Recovery of cobalt by Aliquat 336 as ionic liquid extractant: a statistical study by Taguchi design

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ABSTRACT

Liquid–liquid extraction of Co(II) from acidic chloride solutions was studied with Aliquat 336 extractant, a quaternary ammonium salt in dodecane. Oleyl alcohol modifier was added to the organic phase to enhance the extraction process and avoiding the third phase formation. The extraction experiments were realized by contacting the organic phase with an aqueous feed phase of concentrated hydrochloric acid containing the Co(II) ions. The optimization of Co(II) recovery was determined by optimizing one parameter at a time. Therefore, several experimental parameters such as Aliquat 336 concentration, extraction time, hydrochloric acid concentration and initial concentration of metal ion were studied. The cobalt(II) ions were stripped from the metal loaded organic phase at 94% by distilled water as stripping agent. The mass balances were checked for all studied parameters with an average deviation percentage of 2%. The separation tests of Co(II) and Ni(II) were carried on the basis of the optimal conditions of Co(II) recovery. It showed that the nickel(II) ions were slightly extracted (<10%) whatever the composition of mixture. A Taguchi design with an orthogonal array L4 was used for the statistical study for determining the influence and contribution percentage of certain experimental parameters on the Co(II) recovery process.

Keywords: Liquid–liquid extraction; Cobalt; Nickel; Aliquat 336; Ionic liquid; Taguchi modeling

1. Introduction

Cobalt is mainly obtained as an extraction product of nickel, copper, zinc and lead from their ores [1,2]. Certain raw materials such as oxidic and sulfide ores/concentrates, and sludges/wastes/scrap/dust/spent catalysts, constitute a major source for the production of cobalt and nickel together [3]. These nonferrous metals are most widely used in various industries due to the superior properties they possess. They are used in the pure metal form or in alloys [1]. At hydrometallurgical scale, the leaching step using sulfate and/or chloride systems, results in leach liquors containing mainly cobalt and nickel in association with some impurities, such as copper, iron and aluminum [2,4]. Indeed, it is difficult to obtain pure cobalt metal from these leach liquors because of the difficulties in separating cobalt from nickel which have similar physico-chemical properties [3] and are generally found together in minerals and industrial wastes [5].

For this, the simple separation processes such as chemical precipitation by pH adjustment [6], oxidation and crystallization are not sufficient to separate them [7]. There are thus other methods for the removal of these metals; mention may be made of reverse osmosis [8], filtration processes [9], eletrocoagulation [10] and adsorption [11–13]. The chemical processes of metal ions enrichment that have proven to be effective [14] and mostly used in the separation of Co(II) and Ni(II) are liquid–liquid extraction and ion exchange [15].

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Solvent extraction (SX) or liquid–liquid extraction is a hydro-metallurgical separation and purification technique that is a selective, cost efficient and simpler chemical process. In activities of refining and metal recovery, this technique is proving to be a powerful tool, providing new opportunities to exploit low ores of the value metal and of metal recycling [16]. The facilitated transport in liquid–liquid extraction process can constitute a good alternative to development of new extractants with a high selectivity and efficiency. This will be a beneficial process on economic and ecological scale. Di-2-ethylhexyl phosphoric acid (D2EHPA) is the first extractant which was widely used for recovery of Co(II) and Ni(II) from their mixture. Nevertheless, the process requires of very strict pH control and relatively high operating temperatures [17]. The same phenomenon is presented when using other cationic extractants such as Cyanex 272, LIX 860, etc. The main problem is associated with the pH change of aqueous phase after equilibration with organic phase [16]. A new class of extractants such as the ionic liquids (ILs) can replace this type of the organophosphorus compounds. They constitute a class of organic salts [18], called molten salts [19] because they are in liquid state at room temperature [18]. They find several applications [20], for example: as a solvent in metal extraction and wastewater treatment [21] due to their low volatility, tunable viscosity and miscibility, and electrolytic conductivity [20].

Amines are generally used as representative reagents for extracting where the metal ions are extracted according to the ion association and ion pairs principles [1]. Aliquat 336, an IL reagent [22–25], has been mainly used as extractant for the extraction of metal chloride complexes [26–28]. It is also more efficient in extraction than ternary and secondary amines: $R_4N^+ > R_3NH^+ > R_2NH_2^+ > RNH_3^+$ [21]. Generally, the problem which occurs in solvent extraction is the third phase appearance (between organic and aqueous phases), which opposes to mass transfer and to metal ion stripping. This phenomenon can be explained by the low solubility of the formed organo-metallic complex during the extraction process by Aliquat 336. The low solubility value of the metal–IL complex could be justified by the highly non-polar nature of the complex compared with the polar nature of some solvents [29]. For this, the use of modifiers is important. At industrial scale of a nickel and cobalt SX process for laterite leach liquors, modifiers were commonly used to improve phase separation and avoid third phase formation. Thus, long chain esters or alcohols were added to the organic phase (namely in presence of amine reagents as extractants) to increase the polarity or to solvate organic phase metal–reagent species, and thereby decrease the chances of solid precipitation and subsequent third phase formation [30,31]. By respect to hydrometallurgy, oleyl alcohol ($C_{18}H_{36}O$) is used for the first time as a modifier in the process study of liquid–liquid extraction of cobalt ions by Aliquat 336. The extraction of Co(II) and Ni(II) in hydrochloric acid depends on the formed anionic complexes of the metal chloride. In hydrochloric media, nickel forms only cationic complexes of $Ni(H_2O)_6^{2+}$ and $NiCl^+$ [5]. In the presence of chloride excess, cobalt forms anionic complexes $CoCl_4^{2-}$, favorable to its extraction by Aliquat 336 [5,32]. Cobalt is the preferred transition metal of choice for selective extraction, because of the nice visible color that it has in the aqueous phase (red/pink) [19]. In high chloride concentration, the

cobalt changes the color from pink to dark blue. This was due to the geometric structure change from the square-bipyramids cobalt complex to a tetrahedron [7,19].

This present work contains two integral parts, the first part was devoted to the dynamic study of SX process in the extraction and stripping of Co(II) by the Aliquat 336 as IL extractant when using the oleyl alcohol modifier. The process efficiency was given in function of optimum conditions of the Co(II) recovery from concentrated hydrochloric acid medium. However, it was determined by optimizing one parameter at a time. From these results, separation experiments of cobalt from nickel were carried out. The second part involved the comparison between the experimental and statistical optimization of Co(II) recovery. Therefore, Taguchi experimental design with an L4 orthogonal array was used for the statistical optimization of various controllable parameters such as extractant concentration, initial concentration of metal ion and hydrochloric acid concentration by using the approach of analysis of mean (ANOM). On the other hand, analysis of variance (ANOVA) was used to determine the contribution percentage of each factor on the cobalt recovery.

2. Experimental

2.1. Reagents

Tricaprylmethylammonium chloride (Aliquat 336) was used without further purification. It was purchased with hydrochloric acid from Sigma-Aldrich (Taufkirchen, Germany). Dodecane (pure 99%) was provided from Acros organics (Geel, Belgium) where the oleyl alcohol (pure 85%) was supplied from Alfa Aesar (Karlsruhe, Germany). The chloride salts hexahydrate of cobalt(II) and nickel(II) at 98%, extra pure, were supplied from Fisher chemical (Illkirch, France).

2.2. Method for liquid–liquid extraction and stripping

A quantity of Aliquat 336 was diluted in 20 mL of dodecane using 5% w/v oleyl alcohol as modifier phase. This solution constituted the organic solution of liquid–liquid extraction experiments. The metal ion aqueous phases were prepared by dissolving an appropriate amounts of the corresponding salts of Co(II) and Ni(II) in 6.5 M of hydrochloric acid solution. The volume ratio of organic and aqueous phases was equal to 1 where the mixture was magnetically stirred at 500 rpm during the equilibrium time of extraction. After this, the two phases were decanted in a separator funnel where the organic phase was recovered to pre-concentrate the metal ion in the stripping solution, which is the distilled water. To determine the number of stages needed for the maximum recovery of Co(II) in distilled water as stripping solution, extraction experiments were realized at different volumes of the organic and aqueous phases while maintaining the Org/Aq ratio equal to 1. However, the stripping steps followed the extraction steps. Variation of chloride concentrations was achieved by adding required quantities of sodium chloride. All the experiments were carried out at room temperature of 20.0°C. The extraction isotherm study of Co(II) was realized by maintaining constant temperature. Samples of metal ion were taken for atomic absorption spectrometer analysis. Each experiment was repeated three times and the average value was considered in the calculation.

The mass balance (%), distribution ratio (D) at 0% of mass balance and extraction yield (E, %) were calculated from Eqs. (1)–(3), respectively.

$$\text{Mass balance}, \% = \left(1 - \frac{(X_1 + Y_1)}{X_0}\right) \quad (1)$$

$$D = \frac{[Y_1]}{[X_1]} \quad (2)$$

$$E(\%) = \left(1 - \frac{X_1}{X_0}\right) \times 100 \quad (3)$$

where X_0: initial concentration of cobalt in the aqueous phase; X_1: concentration of cobalt in aqueous phase after extraction; Y_1: concentration of cobalt in the stripping phase.

2.3. Apparatus

A magnetic stirrer; type IKA (color squid) was used in the experiments of metal ion recovery. An analytical balance; type Kern ABS (Balingen, Germany), was used in the weighing operation. Atomic absorption spectrometer (Hitachi Z-2300) was used for the metal analysis, after dilution with 1 M HCl. For the cobalt and nickel analysis, two wavelengths were used: 240.73 and 232.0 nm (linearity: 1–7 ppm; $R^2 = 0.98$–0.99), respectively.

3. Results and discussion

3.1. Optimization study of Co(II) extraction

3.1.1. Distribution diagram of Co(II) in HCl media

Formation of cobalt complexes in the aqueous solution may strongly affect the extraction mechanism of Co(II) with Aliquat 336. Therefore, it is essential to study the chemistry of complexation equilibria as well as the molar fraction of Co(II) species in hydrochloric acid solution. In aqueous solutions rich in chloride, cobalt forms several species of chloride complex according to the reaction Eq. (4) [33].

$$Co^{2+} + iCl^- \xleftrightarrow{\beta_i} CoCl_i^{2-i} \quad (4)$$

With β_i: the overall formation constant and i varied from 1 to 4. They are: $\beta_1 = 0.2$ M^{-1}, $\beta_2 = 0.51$ M^{-2}, $\beta_3 = 0.026$ M^{-3}, $\beta_4 = 0.021$ M^{-4} for Co(II) at 25°C [33].

The molar concentrations of Co^{2+}, $CoCl^+$, $CoCl_2$, $CoCl_3^-$ and $CoCl_4^{2-}$ can be calculated by solving the above chemical equation Eq. (4) together with the mass balance equation for the total metal concentration Eq. (5). So, the molar fraction of Co^{2+} in hydrochloric acid solution can be expressed by Eq. (8) using Eqs. (6) and (7).

$$[Co]_{tot} = [Co^{2+}] + [CoCl^+] + [CoCl_2] + [CoCl_3^-] + [CoCl_4^{2-}] \quad (5)$$

$$[Co]_{tot} = [Co^{2+}] + \left(1 + \beta_1[Cl^-] + \beta_2[Cl^-]^2 + \beta_3[Cl^-]^3 + \beta_4[Cl^-]^4\right) \quad (6)$$

$$[Co^{2+}] = \frac{[Co]_{tot}}{1 + \sum_{i=1}^{4} \beta_i[Cl^-]^i} = \frac{[Co]_{tot}}{\alpha} \quad (7)$$

with

$$\alpha = 1 + \sum_{i=1}^{4} \beta_i[Cl^-]^i$$

$$\%Co^{2+} = \frac{[Co^{2+}]}{[Co]_{tot}} = \frac{1}{\alpha} \quad (8)$$

In addition, the molar fractions of the other chloride complexes of Co(II) were given by the Eq. (9). The distribution diagram of these complexes as function of the hydrochloric acid concentration ranging between 0 and 10 M is shown in Fig. 1.

$$\%[CoCl_i^{2-i}] = \frac{\beta_i[Cl^-]^i}{\alpha} \quad (9)$$

According to the speciation diagram, the predominant species was $CoCl_4^{2-}$ when the hydrochloric acid concentration reached 6.5 M. In this case, the $CoCl_2$ fraction (31.50%) was comparative with that of $CoCl_4^{2-}$ (54.70%) where the other species were found at lower proportions in which the molar fraction of Co^{2+} was of 1.50%. The ionic strength of the solution was the factor affecting the species distribution. However, by maintaining the ionic strength at 6.5 M of HCl, the predominant species remains unchanged [34]. Thus, Aliquat 336 (NR$_4$Cl) extracts only the $CoCl_4^{2-}$ species [26]. This study will bring conclusions on the mechanism of Co(II) extraction from hydrochloric acid medium by the Aliquat 336 using SX process.

3.1.2. Effect of Aliquat 336 concentration

To investigate the influence of extractant concentration on the Co(II) ions extraction, we varied the Aliquat 336 concentration in the range of 0.01 to 0.24 M. The oleyl alcohol concentration was maintained at 5% w/v where the initial
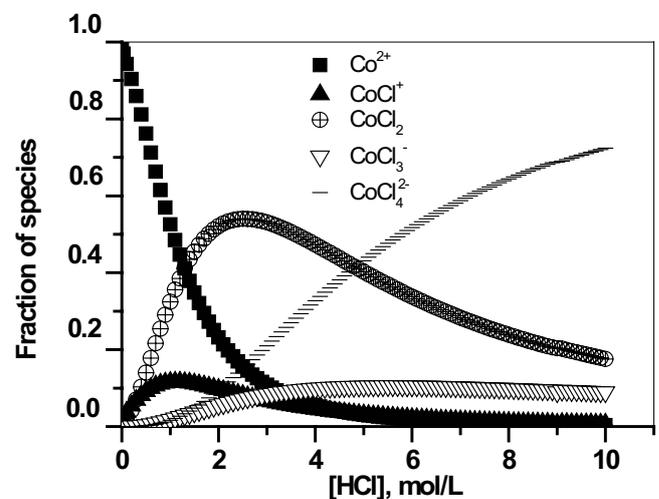
Fig. 1. Speciation diagram for aqueous Co(II) chloro-complexes at different concentrations of hydrochloric acid.

concentration of cobalt ions was of 2 g L^{-1}. Thus, the molar ratio between Co(II) and extractant concentration was varied in the range of 3.4 to 0.14. Fig. 2 shows the evolution of extraction yield of the cobalt ions as function of the Aliquat 336 concentration. It was noted that the extraction yield increased with increasing the extractant concentration due to the presence of more complexing sites which enhanced the Co(II) extraction. It reached a value up 67% at 0.24 M of Aliquat 336. Beyond this extractant concentration, the third phase was appeared due to the precipitation of Co(II) in organic phase. The mass balance was verified with an average deviation percentage of 1.54%.

3.1.3. Mechanism of cobalt(II) extraction

Quaternary ammonium extractants can extract metal ion by two mechanisms, namely by addition reactions or anion exchange [35]. In high hydrochloric acid concentration, cobalt ion forms the anionic complex (CoCl$_4^{2-}$) with large proportions according to the previous results related to the speciation diagram study. Based on these results, one mole of cobalt ion will need a minimum of two moles of Aliquat 336 to neutralize the negative charge of CoCl$_4^{2-}$. Thus, the suggested mechanism of Co(II) extraction by Aliquat 336 can be given by the Eq. (10) [33].

$$CoCl_4^{2-} + \overline{2\left(R_4N^+Cl^-\right)} \quad \overline{\left(R_4N\right)_2 CoCl_4} + 2Cl^- \tag{10}$$
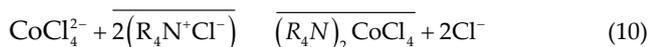
A plot of ln of distribution coefficient versus ln of different concentrations of free Aliquat 336 (Fig. 3) was used to determine the extraction reaction stoichiometry. The concentration of free Aliquat 336 was calculated by Eq. (12) using Eq. (11).

$$\left[Aliquat_{free}\right] = \left[Aliquat_{initial}\right] - \left[Aliquat_{complexing}\right] \tag{11}$$

$$\left[Aliquat_{free}\right] = \left[Aliquat_{initial}\right] - 2Y_1 \tag{12}$$
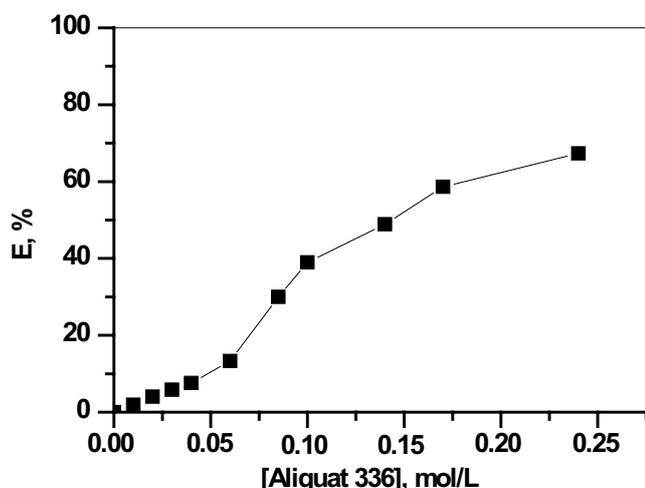
Fig. 2. Extraction yield of Co(II) as function of the extractant concentration. [HCl] = 6.5 M; stirring time: 10 min; [Co(II)] = 2 g L^{-1}; oleyl alcohol: 5% w/v; diluent: dodecane; Vorg/Vaq = 1.
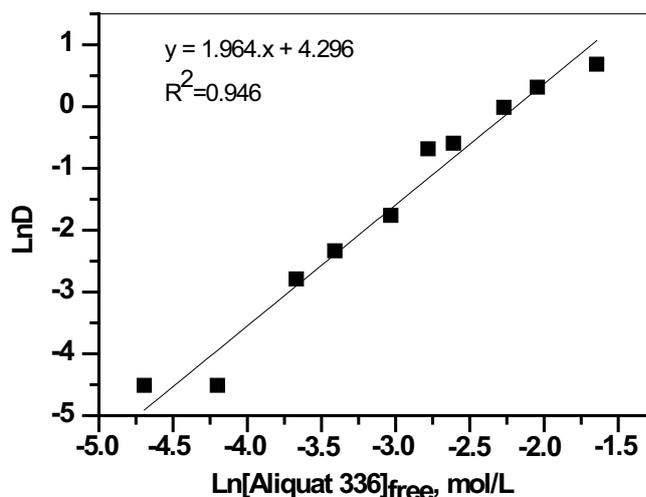
Fig. 3. Plot of ln D vs. ln [Aliquat 336]$_{free}$ for Co(II) extraction. [HCl] = 6.5 M, stirring time: 10 min, [Co(II)] = 2 g L^{-1}, oleyl alcohol: 5% w/v, diluent: dodecane, Vorg/Vaq = 1.

In fact, the ln of distribution coefficient (D) is given by Eq. (15) by using the equation of equilibrium constant K_{ex} Eq. (13) and the equation of distribution coefficient Eq. (14).

$$K_{ex} = \frac{\overline{\left[\left(R_4N\right)_2 CoCl_4\right]}\left[Cl^-\right]^2}{\left[CoCl_4^{2-}\right]\overline{\left[R_4N^+Cl^-\right]}^2} \tag{13}$$

where

$$D = \frac{\overline{\left[Co\right]_{org}}}{\left[Co\right]_{aq}} = \frac{\overline{\left[\left(R_4N\right)_2 CoCl_4\right]}}{\left[CoCl_4^{2-}\right]} \tag{14}$$

$$\ln D = 2\ln\overline{\left[R_4N^+Cl^-\right]} + \ln K_{eq} - 2\ln Cl^- \tag{15}$$

The slope of the linear regression (Fig. 3) was of 1.96 where lnK_{eq} – 2lnCl$^-$ was constant. This slope value is close to two, which suggests that the two moles of Aliquat 336 are associated for the extraction of one mole of cobalt, to form the metal ion-complex in organic phase. These experimental results confirm the proposed mechanism of extraction reaction of Co(II) by Aliquat 336 Eq. (10).

3.1.4. Effect of extraction time

The Aliquat 336 concentration is maintained at 0.17 M instead of 0.24 M in the rest of our study, in order to answer to the economic and ecological interests. Indeed, at 0.24 M we will risk technical problems due to the third phase appearance. The influence of the agitation time on extraction and stripping of the cobalt ions was studied in the range of 0–12 min. The results are shown in Fig. 4. From where, the equilibrium of Co(II) extraction was reached after 2 min where the extraction yield of Co(II) was of 62.5%. The Co(II) extraction was followed by the back-extraction or stripping (Fig. 4). For this, the organic phase, recovered after the extraction step, was brought into contact with distilled water as stripping phase
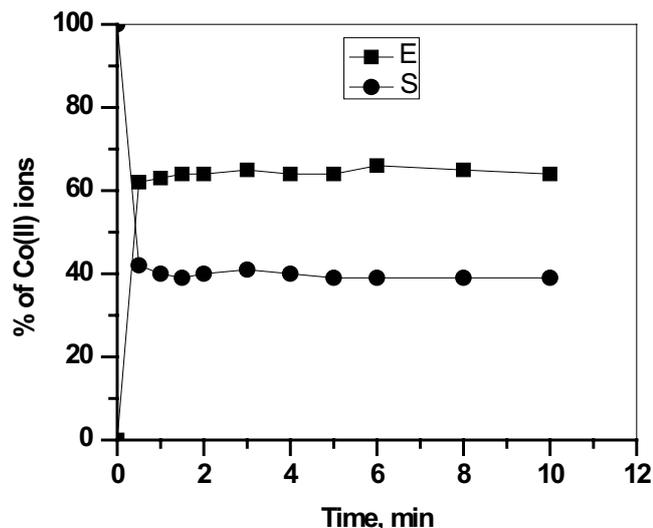
Fig. 4. Effect of agitation time on the recovery of Co(II). [HCl] = 6.5 M, $[Co(II)]_0$ = 2 g L^{-1}, oleyl alcohol: 5% w/v, diluent: dodecane, [Aliquat 336] = 0.17 M, Vorg/Vaq = 1.

Fig. 5. Extraction yield of Co(II) vs. hydrochloric acid concentration. $[Co(II)]_0$ = 2 g L^{-1}, oleyl alcohol: 5% w/v, diluent: dodecane, [Aliquat 336] = 0.17 M, Vorg/Vaq = 1, equilibrium time: 2 min.

at a 1:1 phase ratio. Thus, the stripping equilibrium of Co(II) was reached within 1 min of back-extraction. Therefore, the kinetics of extraction and back-extraction steps were rapid. These results have an advantage for the chemical process of cobalt recovery due to the stripping efficiency in which the Co(II) are stripped at 94%. We noted that the stripping efficiency (*S*) was defined by Eq. (16).

$$S(\%) = \frac{\left[Co\right]_{strip}}{\left[Co\right]_{org}} \times 100 \qquad (16)$$

where $[Co]_{strip}$: Concentration of cobalt in stripping aqueous phase; $[Co]_{org}$: Initial concentration of cobalt in the loaded organic phase

3.1.5. Influence of hydrochloric acid concentration

The influence of hydrochloric acid concentration on the Co(II) extraction by Aliquat 336 was carried out in the range of 4.0 to 8.5 M. According to Fig. 5, it was observed that the extraction yield of cobalt ions increased by increasing the hydrochloric acid concentration in feed phase. Considering these results as well as the speciation diagram, this increase was explained by the fact that the extractable species $CoCl_4^{2-}$ was predominant and its fraction increased when the hydrochloric acid concentration increased. The curve was limited to the concentration of 8.5 M to avoid the third phase formation. In fact, the hydrochloric acid concentration of 6.5 M was effective to obtain a favorable extraction of Co(II). We noted that the mass balance was verified with an average deviation percentage of 2.1%. The chosen acidic concentration was explained by the fact that below 6.5 M of HCl concentration, the extraction yields of Co(II) were not interesting. Therefore, to increase the extraction it would be necessary to increase enormously the stages number in the SX process, which becomes more expensive. The Co(II) extraction remaining quantitative within the range of 6.5–8.5 M of HCl.
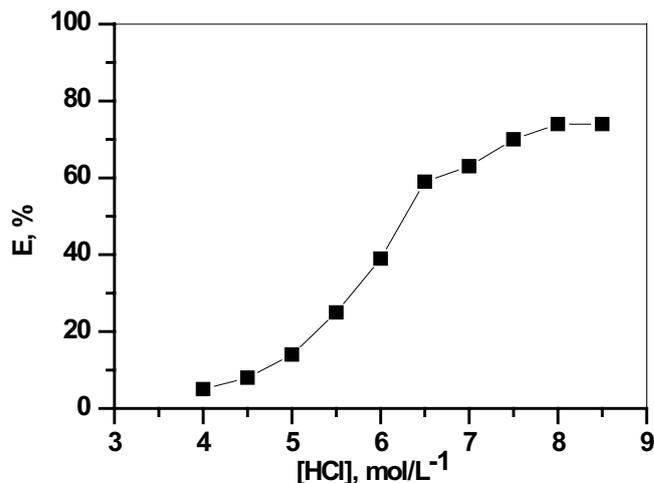
Beyond this last, the third phase formation appears that requires the addition of more modifier quantity or use of heating energy.

3.1.6. Effect of Cl$^-$ concentration

The chlorides concentration is a factor that influences the extraction yield and consequently the efficiency of stripping step in the Co(II) recovery process. For this, we have taken various concentrations ranging from 6.5 to 7.5 M in Cl$^-$ where the hydrochloric acid concentration was constant and equal to 6.5 M. By plotting ln of distribution coefficient as function of ln of chlorides ions (Fig. 6), in the concentration range of 6.5 to 7.5 M, a negative slope (−2.23) was obtained that confirms the suggested mechanism of the Co(II) extraction by
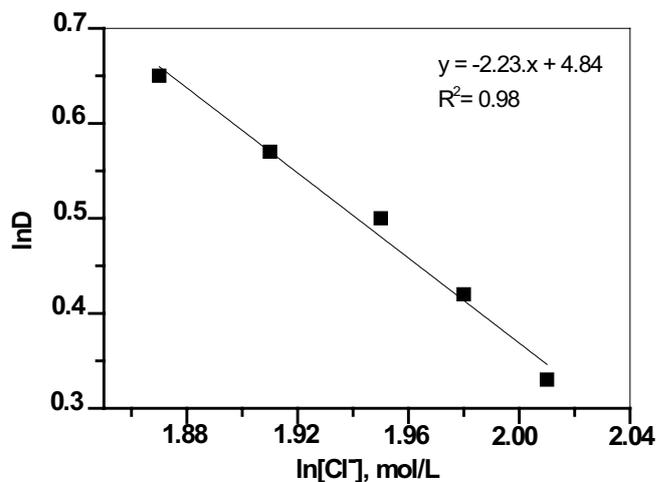
Fig. 6. ln of distribution coefficient as function of the chloride ions concentration. $[Co(II)]_0$ = 2 g L^{-1}, oleyl alcohol: 5% w/v, diluent: dodecane, [Aliquat 336] = 0.17 M, [HCl] = 6.5 M, Vorg/Vaq = 1, equilibrium time: 2 min.

Aliquat 336, cited previously Eq. (10). In fact, the extraction of one mole of Co(II) by Aliquat 336 releases two moles of chlorides ions.

3.1.7. Effect of initial concentration of Co(II)

The feed phase concentration affects the driving force of metal ion transport and consequently the mass transfer rate in liquid–liquid extraction process. However, it influence the metal extractability which can be interpreted as a compromise between the maximum of extracted metal and the minimal consumption of extractant agent [36,37]. The effect of the initial concentration of feed phase on the extraction yield of Co(II) was achieved by varying the concentration of cobalt ions from 1 to 6 g L^{-1} and maintaining the extractant concentration equal to 0.17 M. Thus, the molar ratios between Co(II) and extractant was varied in range of 0.1–0.6 where the operating conditions optimized previously were kept fixed. The mass balance was verified with an average deviation percentage of 2.78%. The results are shown in Fig. 7. From this last, we observed that the extraction yield of Co(II) decreased when the initial concentration of feed phase increased. This can be explained by the exterminating of the extraction sites of extractant or by the saturation of the exchange interface between the organic and aqueous phases.

3.1.8. Extraction isotherm of cobalt (II)

The extraction isotherms were plotted from the SX results given by following the cobalt ions concentration in the organic phase according to that in the aqueous phase while maintaining the constant temperature. When, the initial concentration of feed phase was varied from 1 to 6 g L^{-1}, the evolution of Co(II) concentration in organic phase compared to that in aqueous phase, was not linear (Fig. 8a). From where, the curve begins to bow namely at a high initial concentration of the feed phase. This was in good agreement with the study section on the effect of initial concentration of the feed

Fig. 8. Extraction isotherms for Co(II) extraction using Aliquat 336 as extractant. oleyl alcohol: 5% w/v, diluent: dodecane, [Aliquat336] = 0.17 M, [HCl] = 6.5 M, Vorg/Vaq = 1, equilibrium time: 2 min. (a) [Co(II)]$_i$ = 1–6 g L^{-1} and (b) [Co(II)]$_i$ = 1–3 g L^{-1}.

phase on the Co(II) extraction by Aliquat 336 because beyond a feed concentration of 6 g L^{-1}, the third phase appeared. For initial concentrations of feed phase ranging from 1 to 3 g L^{-1} (Fig. 8b), the quantity of cobalt ions in organic phase was evaluated linearly with that in aqueous phase. Thus, the average value of distribution coefficient, which is the slope of the straight line, was of 1.175. In fact, to enhance the liquid–liquid extraction of Co(II) by Aliquat 336, the initial concentrations of feed phase should range from 1 to 3 g L^{-1} in which interesting values of extraction yields of Co(II) were obtained.

3.1.9. Study of stages number of Co(II) stripping

A McCabe–Thiele diagram was constructed for determining the theoretical plates number needed to reach a maximum stripping of Co(II) after its extraction by Aliquat 336. The diagram was plotted from the equilibrium isotherm of the stripping experiments of Co(II). Fig. 9 shows the equilibrium curve plotted with the cobalt concentration in raffinate, against to that in extract. The working line (Fig. 9) in the chart was limited by the point on the equilibrium curve

Fig. 7. Influence of initial concentration of feed solution on the extraction yield of Co(II). [HCl] = 6.5 M, oleyl alcohol: 5% w/v, diluent: dodecane, [Aliquat 336] = 0.17 M, Vorg/Vaq = 1, equilibrium time: 2 min.
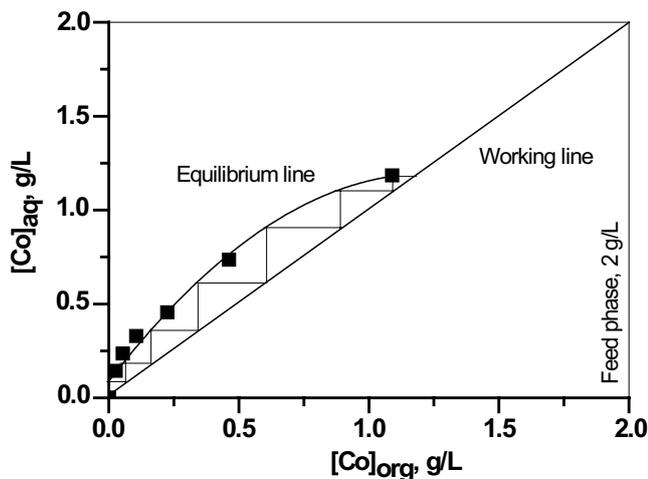
Fig. 9. McCabe–Thiele diagram for Co(II) stripping. Oleyl alcohol: 5% w/v, diluent: dodecane, [Aliquat 336] = 0.17 M, [HCl] = 6.5 M, equilibrium time: 2 min.

corresponding to the initial cobalt content in organic phase and that on the *x*-axis of the initial concentration of feed phase, with a slope equal to Org/Aq ratio. A horizontal line represented each plate in McCabe–Thiele diagram. So, we suggested that it would take six stages for the total stripping of Co(II) in distilled water.

3.2. Comparison of the present study with literature data

Many works were related to the Co(II) extraction by different chemical processes using diverse extractants namely the commercial organophosphoric compounds. Some of them were focused on the use of amine extractants, specially the IL where they are summarized in Table 1. From this last, we showed that our study presented some advantages over the previous data. In fact, we can extract an interesting quantity of cobalt by Aliquat 336 IL starting from its initial concentration corresponding to the range of cobalt ore leach during a short time. Also, we have used a long chain alcohol (oleyl alcohol) as modifier that is desirable at hydrometallurgical scale to enhance the Co(II) extraction and to avoid the third phase formation. Thus, the Co(II) stripping was realized rapidly and only by the distilled water at room temperature. Therefore, besides the Taguchi's modeling, our results have showed an eco-friendly process of cobalt extraction.

3.3. Separation of cobalt from nickel

Before starting the study of selective separation of cobalt and nickel ions from their synthetic mixture by Aliquat 336, experiments tests on the extraction and stripping of nickel(II) were conducted under the optimal conditions of Co(II) recovery (Table 1). The results showed a low extraction and stripping of Ni(II). Based on this result, a series of experiments on separation of the cobalt and nickel ions were carried from different mixtures under the optimal conditions of Co(II) recovery. It showed that the cobalt ions are more extracted than nickel ions whatever the composition of their mixture (Table 2). The liquid–liquid extraction process using Aliquat 336 as IL extractant showed a selectivity for cobalt ions than

nickel ions. This result was in good agreement with the literature about the anionic chloro-complex of cobalt ($CoCl_4^{2-}$), formed in high hydrochloric acid medium, favorable to the extraction by Aliquat 336 unlike the nickel ion which forms only the cationic complexes [5,32]. This will be able to have an advantage in the SX processes for separating the cobalt from nickel in the solutions of hydrochloric acid leachate by Aliquat 336 in presence of oleyl alcohol as modifier.

4. Taguchi modeling of Co(II) extraction

In the classical experimental study, the experiments are carried out by changing one factor at a time and keeping the other parameters constant. The study is advanced by examining the corresponding results, which involve both wasting material and time-consuming [39]. The most applied experimental design methods are response surface methodology [40–42] and Taguchi method [43,44]. Taguchi's technique is a powerful discipline of optimization used as a relevant tool in the engineering process optimization. It is a statistical technique, which estimates the main effects with a minimum number of experimental runs. In fact, it allows the identification of factors that have more influence on the process by using the factorial and an orthogonal arrays where the optimal level of factor for each experiment run is determined [39,45,46]. Thus, the experimental parameters and the number of levels are selected [47] in order to design the matrix of the experiments [48]. The approach of variance analysis (ANOVA) and that of ANOM as well as the signal to noise ratio (*S/N*) were used as the calculation tools of the Taguchi design for analyzing the experimental data and consequently to determine the conditions that give the optimal performance of process [49,50]. The Taguchi's experimental technique presents many advantages; it reduces the cost and improves the quality of the studied process where it provides the robust design solutions. By using the Taguchi method compared with other statistical methods, more quantitative information can be collected from a few experimental trials and a numerous factors can be simultaneously optimized. Taguchi's method is widely used in the recovery field of metal ions [46,51–53] and organic pollutants from wastewater [54–56].

In this paper, Taguchi's experimental design with an orthogonal array (L4) of three parameters and two levels was used in the optimization study, of liquid–liquid extraction of cobalt ions by Aliquat 336 in hydrochloric acid medium. Therefore, the required experiments number was given by the L4 matrix design (Table 3). From the experimental optimization study, we observed that the Co(II) extraction by Aliquat 336 in hydrochloric acid medium was potentially governed by important parameters which considerably affect the metal ion recovery. So, the considered factors in this study are: the Aliquat 336 concentration, hydrochloric acid concentration and initial concentration of the feed phase, designated as the independent variables by the symbols; *A, B* and *C*, respectively (Table 4).

4.1. Statistical study by ANOM approach

4.1.1. Signal-to-noise (S/N) ratio

In Taguchi's methodology, the desirable (signal) and undesirable (noise) values are examined for the characterization

Table 1
Comparison of the Co(II) SX using Aliquat 336/oleyl alcohol with literature data

Extractant	Diluent/modifier	Feed/medium	Strip	Operating parameters	Modeling	Reference
Primene®JMT/ Cyanex 272	Exxol D100	0.25–5 g L⁻¹ NaCl	1 M HCl	JMT/Cyanex 272: 10%/10% v/v $[Cl^-] = 0.4$ M $[Co(II)] = 1$ g L⁻¹ $E = 99\%$ (20 min at 23°C ± 3°C) $S = 95\%$	n/a	[16]
A336/CA-12	Toluene	0.010 g L⁻¹ Na_2SO_4	8×10^{-4} M H_2SO_4	$[[A336][CA-12]] = 2 \times 10^{-2}$ M pH = 5.25 $E = S = 96\%$ (60 min at 25°C)	n/a	[18]
Different forms of Aliquat 336	Kerosene	0.59 g L⁻¹ H_2SO_4 Na_2SO_4	2 M H_2SO_4	$[R4N\text{-}SCN] = 0.36$ M pH = 5.6 $E = 88.8\%$ (20 min at 25°C ± 1°C) $S = > 99.9\%$	n/a	[35]
Alamine 336	*m*-Xylene	1–6 g L⁻¹ HCl	–	Alamine 336 = 0.4 M $[HCl] = 8$ M $[Co(II)] = 1$ g L⁻¹ $E = 78.4\%$ (20 min at 22°C ± 1°C)	DOE	[36]
Alamine 336	Kerosene	0.4–5 g L⁻¹ HCl NaCl	–	Alamine 336 = 0.23 M $[HCl] = 4.5$ M $[Co(II)] = 4.7$ g L⁻¹ $E = 60\%$ (15 min at 25°C)	n/a	[37]
Amine and organophosphoric compounds	Kerosene/ 6% decyl-alcohol	0.54 g L⁻¹ HCl	HCl	$[Aliquat\ 336] = 1.0$ M $E = 63.7\%$ (30 min) $S = 94.4\%$	n/a	[38]
Aliquat 336	Dodecane/ 5% w/v oleyl alcohol	1–6 g L⁻¹ HCl NaCl	Distilled water	$[Aliquat\ 336] = 0.17$ M $[HCl] = 6.5$ M $[Co(II)] = 2$ g L⁻¹ $E = 62.50\%$ (2 min at 20.0°C) $S = 58.75\%$ (1 min)	Taguchi method	Present study

Primene®JMT (JMT): a tertiary alky(C16 to C22) primary amine, Cyanex 272: bis(2,4,4-trimethylpentyl) phosphinic acid, Exxol D100: aliphatic hydrocarbon, A336/CA-12: tricaprylmethylammonium][sec-octylphenoxy acetate, Alamine 336: tri-octyl/decyl amine, n/a: not available.

Table 2
Separation experiments of Co(II) and Ni(II) by Aliquat 336

Mixture composition (Co/Ni)	E%	
g L⁻¹	Co(II)	Ni(II)
2/2	58	5
1/6	59	2
6/1	51	3

of output measures (responses). The term "signal" determines the extent of noise factors on the output experiment [2]. The signal-to-noise (*S/N*) ratios measure the process performance by studying the deviations of the output measures from the desired values. They provide a healthy optimization of the operating parameters by minimizing the deviations in responses [57]. There are three types of ratio (*S/N*) used to

quantify the quality: nominal the better, smaller the better and larger the better [58]. Usually, in the metal ions extraction process, the larger the better was considered [59] according to the Eq. (17). The results are given in Table 5.

$$\frac{S}{N} = -10\log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{E_i^2}\right) \qquad (17)$$

where *n* represents total number of replication of each test run; E_i represents the extraction yield of Co(II) realized in replication experiment *i* carried out under the same experimental conditions of each test run; $\bar{E}$ represents the average extraction yield of Co(II).

4.1.2. ANOM of signal-to-noise

The Co(II) extraction process required optimization of the most influential controlling parameters using an ANOM

Table 3
Test runs for L4 Taguchi model

N° Run	Factors		
	A	*B*	*C*
1	1	1	1
2	1	2	2
3	2	1	2
4	2	2	1

Table 4
Factors and their corresponding levels

Factors	Description	Level 1 (L1)	Level 2 (L2)
A	[Aliquat336], M	0.01	0.24
B	[HCl], M	4	8.5
C	[Co(II)]$_0$, g L^{-1}	1	6

Table 5
Extraction yields of Co(II) corresponding to *S/N* ratios

N° Run	E1	E2	E3	$\bar{E}$	S/N
1	5	3	5	4.33	11.96
2	9	10	7	8.67	18.46
3	19	21	19	19.67	25.85
4	82	84	81	82.33	38.31

approach of the signal-to-noise ratios. Eq. (18) represents the mean value of S/N ratio of each parameter at a level [59].

$$\left(M\right)_{\text{Level}=i}^{\text{Factor}=F} = \frac{1}{n_{Fi}}\sum_{j=1}^{n_{Fi}}\left[\left(\frac{S}{N}\right)_{\text{Level}=i}^{\text{Factor}=F}\right]_j \tag{18}$$

where $\left(M\right)_{\text{Level}=i}^{\text{Factor}=F}$ is the mean of *S/N* ratio with factor *F* at level *i*, $\left[\left(\frac{S}{N}\right)_{\text{Level}=i}^{\text{Factor}=F}\right]_j$ is the S/N ratio value with factor *F* at level *i* in its *j*th appearance in Table 5 and is the *j*th value in Table 6 (*j* = 1,2,3… n_{Fi}); n_{Fi} is the number of appearances of factor *F* in level *i*.

Table 5 illustrates the results of mean values of extraction yield of Co(II) and the S/N ratios according to L4 Taguchi matrix. Thus, from Table 6 we can obtain the optimal level of each factor which contributes to the maximum extraction of Co(II). The results showed that the most influential levels of the considered factors are such as: factor *A* (level 2), factor *B* (level 2) and factor *C* (level l). In fact, for increasing the extraction yield and consequently the recovery of cobalt ions, we must operate with high concentrations in extractant and hydrochloric acid when decreasing the metal ion concentration in feed phase. The experimental study showed that a higher extraction yield of Co(II) can be found of 67% at 0.24 M of Aliquat 336 and 6.5 M of HCl, starting from the initial concentration of feed phase of 2 g L^{-1}. These statistical

Table 6
S/N ratios response table

Factor/level	$\left[\left(\dfrac{S}{N}\right)_{\text{Level}}^{\text{Factor}}\right]_j$		$\left[\left(M\right)_{\text{Level}}^{\text{Factor}}\right]$
	J = 1	J = 2	
A/1	11.96	18.46	15.21
A/2	25.85	38.31	32.07
B/1	11.96	25.85	18.90
B/2	18.46	38.31	28.38
C/1	11.96	38.31	25.13
C/2	18.46	25.85	22.15

results were in good agreement with those obtained experimentally because the extraction yield of Co(II) increased when increasing both the hydrochloric acid concentration in feed phase and extractant concentration.

4.1.3. Cumulative average of extraction yield of Co(II)

The cumulative average of extraction yield of the cobalt ions $(\bar{E})_k^F$ with a certain factor *F* at the *k*th level was given by Eq. (19) where the results are presented in Table 7. We noted that the cumulative average of extraction yield of Co(II) achieved in our study $\left(\bar{E}\right)_k^F$ was equal to 28.75, calculated by Eq. (20).

$$\left(\bar{E}\right)_k^F = \frac{1}{n_{Fk}}\sum_{j=1}^{n_{Fk}}\left[\left(\bar{E}\right)_{\text{Level}=k}^{\text{Factor}=F}\right]_j \tag{19}$$

where $\left[\left(\bar{E}\right)_{\text{Level}=k}^{\text{Facteur}=F}\right]$ represents the average extraction yield of the cobalt ions $(\bar{E})$ with a factor *F* at level *k* in its *j*th appearance sequence in Table 5; n_{Fk} represents the number of appearances of factor *F* at level *k*.

$$\overline{R_T} = \sum_{j=1}^{m}\frac{\left(\sum_{i=1}^{n}E_i\right)_j}{mn} \tag{20}$$

Table 7
Cumulative average of extraction yield of Co(II) according to L4 Taguchi

Factor/level	$\left[\left(\bar{E}\right)_{\text{Level}=k}^{\text{Facteur}=F}\right]_j$		$(\bar{E})_k^F$
	J = 1	J = 2	
A/1	4.33	8.67	6.5
A/2	19.67	82.33	51
B/1	4.33	19.67	12
B/2	8.67	82.33	45.5
C/1	4.33	82.33	43.33
C/2	8.67	19.67	14.16

with m representing the number of experiments carried out in the present study.

4.1.4. Graphical analysis

The individual effects of experimental parameters taken by the Taguchi modeling were plotted in function of the average extraction yields and the signal-to-noise ratios (Fig. 10). The segments of S/N ratios and the average extraction yields are ascending and do not intersect in the studied interval (Fig. 10a). This showed that, to increase the response it is necessary to go toward level 2, which is favored by the L4 model due to important signal-to-noise ratio. Indeed, the best extraction yields of Co(II) by Aliquat 336 are obtained with significant S/N ratios. So, the average extraction yield of Co(II) was of 51% at S/N ratio equal to 32.07. The S/N ratios segment is above of that the average extraction yields. This showed that the Aliquat 336 parameter remains in the respect of the Taguchi L4 model even by changing their concentration in the chosen range. Experimentally, when the Aliquat 336 concentration ranges from 0.17 to 0.24 M, the extraction yield of Co(II) decline by only 4.5%. The same remarks remain valid in the case of the hydrochloric acid concentration parameter (Fig. 10b). From where, the extraction yields of Co(II) increased with increasing the acidic concentration in the aqueous feed phase. Thus, we obtained an average extraction yield equal to 45.5% at S/N ratio of 28.38. This result is in agreement with that obtained through experiment which justifies the choice to work with 6.5 M in acid instead of 8.5 M. From the Taguchi modeling, the extractant concentration parameter remains always predominant of that of hydrochloric acid concentration. In contrast to the individual effects of extractant concentration and acid concentration, the segments of S/N ratios and average extraction yields are downward and intersect within the study interval (Fig. 10c). This indicates that in order to increase the extraction yield of Co(II), it is necessary to go toward low parameter level of the initial concentration of feed phase. Thus, we can expect an average extraction yield of Co(II) equal to 43.33%, from an initial feed concentration of 1 g L^{-1}, at an S/N ratio of 25.13.
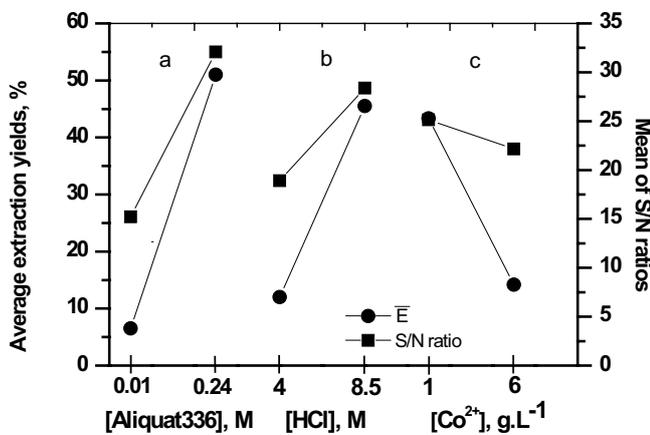
This is in agreement with the experimental results where the best extraction yields of Co(II) were obtained from a feed concentration of 1–2 g L^{-1}.

According to the modeling results, the Taguchi L4 model chosen for the statistical study of liquid–liquid extraction of Co(II) from hydrochloric acidic medium by Aliquat 336 has described our experimental results with accuracy in which the interesting information of factors contribution on the recovery process of Co(II) were given.

4.2. Statistical study by ANOVA approach

ANOVA is a statistical tool used to interpret the experimental data, which gives the optimal performance of factors in the extraction process of Co(II) basing on the determination of significant differences among them [39]. The degree of freedom, sum of squares (SS), variance and the contribution percentage of each experimental factor are included in the ANOVA table [48]. However, the factorial sum of squares (SS_F) was given by Eq. (21) and the total sum of squares (SS_T) was calculated by Eq. (22). These two equations were used in the calculation of variance error Eq. (23) that was used in the determination of the contribution percentage of each factor (ρ_F), given by Eq. (24). We noted that the error variance (V_{Er}) was of 1.83. Table 8 showed the factorial sum of squares and the contribution percentage of each factor. From where, the extractant concentration (50.01%) was an important parameter in the liquid–liquid extraction of Co(II) where the hydrochloric acid concentration (28.33%) becomes in second degree before the feed concentration factor (21.47%). These results were in agreement with those obtained by the ANOM approach. We also observed that the Aliquat 336 extractant contributed more than the other factors in the extraction process of Co(II) in hydrochloric acid medium. We noted that there is no error due to the uncontrollable factors (noise). This concluded that we have taken only all the important and effective factors in our optimization study.

$$SS_F = \frac{mn}{L}\sum_{k=1}^{L}\left(\overline{E}_k^F - \overline{E}_T\right)^2 \tag{21}$$

$$SS_T = \sum_{j=1}^{m}\left(\sum_{i=1}^{n}E_i^2\right)_j - mn\left(\overline{E}_T\right)^2 \tag{22}$$

where L is level number of each factor.

$$V_{Er} = SS_T - \sum_{F=A}^{D}\frac{SS_F}{m(n-1)} \tag{23}$$

$$\rho_F = \frac{SS_F - \left(DOF_F V_{Er}\right)}{SS_T}\times 100 \tag{24}$$

Fig. 10. Effects of the individual experimental parameters on the evolution of the average extraction yields of Co(II) according to *S/N* ratios. (a) Aliquat 336 concentration, (b) hydrochloric acid concentration and (c) cobalt ions concentration.

Table 8
Contribution percentage of factors and their corresponding factorial sum of squares

	SS_F	ρ_F
A	5,940.75	50.01
B	3,366.75	28.33
C	2,552.08	21.47

with DOF$_F$ representing the degrees of freedom for each factor, which is obtained by subtracting one from the number of levels of each factor.

5. Conclusion

The experimental study of liquid–liquid extraction of Co(II) from hydrochloric acid medium by the Aliquat 336 showed that the cobalt ions were extracted at 62.5% and stripped from metal loaded organic phase at 94% by distilled water. Thus, two moles of Aliquat 336 extractant would be required to extract one mole of cobalt where the involved species in the suggested mechanism of extraction reaction was $CoCl_4^{2-}$ that is in accordance with speciation study of cobalt(II) in hydrochloric acid medium. The McCabe–Thiele method showed that six stages were required for complete stripping of Co(II) where the mass balances were checked for all studied parameters with an average deviation percentage of 2%. In fact, the separation experiments of Co(II) and Ni(II) by Aliquat 336 showed a selectivity toward Co(II) whatever the composition of their synthetic mixture. The statistical optimization of experimental data of Co(II) extraction was performed by the Taguchi method. The orthogonal array L4 model showed that the Aliquat 336 concentration parameter (*A*) was more important than the parameters of hydrochloric acid concentration (*B*) and initial concentration of feed phase (*C*) where the maximum of Co(II) extraction can be predicted at: [*A*] = 0.24 M, [*B*] = 8.5 M and [*C*] = 1 g L^{-1}. Indeed, the contribution percentage of each factor in the Co(II) recovery was as follows: *A* (50.01%), *B* (28.33%) and *C* (21.47%). The statistical study was in good agreement with the experimental results where the Co(II) extraction was better in high acidic medium. Therefore, the chosen L4 model has described our extraction process with accuracy.

Acknowledgments

References

[1] A. Surucu, V. Eyupoglu, O. Tutkun, Selective separation of cobalt and nickel by flat sheet supported liquid membrane using Alamine 300 as carrier, J. Ind. Eng. Chem., 18 (2012) 629–634.
[2] F.K. Crundwell, M.S. Moats, V. Ramachandran, T.G. Robinson, W.G. Davenport, Extraction of Cobalt from Nickel Laterite and Sulfide Ores, Extractive Metallurgy of Nickel, Cobalt and Platinum Group Metals, Chapter 29, Elsevier, Amsterdam, Boston, 2011, pp. 365–376.
[3] R.A. Kumbasar, Extraction and concentration of cobalt from acidic leach solutions containing Co–Ni by emulsion liquid membrane using TOA as extractant, J. Ind. Eng. Chem., 16 (2010) 448–454.
[4] R.A. Kumbasar, O. Tutkun, Separation of cobalt and nickel from acidic leach solutions by emulsion liquid membranes using Alamine 300 (TOA) as a mobile carrier, Desalination, 224 (2008) 201–208.
[5] T.Zh. Sadyrbaeva, Separation of cobalt(II) from nickel(II) by a hybrid liquid membrane–electrodialysis process using anion exchange carriers, Desalination, 365 (2015) 167–175.
[6] M.Z. Mubarok, L.I. Hanif, Cobalt and Nickel separation in nitric acid solution by solvent extraction using Cyanex 272 and Versatic 10, Procedia Chem., 19 (2016) 743–750.
[7] R.A. Kumbasar, Selective extraction of cobalt from strong acidic solutions containing cobalt and nickel through emulsion liquid membrane using TIOA as carrier, J. Ind. Eng. Chem., 18 (2012) 2076–2082.
[8] U. Ipek, Removal of Ni(II) and Zn(II) from an aqueous solution by reverse osmosis, Desalination, 174 (2005) 161–169.
[9] E. Katsou, S. Malamis, K.J. Haralambous, M. Loizidou, Use of ultrafiltration membranes and aluminosilicate minerals for nickel removal from industrial wastewater, J. Membr. Sci., 360 (2010) 234–249.
[10] F. Akbal, S. Camci, Copper, chromium and nickel removal from metal plating wastewater by electrocoagulation, Desalination, 269 (2011) 214–222.
[11] B. Li, F. Liu, J. Wang, C. Ling, L. Li, P. Hou, A. Li, Z. Bai, Efficient separation and high selectivity for nickel from cobalt-solution by a novel chelating resin: batch, column and competition investigation, Chem. Eng. J., 195–196 (2012) 31–39.
[12] E. Repo, J.K. Warchol, T.A. Kurniawan, M.E.T. Sillanpää, Adsorption of Co(II) and Ni(II) by EDTA- and/or DTPA-modified chitosan: kinetic and equilibrium modeling, Chem. Eng. J., 161 (2010) 73–82.
[13] M.V. Dinu, E.S. Dragan, Evaluation of Cu^{2+}, Co^{2+} and Ni^{2+} ions removal from aqueous solution using a novel chitosan/clinoptilolite composite: kinetics and isotherms, Chem. Eng. J., 160 (2010) 157–163.
[14] M. Panigrahi, M. Grabda, D. Kozak, A. Dorai, E. Shibata, J. Kawamura, T. Nakamura, Liquid–liquid extraction of neodymium ions from aqueous solutions of $NdCl_3$ by phosphonium-based ionic liquids, Sep. Purif. Technol., 171 (2016) 263–269.
[15] P.V. Vernekar, Y.D. Jagdale, A.W. Patwardhana, A.V. Patwardhana, S.A. Ansarib, P.K. Mohapatrab, V.K. Manchandac, Transport of cobalt(II) through a hollow fiber supported liquid membrane containing di-(2-ethylhexyl) phosphoric acid (D2EHPA) as the carrier, Chem. Eng. Res. Des., 91 (2013) 141–157.
[16] M.T. Coll, A. Fortuny, C.S. Kedari, A.M. Sastre, Studies on the extraction of Co(II) and Ni(II) from aqueous chloride solutions using Primene JMT-Cyanex272 ionic liquid extractant, Hydrometallurgy, 125–126 (2012) 24–28.
[17] R.A. Kumbasar, Selective transport of cobalt (II) from ammoniacal solutions containing cobalt (II) and nickel (II) by emulsion liquid membranes using 8-hydroxyquinoline, J. Ind. Eng. Chem., 18 (2012) 145–151.
[18] X. Sun, X. Ji, L. Zhang, J. Chen, Separation of cobalt and nickel using inner synergistic extraction from bifunctional ionic liquid extractant (Bif-ILE), J. Hazard. Mater., 182 (2010) 447–452.
[19] D. Parmentier, S. Paradis, S.J. Metz, S.K. Wiedmer, M.C. Kroon, Continuous process for selective metal extraction with an ionic liquid, Chem. Eng. Res. Des., 109 (2016) 553–560.
[20] B. Zawisza, R. Sitko, Micro-electrodeposition in the presence of ionic liquid for the preconcentration of trace amounts of Fe, Co, Ni and Zn from aqueous samples, Spectrochim. Acta, Part B, 82 (2013) 60–64.
[21] D. Buachuang, P. Ramakul, N. Leepipatpiboon, U. Pancharoen, Mass transfer modeling on the separation of tantalum and niobium from dilute hydrofluoric media through a hollow fiber supported liquid membrane, J. Alloys Compd., 509 (2011) 9549–9557.
[22] J.P. Mikkola, P. Virtanen, R. Sjöholm, Aliquat 336®—a versatile and affordable cation source for an entirely new family of hydrophobic ionic liquids, Green Chem., 8 (2006) 250–255.
[23] C. Deferm, M. Van de Voorde, J. Luyten, H. Oosterhof, J. Fransaer, K. Binnemans, Purification of indium by solvent extraction with undiluted ionic liquids, Green Chem., 18 (2016) 4116–4127.
[24] Y. Litaiem, M. Dhahbi, Measurements and correlations of viscosity, conductivity and density of an hydrophobic ionic liquid (Aliquat 336) mixtures with a non-associated dipolar aprotic solvent (DMC), J. Mol. Liq., 169 (2012) 54–62.
[25] W. Wei, C.-W. Cho, S. Kim, M.-H. Song, J.K. Bediako, Y.-S. Yun, Selective recovery of Au(III), Pt(IV), and Pd(II) from aqueous

solutions by liquid–liquid extraction using ionic liquid Aliquat-336, J. *Mol. Liq.*, 216 (2016) 18–24.

[26] B. Wassink, D. Dreisinger, J. Howard, Solvent extraction separation of zinc and cadmium from nickel and cobalt using Aliquat 336, a strong base anion exchanger, in the chloride and thiocyanate forms, Hydrometallurgy, 57 (2000) 235–252.

[27] G. Hellé, C. Mariet, G. Cote, Liquid–liquid extraction of uranium(VI) with Aliquat® 336 from HCl media in microfluidic devices: combination of micro-unit operations and online ICP-MS determination, Talanta, 139 (2015) 123–131.

[28] F.D.M. Fábrega, M.B. Mansur, Liquid–liquid extraction of mercury (II) from hydrochloric acid solutions by Aliquat 336, Hydrometallurgy, 87 (2007) 83–90.

[29] E. Quijada-Maldonado, M.J. Torres, J. Romero, Solvent extraction of Molybdenum (VI) from aqueous solution using ionic liquids as diluents, Sep. Purif. Technol., 177 (2017) 200–206.

[30] R.B. Sudderth, G. Kordosky, Some Practical Considerations in the Evaluation and Selection of Solvent Extraction Reagents, D. Malhotra, W.F. Riggs, Chemical Reagents in the Mineral Processing Industry, Society for Mining Metallurgy and Exploration, Colorado, USA, 1986, 181–196.

[31] G.M. Ritcey, Commercial Processes for Nickel and Cobalt, T.C. Lo, M.H.I. Baird, C. Hanson, Handbook of Solvent Extraction, Wiley, New York, 1983, pp. 673–687.

[32] A.H. Blitz-Raith, R. Paimin, R.W. Cattrall, S.D. Kolev, Separation of cobalt(II) from nickel(II) by solid-phase extraction into Aliquat 336 chloride immobilized in poly(vinyl chloride), Talanta, 71 (2007) 419–423.

[33] H.C. Kao, R.S. Juang, Kinetic analysis of non-dispersive solvent extraction of concentrated Co(II) from chloride solutions with Aliquat 336: significance of the knowledge of reaction equilibrium, J. Membr. Sci., 264 (2005) 104–112.

[34] S.Y. Choia, V.T. Nguyenb, J. Lee, H. Kanga, B.D. Pandeyd, Liquid-liquid extraction of Cd(II) from pure and Ni/Cd acidic chloride media using Cyanex 921: a selective treatment of hazardous leachate of spent Ni-Cd batteries, J. Hazard. Mater., 278 (2014) 258–266.

[35] A.A. Nayl, Extraction and separation of Co(II) and Ni(II) from acidic sulfate solutions using Aliquat 336, J. Hazard. Mater., 173 (2010) 223–230.

[36] M. Filiz, N.A. Sayar, A.A. Sayar, Extraction of cobalt(II) from aqueous hydrochloric acid solutions into alamine 336–m-xylene mixtures, Hydrometallurgy, 81 (2006) 167–173.

[37] A. Fernandes, J.C. Afonso, A.J.B. Dutra, Separation of nickel(II), cobalt(II) and lanthanides from spent Ni-MH batteries by hydrochloric acid leaching, solvent extraction and precipitation, Hydrometallurgy, 133 (2013) 37–43.

[38] Y. Liu, M.S. Lee, Separation of cobalt and nickel from chloride leach solution of nickel laterite ore by solvent extraction, Geosyst. Eng., 19 (2016) 214–221.

[39] W. Ferdous, A. Manalo, T. Aravinthan, Bond behaviour of composite sandwich panel and epoxy polymer matrix: Taguchi design of experiments and theoretical predictions, Constr. Build. Mater., 145 (2017) 76–87.

[40] N. Benyahia, N. Belkhouche, J.A. Jönsson, A comparative study of experimental optimization and response surface methodology of Bi(III) extraction by emulsion organophosphorus liquid membrane, J. Environ. Chem. Eng., 2 (2014) 1756–1766.

[41] H. Liu, Y.M. Zhang, J. Huang, T. Liu, Q.H. Shi, Optimization of vanadium (IV) extraction from stone coal leaching solution by emulsion liquid membrane using response surface methodology, Chem. Eng. Res. Des., 123 (2017) 111–119.

[42] M. Mesli, N. Belkhouche, Emulsion ionic liquid membrane for recovery process of lead. Comparative study of experimental and response surface design, Chem. Eng. Res. Des., 129 (2018) 160–169.

[43] G. Taguchi, S. Chowdhury, Y. Wu, Taguchi's Quality Engineering Handbook, Wiley-Interscience, Hoboken, New Jersey, 2005.

[44] A. Nazari, H. Khanmohammadi, M. Amini, H. Hajiallahyari, A. Rahimi, Production geopolymers by Portland cement: designing the main parameters' effects on compressive strength by Taguchi method, Mater. Des., 41 (2012) 43–49.

[45] P.K. Bose, M. Deb, R. Banerjee, A. Majumder, Multi objective optimization of performance parameters of a single cylinder diesel engine running with hydrogen using a Taguchi-fuzzy based approach, Energy, 63 (2013) 375–386.

[46] N.M.S. Kaminari, D.R. Schultz, M.J.J.S. Ponte, H.A. Ponte, C.E.B. Marino, A.C. Neto, Heavy metals recovery from industrial wastewater using Taguchi method, Chem. Eng. J., 126 (2007) 139–146.

[47] R. Azadi, Y. Rostamiyan, Experimental and analytical study of buckling strength of new quaternary hybrid nanocomposite using Taguchi method for optimization, Constr. Build. Mater., 88 (2015) 212–224.

[48] N. Pandey, K. Murugesan, H.R. Thomas, Optimization of ground heat exchangers for space heating and cooling applications using Taguchi method and utility concept, Appl. Energy, 190 (2017) 421–438.

[49] M.K. Balki, C. Sayin, M. Sarıkaya, Optimization of the operating parameters based on Taguchi method in an SI engine used pure gasoline, ethanol and methanol, Fuel, 180 (2016) 630–637.

[50] X. Liu, S. Zhao, Y. Qin, J. Zhao, W.A. Wan-Nawang, A parametric study on the bending accuracy in micro W-bending using Taguchi method, Measurement, 100 (2017) 233–242.

[51] E. Barrado, M. Vega, R. Pardon, P. Grande, J.L.D. Valle, Optimisation of a purification method for metal-containing wastewater by use of a Taguchi experimental design, Water Res., 30 (1996) 2309–2314.

[52] G. Dönmez, Z. Aksu, The effect of copper(II) ions on the growth and bioaccumulation properties of some yeasts, Process Biochem., 35 (1999) 35–142.

[53] T. Mohammadi, A. Moheb, M. Sadrzadeh, A. Razmi, Separation of copper ions by electrodialysis using Taguchi experimental design, Desalination, 169 (2004) 21–31.

[54] G.H.V.C. Chary, M.G. Dastidar, Optimization of experimental conditions for recovery of coking coal fines by oil agglomeration technique, Fuel, 9 (2010) 2317–2322.

[55] A.B. Engin, O. Ozdemir, M. Turan, A.Z. Turan, Color removal from textile dyebath effluents in a zeolite fixed bed reactor: determination of optimum process conditions using Taguchi method, J. Hazard. Mater., 159 (2008) 348–353.

[56] M.R. Sohrabi, S. Jamshidi, A. Esmaeilifar, Cloud point extraction for determination of Diazinon: optimization of the effective parameters using Taguchi method, Chemom. Intell. Lab. Syst., 110 (2012) 49–54.

[57] R.S. Kumar, K. Sureshkumar, R. Velraj, Optimization of biodiesel production from *Manilkara zapota* (L.) seed oil using Taguchi method, Fuel, 140 (2015) 90–96.

[58] M. Sarıkaya, A. Güllü, Taguchi design and response surface methodology based analysis of machining parameters in CNC turning under MQL, J. Cleaner Prod., 65 (2014) 604–616.

[59] R. Pundir, G.H.V.C. Chary, M.G. Dastidar, Application of Taguchi method for optimizing the process parameters for the removal of copper and nickel by growing *Aspergillus* sp., Water Resour. Ind., 20 (2018) 83–92.