unit

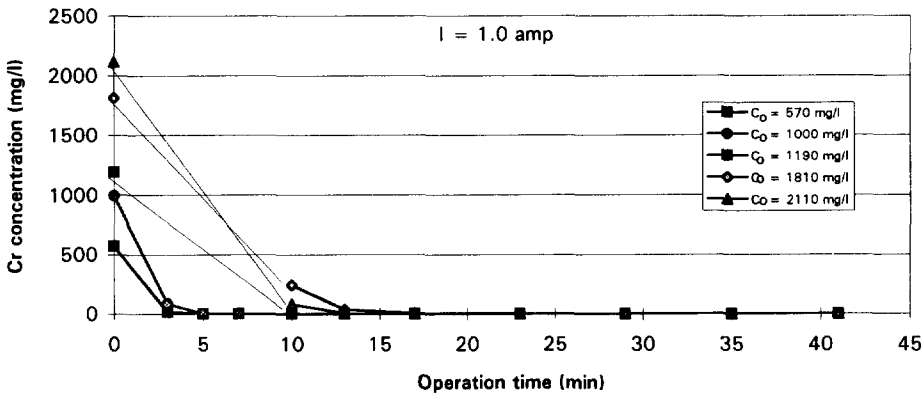
Effects of I. The C_o , pH_i and I values were varied at 1100 mg/l, 4.5 and 0.5-5.0 amp, respectively. Table 2 shows the effects of I on the Min OT required to achieve the Cr concentrations in the mixed liquor filtrate of less than 0.5 mg/l, including the corresponding electrical power consumption (P_c) values in the ECP unit. Increasing the I values inevitably caused higher P_c values (165-185 kWh/m³), especially at the 2.0 and 5.0 amp conditions. The I values of 0.5-1.5 amp resulted in the lower P_c values of 20.0-40.0 kWh/m³. It is apparent that the higher the I values, the faster the Cr removal rates in the ECP unit; this phenomenon was due to the increase in the number and speed of ions and electron movement between the two electrodes, resulting in the rapid reactions of Eq. 8. From Fig. 1, due to the fixed surface area of the electrode plates (or anode), the amount of $\text{Fe}(\text{OH})_3$ produced (Eq. 4 and 5) would be constant at a particular I value. Therefore, if there were high concentrations of Cr ions, the OT required to complete the reactions of Eq. 8 would be longer. The data of Table 2 suggest that, to achieve the lowest P_c , the Min OT and the operation I values should be maintained at 50 min and 1.0 amp (or the i value of 6.7 amp/m²), respectively.

TABLE 2 EFFECTS OF I ON THE MIN I OT AND P_c

Electrical current I, (amp)	Minimum operation time Min OT, (min)	Power consumption P _c , (kWh/m ³)
0.5	90	26.7
1.0	50	20.0
1.5	45	40.0
2.0	40	165.0
5.0	35	185.0

Effects of C₀ Fig. 3 shows the effects of C₀ in the range of 570-2100 mg/l on Cr removal in the ECP unit, which indicated the lower the C₀ values, the shorter the OT required for Cr removal; this was probably due to the reduced amount of Cr to be electro-chemically precipitated (Eq.8), as previously discussed. The Min OT to reach the Cr concentrations of 0.5 mg/l or less was found to be about 20 min.

It is apparent from the above results that the ECP performance was affected by pH_i, I, OT and C₀. The acceptable ECP conditions, based on the experimental results reported herein, were found to be as follows: pH_i of 4.5 and I - 1.0 amp (or i - 6.7 amp/m²); the Min OT would depend on C₀ values. These operating conditions should result in the Cr concentrations in the mixed liquor filtrate of 0.5 mg/l or less and the lowest P_c for the conditions tested.

Fig. 3. Relationships between C₀ and OT in the bipolar ECP unit

Cr Removal Mechanisms in the ECP Unit

Characteristics of the ECP sludge. During the ECP batch experiments, the TSS concentration and production were found to increase with increasing OT, C₀ and I values; the ranges of TSS concentration and sludge production were 2000-7200 mg/l and 2.25-3.15 kg/m³ of Cr wastewater, respectively. Although the density of the precipitated sludge was 1000.8-1002.0 kg/m³ of sludge, the SVI and CST were in the ranges of 60-80 and 20-40 sec, indicating good sludge settleability and dewaterability (Metcalf & Eddy, 1991). The dark

brown color of the ECP sludge was due to the presence of Fe dissolved from the anode (Eq.4 and 5).

Percent content and composition of Cr in the ECP sludge. Chemical compositions of the precipitated sludge determined by X-ray fluorescence analysis, are shown in Table 3. Fe_2O_3 was found to be the major compound (67.9%) contained in the ECP sludge, followed by Cr_2O_3 (25%). From Eq.8, assuming $\text{Fe}(\text{OH})_3$ and FeCr_2O_4 were the major compounds of the ECP sludge, based on mass balance analysis, their percent contents are 67.3 and 23.9, respectively, which are in the same range as those in Table 3.

The X-Ray diffractometric analysis revealed the major types of compounds present in the ECP sludge to be maghemite (Fe_2O_3) and chromite (FeCr_2O_4), thus confirming the results shown in Table 4 and the hypothesis previously proposed in Eq.8. From the mass balance analysis, the percent of Cr removal by precipitation (Eq. 8) in the ECP unit and adsorption on the ECP sludge were 85.1 and 14.8%, respectively.

TABLE 3 CHEMICAL COMPOSITIONS OF DRIED ECP SLUDGE

Chemical composition	% dry weight (expressed as oxide equivalent)
Fe_2O_3	67.9
SO_3	1.8
Cr_2O_3	25.0
NiO	5.5

The presence of FeCr_2O_4 in the ECP sludge sample confirmed the hypothesis that the ECP process could chemically reduce the Cr(VI) ions to the less toxic Cr(III) ions and incorporate them into the iron complex compound form. It can be theoretically calculated from Eq. 8 that removing 1 kg of Cr(VI) by the ECP process would require 2.7 kg of Fe (or steel electrode plate) which is within the experimental range of 1.1-2.8 kg-Fe consumed/kg-Cr removed (Kongsricharoern 1994).

CONCLUSIONS

Based on the experimental results obtained from this study, the following conclusions are made:

1. The bipolar ECP process was found to be feasible in treating a high strength Cr wastewater (Cr concentrations ranging from 570 to 2100 mg/l).
2. The acceptable conditions of the bipolar ECP unit treating the Cr wastewater to achieve the total Cr concentrations in the mixed liquor filtrate of less than 0.5 mg/l and requiring least power consumption were found to be: I - 1.0 amp (or i - 6.7 amp/m²), pH_i - 4.5. At these acceptable conditions, the electric power and iron electrode plate consumptions were 20.0 kWh/m³ and 1.1-2.8 kg-Fe/kg-Cr removed, respectively. The Min OT was found to vary with the C_o value.
3. The mechanisms of Cr removal in the ECP unit were found to be reduction of Cr(VI) to Cr(III) ions, incorporation of the Cr(III) ions into the complex Fe compounds and precipitation. The main compounds of the precipitated sludge were identified as maghemite (Fe_2O_3) and chromite (FeCr_2O_4), whose percent contents in the dried sludge were 68% and 25 %, respectively.

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