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Research Article

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Extraction of manganese(II) from acidic buffer medium using D2EHPA and Cyanex 272 as extractants

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ABSTRACT

Extraction of Mn(II) from an acetic acid-acetate buffer medium was investigated using D2EHPA and Cyanex 272 in kerosene. The effect of different parameters such as equilibrium pH, extractant concentrations, metal ion concentration, sodium acetate concentration and temperature on the extraction system was studied. The percentage extraction of manganese was 96% with 0.1M D2EHPA corresponding to equilibrium pH 4.52 whilst it was 76% with 0.1M Cyanex 272 corresponding to equilibrium pH 4.86. Quantitative extraction of manganese was achieved with 0.8M D2EHPA. The loading capacities of both the extractants were found out. On the basis of slope analysis results, the species extracted into the organic phases were proposed to be $MnA_2.2HA$ and $MnA_2.4HA$ for both D2EHPA and Cyanex 272.When a ternary mixture containing 0.02M Mn(II), 0.01M Cu(II) and 0.01M Co(II) was extracted with D2EHPA, the order of extraction of metal ions is Mn(II)>Cu(II)>Co(II). Highest separation factors of 52.5($\beta_{Mn/Cu}$) and 280.3($\beta_{Mn/Co}$) was obtained from aqueous solution having pH 5.0 and extractant concentration of 0.05M D2EHPA in kerosene.

Key words: Manganese, Extraction, Acetate buffer, D2EHPA, Cyanex 272

INTRODUCTION

Di-2-ethylhexyl phosphoric acid (D2EHPA) and 2,4,4-trimethylpentyl phosphinic acid (Cyanex 272) have been widely used for extraction and separation of first row transition elements from different aqueous medium[1-8]. Cheng investigated the purification of synthetic laterite leach solutions by solvent extraction with D2EHPA in kerosene. He obtained the extraction behavior of seven non-ferrous elements that follows the order: $Zn^{2+} > Ca^{2+} > Mn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+} > Mg^{2+}$ at $pH_{0.5}$ values[2]. Park and Mohapatra [3] proposed a complete hydrometallurgical process for the separation and recovery of cobalt from cobalt-nickel solution using Cyanex 272 in kerosene. Darvishi et al. [4] studied the synergistic effect of Cyanex 272 and Cyanex 302 with D2EHPA for cobalt nickel separation. Many researchers have used the saponified form of these extractants. The reason being in case of sodium salts of these extractants, metal to sodium exchange took place instead of metal to H^+ ion and reserved the pH change to facilitate the metal extraction. In our earlier studies, extraction of cobalt (II) and extraction and separation of Co(II) and Ni(II) from sulfate solution were reported using sodium salts of D2EHPA, PC 88A and Cyanex 272 [9-10]. It was observed that 100% of cobalt extraction was obtained with 0.04 molarity of the above three extractants in benzene. Whilst separation of cobalt from nickel was achieved in two stages at equal phase ratio using 0.05M NaCyanex 272 and 0.05M NaPC 88A in kerosene. Reddy et al. [11] studied the extraction behavior of Cd(II) from sulfate solution using the sodium salts of TOPS 99, PC 88A and Cyanex 272 and their mixtures. Recently Staszak et al. [12] studied the extraction of copper from sulfate solution using Cyanex 272 and its sodium salts in the initial pH range 2-4. They explained much lower extraction of copper in case of Cyanex 272 was due to poor cationic exchange property of the extractant in the pH range studied. The extraction of iron using TOPO from various acid medium and found quantitative extraction of iron from sulfuric acid medium was presented by Hariharan et al [13]. Devi et al [14] reported the extraction of copper and separation from other metals using LIX 973NS-LV.

Manganese which is the fifth element in the first row transition elements has a wide range of applications. It is used in standard disposable batteries, production of steel to improve its workability at high temperature, an alloying agent for aluminum and also in many industries such as glass, ceramics etc. So, its extraction and separation from different leach liquors of secondary sources such as Mn-bearing steel scraps, spent electrodes, spent catalysts and industrial mineral processing waste effluents, lithium ion batteries etc., has a challenge for separation scientists. For this solvent extraction technique plays a vital role for its simplicity in application. The extraction and separation of manganese using organophosphorus extractants such as D2EHPA, PC 88A, Cyanex 272, Cyanex 302 has been reported by many researchers [15-21]. Wang et al. [22] reported the extraction and separation of cobalt(II), copper(II) and manganese(II) having concentrations of 0.004M each from sodium sulfate solution by Cyanex 272, PC-88A and their mixture in n-heptane where acetate buffer is used to maintain the aqueous phase pH. They found that equilibrium pH and sodium sulphate concentration were two important factors which influenced the separation factor among Mn, Co and Cu. Comparison on the extraction efficiency of D2EHPA and Cyanex 272 to extract the divalent manganese cation from a leaching solution of low grade chalcopyrite was reported by Perez-Garibay et al [23]. They found that D2EHPA is more efficient extractant than Cyanex 272 in the aqueous pH range of 8.0-8.5. Batchu et al [24] reported the synergistic solvent extraction of manganese (II) from chloride solutions using the mixture of Cyanex 272 and Cyanex 301. A synergistic enhancement factor of 14.1 was obtained when the mole fraction of Cyanex 272 is 0.6. Organophosphorus extractants extract the metal ions at higher pH ranges where hydrolysis of metal occurs. The alkali salts of these extractants leads to a higher pH of the solution where other metals like Co, Ni etc., were co-extracted [25]. An attempt has been made in the present article to study the extraction of 0.02M manganese (II) (as there were reports of leach liquors containing high concentration of the metal values [26-27]) from acetic acid-sodium acetate buffer medium by D2EHPA and Cyanex 272 using kerosene as the diluent. The influence of pH, extractant concentration, metal concentration, acetate ion concentration and temperature on the extraction of Mn(II) has been investigated. The feasibility of separation in presence of copper and cobalt also investigated. The extracted organic species for manganese extraction was proposed from slope analysis and by graphical methods.

EXPERIMENTAL SECTION

2.1. Reagents

The stock solutions of manganese (II) (0.5M), copper(II) and cobalt (II) each 0.1M were prepared by dissolving required amount of AR grade sulphates in double distilled water. One mL of concentrated sulphuric acid was added to prevent hydrolysis of metal ions. The solution was estimated against 0.1M EDTA. The metal solution used in extraction studies was prepared from the stock solution. Cyanex 272 supplied by the Cytec Industries (as gift sample) and D2EHPA procured from Fulka were used without further purification. Distilled kerosene was used as diluent. Organic phase solutions were prepared by dissolving the required amount of extractants in kerosene and then diluting to the required concentration. All other reagents used were of analytical reagent grade.

2.2. Experimental Procedure

The aqueous solution pH was maintained to the desired value by adding calculated amount of acetic acid-sodium acetate buffer with manganese ion and making the total volume to 50 mL. The initial concentration of manganese ion was kept 0.02M except for variation study of metal ions. Then the aqueous phase (20 mL) was equilibrated with an equal volume of D2EHPA and Cyanex 272 in kerosene for 5 minutes in a separating funnel. After the phase disengagement the aqueous phase was collected and the equilibrium pH was measured. The manganese content in the aqueous phase after extraction was determined by titration with EDTA using Eriochrome Black T as the indicator and for separation studies the metal ions were analyzed using Atomic Absorption Spectrophotometer. The concentration of the metal ion in the organic phase was determined by mass balance. The distribution ratio(D) was calculated using the ratio of the concentration of the metal ions in the organic to that of in aqueous phase at equilibrium. From D values, the percentage of extraction was calculated (%E=100(D/D+1)) and the separation factor ($\beta = D_{M1}/D_{M2}$), where M1 and M2 represents two metals. The temperature variation experiment was carried out by mixing equal volumes of aqueous and organic phases in a flat-bottomed water-jacketed equilibration tube with the help of a magnetic stirring bar. The temperature was maintained constant(±0.1K) by circulating water from a constant temperature bath through the jacket. All the extraction experiments were carried out at 30±1°C.

RESULTS AND DISCUSSION

3.1. Influence of equilibrium pH

Experiments were carried out at room temperature to investigate the effect of pH on the extraction of manganese using 0.1 M D2EHPA and 0.1 M Cyanex 272 in kerosene in the initial pH range 4.0- 6.0. The percentage extraction versus equilibrium pH plot [Fig.1] showed that the percent extraction of manganese increased with increasing equilibrium pH for both D2EHPA and Cyanex 272. With D2EHPA the percentage extraction of manganese increased from 30 to 96% in the equilibrium pH ranges 3.0-4.52, whereas with Cyanex 272 it increased from 11 to 76% in the equilibrium pH range 3.75-4.86. The extraction of manganese was higher in case of D2EHPA, so more number of H^+ ions entered to the aqueous phase shifting the extraction curve to lower pH value compared to Cyanex 272. The $pH_{0.5}$ values were 3.15 and 4.44 for D2EHPA and Cyanex 272, respectively.

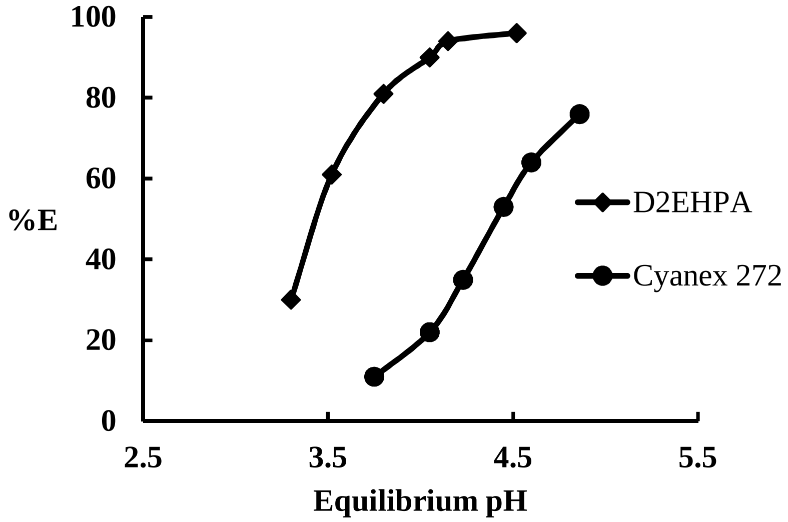

Fig. 1.: Effect of equilibrium pH on percentage extraction of manganese. $[Mn]_{aq}$ = 0.02M, [D2EHPA] and [Cyanex 272] = 0.1M in kerosene

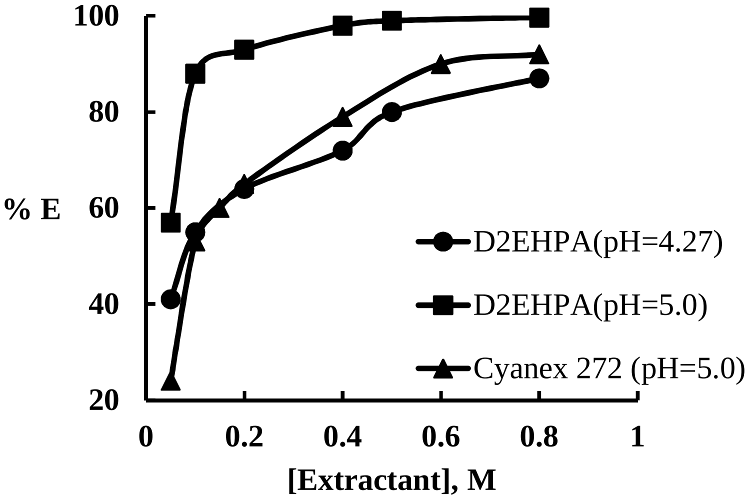

Fig. 2.: Effect of D2EHPA and Cyanex 272 concentration on extraction of manganese. $[Mn]_{aq}$ = 0.02M, $pH_{0.5}$ (Initial) =4.27 for D2EHPA and 5.0 for Cyanex 272, respectively

3.2. Effect of extractant concentration

Extraction of 0.02M Mn(II) was carried out at $pH_{0.5}$ values with various extractant concentrations going from 0.05 to 0.8M D2EHPA and Cyanex 272 in kerosene. Extraction was found to increase with increasing concentrations for both the extractants. With 0.4 M extractant concentrations, the percentage extraction of Mn(II) was 74% for D2EHPA and 79% for Cyanex 272. As the extraction of manganese was pH dependent, the extraction of it was not so much influenced with increase in D2EHPA concentration because the initial pH of the aqueous solution was lower than that of Cyanex 272 (corresponding to their $pH_{0.5}$ values, the initial pH values are 4.27 for D2EHPA and 5.0 for Cyanex 272). When the extraction of manganese (II) was carried out at pH 5.0, the extraction was 95% with 0.04 M D2EHPA. The results were plotted in Fig.2, which showed quantitative of extraction of manganese with 0.8M D2EHPA and 92% extraction of manganese with 0.8M Cyanex 272, respectively.

3.3. Effect of metal ion concentration

Samples containing different concentrations of Mn(II) in the range 0.02-0.3M were prepared and the aqueous phase pH was maintained at 6.0 by adding calculated amount of the buffer solution. The extraction was studied with 0.5 M D2EHPA and Cyanex 272 in kerosene at room temperature. The results were plotted in Fig.3 as a relation between the equilibrium concentrations of Mn(II) in the organic phase to that of initial concentrations of Mn(II) used for the investigation. It was observed that the concentration of manganese (II) in the organic phase increased steadily with increasing aqueous Mn(II) concentration up to 0.2 M with D2EHPA and up to 0.1M with Cyanex 272, respectively. The loading capabilities of 0.5 M D2EHPA and 0.5 M Cyanex 272 for Mn(II) was found to be 3.25 kg m^{-3} and 2.05 kg m^{-3}, respectively. The higher loading value of D2EHPA proven to be a better extractant for manganese compared to Cyanex 272.

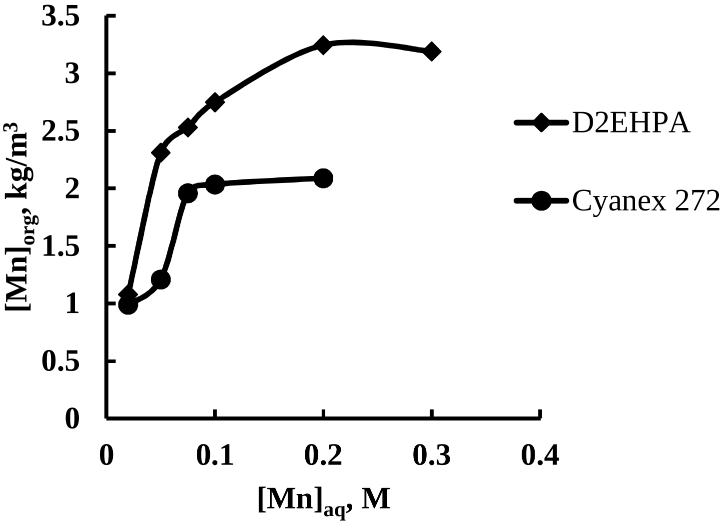

Fig. 3.: Plot of $[Mn]_{org}$, kg/m^3 versus $[Mn]_{aq}$, kg/m^3 with 0.1M D2EHPA and Cyanex 272. Initial pH = 6.0

3.4. Effect of acetate ion concentration

To study the effect of acetate ion (in the concentration range 0.1-0.8M) on the extraction efficiency of 0.1M extractants, the extractions were carried out with 0.02 M Mn(II) ion at their $pH_{0.5}$ values. The analysis of the results showed that the acetate ion influenced the percentage extraction of manganese for both the extractants. However, the effect was more prominent in case of D2EHPA (68-96%) than with Cyanex 272(62-71%) under the concentration range studied [Fig.4]. The increase in extraction could be explained on the research results of Gu et al. [26]. According to them, addition of some ligands like acetate, formate, tartarate etc., to the aqueous phase slightly decreases the interfacial tension between the aqueous phase and the organic phase. Furthermore, anionic ligands have a hydrophobic-hydrophilic molecular structure; with hydrophobic end directed towards the organic phase of the interface resulting in population of the metal ligand complex at the interface more than that of hydrated metal ions enhancing the metal extraction.

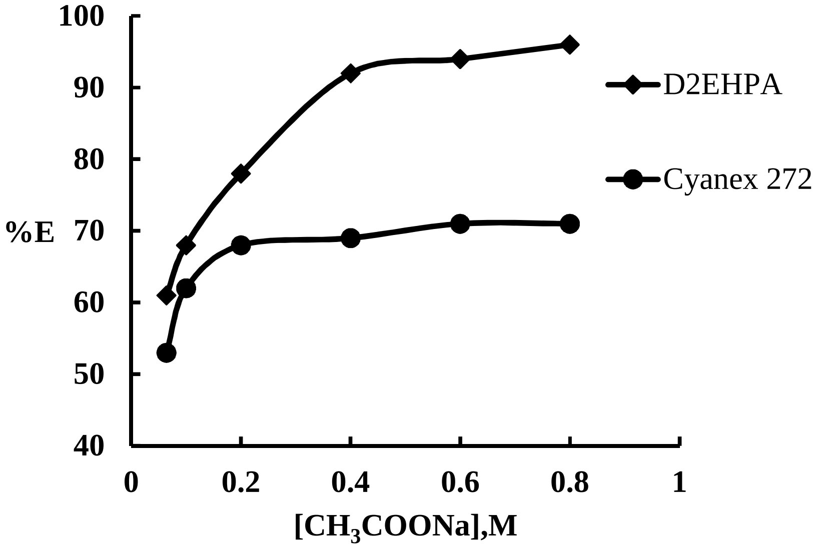

Fig.4.: Effect of sodium acetate concentration on manganese extraction. $[Mn]_{aq}$ = 0.02M, $pH_{0.5}$ (Initial) =4.27 for 0.1 M D2EHPA and 5.0 for 0.1M Cyanex 272, respectively

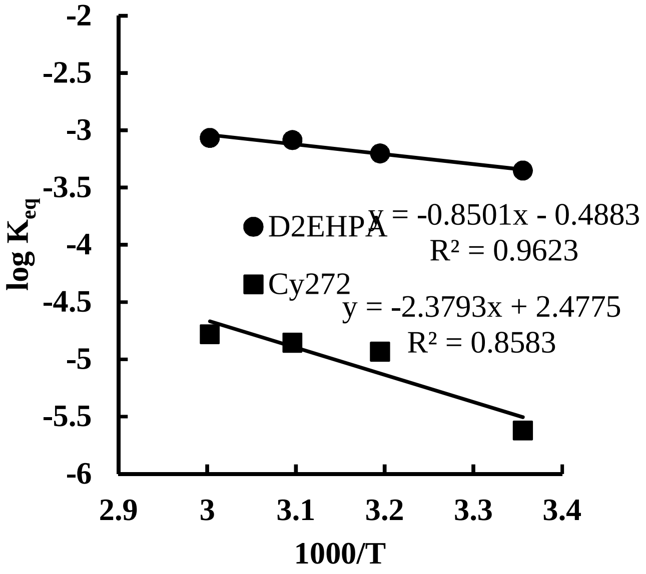

Fig.5.: Plot of log K_{eq} versus 1000/T for manganese extraction. $[Mn]_{aq}$ = 0.02M, $pH_{0.5}$ (Initial) =4.27 for 0.1M D2EHPA and 5.0 for 0.1M Cyanex 272, respectively

3.5. Effect of temperature

The extraction efficiency sometimes depends on temperature. So to know the effect of temperature on the extraction of 0.02 M Mn(II) with 0.1M D2EHPA and 0.1M Cyanex 272 in kerosene, the extraction was carried out at their $pH_{0.5}$ values in the temperature range 298 K- 333K. It was observed that with increasing temperature the distribution ratio of manganese extraction increased from 1.22(298K) to 1.45(333K) for D2EHPA and 1.17(298K) to 1.423(333K) for Cyanex 272, respectively. This concludes that this extraction is endothermic for both cases of the extractants. The thermodynamic parameters such as enthalpy change (ΔH) and entropy change (ΔS) were calculated by plotting log K_{eq} vs.1000/T as presented in Figure 5. From the plot, ΔH and ΔS were calculated and found to be 16.27 kJ mol^{-1} and 9.34 J $K^{-1}mol^{-1}$ for D2EHPA 45.55 kJ mol^{-1} and 47.43 J $K^{-1}mol^{-1}$ and using vant' Hoff equation given below.

$$\log K_{eq} = -\frac{\Delta H}{2.303RT} + \frac{\Delta S}{2.303R}$$

3.6. Extraction stoichiometry

It is well known that organophosphoric acid extractants exist as dimmers in organic non polar diluents [27-28]. D2EHPA and Cyanex 272 are also likely to exist as dimers. The extraction reaction of divalent manganese (Mn^{2+}) by the organophosphorus extractants can be represented as follows:

$$Mn^{2+}_{(aq)} + n\,(H_2A_2)_{(org)} \rightleftharpoons MnA_{2.}(HA)_{n-2(org)} + 2H^{+}_{\ (aq)} \qquad (1)$$

Where HA stands for D2EHPA or Cyanex 272.

The extraction equilibrium constant for the above reaction is given as

$$K_{ex} = \frac{[MnA_2(HA)_{n-2}]_{org}[H^+]^2_{eq}}{[Mn^{2+}]_{aq}[H_2A_2]^n{}_{eq}} \qquad (2)$$

The distribution ratio is the ratio of metal concentration in organic phase to the metal concentration in aqueous phase at reaction equilibrium and substituting it in the equation (2), it becomes

$$K_{ex} = \frac{D[H^+]^2_{eq}}{[H_2A_2]^n{}_{eq}} \qquad (3)$$

Therefore,

$$\log D = \log K_{ex} + 2pH + n \log [H_2A_2]_{eq} \qquad (4)$$

Considering the amount of extracted manganese into the organic phase, the extractant concentration at equilibrium would be given as

$$[H_2A_2]_{equilibrium} = [H_2A_2]_{initial} - n[Mn^{2+}]_{org} \qquad (5)$$

The plot of log D- n log $[H_2A_2]_{eq}$ versus equilibrium pH for different values of number of extractant molecules (n) for D2EHPA and Cyanex 272 concentrations is shown in Fig. 6a and 6b. The line which has a slope of ~2.0 has been selected. The slope is equal to the number of H^+ ions in equation (1). For D2EHPA and Cyanex 272, n=3 have been obtained.

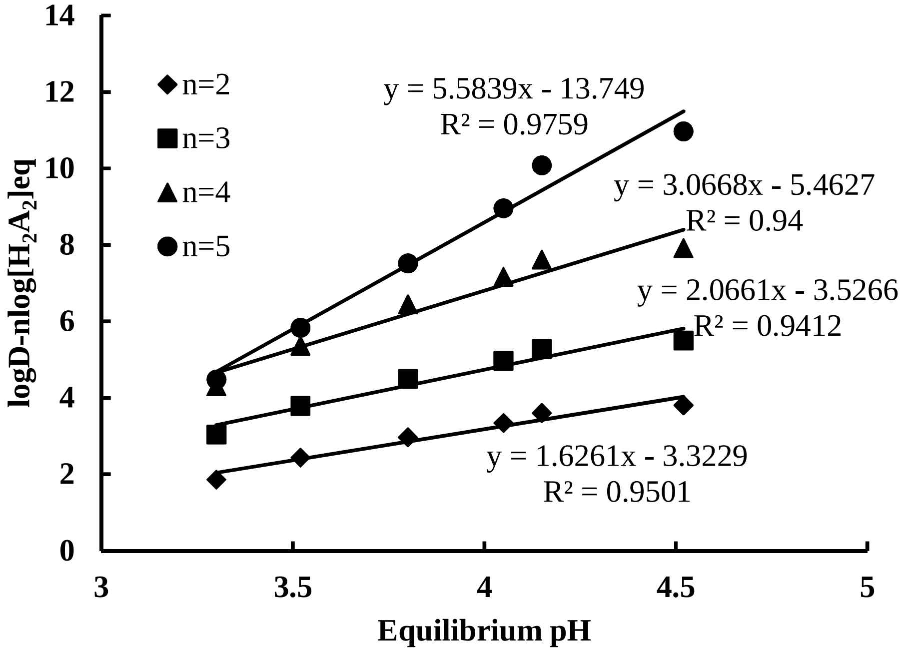

Fig. 6a.: Plot of log D-n log $[H_2A_2]_{eq}$ versus equilibrium pH for 0.1M D2EHPA

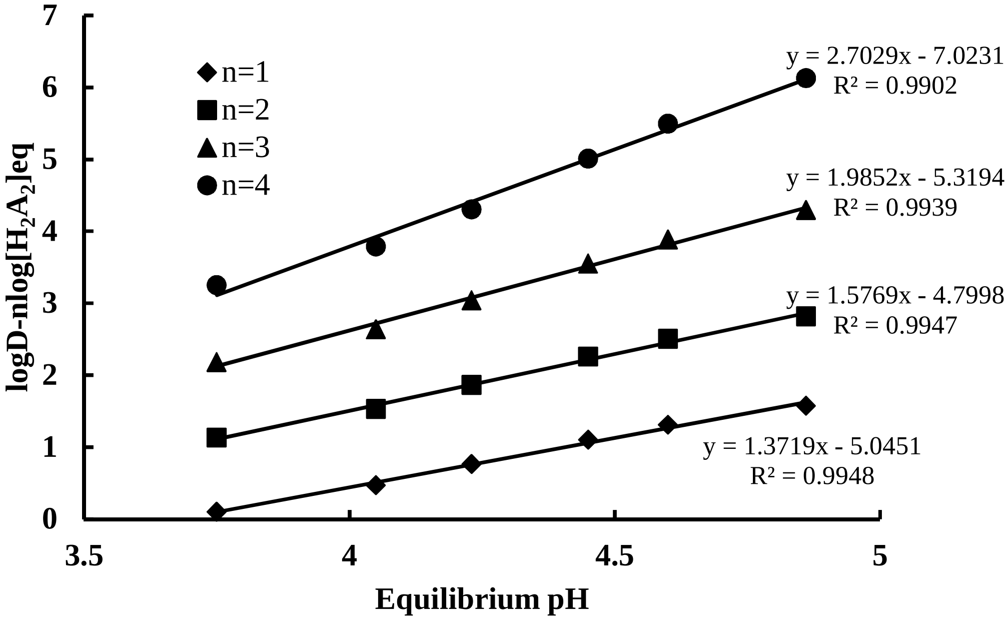

Fig. 6b.: Plot of log D-n log $[H_2A_2]_{eq}$ versus equilibrium pH for 0.1M Cyanex 272

3.6.1. Extraction equilibrium model

The divalent manganese ion can form a number of complexes having coordination number four to eight. Assuming y-merzied manganese (II) complexes are extracted into D2EHPA and Cyanex 272 in kerosene, the extraction equilibrium can be written as

$$\mathrm{yMn}^{2+}_{aq} + \frac{y(a+b)}{2}(\mathrm{H_2A_2})_{eq} \rightleftharpoons (\mathrm{MnA_a(HA)_b})_{y,org} + \mathrm{yaH}^{+}_{aq} \tag{6}$$

The extraction constant (K_{ex}) can be written as

$$K_{yab} = \frac{[(\mathrm{MnA_a(HA)_b})_y]_{org}[\mathrm{H}^+]^{ya}_{eq}}{[\mathrm{Mn}^{2+}]^{y}_{aq}[\mathrm{H_2A_2}]_{eq}^{y(a+b)/2}} \tag{7}$$

$$D = \frac{[(\mathrm{MnA_a(HA)_b})_y]_{org}}{[\mathrm{Mn}^{2+}]_{aq}} \tag{8}$$

$$\log D = \log K_{yab}[\mathrm{Mn}^{2+}]^{y-1}_{aq}[\mathrm{H_2A_2}]^{y(a+b)/2}_{eq} - (ya)\log[\mathrm{H}^+]_{eq} \tag{9}$$

From the variation of log D- n log $[H_2A_2]_{eq}$ vs equilibrium pH, the slope was 2.0 for D2EHPA and Cyanex 272 which implies ya=2.0. Thus equation (9) can be written as

$$D = K_{yab}[\mathrm{Mn}^{2+}]^{y-1}_{aq}[\mathrm{H_2A_2}]^{y(a+b)/2}_{eq}[\mathrm{H}^+]^{2}_{eq} \tag{10}$$

$$[\mathrm{Mn}^{2+}]_{org}[\mathrm{H}^+]^{2}{}_{eq} = K_{yab}[\mathrm{Mn}^{2+}]^{y}_{aq}[\mathrm{H_2A_2}]^{y(a+b)/2}_{eq} \tag{11}$$

$$\log[\mathrm{Mn}^{2+}]_{org}[\mathrm{H}^+]^{2}{}_{eq} - \frac{y(a+b)}{2}\log[\mathrm{H_2A_2}]_{eq} = \log K_{yab} + y\log[\mathrm{Mn}^{2+}]_{aq} \tag{12}$$

The degree of polymerization was found to be 1.0 for both D2EHPA and Cyanex 272 from the plot of $\log[Mn^{2+}]_{org}[H^+]^2{}_{aq}$-y(a+b)/2$\log[H_2A_2]_{eq}$ vs log $[Mn^{2+}]_{aq}$ which was shown in Fig.7. Now a=2, as y=1. Putting this value the extraction equilibrium constant in eqn. (7) is

$$K_{2b} = \frac{[\mathrm{MnA_2(HA)_b}]_{org}[\mathrm{H}^+]^{2}_{aq}}{[\mathrm{Mn}^{2+}]_{aq}[\mathrm{H_2A_2}]_{eq}^{(2+b)/2}} \tag{13}$$

And

$$\log D[\mathrm{H}^+]^{2}{}_{eq} = \log K_{2b} + \frac{(2+b)}{2}\log[\mathrm{H_2A_2}]_{eq} \tag{14}$$

The plot of log $D[H^+]^2{}_{aq}$ vs. $\log[H_2A_2]_{eq}$ gave slopes of 2.07 and 2.05 for D2EHPA and Cyanex 272, respectively. So, the value of b was 2.0 for both extractants[Fig. 8].

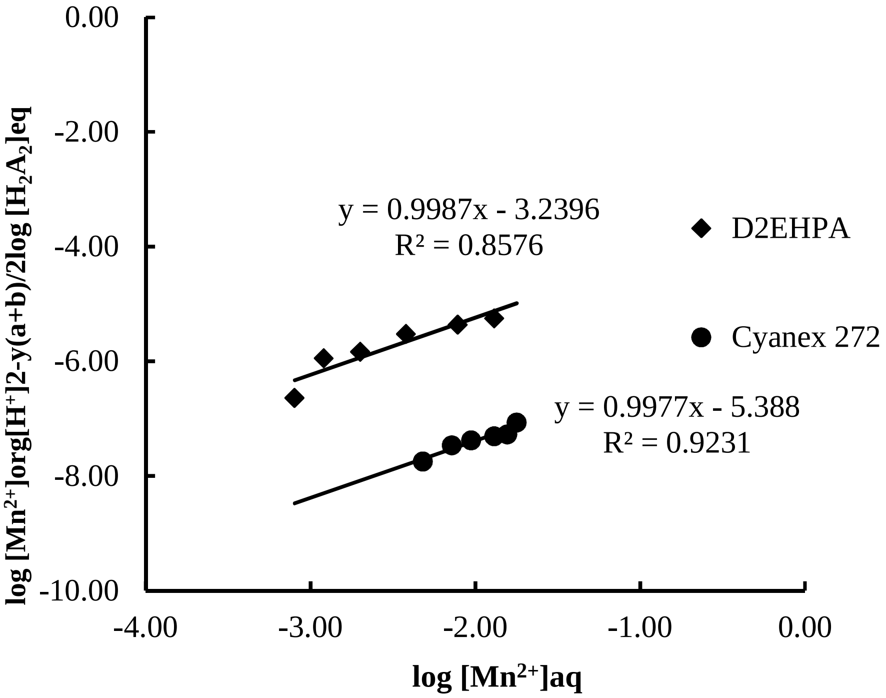

Fig. 7. Plot of log $[Mn^{2+}]_{org}[H^+]^2_{aq} - y(a+b)/2$ log $[H_2A_2]_{eq}$ versus log $[Mn^{2+}]_{aq}$

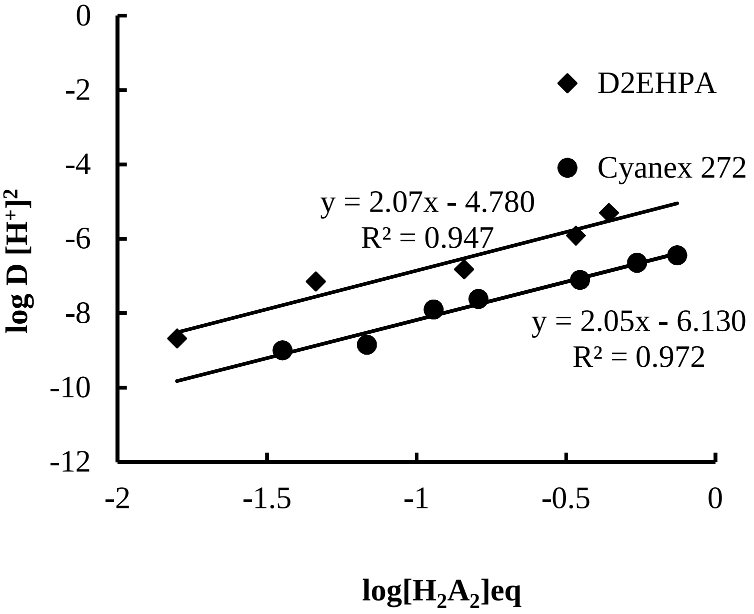

Fig.8: Plot of log $D[H^+]^2_{aq}$ versus log $[H_2A_2]_{eq}$ for extraction of manganese with D2EHPA and Cyanex 272

The above results showed that monomeric species were extracted into the organic phase and the extractant molecules involved in the extraction process were 3.0 and 2.0 for both D2EHPA and Cyanex 272. Basing on these results the extraction equation of manganese can be represented as follows:

$Mn^{2+}_{(aq)} + 3(H_2A_2)_{(org)} \rightleftharpoons (MnA_2.4HA)_{org} + 2H^+_{(aq)}$

$Mn^{2+}_{(aq)} + 2(H_2A_2)_{(org)} \rightleftharpoons (MnA_2.2HA)_{org} + 2H^+_{(aq)}$

3.7. Separation of Mn(II) in presence of Cu(II) and Co(II)

It is reported that the sulfate leach liquor of waste lithium ion batteries contain Mn, Cu and Co with other impurities [22]. Other leach liquors like complex sulfides also contain Mn and Cu. In the present investigation it is found that D2EHPA is a better choice for manganese compared to Cyanex 272 and the separation possibilities of Mn(II), Cu(II) and Co(II) from a ternary mixture was studied using 0.025 and 0.05M D2EHPA from three different pHs namely 4, 4.63 and 5.0. The results presented in Fig. 9 showed that the order of extraction of the three metal ions were in the order Mn(II)>Cu(II)>Co(II) and the order is independent of pH. Highest separation factors of 52.5($\beta_{Mn/Cu}$) and 280.3($\beta_{Mn/Co}$) was obtained from aqueous solution having pH 5.0 and extractant concentration of 0.05M D2EHPA in kerosene.

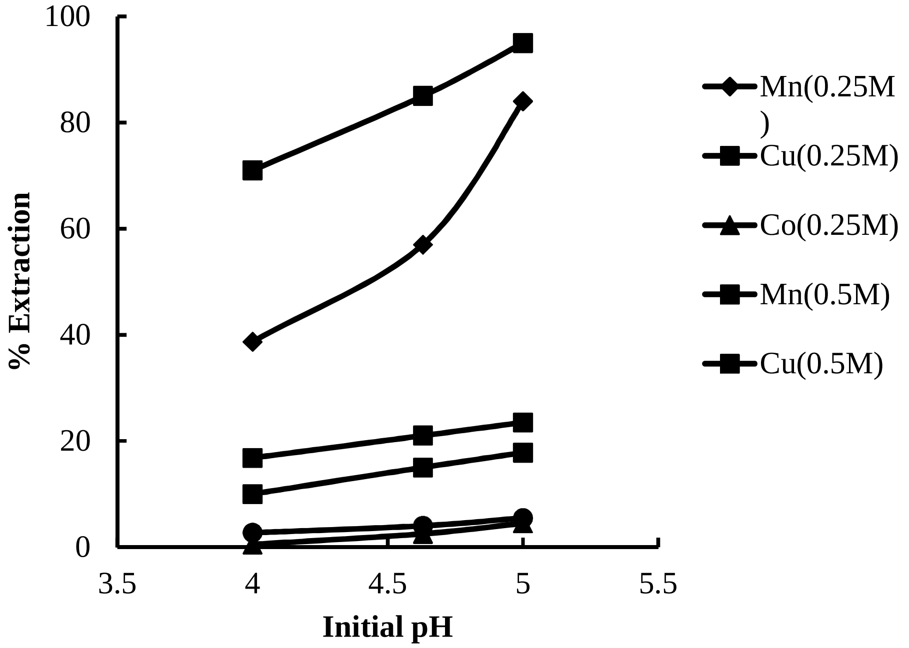

Fig.9.: Effect of pH on percentage extraction of manganese, copper and cobalt using 0.25M and 0.5M D2EHPA in kerosene from a ternary mixture containing $[Mn]_{aq}$ = 0.02M, $[Cu]_{aq}$ = 0.01M and $[Co]_{aq}$ = 0.01M

CONCLUSION

The extraction of manganese (II) from acetic acid-acetate buffer medium using D2EHPA and Cyanex 272 has been investigated. The percentage extraction of manganese (II) increased with increase in equilibrium pH and extractant concentrations. But the extraction efficiency of D2EHPA towards manganese is higher than that of Cyanex 272. Quantitative (100%) extraction of manganese was achieved with 0.8M D2EHPA. The loading capacities of 0.5M D2EHPA and Cyanex 272 were 3.25 kg/m^3 and 2.05 kg/m^3, respectively. The extraction efficiency increased with increase in sodium acetate concentration for both D2EHPA and Cyanex 272, but there is a sharp increase of manganese extraction 68% (0.1M sodium acetate) to 92% (0.4M sodium acetate) in case of D2EHPA. The extraction of manganese was found to be endothermic for both D2EHPA and Cyanex 272. From slope analysis methods the species extracted to the organic phases were proposed to be $MnA_2.4HA$ and $MnA_2.2HA$ for D2EHPA and Cyanex 272. D2EHPA found to be more powerful extractant than Cyanex 272 for manganese extraction. The selectivity of manganese over cobalt is better than manganese over copper corresponding to highest separation factors of 52.5($\beta_{Mn/Cu}$) and 280.3($\beta_{Mn/Co}$).

Acknowledgements

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REFERENCES

[1] S Amer; JM Figueiredo, A. Luis, *Hydrometallurgy*, **1995,** 37(3), 323–337.
[2] CY Cheng, *Hydrometallurgy*, **2000,** 35(3), 369–386.
[3] KH Park; D. Mohapatra, *Met. Mater. Inter*., **2006,** 12(5), 441-446.
[4] D Darvishi; DF Haghshenas; EK Almadari; SK Sadrnezhaad; M Halali, *Hydrometallurgy*, **2005, 77**, 227-238.
[5] MN Gandhi; NV Deorkar; SM Khopkar, *Talanta*, **1993,** 40, 1535–1539.
[6] DS Flett, *J. Organomet. Chem*., **2005,** 690, 2426–2438.
[7] WA Rickelton; DS Flett; DW West, *Solv. Extr. Ion Exch*. **1984, 2**(6), 815–838.
[8] BR Reddy; PVRB. Sarma, *Miner. Metall. Process*., **2001,** 18, 172–176.
[9] NB Devi; KC Nathsarma; V Chakravortty, *Hydrometallurgy***, 1994**, 34, 331-342.
[10] NB Devi; KC Nathsarma; V Chakravortty, *Hydrometallurgy,* **1998,** 49, 47-61.
[11] BR Reddy; D Neel Priya; JR Kumar, *Hydrometallurgy*, **2004,** 74, 277-283.
[12] K Staszak; M Regel-Rosocka; K Wieszczycka; P Burmistrzak, *Sep. Purif. Technol*., **2012,** 85, 183–192.
[13] AVLNSH Hariharan; Ch Sudhakar, A Srinivasanaidu, *J. Chem. Pharm. Res.*, **2011**, 3(4), 945-950.
[14] AP Devi, N Swain; NB Devi, *J. Chem. Pharm. Res*., **2014,** 6(4):1047-1052.
[15] NB Devi; KC Nathsarma; V Chakravortty, *Hydrometallurgy*, **2000**, 54(2-3), 117–131.
[16] KC Nathsarma; NB Devi, *Hydrometallurgy*, **2006,** 84, 149–154.
[17] D Darvishi; M Teimouri; EK Almadari; DF Haghshenas; SK Sadrnezhaad; K Nazri; ISEC 05,"Solvent extraction of sustainable development" Beijing, PR China, **2005**,19-23 September.
[18] DH Fatmeshari; D Darvishi; S Etenadi; ARE Hollagh; EK Almadri; AA Salardini, *Hydrometallurgy*, **2009**, 98, 143-147.
[19] NS Awwad; SI El-Dessouky; EH Borai; EA El-Sofany, *Solv. Extr. Ion. Exch*., **2009**, 27, 408–422.
[20] JM Zhao; XY Shen; FL Deng; FC Wang; Y Wu; HZ Liu, *Sep. Purif. Technol*., **2011,** 78, 345-351.
[21] DV Koladkar; PM Dhadke, *Chem. Anal*., **2001**, 46(3), 411.
[22] F Wang; F He; Z Junmei; N Sui; L Xu; H Liu, *Sep. Purif. Technol*., **2012,** 93, 8–14.
[23] MR Hossain; S Nash; G Rose; S Alam, *Hydrometallurgy*, **2011,** 107, 137-140.
[24] R Perez-Garibay; J Martínez-Jiménez; A Uribe-Salas; A Martínez-Luévanos, *Engineering*, 4, **2012,** 526-531.
[25] NK Batchu; CH Sonu, MS Lee, *Hydrometallurgy*, **2013,** 140, 89–94.
[26] T Jiango; Y Yang; Z Huang; G Qiu, *Hydrometallurgy*, **2003**, 69, 177-186.
[27] J Li; X Li; Q Hu; Z Wang; J Zheng; L Wu; L Zhang, *Hydrometallurgy*, **2009,** 99, 7-12.
[28] ZM Gu; DT Wasan; NN Li, *J. Membr. Sci*, **1986,** 26, 129-142.
[29] BK Tait, *Solv. Extr. Ion Exch*., **1992,** 10 (5), 799–809.
[30] Y Binghua; Y Nagosa; M Satake; A Nomura; K Horita; *Solvent. Extr. Ion. Exch*, **1996,** 14, 849-870.