A Solvent Extraction Design for Separation-Recovery of Heavy Metals Using Amic Acid Extractants

[M. R. Yaftian,* H. Soltani, A. A. Zamani. M. Ghorbanloo]

Abstract — **A multistep solvent extraction design based on the application of two amic acid extractants, named 2-(dibutylcarbamoyl)benzoic acid and 4-(dibutylamino)-4-oxobut-2-enoic acid, and their mixtures with 2-thenoyltrifluoro acetone and tributylamine is presented for the separation and recovery of Pb^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+} ions from industrial wastes and end-of-life products.**

Keywords—Amic acid ligands, Solvent extraction, Heavy metals

I. Introduction

The world demand for various metals is increasing. This enforces the use of raw materials to be extended to the industrial wastes and spent products. In addition to economical aspect, the environmental requirements impose the development of effective methods for the recovery of certain metals from secondary sources [1]. There is a variety of spent products containing economically valuable, and environmentally toxic, metals which can be considered as secondary sources. Solvent extraction is known as an effective method widely used for separation and removal of different target metal ions [2]. A key point for achieving to a successful extraction procedure is the selection of appropriate extractants. The control of selectivity of an extractant process by aquous phase pH is a grand advantage of acidic ligand [3]. The potential of amic acids as selective extractants for lanthanides has been demonstrated [4]. Besides, the binding abilities of 2-thenoyltrifluoro acetone (HTTA) [5] and the synergistic effect of tributyl amine (TBA) [6] towards metal ions are well documented. By considering these potentials, the application of these extractants for separation of heavy metal ions from industrial wastes was realized and following to our previous works on the recovery of economically and environmentally important metals from end-of-life products [7], the present communication reports an extraction multistep design for separation of Pb, Cd, Zn, Co and Ni from leach solution of the above mentioned secondary sources.

II. Experimental

A. Reagents and materials

Phthalic anhydride, dibutylamine, sodium solfate

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anhydrous, maleic anhydride, cyclohexane and dichloromethane (Fluka) were used for preparation of the amic acids 2-(dibutylcarbamoyl)benzoic acid and 4-(dibutylamino)-4-oxobut-2-enoic acid. Metal nitrates, HTTA and TBA were analytical reagent grade (Merck). A stock solution of 1000 ppm of the metal ions was prepared from the nitrate salts (Merck). The working solutions were prepared by diluting the stock solutions with deionized water to appropriate volumes. The pH of the solutions were adjusted with HCl acid or NaOH (Merck) solutions.

B. Instrumentation

Fourier transform infrared (FT-IR) spectra was recorded on a Thermo-Nicolet-is10 FT-IR spectrometer. NMR data obtained from a Bruker NMR 250MHz. Separation of the phases was performed using a centrifuge Heraeus Labofuge 300. A Metrohm pH meter (model 780) with a combined pH electrode was used for pH measurements. A flame atomic absorption spectrometry (Varian 220), was used for determination of metal ions.

C. Synthesis of amic acids

The extractant 2-(dibutylcarbamoyl)benzoic acid (HL^1) obtained by reaction of phetalic anhydride and dibutylamine in dichloromethane. The second amic acid 4-(dibutylamino)-4-oxobut-2-enoic acid (HL^2) was synthesized by reaction of maleic anhydride and dibutylamine in dichloromethane. The resulting products was washed repeatedly with n-hexane, dried in air and characterized by IR spectroscopy and $^1H(^{13}C)$ NMR.

D. Extraction procedures

Equal volumes of organic phase (single ligand or a mixture with synergistic agent in dichloromethane) and aqueous phase containing metal ions in 0.1 M sodium chloride, were contacted for 20 min. at 25°C. The phases were then disengaged with help of centrifugation. The metal ions in the aqueous phase and those in the organic phase after stripping with 0.1 M nitric and sulphuric acids were measured by FAAS method.

III. Results and discussion

Application of HL^1 dissolved in dichloromethane showed that it can extract selectively lead ion from its mixture with Cd, Zn, Co and Ni ions and 0.1 M sodium chloride (Fig. 1). Log-log analysis was used for determination of the extracted complexes. It was shown a 1:2 metal to ligand ratio for the extracted species.
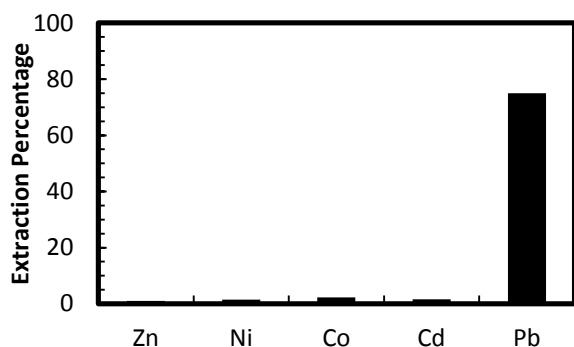
Fig. 1. Extraction of Pb(II) from Co(II), Cd(II), Zn(II) and Ni(II) ions (1×10^{-4} M) from NaCl (0.1 M) solution by HL^1 (0.05 M), aqueous phase pH=4, at 25 °C, stirring time 20 min.

After removing lead ions from the mixture containing Pb, Ni, Co, Cd and Zn ions, by HL^1 dissolved in dichloromethane, the aqueous phase was contacted with a mixture of HL^1 and tributylamine (1:1 ratio) which showed a selective attitude for removal of zinc ions. The results are shown in Fig. 2. The extracted zinc ions were quantitatively stripped with a 0.1 M solution of sulfuric acid. A high selectivity towards zinc ions was observed by using the mixture of HL1 and TBA with respect to their use alone. It was found that the extracted species have a stoichiometry of 1:2:1 metal:HL^1:TBA.
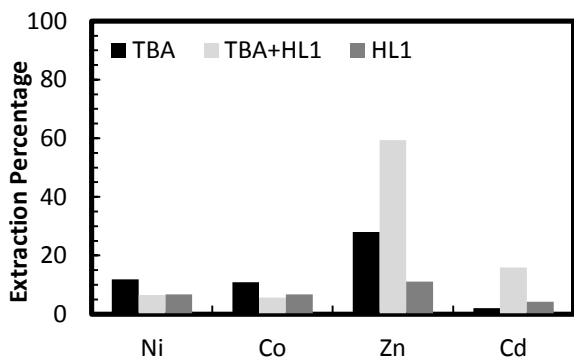

Fig. 2. Investigation of synergism effect by mixture of HL^1 (0.01M) and TBA(0.01M) for the extraction of Co(II), Cd(II), Zn(II) and Ni(II) ions (1×10^{-4} M) from NaCl (0.1 M) solution, aqueous phase pH=4, at 25 °C, stirring time 20 min.

Although HL^2 was not able in extent to extract the investigated metal ions under the experimental conditions used, its mixture with HTTA selectively extract nickel ions. It means a synergistic effect can be taken place towards these ions by the mixture of HL^2 and HTTA (Fig. 3). Log-log analysis revealed the nickel ions are extracted by formation of 1:1:2 metal:HL^2:HTTA ratio. Back extraction of nickel ions was successfully performed by using a 0.1 M solution of sulfuric acid.
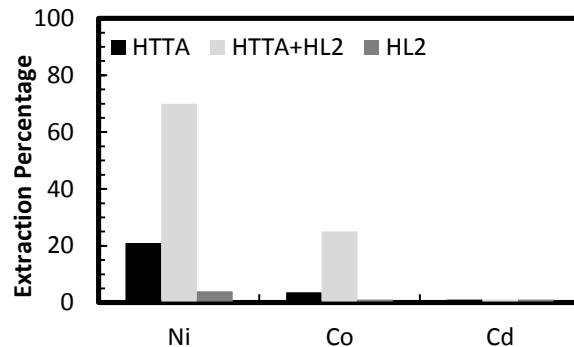

Fig. 3. Synergistic extraction of Ni(II), Co(II) and Cd(II) ions (1×10^{-4} M) from NaCl (0.1 M) solution, aqueous phase pH=4by mixture of HL^2 (0.01 M) and HTTA (0.01 M), for, at 25 °C, stirring time 20 min.

A selective attitude was observed towards cobalt ions for the extraction of these ions from their mixtures with cadmium ions, by using a 1:1 mixture of HL^1 and HTTA (Fig. 4). Thus it is possible to separate cobalt ions from cadmium ions at the last step of the separation design of the studied ions. The loaded organic phase by cobalt ions was quantitatively stripped by using a diluted sulfuric acid solution (0.1 M).

It is noteworthy that the analysis of the extraction data revealed that the 2-thenoyltrifluoroacetone in the synergistic adducts has mutual roles as neutral donor and chelating.
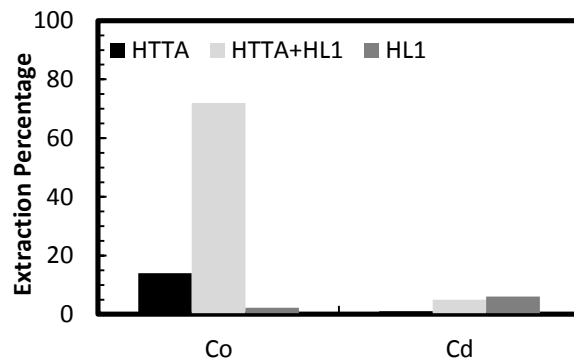

Fig. 4. Investigation of synergism effect of mixture of HL^1 (0.01 M) and HTTA (0.01M) on the extraction of Co(II), Cd(II) ions (1×10^{-4} M) from NaCl (0.1 M) solution, aqueous phase pH=4, at 25 °C, stirring time 20 min.

By separation of lead, zinc, nickel and cobalt, a major amount of cadmium remained in the aqueous phase and thus a separation of the studied metal ions can be achieved. These results conduct us to examine other concentration of the ligands for improving the efficiency of the target separation process. The outcome was a design shown in Fig. 5, for the separation of the investigated metal ions from a synthetic solution containing these ions.
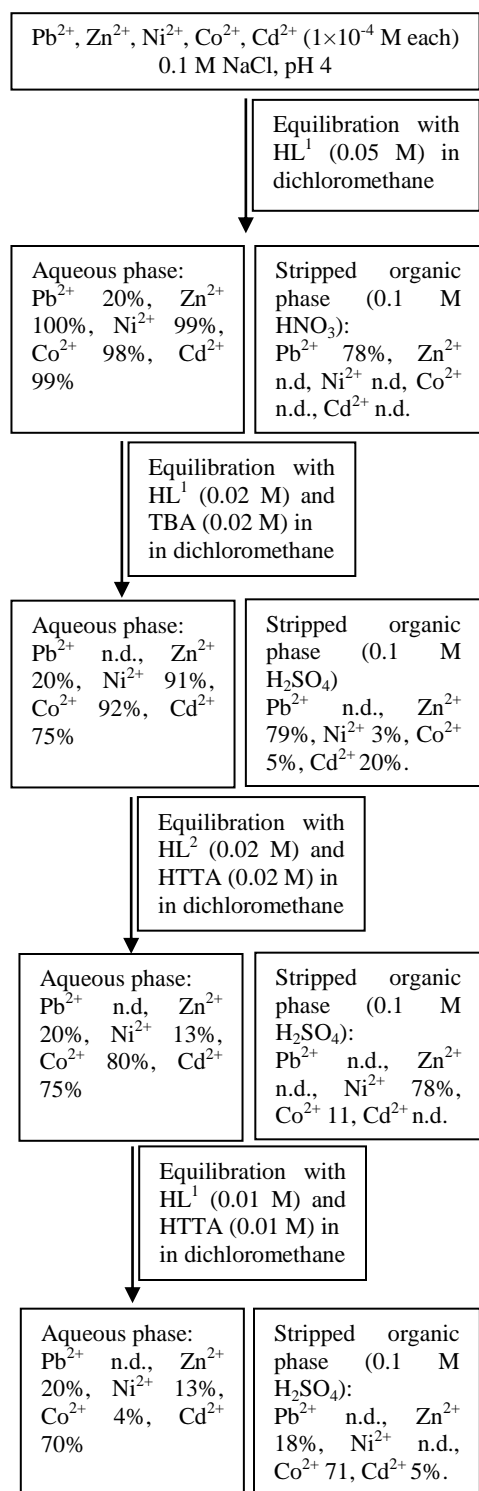
IV. CONCLUSIONS

The presented work is an introduction for designing a solvent extraction procedure for separation of heavy metal ions Pb(II), Zn(II), Ni(II), Co(II) and Cd(II) ions by using newly synthesized extractants 2-(dibutylcarbamoyl)benzoic acid (HL^1) and acid 4-(dibutylamino)-4-oxobut-2-enoic acid (HL^2). It is found that mixture of these with 2-thenoyltrifluoro acetone and tributylamine shows different extracting properties with respect to the amic acid alone. With help of this attitude a design for the extraction of the target ions was proposed and examined on a simulated mixture of the studied metal ions. The progress of the work particularly for using it on industrial wastes and used products is due course.

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Fig. 5. Proposed design for separation of Pb(II), Zn(II), Ni(II), Co(II) and Cd(II) from sodium chloride solution (0.1 M) by HL^1, HL^2 and their mixtures with TBA and HTTA.