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ScienceDirect
Journal of Hazardous Materials 145 (2007) 221–226
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Processing of rayon waste effluent for the recovery of zinc and separation of calcium using thiophosphinic extractant

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Received 20 July 2006; received in revised form 9 November 2006; accepted 10 November 2006
Available online 16 November 2006

Abstract

Zinc is used in various metallurgical, chemical and textile industries. In textile industries, waste effluent containing zinc is generated during the manufacture of rayon yarn. Due to the strict environmental regulations and the presence of toxic metallic and other constituents, the discharge of effluents in sewage is restricted. In view of above a process has been developed for the recovery of zinc from rayon waste effluent following solvent extraction technique using thiophosphinic extractants Cyanex 272 and 302. Before recycling of zinc sulphate solution in spinning bath, solution must be free from calcium, which is deleterious to the process as gypsum precipitates and forms scale. The extractant Cyanex 302 has been found selective for the recovery of 99.99% of zinc in the form of $[R_2Zn]_{org}$ from the effluent above equilibrium pH 3.4 maintaining the O/A ratio of 1/30 leaving all the calcium in the raffinate. The zinc from the loaded Cyanex 302 can be stripped with 10% sulphuric acid at even O/A ratio of 10. The stripped solution thus obtained could be recycled in the spinning bath of the rayon plant and raffinate could be disposed safely without affecting environment.

Keywords: Zinc recovery; Rayon effluent; Solvent extraction; Cyanex 272/302

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]. The composition of the effluent of the different industries is given in Table 1 which shows that the zinc content in the effluent varies between 30 and 100 mg/L Zn [2]. The quantity of the effluent generated also varies depending on the capacity of the yarn production and processing route followed. These effluents are usually neutralised to precipitate zinc before discharging in the sewage. The sludge thus generated is disposed as waste. The disposal of sludge also causes environmental pollution. Alternatively, the effluent may be treated to recover zinc value following solvent extraction or ion exchange process which is emerging technique in the hydrometallurgical treatment of such effluents containing low metallic value. In the present studies, an attempt has been made to recover zinc from such effluents containing low metallic value using solvent extraction technique.

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 as extractant [3–9]. The extraction takes place as cationic liquid ion exchange mechanism. Di(2-ethylhexyl) 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 [10]. It has also been used for extraction of zinc from the effluent of rayon plant [11] and leach liquor of zinc plant residue [12]. It forms ZnR_2 complex in the organic phase [13]. The studies were also made for zinc extraction using phosphonic acid based extractants,

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doi:10.1016/j.jhazmat.2006.11.015

Table 1
Analysis of zinc in the effluent of different rayon industries of India [2]

Serial number	Rayon industries of India	Average analysis of zinc in effluent (mg/L)	Quantity (m^3/day)	Zinc content (kg/day)
1	M/s Baroda Rayon, Fateh Nagar, Surat	100	960	96
2	M/s National Rayon Corporation, Thane	40	3250	130
3	M/s Indian Rayon Ind. Ltd., Gujrat	40	4500	180
4	M/s SIV Industries Ltd., Coimbatore	30	5000	150

viz. bis(2,4,4-trimethylpentyl) phosphinic acid [Cyanex 272], bis(2,4,4-trimethylpentyl) dithiophosphinic acid [Cyanex 301] and bis(2,4,4-trimethylpentyl) monothiophosphinic acid [Cyanex 302] [6–8,14–17] 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 [14]. The formation of species R_2Zn and $Zn(R_2H)_2{\cdot}(RH)_2$ with Cyanex 302 [8,14] and $Zn(R_2H)_2$ and $ZnR_2{\cdot}3RH$ in Cyanex 272 [8] have been reported. The extractant, Cyanex 302 has also been studied for zinc extraction from the solution containing calcium [15,16]. 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

2.1. Materials

The waste effluent 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:

$$\underset{\text{Cyanex 272}}{R_2\overset{\overset{\displaystyle O}{\|}}{P}\text{-}OH} \qquad \underset{\text{Cyanex 302}}{R_2\overset{\overset{\displaystyle S}{\|}}{P}\text{-}OH}$$

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 magnetically stirred conical flask at room temperature. The organic and aqueous phases were mixed and then separated in a separating funnel. The effects 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 2 indicate that calcium is also extracted along with zinc when 5% Cyanex 272 and 1% isodecanol diluted in kerosene is used. 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 [7]. 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.

Table 2
Extraction and separation of Zn/Ca using different solvent

Serial number	Extraction (%)					
	(A) with Cyanex 272			(B) with Cyanex 302		
	Equilibrium pH	Zn	Ca	Equilibrium 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

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. Organic/aqueous = 1; mixing time, 5 min; temperature, 25–30 °C.

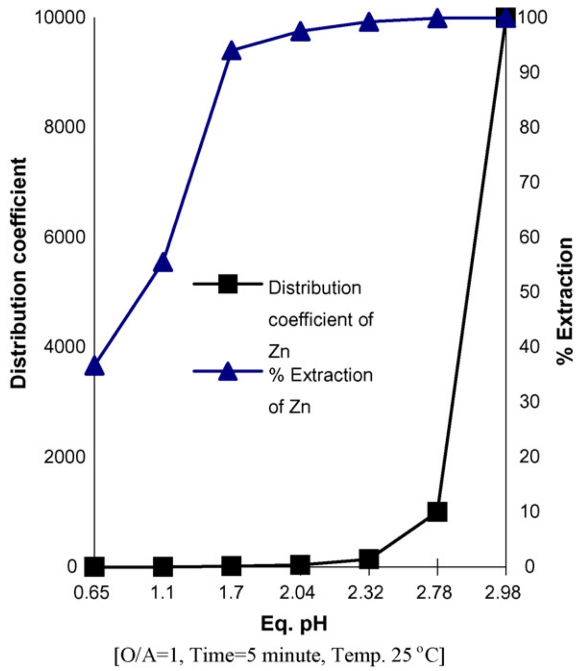


Fig. 1. Extraction of zinc from the aqueous feed containing 0.31 g/L Zn using Cyanex 302 [O/A = 1, time = 5 min, temperature 25 °C].

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 Fig. 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 (Fig. 2). The distribution coefficient of zinc was also found to increase from 4.6 to 102 with increase in pH from 2.24 to 2.98.

Subsequent studies carried out with 0.87 g/L Zn containing solution indicate the similar trend of increase in metal extraction with increasing pH (Fig. 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 coefficient also decreases from 9977 to 56.2 with increase in

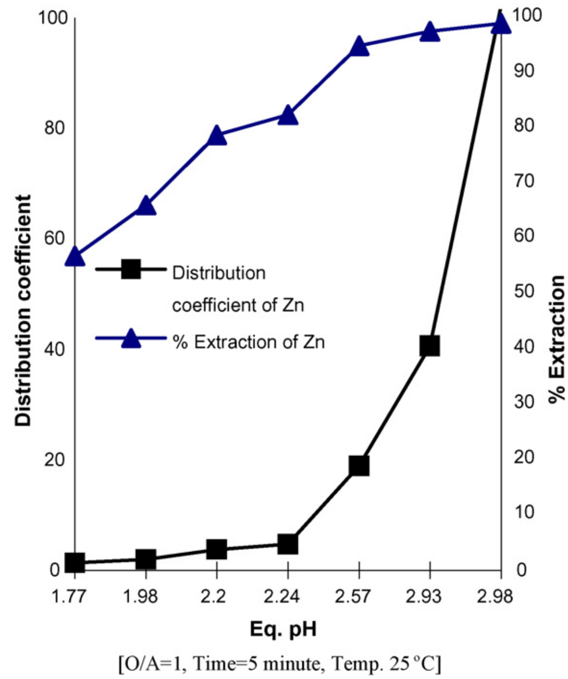


Fig. 2. Extraction of zinc from aqueous solution containing 0.46 g/L Zn using Cyanex 302 [O/A = 1, time = 5 min, temperature 25 °C].

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.

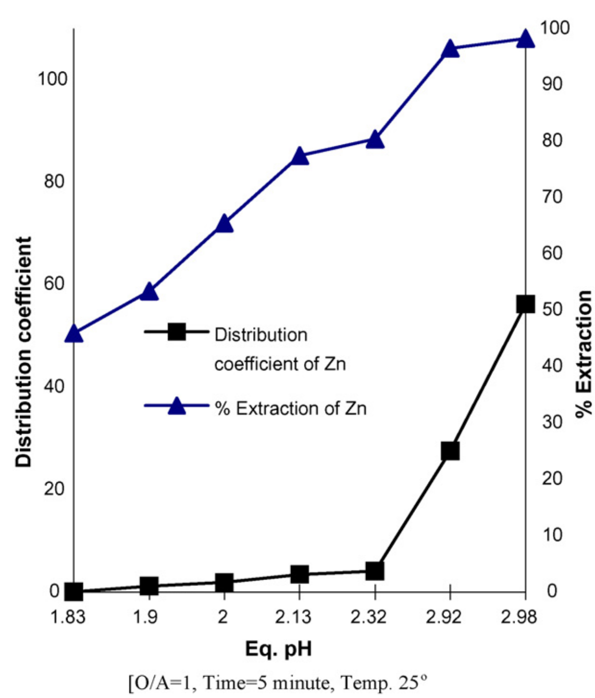


Fig. 3. Extraction of zinc from the aqueous feed containing 0.87 g/L Zn using Cyanex 302 [O/A = 1, time = 5 min, temperature 25 °C].

3.3. Chemistry of zinc extraction

In order to determine the chemistry of the solvent extraction of zinc using Cyanex 302, the studies has been carried out for zinc extraction from low metallic content zinc solution (0.31–0.46 g/L Zn). The zinc exists predominantly as Zn^{2+} and extracted species are in the form of $[R_2Zn]_{org}$. The solvent extracts metal by replacing the hydrogen atoms of the solvent molecules according to the general reaction [16]. The distribution ratio (D) can be calculated from the expression given below:

$$Zn_{aq}{}^{2+} + 2[RH]_{org} \leftrightarrow [R_2Zn]_{org} + 2H_{aq}{}^{+} \quad (1)$$

The equilibrium constant may be written:

$$K = \frac{(R_2Zn)_{org}(H^+)_{aq}{}^2}{(Zn^{2+})_{aq}(RH)_{org}{}^2} \quad (2)$$

$$\left[\frac{R_2Zn}{Zn^{2+}}\right] = K\left[\frac{(RH)^2}{(H^+)^2}\right] \quad (3)$$

Assuming that R_2Zn is the only extracting species in the organic phase and metal ions in the aqueous phase predominantly exist as Zn^{2+}, the distribution ratio [D] is given by the expression

$$D = \frac{(R_2Zn)_{org}}{(Zn^{2+})_{aq}} \quad (4)$$

By taking logarithm of terms in Eq. (3) and rearranging,

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

$$\log[D] = \log K + 2\text{pH} + 2\log[(RH)] \quad (6)$$

Eq. (3) shows that at low acid concentration (H^+) in the aqueous phase, it will result high equilibrium proportion of the zinc in the organic phase (as R_2Zn). A high acid concentration will have the opposite effect, i.e. the stripping of metal takes from the organic phase. The plots have been made $\log D$ against pH of the solution as presented in Fig. 4. Good regression coefficient was obtained. The slope analysis 1.8 and 1.6 is obtained for the zinc solution of concentration 0.31 and 0.46 g/L, respectively. The slope value is near to 2 that mean two molecules of organic required for the extraction of one molecule of zinc. Thus, it suggests that a complex of the form $[R_2Zn]_{org}$ 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 extraction of zinc 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 Fig. 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 coefficient presented in Fig. 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 Fig. 6, which shows that the metal could be recovered from the effluent in one stage at O/A ratio 1.

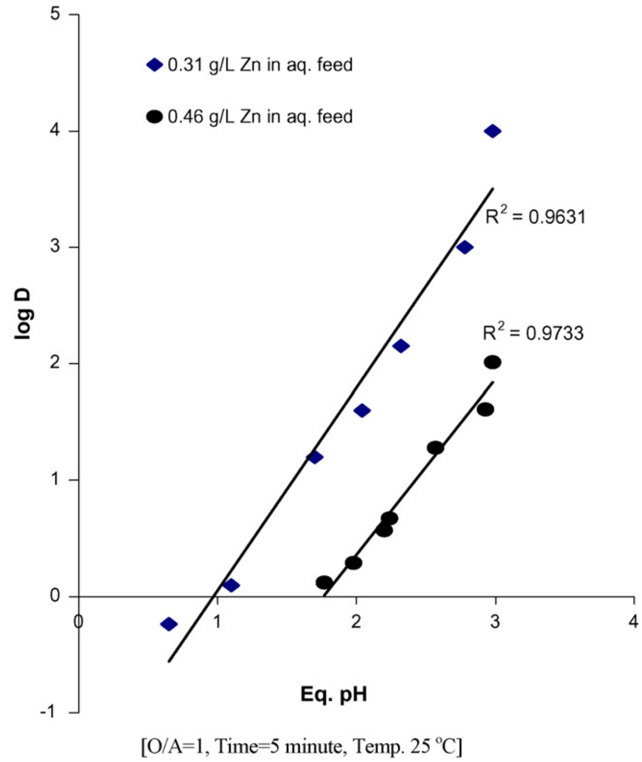


Fig. 4. $\log D$ vs. equilibrium pH for the extraction of zinc using 5% Cyanex 302 [O/A = 1, time = 5 min, temperature 25 °C].

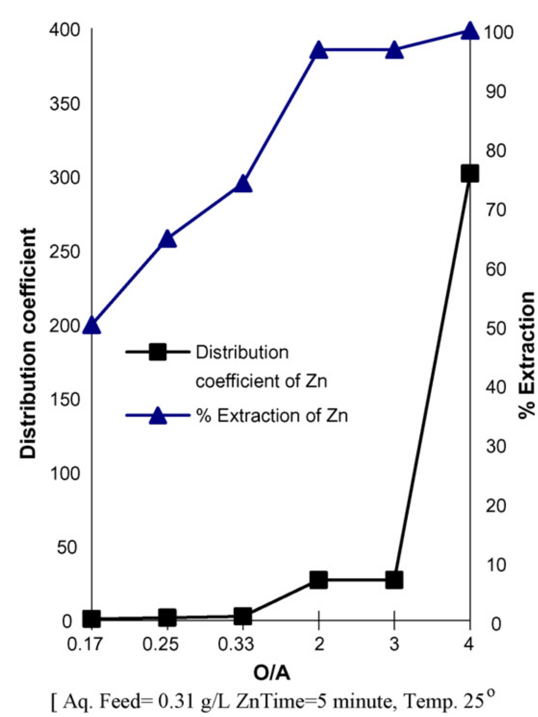


Fig. 5. Effect of O/A ratio on the extraction of zinc using 5% Cyanex 302 [aqueous feed = 0.31 g/L Zn, time = 5 min, temperature 25 °C].

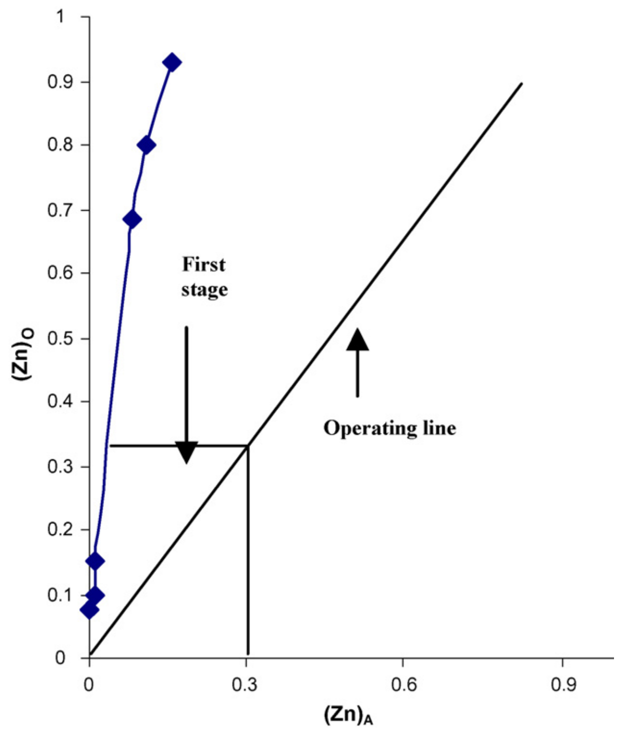
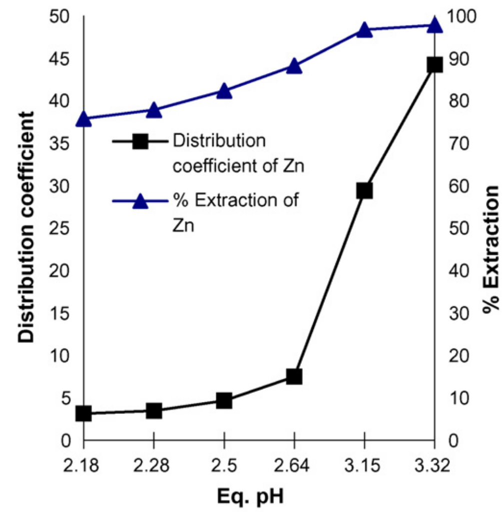


Fig. 6. Extraction isotherm for extraction of zinc with Cyanex 302.



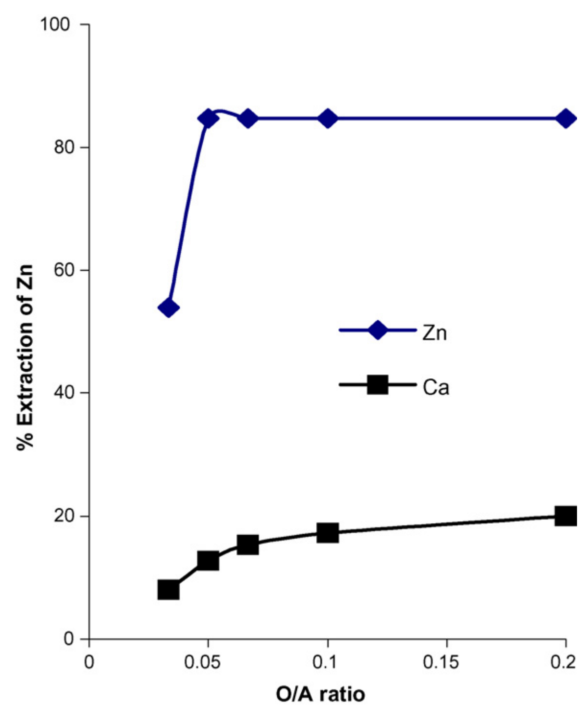
[Aq. Feed=0.085 g/L Zn and 0.025 g/L Ca, Time=5 minute, Temp. 25 °C]

Fig. 7. Extraction of zinc from Baroda rayon effluent using 5% Cyanex 302 [aqueous feed = 0.085 g/L Zn and 0.025 g/L Ca, time = 5 min, temperature 25 °C].

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 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 Fig. 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.

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 2). The extraction of zinc was constant (84.7%) in the O/A range 1:5–1:20; further, decrease in O/A ratio to 1:30 decreased the extraction to 53.9% (Fig. 8). Initially O/A was studied at equilibrium pH 2 using 5% Cyanex 302 and 1% isodecanol in kerosene. The results presented in Fig. 9 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% (Fig. 8) 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. 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



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

Fig. 8. Extraction of zinc from Baroda rayon effluent using 5% Cyanex 272 at different O/A ratio [aqueous feed = 0.085 g/L Zn and 0.025 g/L Ca, time = 5 min, equilibrium pH 3.4, temperature 25 °C].

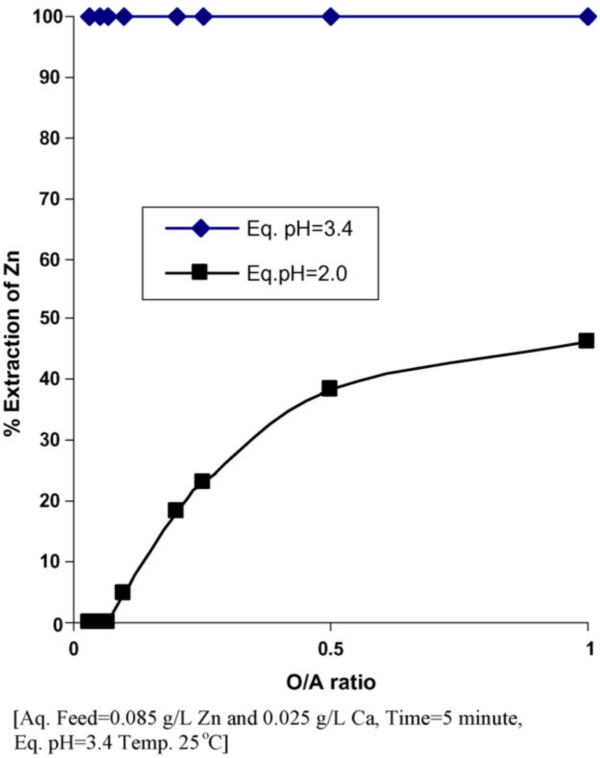


Fig. 9. Extraction of zinc from Baroda rayon effluent using 5% Cyanex 302 at different O/A ratio [aqueous feed = 0.085 g/L Zn and 0.025 g/L Ca, time = 5 min, equilibrium pH 3.4, temperature 25 °C].

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. 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 $[R_2Zn]_{org}$ 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.

Acknowledgements

Authors are very grateful to reviewers and Prof. Merv Fingas, Editor, Journal of Hazardous Materials, for their constructive comments for the improvement of manuscript. One of the authors, M.K. Jha is thankful to Council of Scientific & Industrial Research, New Delhi, Government of India, for financial assistance to carryout this research work. The thanks are also extended to Dr. Jae Min Yoo, Sr. researcher, KIGAM for his cooperation.

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