

*Full Length Research Paper*

## Purification of cobalt solutions in several solvent extraction steps: Using MEXTRAL and D2EHPA as extractants

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Received 17 January, 2021; Accepted 8 March, 2021

A sulphate solution of cobalt (18.93 g/L  $\text{Co}^{2+}$ ) containing major impurities such as copper (1.35 g/L  $\text{Cu}^{2+}$ ), iron (0.28 g/L  $\text{Fe}^{\text{tot}}$ ), zinc (0.70 g/L  $\text{Zn}^{2+}$ ) and manganese (4.83 g/L  $\text{Mn}^{2+}$ ) was purified through the solvent extraction method using two extractants; MEXTRAL and D2EHPA for the removal of copper and for the removal in two stages of a zinc-iron-manganese complex respectively. The effects of the solution's pH, O/A ratio, extraction time and stirring intensity were investigated. The purification extent was enhanced by optimizing these four parameters through Taguchi's L16 ( $4^4$ ) experimental. The final solution obtained through sequential extractions showed a reduction in Cu, Fe, Zn and Mn content of 98.7, 97.5, 98.2, and 80.5% respectively. This study showcased the possibility of obtaining high purity cobalt as a precursor for Lithium ion battery applications, representing 49% of its current global use. The coextraction value of cobalt was estimated at 6.2%.

**Key words:** Purification, MEXTRAL 984N, D2EHPA, cobalt, SX.

### INTRODUCTION

The purity requirements of cobalt in electrical and electrochemical applications are of high standards (Audion et al., 2014). This has driven the development of various purification methods of cobalt solutions for the past years as highlighted in literature. These methods include selective precipitation of impurities, sulphurous precipitation, ion exchange, molecular recognition technology and solvent extraction (Rumbu, 2012).

The extent of impurity removal depends on the specifications of the desired final product; however, it is recommended to remove most of the impurities commonly

commonly found in cobalt's solutions prior to refining it further (Alves Dias et al., 2018). This includes (Fisher and Treadgold, 2007):

- i) Fe, Mn, Al, Cu, Zn, Pb, Cd, Ni; and
- ii) Ca, Mg and other various metals.

of all these methods, the use of solvent extraction as purification method has become the technique of choice owing to its ability to yield high purity grade Co that matches the specs required by today's industry

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**Table 1.** Levels of parameter study.

Level	1	2	3	4
pH	1.6	1.8	2	2.2
O/A ratio	1/1	2/1	3/1	4/1
Time (min)	2	3	4	5
Agitation (rpm)	1650	1700	1750	1800

**Table 2.** Taguchi plan of the tests to be carried out.

Test	pH	O/A ratio	Time [min]	Agitation [rpm]
Test 1	1.6	1/1	2	1650
Test 2	1.6	2/1	3	1700
Test 3	1.6	3/1	4	1750
Test 4	1.6	4/1	5	1800
Test 5	1.8	1/1	3	1750
Test 6	1.8	2/1	2	1800
Test 7	1.8	3/1	5	1650
Test 8	1.8	4/1	4	1700
Test 9	2.0	1/1	4	1800
Test 10	2.0	2/1	5	1750
Test 11	2.0	3/1	2	1700
Test 12	2.0	4/1	3	1650
Test 13	2.2	1/1	5	1700
Test 14	2.2	2/1	4	1650
Test 15	2.2	3/1	3	1800
Test 16	2.2	4/1	2	1750

(Roux et al., 2007; Kopper Chemical Industrial, 2019b; Kitobo, 2009)). Many projects are planning to follow the SX path and are considering including up to three or four SX plants in series, with each of them using a different reagent.

Ketoximes and aldoximes based extractants such as LIX 984N and MEXTRAL 984N are a judicious choice for removal of copper while D2EHPA is mainly used for the purification of cobalt sulphate solutions in order to remove iron, zinc and manganese (Roux et al., 2007; Kopper Chemical Industry, 2019a; Sato et al, 1985; Zhang et al., 2018).

## MATERIALS AND METHODS

### Reagents used

An impure cobalt sulfate solution ( $\text{Co}^{2+}$ : 18.93 g/L;  $\text{Cu}^{2+}$ : 1.35 g/L;  $\text{Fe}^{\text{tot}}$ : 0.28 g/L;  $\text{Zn}^{2+}$ : 0.70 g/L and  $\text{Mn}^{2+}$ : 4.83 g/L) from an impure cobalt carbonate (Co : 24.1% ; Cu : 1.2%; Fe : 2.1%; Zn : 0.8%; Mn : 6.3%) and two extractants amongst which MEXTRAL 984N supplied by Kopper Company Industry Co., Ltd. was used in the organic phase with the oil (Petroleum) as diluent and D2EHPA (Di-2 Ethyl Hexyl Phosphoric Acid) provided by the American firm Cognis was used to 25% in its organic phase still with the oil (Petroleum) as diluent.

The following equipment was used: a beaker of 600 mL, separating funnels, stemware and a Kika Werk branded mechanical

stirrer for purification tests; and a Perkin Elmer AA800 Atomic Absorption Spectrometer for chemical analysis of solutions.

### Extraction tests

Several purification tests were carried out by using separately MEXTRAL 984N and D2EHPA to remove copper and other impurities (iron, zinc and manganese) contained in the solution of sulphate cobalt respectively, while minimizing cobalt loss.

Thus, four parameters were varied using MEXTRAL 984N as extractant as shown in Table 1. The same parameter changes were applied for D2EHPA with the exception of pH values that were set at 2; 2.5; 3 and 3.5, respectively. The experimental procedure followed Taguchi's L16 ( $4^4$ ) plan as given in Table 2.

## RESULTS AND DISCUSSION

### Removal of copper by MEXTRAL 984N

The results obtained with *MEXTRAL 984N* are presented in Table 3. The interpretation of the results focuses on the effects that the four parameters varied throughout this study have on the Cu extraction extent.

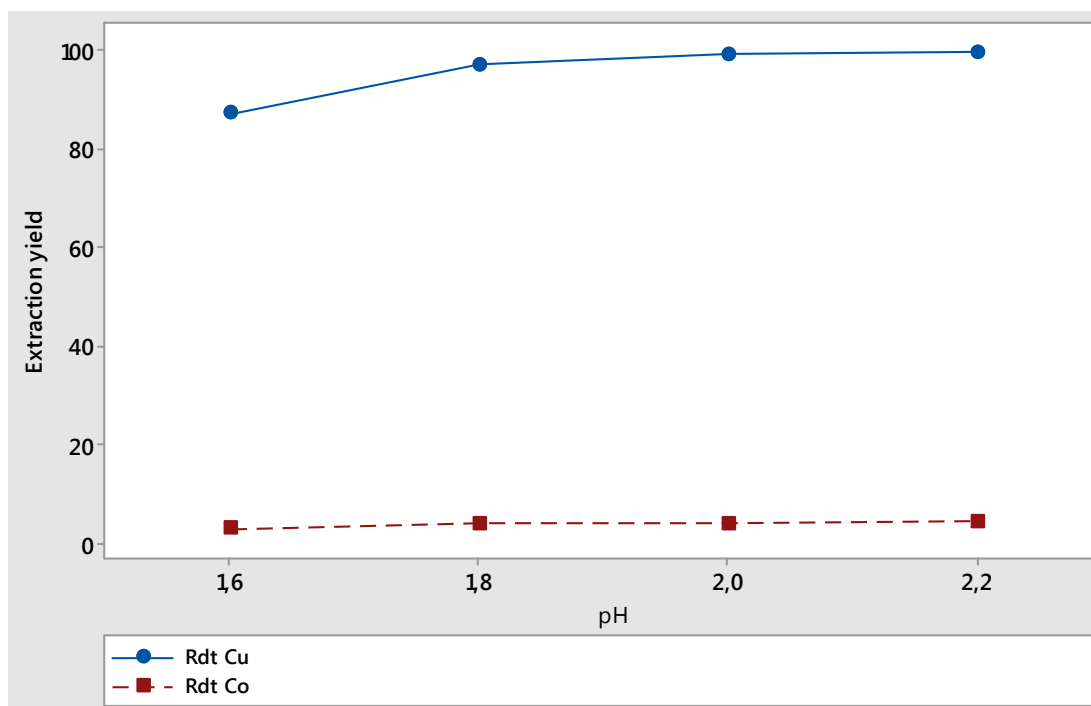
#### pH effect

The curves obtained (Figure 1) summarises the trend

**Table 3.** Results with the MEXTRAL.

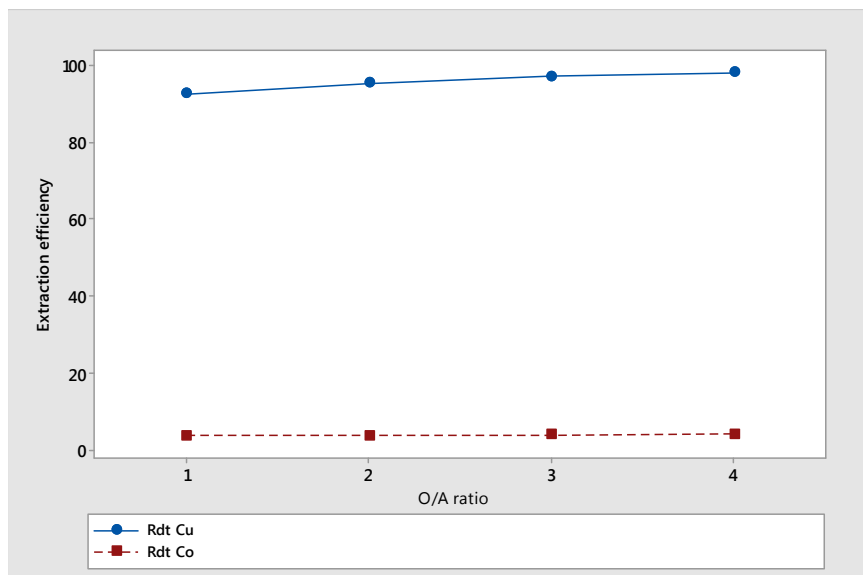
	Rdt Co	Rdt Cu	D <sub>Cu</sub>	D <sub>Co</sub>	S <sub>Cu/Co</sub>
1	2.8	76.9	3.6	0.03	123.2
2	3.0	86.0	6.2	0.03	203.7
3	3.0	90.9	10.2	0.03	333.2
4	3.0	94.5	17.3	0.03	556.5
5	3.9	94.9	19.4	0.04	483.3
6	3.8	96.6	28.4	0.04	719.4
7	4.0	98.4	63.2	0.04	1533.0
8	4.0	98.5	67.4	0.04	1611.1
9	4.0	99.1	110.6	0.04	2643.7
10	4.1	99.1	116.8	0.04	2754.1
11	4.0	99.2	116.8	0.04	2791.9
12	4.1	99.2	131.5	0.04	3059.9
13	4.2	99.5	211.0	0.04	4781.8
14	4.2	99.5	211.0	0.04	4781.8
15	4.7	99.6	264.0	0.05	5415.0
16	4.8	99.8	423.0	0.05	8376.3

Rdt: Extraction yield; D: Distribution coefficient; S: Selectivity.

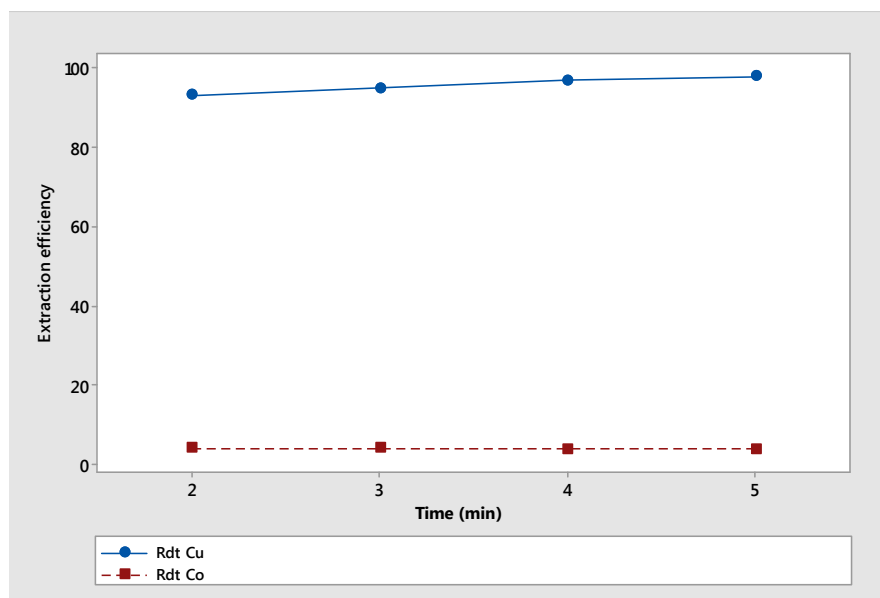
**Figure 1.** Effect of pH on the extraction yield (MEXTRAL 984N).

observed in Cu and Co extraction as function of pH. The Cu extraction extent using MEXTRAL 984N is influenced by the pH of the solution. At pH values between 1.8 and 2.2, more than 95% in Cu extraction was achieved. The optimum extraction percentage was recorded at a pH value of 2.2. This could be explained by the higher Cu

selectivity at pH value below 2.5 for solutions with a minimum concentration of 5.1 g/L as indicated by Cu's curve of isotherms that predicts good Cu extraction at those pH values (MCT Cognis Redbook, 2007). pH values beyond 2.2 lead to the coextraction of other elements, decreases Cu extraction yield and results in a



**Figure 2.** Effect of O/A ratio on extraction efficiency (MEXTRAL 984N).



**Figure 3.** Effect of time on extraction efficiency (MEXTRAL 984N).

considerable Co loss.

#### **Effect of O/A ratio**

The effect of the O/A ratio on the extraction of copper and cobalt is given in Figure 2. The ratio O/A has a positive influence on the extraction yield, that is, the higher the ratio O/A, the greater the extent of Cu extraction. This observation could be explained by the high quantity of available molecules in the organic phase advantageous

for high O/A ratios. Indeed, these molecules ensure enough extraction of Cu and thus promote better yields at high ratios O/A. The slight improvement in yield noticed at a ratio of 2/1 led to its adoption as optimal value.

#### **Effect of time**

Effect of time was also studied in this research. Figure 3 shows the influence of time on copper-cobalt extraction.

The contact time of the organic and aqueous phases

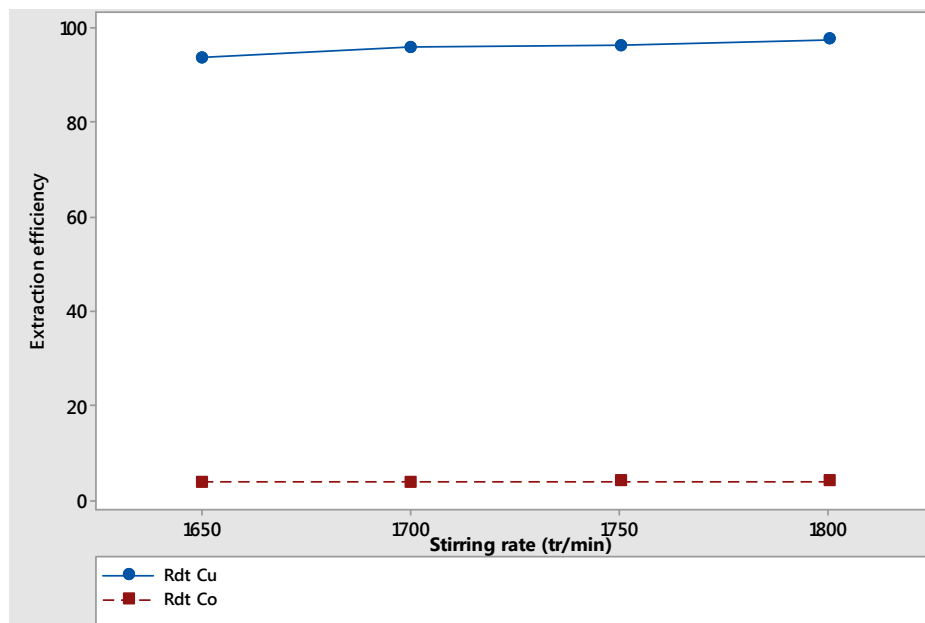


Figure 4. Effect of stirring rate on extraction efficiency (MEXTRAL 984N).

had also an influence on the extraction yield. Within the first 4 min of the purification, the Cu extraction rate is very fast. Beyond that value, the extraction curve reaches a plateau. This could be explained by the equilibrium reaction governing the extraction-stripping system during a liquid-liquid extraction. Indeed, during the extraction of a metal cation by an extractant based on ketoximes and aldioximes, a re-generation of  $H^+$  ions as product of the reaction was noticed. As the reaction proceeds, the presence of  $H^+$  ions become significant in the system, thus lowering the pH of aqueous phase and subsequently limits the extraction reaction.

#### Effect of stirring speed

The stirring speed has a slight influence on the Cu extraction efficiency as shown in Figure 4. Better results were achieved at higher stirring speed (1800 rpm). This could be justified by studies conducted by Cognis where the author concluded that high stirring speed accelerates and facilitates aqueous- organic contact. However, excessive speed must be avoided as it could lead to strong cation losses through Cu entrainment.

The optimal conditions of extraction of copper with MEXTRAL 984N are thus: pH = 2.2; the ratio O/A = 3/1; time t = 5 min and stirring speed = 1 800 rpm.

#### Removal of manganese and zinc by the D2EHPA

The extraction of iron, zinc, manganese and cobalt with the D2EHPA led to a distributivity and selectivity with

respect to cobalt as t summarized in the Table 4.

#### pH effect

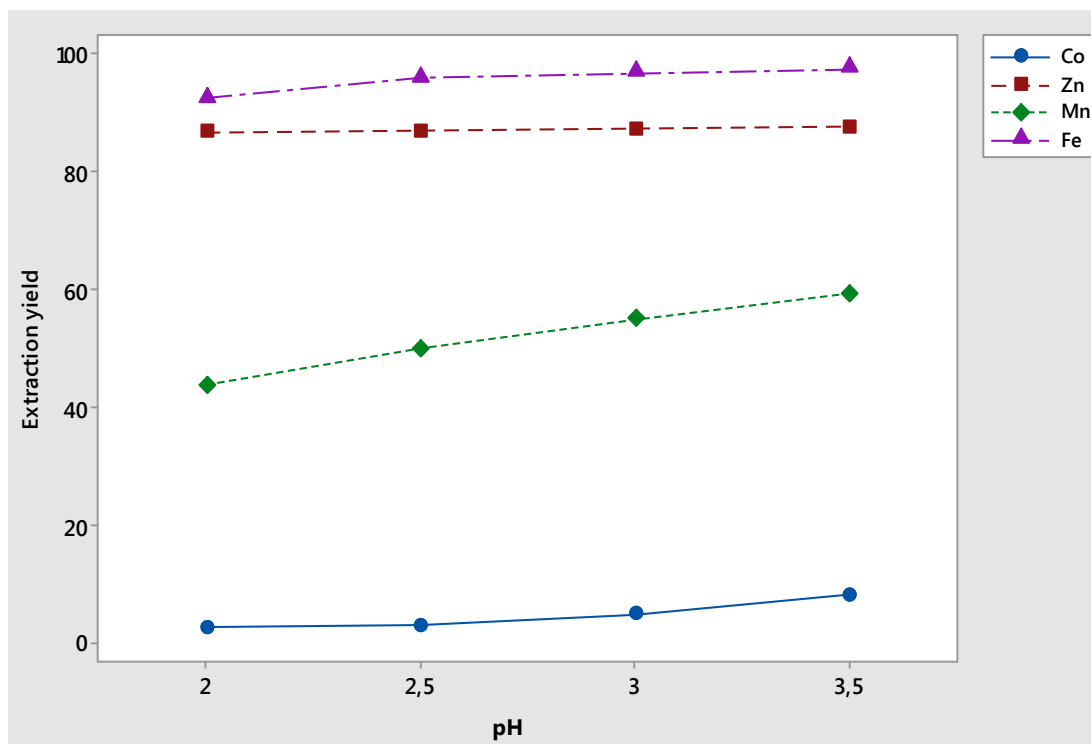
The effect of the pH on iron, zinc, manganese and cobalt extraction is given in the Figure 5. The relative position of each performance curve of a metal cation in Figure 5 is justified by the selectivity of D2EHPA towards each of the components and follows the sequence: Fe>Zn>Mn>Co (Kopper Chemical Industry, 2019a; Niinae et al., 1991; Khaironie et al., 2014; Qiu et al., 2016).

The large zinc extraction at pH values higher than 2 could be justified by extraction isotherms relative to D2EHPA that predict yields greater than 80% for extraction at pH greater than 2 (Kopper Chemical Industry, 2019b). The extraction of almost all of the remaining iron is also justified by the fact that its isotherm achieves excellent extraction at pH values higher than 1 with D2EHPA. The extraction of half of the manganese from pH = 3 could be justified by the fact that the extraction begins with two metal cations ( $Fe^{3+}$ ,  $Zn^{2+}$ ) prior to extracting Mn. A second extraction would be required in order to refine further the resulting raffinate product. It is also worth mentioning that beyond a pH value of 3, Co will be extracted in large amount (>8%), resulting in a significant loss.

The decrease in extraction efficiency at low pH levels could be explained through analysis of the equilibrium equation for solvent extraction system. Indeed, the extraction of metallic cations produces  $H^+$  ions which results in a reduction of pH. The latter does not favour the

**Table 4.** Results obtained after all purification experiments with the D2EHPA.

S/N	Rdt Co	Rdt Zn	Rdt Mn	Rdt Fe	D <sub>Zn</sub>	D <sub>Mn</sub>	D <sub>Fe</sub>	D <sub>Co</sub>	S <sub>Zn-Co</sub>	S <sub>Mn-Co</sub>	S <sub>Fe-Co</sub>
1	2.6	86.5	41.6	89.1	6.4	0.7	8.2	0.03	238.8	26.5	304.1
2	2.6	86.6	43.3	92.7	6.5	0.8	12.8	0.03	240.7	28.4	474.7
3	2.5	86.7	45.0	93.4	6.5	0.8	14.2	0.03	242.7	30.5	527.7
4	2.6	86.8	45.0	94.6	6.6	0.8	17.3	0.03	244.7	30.5	645.7
5	2.3	86.9	47.5	95.5	6.6	0.9	21.0	0.02	246.7	33.6	781.9
6	2.9	86.9	49.9	95.7	6.7	1.0	22.2	0.03	248.8	37.1	825.0
7	2.9	86.8	50.1	96.4	6.6	1.0	26.5	0.03	244.7	37.4	986.7
8	3.1	86.9	51.8	96.4	6.6	1.1	26.5	0.03	246.7	40.1	986.7
9	3.6	87.1	53.5	96.4	6.7	1.2	26.5	0.04	250.9	42.8	986.7
10	3.7	87.2	54.9	96.8	6.8	1.2	30.4	0.04	252.9	45.5	1132.9
11	5.7	87.3	55.5	96.8	6.9	1.3	30.4	0.06	255.1	46.4	1132.9
12	5.8	87.4	55.7	96.8	6.9	1.4	30.4	0.06	257.3	46.9	1132.9
13	6.9	87.4	57.2	97.1	6.9	1.3	32.9	0.07	257.3	49.7	1223.0
14	7.1	87.4	57.9	97.3	6.9	1.4	35.7	0.08	257.3	51.2	1328.0
15	7.4	87.9	58.4	97.5	7.3	1.4	39.0	0.08	271.1	52.3	1452.1
16	10.6	87.9	63.5	97.7	7.3	1.7	43.0	0.12	271.1	64.8	1601.1

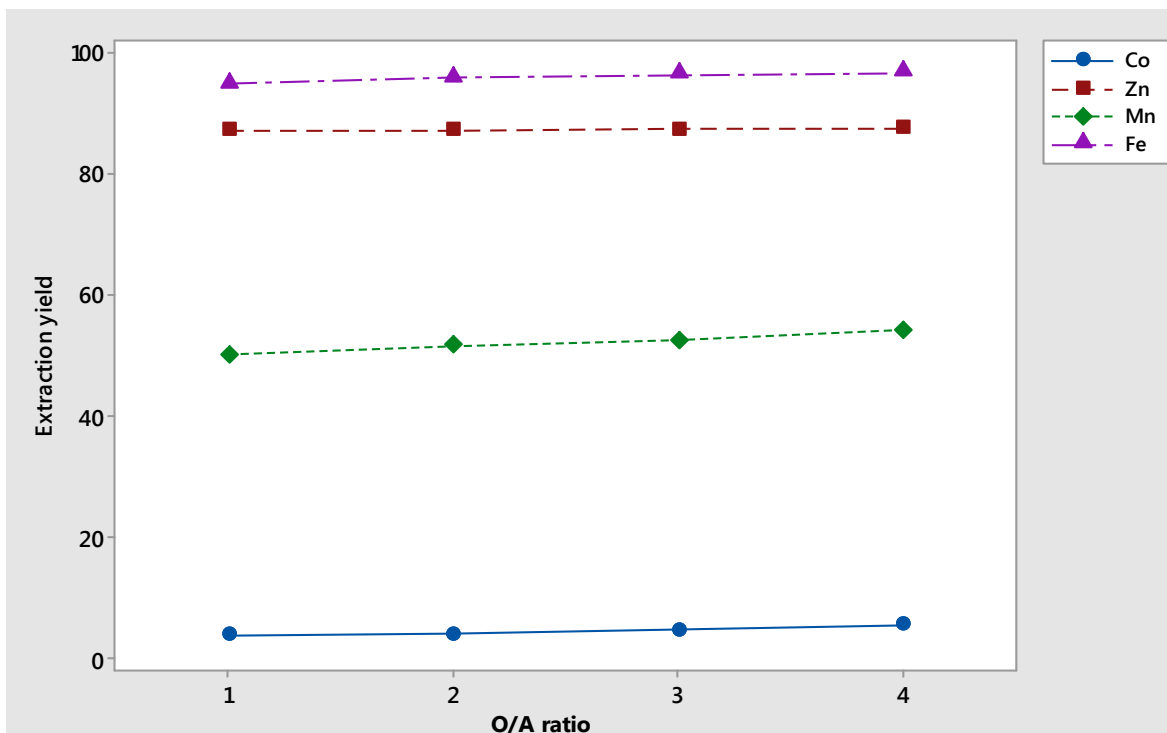
**Figure 5.** Effect of pH on the extraction yield (D2EHPA).

extraction reaction as per Le Chatelier's principle and thus limits the extraction yield prior to reaching an optimal pH value. This result is also supported by studies conducted by Correa et al. (2018) and Pospiech et al. (2004).

#### **Effect of O/A ratio**

The effect of the O/A ratio on the extraction yields of iron, zinc, manganese and cobalt is shown in the Figure 6.

Good extraction of iron, zinc and manganese were



**Figure 6.** Effect of O/A ratio on iron-zinc-manganese-cobalt extraction yields with D2EHPA.

observed at a O/A high ratio (greater than 1/1), which could be justified by studies conducted by Fisher and Treadgold (2007) confirming that these metal cations are extracted at high values of O/A ratio.

The large values of this ratio for zinc and manganese extraction could also be explained by studies conducted by Correa et al. (2018). Indeed, these studies have shown an increase in the extraction efficiency of the aforementioned metal cations when it is greater than 1/1. At constant values of other parameters, the cation behavior of these metals changes as the O/A ratio is changed. The quantity of molecules in the organic phase must be sufficient enough to ensure Fe, Zn and Mn extraction. Thus, better returns are achieved at high ratios.

#### **Effect of time**

The effect of time on the different extractions is shown in the Figure 7. The contacting time of the organic phase and the aqueous phase has a slight influence on the extraction yield of iron, zinc and manganese. After a period of three minutes, there was a slow evolution of the extraction reaction. This phenomenon could also be explained by the equilibrium reaction governing the extraction-stripping system during a liquid-liquid extraction. And because D2EHPA is less selective towards all of the metal cation present, there is an extraction of all the cations in the order of priority leading

to a significant regeneration of  $H^+$  ions as product of the reaction as the reaction proceeds. The presence of  $H^+$  ions rapidly lowers the pH of the aqueous phase to values below 1 (final pH = 0.95). This phenomenon would cause almost a bearing on the curves of the extraction yields or even a decrease of the curves trend.

#### **Effect of stirring speed**

Figure 8 shows the influence of the stirring rate on the extraction yields of iron, zinc, manganese and cobalt. The stirring speed also does not have a strong influence on the extraction yields of the targeted metal cations. Thus, the optimal value is taken at a speed of 1700 rpm. This value could be justified by the lower viscosity of D2EHPA (0.56 poise) as compared to MEXTRAL 984N; which facilitates a good aqueous-organic contact with medium agitation.

The optimum conditions for zinc extraction with D2EHPA are thus: pH = 2; O/A ratio = 2/1; time (t) = 4 min, and stirring speed (v) = 1,700 rpm; while those of manganese are: pH = 3; O/A ratio = 2/1; time (t) = 4 min and the stirring speed (v) = 1,700 rpm. Iron being strongly extracted under the conditions (>95%).

With manganese already extracted almost in half, we proceeded to a second stage of its extraction under the same operational conditions in order to avoid considerable loss of cobalt. The results of the last raffinate constituting the final pure solution are given in

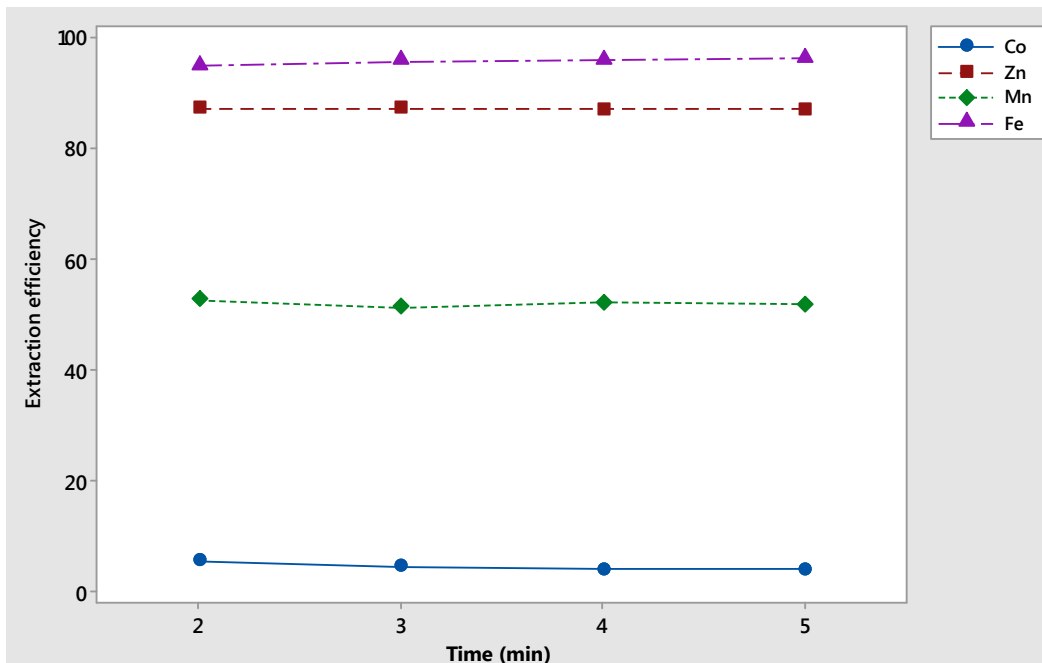


Figure 7. Effect of time on extraction efficiency (D2EHPA).

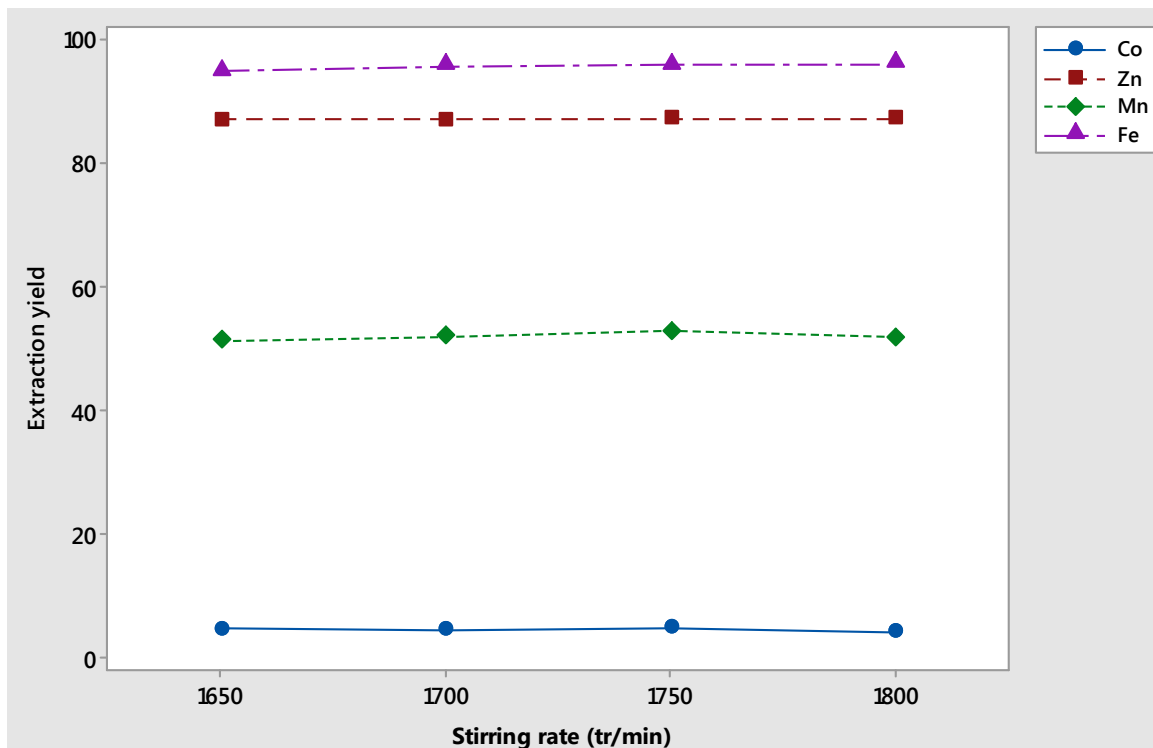


Figure 8. Effect of Agitation on Extraction (D2EHPA).

Table 5. The decrease in cobalt concentration is mainly due to the addition of a considerable volume of NaOH \

(>40 mL) in order to adjust the pH to the required test values and to a low coextraction value that was estimated



**Table 5.** Chemical analysis of the final raffinate.

El (g/L)	Co <sup>2+</sup>	Cu <sup>2+</sup>	Fe <sup>tot</sup>	Zn <sup>2+</sup>	Mn <sup>2+</sup>
Raffinate	16.8	0.017	0.007	0.01	0.94

to be 6.24%.

## Conclusion

In this present research, optimal extracting conditions were determined for different impurities (Cu, Fe, Zn and Mn) contained in a cobalt sulphate solution by consecutively using two extractants MEXTRAL 984N and D2EHPA. A systematic study was conducted in accordance with Taguchi's L16(4<sup>4</sup>) experimental plan by varying four main parameters (pH, O/A ratio, time and stirring speed) at four levels for each series of tests.

Chemical analysis of the final raffinate obtained gave the following composition (Co<sup>2+</sup>: 16.80 g/L; Cu<sup>2+</sup>: 0.017 g/L; Fe<sup>tot</sup>: 0.007 g/L; Zn<sup>2+</sup>: 0.0125 g/L and Mn<sup>2+</sup>: 0.940 g/L) which demonstrates removal of almost all major impurities namely: 98.74% of copper, 97.5% of iron, 98.1% of zinc and 80.53% of manganese. The decrease in cobalt concentration is mainly due to the addition of a considerable volume of NaOH (>40 mL) to adjust pH to the required test values and low coextraction value that was estimated to be 6.2%. The approach proposed in this study allows purification of industrial cobalt solutions in order to produce high purity compounds.

## CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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