Recycling of rayon industry effluent for the recovery and separation of Zn/Ca using Thiophosphinic extractant

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Abstract:

In textile industries, waste effluent containing zinc is generated during the manufacture of rayon yarn from the wood pulp or cotton linters. Due to the strict environmental regulations and the presence of toxic metallic and other constituents, the discharge of industrial effluents in the sewage or disposal of solid sludge as landfill is restricted. Before recycling of zinc as zinc sulphate solution to the spinning-bath of the rayon manufacturing plant the zinc sulphate solution must be free from calcium, which is deleterious to the process as gypsum precipitates with the increase in concentration and forms scale in the bath. In the present work an attempt has been made to develop a process following solvent extraction technique using thiophosphinic extractants, Cyanex 272 and 302 modified with isodecanol and diluted in kerosene to recover zinc from rayon effluent. Various process parameters viz. extraction of zinc from different concentration of solution, distribution ratio, selective extraction, O/A ratio on extraction and stripping from the loaded organic, complex formation in the organic phase etc. have been studied to see the feasibility of the process. The extractant Cyanex 302 has been found selective for the recovery of 99.99% of zinc from the effluent above equilibrium pH 3.4 maintaining the O/A ratio of 1/30 leaving all the calcium in the raffinate. It selectively extracted zinc in the form of complex $[R_2Zn.3RH]_{org}$ and retained all the calcium in the aqueous raffinate. The zinc from the loaded Cyanex 302 can be stripped with 10% sulphuric acid at even O/A ratio of 10 without affecting the stripping efficiency. The stripped solution thus obtained could be recycled in the spinning bath of the rayon plant. The raffinate obtained after the recovery of zinc could be disposed safely without affecting environment.

Keywords: Zinc recovery, Rayon effluent, solvent extraction, Cyanex 272 / 302

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1. INTRODUCTION

In textile industries, waste effluent containing zinc is generated from the spinning bath during the manufacture of rayon yarn from the wood pulp or cotton linters.[1] Due to the strict environmental regulations and the presence of toxic metallic and other constituents, the discharge of industrial effluents in the sewage or disposal of solid sludge as landfill is restricted. In view of waste recycling and conserve the natural resources the extraction of zinc from this waste is necessary.

Solvent extraction process is more effective for the separation and recovery of metals from the complex and low metallic containing solutions. Attempts have been made for the solvent extraction of zinc from sulphate solutions using alkyl carboxylic, phosphoric and phosphonic acids extractant. [2-4, 5-8] The extraction takes place as cationic liquid ion exchange mechanism. Di-(2ethylhexyl) phosphoric acid (D2EHPA) has been extensively studied for extraction and separation of transition metals. The extraction of metal is pH dependent and their separation could be achieved by precise control of the pH of solution.[9] It has also been used for extraction of zinc from the effluent of rayon plant[10] and leach liquor of zinc plant residue.[11] It forms ZnR_2 complex in the organic phase.[12] The studies were also made for zinc extraction using phosphonic acid based extractants viz. bis(2,4,4-trimethylpentyl) phosphinic acid [Cyanex 272], bis(2,4,4-trimethylpentyl) dithiophosphinic acid [Cyanex301] and bis(2,4,4-trimethylpentyl) monothiophosphinic acid [Cyanex302][5-7, 13] and behaviour of the Cyanex 302 was compared with D2EHPA and Cyanex 272. The order of extraction was found to be Cyanex 302 >= D2EHPA > Cyanex 272.[13] The formation of species R_2Zn and $Zn(R_2H)_2.(RH)_2$ with Cyanex 302.[7, 13] and $Zn(R_2H)_2$ and $ZnR_2.3RH$ in Cyanex 272 [7] have been reported. The extractant, Cyanex 302 has also been studied for zinc extraction from the solution containing calcium.[14-15] The loaded zinc was stripped from organic phase with sulphuric acid. But there is no detail information regarding the recovery of zinc from the rayon waste effluent has been found.

In the present paper solvent extraction studies have been made for the recovery of zinc from the effluent of rayon plant containing low metallic value. The solution contains calcium as major impurity, which is required to be removed before recycling in the spinning bath of rayon industry because it will precipitate as gypsum and forms scale in the bath with the increase in concentration. Various process parameters viz. extraction of zinc from different concentration of solution, pH of the solution, distribution ratio, selective extraction, O/A ratio on extraction and stripping from loaded organic, complex formation in the organic phase etc have been studied using Cyanex 302 and Cyanex 272. Based on the studies a process is developed to recycle zinc and could be simulated for the operation in continuous mode.

2. EXPERIMENTAL SECTION

2.1 Materials: The waste effluents supplied by M/s Baroda Rayon Co., Gujrat, India was used for the extraction and separation of zinc from the impurities particularly calcium. The effluent (pH=6.23) contains 0.085 g/L Zn and 0.025 g/L Ca. Initially the synthetic solution containing the metals in the required proportion was prepared from their respective sulphate salts. Aqueous solutions were made using distilled water. The chemical reagents such as sulphuric acid, sodium hydroxide etc used for the experiment were of laboratory reagent (L.R.) grade. The extractants Cyanex 272 and Cyanex 302 were supplied by Cyanamid Canada, Inc., and were used without further purification.

The extractants have following structures:

O	S
‖	‖
R_2 P-OH	R_2 P-OH
Cyanex 272	Cyanex 302

Where, R = C_8H_{17}

All other chemicals were reagent grade. The analyses of the samples were carried out by EDTA-Titration using xylenol orange as indicator, Atomic Absorption Spectrophotometer and Inductively Coupled Plasma Spectrophotometer.

2.2 Procedure. Solvent extraction experiments were carried out in a mangnetically stirred conical flask at room temperature. The organic and aqueous phases were mixed and then separated in a separating funnel. The effect of various process parameters viz. time, organic : aqueous ratio, pH were studied during the extraction and separation of Zn-Ca. The aqueous raffinate was analysed to know metals present. The stripped solution was also analysed to check the material balance.

3. RESULTS AND DISCUSSION

3.1 Separation behavior of Cyanex 272 and 302 towards Zn/Ca

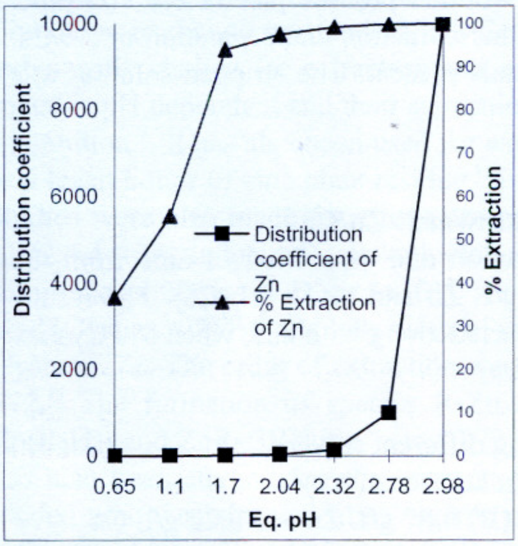
The studies have been carried out for the extraction and separation of zinc from the aqueous feed solution containing calcium (2.13 g/L Zn and 0.118 g/L Ca). The results given in Table-1 indicate that calcium is also extracted along with zinc when 5% Cyanex 272 and 1% isodecanol diluted in kerosene is used.

Table-1 : Extraction and separation of Zn/Ca using different solvent
Organic : 5 % Cyanex and 1% isodecanol in kerosene (v/v)
Aqueous feed: (A) 2.13 g/L Zn and 0.118 g/L Ca (B) 0.87 g/L Zn and 0.22 g/L Ca
Org / Aq.= 1, Mixing time : 5 minutes, Temperature : 25-30°C

S.N.	% Extraction					
	A with Cyanex 272			B with Cyanex 302		
	Eq. pH	Zn	Ca	Eq.pH	Zn	Ca
1.	2.16	17.84	11.86	1.83	45.97	Nil
2.	2.67	56.61	12.45	1.90	53.44	Nil
3.	2.76	60.32	13.29	2.0	65.51	Nil
4.	2.99	69.62	15.22	2.13	77.47	Nil
5.	3.58	93.66	17.50	2.32	80.45	Nil
6.	4.21	99.71	23.72	2.92	96.5	Nil

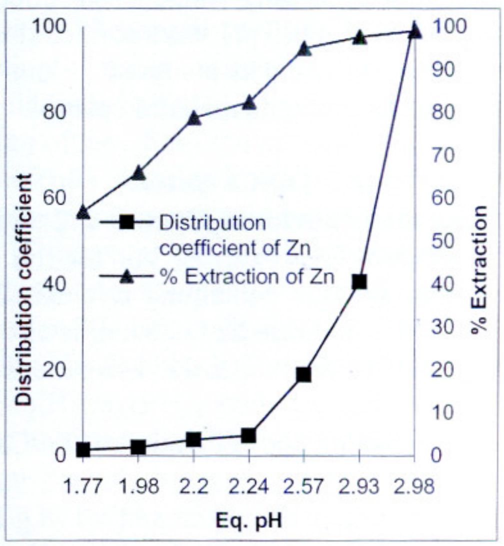
The extraction of calcium has been found to increase from 11.86% to 23.72% with increase in the equilibrium pH of the aqueous solution from 2.16 to 4.21. The calcium extraction has also been reported by Rickelton and Boyle.[6] The extracted calcium in the organic phase is stripped with sulphuric acid. It will precipitate as gypsum when its concentration increases with recycling of the stripping solution in the bath. The studies carried out from the aqueous solution containing 0.87 g/L Zn and 0.22 g/L Ca with 5% Cyanex 302 and 1% isodecanol in kerosene indicated selective extraction of zinc leaving all the calcium in the raffinate. The stripped solution obtained is free from the calcium which could be recycled in the spinning bath of the rayon plant. Thus Cyanex 302 is the selective reagent for the purification of solution containing calcium. The subsequent studies have been carried out with Cyanex 302.

3.2 Extraction of zinc from aqueous solutions. The effect of pH on zinc extraction has been studied using different zinc concentration in the aqueous feed solution at organic to aqueous ratio 1 using 5% Cyanex 302 and 1% isodecanol in kerosene. The results presented in Figure-1 indicate that the extraction of zinc increases from 36.7% to 99.98% with increase in pH of the solution from 0.65 to 2.98 for the solution containing 0.31 g/L Zn. The results also indicate a steep rise in distribution ratio above 2.78 pH and reaches maximum value at 2.98 pH. The studies carried out with 0.46 g/L Zn containing solution at varying pH also show an increase in zinc extraction from 56.86% to 99.03% with rise of pH from 1.77 to 2.98 (Figure-2). The distribution co-efficient of zinc was also found to increase from 4.6 to 102 with increase in pH from 2.24 to 2.98.



[O/A=1, Time=5 minute, Temp. 25 °C]

Figure-1: Extraction of zinc from the aq. Feed containing 0.31 g/L Zn using Cyanex 302.



[O/A=1, Time=5 minute, Temp. 25 °C]

Figure-2 : Extraction of zinc from aqueous solution containing 0.46 g/L Zn using Cyanex 302.

Subsequent studies carried out with 0.87 g/L Zn containing solution indicate the similar trend of increase in metal extraction with increasing pH (Figure-3). On comparing the three solutions for zinc extraction at 2.98 pH, the metal extraction decreases slightly from 100% to 98.25% with increase in metal content from 0.31 to 0.87 g/L Zn in aqueous feed solution. The distribution co-efficient also decreases from 9977 to 56.2 with increase in aqueous feed zinc content. The pH values for 50% extraction for three different solutions was found to increase from 0.96 to 1.86 with increase in the aqueous feed metal content from 0.31 to 0.87 g/L Zn. Thus, higher pH is required for the effective extraction of zinc from the concentrated aqueous feed solution containing zinc.

3.3 Chemistry of zinc extraction. In order to see the complex formation in the organic phase during the extraction of zinc from the low metallic content zinc solution (0.31-0.87 g/L Zn), the monomers and dimers form of extractant have been considered.[16] The zinc exists predominantly as Zn^{2+} and extracted species are in the form of $[R_2Zn.3RH]_{org}$. The distribution ratio (D) can be calculated from the expression given below:

$$Zn^{2+}_{aq} + 2[(RH)_2]_{org} + [R^-]_{org} \leftrightarrow [R_2Zn.3RH]_{org} + H^+_{aq} \quad [1]$$

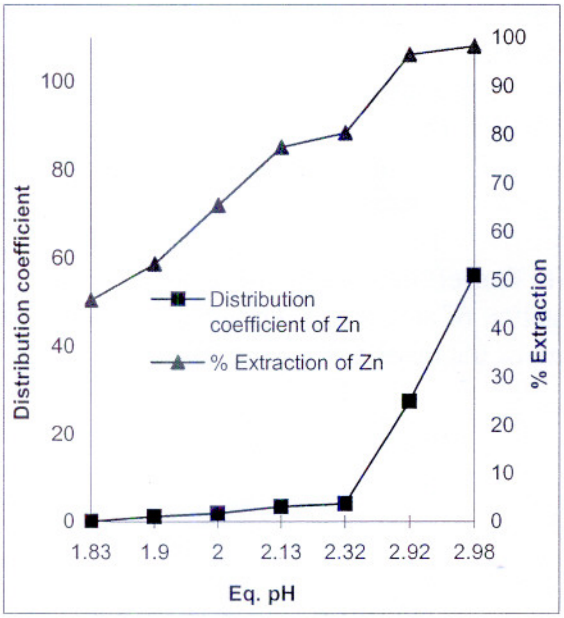
For which equilibrium constant may be written:

$$K = [(R_2Zn.3RH)_{org} (H^+)_{aq}]/[(Zn^{2+})_{aq} \{(RH)_2\}^2_{org} \cdot (R^-)] \quad [2]$$

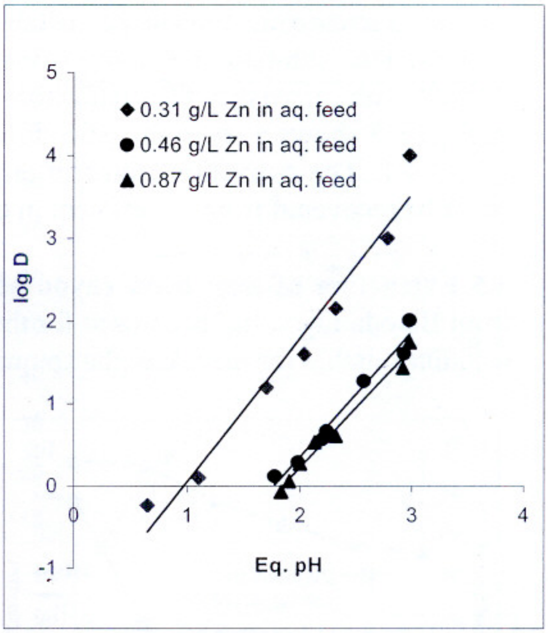
$$K = D [(H^+)_{aq}]/ [\{(RH)_2\}^2_{org} \cdot (R^-)] \quad [3]$$

$$\log K = \log D + \log H^+ - \log [R^-] - 2\log[(RH)_2] \quad [4]$$

$$\log D = \log K + pH + \log [R^-] + 2\log[(RH)_2] \quad [5]$$



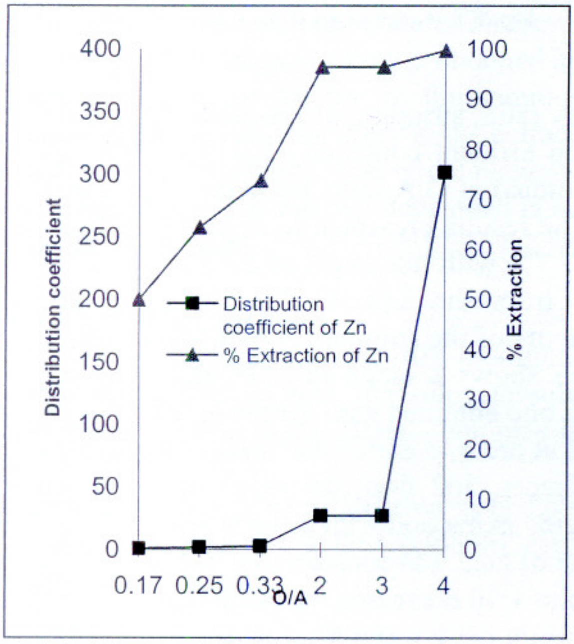
[O/A=1, Time=5 minute, Temp. 25 °C]
Figure-3: Extraction of zinc from the aq. Feed of zinc containing 0.87 g/L Zn using Cyanex 302



[O/A=1, Time=5 minute, Temp. 25 °C]
Figure-4 : log D vs Equilibrium pH for the extraction using 5% Cyanex 302

The plots have been made log D against pH of the solution as presented in Figure-4. The slope analysis of these plots show 0.75, 0.83 and 0.85 for the concentration of solutions 0.31, 0.46 and 0.87 g/L Zn respectively. Thus, it suggests that a complex of the form $[R_2Zn.3RH]_{org}$ is formed in the organic under this condition with Cyanex 302.[16]

3.4 Effect of O/A ratio on zinc extraction. *The organic to aqueous ratio is used for the*



[Aq. Feed= 0.31 g/L ZnTime=5 minute, Temp. 25 °C]
Figure-5: Effect of O/A ratio on the extraction of zinc using 5% Cyanex 302

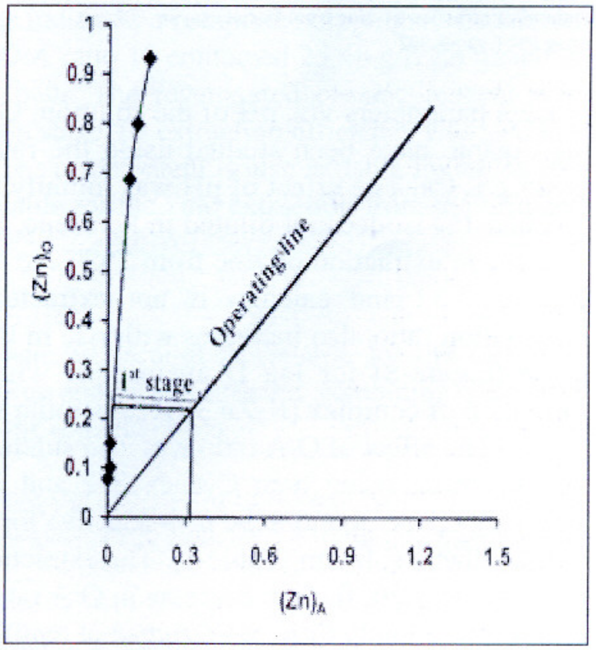
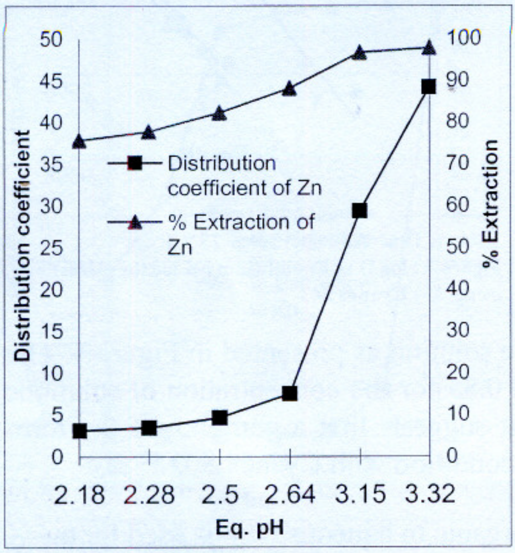


Figure-6 : Extraction isotherm of zinc from effluent using 5% Cyanex 302

from the aqueous solution. The studies have been carried out using 5% Cyanex 302 and

1% isodecanol diluted in kerosene at room temperature. The results presented in Figure-5 indicate increase in percentage metal extraction with increase in O/A ratio from the aqueous feed solution containing 0.31 g/L Zn. The extraction increased from 50.0% to 99.67% with increase in O/A ratio from 1:6 to 4:1. The distribution co-efficient presented in Figure-5 shows a sharp increase from 27.1 to 302 with increase in the O/A ratio from 2:1 to 4:1. The extraction isotherm is plotted in Figure-6, which shows that the metal could be recovered from the effluent in one stage at O/A ratio 1.

3.5 Extraction of zinc from rayon effluent. The effluent of textile industry obtained from Baroda rayon has been used for the extraction of zinc and its enrichment to produce solution suitable for recycle in the spinning bath of the rayon processing. Different



[Aq. Feed=0.085 g/L Zn and 0.025 g/L Ca, Time=5 minute, Temp. 25 °C]

Figure-7: Extraction of zinc from Baroda rayon effluent using 5% Cyanex 302

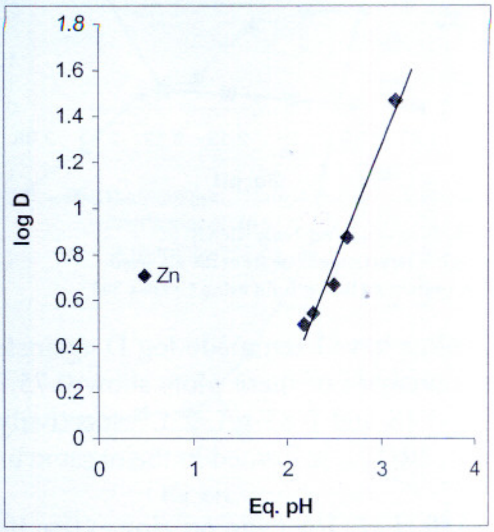
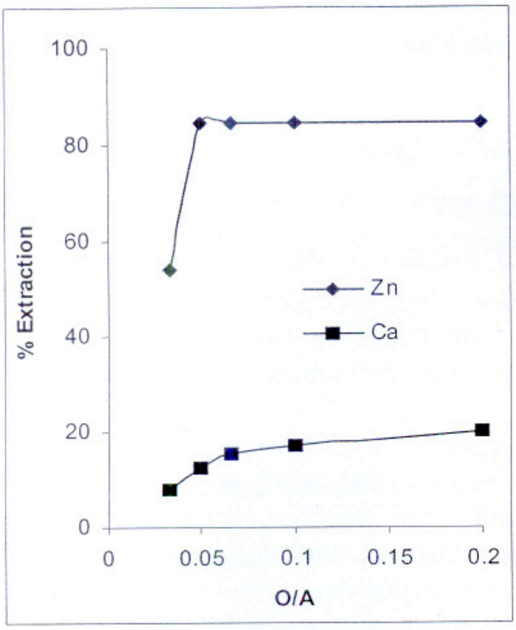


Figure- 8 : Graph of log D Vs. equilibrium pH

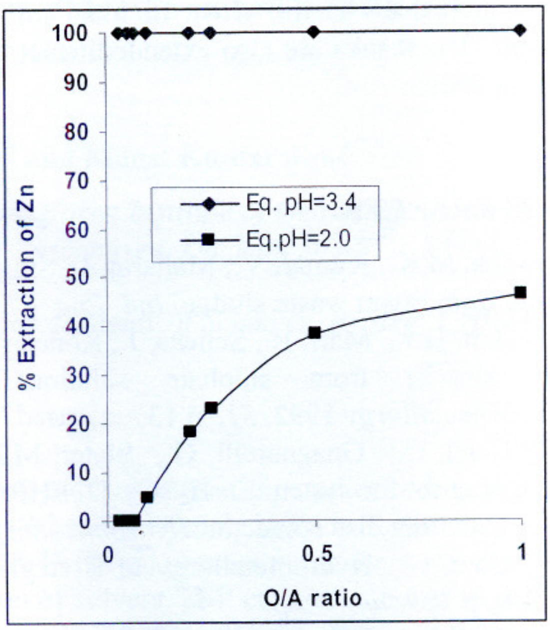
process parameters viz. pH of the solution, O/A ratio, stripping of the loaded zinc from the organic have been studied using the rayon effluent containing 0.085 g/L Zn and 0.025 g/L Ca. The effect of pH was initially studied at O/A ratio 1/3 using 5% Cyanex 302 and 1% isodecanol diluted in kerosene. The results presented in Figure-7 indicate increase in extraction of zinc from 75.7% to 97.7% with rise in pH of the solution from 2.18 to 3.32 and calcium is not extracted from the aqueous feed solution. The distribution ratio also increases with rise in the pH of the solution. A plot has also been made (Figure-8) for log D against pH which shows a slope of 1.08 indicating the formation of complex $[R_2Zn.3RH]_{org}$ similar to one obtained with synthetic solution.

The effect of O/A ratio was also studied in order to enrich the metal content in the organic phase using both Cyanex 272 and Cyanex 302 from the rayon effluent. The Cyanex 272 was found to be non-selective for zinc extraction with effluent similar to one with synthetic solution (Table-1). The extraction of zinc was constant (84.7%) in the O/A range 1:5 to 1:20; further, decrease in O/A ratio to 1:30 decreased the extraction to 53.9% (Figure-9). Initially O/A was studied at equilibrium pH 2 using 5% Cyanex 302 and 1% isodecanol in kerosene. The results presented in Figure-10 indicate increase in zinc extraction from 23.0% to 46.1% with increase in O/A ratio from 0.25 to 1.0. As the low pH 2.0 was not effective for the metal extraction, the extraction studies carried out at higher pH 3.4 showed complete extraction of zinc even at O/A ratio 1/30. On comparing the extraction property of Cyanex 272 with Cyanex 302 of similar strength, Cyanex 272 extracted only 87.7% (Figure-9) of zinc even O/A ratio 1/5. Thus, the Cyanex 302 is more effective reagent for the extraction of zinc from the effluent solution of rayon industry.



[Aq. Feed=0.085 g/L Zn and 0.025 g/L Ca, Time=5 minute, Eq. pH=3.4 Temp. 25 °C]

Figure-7: Extraction of zinc from Baroda rayon effluent using 5% Cyanex 272 at different O/A ratio



[Aq. Feed=0.085 g/L Zn and 0.025 g/L Ca, Time=5 minute, Eq. pH=3.4 Temp. 25 °C]

Figure- 8 : Extraction of zinc from Baroda rayon effluent using 5% Cyanex 302 at different O/A ratio

The stripping studies of the loaded zinc was also carried out after extracting the zinc in 5% Cyanex 302 and 1% isodecanol in kerosene. The zinc content in the organic phase was 2.549 g/L which was stripped with 10% sulphuric acid at different O/A ratio from 1/1 to 10/1 at room temperature. The results indicated a complete stripping of the zinc in one stage.The stripped solution obtained at O/A ratio 10 contained 25.48 g/L Zn which is quite suitable for the use in the spinning bath. The regenerated organic reagent was recycled for the zinc recovery in the extraction stage. Its extraction efficiency was also not affected by repeated recycle of the reagent. The acid content is also suitable for use in the spinning bath. The process developed is suitable for the zinc extraction from the effluent of the rayon plant.

4.0 CONCLUSIONS

The extractant, Cyanex 302 modified with isodecanol is suitable for the selective extraction of zinc from the sulphate solution and rayon effluent containing zinc and calcium. It forms $(R_2Zn.3RH)_{org}$ complex in the organic phase.

Zinc is effectively extracted above pH 3.4 from the effluent at O/A ratio of 1/30 and from the organic phase with 10% sulphuric acid at even O/A ratio of 10 without affecting the stripping efficiency.

The solvent is suitable for the extraction and enrichment of zinc from the rayon effluent. The stripped solution 25.48 g/L zinc could be recycled in the spinning bath of rayon plant.

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