Extraction, Stripping and Precipitation Studies of Chromium (VI) Using TRPO (Cyanex923) as The Ligand

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***Abstract*—The toxicity imparted to the water and the occupational safety problems associated with the release of chromic acid into the atmosphere is making the electroplating industry to look for an alternative to Chromium(VI). The conventional method for treatment of metal waste is precipitation and the sludge obtained is often disposed as landfills, resulting in loss of useful resources and more importantly creating environmental problems associated with solid waste disposal. Solvent extraction is a widely employed commercial technique for the selective separation of metals from industrial waste streams. Herein, reporting an an investigation on the extraction behavior of chromium(VI) from dilute acidic solutions using trialkyl phosphine oxide (TRPO = Cyanex 923). The effect of various parameters such as concentration of the extractant, acidity, concentration of the metal ion and the nature of the diluent on the extraction of chromium(VI) has been investigated. The results demonstrate that chromium(VI) extracted into the organic phase as H_2CrO_4. 2TRPO. The nature of the extracted complex in the organic phase was further confirmed by UV-VIS spectra of the extracted complex. The stripping and precipitation of Chromium(VI) has also been examined. Chromium from the loaded organic phase is precipitated as CrO_3 using NaOH at pH 9 and is characterized using XRD and SEM. The mutual separation possibilities of chromium(VI) and chromium(III) has also been explored with a view to recover chromium species from industrial wastes.**

***Index Terms*—Chromium(VI), solvent extraction, TRPO, Cyanex923, CrO_3**

I. INTRODUCTION

Based on the differing toxicities chromium is important compared to the other toxic elements in the environment in that different species of chromium, specially chromium(III) and chromium(VI) are regulated in different ways [1, 2]. All other toxic metals, such as lead, cadmium and arsenic are regulated based on their total concentrations, irrespective of their oxidation state. For example, United States Environmental Protection Agency (USEPA) classifieds materials as hazardous waste if they contain leachable chromium, but excluded those materials from classification if it can be shown that the leachable chromium is not chromium(VI). Chromium(VI) is recognized to be much more toxic than chromium(III), and is found to be toxic to bacteria, plants, animals and people.imparting toxicity to cause lung cancer as well as kidney, liver and gastric damage. Hence, the world health organization (WHO) recommended toxic limits of chromium(VI) in waste water is at the level of 0.005ppm. Theres strict regulations regarding the maximum permissible concentration of chromium(VI) in natural or drinking water [3, 4].

Because of the simplicity, versatility, easy recovery of the metal ion and ready adaptability to scaling up of the process, methods based on liquid-liquid extraction has emerged as a widely employed technique [5] for the separation of metal ions [6-8]. Recycling of the spent organic solvent is yet another attractive feature of this technique. Hence in the present work an attempt has been made to develop a selective separation method for the recovery of chromium using liquid - liquid extraction by employing commercially available extractant system. The solvent extraction of chromium(VI) from aqueous acidic sulphate solutions with bis-2,4,4-trimethylpentylphosphinic acid in kerosene has been investigated as a function of aqueous phase acidity, extractant concentration and temperature [9]. The distribution ratio increases with increase in concentration of the extractant, aqueous phase acidity and temperature. Cyanex 272 forms a 1:1 solvated complex with the metal ion in its dilute solutions. The extraction of chromium(VI) from various aqueous solutions by 1-phenyl-3-methyl-4-

butylpyrazolone has been studied by Uzoukwnn and Ukegbun [10], and proposed a separation method for chromium(VI) from Fe(III). The recovery and separation of chromium(VI) from aqueous solutions with solvent extraction have been studied by a number of researchers [11-13]. The mechanism of the extraction of chromium(VI) is quiet complicated because chromium(VI) forms in aqueous solutions a variety of complexes with varying metal concentrations and pH in the aqueous phase [14]. The chemical equilibria for the extraction of chromium(VI) from aqueous solutions with tri-n-octylphosphine oxide (TOPO) has been investigated by Ting-Chia Huang and co-workers [15, 16]. The investigations on the UV - Visible spectra of chromium(VI) in the kerosene solution of TOPO indicated the presence of the complexes $HCrO_4^-$ and $Cr_2O_7^{2-}$ with TOPO in the organic phase. The extracted complexes were also further confirmed by analyzing the extraction data by numerical methods. The corresponding extraction constants were reported as 2019 and 3.69 x 10^8, respectively. Tris (2-ethyl hexyl) phosphate (TEHP) has been used for the extraction of chromium(VI) from dilute solutions and reported the extracted complexes as $HCrO_3Cl$. 3TEHP [17]. In this article, the development of a liquid-liquid extraction method for chromium(VI) from aqueous solutions using commercially available extractant trialkyl phosphine oxide (Cyanex 923 = TRPO) is discussed.

II. EXPERIMENTAL

Materials

The acid chloride (Trialkylphosphine oxide (TRPO) with the trade name Cyanex 923, supplied by Cytec, Canada was used after purification (purity = >99 %; average mol. wt. = 348 g) [18]. Tthe diluent in the present work is purified kerosene (boiling range 160-200°C, composed of aliphatic hydrocarbons). All other chemicals used were of analytical reagent grade.

Instruments

For routine analysis of metal ions A Perkin Elmer AAnalyst 100 atomic absorption spectrophotometer and a Hitachi (Tokyo, Japan) 220 double beam microprocessor-controlled spectrophotometer were used. An Orion (USA) 720A Ion Analyzer was used for the pH measurements.

Extraction and Analytical Procedure

Known volumes of aqueous and organic phases in a glass stoppered vial was shaken using a mechanical shaker at room temperature to do the extraction and back extraction (stripping). From the time of extraction experiment it was confirmed that the equilibrium was obtained within two minutes. The aqueous phase metal concentrations were measured using spectroscopic techniques and the concentration in the organic phase was calculated considering material balance. The ration between the concentration of metal ions in the organic phase to that in the respective aqueous phase ids calculated as distribution ratio, D. All the extraction experiments were performed in duplicate and the general agreement in the distribution ratio values obtained was within ± 5%.

III. RESULTS AND DISCUSSION

Time of extraction

The effect of phase contact time on the distribution data for the extraction of chromium(VI) (0.001 mol/dm^3) from aqueous solutions of pH= 2 using 0.1 mol/dm^3 cyanex 923 in kerosene has been measured and the results are given in the Table1. It is clear from the results that the extraction equilibrium is found to be reached within 5 minutes.

Table 1. Extraction of Chromium (VI) from aqueous solutions of pH = 2 with TRPO (cyanex 923). [Cr (VI)] =0.001 mol/dm^3 ; [Cyanex 923] = 0.1 mol/dm^3.

Time (min)	Distribution ratio
5	3.52
10	3.50
15	3.52
30	3.54
60	3.52

Effect of Cyanex 923 Concentration

The effect of concentration of Cyanex 923 concentration (0.01 - 0.1 mol/dm^3) on the extraction of chromium (VI) (0.001 mol/dm^3 and 0.002 mol/dm^3) from aqueous solutions of pH = 2 has been investigated and the results are depicted in Figs. 1(a and b, respectively). It is clear from the figures that

the extraction of chromium(VI) increases linearly with increase in concentration of the extractant. From the slopes of the plots, log D vs log [Cyanex 923], it is inferred that two molecules of Cyanex923 are involved in the extracted complex.

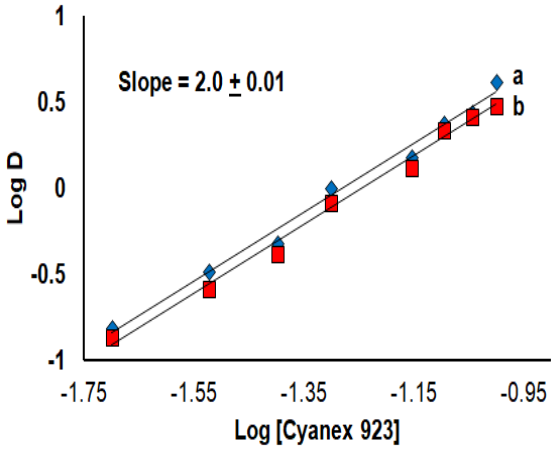

Fig. 1 Effect of TRPO (Cyanex 923) concentration on the extraction of chromium(VI). (a) aqueous phase = 0.001 mol/dm^3 Cr(VI) of pH = 2 and (b) aqueous phase = 0.002 mol/dm^3 Cr(VI), pH = 2.

Effect of pH

The extraction of chromium(VI) (0.001 and 0.002 mol/dm^3) with 0.1 mol/dm^3 Cyanex 923 has been investigated as a function of pH of the aqueous phase and the results are given in Figs. 2 and 3. The extraction behavior of chromium(VI) showed an inverse dependence with pH. The plots of log D vs pH gave slopes of -1, indicating the formation of the complex, H_2CrO_4.

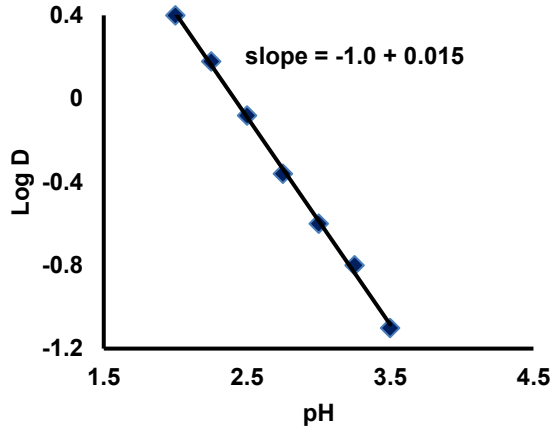

Fig. 2 Effect of pH on the extraction of chromium(VI). Aqueous phase = 0.001 mol/dm^3 Cr(VI), organic phase = 0.1 mol/dm^3 Cyanex 923.

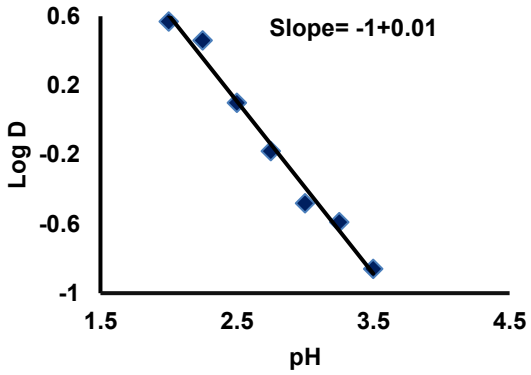

Fig. 3 Effect of pH on the extraction of chromium(VI). Aqueous phase = 0.002 mol/dm^3 Cr(VI), organic phase = 0.1 mol/dm^3 Cyanex 923.

Effect of metal ion concentration

The effect of chromium(VI) concentration on the extraction process has been investigated using Cyanex 923 (0.1 mol/dm^3) in kerosene from aqueous solutions of pH 2 and the results are shown in Fig.4. It is clear from the results that the extraction efficiency of chromium(VI) decreases with the initial metal concentration in the aqueous phase. From the log - log plots of equilibrium metal ion concentrations in the organic to that in the aqueous phase with a slope of unity it was evident that a mononuclear species was extracted in to the organic phase.

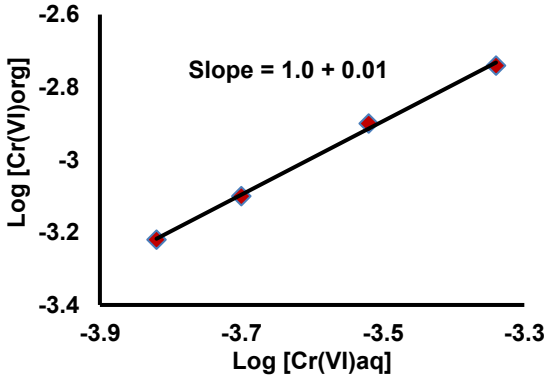

Fig. 4 Effect of metal ion concentration on the extraction of chromium(VI). Organic phase = 0.1 mol/dm^3 Cyanex 923, pH = 2.

UV Absorption Spectra

To study the nature of the complex with Cyanex 923 in the organic phase, the UV-VIS spectrum of chromium(VI) in kerosene solution of TRPO

(Cyanex 923) has been investigated. The loaded organic phases were prepared by conducting the extraction of chromium(VI) with Cyanex 923 in kerosene. ([Cr(VI)] = 0.001 mol/dm^3 , pH = 2 and [Cyanex 923] = 0.1 mol/dm^3, and at [Cr(VI)] = 0.002 mol/dm^3, pH = 2 and [Cyanex 923] = 0.1 mol/dm^3). The equilibrium concentrations of chromium(VI) in the organic phases were found to be 7.75 x 10^{-4} mol/dm^3 and 1.5 x 10^{-3} mol/dm^3, respectively. The UV-VIS spectra is shown in Fig. 5. A distinct peak at 345nm in the spectrum clearly indicates the existence of $HCrO_4^-$ species in the organic phase.

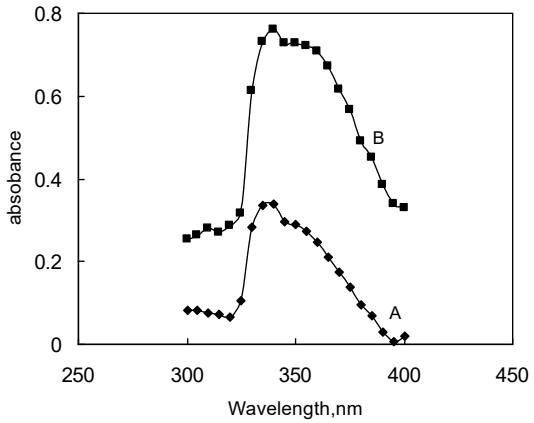

Fig.5 UV-VIS spectra of chromium(VI)in kerosene solution of cyanex 923. A = [Cr(VI)] = 7.75 x 10^{-4} mol/dm^3 , B = [Cr(VI)] = 1.15 x 10 $^{-3}$ mol/dm^3 .

Extraction Equilibrium

Based on the preceding studies, the extraction equilibrium for the extraction of chromium(VI) from aqueous solutions with TRPO (Cyanex 923) in kerosene can be expressed as follows:

$$HCrO_4^- + H^+ + 2TRPO \overset{Kex}{\Longleftrightarrow} H_2CrO_4.2TRPO$$

Where K_{ex} denotes the equilibrium constant value and is given by,

$K_{ex} = [H_2CrO_4.\ 2TRPO] / [HCrO_4^-] [H^+] [TRPO]^2$

The equilibrium constant, $K_{ex,}$ was calculated and found to be equal to 4.3 x 10^4.

Effect of diluents

The effect of various diluents on the extraction of Cr(VI) has been examined using 0.1 mol/dm^3 Cyanex 923 in various commercially employed solvents that are shown in table 2. From the results it was evident that the nature of the solvent has an effect on the extraction. Higher extraction efficiency for chromium(VI) was detected when solvents with low dielectric constants such as xylene, toluene, benzene and kerosene were used. While poor extraction effiecienies were observed when solvents with high dielectric constants were used.This may be due to the strong interaction between the extractant and chloroform through hydrogen bonding. However in the present study, methyl isobutyl ketone, having high dielectric constant showed higher extraction and is due to the synergistic effect of the mixed-solvent system. Among aromatic hydrocarbons, the extraction efficiency of chromium(VI) varies in the order; xylene > toluene > benzene.

Table.2 Effect of nature of the various solvents on the extraction of chromium(VI).

Diluent	Dielectric constant(ε)[20]	% Extraction
MIBK	13.11	97
Chloroform	4.90	23
Xylene	2.26	80
Toluene	2.24	77
Benzene	2.28	76
Kerosene	2.00	78

Stripping studies

Various stripping agents of different concentrations were examined to recover the chromium(VI) from the loaded organic phase (0.1 mol/dm^3 Cyanex 923 in kerosene containing 7.75 x 10^{-4} mol/dm^3 chromium(VI)) and the results are given in Table 3.

Table. 3 Stripping behavior of chromium(VI)

Stripping agent	% recovery of chromium(VI)	Phase ratio (Org. : Aq.)	No. of stages
1-6 mol/dm^3 HCl	Nil	1 : 1	1
1-2mol/dm^3 H_2SO_4	Nil	1 : 1	1
1-2mol/dm^3 HNO_3	Nil	1 : 1	1
Buffer of pH = 6	99.9	1 : 1	4

It is clear from the results that chromium(VI) can be recovered > 99% from loaded organic phase in four stages of stripping using buffer solution of pH = 6.

Precipitation studies

From the stripping studies 99.9 % the extracted Cr was getting stripped while using a solution of pH 6. In order to explore the possibility of recovering Cr by direct precipitation is tested at various pH conditions, pH 6, 7, 8, 9 and 10. The precipitate obtained was calcined and used for further characterizations. The percentage precipitations were determined by analyzing the supernatant solution to find the residual Cr concentration. The percentage of Cr precipitation increased with increasing pH. The precipitations experiments were done three times and the averages with the error are shown in the figure.

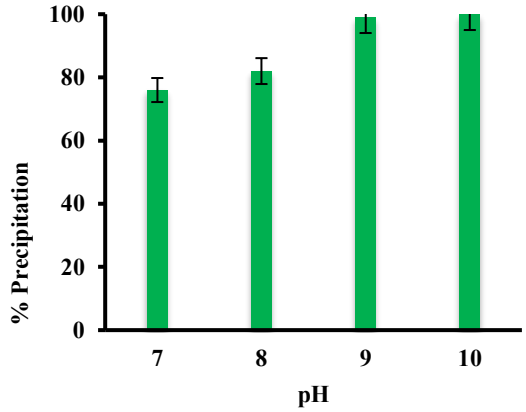

Fig. 6. Precipitation of Cr(VI) from the loaded TRPO(Cyanex 923) phase at different pH.

The effect of various precipitating agents like NaOH, $Ca(OH)_2$, NH_4OH and precipitation time are studied at pH 9 and NaOH was found to be the best precipitating reagent and also the maximum precipitation was observed within 30min in all the cases [21].

The precipitates were washed and calcined at 500^0C overnight before doing the characterization. The calcined precipitate was characterized using XRD, SEM, UV and IR. The XRD pattern of the precipitate after calcinations is shown in the Fig. which shows the characteristic peaks of a pure hexagonal CrO3, with no impurity peaks of any other phase or material. The XRD patter shows the characteristic peaks at 2T = =21.53°, 26.32°, 31.82°, 38.13°, and 40.1°. The values were in agreement with the earlier reported values of nanocrystalline hexagonal CrO_3 [22]. In order to study the surface morphology of the CrO3, the SEM image of the CrO_3 after precipitation calcination is recorded. The SEM image shows pure CrO_3 particles.

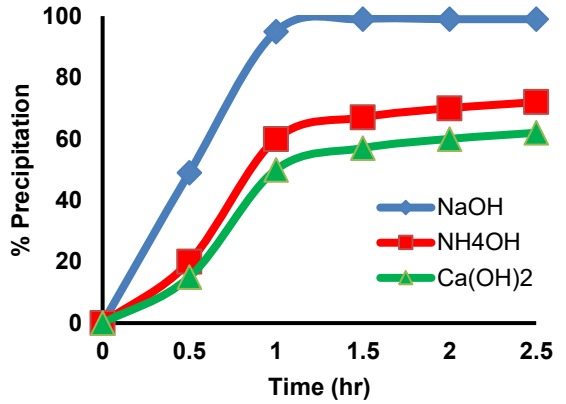

Fig. 7. Effect of time on the Precipitation of Cr(VI) from the loaded TRPO with various precipitating agents

Comparison of extraction behavior of chromium(VI) and chromium(III)

The extraction behavior of chromium(VI) (0.001 mol/dm^3) and chromium(III) (0.001 mol/dm^3) from acidic solutions has been investigated using cyanex 923 (0.1 mol/dm^3) in kerosene as the extractant. It is clear from the results that chromium(VI) gets extracted into the organic phase whereas, chromium(III) remains in the aqueous phase unextracted. Thus chromium(III) can be easily separated from a mixture of chromium(III) and chromium(VI) from dilute acidic solutions by employing Cyanex 923 as an extractant.

IV. CONCLUSION

The liquid-liquid extraction behavior of chromium(VI) and chromium(III) has been investigated from dilute acidic solutions using Cyanex 923 (TRPO) in kerosene as an extractant. The results clearly indicate that chromium(VI) is extracted as, H_2CrO_4. 2 TRPO. On the other hand, chromium(III) was found to be not extracted under the present experimental conditions. Thus chromium(III) and chromium(VI) can be separated by employing Cyanex 923 as an extractant from dilute acidic solutions (pH = 2). Further, the results also demonstrate that Cyanex 923 can be used as a potential extractant for the extraction and separation of chromium(VI) from industrial wastes. The stripping and the precipitation studies revealed that, Cr(VI) can be precipitated from the loaded organic

phase using NaOH as the precipitating agent. At pH 7, 8, 9 and 10 Cr(V)) was precipitated directly from the loaded organic phase. 100 % precipitation and recovery of Cr(VI) was observed at a pH 10. The precipitated Cr(VI) was then washed and calcined at 500^0C overnight and is then characterized using XRD and SEM. The XRD and SEM data suggests the formation of pure nanocrystalline CrO3 with no other impurities.

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CONFLICT OF INTEREST

There is no conflict of interest in submitting the manuscript and the same has not been submitted anywhere else for publication

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