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SOLVENT EXTRACTION OF HEXAVALANT CHROMIUM FROM ELECTROPLATING WASTE SOLUTION WITH TBP

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Abstract

The present work aims to recover hexavalent chromium from an electroplating effluent by using solvent extraction with tributylphosphate (TBP) as an extractant. The results demonstrate that chromium(VI) is extracted as $HCrO_3Cl.2TBP$ in acidic chloride medium and loading capacity of TBP for chromium(VI) was found to be 178 g/L. Stripping of chromium(VI) form loaded TBP has also been studied. With 0.1N NaOH solution chromium(VI) was stripped quantitatively from loaded organic. TBP was also used to recover chromium(VI) and zinc from real electroplating effluent collected from an electroplating industry of Jamshedpur. By solvent extraction with TBP and selective stripping with 10% H_2SO_4 and 1N NaOH 76.1% of zinc and 92.58% chromium(VI) were recovered.

Introduction

Treatment of industrial wastewater containing toxic heavy metals and their compounds has received greater attention over the past decades, since they pose grave threat to environment and consequently to the living organism including human being because of their accumulation and also non-biodegradability [1-3]. Chromium is an important metal in this category. Its wide and exhaustive industrial applications in electroplating, tanning, metal alloy manufacturing industry, catalysis, pigments making etc. not only lead to depletion of natural resources but critically damages the ecological balance as well [4-6]. Environmentally, hexavalent chromium ions are strongly toxic carcinogenic, mutagenic and notoriously mobile in nature because they are weakly bounded to inorganic surface [7-8]. Conventional treatment of waste water containing Chromium(VI) involves chemical reduction of Chromium(VI) to Cr(III) by SO_2, Na_2SO_3 or a ferrous ion compound ($FeSO_4$) following the precipitation of $Cr(OH)_3$ [9]. However, the frustrating aspects of the reduction precipitation method are the significant sludge production and the long-term environmental consequences [10]. According to Central Pollution Control Board (CPCB), Govt. of India discharge limit for total chromium in the industrial effluent is 2 mg/L.

Among the alternative methods [11] being developed to meet the environmental regulations while generating value-added products, solvent extraction technique is widely referred which has been successfully applied in the solution purification and extraction of several non-ferrous and toxic metals [12-15]. Extensive studies have been carried out on solvent extraction of chromium(VI) using basic (quaternary and tertiary amines) [16-18], neutral {tri-n-octyl phosphine oxide (TOPO) and tri-n-butyl phosphate (TBP)} [19-20] and acidic extractants (Cyanex 272, DEHPA and LIX-84) [21-26]. But literature dealing with true electroplating effluents to recover chromium(VI) by using solvent extraction method is quite scanty [27-30]. The present investigation relates to the solvent extraction and stripping behaviour of chromium(VI) with TBP from a model solution similar to that of an electroplating waste solution with the aim of recovering the metal.

Experimental

A stock solution containing 1g/L chromium(VI) was prepared by dissolving appropriate amount of CrO_3 in distilled water. From the stock solution chromium solution of desired concentrations were prepared by appropriate dilution with distilled water and further used for solvent extraction studies. Tri-n-butyl phosphate (TBP) obtained from BDH, England was used as an extractant. All other chemicals used were of analytical grade reagent. Solvent extraction studies were carried out by mixing equal volumes of chromium(VI) solution and TBP with the help of glass stirrer for a specified time. After equilibration the phases were allowed to separate and chromium content of raffinate was estimated with the help of Atomic Absorption Spectrometer (ECIL, India). Concentration of chromium in the organic phase was deduced from the difference between initial concentration of chromium(VI) in the aqueous phase and the concentration of chromium in the raffinate. A solution of 0.1N NaOH was used for stripping of chromium from the loaded TBP and satisfactory material balance was obtained in all the experiments.

Results and Discussion

Solvent Extraction of Chromium(VI) with TBP

(a) Effect of Contact Time:

The kinetics of chromium(VI) extraction was studied by contacting aqueous solution containing 195ppm Chromium(VI) at pH 1.0 with undiluted TBP. The results obtained are shown in Fig.1. The extraction of chromium(VI) with TBP was quite rapid and quantitative; equilibrium reached within 1 min time. It was also observed that prolonged contact time had no adverse effect on extraction. However, to ensure equilibrium, 5 min. contact time was maintained during the extraction studies.

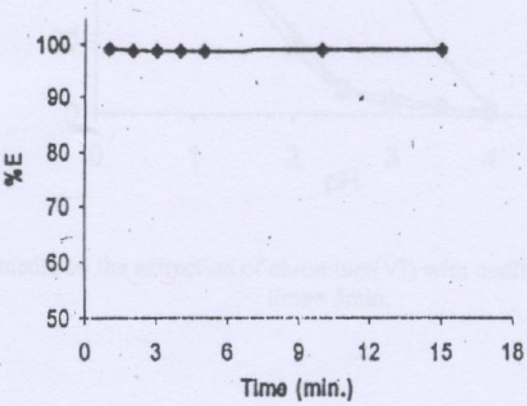

Fig.1. Effect of contact time on extraction of chromium(VI) with undiluted TBP at A:O ratio=1:1,

(b) *Effect of pH and Type of Acidic Media on Extraction of Chromium(VI):*

The extraction of chromium(VI) (195 ppm) with TBP was studied by varying pH in the range 1-4 in chloride, nitrate and sulphate media. The results depicted in Fig. 2 show that in chloride medium at pH 1 quantitative extraction of chromium was observed. In general, irrespective of the aqueous media taken extraction of chromium(VI) decreased with increase in pH of the aqueous phase. This may be due to the fact that at pH ≤ 1 chromium(VI) in aqueous phase exists as H_2CrO_4 [31-33] as shown below:

$$Cr_2O_7^{2-}{}_{(aq)} + H_2O_{(aq)} \leftrightarrow 2HCrO_4^-{}_{(aq)} \quad K_1 = 10^{-2.2} \quad .....(1)$$

$$H_2CrO_{4(aq)} \leftrightarrow H^+ + HCrO_4^-{}_{(aq)} \quad K_2 = 4.1 \quad .....(2)$$

Chromium thus gets extracted into the organic phase as $H_2CrO_4.nTBP$ in the absence of any chloride ion. The extraction equilibrium can be written as:

$$[HCrO_4^-]_{(aq)} + [H^+]_{(aq)} + n\,[TBP]_{(org)} \leftrightarrow [H_2CrO_4.nTBP]_{(org)} \quad ...(3)$$

At pH > 2 chromium(VI) in the aqueous phase predominantly exists as $HCrO_4^-$ and $Cr_2O_7^{2-}$ and are not likely to be extracted with TBP.

The plot (Fig. 3) of log D vs. log $[H^+]$ in chloride media had a slope of 1.9 indicating involvement of two H^+ ions in the extraction of chromium(VI) with TBP. This is in contrast to the equation (3) and this deviation may be attributed to the presence of 0.5 mole/L chloride ion in the extraction system.

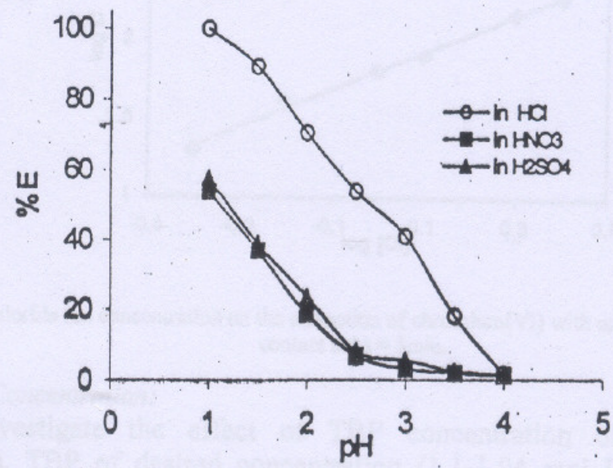

Fig. 2: Effect of acidic media on the extraction of chromium(VI) with undiluted TBP at A:O ratio = 1:1; contact time= 5min.

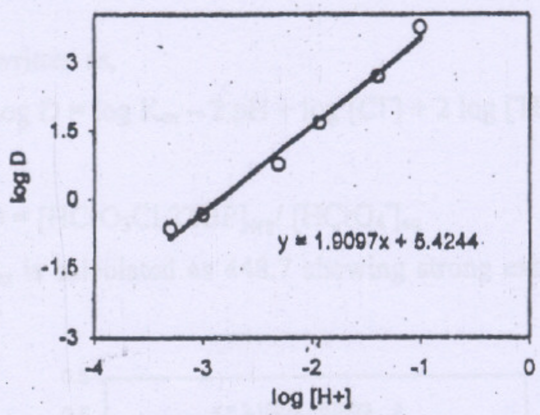

Fig. 3 Effect of the hydrogen ion concentration on the extraction of chromium(VI) with undiluted TBP at A:O ratio=1:1; contact time= 5min.

(c) *Effect of Chloride Ion on the Extraction of Chromium(VI):*

The effect of variation of chloride ion concentration on the extraction of chromium(VI) with undiluted TBP at pH 1.0 was also studied. As shown in Fig.4 the plot of log D vs. log [Cl$^-$] had a slope of 1.19 indicating extraction of 1 mole of chloride ion along with 1 mole of chromium(VI) into the organic phase.

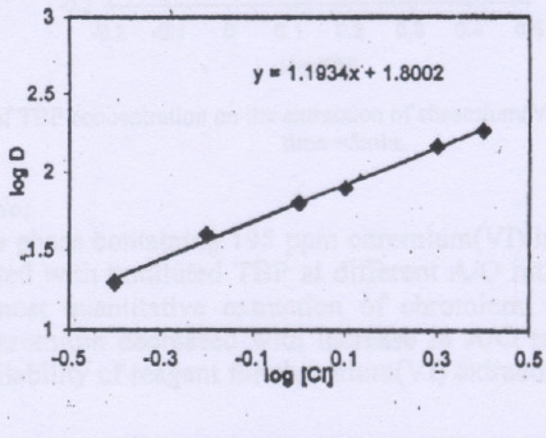

Fig. 4: Effect of chloride ion concentration on the extraction of chromium(VI) with undiluted TBP, A:O ratio=1:1; contact time = 5min.

(d) *Effect of TBP Concentration:*

To investigate the effect of TBP concentration on the extraction of chromium(VI), TBP of desired concentration (1.1-1.94 mol L^{-1}) was prepared by diluting with kerosene and contacted with equal volume of chromium(VI) solution at pH 1. It is clear from Fig. 5 that extraction of chromium(VI) increased with increase in TBP concentration and log D vs. log [TBP] had slope of 2.15 indicating involvement of two moles of TBP for extraction of one mole of chromium(VI). Therefore, the extraction equilibrium can be written as:

$$[HCrO_4^-]_{aq} + 2[H^+]_{aq} + [Cl^-]_{aq.} + 2[TBP]_{org.} \leftrightarrow [HCrO_3Cl.2TBP]_{org.} + [H_2O]_{aq.}$$

……………………K_{ex} .(4)

The equilibrium constant K_{ex} of chromium(VI) can be given by:

$$K_{ex} = [HCrO_3Cl.2TBP]_{org} / [HCrO_4^-]_{aq} [H^+]^2_{aq} [Cl^-]_{aq.} [TBP]^2_{org.} \quad (5)...$$

Eq. 2 can be re-written as,

$$\text{Log } D = \log K_{ex} - 2\,\text{pH} + \log [Cl^-] + 2 \log [TBP]$$

Where,

$$D = [HCrO_3Cl.2TBP]_{org} / [HCrO_4^-]_{aq}$$

The value of K_{ex} is calculated as 448.7 showing strong extraction of chromium(VI) with the solvent.

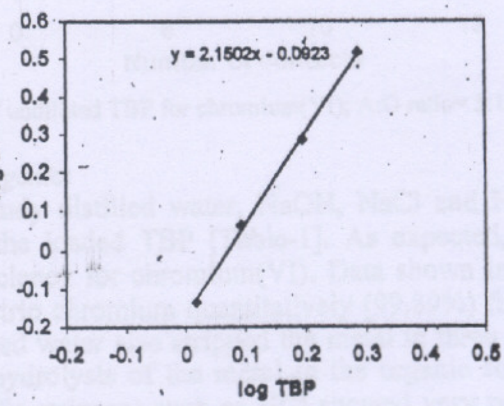

Fig. 5: Effect of TBP concentration on the extraction of chromium(VI) at A:O ratio= 1:1; contact time =5min.

(e) *Effect of A/O Ratio:*

Aqueous phase containing 195 ppm chromium(VI) in HCl medium and at pH 1.0 was contacted with undiluted TBP at different A/O ratio (Fig.6). At phase ratio A:O = 1:1 almost quantitative extraction of chromium was observed. However, extraction of chromium decreased with increase in A/O ratio. This may be due to decrease in availability of reagent for chromium(VI) extraction.

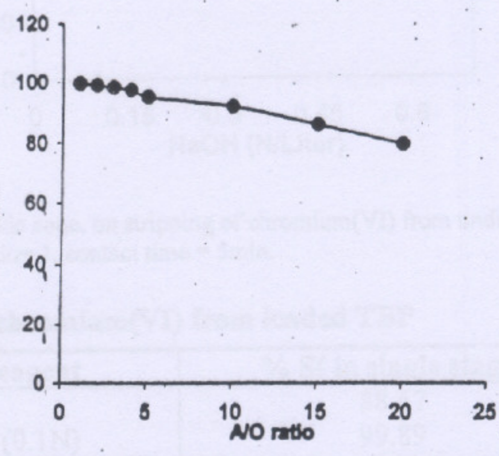

Fig.6: Effect of A/O ratio on the extraction for chromium(VI) with undiluted TBP; contact time= 5min.

To investigate the loading capacity, undiluted TBP was equilibrated with aqueous feed containing 195 ppm chromium(VI) up to ten contacts at an aqueous pH of 1.0. Fig. 7 shows that TBP has an excellent loading capacity and can extract 178g chromium(VI)/ L of TBP.

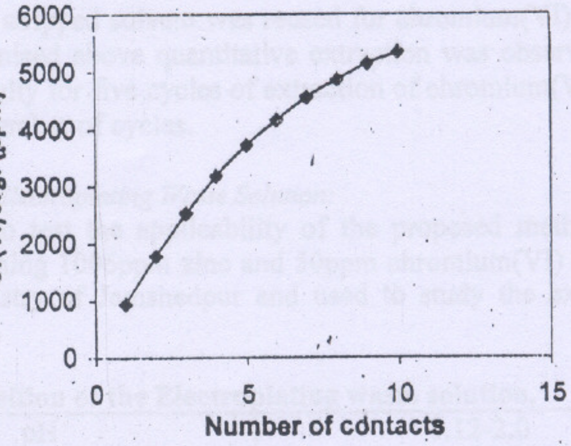

Fig. 7: Loading capacity of undiluted TBP for chromium(VI); A:O ratio= 5:1;contact time= 5min.

(f) *Stripping of the Loaded Organic:*

In the present study distilled water, NaOH, NaCl and HCl were tested for chromium(VI) stripping from the loaded TBP [Table-1]. As expected, sodium hydroxide showed excellent stripping efficiency for chromium(VI). Data shown in Fig.8 indicate that 0.1M NaOH was sufficient to strip chromium quantitatively (99.89%) from the loaded TBP in single stage. Although distilled water also stripped the metal in three stages but it caused delayed phase separation and hydrolysis of the metal in the organic solvent. On the other hand, sodium chloride and acidic strippant such as HCl showed very poor stripping ability even at very high concentration. Hence, NaOH was selected as stripping agent in further experiments.

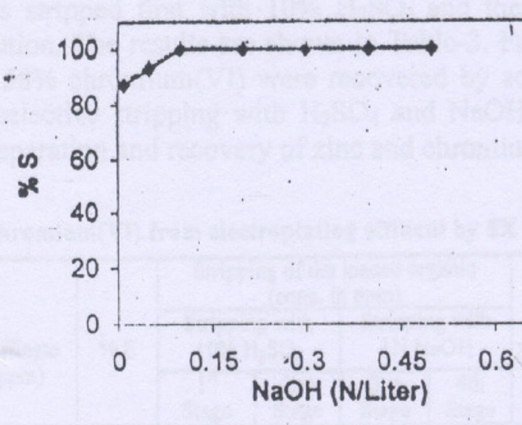

Fig. 8: Effect of sodium hydroxide conc. on stripping of chromium(VI) from undiluted TBP; A:O ratio= 1, contact time = 5min.

Table1- Stripping study of chromium(VI) from loaded TBP

S. No.	Stripping reagent	% S(in single stage)
1.	Distilled water	88.57
2.	Sodium hydroxide (0.1N)	99.89
3.	Sodium chloride (1N)	3.7
4.	Hydrochloric acid (5.5N)	4.53

(g) *Recycling of the solvent :*

When the stripped solvent was reused for chromium(VI) extraction under the same conditions as optimised above quantitative extraction was observed. The regenerated TBP was tested successfully for five cycles of extraction of chromium(VI) and as expected it can be reused for more number of cycles.

(h) *Application to the Electroplating Waste Solution:*

In order to test the applicability of the proposed method an electroplating effluent [Table-2] containing 1006ppm zinc and 50ppm chromium(VI) was collected from a local electroplating industry of Jamshedpur and used to study the extraction of zinc and chromium(VI) with TBP.

Table-2: Composition of the Electroplating waste solution.

pH	1.12-2.0
Zinc	1004 ppm
Chromium(VI)	50 ppm
Iron	3-5 ppm
Chloride	100 g/L
Sulphate	10 g/L

Under the optimised conditions as with synthetic solution undiluted TBP exhibited higher extraction efficiency for chromium(VI) over zinc; chromium(VI) extraction was found to be 93.05% as against 76.9% zinc extraction at pH 1.13 in single contact. Chromium in raffinate in single contact was found to be 3.5 ppm which can further be reduced either by one more stage of solvent extraction with TBP or by increasing the O/A ratio, thereby meeting the specification for discharge limit of chromium in the stream. From the loaded organic zinc was stripped first with 10% H_2SO_4 and then chromium(VI) was stripped with 1N NaOH solution. The results are shown in Table-3. From the electroplating effluent 76.1% zinc and 92.58% chromium(VI) were recovered by solvent extraction with TBP in single contact and selective stripping with H_2SO_4 and NaOH, respectively. In the continuous mode complete separation and recovery of zinc and chromium may be possible.

Table-3: Recovery of zinc and chromium(VI) from electroplating effluent by SX with TBP

Radical	Aq. Feed (ppm)	Raffinate (ppm)	% E	Stripping of the loaded organic (conc. in ppm)				% Stripping	% Recovery
				Stripping with 10% H_2SO_4		Stripping with 1N NaOH			
				1st Stage	2nd Stage	3rd Stage	4th Stage		
Zinc	1006	232.89	76.9	719.45	45.7	0	0	98.9	76.1
Chromium(VI)	50	3.48	93.05	0	0	44.19	2.1	99.3	92.58

Conclusion

Following conclusions are drawn from solvent extraction studies of chromium(VI) with TBP from a model and real electroplating effluent generated in an electroplating industry.

1. From acidic chloride solution chromium(VI) can be extracted quantitatively at pH 1.0 using TBP as an extractant. The extracted species is found to be $HCrO_3Cl.2TBP$ under this condition.

ii. With 0.1N NaOH solution chromium(VI) is stripped quantitatively in single stage from the loaded organic phase showing complete recovery of the metal from the waste stream.
iii. From electroplating effluent 76.1% of zinc and 92.58% chromium(VI) are recovered by SX with TBP and selective stripping with 10% H_2SO_4 and 1N NaOH.
iv. The raffinate from the extraction process contains 3.5 ppm chromium which may be safely discharged in the stream after one more stage of SX with TBP.

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