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Recovery of Chromium from Electroplating Wastewater Using DI 2-(Ethylhexyl) Phosphoric Acid

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Recovery of Chromium from Electroplating Wastewater Using DI 2-(Ethylhexyl) Phosphoric Acid

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Abstract: Extraction of chromium (III) using D2EHPA (di 2-ethylhexyl phosphoric acid) in kerosene was carried out. A study was carried out to optimize the conditions, namely pH, carrier D2EHPA, aqueous and organic ratio, and reaction time. The effect of chloride and sulphate concentration on the extraction process was studied. The tri-butyl phosphate (TBP) was used as a phase modifier to facilitate the extraction process. In the stripping process, remarkable amount of chromium was recovered from the loaded organic phase using hydrogen peroxide as a stripping agent. When the stripped organic solution was reused for chromium extraction, it showed appreciable extraction efficiency under optimum conditions. The chromium (VI) present in the electroplating wastewater was reduced to chromium (III) with ascorbic acid, and under optimized conditions the removal of chromium from electroplating wastewater was found to be satisfactory.

Keywords: Solvent extraction, chromium (III), di 2-(ethylhexyl) phosphoric acid, tri-butyl phosphate, stripping

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INTRODUCTION

Heavy metals originating from electroplating industry have received considerable attention and studies over the past decade. Several attempts have been made to develop methods to effectively control the release of toxic and hazardous materials into the environment. There is continued concern over the potential adverse effects on humans, animals and crops from the toxic heavy metal contaminants found in wastewater, especially in the case of wastewater arising from metal finishing industries. Although many sources can be attributed as a cause for chromium-contamination, the electroplating industry is probably one of the largest contributors of chromium containing wastewater. Realizing the high toxic potential of chromium (VI), regulatory agencies are keen in restricting the disposal of chromium containing wastewater into land and aquatic systems. A versatile technique adopted for removal of chromium from industrial waste is by the reduction of chromium (VI) to chromium (III) using ferrous sulphate, sulphur dioxide and ascorbic acid followed by precipitation (1, 2). But this technique is tedious.

D2EHPA is a well-known solvent extraction reagent showing favorable extraction and stripping properties for a range of metals like Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, and Cr^{3+} (3). It is chemically stable and relatively cheap. The purity of D2EHPA can be easily determined by a potentiometric method of acid – base titration (4, 5). In addition, this reagent can be purified to achieve purity of over 98%, which is essential for rigorous equilibrium and kinetics investigation. D2EHPA molecules predominate as monomers in aromatic diluents and as dimmers when dissolved in aliphatic ones (6). Aliphatic diluents are preferred for extraction process because of their lower toxicity (7).

The extraction of chromium (III) with D2EHPA has been reported previously (1). Islam and Biswas (8) reported that chromium (III) could not be stripped from an organic phase of D2EHPA. In contrast Pandey et al. (1) found that considerable amount of chromium (III) could be stripped with mineral acid from the loaded organic-phase containing D2EHPA. The stripping of chromium (III) was less effective with dilute mineral acid and 8M HCl was required to obtain 80% recovery in 30 min at room temperature (1). Extraction of chromium (III) with D2EHPA reported in the present work is the first under these experimental conditions such as extraction followed by stripping of chromium (III) by oxidation to chromium (VI) from loaded organic phase. The present study investigates the solvent extraction and stripping behavior of standard chromium (III) solution with ammonium salt of D2EHPA. The chromium (VI) present in the electroplating wastewater was reduced to chromium (III) with ascorbic acid. The reduced chromium (III) in plating wastewater was utilized for the extraction and recovery studies for chromium in real effluent.

EXPERIMENTAL PROCEDURE

Reagents and Apparatus

D2EHPA of 98% purity kindly donated by Venus Ethoxy ether, Goa, India, was used without further purification. Tri-butyl phosphate of 99% (CDH, India) purity was used as the third phase modifier and commercial grade kerosene of specific gravity 0.8 was used as a diluent. All the other chemicals used were of analytical reagent grade. A stock solution containing 100 ppm of chromium (III) was made from chromium chloride with distilled water. Standard working solution was prepared on a daily basis. All organic phase solutions were prepared by dissolving weighed amount of D2EHPA and TBP in a minimum volume of kerosene and then diluting to the required volume. A Techcomp UV-VIS spectrophotometer model 8500 was used for measuring absorbance. The investigation of chromium D2EHPA complex present in the organic phase was performed using a Perkin-Elmer FT-IR spectrometer (model spectra −1).

Extraction and Analytical Procedures

Solvent extraction and stripping experiments were carried out by shaking equal volumes of aqueous and organic phase (1 : 1 ratio) in a glass-stoppered bottle using a mechanical shaker at 100 rpm. Standard chromium (III) solution with initial concentration of 100 ppm was used for the extraction studies. During the preliminary extraction studies an emulsion was formed in between the aqueous and organic phase. 0.15 M TBP was added to organic phase to avoid the formation third phase (9). After phase separation, the concentration of a chromium (III) ion remaining in the aqueous phase was determined using standard procedures. The chromium (III) was oxidized to chromium (VI) with dilute sulphuric acid and potassium permanganate solution and analyzed by diphenyl carbazide method (10). The distribution ratio, K_d, was taken as the ratio of the concentration of the metal ion in the organic phase to that present in the aqueous phase.

The stripping process was carried out with sodium hydroxide and hydrogen peroxide solutions. During the analysis, hydrogen peroxide was expelled from the aqueous phase by heating at 40°C for a few minutes (11).

RESULTS AND DISCUSSION

Extraction Equilibrium

The extraction of trivalent chromium ion with an organic-phase containing D2EHPA in kerosene can be expressed as follows:

$$Cr^{3+} + 3HR_{org} \longleftrightarrow CrR_{3org} + 3H^{+} \qquad (1)$$

$$K_{ex} = \frac{[CrR_{3_{org}}][H^+]^3}{[Cr^{3+}][HR_{org}]^3} \tag{2}$$

$$K_d = \frac{[Cr_{org}]}{[Cr^{+3}_{aq.}]} \tag{3}$$

The HR stands for the carrier D2EHPA, K_{ex} is the extraction equilibrium constant and K_d is the distribution coefficient.

Effect of pH on Extraction

The extraction study of aqueous phase containing 100 ppm of chromium (III) was carried out with organic-phase containing 0.45 M solutions of D2EHPA and 0.15 M tri-butyl phosphate in kerosene. The pH optimization was carried out with equal volume of aqueous (20 mL) and organic phase (20 mL). The initial pH of aqueous phase was varied from 1.0 to 4.5 and the extraction was carried out. The percentage of chromium extraction increased with increasing feed pH and the maximum extraction of 38.8% was observed when the initial pH was 4.5. The pH of the solution after extraction was found to be 2.2. This final pH is referred to as equilibrium pH. Reduction in initial pH to equilibrium pH may be due to the acidic nature of D2EHPA (12). To neutralize the organic phase it was stirred with 20% v/v ammonium hydroxide solution for 10 min at 100 rpm and organic phase was separated. This ammoniated organic phase was used for further extraction studies. When ammoniated D2EHPA solution was used for extraction, both the initial and equilibrium pH remained same. The results depicted in Fig. 1 give the extraction of chromium (III) at different pH values by the organic

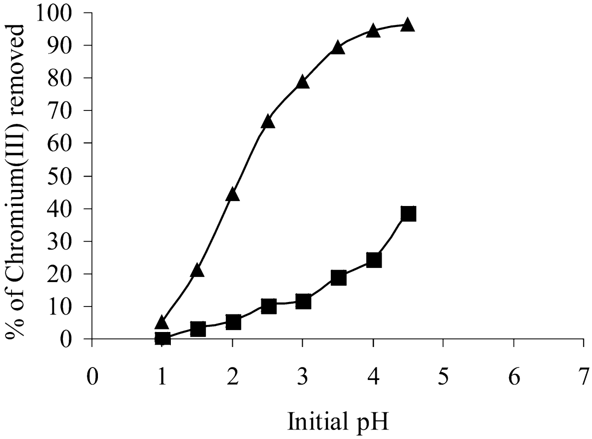

Figure 1. Effect of pH on extraction. ▲ D2EHPA solution after treatment with ammonium hydroxide; ■ before treatment with ammonium hydroxide, 0.45 M D2EHPA, 0.15 M TBP in kerosene and 100 ppm chromium standard solution were used.

phase before treatment with ammonium hydroxide and after treatment with ammonium hydroxide solution. The results were similar to those reported by Pandey et al. (1) where 35% chromium extraction was observed at equilibrium pH of 2.1. At the equilibrium pH of 4.5 a removal efficiency of 96.5% was observed. When pH was increased further, $Cr(OH)_3$ was precipitated. From this study, it was found that optimum pH for the solvent extraction studies for chromium (III) in ammoniated D2EHPA system was 4.5.

Effect of Extractant Concentration

A study was carried out with standard chromium (III) solution with different concentrations of D2EHPA. The concentration was varied from 0.25 to 0.6 M. The effect of D2EHPA concentration in organic phase is presented in Table 1. The extraction efficiency was found to increase with increase in D2EHPA concentration and maximum extraction of 96.3% was obtained at a concentration of 0.45 M. With further increase in concentration there was no significant change in extraction efficiency. Analyzing the experimental data of the distribution ratio K_d and extractant (D2EHPA) concentration at a constant value of other parameters allows an estimation of the number of extractant molecule associated with the extracted metal complex (13). The distribution ratio (K_d) of chromium (III) was calculated with different molar concentrations of D2EHPA. The distribution ratio of log K_d vs. log D2EHPA concentration is given in Fig. 2. The plot of log K_d vs. log D2EHPA gave a straight line with a slope of 3.25 indicating a metal to reagent mole ratio of 1 : 3. The results were similar to those reported by Islam et al. and Rao et al. (8, 12).

Extraction of Chromium (III) as a Function of Time

The extraction time of an aqueous to organic ratio 1 : 1 was varied from 15 sec to 300 sec and 120 sec was found to be adequate to get maximum extraction efficiency.

Table 1. Effect of extractant concentration

S. No	D2EHPA (moles)	Extraction of chromium (III) (%)
1	0.25	78.0
2	0.3	83.3
3	0.35	90.9
4	0.4	94.8
5	0.45	96.3
6	0.5	96.3
7	0.6	95.9

0.15 M TBP in kerosene solution was used, equilibrium pH 4.5 ± 0.1 was maintained.

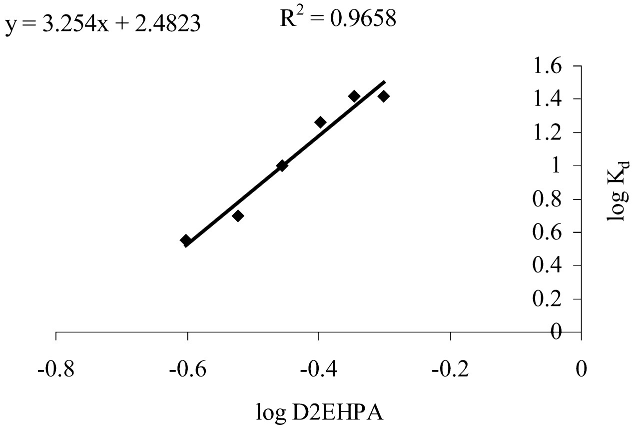

Figure 2. Relationships between $\log K_d$ and log D2EHPA. $\log K_d = 3.254 \log \text{D2EHPA} + 2.4823$.

Effect of Aqueous and Organic Phase Ratio

The removal efficiency was studied using different ratios of aqueous and organic phase at 120 sec. The aqueous to organic (A/O) ratio and their efficiencies are presented in Table 2. The results indicate that the maximum extraction 96.5% was achieved with 1 : 1 ratio. Further increase in A/O ratio above 2 : 1 resulted in decrease in extraction efficiency. The extraction time was increased from 120 to 1800 sec for 3 : 1, 4 : 1, and 5 : 1 aqueous to organic ratios but the maximum efficiency of 96.5% was not achieved. Therefore, 1 : 1 volume ratio of aqueous and organic phase was used for the solvent extraction studies to attain maximum extraction efficiency with minimum time of 120 sec.

Table 2. Effect of aqueous and organic ratio on extraction

S. No	Aqueous to organic phase ratio	Extraction of chromium (%)
1	1 : 1	96.5
2	2 : 1	96.0
3	3 : 1	94.9
4	4 : 1	92.5
5	5 : 1	81.8

0.45 M D2EHPA and 0.15 M TBP phase modifier in kerosene solution were used. Equilibrium pH of 4.5 ± 0.1 was maintained and the extraction time was 120 sec.

Extraction Efficiency of Chromium in the Presence of Chloride and Sulphate

The sulphate and chloride concentration in the aqueous solution was varied from 0 to 2500 ppm. The extraction efficiency in the presence of chloride and sulphate with standard chromium (III) solution is given in Table 3. With the increase in chloride and sulphate the extraction efficiency slightly decreased from 96.4% to 93.8% and 91.4%, respectively. The extraction efficiency decreased in the presence of sulphate and chloride ions as reported by other workers (8, 14). The work by Schugerl et al. (15) suggested that the depression of chromium (III) extraction by sulphate was due to complex formation but provided no supporting details or data.

Stripping of Chromium (III) from Loaded Organic Phase

The recovery of extracted chromium (III) from organic-phase containing D2EHPA was reported to be very difficult and slow process. The reason for incomplete stripping of chromium (III) was attributed to the extraction of some hydrolyzed/polymeric species, which could not be easily destabilized (16). Pandey et al. (1) noted that a much lower concentration of chromium (III) ($2 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$) could be completely stripped from an organic-phase containing D2EHPA. The stripping of chromium (III) with highly concentrated mineral acid was reported in the literature (1). In this present study, the stripping of chromium (III) from loaded organic phase was carried out by oxidation process using dilute sodium hydroxide and hydrogen peroxide solution.

Table 3. Extraction efficiency of chromium (III) in the presence of chloride and sulphate

S.No	Sulphate and chloride concentration (ppm)	Chromium recovered in the presence of chloride (%)	Chromium recovered in the presence of sulphate (%)
1	0	96.4	96.4
2	250	96.1	95.1
3	500	95.5	94.2
4	1000	94.8	93.5
5	1500	94.5	92.8
6	2000	94.2	92.1
7	2500	93.8	91.4

0.45 M D2EHPA and 0.15 M TBP in kerosene solution were used. Equilibrium pH 4.5 ± 0.1 and 120 sec equilibrium time was maintained.

Optimization of Sodium Hydroxide Concentration

In the stripping process, the concentration of sodium hydroxide was optimized by keeping a fixed amount of 4% hydrogen peroxide solution. The stripping of chromium (III) from the loaded organic phase with different concentrations of sodium hydroxide solution is shown in Fig. 3. Maximum stripping of 98.5% of chromium (III) was achieved from the loaded organic phase using 0.6 M sodium hydroxide and 4% hydrogen peroxide solution in 300 sec at 27°C.

Optimization of Hydrogen Peroxide Concentration

The hydrogen peroxide concentration was varied from 1.0 to 5.0% and optimized for the stripping process with 0.6 M sodium hydroxide solutions. The stripping of chromium (III) from loaded organic phase with different concentration of hydrogen peroxide is shown in Table 4. The maximum extraction of 98.9% chromium (III) was achieved from the loaded organic phase using 3.5% hydrogen peroxide in 300 sec stripping time. This oxidation method of stripping involves mild conditions and relatively short time when compared to those reported in literature (1).

Effect of Stripping Time

It was found that the stripping time of 300 sec for the chromium-loaded organic phase with 0.6 M sodium hydroxide and 3.5% solution of hydrogen peroxide was sufficient to completely strip the chromium.

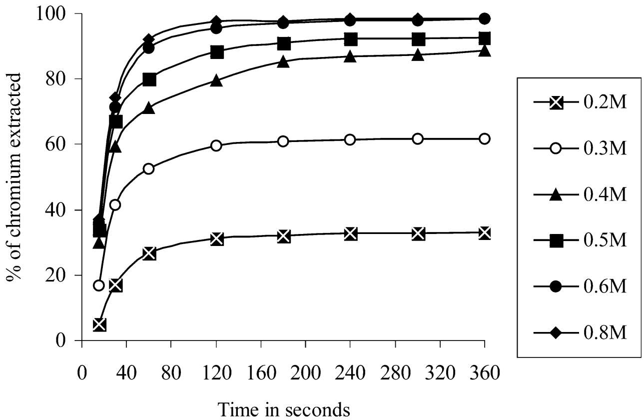

Figure 3. Optimization of sodium hydroxide concentration. 4% hydrogen peroxide was added to the stripping solution.

Table 4. Optimization of hydrogen peroxide concentration

S. No	Hydrogen peroxide (%)	Chromium recovered (%)
1	1.0	66.4
2	1.5	81.9
3	2.0	90.1
4	2.5	94.8
5	3.0	97.5
6	3.5	98.9
7	4.0	98.9
8	5.0	98.8

0.6 M sodium hydroxide solution and 300 sec stripping time was maintained.

Reuse of Organic Phase

The stripped organic layer was reused for chromium (III) extraction under the optimized conditions such as volume, pH, and chromium concentration as in the first trial and it was found that 80.8% of chromium (III) was extracted into the organic layer. At the end of the first extraction and stripping studies there was 3% reduction in original volume of the organic phase. The decrease in extraction efficiency in the second trial may be due to the loss of organic phase during the extraction and stripping process. When 3% of fresh organic solution was added to make up to the original volume of the organic phase, the extraction efficiency was restored to the original value. Thus, it is possible to restore original ability by adding required fresh organic solution in each recycling process.

FT-IR Spectroscopic Analysis of the Organic Phase

The FT-IR spectra for pure D2EHPA, loaded organic phase and stripped organic phase are given in Fig. 4. For pure D2EHPA, P–O–C group showed intense absorption band around 1037 cm^{-1}. This group appears to have two stretching frequencies, one primarily due to the stretching of the P=O bond and the other due to the O–C stretching, but it was not possible to specifically distinguish them. This is because P–O–H group may overlap in the same frequency. These results are similar to Morais and Mansur (17). The P=O stretching frequency was assigned at 1229 cm^{-1}. When the D2EHPA interacts with any metals, the phosphoryl bond is highly affected (17). The FT-IR spectra of the free D2EHPA and loaded organic phases show that the P=O band occurred at 1229 and 1203 cm^{-1} respectively. The intensity of

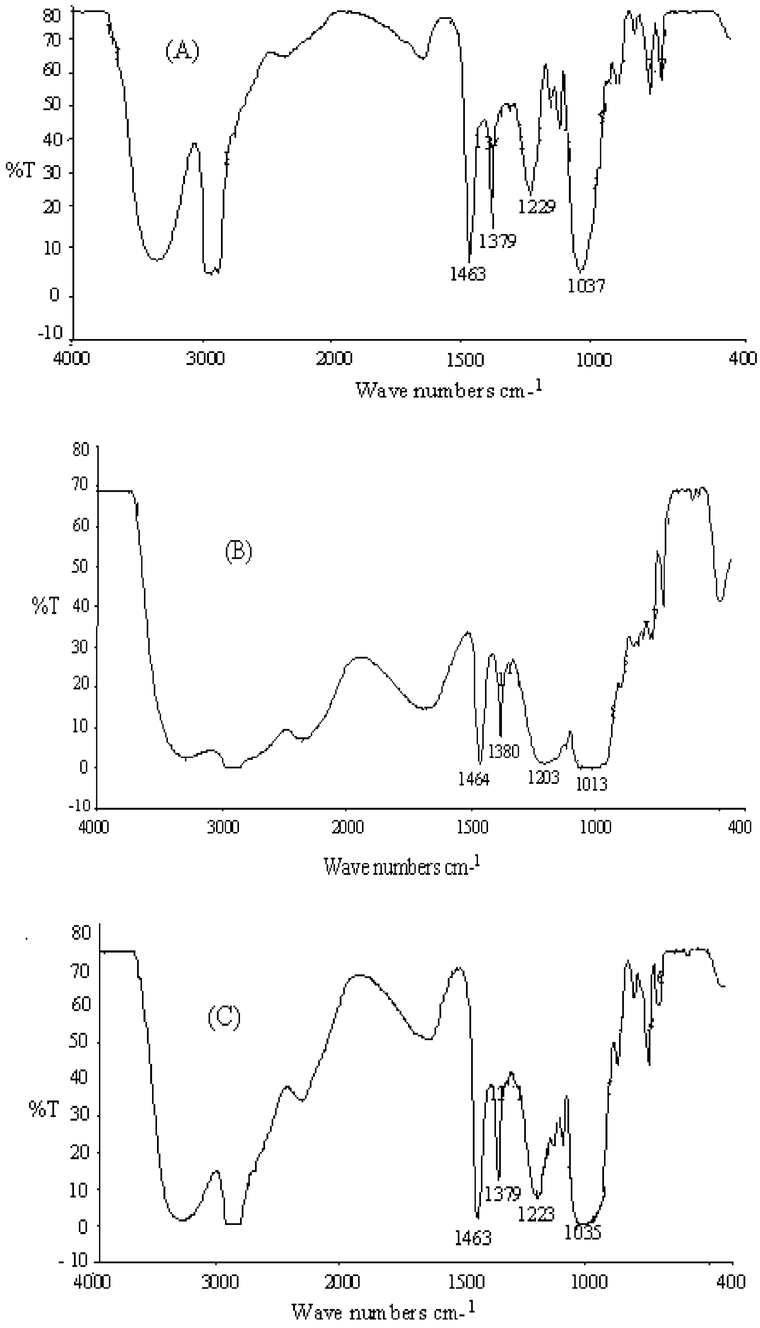

Figure 4. FT-IR spectra for pure D2EHPA, loaded organic phase and stripped organic phase. (A) FT-IR spectra for pure D2EHPA (with out solvent). (B) FT-IR spectra for Cr (D2EHPA) 3 complex (with out solvent). (C) FT-IR spectra for stripped D2EHPA.

the P=O band corresponding to the free D2EHPA was clearly shifted with increase of chromium concentration in the organic phase. The relative intensity of the band for free D2EHPA (P–O–H) 1037 cm^{-1} shifted to 1013 cm^{-1} with the increase in chromium concentration. This indicates that the free P–O–H bonds are reduced. It appears that the complex Cr $(D2EHPA)_3$ is preferentially formed since more stable Cr–O bonds are produced (16). After stripping of chromium from the loaded organic phase it was analyzed by FT-IR spectra. The spectra shows bands at 1035 and 1223 cm^{-1} for P–O–H and P=O, respectively. The FT-IR study reveals that chromium (III) is extracted from aqueous to organic phase by forming a complex with phosphate group of D2EHPA. During stripping chromium (III) is oxidized to chromium (VI) leading to the breakage of the complex.

Application to Electroplating Wastewater

The electroplating wastewater was collected from Ambatur industrial area in Chennai, India. The electroplating wastewater contained both chromium (VI) and chromium (III) with a high amount of chloride and sulphate. The physical and chemical parameters for the electroplating wastewater were analyzed and the results are given in Table 5. The D2EHPA present in organic-phase selectively extracts chromium (III) alone. Hence the chromium (VI) was reduced to chromium (III) by the addition of 0.1% ascorbic acid. The reduced plating wastewater was diluted to required concentration and utilized for solvent extraction and recovery process under optimum condition. The maximum extraction of 90.3% and maximum stripping of 98.5% was observed for the electroplating wastewater. The slight decrease in extraction efficiency may be because of the presence of chloride, sulphate, and other impurities present in the real effluent.

Table 5. Characteristics of electroplating wastewater

S. No	Parameters	Electroplating wastewater
1	pH	2.65
2	Conductivity µ mho/cm	2670
3	Total hardness mg/l	160
4	Calcium mg/l	48.5
5	Magnesium mg/l	9.74
6	Chloride mg/l	750
7	Sulphate mg/l	500
8	Chromium (VI) mg/l	485
9	Chromium (III) mg/l	36

CONCLUSIONS

The present work investigated the recovery of chromium by solvent extraction using D2EHPA from aqueous solution and electroplating wastewater. Maximum extraction of 96.5% was achieved from standard chromium (III) chloride solution by using 0.45 M D2EHPA with 0.15 M tri-butyl phosphate as phase modifier in kerosene, at an equilibrium pH of 4.5. The maximum stripping efficiency of 98.9% of chromium (III) was achieved from loaded organic phase using 0.6 M of sodium hydroxide and 3.5% of hydrogen peroxide solution at 300 sec. Under optimized condition, the maximum extraction and stripping of chromium was achieved from electroplating wastewater as 90.3% and 98.5% respectively.

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