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Liquid-liquid extraction studies on Zn(II) and Cd(II) using phosphonium ionic liquid (Cyphos IL 104) and recovery of zinc from zinc plating mud

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ABSTRACT

The present study describes partition behavior of Zn(II) and Cd(II) from acidic chloride medium using Cyphos IL 104 [trihexyl(tetradecyl)phosphonium bis 2,4,4-(trimethylpentyl)phosphinate] diluted in toluene. Factors affecting the extraction such as concentration of extractant and H^+, nature of diluent, equilibration time and temperature have been evaluated. Loading and regeneration capacity along with the stability of extractant have also been assessed. The data obtained have been used to determine the stoichiometry of the extracted complex that was found to be 1:2 i.e., two moles of extractant per mole of Zn(II)/Cd(II). Effect of temperature on distribution suggested the process to be exothermic and spontaneous with ΔG° values of -39.63 ± 4.27 kJ/mol and -65.91 ± 0.4 kJ/mol for zinc and cadmium, respectively. The extraction behavior of associated metal ions namely Cu(II), Ni(II), Co(II), Fe(II)/(III) and Mn(II) has been studied and conditions for their separation from zinc and cadmium have been optimized. Based on the extraction data a separation scheme was designed and applied to a synthetic multi element mixture for the recovery of zinc and cadmium. The potential of the extractant for the recovery of zinc from zinc plating mud is assessed.

1. Introduction

With the increasing demand and limited sources of transition metals, recycle of these metals from waste has assumed significance. Heavy transition metals have a broad area of applications and improper disposal of their waste leads to serious environmental problems and health issues. To develop techniques or methods which address these issues has become a challenge. A lot of efforts are being made in this area [1]. Zinc and cadmium are the two transition metals which find applications in metallurgical, chemical, alloy, electroplating, battery and mining industries. Waste containing zinc and cadmium are produced during the manufacturing of products and at the end of their life cycle. Major sources of zinc waste are spent batteries [2,3], plating mud [4], pickling solutions [5,6], zinc ash, zinc dross, flue dusts of electric arc furnace, brass smelting, automobile shredder scrap, electroplating and rayon industry sludge [7,8]. Sources of cadmium waste are discharge from metal refineries, waste batteries, mining, smelting, refining of non ferrous metals, Cd-plated steel scrap and pigments [9,10]. Cadmium has been listed as a carcinogen by International Agency for Research on cancer and by US Environmental Protection Agency (EPA) [11]. Recovery and recycling of these metals is important which will help to fulfill the demand and solve economical and environmental issues. Various methods such as precipitation, coagulation, adsorption, ion exchange, membrane separation and liquid-liquid extraction have been used for the recovery and environmental remediation of various metal ions [12]. Most of these techniques are time consuming, complex and require high cost. Liquid-liquid extraction, on the other hand is a simple, less time consuming technique with low operational cost.

Extraction studies on Zn(II) and Cd(II) from acidic solutions have been reported using organophosphorous [13,15,18], amine [13,18] and ketoximes [14,16,17] extractants. Recently, a new class of extractants called ionic liquids has come on the forefront. These are considered green solvents and have various advantages over traditional organic solvents such as good thermal stability, non-flammability, negligible vapor pressure, tunable viscosity and miscibility with organic solvents [19,20]. Ionic liquids have fruitful applications in various fields such as extraction, chromatography, electroanalytical studies, chemosensing and spectrometry.

In the last two decades many reports have appeared on the use of different ionic liquids for the extraction of various metal ions [21–24]. Lately, separation chemists have focused attention on phosphonium ionic liquids which are marketed by Cytec industries under the trade name of Cyphos IL. Phosphonium ionic liquids

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have gained increasing attention due to their increased hydrophobicity and thermal stability compared to ammonium based analoges. Moreover, the kinetics of salt formation is faster [25].

Among these, Cyphos IL 101 (tetradecyl-(trihexyl) phosphonium chloride) has been extensively investigated for the extraction of various transition metals and rare earths [26–48]. A few studies have also been reported on the use of Cyphos IL 104 (tetradecyl-(trihexyl) phosphonium bis-(2,4,4-trimethylpentyl)-phosphinate) for the extraction and recovery of Pd(II) [42–44,49], Ru(III), Rh (III) [45], Fe(II), Fe(III) and Zn(II) [46,48], Cu(II) [29], Au(III) [50,51], Ni(II), Co(II) [52] and rare earths [53–55]. Literature review reveals that Cyphos IL 104 has not been explored in detail for Zn(II) and Cd(II) except some scanty references. Gallardo et al. [37] reported efficient removal of zinc with Cyphos IL 101 impregnated resin Amberlite XAD-7 at 2.0–4.0 M HCl. They further observed that the performance of impregnated resin remains unchanged up to 5 cycles. Regel-Rosocka [34] reported extraction studies on Zn(II) with Cyphos IL 101 and 109 and found Cyphos IL 101 to be a better extractant than Cyphos IL 109. Regel-Rosocka and coworkers have explored different phosphonium ionic liquids for the extraction of Zn(II) and Fe(III) from aqueous phase [46] and model pickling solution [48]. Quantitative extraction of both the metal ions was achieved with Cyphos IL 101 and 104 whereas less than 10% was achieved with Cyphos IL 109 and 111. Baczynska et al. [28] studied the effect of structure of poly inclusion membranes on the transport of Zn(II) from chloride medium using Cyphos IL 101,104 and 167 and found cellulose triacetate based membrane to be most effective. Same group also examined [47] the transport of Zn(II), Fe(II) and Fe(III) ions from chloride aqueous solutions across polymer inclusion membranes (PIMs) and supported liquid membranes using Cyphos IL 101,104 and 167 and found that Zn(II) and Fe(III) are effectively transported through both PIMs and SLMs.

Beata Pospiech explored both, Cyphos IL 101 [38] and Cyphos IL 104 [56] as ion carrier for polymer inclusion membrane. Cd(II) was separated from Co(II) and Ni(II) using Cyphos IL 101 as ion carrier. With Cyphos IL 104 as ion carrier Cd(II) was separated from Co(II), Ni(II) and Cu(II), achieving highest selectivity coefficients for Co(II) and Cu(II). The data generated for the permeation of Cd(II) has been compared with solvent extraction data in case of Cyphos IL 104. Swain and coworkers [41] investigated Cyphos IL 101 for the extraction of cadmium from sulphate medium and carried out separation of cadmium from nickel and zinc from a ternary mixture.

In the present study, Cyphos IL 104 was investigated for the extraction, separation and recovery of Zn(II) and Cd(II). Extraction of both the metal ions was performed in chloride medium and the influence of various parameters such as shaking time, concentration of H^+, Cl^- and extractant, temperature, nature of acid and diluents on the partition of Zn(II) and Cd(II) has been assessed. Based on the extraction data a probable extraction mechanism has been proposed. Stripping studies were conducted to select suitable stripping agent for the said metal ions. Recycling capacity and loading capacity of Cyphos IL 104 have been evaluated. The extraction behavior of some associated metal ions namely Ni(II), Co(II), Fe(II), Mn(II) and Cu(II) have been studied. Binary separations of Zn(II) and Cd(II) from one another and from associated metal ions were studied. The optimised experimental conditions are extended for the recovery of Zn(II) and Cd(II) from synthetic mixture. In addition, zinc was quantitatively recovered from zinc plating mud.

2. Experimental

2.1. Materials

All the reagents and chemicals used were of analytical grade. Salts of desired metal ions were dissolved in millipore water containing minimum amount of corresponding acid to prepare stock solutions of metal ions which were standardized by using suitable standardization method. Kerosene fraction collected at 160–200 °C was used for diluent effect. Cyphos IL 104 was received from Cytec Inc., Netherlands as a gift sample and used as such without any further purification. Important properties of Cyphos IL 104 are shown in (Table 1). Sample of zinc-plating mud was obtained from Hindustan Zinc Ltd., Udaipur, Rajasthan (India).

2.2. Instruments used

A flask shaker with wrist action (Perfit) was used for equilibrating aqueous and organic phases. Julabo FT-200, Germany shaking water bath with temperature controlled programming (±0.1 °C) was used for temperature effect. Metal concentrations in aqueous phase were determined using Atomic Absorption Spectrometer (AAnalyst 800, Perkin Elmer, Germany). FTIR spectra of neat and loaded organic phases were recorded on a Nicolet 6700 FTIR spectrometer.

2.3. Distribution studies

Equal volumes of aqueous (2.0×10^{-2} g/L of metal ion) and organic phases (2.0×10^{-3} mol/L of Cyphos IL 104 diluted with toluene/unless mentioned otherwise) were equilibrated at room temperature (25 ± 3 °C) for 6 min and allowed to separate. Concentrations of metal ions before and after extraction in aqueous phase were checked by AAS. Concentrations of metal ions in organic phase were calculated by mass balance. All analyses were done in triplicate.

3. Results and discussion

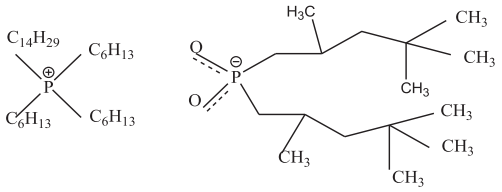
3.1. Partition behavior of Zn(II) and Cd(II) in different acid media

Partition behavior of both the metal ions from three different acid media (HCl, HNO_3, H_2SO_4) was studied using 2.0×10^{-3} mol/L Cyphos IL 104 solution in toluene. Acid molarity was varied from 1.0×10^{-3} to 2.0 mol/L HCl/HNO_3/H_2SO_4. Extraction of Zn(II) and Cd(II) from HNO_3 and H_2SO_4 media in the investigated acid molarity range is insignificant. As illustrated in Fig. 1, there is a significant rise in percentage extraction of both the metal ions with the increase in HCl concentration. Extraction of Cd(II) at 1.0×10^{-3} mol/L HCl is around 22% and increases with increasing acid molarity attaining a quantitative value at 0.1 mol/L HCl. Zn(II) shows negligible extraction up to 0.01 mol/L HCl which increases sharply to around 98% at 1.0 mol/L HCl.

As quantitative extraction of Zn(II) and Cd(II) is achieved only from HCl medium, the effect of various experimental variables on the distribution of Zn(II) and Cd(II) has been investigated in HCl medium. Cyphos IL 104 has a tendency to extract protons from aqueous solution causing increase in pH of the aqueous solution and decrease in the availability of free extractant for metal extraction [29,54]. A plot was drawn between H^+/Zn(II)/Cd(II) concentration in the organic phase after extraction and HCl molarity (Fig. 2) to understand the relation between extraction of HCl and Zn(II)/Cd (II) with Cyphos IL 104 at different HCl molarities The percentage of acid transferred to the organic phase was calculated from acid base titration of the aqueous phase or by difference in initial and equilibrium pH.

In case of Cd(II) the extraction of acid is around 83% at 1.0×10^{-3} mol/L HCl which gradually decreases to around 6% at 1.0×10^{-2} mol/L HCl and is negligible thereafter. On the other hand, extraction of Cd(II) is around 22% at 1.0×10^{-3} mol/L HCl and increases with the increasing HCl molarity attaining a

Table 1
Characteristics of Cyphos IL 104.

CYPHOS IL 104	Properties	
	Physical state (25 °C)	Liquid
	Molar mass (g/moL)	773.27
	Specific gravity (g/cm^3)	0.892
[trihexyl(tetradecyl)phosphonium bis 2,4,4-trimethylpentylphosphinate]	Viscosity (cP at 25 °C)	805.8
Molecular formula: $C_{48}H_{102}O_2P_2$	Solubility	Organic solvents
Abbreviated formula: $[R_3R'P^+A^-]$	Flammability	Nonflammable

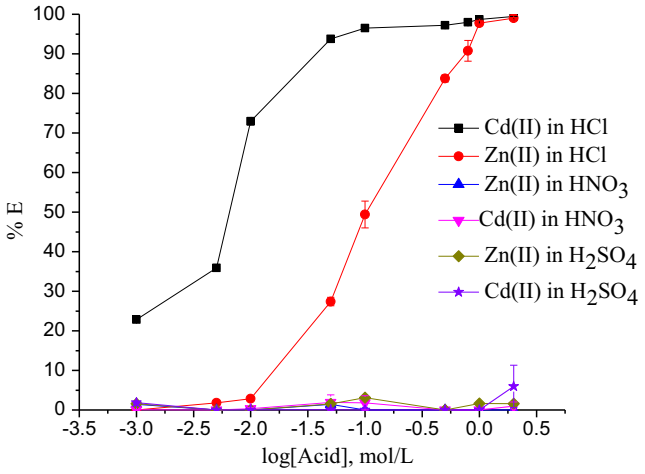


Fig. 1. Effect of concentration of different acids on the partition of Cd(II) and Zn(II) using Cyphos IL 104. Conditions: [Zn(II)/Cd(II)] = 2.0×10^{-2} g/L, [Cyphos IL 104] = 2.0×10^{-3} mol/L.

quantitative value (96%) at 1.0×10^{-2} mol/L HCl. Almost similar trend was observed in case of Zn(II) as shown in Fig. 2(b). Detailed partition studies on Cd(II) have been investigated at 1.0×10^{-2} mol/L HCl where acid and metal are extracted 6% and 83%, respectively. In case of Zn(II), detailed studies were carried out at 0.5 mol/L HCl where extraction of HCl is negligible and that of Zn(II) is 83%.

Previous reports [57] and our preliminary studies have shown that acid is extracted forming a 1:1 complex with the extractant.

3.2. Influence of equilibration time

Shaking time was varied from 30 s to 15 min to study the effect of equilibration time on the extraction of both the metal ions and the results are shown in Fig. 3. Results reveal that kinetics of extraction for both the metal ions with Cyphos IL 104 is very fast and the equilibrium is attained within 5 min. Moreover, longer equilibration time had no adverse effect on partition. Therefore, equilibration time of 6 min was observed for all further studies.

3.3. Influence of different diluents

Hexane, butyl alcohol, kerosene, cyclohexane, benzene, toluene, xylene, and cyclohexanone were used to discern the effect of

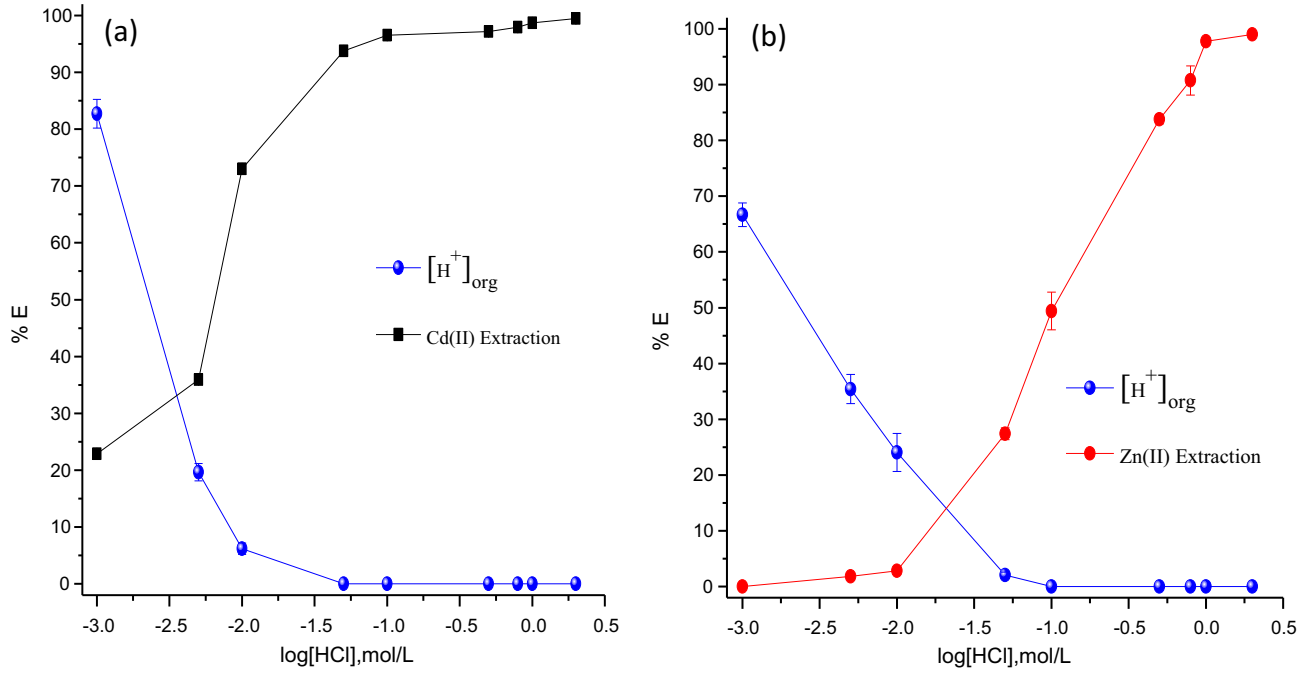


Fig. 2. Effect of HCl molarity on the extraction of H^+, Cd(II) [a] and Zn(II) [b] Conditions: [Zn(II)/Cd(II)] = 2.0×10^{-2} g/L, [Cyphos IL 104] = 2.0×10^{-3} mol/L, [HCl] = 1.0×10^{-3} to 2.0 mol/L.

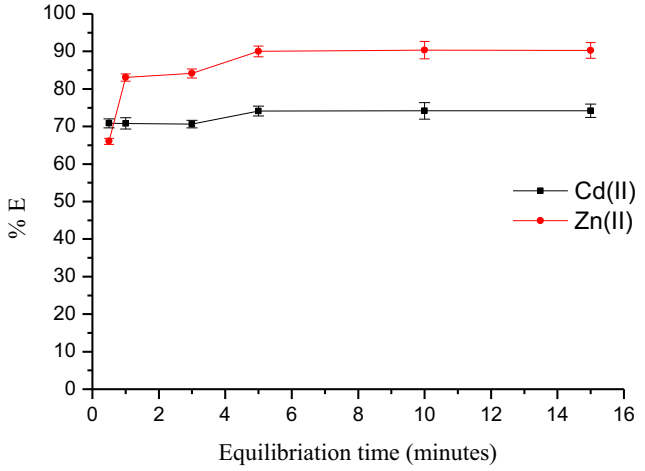


Fig. 3. Effect of equilibration time on Cd(II) and Zn(II) extraction with Cyphos IL 104. Conditions: [Cd(II)] = 2.0×10^{-2} g/L in 0.01 mol/L HCl, [Zn(II)] = 2.0×10^{-2} g/L in 0.5 mol/L HCl, [Cyphos IL 104] = 2.0×10^{-3} mol/L.

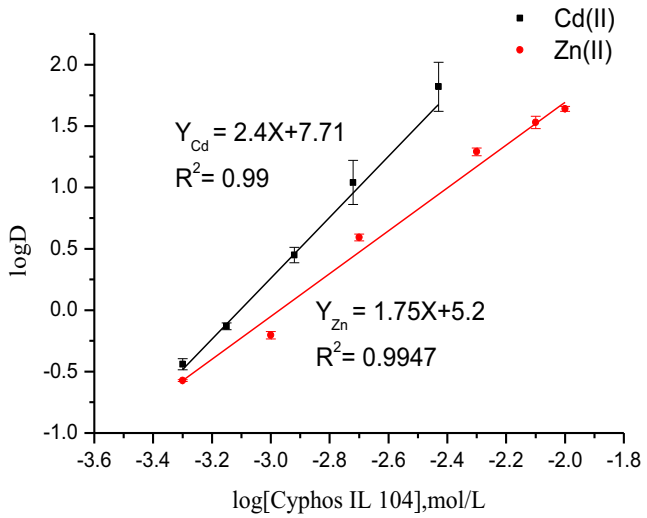


Fig. 4. Effect of Cyphos IL 104 concentration on the distribution of Zn(II) and Cd(II). Conditions: [Zn(II)/Cd(II)] = 2×10^{-2} g/L, [HCl] = 0.5 mol/L (for Zn(II)) and 0.01 mol/L (for Cd(II)).

different diluents on the extraction of Zn(II) and Cd(II). The results (Table 2) indicate that there is no significant correlation between the partition of metal ion and dielectric constant of diluent. However, partition of both the metal ions is very low or negligible with diluents of high dielectric constant. Cyclohexane, benzene and toluene give comparable and high extraction for both the metal ions. Toluene was selected as a diluent for further studies because of better phase separation, low volatility and economic considerations.

3.4. Effect of extractant concentration

Cyphos IL 104 concentration was varied between 5.0×10^{-4} and 1.0×10^{-2} mol/L while keeping the concentration of Zn(II) (2.0×10^{-2} g/L in 0.5 mol/L HCl) and Cd(II) (2.0×10^{-2} g/L in 0.01 mol/L HCl) constant. It was observed that with the increase in extractant concentration percentage extraction of both the metal ions increases. Plots of logD as a function of log[Cyphos IL 104] gave straight line with a slope of around two for both the metal ions (Fig. 4). This confirms the involvement of two molecules of extractant per metal atom in the formation of the extracting species in both the cases.

3.5. Effect of chloride ion concentration

To investigate the effect of chloride ion concentration on the extraction of Zn(II) and Cd(II), Cl^- ion concentration was varied with NaCl solution keeping H^+ concentration constant with H_2SO_4. 2.0×10^{-3} mol/L Cyphos IL 104 solution in toluene was used to extract both the metal ions. In case of Zn(II), chloride ion concentration was varied from 0.1 mol/L to 1.5 mol/L at 0.5 mol/L H^+ concentration and for Cd(II) from 5.0×10^{-3} to 0.1 mol/L at 0.01 mol/L H^+ concentration. The distribution of both the metal ions increases with increase in chloride ion concentration. Plots between logD and log[Cl^-] (Fig. 5) give straight lines having slope of around two suggesting the incorporation of two chloride ions in the formation of extracting species for both Zn(II) and Cd(II).

Table 2
Influence of different diluents on the extraction of Zn(II) and Cd(II).

Diluent	Dielectric constant	% Extraction	
		Cd(II)	Zn(II)
Cyclohexane	2.02	81.6 ± 1.28	80.52 ± 2.62
Kerosene	2.02	44.35 ± 1.12	77.49 ± 3.23
Benzene	2.3	80.18 ± 2.34	82.36 ± 1.46
Toluene	2.44	81.56 ± 2.02	82.59 ± 1.87
Xylene	2.2	77.30 ± 1.08	77.09 ± 1.19
Hexane	1.891	69.57 ± 2.58	84.52 ± 1.93
Butyl alcohol	17.51	3.7 ± 0.09	0.2 ± 0.008
Cyclohexanone	18.3	–	1.32 ± 0.02

3.6. Extraction equilibrium

It is well documented that different species of Cd(II)/Zn(II) exist in aqueous phase at different HCl concentrations. At low HCl molarities cadmium and zinc exist as M^{2+}, MCl^+, MCl_2 [10,58]. Fig. 6 represents contribution of different Zn(II) and Cd(II) species in chloride media at fixed metal and H^+ concentration [59]. At 2×10^{-2} g/L metal ion and 0.5 mol/L chloride ion concentration the predominant species for Zn(II) is Zn^{2+}. In the case of cadmium at 2×10^{-2} g/L metal ion and 0.01 mol/L chloride ion concentra-

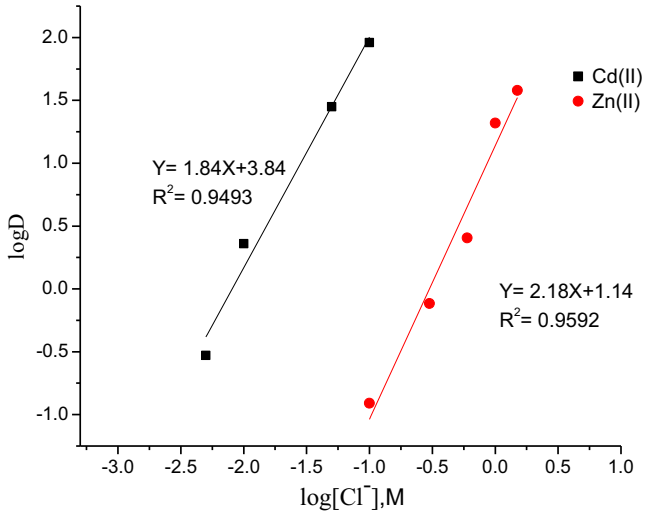


Fig. 5. Effect of chloride ion concentration on the extraction of Zn(II) and Cd(II). Conditions: [Zn(II)/Cd(II)] = 2×10^{-2} g/L, [Cyphos IL 104] = 2.0×10^{-3} mol/L, [H^+] = 0.5 mol/L (for Zn(II)) and 0.01 mol/L(for Cd(II)).

tion, Cd^{2+} is the dominating species. ConsideringZn^{2+} and Cd^{2+} as the dominating species and the slope values obtained from extractant and chloride ion effect, the mechanisms proposed for the extraction of Zn(II) and Cd(II) are as follows-

$$Zn^{2+}_{aq} + 2Cl^{-}_{aq} + 2[R_3R'P^+A^-]_{org} \leftrightarrow [(R_3R'P)_2ZnCl_2A_2]_{org} \quad (1)$$

$$Cd^{2+}_{aq} + 2Cl^{-}_{aq} + 2[R_3R'P^+A^-]_{org} \leftrightarrow [(R_3R'P)_2CdCl_2A_2]_{org} \quad (2)$$

Similar species for Zn(II) and Cd(II) have been proposed by Wassink et al. [60] with Aliquat 336.

The extraction equilibrium constant, K_{ex}, can be derived from Eqs. (1) and (2):

$$K_{ex} = \frac{[(R_3R'P)_2MCl_2A_2]_{Org}}{[M^{2+}]_{aq} \cdot [Cl^-]^2_{aq} \cdot [R_3R'P^+A^-]^2_{Org}} \quad (3)$$

where M = Zn/Cd.

$$K_{ex} = \frac{D}{[Cl^-]^2_{aq} \cdot [R_3R'P^+A^-]^2_{Org}} \quad (4)$$

Log K_{ex} values have been calculated for varying extractant and chloride concentrations using Eq. (4) and the values are given in Table 3. Data clearly indicate that almost constant log K_{ex} values are obtained for the two conditions for each metal ion. This confirms that the proposed extraction mechanism is valid under the investigated partition conditions.

The average log K_{ex} values 6.621 ± 0.243, 6.67 ± 0.269 for Zn(II) and 10.53 ± 0.21, 10.16 ± 0.38 for Cd(II).

FTIR spectroscopic analysis was performed to characterize the extracted species. FTIR spectra of neat and loaded Cyphos IL 104 were recorded and are shown in Fig. 7. In FTIR of neat Cyphos IL 104 peaks at 1465 cm^{-1} and 1384 cm^{-1} are due to P-C stretching and C—H in plane bending, respectively, at 1347 cm^{-1} and 1251 cm^{-1} due to P═O stretching, at 1027 cm^{-1} due to P—O asymmetric stretching and at 729 cm^{-1} and 694 cm^{-1} due to C—H and P—C deformation [61,62]. The FTIR spectra of neat and loaded organic phases are not very different but major change observed is the disappearance of peaks at 1347 cm^{-1} and 1251 cm^{-1}. Disappearance of peaks due to P═O stretching (1347 cm^{-1} and 1251 cm^{-1}) indicates the involvement of P═O in the formation of extracted complex in both the cases.

3.7. Effect of temperature

Variation in the partition behavior of zinc and cadmium with the change in temperature (293–333 K) was studied. Results along with the experimental conditions are shown in Fig. 5. It is observed that with rise in temperature, partition of both the metal ions decreases, indicating the process to be exothermic. Plots of log K_{ex} vs. 1000/T for zinc and cadmium gave straight lines as shown in Fig. 8.

The thermodynamic parameters for Zn(II) and Cd(II) are calculated using Gibb's Helmholtz equation-

$$\log K_{ex} = -\frac{\Delta H^\circ}{2.303\ RT} + \frac{\Delta S^\circ}{2.303\ R} \quad (5)$$

Eq. (5) shows that the slope of each line is equal to (ΔH°/2303R) and intercept is equal to (ΔS°/2.303R). The change in enthalpy (ΔH°) for Zn(II) and Cd(II) is found to be −30.05 ± 0.96 kJ/mol and −48.8 ± 2.68 kJ/mol, respectively. Similarly, the change in entropy (ΔS°) for Zn(II) and Cd(II) is found to be 32.15 ± 2.39 J/K mol and 57.41 ± 7.66 J/K mol, respectively.

The apparent change in Gibb's free energy can be calculated by using Eq. (6)-

$$\Delta G^\circ = \Delta H^\circ - T \cdot \Delta S^\circ \quad (6)$$

At room temperature (25 °C), apparent change in Gibb's free energy for Zn(II) and Cd(II) is −39.63 ± 4.27 kJ/mol, −65.91 ± 0.4 kJ/mol, respectively.

3.8. Loading capacity of Cyphos IL 104

Loading capacity of the extractant was checked by equilibrating equal volumes of organic (2.0×10^{-3} mol/L in toluene) and aqueous phase (2.0×10^{-2} g/L Zn(II)/Cd(II)) for 6 min at room temperature. The two phases were allowed to separate and aqueous phase was checked for remaining metal content. The loaded Cyphos IL 104 was contacted with a fresh aqueous phase several times till it was saturated i.e. till percentage extraction efficiency approaches

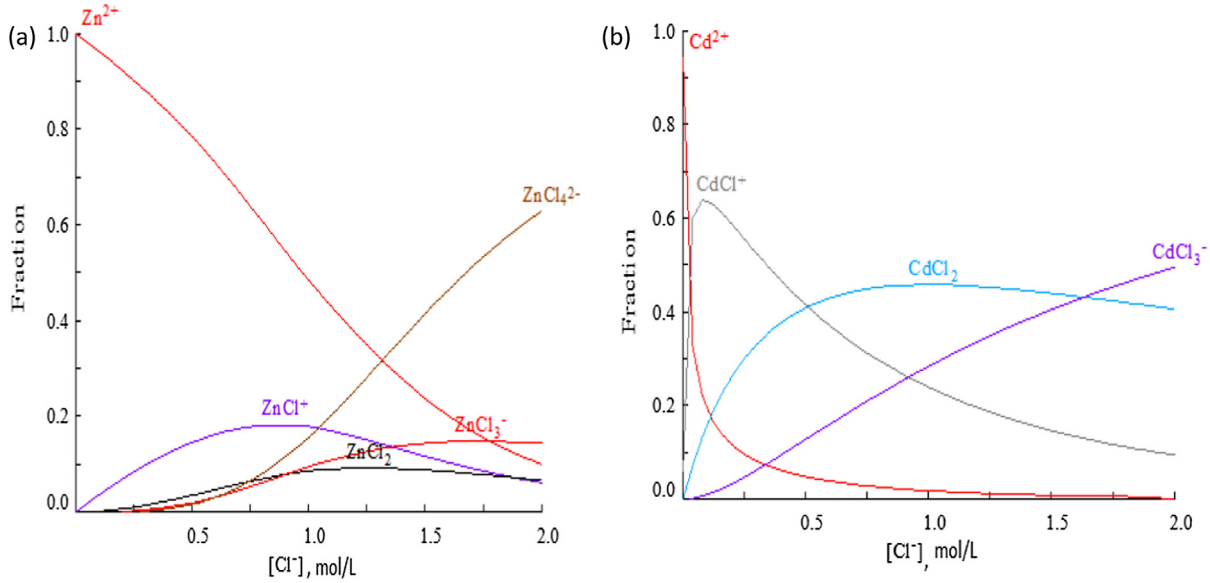


Fig. 6. Speciation diagrams for (a) Zn(II) and (b) Cd(II) species in chloride media. Conditions: [Zn(II)/Cd(II)] = 2×10^{-2} g/L, [H^+] = 0.5 mol/L (for Zn(II)) and 0.01 mol/L (for Cd(II)).

Table 3
The equilibrium constant (log K_{ex}) of Zn(II) and Cd(II) at (a) different concentrations of Cyphos IL 104 and (b) different concentrations of chloride ion.

	Zn(II)				Cd(II)			
	[Cyphos IL 104], mol/L	[Cl^-], mol/L	log K_{ex}	Average	[Cyphos IL 104], mol/L	[Cl^-], mol/L	log K_{ex}	Average
(a)	0.0005	0.5	6.92		0.0005	0.01	10.36	
	0.001	0.5	6.65		0.001	0.01	10.29	
	0.002	0.5	6.85	6.621 ± 0.243	0.002	0.01	10.53	10.53 ± 0.21
	0.005	0.5	6.61		0.005	0.01	10.68	
	0.008	0.5	6.40		0.01	0.01	10.8	
	0.01	0.5	6.3					
(b)	0.002	0.1	6.53		0.002	0.001	10.78	
	0.002	0.3	6.45		0.002	0.005	9.85	
	0.002	0.6	6.46	6.67 ± 0.269	0.002	0.01	10.26	10.16 ± 0.38
	0.002	1.0	7.0		0.002	0.05	10.01	
	0.002	1.5	6.93		0.002	0.1	9.92	

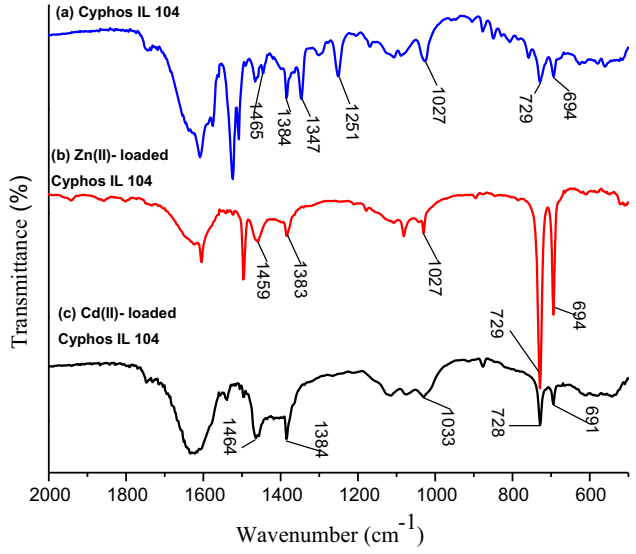


Fig. 7. FTIR spectra of (a) 2.0×10^{-3} mol/L Cyphos IL 104 in toluene, (b) Zn(II) loaded Cyphos IL 104 in toluene at 0.5 mol/L HCl, (c) Cd(II) loaded Cyphos IL 104 in toluene at 0.01 mol/L HCl.

to zero. After each contact the remaining aqueous phase was analysed for its metal content.

The results (Fig. 9) explain that saturation of organic phase with respect to Zn(II) and Cd(II) is achieved after nine and seven contacts, respectively. It is found that 2.0×10^{-3} mol/L of extractant can hold a maximum of 1.41 mM of Zn(II)(0.705 mol Zn(II)/mole Cyphos IL 104) and 0.944 mM Cd(II)(0.472 mol Cd(II)/mole Cyphos IL 104).

3.9. Stripping studies

Different stripping agents were examined for the back extraction of Zn(II) and Cd(II) from the respective loaded organic phases. Stripping efficiencies of different reagents for Zn(II) and Cd(II) are shown in Table 4. It was observed that 0.01 mol L^{-1} EDTA/1.0 mol L^{-1} HNO_3 are effective for Zn(II) and 1.0 mol L^{-1} nitric acid/sulphuric acid are suitable for quantitative stripping of Cd(II). For further studies 0.01 mol L^{-1} EDTA and 1.0 mol L^{-1} HNO_3 were used as stripping agents for Zn(II) and Cd(II), respectively.

Stripping of Zn(II) and Cd(II) from the loaded organic phase may be represented as-

$$[(R_3R'P)_2ZnCl_2A_2]_{Org} + [EDTA]^{4-}_{aq} \leftrightarrow [Zn-EDTA]^{2-}_{aq} + R_3R'PA_{org} + 2Cl^-_{aq} \quad (7)$$

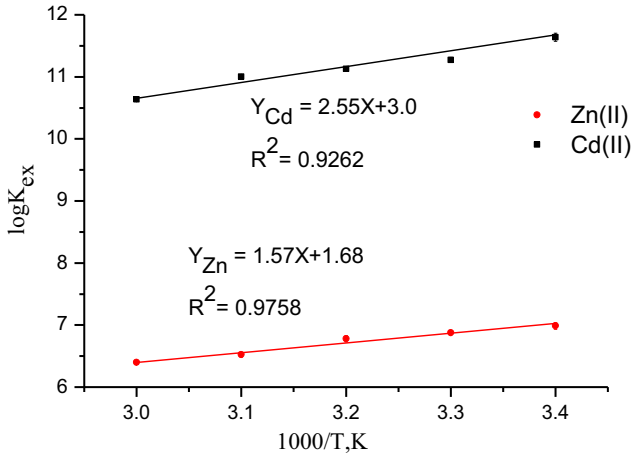


Fig. 8. Effect of temperature on the extraction of Zn(II) and Cd(II). Conditions: for Zn (II)([metal ion] = 2×10^{-2} g/L, [Cyphos IL 104] = 2.0×10^{-3} mol/L, [HCl] = 0.5 mol/L)/for Cd(II)([metal ion] = 2×10^{-2} g/L, [Cyphos IL 104] = 2.0×10^{-3} mol/L, [HCl] = 0.01 mol/L).

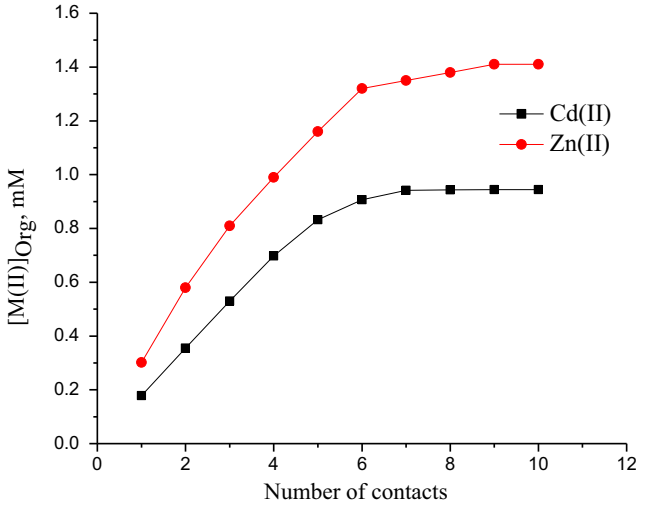


Fig. 9. Loading capacity of Cyphos IL 104. Conditions: [Zn(II)/Cd(II)] = 2.0×10^{-2} g/L, [Cyphos IL 104] = 2.0×10^{-3} mol/L, [HCl] = 1.0 mol/L.

Table 4
Efficiencies of various stripping agents for Zn(II) and Cd(II).

Stripping solution	% Stripping	
	Zn(II)	Cd(II)
Water	44.25 ± 1.89	8.66 ± 1.02
0.5 M NH_4OH	49.56 ± 0.97	89.59 ± 1.44
1 M H_2SO_4	87.43 ± 1.25	93.38 ± 1.56
1 M HNO_3	93.81 ± 1.06	97.74 ± 0.85
0.01 M EDTA	100 ± 0.66	Turbidity appears

$$[(R_3R'P)_2CdCl_2A_2]_{Org} + 2HNO_{3aq} \leftrightarrow Cd^{2+}_{aq} + 2NO_{3aq^-} + 2Cl^-_{aq} + 2R_3R'PA_{org} + 2H^+_{aq} \quad (8)$$

3.10. Hydrolytic stability and regeneration capacity of Cyphos IL 104

Hydrolytic stability and reusability of an extractant are important for determining its applicability on commercial scale. To check the hydrolytic stability of the extractant towards hydrochloric and nitric acid, 2.0×10^{-3} mol/L Cyphos IL 104 was kept in contact with 1.0 mol/L HCl and 1.0 mol/L HNO_3 for fifty days with sporadic shaking. The partition of metal ions (2.0×10^{-2} g/L in 1.0 mol/L HCl) was checked periodically after five days. An insignificant variation of ±2% was observed after a contact period of fifty days in each case.

The regeneration power of Cyphos IL 104 for Zn(II) and Cd(II) was checked. Ten consecutive extraction-stripping cycles were carried out and after every cycle, stripped Cyphos IL 104 was regenerated by washing with water till neutral. Plot of percentage extraction as a function of number of cycles (Fig. 10) indicates an insignificant change in percentage extraction of Zn(II) and Cd(II) up to ten cycles. Results thus suggest that Cyphos IL 104 has good regeneration capacity and can be used as a commercial extractant.

3.10.1. Partition studies of associated metal ions in HCl medium

Distribution of associated metal ions was studied using 2×10^{-3} mol/L Cyphos IL 104 in the acidity range of 1×10^{-3} to 2.0 mol/L HCl. The results (Fig. 11) indicate that Mn(II) shows negligible extraction (<5%) whereas Co(II), Ni(II) and Fe(II) show low extraction(0–20%) in the investigated range of acidity. Extraction of Cu(II) is also low except at 5.0×10^{-3} mol/L HCl where it reaches around 50%. Fe(III) shows poor extraction (<20%) in low acidity range (1.0×10^{-3} to 5.0×10^{-1} mol/L) which increases sharply at high acidity attaining 88% value at 2.0 mol/L HCl.

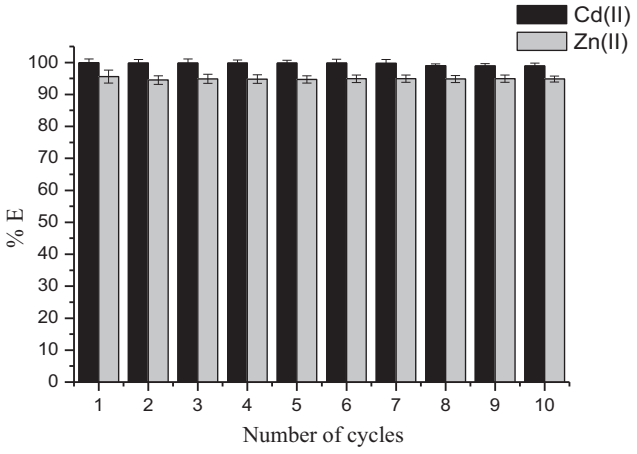


Fig. 10. Regeneration capacity of extractant. Conditions: [Cyphos IL 104] = 2.0×10^{-3} mol/L, [Zn(II)/Cd(II)] = 2.0×10^{-2} g/L, [HCl] = 1.0 mol/L.

4. Separations

The data obtained from distribution studies suggest suitable conditions for the mutual separation of Zn(II) and Cd(II) and their separation from other associated metals. A number of binary separations involving Zn(II) and Cd(II) were carried out and results along with separation factors are summarized in Table 5.

4.1. Binary separations involving Zn(II)

Binary separations of Zn(II) from associated metal ions were performed at 0.8 mol/L HCl. Zn(II) was separated from Cu(II)/Ni(II)/Co(II)/Fe(II)/Mn(II) (2.0×10^{-3}g/L each) by carrying out extraction at 0.8 mol/L HCl using 2.0×10^{-3} mol/L Cyphos IL 104. A major fraction of Zn(II) (~93%) is extracted leaving all the other metal ions in the aqueous phase. The Loaded organic phase was scrubbed with 0.8 mol/L HCl solution to remove co-extracted associated metal ions followed by stripping of Zn(II) using 0.01 mol/L EDTA.

4.2. Binary separations involving Cd(II)

Cd(II) was separated from Zn(II)//Cu(II)/Fe(II) at 0.01 mol/L HCl using 2.0×10^{-3} mol/L Cyphos IL 104. Under these conditions ~78% of Cd(II) is transferred to the organic phase leaving behind other metal ions in the aqueous phase. However, around 2.5% of Zn(II) was co extracted with Cd(II) which was removed by scrubbing the loaded organic phase with 0.01 mol/L HCl. Finally, the loaded organic phase which contained only Cd(II) which was stripped using 1.0 mol/L HNO_3. Separation of Ni(II)/Co(II)/Mn(II) from Cd(II) was achieved by performing extraction at 0.1 mol/L HCl using 2.0×10^{-3} mol/L Cyphos IL 104. Cd(II) is quantitatively transferred to the organic phase leaving other associated metal ions in the aqueous phase. Cd(II) was recovered using 1.0 mol/L HNO_3 as stripping agent.

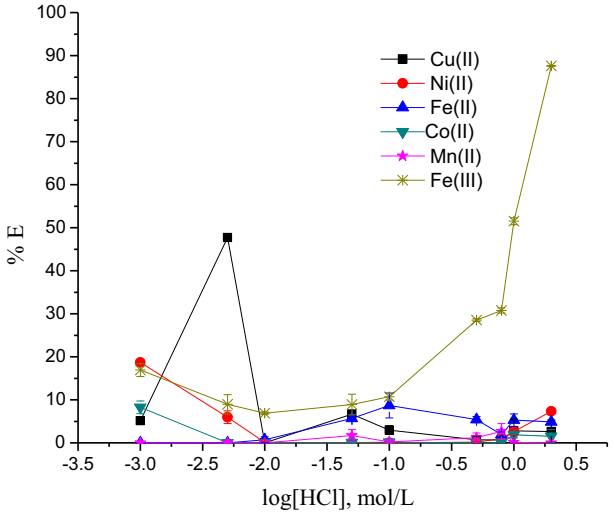


Fig. 11. Effect of HCl concentration on the partition of associated metal ions using Cyphos IL 104. Conditions: [Metal ion] = 2.0×10^{-2} g/L; [Cyphos IL 104] = 2.0×10^{-3} mol/L.

Table 5
Binary separations of Zn(II) and Cd(II) using 2.0×10^{-3} mol/L Cyphos IL 104.

Metal ions	Concentration ratio	Acid molarity (mol/L), HCl	Metal ion remaining in the aqueous phase (%)	Metal ion transferred into the organic phase (%)	[a]Zn(II) and Cd(II) recovered from organic phase (%)	Separation Factor(based on single extraction)
Zn(II):Cu(II)	1:1	0.8	6.91 ± 0.04,Zn 99.04 ± 0.09,Cu	93.04 ± 0.18,Zn 0.94 ± 0.05,Cu	99.78 ± 0.12,Zn	1.41×10^3
Zn(II):Ni(II)	1:1	0.8	6.83 ± 0.045,Zn 99.29 ± 0.05,Ni	93.34 ± 0.26,Zn 0.71 ± 0.28,Ni	99.89 ± 0.09,Zn	2.0×10^3
Zn(II):Co(II)	1:1	0.8	6.24 ± 0.035,Zn 99.04 ± 0.02,Co	94.21 ± 0.14,Zn 0.96 ± 0.1,Co	99.28 ± 0.1.1,Zn	1.68×10^3
Zn(II):Fe(II)	1:1	0.8	6.96 ± 0.2Zn 98.94 ± 0.16,Fe	93.04 ± 0.12,Zn 1.1 ± 0.82,Fe	99.89 ± 0.23,Zn	1.21×10^3
Zn(II):Mn(II)	1:1	0.8	5.91 ± 0.035,Zn 99.85 ± 0.01,Mn	94.64 ± 0.18,Zn 0.15 ± 0.05,Mn	99.99 ± 0.08,Zn	1.18×10^4
Cd(II):Zn(II)	1:1	0.01	98.4 ± 0.24,Zn 23.1 ± 0.02,Cd	2.2 ± 0.11,Zn 76.95 ± 0.02,Cd	99.99 ± 0.12,Cd	1.452×10^2
Cd(II):Cu(II)	1:1	0.01	22.8 ± 0.1,Cd 100 ± 0.05,Cu	77.24 ± 0.02,Cd –	99.99 ± 0.42,Cd	3.4×10^5
Cd(II):Fe(II)	1:1	0.01	22.1 ± 0.08,Cd 99.78 ± 0.04,Fe	77.59 ± 0.12,Cd 1.2 ± 0.6,Fe	99.99 ± 0.22,Cd	2.88×10^2
Cd(II):Ni(II)	1:1	0.1	3.49 ± 0.51,Cd 99.99 ± 0.02,Ni	96.51 ± 0.71,Cd –	99.99 ± 0.12,Cd	2.8×10^6
Cd(II):Co(II)	1:1	0.1	3.1 ± 0.02,Cd 99.91 ± 0.08,Co	95.8 ± 0.02,Cd 0.145 ± 0.01,Co	99.99 ± 0.11,Cd	1.521×10^4
Cd(II):Mn(II)	1:1	0.1	2.64 ± 0.02,Cd 99.7 ± 0.28,Mn	97.22 ± 0.71,Cd 0.225 ± 0.02,Mn	99.99 ± 0.05,Cd	1.52×10^4

Note: ± stands for standard deviation.
[a] Zn(II) stripped using 0.01 mol/L EDTA and Cd(II) using 1.0 mol/L HNO_3.

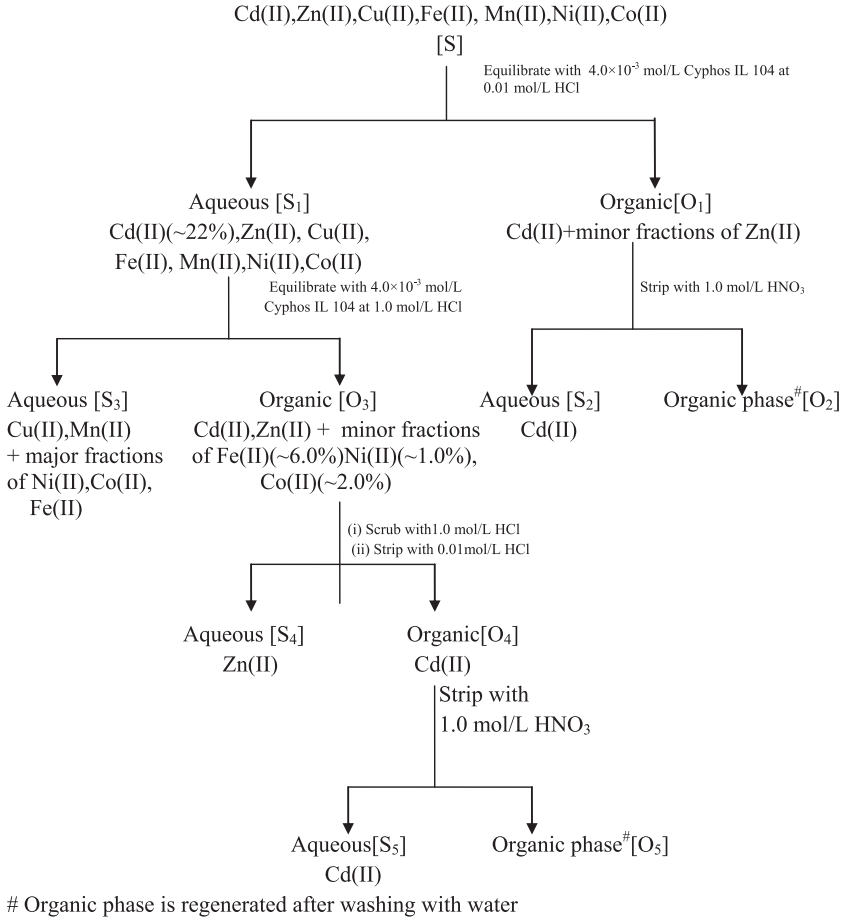


Fig. 12. Recovery of Cd(II) and Zn(II) from synthetic mixture using Cyphos IL 104.

Table 6
Recovery of Zn(II) and Cd(II) from a synthetic multi element mixture using 4.0×10^{-3} mol/L Cyphos IL 104.

Metal ions	Composition of initial solution [S] (mg/L)	Metal ions in solution [S_1] (mg/L)	Metal ions in solution [S_2] (mg/L)	Metal ions in solution [S_3] (mg/L)	Metal ions in solution [S_4] (mg/L)	Metal ions in solution [S_5] (mg/L)	Recovery (%)
Cd(II)	52.5	12.1 ± 0.02	41.58 ± 0.21	–	<2.0	8.2 ± 0.03	94.82 ± 0.18
Zn(II)	46.05	44.55 ± 0.24	<1.0	–	40 ± 0.22	–	86.86 ± 0.21
Cu(II)	53.33	53.33 ± 0.05	–	49.81 ± 0.1	–	–	
Co(II)	47.75	47.28 ± 0.08	–	42.2 ± 0.24	–	–	
Ni(II)	50.38	50.03 ± 0.02	–	45.2 ± 0.04	–	–	
Fe(II)	51.15	50.5 ± 0.04	–	43.8 ± 0.2	–	–	
Mn(II)	51.8	51.63 ± 0.3	–	48.2 ± 0.16	–	–	

Recovery of Cd(II) calculated by combining Cd(II) content in [S_2] and [S_5].

Table 7
Composition of digest and leach liquors obtained from Zn-plating mud.

Sample	Metal	Concentration of metal in digested sample (mgL^{-1})	Concentration of metal in leached sample (mgL^{-1})	% Leaching
Zinc-plating mud	Zn	440.8 ± 2.2	426.5 ± 3.0	96.76
	Mn	8.522 ± 0.02	8.232 ± 0.1	96.6
	Fe	239.6 ± 1.15	232.4 ± 2.05	96.99
	Cd	1.75 ± 0.04	1.3 ± 0.2	74.29

Table 8
Recovery of Zn(II) from zinc plating mud leach liquor.

Metals analysed	Metal ions in solution [ZP_1] (mg/L)	Metal ions in solution [ZP_2] (mg/L)	Metal ions in solution [ZP_3] (mg/L)	Metal ions in solution [ZP_4] (mg/L)	Metal ions in solution [ZP_5] (mg/L)	Recovery (%)	Purity (%)
Zinc	426.5 ± 3.0	7.18 ± 1.41	409 ± 2.1	–	399.5 ± 4.2	93.0 ± 1.2	~99
Cadmium	1.3 ± 0.2	0.911 ± 0.08	–	–	–	–	
Iron	232.4 ± 2.05	–	231 ± 2.5	225.8 ± 3.5	2.532 ± 0.41	–	
Manganese	8.232 ± 0.1	–	8.012 ± 0.2	7.12 ± 1.02	–	–	

5. Recovery

5.1. Recovery of Zn(II) and Cd(II) from synthetic multi element mixture

Based on the extraction data a flow sheet (Fig. 12) was designed to recover Zn(II) and Cd(II) from a multi element mixture containing Cd(II)/Zn(II)/Cu(II)/Ni(II)/Co(II)/Fe(II)/Mn(II). Various steps of the scheme are described below.

50 mL of an aqueous solution [S] containing around 5.0×10^{-2} g/L of each Cd(II), Zn(II), Cu(II), Ni(II), Co(II), Fe(II)and Mn(II) at 0.01 mol/L HCl were equilibrated with equal volume of 4.0×10^{-3} mol/L Cyphos IL 104 in toluene. Almost 78% of Cd(II) leaving other metal ions in the aqueous phase [S_1] is transferred to the organic phase [O_1]. The organic phase [O_1] was then stripped using 1.0 mol/L HNO_3 to recover Cd(II) [S_2]. The raffinate [S_1] containing Cd(II) (~22%), Zn(II), Cu(II), Ni(II), Co(II), Fe(II) and Mn(II) was equilibrated at 1.0 mol/L HCl with equal volume of 4.0×10^{-3} mol/L Cyphos IL 104. Zn(II) and Cd(II) are completely transferred to the organic phase with small portions of Co(II), Ni (II) and Fe(II) while Cu(II), Mn(II) and major portions of Co(II), Ni (II) and Fe(II) remained in the aqueous phase [S_3]. Co(II), Ni(II) and Fe(II) were scrubbed from organic phase [O_3] with 1.0 mol/L HCl. The remaining organic phase containing Cd(II) and Zn(II) was equilibrated with 0.01 mol/L HCl to recover Zn(II) from the organic phase [S_4]. Cd(II) left in the organic phase was then stripped with 1.0 mol/L HNO_3 [S_5]. The organic phases remaining after stripping [$O_2 + O_5$] were regenerated by washing with water and the concentrations of the metal ions in aqueous phase at different stages of separation scheme are given in Table 6.

6. Recovery of Zn(II) from zinc plating mud

Zinc plating mud sample was first dried in an oven at 80 °C for 24 h. 1.0 g of powdered sample was digested with 20 mL of aqua-regia, evaporated to near dryness, cooled and filtered. Filtrate and the washings were collected and made up to 100 mL. The digested sample solution was assayed by AAS for the determination of metal contents (Table 7). For leaching, 1.0 g of powdered sample of zinc plating mud was treated twice with 5.0 mL of conc. HCl containing few drops of conc. nitric acid [4]. The resulting solution was heated to boil at 60 °C, cooled and filtered. The filtrate and washings were collected and diluted to 100 mL maintaining the acidity at 0.01 mol/L HCl. Resulting leach liquor [ZP_1] was analysed for its metal contents using AAS (Table 7). It is clear from the results that almost 97% of the zinc content is leached into the aqueous phase. The separation scheme developed for synthetic mixture (Fig. 12) was applied to zinc plating mud leach liquor for the recovery of Zn(II). As leach liquor contains reasonably high concentration of Fe(III), a minimum of 100-fold molar excess of ascorbic acid was added to reduce Fe(III) to Fe(II) to minimize the co-extraction of Fe(III) along with Zn(II) [63].

30 mL of the leach liquor [ZP_1] were equilibrated with equal volumes of 2.0×10^{-3} mol/L Cyphos IL 104 for 5 min. Major portion of Cd(II) is extracted in the organic phase leaving Fe(II), Mn(II) and major portion of Zn(II) in the equilibrated aqueous phase. The organic phase was then stripped using 1.0 mol/L HNO_3 to recover Cd(II) [ZP_2]. The acidity of the raffinate containing Zn(II), Fe(II) and Mn(II) [ZP_3] was raised to 1.0 mol/L HCl and equilibrated with equal volume of 0.05 mol/L Cyphos IL 104. In this step Zn(II) is completely transferred to the organic phase with small portion of Fe(II) while Mn(II) and major portion of Fe(II) remained in the aqueous phase [ZP_4]. The remaining organic phase containing Zn(II) and minor fraction of Fe(II) is scrubbed with 1.0 mol/L HCl to remove Fe(II) from the loaded organic phase. Zn(II) was then recovered from the organic phase with 1.0 mol/L HNO_3 [ZP_5]. The concentrations of the metal ions in the initial and successive aqueous phases recovered at different stages of the scheme are given in Table 8. Results indicate that around 93% zinc with >99% purity is recovered.

Table 9
Comparison of various extraction systems for zinc and cadmium.

S. No.	Extractant	Diluent	Equilibration tim ze (min)	Loading Capacity mole/mole	Extraction studies	Separations	Recovery from real sample	References
1.	Cyphos IL101 Cyphos IL109	Toluene	15	0.537, 0.716	Zn(II)	–	–	[34]
2.	Cyphos IL 101, 104, 109, 111	Toluene	30	–	Zn(II), Fe(III)	–	–	[48]
3.	Pridyl ketoximes	Chloroform, Toluene + 10% decanol	30	0.33,0.37 0.36	Cd(II)	–	–	[14]
4.	Cyanex 301 Cyanex 302	Toluene	30	0.35 0.1	Cd(II)	–	–	[15]
5.	Cyphos IL 101 Cyphos IL 104	Toluene	30	–	Zn(II), Fe(II), Fe(III)	Separation of Zn(II) from Fe(III)	–	[46]
6.	Imidazolium and ammonium ILs	–	5	–	Zn(II), Cd(II), Cu(II), Fe(III)	Separation of Cd(II), Zn(II), Cu(II), Fe(III)	–	[22]
7.	3-pyridine ketoxime	Toluene + 10% Decanol or Toluene + 10% Decanol + 1% TBP	20	0.7–0.76 0.5	Zn(II)	Separation of Zn(II) from Fe(II), Fe(III) and Cu(II)	–	[16]
8.	Alkyl-Pyridyl Ketoximes	Toluene + 10% decanol	30		Zn(II)		–	[17]
	(a) 2PC10			0.73, 0.87		–		
	(b) 2PC12			0.7, 1.0		Separation of Cu(II)from Zn(II), Cd(II)		
	(c) 2PC14			0.86, 0.7		–		
9.	Cyphos IL 109	Kerosene + Decanol	60	–	Zn(II), Fe(III)	Zn(II) from Fe(III)	–	[64]
10.	Cyphos IL 104	Toluene	20	–	Cd(II)	Separation of Cd(II) from Cu(II), Co(II), Ni(II)	–	[56]
11.	Cyanex 272 and Aliquat - 336 mixture	Kerosene	20	–	Zn(II), Cu(II)	Separation of Zn(II) from Cu(II)	–	[18]
12.	Cyphos IL 101	Kerosene	5	–	Cd(II)	Separation of Cd(II) from Ni(II), Zn(II)	–	[41]
	Aliquat 336					–		
13.	Cyphos IL 104	Toluene	6	0.705(Zn) 0.472(Cd)	Zn(II), Cd(II)	Mutual separation of Zn(II) and Cd(II) and Zn(II)/Cd(II) separation from Cu(II), Ni(II), Co(II), Fe(II), Mn(II)	Zn-plating mud	Present Study

7. Comparative study

The details of some previously studied extraction systems for Zn(II)/Cd(II) and the present extraction system have been summarized in Table 9. Most of the studies report extraction of Zn(II)/Cd(II) either without any separations or their separation from one to three associated metal ions namely Cu(II)/Fe(II) or Fe(III)/Co(II)/Ni(II). Generally studies on loading capacity are missing and longer equilibration time of 10–60 min has been used as compared to 6 min in the present study. Moreover, the developed separation conditions have not been applied to a real sample to illustrate the recovery of pure Zn(II)/Cd(II). Loading capacities achieved in the present study for Zn(II)/Cd(II) are either comparable or higher than the reported values. Oxime extraction systems [16,17] which report comparable or slightly higher loading capacities for Zn(II) have used modifier where as in the present extraction system no modifier is required. In present study 99% pure Zn(II) has been recovered quantitatively from zinc plating mud.

8. Conclusions

Cyphos IL 104 can be considered as a promising reagent for the extraction of Zn(II) and Cd(II) and their separation from commonly associated metal ions. The quantitative extraction of Zn(II) and Cd(II) can be achieved from HCl medium. The extraction studies have been carried out at 25 ± 3 °C without any synergist or modifier. Simple and convenient stripping agents are used for the recovery of metal ions. The composition of the extracted species has been proposed. The calculated thermodynamic parameters suggest that the extraction of zinc and cadmium is fast and the process is exothermic. The developed conditions of separations have been successfully fused to recover Zn(II) and Cd(II) from multi element mixture. Zinc with 99% purity was quantitatively recovered from zinc plating mud at laboratory scale using Cyphos IL 104. The feasibility of Cyphos IL 104 based separation process is proven due to insignificant decline in its extraction efficiency after several extraction-stripping cycles. Finally, the present approach demonstrates the recovery of valuable metals from industrial waste.

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