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Studies on the use of CYANEX 272 for Cr(III) / Cr(VI) separation from different aqueous solutions

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Summary : The extraction of Cr(III) and Cr(VI) from aqueous chloride, sulphate and nitrate media by bis(2,4,4-trimethlypentyl) phosphinic acid (CYANEX 272) in kerosene was studied under equilibrium conditions. The effect of pH, shaking time, extractant, anions and metal concentrations were separately investigated. Experimental results indicated that CYANEX 272 is more selective for Cr(III) than Cr(VI) from the investigated aqueous solutions, with relatively higher separation from chloride medium. Stripping of Cr(III) from loaded organic solutions using different stripping agents was also tested. The results are used to assess the conditions for maximum Cr(III)/Cr(VI) separation from the investigated aqueous solutions.

Introduction

Chromium is used in many industries as the production of stainless steel, in tanning process and in plating of metal surface; CrO_3 is a strong oxidizing agent commonly used in the industry of paper , sugar, ….. etc . Cr(VI) is highly toxic and must be removed from wastewater before it is discharged into surface water(1). Cyanex (272) was found to be an effective extractant for the separation and purification of a number of metals (2,3) and organic acids due to its excellent chemical stability, high boiling point and low solubility in water. It is highly selective for the extraction of Cr(III) (3).

The chromium available in the waste spent liquor often creates disposal problems. The versatile technique adopted (4) for removal of the metal from such solutions is based on the reduction of the toxic Cr(VI) ions to Cr(III) by a reducing agent, such as ferrous sulphate or sulphur dioxide, in the pH range 2,5-3. Although in the recent years decontamination of industrial liquid streams from toxic metals by ion exchange (5) proved to be economically competitive, and hence is practised, the application of solvent extraction [6] for removal, recovery of metals from such sources has also been explored. Brooks [7] has studied the removal of several metal ions, including Cr(III), from simulated and industrial metal finising wastewater by solvent extraction. Preliminary studies on the treatment of leather manufacture waste water by solvent extraction have been performed by Wu et al. [8] who reported the removal of 0.5-1.0 g/l Cr(III) by P_2O_4 phosphatic solvent . The use of solvent extraction for the extraction of Cr(III) has been patented [9] with a view to recovering the metal from the sulphate solution. Liquid emulsion membrane have been used [10] to recover chromium from wastewater containing sulphuric acid. Most of the other publications deal with the liquid-liquid extraction of Cr(III) from different aqueous solutions and give the details of extraction kinetics and mechanism, the species extracted and its estimation. Recovery of Cr(VI) from liquid wastes was achieved by electrodialsis [11,12] . Solid phase extraction of Cr(VI)- APDC chelate on the Ambersorb 563 cabonaceous resin was used for the speciation and recovery of chromium in tannery wastewater [13].

Due to the known toxicity of Cr(VI), its separation from Cr(III) in the commonly used aqueous solutions is of major importance for environmental pollution control. In this context the present work aims to understand the chemistry of Cr(III) extraction by the commercial extractant CYANEX 272 bis(2,4,4-trimethylpentyl) phosphinic acid from aqueous solutions and the factors enhancing the separation factor between Cr(III) and Cr(VI) from these solutions.

Experimental

The extractant CYANEX 272 was kindly supplied from Cytec company, Canada. Odourless kerosene was obtained from Misr Petroleum company, Egypt. Chromium chloride, potassium dichromate and sodium nitrate are analytical grade reagents (AR) supplied by Merck. Ammonium chloride, and ammonium sulphate were obtained from Prolabo.

Colorimetric determination of the yellow chromate CrO_4^{2-} was carried out at pH >9.5, whereby Cr(III) was oxidized to Cr(VI) in an alkaline medium . The spectra of Cr(III) and Cr(VI) show maximum absorption peak at 374 nm using the chromate method[(14)]. The molar absorpitivity **ε** was found to be $0.38x10^4$ for Cr^{III} and $0.52x10^4$ for Cr^{vf}

Procedure

In this work, the extraction behavior was investigated by solvent extraction technique using CYANEX 272 bis- (2,4,4-trimethylpenty) phosphinic acid in kerosene at 25 ±1^{o}C. These experiments were carried out by equilibrating equal volumes of 2% CYANEX 272 in kerosene and aqueous solution which contains 100Mg/ml of the metal ion under consideration in stoppered glass bottles using a thermostated mechanical shaker. After equilibration and phase separation, a suitable volume of the aqueous phase was spectrophotometrically measured. The concentration of the metal in the organic phase was calculated by the difference between its concentration in the aqueous phase before and after extraction. The extraction percent was calculated from the relation :

$$E , \% = C_b – C_a /C_b \text{ x } 100$$

where C_b is the original metal concentration before extraction and C_a its concentration after extraction.

$$D = C_o/C_A$$

where D is the distribution coefficient, C_o the concentration of the organic phase after extraction, C_A the concentration of the aqueous phase after extraction.

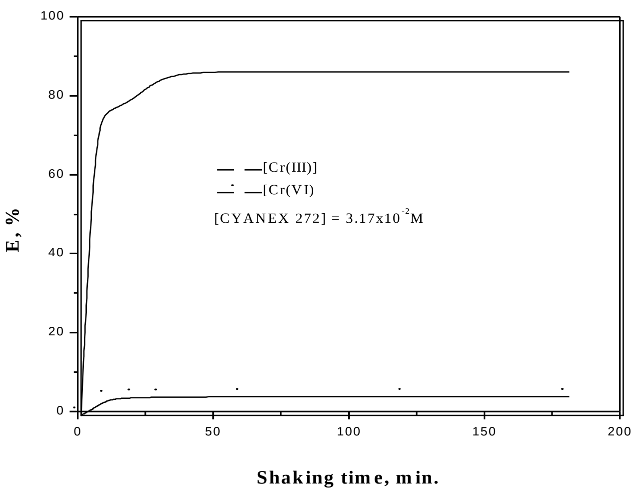
Results and discusions

3.1 Extraction of Chromium (III) and Chromium (VI)

Different parameters affecting the extraction of Cr(III) and Cr(VI) were investigated. These include the effect of pH, shaking time, CYANEX 272 concentration, Cr(III), Cr(VI) concentration, loading capacity of the extractant, the effect of different anions such as sulphate, nitrate and chloride. Stripping investigations on the recovery of Cr(III) from the loaded organic phase were also carried out.

3. 1. 1 Effect of shaking time

The effect of shaking time on the extraction of Cr(III), Cr(VI) from aqueous solution of pH 5 using 2% (3.17×10^{-2} M) CYANEX 272 in kerosene was investigated in the range 5-180 min. The relations between the shaking time and the extraction percentage of Cr(III) and Cr(VI) which are illustrated in Fig.(1) indicate an increase in the extraction of Cr(III) with shaking time and equilibrium was reached after 30 min while for Cr(VI) extraction was very low and slightly increased with time.



(Fig.(1) : Effect of shaking time on the extraction of 100 ppm Cr(III) and Cr(VI) from aqueous solution

3.1.2 Effect of pH

The effect of pH on the extraction of Cr(III) or Cr(VI) using 3.17×10^{-2} M CYANEX 272 in kerosene was studied in the range 1-10. It was observed that for Cr(III) no extraction was detected till pH 3, then the extraction

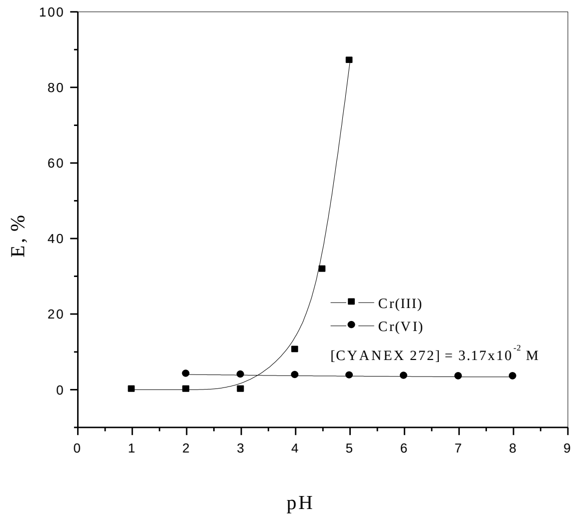


Fig. (2) : Effect of pH on the extraction of 100 ppm of Cr(III) and Cr(VI) from aqueous solution

increased effectively from pH^4 to 5 while at higher pH values hydrolysis of Cr(III) occurred. For Cr(VI) extraction was quite low and the results showed a slight decrease in the extraction with the increase in pH.

3.1.3 Effect of CYANEX 272 concentration

The influence of CYANEX 272 concentration on the extraction of Cr(III) or Cr(VI) from aqueous solution of pH 5 in the range of 0.25-5% (0.004-0.079 M) is illustrated in Fig. (3). It's clear that Cr(III) extraction increases with the concentration of CYANEX 272 and complete extraction is obtained with 5% extractant concentration while in the investigated range, Cr(VI) extraction was too low and slightly increased with extractant concentration.

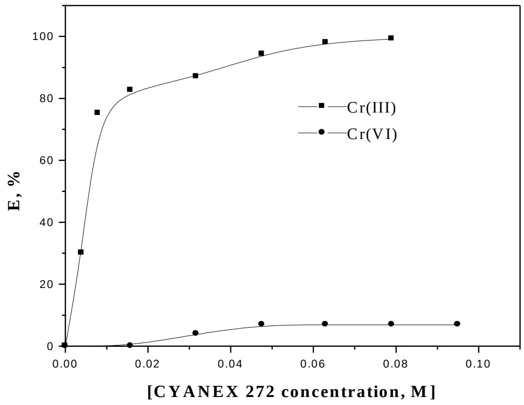


Fig.(3) : Effect of CYANEX 272 concentration on the extraction of Cr(III) and Cr(VI) from aqueous medium

3.1.4 Effect of Cr(III) & Cr(VI) concentration

The effect of initial Cr(III) and Cr(VI) concentration on the extraction of Cr(III) and Cr(VI) using 3.17×10^{-2} M CYANEX 272 in kerosene was studied over the range 100-1500 Mg/ml from an aqueous solution of pH 5. The results obtained and represented in Fig. (4) indicate that the extraction percent of

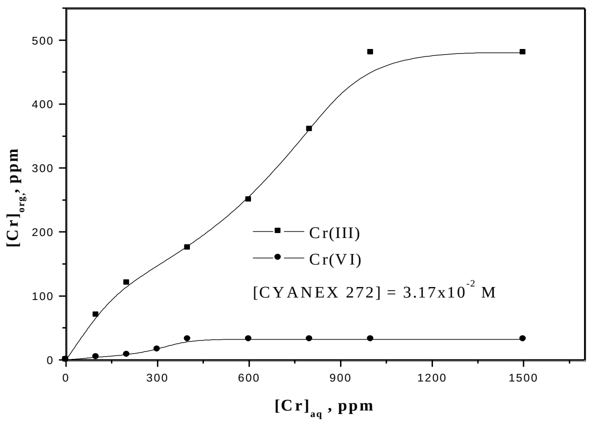


Fig. (4) : Effect of Cr(III) and Cr(VI) concentration on their extraction from aqueous solution

Cr(III) increases with the increase of initial Cr(III) concentration within the range 100-1000 Mg/ml then remains constant with further increase in its concentration.

The effect of anions concentration

The effect of anions concentration on the extraction of 100 Mg/ml Cr(III) or Cr(VI) in the range 0.1-2 M using 3.17×10^{-2} M CYANEX 272 in kerosene was investigated. The results show a slight increase in the extraction of Cr(III) in presence of NO_3^-, a negligible effect of Cl^- and a drastic decrease in presence of SO_4^{2-} ions, Fig. 5. On the other hand, the extraction of Cr(VI) was found to decrease in the presence of nitrate and chloride ions till nearly no extraction was observed at 2M concentration;. in the presence of sulphate ions a slight increase in the extraction was observed, Fig. 6.

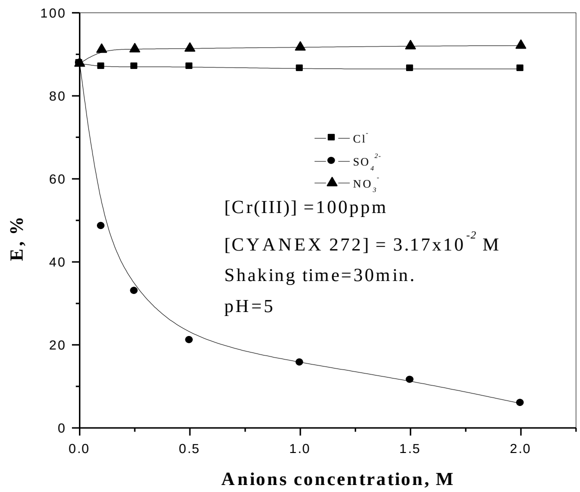


Fig. (5) : Effect of anions concentration on the extraction of Cr(III) by CYANEX 272 in kerosene

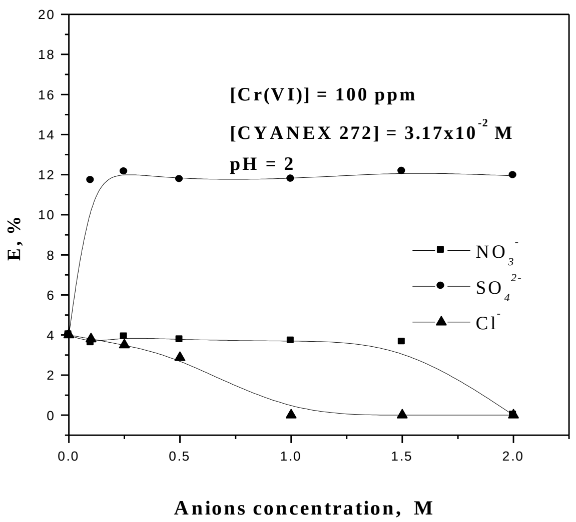


Fig. (6) : Effect of anion concentration on the extraction of Cr(VI) by CYANEX 272 in kerosene

3. 2 Separation of Cr(III) from Cr(VI)

The separation between Cr(III) and Cr(VI) is expressed by the separation factor (S) which is evaluated from their distribution ratios $D_{Cr(III)}$ and $D_{Cr(VI)}$ and represented by S = $D_{Cr(III)/}$ $D_{Cr(VI)}$. The value of S was found to increase by increasing the nitrate and chloride concentrations, and decrease by increasing the sulphate concentration which indicate the increase in the selectivity of the investigated system by increasing the nitrate and chloride concentrations. Table1. represents the effect of anions concentration on the distribution ratio of Cr(III) with respect to Cr(VI) from aqueous nitrate, sulphate and chloride media. The tabulated data show that in nitrate and chloride media $S_{Cr(III) / Cr(VI)}$ reached its maximum values at 2 M nitrate and 1 M chloride concentration. Maximum separation can be achieved after 5 minutes shaking.

Table 1. Effect of anions concentration on the separation factor $S_{Cr(III)/Cr(VI)}$ from aqueous nitrate, sulphate and chloride media.*

Concentration	**$S_{Cr(III)/Cr(VI)}$**		
	NO_3^-	**SO_4^{2-}**	**Cl^-**
0.1 M	21.9	4.2	27.6
0.25 M	22.5	2.7	26.1
0.5 M	23.5	1.8	31.8
1M	23.4	1.3	84
1.5 M	23.8	0.9	84
2 M	1315	0.5	84

*Shaking time 30min
CYANEX 272 = (3.17 x 10^{-2} M)
pH=5
Cr(III) or Cr(VI) = 100 Mg/ml

Extraction equilibrium

Based on the above results and assuming that at higher pH values, Cr^{3+} exists as a mixture of hydrolysed forms $Cr(OH)_j$, where j = 1, 2, or 3 over the pH range 2.5-5.5 [15], taking into consideration that CYANEX 272 is mainly found as a dimer in aliphatic diluents [2]. The extraction of Cr(III) by CYANEX 272 in kerosene could be represented by the equilibrium :

$$Cr(OH)^{2+} + 1.5\overline{(HA)_2} = \overline{CrA_3} + H_2O + 2H^+$$

and

$$K_{ex} = \frac{D\,[H^+]^2}{\overline{[(HA)_2]}^{1.5}}$$

Where $\overline{(HA)}_2$ denotes CYANEX 272, D is the distribution ratio of chromium(III) species and K_{ex} represents the extraction constant. Different values of the extraction constant evaluated at different CYANEX 272 and hydrogen ion concentrations, indicate that the average value of K_{ex} is $(1.66 \pm 0.36)\times10^{-7}$.

Loading capacity

The loading capacity of CYANEX 272 in kerosene was studied by repeating the extraction step for the same organic phase with fresh aqueous solutions at fixed aqueous : organic ratio of 1 : 1. In this concern, 1000 Mg/ml Cr(III) in aqueous solution of pH=5 was shaken with equal volume of $3.17x10^{-2}$ M CYANEX 272-kerosene solution. The two phases were separated, Cr(III) concentration was determined, and the same organic phase was used again for the extraction with fresh Cr(III) solution, Fig(7). The maximum concentration of Cr(III) in the organic phase was found to be 810 ppm and reached after three extraction stages. In this case, the maximum loading is (0.49 M) Cr(III) per mole extractant

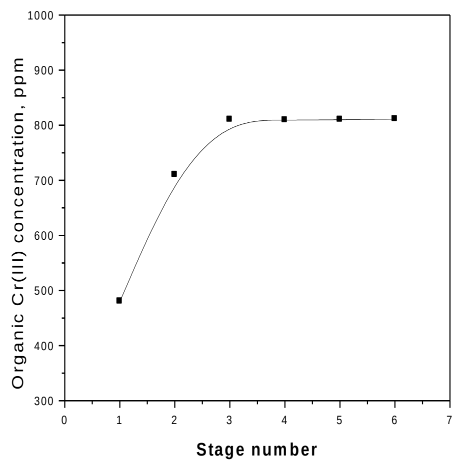


Fig. (7): Effect of number of stages on the extracton of Cr(III))
by $3.17x10^{-2}$ M CYANEX 272 in kerosene from aqueous)
solution of pH 5

3.3 Stripping of Cr(III) from loaded organic phase

The results of the effect of pH on the extraction indicated that Cr(III) could be stripped at pH values < 1. In this case, different concentrations of H_2SO_4, HNO_3 and HCl from (1-9) M were contacted with equal volumes of the organic phase after extraction of 1000ppm Cr(III) by 2%(0.063)M CYANEX 272. Preliminary experiments showed that 30 min were enough to reach maximum stripping. The results obtained (Table 2) show a gradual increase in the stripping percent with the increase of the strip acid concentration reaching 80% with 6M H_2SO_4.

Table (2) : The effect of strip concentration on the stripping percent of 810 ppm Cr(III) from the loaded organic phase.

Concentration , M	H_2SO_4	HCl	HNO_3
	Stripping %		
1	16	13	9
3	34	29	25
6	80	76	61

3.4 Effect of interfering ions

In tanning bath waste solution, in addition to Cr(III) there are traces of Fe(III) , Al(III) and high concentration of chloride ion [16]. Where at pH 5 aluminum is precipitated as AlO(OH) [17] and iron is precipitated as red brown hydrous oxide; the hydrolysis of iron is more complicated giving hydroxyl species as well as $FeCl_4^-$ [15] . This indicates that the effect of these interfering ions could be neglected when carrying out the extraction of Cr (III) from solutions of pH =5 which was found to be optimum for this extraction process.

CONCLUSIONS

- The extraction of Cr(III) from nitrate, sulphate and chloride media by CYANEX 272 is pH dependent and maximum extraction is obtained at pH 5, with negligible extraction of Cr(VI) in the pH range 2-8.
- The selective separation of Cr(III) from Cr(VI) by CYANEX 272 reaches its maximum values at 2M nitrate and 1M chloride concentration.
- The loaded capacity of 0.063M CYANEX272 in kerosene for Cr(III) is 0.81g/l at phase ratio org. : aq. = 1 :1 after three stages.

-Stripping of Cr(III) from loaded organic phase is quantitative using 6M H_2SO_4.

-The recovered Cr(III) from the strip liquor is highly pure (99%) and could be used for industrial purpose .

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