Recovery of chromium (VI) from electroplating effluent by solvent extraction with tri-*n*-butyl phosphate

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Recovery of hexavalent chromium from a model and real electroplating effluent by solvent extraction with tri-*n*-butyl phosphate (TBP) was studied. In different acid media chromium(VI) extraction with TBP followed the order HCl > H_2SO_4 ~ HNO_3. In acidic chloride medium chromium(VI) was extracted as $HCrO_3Cl.2TBP$. The loading capacity of TBP for chromium(VI) was found to be 5.35 g/L. Stripping of chromium(VI) from loaded TBP was also studied. With 0.1 N NaOH solution chromium(VI) was stripped quantitatively from loaded organic. TBP was also used to recover chromium(VI) and zinc from electroplating effluent collected from an electroplating industry. By simultaneous extraction with TBP, and stripping with 10% H_2SO_4 and 1 N NaOH zinc and chromium(VI) were recovered, quantitatively.

Keywords: Chromium(VI), Electroplating effluent, Solvent extraction, TBP

Heavy metals are toxic substances that once discharged into water bodies as industrial waste cause environmental pollution. Chromium is an important non-ferrous metal finding its application in electroplating industries for surface treatment and finishing of metals/plastics. This leads to the generation of effluents and solid wastes containing chromium. Environmentally, hexavalent chromium ions are strongly toxic, carcinogenic, mutagenic and notoriously mobile in nature because they are weakly bound to inorganic surface[1,2]. Due to stringent laws, which have come into existence world over, pollution related problems and their control are of prime concern. According to Central Pollution Control Board (CPCB), Govt. of India, discharge limit for total chromium in the industrial effluent is 2 mg/L.

Conventional treatment of waste water[3] containing chromium(VI) involves chemical reduction of chromium(VI) to chromium(III) by SO_2, Na_2SO_3 or a ferrous ion compound ($FeSO_4$) followed by precipitation of $Cr(OH)_3$. However, the frustrating aspects of the reduction-precipitation method are the significant sludge production and the long-term environmental consequences[4]. Besides environmental aspects, sufficiently large amounts of metals are disposed off resulting in enhanced burden on the depleting primary resources like ores and minerals. It is, therefore, essential to look for not only removal-

disposal approaches mostly employed as a versatile technique but also to explore recover-reuse methods which can meet the twin objectives of achieving pollution norms and producing value added products/resources recovery from the waste streams thus conserving the natural resources.

Among the alternative methods[5] 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[6-9]. Extensive studies have been carried out on solvent extraction of chromium(VI) using basic (quaternary and tertiary amines)[10-12], neutral {tri-*n*-octyl phosphine oxide (TOPO) and tri-*n*-butyl phosphate (TBP)}[13,14] and acidic extractants (Cyanex 272, DEHPA and LIX-84)[15-20]. But literature dealing with true electroplating effluents to recover chromium(VI) by using solvent extraction method is quite scanty[21-24]. The present investigation relates to the solvent extraction and stripping behaviour of chromium(VI) with TBP from an electroplating waste solution with the aim of recovering the metal.

Experimental Procedure

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. The pH of the aqueous solution was adjusted by adding sodium hydroxide solution. 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 at temperature 303 K with the help of glass stirrer for a specified time. The speed of glass stirrer was fixed at 250 rpm. 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. At times, from the organic phase chromium(VI) was stripped with NaOH solution and material balance was checked.

Results and Discussion

Solvent extraction of chromium(VI) with tri-n-butyl phosphate

Effect of contact time

The kinetics of chromium(VI) extraction was studied by contacting aqueous solution containing 195 ppm 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.

Effect of pH and type of acidic media

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 showed quantitative extraction of chromium at pH 1 in chloride medium. In general, irrespective of the aqueous media taken extraction of chromium(VI) decreased with increase in pH of the aqueous phase. This may be explained by dependence of pH on the existence of various chromium(VI) species in the aqueous solution[25-28]. In the acid media $HCrO_4^-$, $Cr_2O_7^{2-}$ and H_2CrO_4 are the predominant
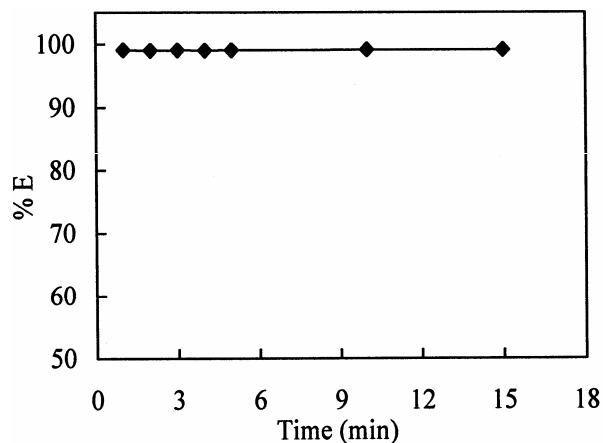

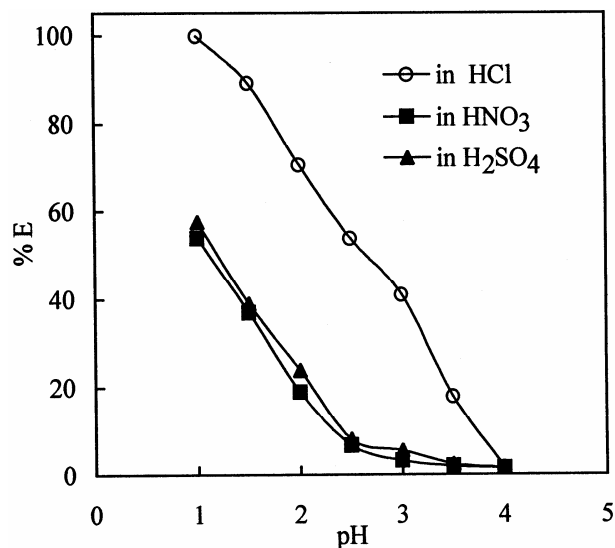Fig. 1–Effect of contact time on extraction of chromium(VI) with undiluted TBP at A:O ratio = 1:1; Eq. pH = 1.0.
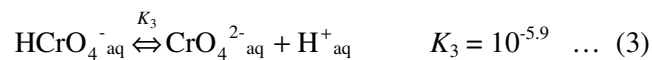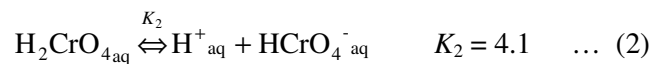

Fig. 2–Effect of acid media on the extraction of chromium(VI) with undiluted TBP at A:O = 1:1; contact time = 5 min.

species. In basic solutions above pH 6 chromium(VI) exists in the form of CrO_4^{2-}. In the pH range 2-6 $HCrO_4^-$ and $Cr_2O_7^{2-}$ remain in equilibrium, and at pH $\leq$ 1 the main species is H_2CrO_4. The equilibria among various species of chromium(VI) are given below.

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

$$H_2CrO_4{}_{aq} \overset{K_2}{\Leftrightarrow} H^+{}_{aq} + HCrO_4^-{}_{aq} \quad K_2 = 4.1 \quad \dots \ (2)$$

$$HCrO_4^-{}_{aq} \overset{K_3}{\Leftrightarrow} CrO_4^{2-}{}_{aq} + H^+{}_{aq} \quad K_3 = 10^{-5.9} \ \dots \ (3)$$

where K_1, K_2, K_3 are equilibrium constants

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:

$$[HCrO_4^-]_{aq} + [H^+]_{aq} + n[TBP]_{org} \Leftrightarrow$$
$$[H_2CrO_4.nTBP]_{org} \quad \dots \text{(4)}$$
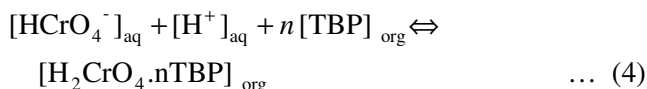
At $pH > 2$ chromium(VI) in the aqueous phase predominantly exists as $HCrO_4^-$ and $Cr_2O_7^{2-}$, which are not likely to be extracted with TBP[29].

The plot (Fig. 3) of log D versus log $[H^+]$ (where D is the distribution ratio) 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 Eq. (4) and this deviation may be attributed to the presence of 0.5 mole/L chloride ion in the extraction system. Because, in the acidic chloride medium chromium(VI) exists in the form of chlorochromate ion (CrO_3Cl^-)[28,30]. Therefore, in the presence of chloride ion chromium(VI) may be extracted into the organic phase as $HCrO_3Cl.nTBP$.

$$CrO_3(OH)^-_{aq} + H^+ + Cl^- \rightarrow CrO_3Cl^-_{aq} + H_2O \quad \dots \text{(5)}$$
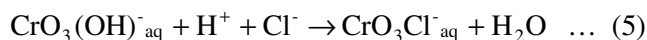
Effect of chloride ion

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 versus 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, and confirming the extracted phase as $HCrO_3Cl.nTBP$.

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 versus 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:
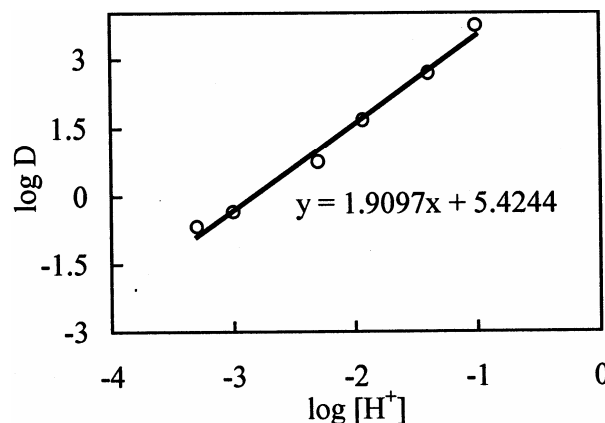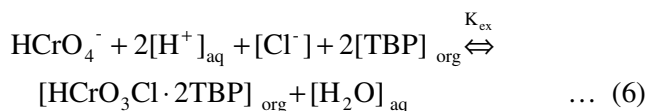
$$HCrO_4^- + 2[H^+]_{aq} + [Cl^-] + 2[TBP]_{org} \overset{K_{ex}}{\Leftrightarrow}$$
$$[HCrO_3Cl \cdot 2TBP]_{org} + [H_2O]_{aq} \quad \dots \text{(6)}$$

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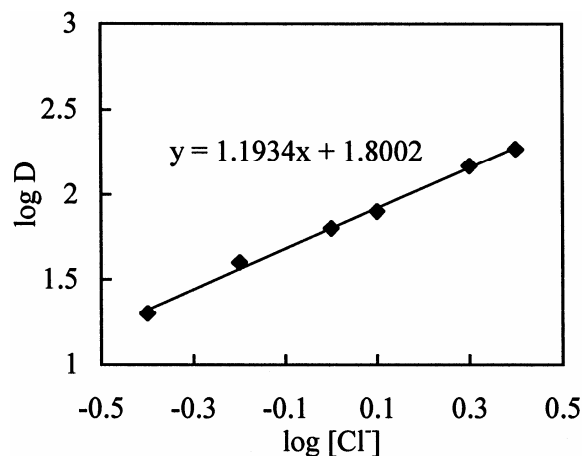

Fig. 4–Effect of chloride ion concentration on the extraction of chromium(VI) with undiluted TBP; A:O = 1:1; Eq. pH = 1.0; contact time = 5 min.
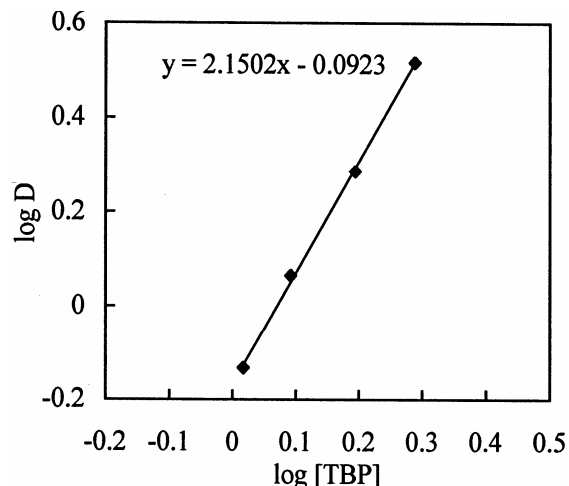

Fig. 5–Effect of TBP concentration on the extraction of chromium(VI) at A:O = 1:1; Eq. pH = 1.0; contact time = 5 min.

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

$$K_{ex} = \frac{[HCrO_3Cl \cdot 2TBP]_{org}}{[HCrO_4^-]_{aq}\,[H^+]^2_{aq}\,[Cl^-]_{aq}.[TBP]^2_{org}} \quad \ldots (7)$$

Eq. (4) can be re-written as,

$$\mathrm{Log}\,D = \log K_{ex} - 2\,pH + \log[Cl^-] + 2\log[TBP] \quad \ldots (8)$$

where

$$D = \frac{[HCrO_3Cl \cdot 2TBP]_{org}}{[HCrO_4^-]_{aq}} \quad \ldots (9)$$

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

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.

To investigate the loading capacity, undiluted TBP was equilibrated repetitively with aqueous feed containing 195 ppm chromium(VI) up to ten contacts at an aqueous pH of 1.0. Figure 7 shows that TBP has an excellent loading capacity and can extract 5.35 g chromium(VI)/ L of TBP.

Stripping of loaded organic phase

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 0.1 M NaOH was sufficient to strip chromium
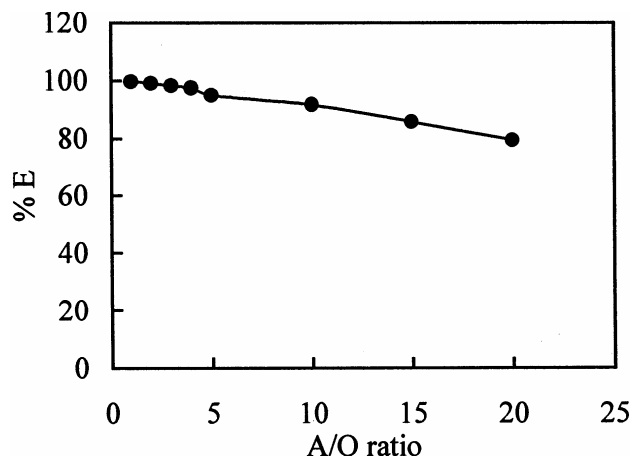
Table 1—Stripping study of chromium(VI) from loaded TBP
O/A=1; Contact time, 5 min; Loaded organic, 190 ppm Cr(VI)

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

Fig. 6—Effect of A/O ratio on the extraction of chromium(VI) with undiluted TBP; Eq. pH = 1.0; contact time = 5 min.
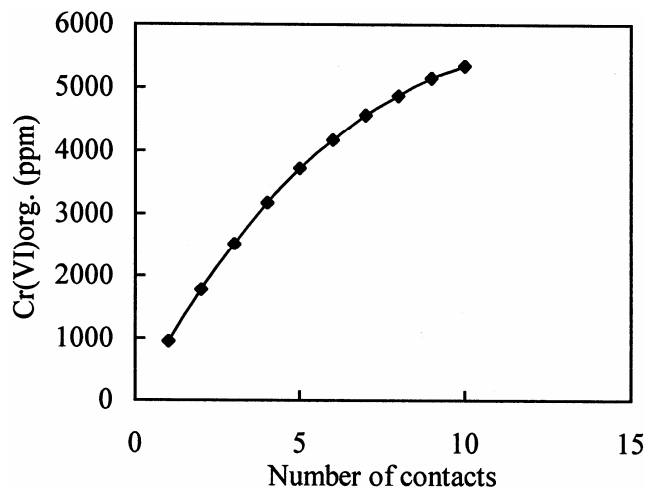

Fig. 7—Loading capacity of undiluted TBP for chromium(VI); A:O = 5:1; Eq. pH = 1.0; contact time = 5 min.
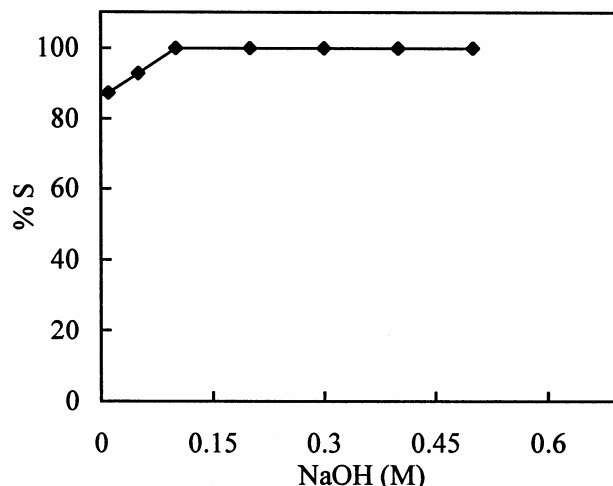

Fig. 8—Effect of sodium hydroxide concentration on stripping of chromium(VI) from loaded TBP; A:O = 1:1, contact time = 5 min.

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.

Recycling of 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.

Recovery of chromium(VI) from electroplating effluent of industry

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

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 at O/A ratio of 1. 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. The Raffinate obtained above was contacted with TBP at O/A ratio of 1 yielding waste solution containing 0.03 ppm chromium(VI). This meets the specification for discharge limit of chromium in the stream (2 mg/L). From the loaded organic phase zinc was stripped first with 10% H_2SO_4 and then chromium(VI) was stripped with 1 N 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.

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.

(i) Chromium(VI) can be extracted quantitatively from acidic hloride solution at pH 1.0 using TBP as an extractant. The extracted species is found to be $HCrO_3Cl.2TBP$ under this condition.

(ii) Chromium(VI) is stripped quantitatively with 0.1 M NaOH solution in single stage from the loaded organic phase showing complete recovery of the metal from the waste stream.

(iii) From electroplating effluent 76% of zinc and 92.6% chromium(VI) are recovered by SX with TBP and selective stripping with 10% H_2SO_4 and 1 M NaOH.

(iv) The raffinate contains 3.5 ppm chromium. In the 2nd stage of extraction with TBP at phase ratio of 1, chromium content of the raffinate was reduced to 0.03 ppm which can be discharged into the stream.

(v) Thus the process can be used to recover chromium from electroplating effluent meeting environmental regulatory norms, and making suitable for discharge into streams.

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

Table 3—Recovery of Zn and Cr(VI) from electroplating effluent by SX with TBP

Radical	Aq. feed (ppm)	Raffinate (ppm)	%E	Stripping of loaded organic (ppm)				% Stripping
				Stripping with 10% H_2SO_4		Stripping with 1 N NaOH		
				1st Stage	2nd Stage	3rd Stage	4th Stage	
Zn	1006	132.89	76.9	719.5	45.7	0	0	98.9
Cr(VI)	50	3.48	93.05	0	0	44.2	2.1	99.3

References
1 Lewandowski Z, *Water Res,* 19 (1985) 589.
2 Losi M E, Amrhein C & Frankenberger W T, *Environ Toxicol Chem*, 13 (1994) 1727.
3 Kato I & Nagai S, *Japan Kokai Tokkyo Koho*, JP03 (1991) 224.
4 Unnithan M R & Anirudhan T S, *Ind Eng Chem Res*, 40 (2001) 2693.
5 Agrawal A, Kumar V & Pandey B D, *Mineral Processing & Extractive Metallurgy Rev*, 27 (2006) 99.
6 Amezaga A S, *Ing Quim*, 16 (1984) 75.
7 Brooks C S, *Metal Finish*, 85 (1987) 55.
8 Chemielewski A G, Urbanski T S & Migdal W, *Hydrometallurgy*, 45 (1997) 333.
9 McDonald C W & Bajwa R S, *Sep Sci Technol,* 12 (1977) 435.
10 Senol A, *Sep Purif Technol*, 36 (2004) 63.
11 Someda H H, El-Shazly E A & Sheha R R, *J Hazard Mater*, B117 (2005) 213.
12 Salazar E, Ortiz M I, Urtiaga A M & Irabien J A, *Ind Eng Chem Res*, 31 (1992) 1516.
13 Huang T C, Chen C C & Chen D H, *Solv Extract Ion Exch,* 15 (1997) 837.
14 Ouejhani A, Dachraoui M, Lelleve G & Fauvarque J F, *Anal Sci*, 19 (2003) 1499.
15 Lanagan M D & Ibana D C, *Minerals Eng*, 16 (2003) 237.
16 Pandey B D, Cote G & Bauer D, *Hydrometallurgy*, 40 (1996) 343.
17 Flett D S, *J Organomet Chem*, 690 (2005) 2426.
18 Preston J S, *Hydrometallurgy*, 10 (1983) 187.
19 Henkel Co, LIX reagents and systems: chromium, Technical Bulletin, 1961.
20 Deptula C, *Int Solv Ext Conf*, Society of Chemical Industry, The Hague, 1, 1971, 638.
21 Clevenger T E & Novak J T, *J Water Pollut Control Fed*, 55 (1983) 984.
22 Venkateswaran P & Palanivelu K, *Sep Purif Technol*, 40 (2004) 279.
23 Ajmal M, Rao R A K & Siddiqui B A, *Water Res*, 30 (1996) 1478.
24 Senthilnathan J, Mohan S & Palanivelu K, *Sep Sci Technol*, 40 (2005) 2125.
25 Sengupta A, Subramanian S & Clifford D, *J Environ Eng*, 114 (1988) 137.
26 Tandon R K, Crisp P T & Ellis J, *Talanta*, 31 (1984) 227.
27 Sperling M, Xu S & Welz B, *Anal Chem*, 64 (1992) 3101.
28 Cotton F A & Wilkinson G, *Advanced Inorganic Chemistry,* 4th edn (John Wiley & Sons, New York), 1980.
29 Saha B, Gill R J, Bailey D G, Kabay N & Arda M, *React Funct Polym*, 60 (2004) 223.
30 Marrison G H & Freiser H, *Anal Chem*, 36 (1964) 93.