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Selective extraction and recovery of copper from chloride solution using Cextrant 230

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ABSTRACT

The extraction behavior of Cu(II) from chloride solution was investigated using di(2-ethylhexyl) [N-(2-ethylhexyl)aminomethyl] phosphonate (Cextrant 230, L). Cextrant 230 has a higher selectivity for Cu(II) over other divalent metal ions, e.g. Co(II), Ni(II), Mg(II) and Ca(II). The effect of the concentration of chloride ion and the extractant, aqueous pH values and temperature on the Cu(II) extraction was studied in detail. A possible extraction mechanism was proposed and the extracted complex was determined to be $CuCl_2 \cdot 3L$ by the slope analysis method. Thermodynamic parameters (ΔG, ΔH and ΔS) were calculated, suggesting that the copper extraction was an exothermic process. The loading capacity of 30% (v/v) Cextrant 230 was 16.9 g Cu/L. The loaded Cu(II) can be stripped efficiently by HCl, HNO_3 and H_2SO_4. A extraction process for the selective extraction and recovery of Cu(II) from a raffinate obtained after the recovery of rare earths from the waste NdFeB magnets was proposed, by which the purity of copper product reached 99.5% with a yield of 98.0%.

1. Introduction

Copper, as a ductile, corrosion resistant and malleable non-ferrous metal, is widely used in electrical, light industry, machinery manufacturing, construction industry, defense industry and other fields (Baba et al., 2015; Elsentriecy et al., 2015). It is also added to improve the performance of magnets. With the booming development of mechanical and electronic products, a large amount of rare earth permanent magnets have been produced and used. As a result, a large amount of waste magnets will be produced during the manufacture of the magnets or by the end-of-life motors. In order to save precious resources and protect the environment, it is important to recover and reuse these secondary resources, not only rare earths but also the additives such as copper (Smolinski et al., 2017).

Compared to other separation methods such as precipitation, ion exchange and adsorption, solvent extraction is a cheap and high-efficiency technique for preparing high purity copper (Liao et al., 2001; Sinha et al., 2016; Xu et al., 1992). Various extractants have been applied in the copper extraction from sulfate medium (Sole and Hiskey, 1995; Devi, 2016; Kumar et al., 2013; Navarro and Alguacil, 1999; Reddy and Priya, 2005; Sandhibigraha and Sarma, 1997). Borowiak-Resterna (1994) reported the copper extraction from chloride medium using N-alkyl-3-pyridinecarboxamides and *N,N*-di-alkyl-3-pyridinecarboxamides and determined the extracted species being $CuCl_2L_2$, where L stands for the extractant. Strikovsky et al. (1996) studied the extraction of copper from chloride solution by solvent impregnated resins containing di-(2-ethylhexyl) dithiophosphoric acid (HL), and deduced the extracted complexes to be $CuCl_2(HL)_8$ and $CuClL(HL)_8$. However, it is more difficult to obtain high quality copper from chloride medium than from sulphate solutions (Lu and Dreisinger, 2013).

Recently, aminophosphonates have drawn considerable attention and widely used as fungicide, plant virucide, anti-tumor agents, extractants, and so on (Hu et al., 2008; Mucha et al., 2011; Ranu and Hajra, 2002). This kind of extractants have many advantages including easy synthesis, good thermal stability, low emulsification ability and high extraction capacity towards the metal ions (Lu et al., 2017). In our previous work, a series of neutral α-aminophosphonates were synthesized for the extraction and separation of Ce(IV)/Th(IV)/RE(III) and Zr(IV)/Hf(IV) (Chen et al., 2017; Kuang et al., 2017; Le et al., 2018; Lu et al., 2017; Wei et al., 2017). For instance, Ce(IV) and Th(IV) can be selectively extracted and separated from trivalent rare earths using di(2-ethylhexyl) [N-(2-ethylhexyl)aminomethyl] phosphonate (Cextrant 230). And 99.9% CeO_2 and 99% ThO_2 can be obtained from the bastnasite leaching by two step extraction process (Lu et al., 2017). The

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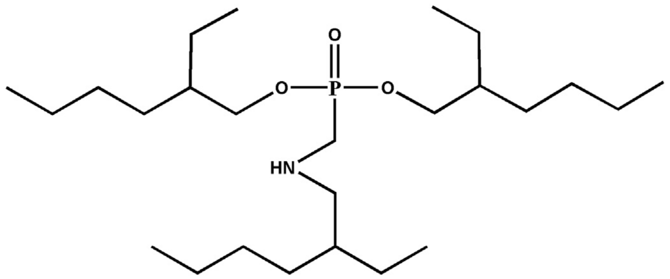

Fig. 1. Molecular structure of Cextrant 230.

alkyl steric hindrance of the amino group has little effect on the extraction performance of the extractants towards Ce(IV), Th(IV) and RE (III) (Kuang and Liao, 2018). However, up to now, to the best of our knowledge, α-aminophosphonates have not been applied in the copper extraction. Herein Cextrant 230 (abbreviate as L, shown in Fig. 1) was chosen as the extractant for the selective extraction of copper from chloride medium. The extraction ability and separation performance of Cextrant 230, the extraction mechanism of copper, loading capacity and stripping properties were investigated. A process for extracting and recovering copper from a raffinate after the recovery of rare earths from the waste NdFeB magnet was also proposed.

2. Experiment

2.1. Reagents and apparatus

Cextrant 230 was synthesized and purified as reported by Lu et al. (2017). The extractant dissolved in *n*-heptane was used as the organic phase. Aqueous solutions were prepared by dissolving $CuCl_2·2H_2O$, $CoCl_2·6H_2O$, $NiCl_2·6H_2O$, $MgCl_2·6H_2O$ and anhydrous $CaCl_2$ with deionized water respectively and diluting to the required concentrations. All other chemical reagents were of reagent grade.

FT-IR spectra were recorded on a Vector22/N spectrometer (Bruker, Fllanden, Switzerland). The sample was prepared by dabbing the organic phase over a KBr crystal and then heating it under an infrared lamp to remove the solvent. The pH of the aqueous phase was carried out with a model PHS-3C digital pH meter (Shanghai REX Instrument Factory). The metal concentrations were analyzed by an inductively coupled plasma-optical emission spectrometer (ICP-OES, PerkinElmer Optimal 8000).

2.2. Extraction procedures

The extraction equilibrium experiments were carried out by mixing equal volumes (3 mL) of aqueous solution and organic phase in equilibrium tubes placed in a thermostatic air bath chamber and then shaking vigorously for 30 min at 298 ± 1 K (unless specifically stated). After the phases were separated, the equilibrium concentrations of metal ions in the aqueous solutions, $[M]_{(a)}$, were measured by ICP-OES. The metal concentrations in the organic phase, $[M]_{(o)}$, were calculated by mass balance. The stripping was performed by contacting equal volumes of loaded organic phase with mineral acids of different concentrations in a funnel and shaking for 30 min at 298 ± 1 K.

The extraction percentage (*E*%), distribution ratio (*D*), separation factor (*β*) and stripping ratio (*St%*) are expressed in the following Eqs. (1)–(4).

$$E\% = \frac{[M]_{(o)}}{[M]_{(a)} + [M]_{(o)}} \times 100 \tag{1}$$

$$D = \frac{[M]_{(o)}}{[M]_{(a)}} \tag{2}$$

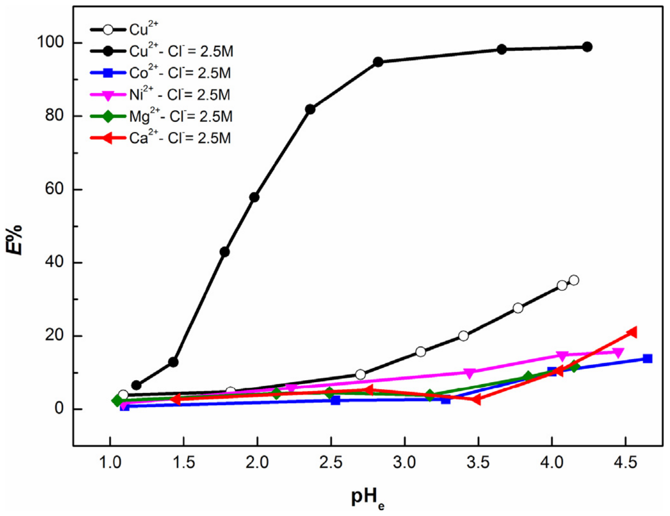

Fig. 2. Effect of the equilibrium pH on the extraction of Cu(II), Co(II), Ni(II), Ca (II) and Mg(II). Organic phase: [L] = 0.10 mol/L. Aqueous phase: $[M^{2+}]$ = 0.010 mol/L, with/without 2.5 mol/L NaCl.

$$\beta = \frac{D_1}{D_2} \tag{3}$$

$$St\% = \frac{[M]_{(a)}}{[M]_{(o,init)}} \times 100 \tag{4}$$

where D_1 and D_2 are the distribution ratios of two metal ions M_1 and M_2, respectively. $[M]_{(o,\ init)}$ denotes the initial concentration of metal ions in the loaded organic phase.

3. Results and discussion

3.1. Effect of the equilibrium pH on the copper extraction

The effect of the equilibrium pH on the copper extraction was investigated using 0.10 mol/L Cextrant 230 in the presence or absence of salting-out reagent (2.5 mol/L NaCl). Meanwhile, for comparison, the extraction of Co(II), Ni(II), Ca(II) and Mg(II) by Cextrant 230 was also studied under the same conditions. All the initial concentrations of the metal ions were of 0.010 mol/L.

As shown in Fig. 2, the pH values have obvious influence on the extraction of copper. In the absence of the NaCl salting-out reagent, the copper extraction increases slowly with the increasing aqueous equilibrium pH to about 40% at pH = 4.2. However, in the presence of the NaCl salting-out reagent, the copper extraction increases sharply with the increasing aqueous equilibrium pH to 94.8% at pH = 2.8 and then nearly keeps unchanged afterward. It can be explained that the addition of the salting-out reagent promotes the formation of copper-chloride complex species which are easier to be extracted. For comparison, the extraction of other divalent metal ions, e.g. Co(II), Ni(II), Ca(II) and Mg (II) was also investigated in the presence of the salting-out reagent. The extraction of these divalent ions increases slightly with the increasing equilibrium pH to ≤ 20% at pH = 4.5.

The separation factors (*β*) between copper and other divalent metal ions in the presence of the salting-out reagent at different equilibrium pH value are tabulated in Table 1. It is found that the separation factors increase sharply with increasing equilibrium pH values. For example, the $\beta_{Cu/Co}$ value increases obviously from 7.8 at pH = 1.18 to 779 at pH = 3.66. Therefore, Cextrant 230 would be used to separate Cu(II) efficiently from the impurities such as Co(II), Ni(II), Ca(II) and Mg(II) in the presence of the salting-out reagent.