A Study on the Extraction of Cd(II), Co(II) and Ni(II) Ions by Bis(2-ethylhexyl)phosphoric Acid and 2-Thenoyltrifluoroacetone

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ABSTRACT: Keep in mind the importance of cadmium, cobalt and nickel ions as environmentally and economically strategic heavy metals, the application of two acidic extractants, named bis(2-diethylhexyl)phosphoric acid (DEHPA) and 2-thenoyltrifluoroacetone (HTTA), was assessed for the extraction-recovery of these ions from leached solution of spent rechargeable Ni-Cd batteries. The conditions for leaching of metal contents in solid materials of the batteries were optimized. The effect of parameters influencing the process for achieving to an efficient and selective extraction of Cd, Co and Ni ions from synthetic samples and leach liquor of spent Ni-Cd batteries was investigated.

KEY WORDS: Liquid-liquid extraction, Bis(2-ethylhexyl)phosphoric acid, 2-Thenoyltrifluoroacetone, Cadmium, Cobalt, Nickel.

INTRODUCTION
The world demand for metals is progressively increasing, while primary sources are being depleted. Thus, the range of raw materials is expanded to the end-of-life products. Beside this 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 end-of-life products which can be considered as secondary sources. Spent rechargeable nickel-cadmium batteries form an important group of these products. This type of batteries is used in various devices such as cordless power tools, cordless telephones, communications devices and emergency lighting [2]. These batteries are classified as hazardous waste, because nickel and cadmium are suspected carcinogens [3,4]. Hydrometallurgical processes are among the most applied methods for the recovery of heavy metal ions from various sources. Xue et al. [5] published a review on the methods for recovering heavy metals from different real waste samples. Commercial extractants Cyanex 272 [6] and Cyanex 923 [7] have been examined for the extraction of nickel and cadmium ions from synthetic mixtures. These extractants were used by Reddy et al. [8] for the solvent extraction of cadmium and nickel ions from chloride leach liquor of spent nickel-cadmium batteries. A hydrometallurgical method was developed for recovery of nickel and cadmium from used rechargeable batteries by Rudnik & Nikiel [9]. Recently, the separation-recovery of cadmium and nickel ions from sulfate solutions with TOPS 99 as extractant alone...
and in combination with Cyanex 471X as a synergistic reagent was studied [10]. Following to our studies on the separation, concentration and recovery of hazardous metal ions [11-16], the present work deals with the acid leaching of cadmium, cobalt and nickel from spent nickel-cadmium batteries followed by solvent extraction separation by bis(2-ethylhexyl)phosphoric acid (DEHPA) and 2-thenoyltrifluoroacetone (HTTA) extractants. To the best of our knowledge this the first report on the application of HTTA for the recovery of Cd, Co and Ni ions from leach liquor of rechargeable batteries. In addition, the results allow a comparison of the extraction properties of these ligands towards target ions.

EXPERIMENTAL SECTION

Apparatus and materials
A Varian atomic absorption spectrometer (model AA220) and a pH-meter Metrohm (model 780) were used for metal determinations and pH adjustments, respectively. Bis(2-ethylhexyl)phosphoric acid (DEHPA), 2-thenoyltrifluoroacetone (HTTA) and tri-n-octylphosphine oxide (TOPO), from Merck, were used as received. Solvents (Merck) used were washed three times with distilled water in order to remove the solvent stabilizers and saturate them by water. The stock solution of cadmium, cobalt and nickel solutions were prepared by dissolving the requisite quantity of the corresponding sulfates (Fluka). The solutions then were standardized complexometrically. All other reagents were of laboratory reagent grade and were from Merck or Fluka chemical companies.

Extraction experiments
The solvent extraction experiments were carried out in stoppered glass tubes immersed in a thermostated water bath (22 °C) using equal volumes (10 mL) of the organic and the aqueous phases. The extraction equilibrium was reached after 30 min under continuous magnetic stirring. After equilibration, the concentration of remained metal ions in the aqueous phase was determined by atomic absorption spectrometry. The metal content in the organic phase was measured similarly, after back-extraction with diluted solution of sulfuric acid (0.5 M).

Leaching studies
Leaching experiments of metals from solid materials of spent batteries (Panasonic, Sony, Philips) were carried out with varying sulfuric acid concentration (0.25-6 M), solid-to-liquid ratios (1:7 to 1:40), leaching time (5-21 h) and temperature (25-50°C). The batteries were first dismantled to remove the battery materials. The results of these tests indicate that the percentage dissolution of cadmium, cobalt and nickel increases with concentration of acid, temperature and time, and decreases with increase in the solid-to-liquid ratio. Five replicate leaching experiments on the separated materials under selected conditions, i.e. 3.5 M sulfuric acid, 1:10 solid-to-liquid ratio, 11 h of stirring and at 50°C, show the percentage of cadmium, cobalt and nickel being removed from the solid materials equals to 17.3 (±0.2), 3.4 (±0.2) and 34.1 (±0.3) weight percent, respectively. The resulted solution was diluted with distilled water and adjusted at desired pH for performing the extraction experiments.

RESULTS AND DISCUSSION

Effect of pH
In order to ascertain extractive abilities of DEHPA and HTTA, the extraction of Cd (3.1×10⁻⁴ M), Co (1.2×10⁻⁵ M) and Ni (1.2×10⁻⁴ M) from synthetic aqueous samples into dichloromethane solution of one of the extractants was performed at 22 °C. The results are shown in Fig. 1.

The variation of extraction percentage versus pH reveals a cation exchange mechanism for the process. The existence of considerable extraction percentages at lower pH values, particularly by HTTA, may be attributed to an extraction via a solvation mechanism at these pH ranges. A decrease in the extraction at higher pH value is envisaged as a result of the metal hydroxide formation.

For both extractants the maximum extraction percentage of cadmium is observed at pH 5.13. However this maximum for cobalt and nickel ions was located at pH 3.82. The extraction values, the corresponding distribution ratios and the selectivity factors towards cadmium ions (at pH 5.13) and cobalt ions (at pH 3.82) in comparison to the two other metal ions are presented in Table 1.

The results demonstrate at pH 5.13 both of the extractants are selective towards cadmium ions. However, a better separation can be achieved by using DEHPA with respect to HTTA. At pH 3.82 both of the extractants present a similar selectivity towards cobalt ions.
Table 1: Extraction percentage, distribution ratio and selectivity factor of cadmium, cobalt and nickel ions by DEHPA and HTTA (0.25 M) in dichloromethane.

<table>
<thead>
<tr>
<th>pH</th>
<th>Parameter</th>
<th>DEHPA</th>
<th>HTTA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cd</td>
<td>Co</td>
</tr>
<tr>
<td>5.13</td>
<td>E%</td>
<td>99.7</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td>D_M</td>
<td>3332.3</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>SF_Co/M</td>
<td>-</td>
<td>3.64</td>
</tr>
<tr>
<td>3.82</td>
<td>E%</td>
<td>46</td>
<td>70.8</td>
</tr>
<tr>
<td></td>
<td>D_M</td>
<td>0.85</td>
<td>2.40</td>
</tr>
<tr>
<td></td>
<td>SF_Co/M</td>
<td>0.45</td>
<td>-</td>
</tr>
</tbody>
</table>

*Extraction percentage. ‡Distribution ratio, D_M=[M]_org/[M]_aq. §Selectivity factor, SF_M/M’=log[D_M/D_M’].

Fig. 1: Solvent extraction of Cd(II), Co(II) and Ni(II) ions from a synthetic sample containing 3.1×10^-4, 1.2×10^-5 and 1.2×10^-4 M, respectively by a 0.25 M solution of DEHPA (a) and HTTA (b) in dichloromethane as a function of the aqueous phase pH.

Effect of organic diluent

Organic diluents influence both the selectivity and efficiency of the extraction processes. In order to investigate the effect of this parameter a series of extraction experiments was carried out by using chloroform, ethylacetate, xylene (mixture of isomers) and kerosene. The results, together with those obtained by using dichloromethane, are shown in Table 2.

The results obviously comport the effect of diluent on both extraction efficiency and extraction selectivity of the extractants. Although the extraction percentage of cadmium ions by DEHPA in kerosene and dichloromethane at pH 5.13 is higher than cobalt and nickel ions, the selectivity towards Cd(II) ions is more pronounced in dichloromethane. The application of chloroform, in place of dichloromethane, lowers the extraction of cadmium ions by both of the extractants at pH 5.13. In contrast, chloroform enhances significantly the extraction percentage of cobalt and nickel ions with a preference towards cobalt ions. By using ethylacetate, DEHPA prefers to extract cadmium and nickel ions at pH 5.13, whereas the extraction of cobalt ions decreases sharply in comparison to its solution in chloroform.

At both pH values, HTTA dissolved in ethylacetate extracts more efficiently cobalt and nickel ions. No pronounced selectivity is found by using xylene as diluent for both of the extractant at pH 5.13. The comparison of the results obtained in the extraction of the studied ions by HTTA in dichloromethane, chloroform, xylene and kerosene at pH 5.13 is near to those described for DEHPA. The lowest extraction efficiency is observed towards cadmium ions by HTTA in ethylacetate.
Table 2: Extraction percentage of cadmium, cobalt and nickel ions by DEHPA and HTTA dissolved in different diluents.

<table>
<thead>
<tr>
<th>pH</th>
<th>Diluent</th>
<th>DEHPA</th>
<th>HTTA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Cd</td>
<td>Co</td>
</tr>
<tr>
<td>5.13</td>
<td>Dichloromethane</td>
<td>99.7</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td>Chloroform</td>
<td>65.1</td>
<td>80.3</td>
</tr>
<tr>
<td></td>
<td>Ethylacetate</td>
<td>58.5</td>
<td>0.9</td>
</tr>
<tr>
<td></td>
<td>Xylene</td>
<td>71.2</td>
<td>68.5</td>
</tr>
<tr>
<td></td>
<td>Kerosene</td>
<td>60.1</td>
<td>7.9</td>
</tr>
<tr>
<td>3.82</td>
<td>Dichloromethane</td>
<td>46.1</td>
<td>70.8</td>
</tr>
<tr>
<td></td>
<td>Chloroform</td>
<td>69.2</td>
<td>70.8</td>
</tr>
<tr>
<td></td>
<td>Ethylacetate</td>
<td>47.4</td>
<td>72.5</td>
</tr>
<tr>
<td></td>
<td>Xylene</td>
<td>68.3</td>
<td>75.6</td>
</tr>
<tr>
<td></td>
<td>Kerosene</td>
<td>50.1</td>
<td>12.2</td>
</tr>
</tbody>
</table>

Experimental conditions were similar to those presented in the caption of Fig. 1. The values are the mean of three independent extraction experiments with $\sigma_{N-1} \leq 0.6\%$.

A different attitude of the tested diluents on the extraction properties of DEHPA and HTTA at pH 3.82 was obtained. The performance of the extraction process by DEHPA at this pH is very similar in dichloromethane and ethylacetate. Similar selectivity order i.e. $\text{Co}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$ was found for HTTA dissolved in dichloromethane and ethylacetate. The efficiency of this extractant in ethylacetate towards cadmium ions is lower than that in dichloromethane. It is noteworthy that, DEHPA and HTTA dissolved in kerosene show the lowest selectivity towards cobalt ions at pH 3.82. At this pH both of the extractants in other tested diluents are selective for cobalt ions.

**Design of an extraction scheme**

Based on the results obtained in the previous sections, a separation scheme for recovery of cadmium ($3.5 \times 10^{-3}$ g/L), cobalt ($7.1 \times 10^{-4}$ g/L) and nickel ($7.0 \times 10^{-3}$ g/L) ions from a synthetic sample by using DEHPA in dichloromethane and HTTA in xylene was designed (Fig. 2a). In this design an aqueous phase (20 mL, pH 5.13) was equilibrated with a solution of DEHPA in dichloromethane (0.25 M, 20 mL). After equilibration (30 min.), the phases were separated and the organic phase was stripped with a 0.5 M sulfuric acid solution. The results show an extraction value $>99\%$ of cadmium ions, whereas the percentage of cobalt and nickel ions extracted into the stripping solution was found to be $3.7\%$ ($2.6 \times 10^{-2}$ g/L) and $5.1\%$ ($3.6 \times 10^{-1}$ g/L), respectively. The analysis of the aqueous phase after equilibration show the remained cadmium is negligible. However, the remaining content of cobalt and nickel ions was found to be $96.3\%$ ($6.84 \times 10^{-4}$ g/L) and $94.9\%$ ($6.64 \times 10^{-3}$ g/L) with respect to their initial concentration, respectively.

In the second step, the latter aqueous phase was equilibrated with a solution of HTTA in xylene (0.25 M). The phases were separated and the metal ions in the aqueous phase were analyzed. The results show that the raffinate contains only nickel ions with a concentration of $4.64 \times 10^{-3}$ g/L ($66.3\%$ of its initial value). The analysis of the organic shows that the recovered cobalt and nickel ions equals to $6.83 \times 10^{-4}$ and $2.0 \times 10^{-3}$ g/L ($96.2$ and $32.3\%$ the initial concentrations), respectively.

The analysis of “aqueous solution I” show an increase in the $[\text{Cd}]/[\text{Ni}]$ ratio from 0.5 to near $10$ ($\sim 18$ times enrichment) and that of $[\text{Cd}]/[\text{Co}]$ ratio from about 5 to 122 ($\sim 24$ times enrichment). The proposed design allows separation and purification of nickel ions with a recovery of $65.7\%$ (aqueous solution II). It permits to remove the cadmium ions from the solution containing two other metal ions and increases the $[\text{Co}]/[\text{Ni}]$ ratio from 0.1 to 0.3 (aqueous solution III).

Although the synthetic sample was prepared considering the concentration of cadmium, cobalt and nickel ions in the leached solution of spent batteries, the applicability of the designed method was assessed by performing the separation of studied metal ions from the real sample. The results are shown in Fig. 2b. It is seen the existence of some differences between the results obtained for the separation of Cd, Co and Ni ions for synthetic and those
Fig. 2. Scheme of the separation of cadmium, cobalt and nickel ions from a synthetic sample (a) and a real sample prepared by leaching the residue of the material of spent rechargeable Ni-Cd batteries (b) by consecutive extraction using DEHPA in dichloromethane and HTTA in xylene. In this scheme "n.d." means the amount of the ions is not detectable.
for the real sample. This investigation shows the applicability of the method in some extent for the real sample.

**Effect of the presence of TOPO as synergistic agent**

The extraction of cadmium, cobalt and nickel ions from the leach liquor of spent batteries was tested by DEHPA and HTTA in the absence and in the presence of TOPO as synergistic agent in dichloromethane. The obtained results are regrouped in Table 3. The data confirm a synergistic extraction of cadmium and nickel ions by both extractants in the presence of TOPO. In contrast, an antagonist interaction was observed for cobalt ions. It is noteworthy that the order of selectivity presented in the extraction of the studied ions at pH 3.82 by DEHPA differs from that obtained by the mixture of DEHPA and TOPO. However, this selectivity was remained invariant in the extraction by the acidic extractants DEHPA or HTTA alone or their mixtures with TOPO.

**Multi-step extraction process**

A 50 mL of a synthetic solution of Cd, Co and Ni ions with the concentration of $3.5 \times 10^{-3}$, $7.1 \times 10^{-4}$ and $7.0 \times 10^{-3}$ g/L, respectively, at pH 5.13 was contacted with a dichloromethane solution of DEHPA. After equilibration, the organic phase (50 mL) was stripped with 50 mL of diluted sulfuric acid solution (0.5 M). This latter solution contains $3.47 \times 10^{-3}$ (99.7%), $5 \times 10^{-3}$ (7.1%) and $8.7 \times 10^{-4}$ (12.4%) g/L of cadmium, cobalt and nickel, respectively. The raffinate contained $6.4 \times 10^{-4}$ (90.1%) and $6.0 \times 10^{-3}$ (85.7%) g/L of cobalt and nickel. Two 25 mL portions of this solution were selected. The metal ions in one of these portions were extracted by 25 mL of DEHPA solution (0.25 M) in dichloromethane. Determination of the metals in the organic phase after performing a back-extraction step showed the extraction values of cobalt and nickel ions to be $3.3 \times 10^{-4}$ (51.6%) and $3.9 \times 10^{-3}$ (65%) g/L, respectively.

For investigating the effect of multi-step extraction on the separation of cobalt and nickel ions, the second 25 mL portion of the raffinate (containing cobalt and nickel) was contacted in five steps with 5 mL of DEHPA in dichloromethane. The amount of metal ions extracted in each step and the variation in the [Ni]/[Co] concentration ratio are presented in Table 4. It is seen that the total amount of cobalt and nickel recovery was enhanced in multi-step extraction process with respect to that of single-step (83.6 and 95.0 percent for cobalt and nickel, versus 51.6 and 65.0 percent, respectively).

It is noteworthy that the nickel to cobalt concentration ratio in the initial raffinate was 9.4. This ratio is enhanced to 11.8 in the single-step process, whereas this value for the total amounts of recovered metal ions in multi-step extraction is reached to a value of 10.7. This shows that the multi-step process demonstrates a poorer selectivity with respect to that of single-step process.

A similar investigation has been performed on the leached solution of spent Ni-Cd batteries (Table 5). As it is seen the separation factor obtained by performing a single-step extraction process is higher than that found by multi-step process (i.e the ratio of [Ni]/[Co] increases...
from 9.4 to 12.8 and 11.1 by the single-step and multi-step process, respectively). In contrast the extraction efficiency is enhanced by using the multi-step extraction. In fact, the recovery of cobalt and nickel enhances from 51.6 and 65.0 percent in single-step process to 73.1 and 87.9 percent by multi-step extraction process.

**CONCLUSIONS**

Bis(2-ethylhexyl)phosphoric acid (DEHPA) and 2-thenoyltrifluoroacetone (HTTA) are efficient extractants for Cd, Co and Ni ions. The selectivity and efficiency of the process are profoundly affected by the aqueous phase pH and the type of organic diluent. It is shown that the presence of tri-n-octylphosphine oxide (TOPO) influences synergistically the extraction of nickel and cadmium ions by DEHPA and HTTA. This effect was also observed for the extraction of cobalt by the mixture of HTTA and TOPO. In contrast, an antagonist effect was found for the extraction of cobalt by the mixture of DEHPA and TOPO. An extraction scheme using DEHPA in dichloromethane and HTTA in xylene allows decontamination of the leach liquor of the spent rechargeable batteries from hazardous cadmium ions, and a near 50% recovery of nickel with respect to its initial amount. Multi-step process enhances the extraction efficiency in comparison with a single-step process. However, this advantage is not accompanying with a better separation factor.

**REFERENCES**


