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Technical note

Synergistic solvent extraction of manganese(II) with a mixture of Cyanex 272 and Cyanex 301 from chloride solutions

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ABSTRACT

The solvent extraction of manganese(II) has been studied from chloride solutions using a mixture of Cyanex 272 and Cyanex 301 dissolved in kerosene. The mixture has shown a significant synergistic effect at $X_{Cyanex\ 272} = 0.6$. The synergistic enhancement factor was calculated to be 14. The extracted species in the organic phase was found to be $MnH_2A_2B_2$ using slope analysis method. Stripping experiments showed that manganese could be recovered using dilute sulphuric acid solutions from the loaded mixture. The mixture has a potential for the separation of Mn(II) from other associated metals.

1. Introduction

Manganese is an important metal used in industries such as steel, iron, battery, nonferrous alloys, and fine chemicals. The physical properties of steel like strength, hardness and resistance are improved by the addition of Mn. Therefore, the demand for manganese has been increased due to growth in steel and battery industry. Separation and recovery of manganese has been carried out using solvent extraction by utilizing various kinds of extractants (Devi et al., 2000; Hosseini et al., 2011; Innocenzi and Veglio, 2012; Lee and Filiz, 2008; Nathsarma and Devi, 2006; Salgado et al., 2003; Tait, 1992; Thakur, 1998; Veloso et al., 2005; Wang et al., 2012; Zhang and Cheng, 2007).

Solvent extraction of manganese from chloride solutions with di(2-ethyhexyl)phosphoric acid (D2EHPA) in kerosene was investigated. The composition of the extracted species in the organic phase was found to be $MnR_2(HR)_2$ (Biswas et al., 2000). Tsai and Tsai (2011) reported the studies on the distribution of manganese between aqueous sulfate solutions and kerosene solutions of D2EHPA. The existence of two species, $MnR_2(HR)_2$ and $MnR_2(HR)_3$ in the organic phase was found by applying both graphical and numerical analyses. The extraction equilibrium of Mn(II) using bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) dissolved in kerosene was investigated by Biswas and Rahman from sulphate-acetato medium (Biswas and Rahman, 2011). The authors proposed the extraction mechanism and reported the complete stripping of Mn(II)-loaded Cyanex 272 with 0.1 M solutions of HCl, HNO_3 and H_2SO_4(Biswas and Rahman, 2011).

The solvent extraction of Mn(II) from sulphate solutions using sodium salt of Cyanex 272 was studied and the extracted species was determined as $MnA_2 \cdot 3HA$ (Devi et al., 1997a). Devi and Mishra (2010) studied the solvent extraction of manganese from sulphate media using bis(2,4,4-trimethylpentyl)monothiophosphinic acid (Cyanex 302) and reported the formation of extracted species as $MnR_2(RH)_4$ based on slope analysis. It was observed that at an equilibrium pH of 5.45, extraction of 0.01 M Mn(II) was quantitative using 0.1 M Cyanex 302. Liquid–liquid extraction of Mn(II) from sulphate solutions using bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301) diluted in toluene was investigated and stoichiometric ratio of the metal:reagent was found to be 1:2 (Shinde and Dhadke, 1999). Alamine 336 diluted in m-xylene was employed for the distribution studies of Mn(II) from hydrochloric acid solutions (Filiz, 2007). Extraction of Mn(II) from chloride solutions with tri-butyl phosphate in xylene was studied and $MnCl_2 \cdot 3TBP$ was reported to be the probable extracted species (Yadav and Khopkar, 1969). Argekar and Shetty (1997) studied the solvent extraction of Mn(II) with bis(2,4,4-trimethylpentyl) monothiophosphinic acid, $R_2P(S)OH$ in toluene and determined the extracted species as $[R_2P(S)O]_2Mn$. Tait (1992) investigated the solvent extraction of some base metal ions including Mn(II) from sulphate media with Cyanex 301, Cyanex 302 and their binary mixture with Aliquat 336 in toluene. It was found that 50% of manganese was extracted at a pH of 4.0. On the other hand, the extraction of Mn(II) was zero from sulphuric acid solutions. Also, Cyanex 301 was more efficient than mixture of Cyanex 301 and Aliquat 336 towards the extraction of Mn(II).

Devi et al. (1997b) investigated the solvent extraction of Mn(II) using sodium salts of D2EHPA, PC 88A and Cyanex 272 and their binary mixtures. It was found that mixture of NaCyanex 272 and NaPC 88A

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demonstrates the best synergism. The separation of zinc and manganese from sulphate solutions using a mixture of D2EHPA and Cyanex 272 was studied. It was suggested that 1/3 (D2EHPA/Cyanex 272) volumetric ratio of extractants is the best mixture for separating zinc and manganese (Ahmadipour et al., 2011). Zhao et al. (2011) have used a mixture of Cyanex 272 and PC 88A for the synergistic extraction of Mn(II) from sulfate media. The maximum synergistic enhancement coefficient of 4.12 was obtained at an equilibrium pH of 4.95.

Table 1 describes the summary of the literature reports regarding Mn(II) extraction studies. Literature review reveals that little work has been done on the synergistic solvent extraction of Mn(II) from chloride solutions. There are no reports describing the synergistic extraction of Mn(II) from chloride solutions. In the present paper, synergistic solvent extraction of manganese has been investigated from chloride solutions using a mixture of Cyanex 272 and Cyanex 301 dissolved in kerosene. The effect of equilibrium pH, extractant concentration, extraction mechanism, diluents, stripping studies and separation possibilities of Mn(II) with other associated metals are discussed.

2. Experimental

2.1. Reagents and chemicals

Bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272, Cytec, Canada), and bis(2,4,4-trimethylpentyl)dithiophosphinic acid (Cyanex 301, Cytec, Canada) were used without purification. Kerosene (Chemically pure grade) was used as diluent. Stock solutions of Mn(II) were prepared by dissolving $MnCl_2.4H_2O$ (Dae Jung, Korea) in deionized water. The pH of the aqueous phase was adjusted to desired value using AR grade hydrochloric acid and sodium hydroxide solutions.

2.2. Apparatus

A Thermo Orion star A211 pH meter was used for the measurement of pH of the aqueous solutions. The concentration of Mn in the aqueous solution was determined using inductively coupled plasma-optical emission spectrometer (Spectro, Arcos). Equilibrium experiments were carried out on a wrist action shaker (Burrel, USA).

2.3. Procedure

Solvent extraction experiments were performed by mixing equal volumes (10 mL) of aqueous and organic phases for 30 min (sufficient to attain equilibrium) using a wrist action shaker at ambient temperature. When the two phases reached the equilibrium, the mixture was separated with a separating funnel and equilibrium pH of the aqueous phase was measured. Metal ion concentrations in the aqueous phase before and after extraction were determined by ICP-OES after suitable dilutions. The concentration of metal in the organic phase was obtained by the difference between concentrations of feed and raffinate. The distribution coefficient, D, was calculated as the ratio of the concentration of metal present in the organic phase to that in the aqueous phase at equilibrium.

3. Results and discussion

3.1. Screening of extractants

The extraction of Mn(II) was investigated as a function of aqueous phase acidity from chloride solutions containing metal concentration of 500 mg/L. The initial pH was varied from 2.8 to 5.7 for extraction with 0.1 M of D2EHPA, PC 88A, Cyanex 272, and 4.16 to 7.33 for Cyanex 301 and Versatic Acid. The corresponding change in equilibrium pH was 2.2 ± 0.1 with D2EHPA, 2.7 ± 0.1 with PC 88A, 2.8–3.2 with Cyanex 272, 2.7 with Cyanex 301 and 4.1–4.9 with Versatic Acid. It was observed that with the increase of the initial pH, increment in the percent extraction of Mn was very low. The percent extraction was ~20, 8, 3, 15 and 8 with 0.1 M of D2EHPA, PC 88A, Cyanex 272, Cyanex 301 and Versatic Acid, respectively. Therefore, mixture of extractants was considered to examine the enhancement in the extraction of Mn(II). Several mixtures with different combinations have been studied, among these, a mixture of Cyanex 272 and Cyanex 301 has shown synergism. Hence,

Table 1
Summary of the literature reports on the extraction of Mn(II).

Feed composition	Medium	Extractant system	Remarks	Ref.
0.01 M Mn(II)	Sulphate solutions	Sodium salts of D2EHPA, PC 88A, and Cyanex 272 and their binary mixtures	Proposed extraction mechanism with singles extractants Mixture of NaCyanex 272 and NaPC 88A found to be the best synergistic mixture	Devi et al., 1997b
Cu(II), Zn(II), Fe(III), Fe(II), Co(II), Ni(II) and Mn(II)(each 0.02 M, single systems)	Sulphate solutions	Cyanex 301, Cyanex 302 and their binary mixtures with Aliquat 336	The pH0.5 values are 4.0, 5.1, 5.6, and 8.9 for Cyanex 301, Cyanex 302, Cyanex 301/Aliquat 336, Cyanex 302/Aliquat 336. Cyanex 301 is more efficient than Cyanex 302 and binary mixtures with Aliquat 336 are less efficient than single acid reagents	Tait, 1992
Mn(II)	Sulphate-acetato medium	Cyanex 272	Proposed mechanism of extraction and extracted species	Biswas and Rahman, 2011
Mn(II)	Sulphate solutions	Cyanex 302	Reported the mechanism of extraction and calculated the extraction equilibrium constant	Devi and Mishra, 2010
Mn(II)	Sulphate solutions	D2EHPA	Extraction equilibrium was established on the basis of graphical and numerical methods.	Tsai and Tsai, 2011
Zn(II) and Mn(II)	Sulphate solutions	Cyanex 272	Studied the solvent extraction reaction and mechanism	Devi et al., 1997a
Co(II), Mn(II)	Sulphate solutions	Mixture of Cyanex 272 and PC 88A	The extraction mechanism and possible extracted species were proposed	Zhao et al., 2011
Co(II), Mn(II), Cu(II)	Sulphate solutions	Mixture of Cyanex 272 and PC 88A	Investigated the synergistic extraction reaction and extracted species	Wang et al., 2012
Zn(II) and Mn(II)	Sulphate solutions	Mixture of D2EHPA and Cyanex 272	Investigated the synergistic effect on the separation of Zn and Mn. Also determined the extraction stoichiometry	Ahmadipour et al., 2011
Mixture of Ni(II), Co(II), Zn(II), Mn(II), Mg(II), Ca(II), Si, Na	Chloride solutions	Mixture of LIX 63, Versatic 10 and TBP	Investigation on the selection of best synergistic mixture and optimization of parameters	Cheng et al., 2010
Mixture of Cu(II), Ni(II), Co(II), Zn(II), Mn(II), Ca(II)	Chloride solutions	Mixture of LIX 63, Versatic 10 and TBP	Proposed process flowsheet for the recovery of Cu(II), Ni(II), Co(II), and Zn(II)	Zhu et al., 2012
Mn(II)	Chloride solutions	TBP	Proposed extracted species as MnCl3.3TBP	Yadav and Khopkar, 1969