



## Synergistic Extraction of Chromium (III) using TPPO and TMA

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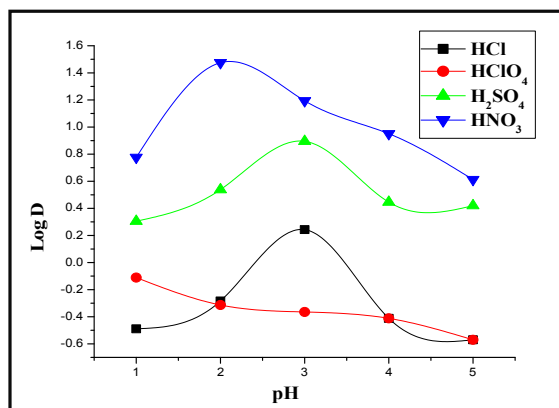
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Accepted on 9<sup>th</sup> June, 2018

### ABSTRACT

The extraction of chromium (III) from sulphuric, nitric, hydrochloric and perchloric acid solutions has been studied using mixtures of Triphenylphosphine oxide (TPPO) and Trimethylamine (TMA) in chloroform. The investigations were carried out to study the effect of various parameters like shaking time, pH, concentration of synergistic mixture, temperature, diluents on the extraction of chromium (III). Stoichiometries of extracted species in both individual and mixed extraction were ascertained by slope ratio analysis. Thermodynamic parameters controlling the nature of the extraction were also evaluated from the distribution ratio values obtained at different temperatures in order to explain the extraction mechanism.

### Graphical Abstract



Effect of pH by mixture of TPPO+TMA and synergistic extractants.

**Keywords:** Chromium (III), TPPO, TMA, Synergistic extraction, separation.

## INTRODUCTION

Synergistic systems involve the formation of a more hydrophobic ternary adduct which is mostly responsible for enhanced transfer of metal complex into organic phase [1]. Sushanta Kumar *et al.*, attempted synergistic extraction and separation studies of Ce(III) from acidic nitrate medium using

binary mixture of Cyanex 921 and Cyanex 923 in kerosene [2]. Synergistic solvent extraction of Co (II) and Li (I) from aqueous chloride solutions with mixture of cyanex 272 and TBP [3], Mangesh H Chhatre *et al.*, used synergistic extraction of Cerium (III) in salicylate media with tris (2-ethylhexyl) phosphate and TBPO, Y. G. Wang *et al.*, Synergistic Extraction of Zinc(II) using Mixtures of CA-100 and Cyanex 272 has been attempted [4, 5]. There are few examples available on synergistic Cr (III) extraction [6, 7]. In the present communication we describe our results obtained on the synergistic extraction of Cr (III) using TPPO and TMA in order to study the effects of several parameters - temperature dependence as well as nature of Cr (III) extraction.

## MATERIALS AND METHODS

**Reagents and equipments:** Chromium sulphate [ $\text{Cr}_2(\text{SO}_4)_3$ ](E Merck grade) was used for preparing chromium stock solution (1M) and standardized titrimetrically [8], with a standard solution of ferrous ammonium sulphate after oxidation of Cr(III) to Cr (VI) (using ceric ammonium nitrate as oxidant) with n-phenyl anthranilic acid (NPA) as indicator. 0.25 M (stock solution) of each Triphenylphosphine oxide (TPPO) and Trimethylamine (TMA) in chloroform was prepared and diluted appropriately to get the required concentration. All other chemicals used were of AR grade and purified according to the standard methods and are used as such without any further purification.

A digital pH meter equipped with single electrode was used for pH measurements, A temperature controlled mechanical shaker, made by KEMI was used for the equilibration studies, Atomic Absorption Spectrophotometer type AAS-SVL Spectronics Model 205 was used for the determination of chromium content in the samples.

**General Extraction Procedure:** 10.0 mL of chromium (III) having concentration  $1.0 \times 10^{-3}$  M of the corresponding mineral acid in a 150 mL separating funnel was shaken with 10 mL portions of each 0.025 M of TPPO+TMA mixture in chloroform (pre-equilibrated with 0.1M mineral acid). This was shaken thoroughly for five minutes and was allowed to settle for few min. Chromium (III) concentrations in both the phases were estimated. The equilibrium chromium (III) concentration in the organic phase was determined by taking the difference in the initial chromium (III) concentration and the equilibrium chromium (III) concentration in the aqueous phase using AAS. It was clearly noticed that chromium (VI) could not be extracted under the experimental conditions. In order to study the effect of temperature, equilibrations were carried out in a temperature controlled mechanical shaker, after which distribution ratio (D) was determined.

## RESULTS AND DISCUSSION

**Effect of shaking time:** The extraction of Cr (III) using a mixture of TPPO + TMA in chloroform has been studied by varying the shaking time from 5 to 30 min. With increase in shaking time from 5 to 15 min, the percentage extraction of Cr (III) was increased from 74.11% to 96.76% and then remains unchanged. Further increase in the time of equilibration does not affect the extraction equilibrium (Fig. 1). Therefore, for all experiments the shaking time was considered as 15 min.

**Effect of pH in extraction process:** The pH is a very important parameter for extraction studies. Experiments were carried out with different pH of aqueous phase, extractant concentration of 0.025 M. At first, it was observed that the percentage of extraction increased with increasing pH from 1.0 to 3.0 in case of sulphuric and hydrochloric acid media and there is a gradual decrease in pH (1.0 -5.0) in case of perchloric acid but in the case of nitric acid solutions there is an increase in pH from 1.0-2.0 and above pH 3.0 the extraction efficiency decreases perhaps due to hydrolysis of chromium. Extraction efficiency was maximum (96.76%) in the range 2.0 pH in nitric acid media (Fig. 2, Fig. 3).

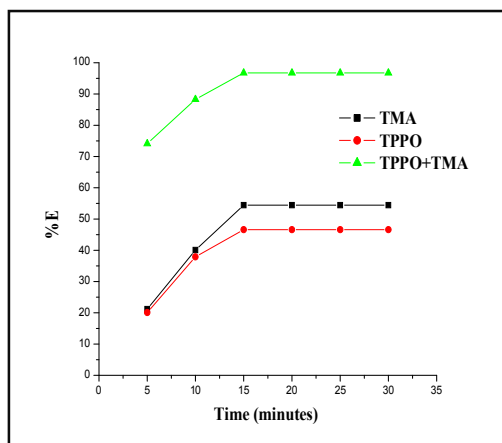


Figure 1. Effect of Time by the individual.

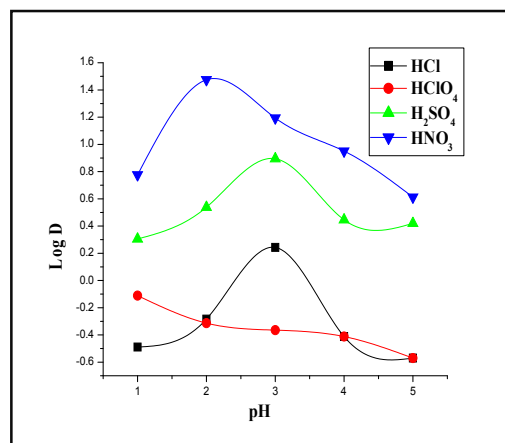


Figure 2. Effect of pH by mixture of TPPO+TMA and synergistic extractants.

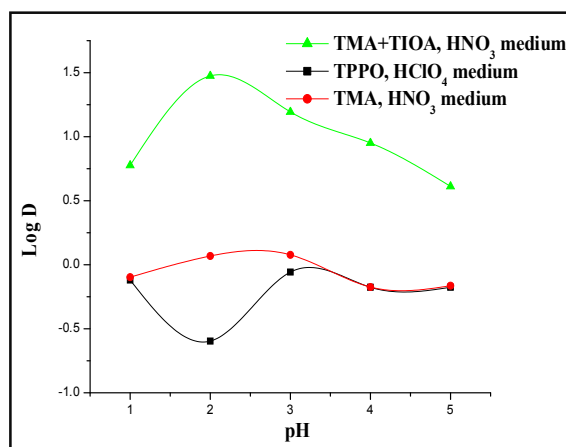


Figure 3. Effect of pH by the individual and synergistic extractants.

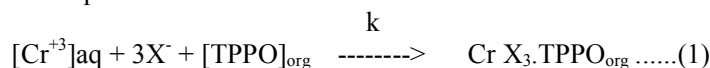
**Effect of diluents:** Effect of diluents on the extraction by with 0.025M of TPPO+TMA was studied with different organic solvents. It was found that maximum extraction was obtained with chloroform. The order of extraction by different solvents was given below (Table 1).

Table 1. Distribution ratio and %E in different solvents.

Solvent	TPPO		TMA		TPPO+TMA	
	Distribution ratio (D)	%E	Distribution ratio (D)	%E	Distribution ratio (D)	%E
Chloroform	0.875	46.66	1.195	54.44	29.871	96.76
Toluene	0.694	40.96	0.308	23.54	2.063	67.35
Benzene	0.678	40.40	0.621	38.30	3.154	75.92
Cyclohexane	0.615	38.08	0.514	33.94	3.946	79.78
Nitrobenzene	0.542	35.14	0.645	39.20	2.636	72.49
Carbon tetrachloride	0.397	28.41	0.428	29.97	2.911	74.43

**Variation of extraction of Cr (III) with TPPO:** Extraction of Cr (III) by TPPO in chloroform in the concentration range (0.025 to 0.005 M) indicates that the distribution ratios were very poor (46.66%). The composition of extractable species was obtained from the plot of log D vs. Log [TPPO] and the

data are fitted to a straight line with slope of unity (Fig. 4), indicating one molecule of TPPO is involved in the extraction process.



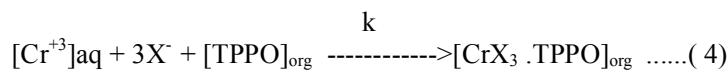
$$k = \frac{[\text{Cr X}_3 \cdot \text{TPPO}]_{\text{org}}}{[\text{Cr}^{+3}]_{\text{aq}} [\text{X}]^{3-} [\text{TPPO}]} \dots\dots(2)$$

And Distribution ratio,  $D = \frac{[\text{Cr X}_3 \cdot \text{TPPO}]_{\text{org}}}{[\text{Cr}^{+3}]_{\text{aq}}}$

Taking logarithm and putting the value of D in eq. (1) we have,

$$\log D = \log k + \log [\text{TPPO}]_{\text{org}} \dots\dots(3)$$

Stoichiometric co-efficients for the extraction reaction can be determined from the plot of log D against log [TPPO]<sub>org</sub>. Slope of unity is observed from all the acids employed in the study (Fig. 4) and hence individual extraction reaction of Cr (III) by TPPO is described as,



$$\text{Thus, } \log k = \log D - \log [\text{TPPO}]_{\text{org}} \dots\dots(5)$$

**Extraction of chromium (III) with TMA:** Extraction of Cr (III) by TMA in chloroform was also investigated in the concentration range as mentioned above. Plot of log D vs. log [TMA] gave a straight line with slope of 1 (Fig. 5), indicating one molecule of TMA is involved in the extraction process.

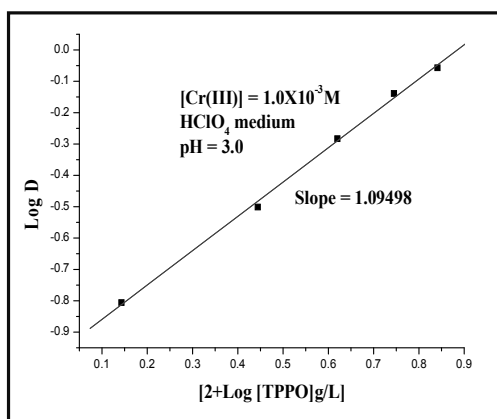


Figure 4. Extractant Variation of Cr (III) with TPPO.

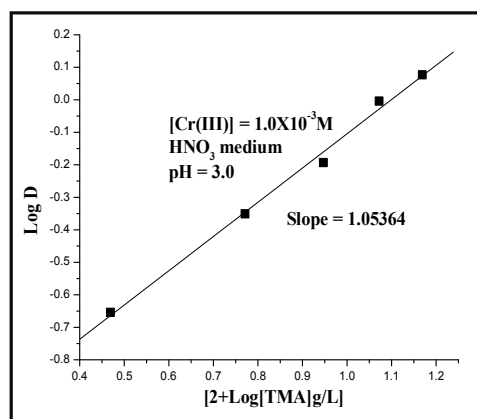
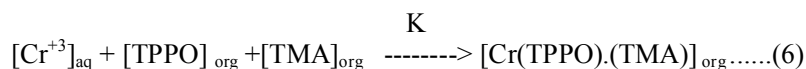


Figure 5. Extractant Variation of Cr (III) with TPPO.

**Synergistic extraction of chromium (III) in presence of TPPO and TMA:** Preliminary experiments show that the extent of extraction is poor in case of TPPO and TMA, used in the present study. However, when TPPO is mixed with TMA, a marked enhancement in the extent of Cr (III) extraction takes place. As  $D_{\text{mix}}$  is always greater than  $D_{\text{TPPO}}$  and  $D_{\text{TMA}}$ , mixed extraction definitely leads to synergism. If synergistic coefficient (S.C) and extent of synergism ( $\Delta D$ ) are positive, then synergism occurs. The extent of synergism is expressed in terms of  $\Delta D [D_{\text{mix}} - (D_{\text{TPPO}} + D_{\text{TMA}})]$  and synergistic coefficient ( $\text{S.C} = \log D_{\text{mix}} / (D_{\text{TPPO}} + D_{\text{TMA}})$ ).  $\Delta D$  and S.C were defined to evaluate synergistic effect as mentioned below (Table 2).

Where,  $D_{\text{mix}}$  = distribution ratios in presence of mixed extractants.  $D_{\text{TPPO}}$  = distribution ratios in presence of TPPO only.  $D_{\text{TMA}}$  = distribution ratios in presence of TMA only.

The plot of  $\log (D_{\text{mix}})$  against both  $\log [\text{TPPO}]$  and  $\log [\text{TMA}]$  shows straight lines of slope values 1 (Fig. 6) and (Fig. 7) respectively. Thus one TPPO molecule and one TMA molecule are present in ternary extracted species. Thus, mixed extraction could be shown as,



Therefore,

$$K = \frac{[\text{Cr}.(\text{TPPO}).(\text{TMA})]_{\text{org}}}{[\text{Cr}^{+3}]_{\text{aq}} \times [\text{TPPO}]_{\text{org}} \times [\text{TMA}]_{\text{org}}} \dots (7)$$

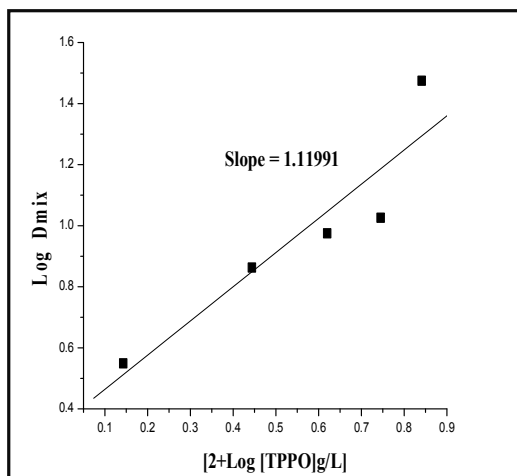
$$D_{\text{mix}} = \frac{[\text{Cr}.(\text{TPPO}).(\text{TMA})]_{\text{org}}}{[\text{Cr}^{+3}]_{\text{aq}}} \dots (8)$$

Substituting values of  $D$  in  $D_{\text{mix}}$  expression and taking log values of both sides,

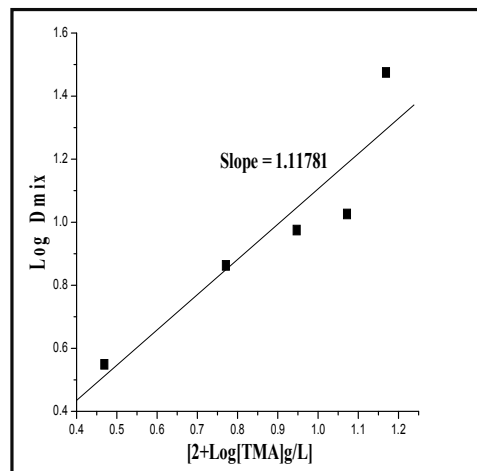
$$\log K = \log [D_{\text{mix}} - D]_{\text{org}} - \log [\text{TPPO}]_{\text{org}} - \log [\text{TMA}]_{\text{org}} \dots (9)$$

Table 2. Results of synergistic extraction of Cr (III).

Solvent	Concentration of TMA (M)	$D_{\text{TPPO}}$	$D_{\text{mix}}$	%E	S.C	$\Delta D$
Chloroform	0.025	0.875	29.871	96.76	1.1	27.80
	0.02		10.630	91.40	0.7	8.91
	0.015		9.449	90.42	0.8	8.12
	0.01		7.306	87.96	0.8	6.21
	0.005		3.543	77.98	0.6	2.68
Cyclohexane	0.025	0.615	3.946	79.78	0.5	2.81
	0.02		3.143	75.86	0.5	2.18
	0.015		2.614	72.32	0.5	1.88
	0.01		2.060	67.32	0.6	1.54
	0.005		1.333	57.13	0.7	1.11
Nitrobenzene	0.025	0.542	2.636	72.79	0.3	1.44
	0.02		2.011	66.78	0.3	1.05
	0.015		1.747	63.59	0.4	1.14
	0.01		1.209	54.73	0.4	0.73
	0.005		0.863	46.32	0.4	0.54
Benzene	0.025	0.678	3.154	75.92	0.3	1.85
	0.02		2.614	72.32	0.3	1.45
	0.015		2.190	68.65	0.4	1.34
	0.01		1.321	56.91	0.3	0.69
	0.005		1.106	52.51	0.5	0.80
Carbon tetrachloride	0.025	0.397	2.911	74.43	0.5	2.08
	0.02		1609	61.67	0.3	0.88
	0.015		1.201	54.56	0.3	0.66
	0.01		1.113	52.67	0.4	0.69
	0.005		0.063	5.92	-0.6	-0.22
Toluene	0.025	0.694	2.063	67.35	0.3	1.06
	0.02		1.466	59.44	0.2	0.65
	0.015		1.091	52.17	0.2	0.54
	0.01		0.932	48.24	0.3	0.49
	0.005		0.919	47.88	0.4	0.58

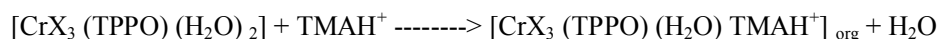


**Figure 6.** The plot of Log Dmix vs. [2+Log [TPPO] gL<sup>-1</sup>] in synergistic extraction of Cr (III).



**Figure 7.** The plot of Log Dmix vs. [2+Log [TMA] gL<sup>-1</sup>] in synergistic extraction of Cr (III).

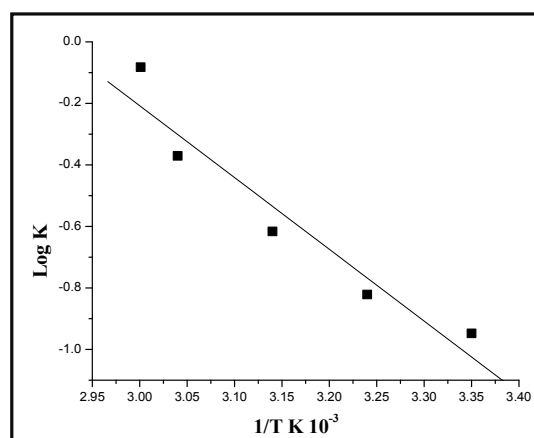
Thus, the adduct formation in the organic phase may be described as,



**Effect of temperature:** The effect of temperature on extraction of chromium (III) using mixture of 0.025M TPPO and TMA in chloroform was studied in the range of 25°C to 60°C (298K – 333K) as it plays an important role. It was found that the percentage extraction chromium (III) increases with aqueous phase acidity. The equilibrium metal ion concentrations in the organic and aqueous phase from equations (5) and (9), the equilibrium extraction constant logK for the complexes studied were calculated.

Standard enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were obtained from slope and intercept of the plot of log K against 1/T (Fig. 8) using Van't Hoff equation,

$$\log K = -\Delta H/2.303RT + \Delta S/2.303R \quad \text{.....(10)}$$



**Figure 8.** Temperature Variation.

The thermodynamic values of  $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  in the above temperature range are shown in table 3.

Table 3. Thermodynamic Parameters.

System	Solvent	$\Delta H^{\circ}$ (kJK <sup>-1</sup> .mol <sup>-1</sup> )	$\Delta S^{\circ}$ (JK <sup>-1</sup> .mol <sup>-1</sup> )	$\Delta G^{\circ}$ (kJK <sup>-1</sup> .mol <sup>-1</sup> )
Cr(III)- TPPO-TMA	Chloroform	19.40	56.49	-16.82
	Cyclohexane	20.48	55.29	-16.46
	Nitrobenzene	20.51	53.76	-16.01
	Benzene	19.73	51.78	-15.42
	Carbon tetrachloride	24.59	17.71	-5.27
	Toluene	13.80	66.94	-19.93

The positive values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  shows that extractions are entropy favoured i.e., (liberation of large number of water molecules leads to enhancement of entropy) and enthalpy disfavoured (due to bond breaking). Therefore, this ternary system is entropy controlled owing to extensive dissociation of the metal ion from its complex containing water or chloride ions as it extracts into the organic phase.

The positive value of  $\Delta H^{\circ}$  suggests that the heat effects involved in the dissociation of the metal cation from its complex containing H<sub>2</sub>O or Cl<sub>2</sub> ion is the main enthalpy factor. The value of  $\Delta H^{\circ}$  is calculated to be 19.40 kJK<sup>-1</sup>.mol<sup>-1</sup>. It indicates that the dissociation of the metal ion and the formation of the synergistic complex are almost similarly responsible for the small value of the enthalpy change in this temperature range.

## APPLICATION

**Determination of chromium in Tannery effluents:** Several attempts were made to determine the chromium content of tannery effluents as well as chrome slag collected from the vicinity of a local industrial area. As described above that the extraction of chromium (III) using TPPO+TMA in chloroform from different mineral acid media was studied and succeeded.

Basic chromic sulphate is generally used for tanning of hides in the leather where the reaction of chromium with collagen raises the hydrothermal stability of the leather and also renders it resistant to bacterial attack. Several workers have made an attempt to remove chromium from tannery effluents [9-16]. A survey on tannery waste characteristics indicates that chromium (VI) is absent, chromium (III) is present in concentrations of 1.3 – 1.5 % of dry solids. Environmental related problems are involved in the incineration process of the tannery waste disposal such as possibility of chromium (III) (present in higher amounts) being oxidized to chromium (VI), thereby increasing the release of chromium (VI) into the environment. In view of this the alternative i.e., dissolution in acid followed by mechanical separation of solid from the acid extract and selective extraction of chromium from the tannery wastes gained importance. An attempt is made to separate chromium from the tannery effluents collected from a chrome tannery industry situated at Nellimarla, Vizianagram district, Andhra Pradesh, India.

The collected samples after acid dissolution and filtration to remove undissolved impurities are adopted the following procedure. An aliquot (250 mL) of the filtered sample is taken and boiled till to reduce its volume to about 1/5<sup>th</sup> of the initial volume (50mL). In this method interference due to iron (III) is separated by following photometric method [17]. 10 mL of this solution is then extracted with 10 ml of 0.025 M TPPO+TIOA in chloroform as per the procedure described earlier.

A synthetic solution with a composition Cr = (0.20 – 0.40) gL<sup>-1</sup>, Al = 2.0 gL<sup>-1</sup>, Fe (III) = 0.5 gL<sup>-1</sup>, SO<sub>4</sub><sup>2-</sup> = 40.0 gL<sup>-1</sup>, pH = 3.0 is subjected to the same procedure and tested for recovery of chromium. It may be recalled that the recovery of chromium is (99.7 ± 0.3 %) both in the presence and in the absence of the impurities usually associated with tannery wastes. Hence the data in table 4 on chromium (III) recovery may safely be considered to be reliable.

**Table 4.** Analysis of chromium in synthetic and tannery effluents

Sample	Chromium(III) added (gL <sup>-1</sup> )	Chromium found after recovery by extraction	
		Recovery Value	S.D
<b>Synthetic samples</b>			
1	0.20	0.195	0.001
2	0.25	0.246	0.003
3	0.30	0.293	0.002
4	0.35	0.344	0.002
5	0.40	0.391	0.002
Tannery Effluent Samples			
1(Inlet of ETP)	-	3.18	0.026
2(Outlet of ETP)	-	4.76X10 <sup>-2</sup>	0.0004

ETP = Effluent treatment plant

S.D = Standard Deviation (Average of four determinations)

## CONCLUSIONS

Thermodynamic parameters obtained from the distribution ratio values of the extraction revealed that it is entropy favoured (endothermic in nature) indicated by release of water molecules in synergistic extraction.

## ACKNOWLEDGEMENTS

Thanks are due to Dr. V. Muralidhara Rao (Retd.), Professor, School of Chemistry, Andhra University, Visakhapatnam for his valuable suggestions. Thanks are due to UGC office for providing financial assistance in the major research project. Thanks are also due to Principal, GIT and Management of GITAM for providing necessary facilities.

## REFERENCES

- [1]. P. Dey, S. Basu, Radiotracer study of the effects of Organo phosphorus donors on the extraction of Iron (III) with 2-hydroxyl-N-phenylbenzamide in n-butanol, *Adiochemistry*, **2011**, 53, 370-374.
- [2]. Sushanta Kumar Sahu, Sujata Mishra, Synergistic extraction and separation studies of Ce(III) from acidic nitrate medium using binary mixture of Cyanex 921 and Cyanex 923 in kerosene, *Separation Science and Technology*, **2016**, 51, 447-456,
- [3]. Beata pospiech, Synergistic solvent extraction of Co (II) and Li (II) from aqueous chloride solutions with mixture of Cyanex 272 and TBP, *Physicochem. probl. miner. Process*, **2016**, 52, 353-364.
- [4]. Mangesh H. Chhatre, V.M. Shinde, Liquid-liquid extraction of Cerium (II) salicylate with tris (2-ethylhexyl) phosphate and tributylphosphineoxide, *Solvent Extraction and Ion Exchange*, **2000**, 18, 41-54.
- [5]. Y. G. Wang, L. G. Wang, D. Q. Li, Synergistic Extraction of Zinc(II) with Mixtures of CA-100 and Cyanex 272, *Separation Science and Technology*, **2003**, 38, 2291-2306.
- [6]. C. F. Baes Jr., H. T. Baker, The Extraction of Iron(III) from Acid Perchlorate Solution by Di-(2-ethylhexyl) Phosphoric acid in n-Octane, *Journal of Physical Chemistry*, **1960**, 64, 89-94.
- [7]. Okatan Ahmet, Eyupoglu Volkan, Kumbasar Recep Ali, Turgut Halil Ibrahim, Synergistic Extraction and Separation of Co(II)/Ni(II) by Solvent Extraction Technique Using TIOA/TOPO as Carriers. *International Conference on Advances in Natural and Applied Sciences*, Proc. AIP Conf., **2016**, 1726, 020111-1-020111-4.
- [8]. J. P. Mckaveney, H. Freiser, Solvent extraction of chromium with acetyl acetone, *Analytical Chemistry*, **1958**, 30, 1965-1968.
- [9]. B. Debabrata, C.Parimal, L. Ray, Continuous removal of chromium from tannery waste water using activated sludge process, *Indian J. Chemical Technology*, **2011**, 19, 32-36.



- [10]. Maher jabari, Fathiaqra, Safashahin and Awni khatib, Monitoring chromium content in tannery wastewater, *The journal of the argentine chemical society*, **2009**, 97, 77-87.
- [11]. S. Kartal, S. Tokalloglu, and b. Ozkan, Speciation of Cr (III)/ Cr (VI) in tannery waste waters by using ion-exchange resins, *Bulletin of the korean chemical society*, **2006**, 27, 694-698.
- [12]. S. F. Lesley sounderraj , Nancy Lesley, P. Senthil kumarint, Studies on the effect of tannery effluent and chromium accumulation in common crop tilapia mossambica, *International journal of pharmaceutical & biological archives*, **2012**, 3, 978-985.
- [13]. A. Rajendran, C. Mansiya, Extraction of chromium from tannery effluents using waste egg shell material as an adsorbent, *British journal of environment & climate change*, **2011**, 1, 44-52.
- [14]. Shajahansiraj, Md. Monarul Islam, Prokashchandra das, Shah Md. Masum, Ismet arajahan, Md. Aminulhasan and **Md. Shajahan**, Removal of chromium from tannery effluent using chitosan-charcoal composite, *Journal of bangladesh chemical society*, **2012**, 25, 53-61.
- [15]. V. Kannan, M. Vijayasanthi, M. Chinnasamy, Bioremediation of chromium in tannery effluent by filamentous cyanobacteria anabaena flos-aquae west, *Int. J. of environmental sciences*, **2012**, 2, 2360-2366.
- [16]. R. Ali Kumbasar, Extraction of chromium (VI) from multicomponent acidic solutions by emulsion liquid membranes using TOPO as extractant, *J. hazard mater*, **2009**, 167, 1141-7.
- [17]. Vijay J. Ghodvinde, S. M. Pitale, S. P. Janwadkar, Prasant P. Lohani, P.K. Rana and D. K. Yadav, New Analytical Technique for Determination of Trace Amount of Fe (III) by Using UV-Visible Spectrophotometric Method with Photometric Reagent. *J. Applicable Chem.*, **2017**, 6, 107-114.