A Solvent Extraction Design
for the Selective Separation of Cadmium, Nickel, and Cobalt
from Spent Rechargeable Ni-Cd Batteries

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ABSTRACT: *The hydrochloric acid leaching of cadmium, nickel, and cobalt from the dismantled powder of spent rechargeable nickel-cadmium batteries was optimized by the response surface methodology. The optimized parameters included HCl concentration, powder mass, temperature, and solid/solution contact time. The optimal values were 100 mL of 2.6 M HCl, 4.4 g of powder, temperature 48.6 °C, and time 3.19 h. The concentrations of Cd, Ni, and Co in the leach solution were 13500, 12150, and 900 mg/L, respectively. The designed process involved a two-step solvent extraction/back-extraction procedure using 0.5 mol/L trioctylamine (TOA) in dichloromethane as the organic phase. The first step consisted of four successive extraction experiments of the metals from the aqueous phase into the organic phase. The results of this step showed that 92.7% of cadmium and 26.7% of cobalt are extracted into the organic phase. In contrast, nickel ions remain quantitatively in the source phase. The different stability of the anionic chloride complexes of cadmium and cobalt leads to different extractability of these metals. By employing an appropriate back-extraction procedure a selective separation of these ions was achieved. The extracted Cd(II) and Co(II) ion pairs (i.e. $[TOAH^+][MCl^-_3]$, M is Cd or Co) were back-extracted into the stripping phase by using ammonia solutions as a suitable complexing reagent for these metal ions. Selective back-extraction of cadmium (86.3%) from the organic phase by using 0.5 M NH_3 solution has resulted. The second step included five consecutive extraction experiments on the raffinate of the preceding step. The total extraction of cobalt into the accumulated organic phase reached 83.0%. Efficient recovery of the extracted cobalt (79.3%) was obtained by a single back-extraction experiment using 7 M NH_3. The investigated design allows for improving Ni/Co ratio from 13.9 in the starting aqueous solution to 106 in the ultimate raffinate.*

KEYWORDS: *Spent Ni-Cd batteries; Metals recovery, Leaching; Response surface methodology optimization; Solvent extraction.*

INTRODUCTION

The increasing presence of electric and electronic devices in everyday life of the people who live in both developed and under developing countries[1] results in the increase of demands for different type of batteries, especially those are rechargeable [2-4]. Regardless to the type of batteries, they have a limited lifetime, and must be

then discarded. The contents of these batteries are usually composed of a variety of toxic heavy metals which can be a menace for the environment [5, 6]. Nevertheless, the metals contents of such batteries are important and valuable from both industrial and economical points of view [7-9]. These points stimulated many research groups around the world to establish efficient methods for the recovery of metals from spent batteries [10, 11].

Although, a variety of new rechargeable batteries are developed and are found in the market [4], nickel-cadmium batteries remain as one of the most used of this type of batteries. They are applicable for many electronic devices, and thus they have a prominent position for the electronic industries. These batteries are contained considerable amount of nickel, cadmium, and cobalt.

A bulk of studies have been devoted to the leaching and recovery of these metals from the spent nickel-cadmium batteries [12]. Leaching as the first chemical step of the recovery of metals from Ni-Cd batteries has been studied by *Nogueira* and *Margarido* [13]. They have reported the leaching efficiency of cadmium, nickel and cobalt from the batteries with sulfuric acid solutions. Application of hydrated ferric sulfate for dissolving heavy metals in the same type of batteries has also been reported [14]. Reddy and Priya studied the leaching and solvent extraction of cadmium, nickel and cobalt from spent Ni-Cd batteries [15]. They have used the single factor at a time optimization for leaching process of dismantled powder of these batteries. Following this study, *Reddy et al.* have applied two different type of extractants (*i.e.* Cyanex 923 and Cyanex 272) dissolved in kerosene by designing a relatively complicated solvent extraction/back-extraction processes for the recovery of Cd(II), Ni(II) and Co(II). This group has also examined the solvent extraction of other type of phosphorus containing extractants TOPS 99, Cyanex 302 and Cyanex 301 [16]. The results were encountered with some imperfections such as hard back-extraction step and disadvantage of the uncompleted separation of the investigated metals. A flow sheet liquid-liquid extraction process based on the organophosphorus extractants has been reported for the separation of Cd(II), Ni(II), and Co(II) leached by hydrochloric acid solution from the spent Ni-Cd batteries [17]. To produce metallic nickel from spent Ni-Cd batteries, in a study the batteries were leached by using ultrasonic radiation [18]. The leached

nickel was then recovered by electrodeposion technique. Although the recovery of metals from Ni-Cd batteries wastes is mainly based on hydrometallurgical processes, bio-hydrometallurgical [19] and thermal method are among the other method used for performing such goal [20].

Trioctylamine (TOA), a member of alkyl amine extractants, is well-known as a basic extractant used frequently for the extraction of metals as their oxanionic species [21, 22], or as anionic chloro-complexes [23, 24], via the ion-pair formation mechanism. However, it is worth of note that, although many reports on the extraction of cadmium, cobalt and nickel from chloride or thiocyanate solutions by the amine extractants including TOA have been published [25-30], the target of those reports is not the same envisaged for the presented study in this report. This report intends demonstrating the separation of Cd, Co and Ni from leach solutions of spent Ni-Cd batteries by employing the well-known basic extractant TOA in a new design of solvent extraction/back-extraction process. In this trajectory, the parameters affecting the leaching process has been first optimized by using Response Surface Methodology (RSM). Then, the leach solution has been subjected to a two-step solvent extraction process for separation and purification of the leached metal ions.

EXPERIMENTAL SECTION
Chemical and reagents

Spent rechargeable nickel-cadmium batteries (various trademarks) were collected from the local electronic devices repair shops. Trioctylamine (TOA) (98%, Samchun, Korea), dichloromethane (99%, Merck, Germany), 37 wt% hydrochloric acid (Merck, Germany), cadmium(II) nitrate hexahydrate (98%, Merck, Germany), nickel(II) nitrate hexahydrate (99%, Merck, Germany), cobalt(II) nitrate (99%, Merck, Germany) and 25 wt% ammonia solution (Merck, Germany) were used as received. Nickel, cadmium and cobalt nitrate salts were used for the preparation of standard solutions for using in analysis of the corresponding metals in aqueous solutions. The stock solutions were standardized complexometrically using standard EDTA solution. It is worth of note that the solutions used in the extraction process were obtained by leaching the solid materials of spent Ni-Cd batteries (see section "Leaching procedure").

Instrumentation

The Zolalan water purification system (m–uv–3$^+$, Iran) was used for preparing deionized water. A centrifuge (Labofuge300, Heraeus, USA) assisted the organic/aqueous phases separations. Analysis of the metals were performed on the Varian (AA220, Australia) flame atomic absorption spectrometer (FAAS).

Optimization of the leaching process by the Response Surface Methodology (RSM)

The experimental design composed of three stages including: (a) designing and realizing the experiments, (b) using regression procedure to make a response model, and (c) optimization. The main operating parameters in this investigation were batteries powder, concentration of hydrochloric acid solution, solid/solution contact time, and temperature. To determine the minimum number of required experiments for selecting the optimum values of the target parameters, the central composite design (CCD) which is a fractional factorial design was employed [31]. The data processing has been done by using the general statistical software Minitab 16.1. A set of 22 experiments were designed. To statistical calculations, the variables (X_i) have been convert to codes (x_i) by using Eq. (1):

$$x_i = \frac{X_i - X_0}{\delta X} \tag{1}$$

Where, X_0 is the X_i value at the central point and δX_i is the variation degree. The second order equation 2 was employed for the description of the response by the independent variables:

$$y = \beta_0 + \sum_{i=1}^{K} \beta_i X_i + \sum_{i=1}^{K} \beta_{ii} X_i^2 \tag{2}$$
$$+ \sum \sum_{i<j} \beta_{ij} X_i X_j + \varepsilon$$

In this equation, y is the response (recovery of one of the leached metals, *i.e.* cadmium), β_0 denotes the constant coefficient, β_i the linear coefficients, β_{ij} the interaction coefficients, β_{ii} the quadratic coefficients, and ε signifies the error.

Leaching procedure

The powder separated from the spent batteries (4.4 g) and 100 mL of hydrochloric acid (2.6 mol/L) were poured into a 250 mL round bottom flask and a magnet bar was put in this flask. A condenser was connected to this flask

and the flask was put in an oil bath (48.6 ± 0.2 °C) located on a magnet stirrer. The solution was stirred for 200 min. Then the mixture was filtered off, and the aqueous phase, after appropriate dilution with deionized water, was subjected to the metals analysis by FAAS.

Solvent extraction and back-extraction procedures

Solvent extraction experiments have been performed by entering 15 mL of leach solution (containing 202.5 mg Cd, 187.5 mg Ni, and 13.5 mg Co) and 15 mL of dichloromethane solution of TOA (0.5 mol/L) in a 50 mL-round bottom flask. The concentration of the extractant was selected enough large so that its distribution into the aqueous phase does not affect the extraction efficiency. The mixture was then magnetically stirred. After 60 min, the stirring was stopped, and the phases were separated by centrifugation. For repeating the extraction experiments, a new portion (15 mL) of the organic phase was contacted with the raffinate. This procedure was done four times. The accumulated organic phase (60 mL) was contacted with 15 mL of ammonia solution (0.5 mol/L) and magnetically stirred for 60 minutes to follow the back-extraction process of cadmium. The analysis of metals in the back-extraction aqueous phase was performed by FAAS, after appropriate dilution. The aqueous phase was then subjected to five further extraction procedure as described above by contacting a new portion (15 mL) of the organic phase with the aqueous phase. The separated organic phase in this step with those remained after back-extraction procedure of the first step were mixed and the resulted organic solution (135 mL) was contacted with 15 mL of a 7 mol/L ammonia solution. The mixture was stirred for 60 minutes, and then the phases were separated. The metals in the aqueous phase were analyzed by FAAS. All extraction and back-extraction experiments were carried out in triplicate and at room temperature (22±1 °C).

RESULTS AND DISCUSSION
Leaching study

The optimization of the parameters affecting the leaching process of the powder of dismantled spent batteries by hydrochloric acid is crucial which allows the maximum transfer of cadmium, nickel and cobalt to the solution. Response Surface Methodology (RSM) [32] with Central Composite Design (CCD) was employed to realize this optimization. To this end, cadmium was selected

Table 1: Levels of the experimental variables used for the employed central composite design.

Variable	Key	Levels				
		Lowest (-α)	Low (-1)	Center (0)	High (+1)	Highest (+α)
Concentration HCl (mol/L)	X_1	0.5	1.375	2.250	3.125	4
Solid material (g)	X_2	1	2	3	4	5
Temperature (°C)	X_3	25	41.25	57.50	73.75	90
Time (h)	X_4	1	2.75	4.50	6.25	8

as the indicator element, with the suggestion that the optimized leaching conditions are similar for the other metals. The optimized parameters were hydrochloric acid concentration, the mass of solid material (batteries powder), temperature and time. Table 1 contains the experimental variables and the related levels used in the Central Composite Design (CCD). The levels have been selected by considering the conventional ranges employed in the corresponding studies.

An experimental design including 22 experiments (Table 2) was prepared by Minitab 16.1. The data given in Table 2 were used for the fitting the polynomial model representing the leached amount of cadmium as a function of the variables shown in Table 1.

Equation 3 describes a model for predicting the amount of leached cadmium as a function of the coded variables. This polynomial equation was obtained by employing the least square regression method.

$$y_{Cd} = -7.05317 + 1.44309X_1 + 0.871806X_2 + \quad (3)$$
$$0.109877X_3 + 0.678352X_4 - 0.124349X_1X_1 -$$
$$0.254497X_2X_2 - 7.58191004X_3X_3 -$$
$$0.0579915X_4X_4 + 0.109429X_1X_2 -$$
$$0.00807692X_1X_3 - 0.0692857X_2X_3$$

By removing the terms with the higher probability value (*p*-value) than 0.05, equation 4 was obtained:

$$y_{Cd} = -7.05317 + 1.44309X_1 + \quad (4)$$
$$0.678352X_4 - 0.124349X_1X_1 - 0.254497X_2X_2 -$$
$$7.58191004X_3X_3 - 0.0579915X_4X_4 -$$
$$0.00807692X_1X_3 - 0.0692857X_2X_3$$

The statistic factors resulted by using the analysis of variance (ANOVA) are presented in Table 3. This analysis allowed estimating the significance and validity of the model at 95% confidence level.

The evaluated F- (19.12) and p- (<0.001) values revealed the proposed model is highly significant. It is

noteworthy that the theoretical F-value equals to 2.85 [33]. The greater F-value predicted by the model with respect to the theoretical value (19.12) lets to reject the null hypothesis and it confirmed the significant difference of the regression variations and the residuals. The evaluated p-value of the lack of fit (0.051) demonstrates the suitable precision of the proposed model. It is worth mentioning that the correlation coefficient (R^2) of the plot of experimental signals versus model's predicted signals was found to be 0.955. This revealed that 95.5 percent of the experimental data are predictable by the model.

The three- (3D) and two- (2D) dimensional response surface graphs allow describing the interaction of two variables affecting the leaching process. Fig. 1 demonstrates these graphs for estimating the existence of interaction between the binary parameters solid mass/temperature (Fig. 1 a-b), solid mass/hydrochloric acid concentration (Fig. 1 c-d), solid mass/shaking time (Fig. 1 e-f), shaking time/hydrochloric acid concentration (Fig. 1 g-h), temperature/hydrochloric acid concentration (Fig. 1 i-j), and temperature/shaking time (Fig. 1 k-l), on the leaching efficiency of cadmium from the powder of dismantled spent Ni-Cd batteries. The response surface two-dimensional graphs (Fig. 1-b, 1-d, 1-f, 1-h, 1-j, and 1-l) reveal that although the binary parameters solid mass/temperature and solid mass/shaking time have significant interactions. The other two-dimensional i.e. solid mass/hydrochloric acid concentration, shaking time/hydrochloric acid concentration, temperature/hydrochloric acid concentration, and temperature/shaking time did not confirm effective interactions. These conclusions have been drawn by considering elliptical and symmetrical round form of the two-dimensional graphs for the investigated binary parameters with significant interactions or without interaction, respectively. However, the evaluated *p*-values are helpful to describe the presence or absence of significant interactions between

Table 2: The matrix of central composite design for the optimization of the leaching process.[a]

Run	Solid mass (g)	HCl Conc (mol/L)	Temp. (°C)	Time (h)	y_{Cd} Values (mg/L)	
					Experimental	Predicted
1	3	2.250	57.50	4.50	0.874	0.904
2	1	2.250	57.50	4.50	0.018	0.073
3	3	2.250	57.50	1.00	0.418	0.374
4	3	4.000	57.50	4.50	0.199	0.221
5	3	0.500	57.50	4.50	0.113	0.029
6	3	2.250	57.50	4.50	0.858	0.904
7	3	2.250	25.00	4.50	0.069	0.174
8	5	2.250	57.50	4.50	0.858	0.741
9	3	2.250	90.00	4.50	0.184	0.017
10	3	2.250	57.50	8.00	0.032	0.014
11	4	1.375	73.75	2.75	0.105	0.269
12	4	1.375	41.25	6.25	0.162	0.188
13	4	3.125	73.75	6.25	0.025	0.134
14	3	2.250	57.50	4.50	0.940	0.904
15	4	3.125	40.25	2.75	0.912	0.898
16	3	2.250	57.50	4.50	0.861	0.904
17	3	2.250	57.50	4.50	1.035	0.904
18	3	2.250	57.50	4.50	0.858	0.904
19	2	1.375	41.25	2.75	0.010	-0.037
20	2	3.125	73.75	2.75	0.015	0.051
21	2	3.125	41.25	6.25	0.043	-0.068
22	2	1.375	73.75	6.25	0.133	0.208

[a]*The concentration reported for Cd concentration in the leach solutions are those after 10000 times dilution for FAAS analysis.*

Table 3: The analysis of the experimental response by using ANOVA.

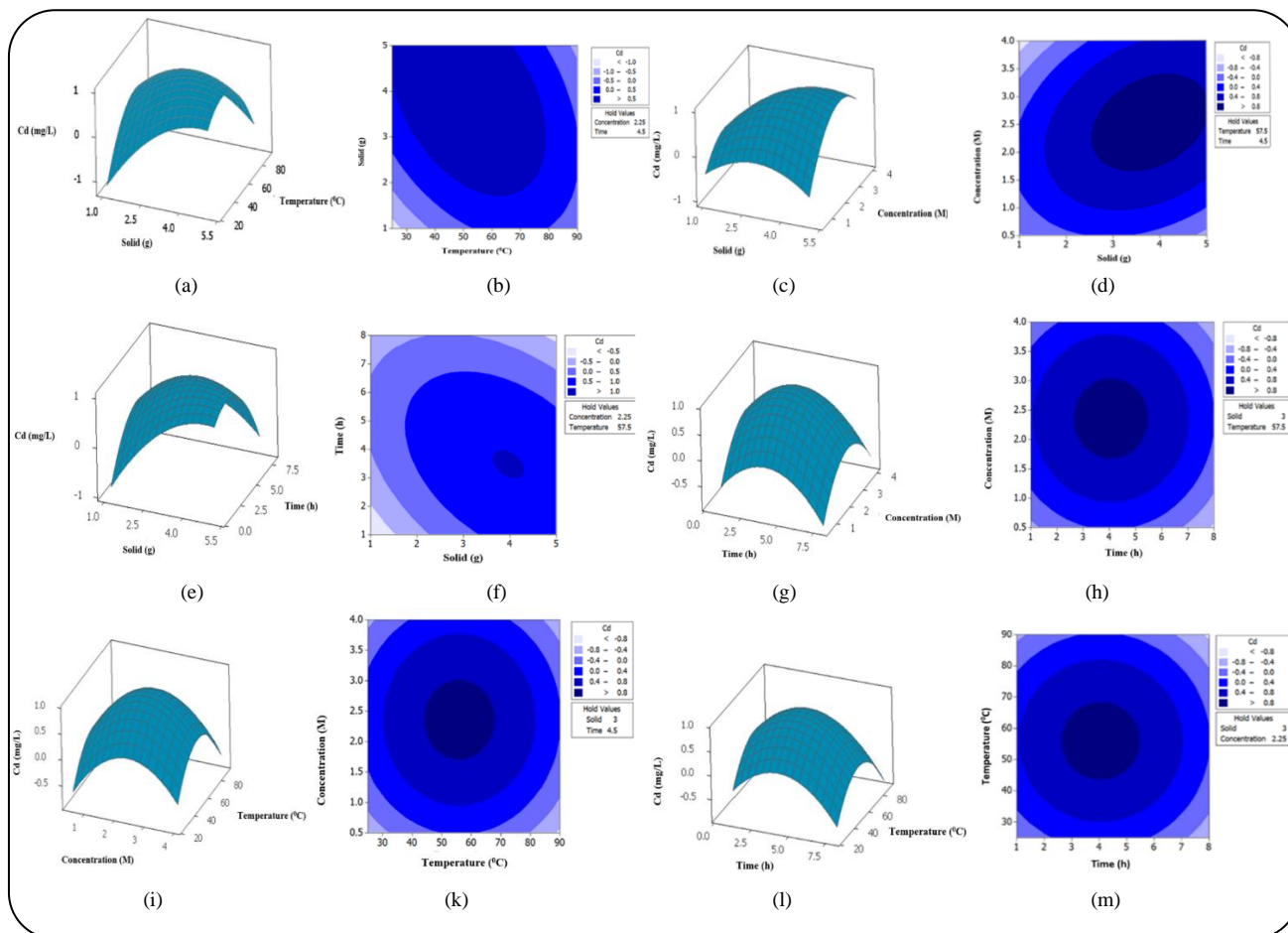| Source	Degree of freedom	Sum of squares	Adjusted mean square	F-value	P-value
Regression	11	3.21710	0.29246	19.12	<0.001
Linear	4	0.3749	0.15937	10.18	<0.001
Square	4	2.25083	0.56271	35.93	<0.001
Interaction	3	0.32877	0.10959	7.00	0.008
Residual error	10	0.15663	0.01566	-	-
Lack of fit	5	0.13119	0.0222624	5.16	0.051
Pure error	5	0.02544	0.00509	-	-
Total	21	3.37372	-	-	-

Fig. 1: Response surface 3D and 2D graphs of the solid mass/temperature (a, b), solid mass/hydrochloric acid concentration (c, d), solid mass/shaking time (e, f), shaking time/hydrochloric acid concentration (g, h), temperature/hydrochloric acid concentration/ (i, j), temperature/shaking time/ (l, m). Other fixed experimental conditions for each investigation: hydrochloric acid volume 100 mL, hydrochloric acid concentration 2.25 mol/L, shaking time 4.5 h, 57.5 °C, solid mass 3 g.

the studied binary parameters. The *p*-values for the interaction of parameters solid mass/temperature and solid mass/shaking time binary parameters were evaluated to be 0.014 and 0.019 at the confidence level 95%.

Three-dimensional graphs (Fig. 1-a, 1-c, 1-e, 1-g, 1-i) allow to predict the efficiency of the leaching process as a function of the investigated parameters. Such analysis showed that the leached amount of cadmium enhances with the amount of solid mass (< 4.5 g) and temperature (< 50 °C). Most likely, the evaporation of the solution results in the reduction of the leaching process efficiency at higher temperatures. The influence of the amount of solid mass and the hydrochloric acid concentration parameters on the cadmium leaching (Fig. 1-c), with a *p*-value of 0.056, showed the lack of interaction between these parameters. It was seen that, an increase in the

hydrochloric acid concentration improves the leaching efficiency. This can be attributed to the formation of cadmium chloro-complexes in such media [34]. However, a decrease in the cadmium leaching when the acid concentration was increased to > 3 mol/L could be described by the reduction of the acid activity at higher electrolyte concentration. The response surface 3D graph of the amount of leached cadmium as a function of the solid mass and the solid-solution contact time (shaking time) is demonstrated in Fig. 1-e. An explanation for the peak form of the cadmium recovery versus time plot may be attributed to the evaporation of leaching solution and thus the decrease in the solution volume at higher contact time of the solid/solution phases.

Based on the above-described experimental design, the best performance of the leaching process by 100 mL

Table 4: Optimal values and ranges within the leaching parameters were studied.

Parameter	Range studied	Optimal value
Solid mass (g)	1 - 5	4.4
Concentration of HCl (M)	0.5 – 4.0	2.6
Temperature (°C)	25 - 90	48.6
Shaking time (h)	1 - 8	3.19

Table 5: Concentration of the leached Cd(II), Ni(II) and Co(II) ions in the solution (mg/L) and their corresponding wt%
in the powder of dismantled Ni-Cd batteries.

Metal	Concentration in the leached solution (mg/L)	Weight percent in the power (wt%)
Cadmium	13500 (±5)	30.5 (±1.9)
Nickel	12150 (±7)	27.2 (±1.6)
Cobalt	900 (±2)	2.2 (±0.1)

solution of hydrochloric acid was achieved by using the optimum values of the influencing parameters as those given in Table 4. Under such conditions the experimental value for the diluted leached cadmium has been found to be 1.35 mg/L which was close to that predicted by the proposed model (1.31 mg/L) with an error of 3.0%.

The analysis of the leach solution showed the concentrations of Cd(II), Ni(II) and Co(II) are 13500, 12150, and 900 mg/L, respectively. These concentrations equal to 30.5 wt% of Cd, 27.2 wt% of Ni, and 2.2 wt% of Co in the power obtained from the dismantled Ni-Cd batteries (Table 5).

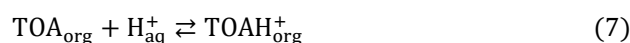***Extraction-separation of Cd(II), Ni(II) and Co(II) from the leach solution***

Keep in mind the presence of chloride ion in the leach solution, it is suggested that the cadmium and cobalt ions are found as their trichloro-complexes i.e. $CdCl_3^-$ and $COCl_3^-$, with the formation constants (K_f) of 3.5×10^4 and 0.24, respectively [35, 36]:

$$Cd^{2+} + 3Cl^- \rightleftarrows CdCl_3^- \tag{5}$$

$$Co^{2+} + 3Cl^- \rightleftarrows CoCl_3^- \tag{6}$$

To the best of the author's knowledge, there is no report on the formation of nickel-chloride complexes. Inability of chloride ions to complex nickel(II), and the superior formation constant for the chloro-complexes of cadmium with respect to that of cobalt, results in purposing a solvent extraction procedure for the selective separation of Cd(II), Ni(II) and Co(II) by selecting an extraction

system based upon the ion-pair formation mechanism of the anionic chloro-complexes of cadmium and cobalt ions by an amine extractant.

Trioctylamine (TOA) dissolved in an organic solvent contacted with an acidic aqueous solution can be protonated at the organic/aqueous interface, and thus the extractable anions from the aqueous phase form the ion-pairs with the protonated TOA. The equilibria presenting the protonation of TOA and the ion-pair formation of TOAH⁺ and anionic chloro-complexes of cadmium and cobalt at the interface of organic/aqueous phases are given in Eqs. 7-9.

$$TOA_{org} + H_{aq}^+ \rightleftarrows TOAH_{org}^+ \tag{7}$$

$$CdCl_{3.aq}^- + TOAH_{org}^+ \rightleftarrows [TOAH^+][CdCl_3^-]_{org} \tag{8}$$

$$CoCl_{3.aq}^- + TOAH_{org}^+ \rightleftarrows [TOAH^+][CoCl_3^-]_{org} \tag{9}$$

In order to study the extraction-separation of Cd(II), Ni(II) and Co(II) ions, 15 mL of the aqueous solution containing 202.5, 187.6 and 13.5 mg of cadmium, nickel and cobalt was contacted with 15 mL of a dichloromethane solution of TOA (0.5 mol/L). The phases were stirred magnetically for 1 h. After equilibration, the phases were separated and the amounts of the metal ions remained in the aqueous phase, after dilution, were determined by FAAS. This procedure was repeated four times by using the raffinate of the previous step and a fresh 15 mL portion of the organic phase. The percentage of remained metals in the aqueous phase and extracted to the organic phase after each extraction experiment are shown in Fig. 2.
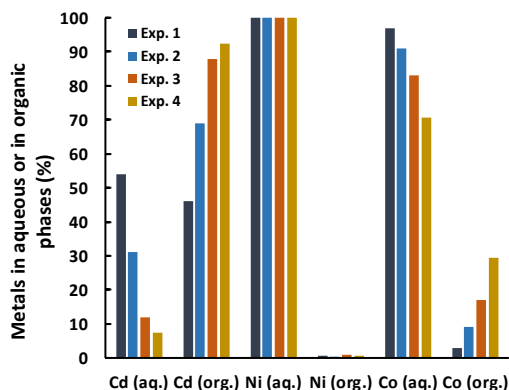
Fig. 2: Percentage of Cd(II), Ni(II) and Co(II) remained in the raffinate and extracted into the organic phases after 4 successive extraction experiments. The percentage of the metals in the organic phases are the accumulated amount of the metals. The aqueous phase was 15 mL of sample solution. Each extraction experiment was performed by the initial aqueous solution with 15 mL of the organic phase (0.5 mol/L TOA in dichloromethane). Step 1 consists of 4 extraction experiments. Initial amounts of Cd, Ni and Co in 15 mL in staring aqueous phase were 202.5, 187.5 and 13.5 mg, respectively, extraction time 1 h, temperature 22±1 °C. The data are given based upon three experiments with the RSD ≤ 2.2 %. The amount of Ni in the organic phase was inferior to the corresponding detection limit of its analysis by FAAS (i.e. Not detectable).
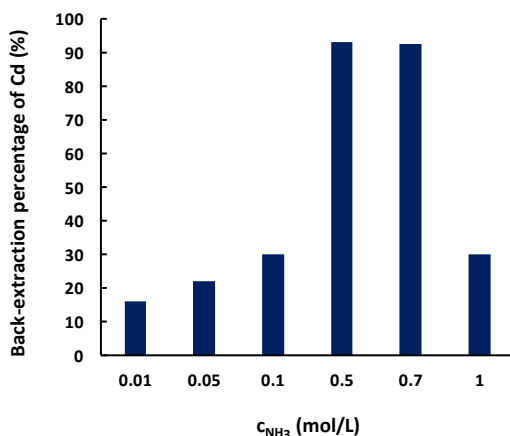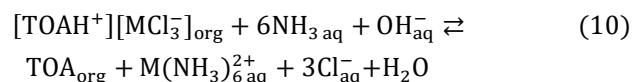

Fig. 3: Back-extraction percentage of cadmium from accumulated organic phase (60 mL) after 4 successive extraction experiments by 0.01 - 1 mol/L ammonia solution (15 mL). Other experimental conditions: back-extraction time 1 h and temperature 22±1 °C. The amounts of cobalt in the back-extraction solution were not detectable. The data are given based upon three experiments with the RSD ≤ 2.6 %.

As it is seen, the amount of cadmium, nickel and cobalt in the ultimate aqueous solution (after subjected to four extraction experiments with the organic phase) was 7.5%, 100% and 70.7%, respectively. Thus, the extraction percentage of cadmium and cobalt after four extraction experiments in the organic phase (60 mL) were 92.5% (187.5 mg) and 29.3% (3.95 mg). The extraction of nickel from the aqueous phase into the organic phase was lower than relative standard deviation. It is noteworthy that, the percentage of metals in the organic phases are accumulative. The raffinate contained 14, 187.4 and 9.5 mg of Cd, Ni and Co, respectively.

Regarding the extraction mechanism, it was assumed that the application of basic solutions with ability to complex cadmium and cobalt may result in stripping of the loaded organic phase. Thus, the equation describing the back-extraction of cadmium or cobalt can be considered as that presented in Eq. 10, in which M is Cd or Co:

$$[TOAH^+][MCl_3^-]_{org} + 6NH_{3\ aq} + OH_{aq}^- \rightleftarrows \qquad (10)$$
$$TOA_{org} + M(NH_3)_{6\ aq}^{2+} + 3Cl_{aq}^- + H_2O$$

In order to recovery the metals extracted into the organic phase, the accumulated organic solution (60 mL) was contacted to 15 mL of ammonia solutions with the concentrations in the range of 0.01 to 1 mol/L. The results (Fig. 3) showed that the back-extraction percentage of cadmium is enhanced by increasing the concentration of ammonia solution from 0.01 - 0.5 mol/L. However, an increase in the ammonia solution concentration beyond 0.5 mol/L (i.e. 0.7 mol/L) did not affect the back-extraction percentage of cadmium. At this stage of study, we do not have an interpretation for lower back-extraction percentage of cadmium when 1 mol/L of ammonia solution is used with respect to those have been achieved by using 0.5 and 0.7 mol/L solution. It is worth noting that the organic phase did not release any detectable cobalt when it was contacted with the tested ammonia solutions.

In fact, by using a solution of 0.5 mol/L of ammonia solution ~93 wt% (~ 174.7 mg) of the extracted cadmium (~ 187.8 mg) was back-extracted into the aqueous solution. This equals to 86.2 wt% with respect to the amount of cadmium in the starting aqueous solution. Besides, the back-extraction solution did not contain any detectable amount of nickel and cobalt.

To increase the extraction separation of cobalt/nickel in the raffinate of the first step, a further five consecutive
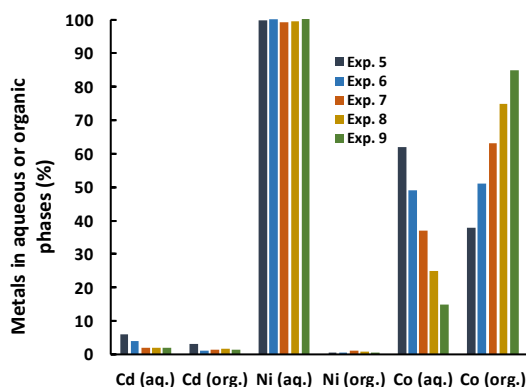
Fig. 4: Percentage of Cd(II), Ni(II) and Co(II) remained in the raffinate and extracted into the organic phases after 5 successive extraction experiments using the raffinate of the first step of the process(See Fig. 2). The percentage of the metals in the organic phases are the accumulated amount of the metals. The aqueous phase was 15 mL of sample solution. Each extraction experiment was performed by the initial aqueous solution with 15 mL of the organic phase (0.5 mol/L TOA in dichloromethane). Initial amounts of Cd, Ni and Co in 15 mL in the raffinate of step 1 were 14, 187.4 and 9.5 mg, respectively, extraction time 1 h, temperature 22±1 °C. The data are given based upon three experiments with the RSD ≤ 2.9 %. The amount of Ni in the organic phase was inferior to the corresponding detection limit of its analysis by FAAS (i.e. Not detectable).
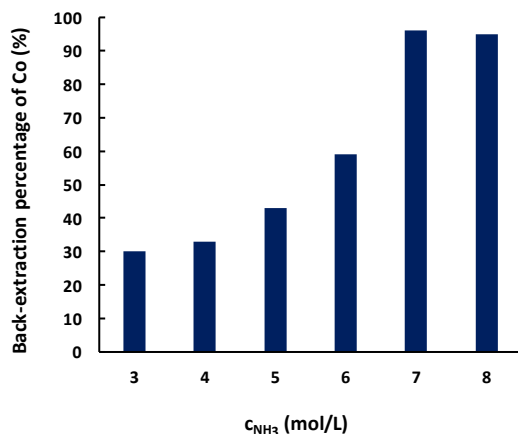

Fig. 5: Back-extraction percentage of cobalt from accumulated organic phase (total organic volume of 135 mL gathered collected from step 1 and step 2) by 3 - 8 mol/L ammonia solutions. Other experimental conditions: back-extraction time 1 h, temperature 22±1 °C. Not detectable cadmium was found in the aqueous stripping solution. The data are given based upon three experiments with the RSD ≤ 3.2 %.

extraction experiments of the cobalt content of the raffinate by new portions of the organic phase (0.5 mol/L of TOA in dichloromethane, 15 mL each experiment) were performed. The results showed the extraction percentage of cobalt from the aqueous into the organic phase is increased after each extraction experiment (Fig. 4). The total extracted cobalt into the accumulated organic phase after 9 extraction experiments was determined to be about 11.2 mg; *i.e.* 83 wt% of its initial content in the starting aqueous solution.

The accumulated organic phase in this step (75 mL) was combined with the free cadmium organic phase obtained in the step 1 (60 mL). To strip the metal contents of this accumulated organic phase (135 mL), it was contacted with 15 mL of 3 - 8 mol/L ammonia solutions, for 1 h. The results are shown in Fig. 5. A quantitative back-extraction of cobalt was attained by using ammonia solution with the concentration greater than 7 mol/L.

CONCLUSIONS

Fig. 6 summarizes schematically the design and the obtained results of the proposed process. This design provides the variation of Ni/Cd ratio from 1.8 in the starting sample solution to 23.6 in the obtained raffinate after 4 consecutive extraction experiments. In spit, the back-extraction of the accumulated organic solutions after primary extraction step (4 successive extraction experiments) allowed achieving to a solution free of nickel and cobalt, and contains 86.3 wt% of cadmium with respect to its amount in the starting solution. Nickel cannot form the chloro-complexes and thus remain quantitatively in the source phase. The different tendency for the formation of chloride complexes of cadmium and cobalt, and employing an appropriate back-extraction procedure, lead to a selective separation of the target ions. The extracted Cd(II) and Co(II) ion pairs (i.e. $[TOAH^+][MCl_3^-]$, M is Cd or Co) may be dissociated and thus back-extracted into the stripping phase by using ammonia solution as a suitable complexing reagent (i.e. ammonia solution) for these metal ions. The second step included five consecutive extraction experiments on the raffinate of preceding step. The total extraction of cobalt into the accumulated organic phase reached to 83.0%. Efficient recovery of the extracted cobalt (79.3%) was obtained by a single back-extraction experiment using 7 M NH_3.
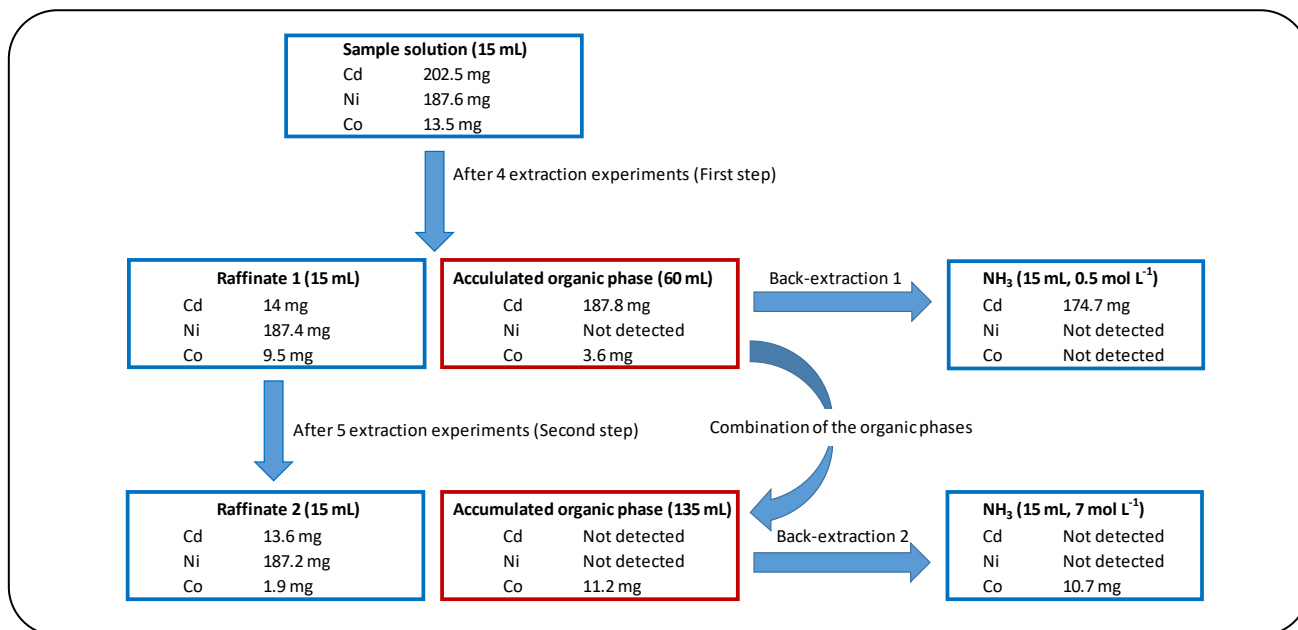
Fig. 6: A schematic summary of the designed solvent extraction method.

The second step of the process, included 5 further successive extraction experiments on the raffinate of the first step, allowed improving the molar ratio of Ni/Co from 13.9 in the starting aqueous solution to 106 in the ultimate raffinate. The solution used for the back-extraction solution of the accumulated organic phase obtaining in both steps (135 mL) contains about 71 wt% of the cobalt with respect to its amount in the starting aqueous solution. This solution contained neither nickel nor cadmium ions.

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