

Recovery of Chromium from Electroplating Wastes by Solvent Extraction

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Abstract

Ultrapure chromium chloride was quantitatively recovered from industrial wastes by solvent extraction using 30% TBP – pure kerosene, a pilot plant flow sheet was proposed on basis of this work, FTIR- analysis for the washed loaded organic extractant prevailed that chromium chloride –TBP complex was formed during mixing of the two immiscible liquids.

Keywords: Solvent extraction; Chromium; Electroplating wastes; Recovery of chromium

Introduction

The ability of a solute to distribute itself between an aqueous solution and an immiscible organic solvent has long been applied to separation and purification solutes either by extraction into the organic phase, leaving undesirable substances in the aqueous phase; or by extraction of the undesirable substances into the organic phase, leaving the desirable solute in the aqueous phase. The properties of the organic solvent require that the dissolved species be electrically neutral. Optimization of separation processes to produce the purest product at highest yield by lowest possible cost under the most favourable environmental conditions [1].

The distribution law

The distribution law, derived in 1898 by Nernst, relates to the distribution of a solute (A) in the organic and in the aqueous phases at equilibrium reaction state:

$$K_{D,A} = \frac{\text{Concentration of Species A in organic phase}}{\text{Concentration of Species A in aqueous phase}} = \frac{[A]_{org}}{[A]_{aq}} \quad (1)$$

where brackets refer to concentrations; KD, A is the distribution, this equation is valid only with pure solvents, if the mutual solubilities of the solvents are small, (<1%) and the activity factors of the system are constant. If the solute is strongly solvated, or at high concentration (mole fraction >0.1), or if the ionic strength of the aqueous phase is large (>0.1 M) or changes, Eq. 1 must be corrected for deviations from ideality according to:

$$K_{D,A}^{\circ} = \frac{y_{A,org}[A]_{org}}{y_{A,aq}[A]_{aq}} = \frac{y_{A,org}}{y_{A,aq}} K_{D,A} \quad (2)$$

The distribution ratio (Coefficient)

The IUPAC definition of the distribution ratio, D, is given:

$$D_M = \frac{M \text{ in organic phase}}{\text{Concentration of all species containing}} = \frac{[M]_{i,org}}{[M]_{i,aq}} \quad (3)$$

When M is present in various complex forms in the aqueous phase and in the organic phase, $[M]_i$ refers to the sum of the concentrations of all M species in a given phase. It is important to distinguish between [2] the distribution constant, KD, which is valid only for a single specified species (e.g., MA₂) and the distribution ratio, DM, which may involve sums of species of the kind indicated by the index, and thus is not constant.

Solvent extraction is a unit operation for the purification and concentration of a wide variety of metals and materials. It consists of a contacting an organic diluent containing an extractant, with an aqueous phase containing the metal or material of interest. The extractant chemically reacts with the metal to form an organic-metal complex that is soluble in the organic phase meanwhile the impurities normally do not react with the extractant thus remain in the aqueous phase. The organic phase, containing the organic-metal complex, is separated from the aqueous phase. The metal is recovered and concentrated into another aqueous phase by reversing the chemical reaction. Solvent extraction was first applied to higher value metals, but now due to availability of new extractants with improved selectivity, faster kinetics and the developed extracting technology is now applicable to lower value metals. Solvent extraction consists of four steps:

Extraction: The operation of transferring the metal of interest from the aqueous phase to the organic phase (extraction cascade).

Scrubbing: The selective removal of impurity metals from the loaded organic phase by treatment with fresh scrub solution. The spent scrub solution is normally combined with the Feed.

Stripping: The process that recover the metal of value from the scrubbed organic phase by reversing the extraction chemical reaction (stripping process) normally conducted under conditions in order to produce a strip liquor containing a high concentration of the metal value (pure product).

Regeneration: The treatment of the stripped organic phase for removal of metals that were not scrubbed or stripped and the degradation products. The operation produces a regenerated organic phase for recycle to the new extraction operation process as organic extractant feed.

The aim of this work is to recover chromium as a valuable metal from industrial wastes e.g., electroplating and electro wining activities

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by solvent extraction technique using tri butyl phosphate in purified kerosene and to save our environment. Solvent extraction is the ever most worldwide technology used in global industries such as phosphoric and phosphates industries, pharmaceutical drug production, different oils purification and production as well as nuclear industries for nuclear fuel reprocessing and fissile uranium enrichment. Novel reliable extractants having interesting chemical and engineering properties such as tri butyl phosphate, amines, di 2-ethyl hexyl phosphoric acid and tri octyl phosphine oxide are used in solvent extraction plants for many years without any chemical changes in their chemical structures [3].

Experimental Work

Requirements

Apparatus: Portable PH-meter model HI 9811-5, HANA Co, FTIR – Spectrometer-Bruker/Alpha Platinum ATR.

Chemicals: Zinc Chloride, Sodium Hydroxide, Hydrochloric acid, Sulphuric Acid, Ferric Chloride, Chromium Tri-oxide, Tri Butyl Phosphate (TBP) all of laboratory reagent and pure grades (Aldrich and Fluka) and commercial crude kerosene.

Glassware: Beakers, Separators funnels, Pipettes, Filter paper no. 542 and Appindorff pipette.

Experiment

Purification of kerosene: 1 liter of commercial crude kerosene added into 2 litre glass beaker, and stirred with 100 ml of concentrated sulphuric acid by mechanical stirrer for 3 hours, then the treated kerosene was separated using a 2 litre separatory funnel, washed 3 times with distilled water, then the purified kerosene [4-6] was distilled using simple distillation apparatus to recover the cut product in the range 120-260 °C.

Preparation of 30% TBP-kerosene, by mixing 30 ml TBP reagent with the purified kerosene in step-1.

Preparation 1 liter of PH solutions 1,2,2,5 and 7 by adding drops of HCl dil. to distilled water meanwhile controlling the PH values with the aid of a PH meter.

Preparation of ~ 1 g/l Chromium solution by dissolving chromium trioxide into the solutions prepared at step 2.

Preparation of ~ 0.5 g/l Zinc solution by dissolving Zinc chloride into the solutions prepared at step 2.

Experiments to determine the residence time of chromium extraction.

Experiments to determine the distribution coefficient of chromium and zinc by 30% TBP-treated Kerosene (organic extractant) respectively by mixing 10 ml of organic extractant with 10 ml of each standard solution at steps 4,5 using 50 ml separatory funnel for 10 minutes as an infinite time [7-12].

Recovery of chrome from simulated waste solution: 50 ml of simulated Feed ($H^+=0.295$ N) extracted 6 times by 50 ml 30% TBP-KER (6 times). Then the loaded organic washed by 10 ml of 0.2 N HCl (3 times), finally the washed loaded extractant stripped off by (50 ml) DMW 5 times.

Results and Discussion

The idea of solvent extraction is based on the complexation of the valuable metal of interest in an aqueous medium by the organic extracting TBP through mechanical mixing process of the two immiscible liquids

to form $HCrO_3 \cdot 2TBP$ complex which dissolves in an organic medium such as kerosene leaving the impurities in the aqueous medium, this fact was approved by FTIR analysis for the very pure chromium chloride (Figure 1) which is showing the peaks of Cr^{+3} and Cl^{-1} , meanwhile Figure 2 is showing all the types of C-H and P-O, C-O bonds for the very pure organic extractant 30% TBP- kerosene and Figure 3 is showing all the bonds of the pure chromium chloride and the organic extractant together.

Very high chemical Tri butyl phosphate was chosen as a novel extractant for its selectivity, negligible mutual solubility, neutral and stability. TBP is used in a suitable diluent in a proportion 30% TBP in purified inert diluent such as kerosene [13] for chemical engineering considerations related to scale up to pilot plant or industrial scale. Table 1 reflects the chromium chloride prepared by different pH solutions which illustrates the acidic solution due to acidity nature of the salt that formed by strong acid, meanwhile Table 2 showing the amphoteric behaviour on $ZnCl_2$ salt. Extraction process proved to be very fast as seen by Figure 4 which is about 3 minutes.

The distribution coefficient of chromium (D_a^{Cr}) was found to increase in the Acid range as seen from Table 3 contrary the distribution coefficient of zinc (D_a^{Zn}) impurity increases towards the PH range (Table 4) which increases the value of the separation factor, for this means that as the value of separation factor increases the purity of the metal of interest increases, taking into account separation can not be possible when separation factor < 1 .

$$\text{Separation factor (S)} = D_a^{Cr} / D_a^{Zn}$$

According to the values of the distribution coefficient of chromium, the number of the theoretical number of extraction stages could be calculated due to the following mathematical formula:

$$Xe \left(\frac{a/D}{D} \right)^n = Xw$$

$$0.1 \left(\frac{1}{5} \right)^n = 10^{-3}$$

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$$n = 4.3 \rightarrow 5 \text{ stages}$$

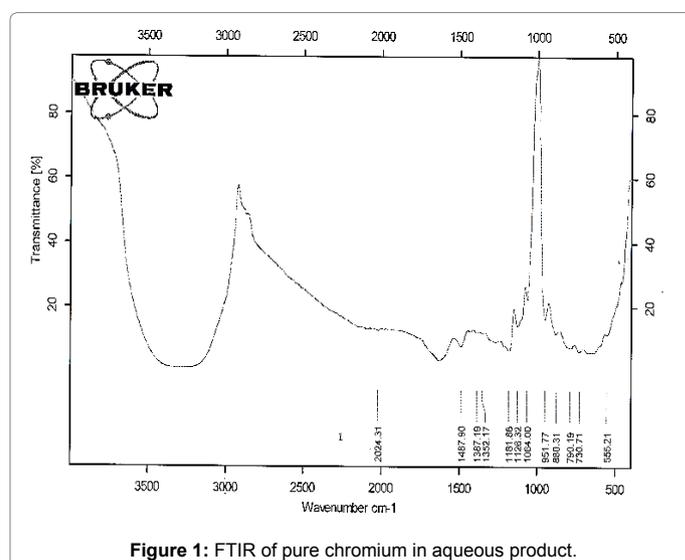


Figure 1: FTIR of pure chromium in aqueous product.

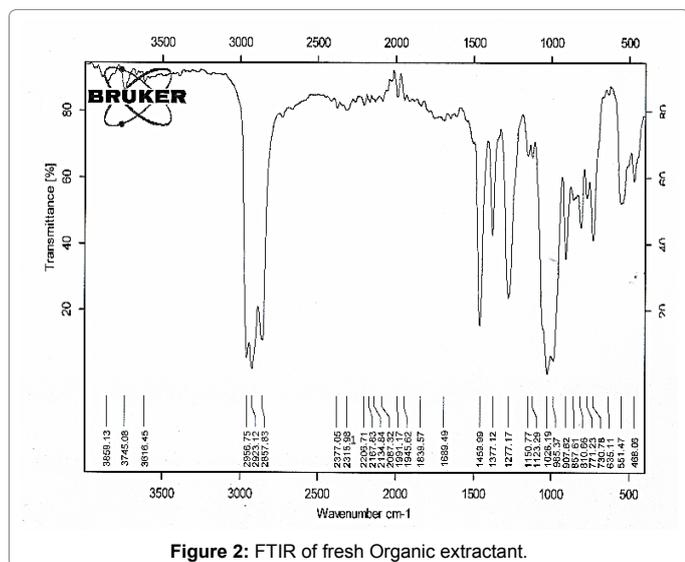


Figure 2: FTIR of fresh Organic extractant.

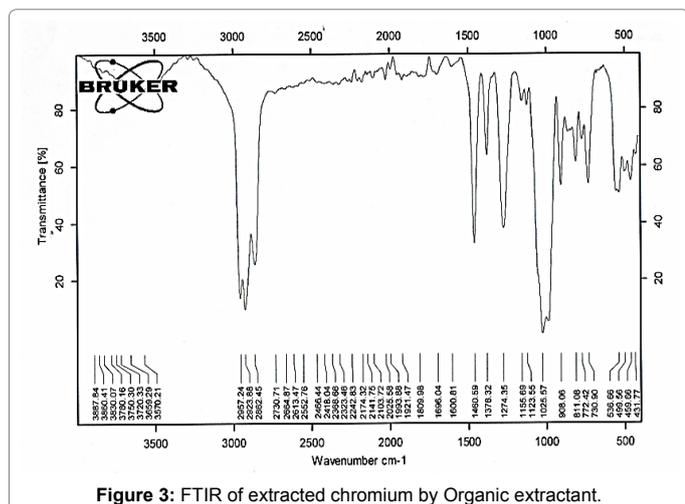


Figure 3: FTIR of extracted chromium by Organic extractant.

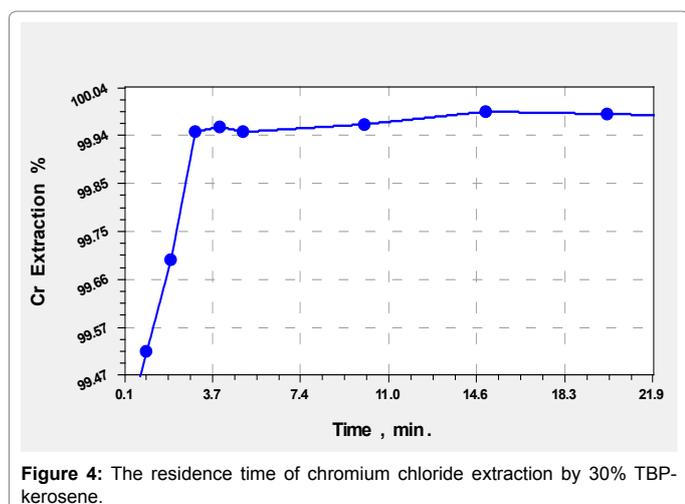


Figure 4: The residence time of chromium chloride extraction by 30% TBP-kerosene.

Theoretical number of stages was found according to McCabe-Thiele diagram (Figure 5) to be equal 5 stages as found previously by the theoretical calculations [14]. The theoretical number of extracting

and stripping stages as seen from McCabe- Thiele diagram based on almost quantitative recovery (>99.99%). The actual recovery was found to be >99.96% for ultrapure chromium product (Table 5).

The batch wise purification process of chromium can be scaled up on bases of mixer settlers facility or columns (packed and/or pulsed) to be constructed as a pilot or industrial plant facilities going on a continuous purification process taking into considerations the efficiency [15,16] of mixer settlers which is <100%.

As seen from Figure 6, the industrial aqueous waste containing chromium chloride (aqueous feed) is fed into the continuous counter current cascade at stage number 6 of the extraction battery (6 extracting stages), meanwhile the washing solution (scrub) is fed through stage number 9 of the scrubbing section of the extraction battery (3 scrubbing stages). The washed loaded organic stream is transferred to the re extraction battery (stripping) to recover the ultrapure chromium product by demineralized water stream. The facility seen at Figure 6 is considered of highly investment which produces 57.6 Tonnes/year of 69120 \$. Figures 7 and 8 showing the traditionally available pilot and industrial plant facilities [17-19].

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pH	pH of Cr Solution after Preparation
1	1
1.5	2
1.6	3
1.6	5
1.7	7

Table 1: Stock solutions of chromium chloride (~1 g/l) prepared at different pH values.

pH	pH of Zn Solution after Preparation
1	1.1
2	1.6
3	2.6
5	4.7
7	5.3

Table 2: Stock solutions of ZnCl₂ (~0.5 g/l) prepared at different pH values.

pH	Cr Conc. in Initial aq. Solution, ppm	Cr Conc. in Final aq. Solution, ppm	Cr Conc. in Org. Solution, ppm	D _o
1	838.6	124.22	714.38	5.75
1.5	838.6	123.6	641.1	5.187

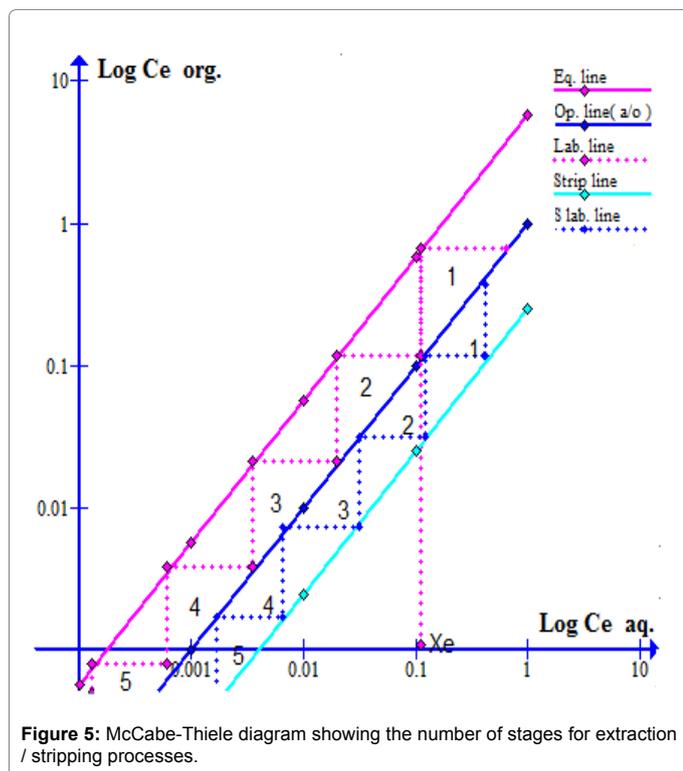
Table 3: The distribution coefficient of chromium in the system 30% TBP-ker/HCl.

pH	Zn Conc. in Initial aq. Solution, ppm	Zn Conc. in Org. Solution, ppm	D _o
1.1	196.96	-----	-----
1.6	226.76	-----	-----
2.6	184.68	-----	-----
4.7	186.28	-----	-----
5.3	224.56	9.6	0.0446

Table 4: The distribution coefficient of Zn in the system 30%TBP-ker/HCl.

Sample	Cr ppm	Zn ppm	Fe ppm
Pure Cr product	112.9	-----	-----
Aqueous	0.1	19.17	6.6
Simulated Feed	113.2	19.2	6.66

Table 5: Mass balance of the purification of chromium by solvent extraction cycle.



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