

Article

# Sequential Recovery of Critical Metals from Leached Liquor of Processed Spent Lithium-Ion Batteries

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**Abstract:** The processing and extraction of critical metals from black mass is important to battery recycling. Separation and recovery of critical metals (Co, Ni, Li, and Mn) from other metal impurities must yield purified metal salts, while avoiding substantial losses of critical metals. Solvent extraction in batch experiments were conducted using mixed metal sulphates obtained from the leach liquor obtained from spent and shredded lithium-ion batteries. Selective extraction of  $Mn^{2+}$ ,  $Fe^{3+}$ ,  $Al^{3+}$  and  $Cu^{2+}$  from simulated and real leached mixed metals solution was carried out using di-2-ethylhexylphosphoric acid (D2EPHA) and Cyanex-272 at varying pH. Further experiments with the preferred extractant (D2EPHA) were performed under different conditions: changing the concentration of extractant, organic to aqueous ratio, and varying the diluents. At optimum conditions (40% *v/v* D2EPHA in kerosene, pH 2.5, O:A = 1:1, 25 °C, and 20 min), 85%  $Mn^{2+}$ , 98%  $Al^{3+}$ , 100%  $Fe^{3+}$ , and 43%  $Cu^{2+}$  were extracted with losses of only trace amounts (<5.0%) of  $Co^{2+}$ ,  $Ni^{2+}$ , and  $Li^{+}$ . The order of extraction efficiency for the diluents was found to be kerosene > Exxal-10 >>> dichloromethane ( $CH_2Cl_2$ ) > toluene. Four stages of stripping of metals loaded on D2EPHA were performed as co-extracted metal impurities were selectively stripped, and a purified  $MnSO_4$  solution was produced. Spent extractant was regenerated after  $Fe^{3+}$  and  $Al^{3+}$  were completely stripped using 1.0 M oxalic acid ( $C_2H_2O_4$ ).

**Keywords:** black mass; critical metals; extractants; diluents; separation; stripping



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## 1. Introduction

Globally, the discussion about climate change and the transition to clean energy is of high importance in academic and research activities. Recently, there has been an exponential increase in the demand for electric vehicles, plug-in electric charging stations, and consumer electronics, all of which require portable batteries [1,2].

State-of-the-art cathode chemistries of lithium-ion batteries have developed significantly in the last few years. Although nickel-manganese-cobalt (NMC) in general remains dominant, popular trends show an increase in the nickel content of the cathode. For instance, NMC 622, NMC 811, and possibly NMC 955, are preferable to NMC 333 or NMC 433 due to higher energy densities. Lithium-iron-phosphate (LFP) batteries are becoming popular again, especially in China, due to increased safety, cost, and ease of recycling. Some lithium nickel-cobalt-aluminum oxide (NCA) batteries continue to be used as well, while lithium-ion manganese oxide (LMO) batteries are no longer widely used in vehicles due to their short life span [2]. It is noteworthy that several of the materials used in these batteries, such as lithium, nickel, cobalt, manganese, aluminum, graphite, and silicon, have been declared critical because of their supply risk [2,3].

The demand for lithium in 2020 reached 429,000 metric tons. If the current policies to meet the International Energy Agency (IEA's) sustainable development goals are rigorously pursued, Li demand is estimated to increase to about 1 million metric tons in 2030 [4]. In 2021, the global demand for nickel amounted to some 2.86 million metric tons and is forecast to reach 3.61 million metric tons worldwide in 2023, representing a 14% increase from the estimated demand in 2022 [5]. Despite the turbulence in cobalt demand experienced in

2022, cobalt prices grew 13%, reaching a production of 187,000 metric tons. The cobalt market prospects remain robust as demand is set to double by 2030. In this context, cobalt, nickel, and lithium remain major critical metals for battery production. Other elements such as manganese, copper, iron, aluminum, and phosphorus, are still needed to improve various properties of the battery [6]. Moreover, the use of nickel in cathode material has been increased recently, based on a consensus within the industry to reduce or phase out cobalt in cathode materials due to its fragile supply chain, price volatility, and legislation on mining [7].

When these devices reach their end of life, tons of waste batteries are generated [8,9] and recycling of the critical metals from this waste will be necessary to meet demand, use resources efficiently, bolster supply chains, and safeguard the environment. Lithium-ion batteries can be processed in one of four ways, via direct recycling, pyrometallurgy, hydrometallurgy, and bio metallurgy [10–17].

Direct recycling is the most cost-efficient technique as it involves direct reuse of materials without disruption to their structure. However, this method has faced serious drawbacks due to loss of lithium (>20%) and recycled cells exhibiting parasitic reactions, causing higher cell impedance and shifts in the electrode potential [18,19]. Direct recycling also produces large volumes of wastewater containing high concentrations of critical metals which may require further downstream processing. It is important to note that these issues can vary depending on the battery type and the intrinsic value of certain cathode chemistries, which may affect the feasibility of direct recycling in high labor-cost countries.

Pyrometallurgy involves roasting, smelting, and refining at high temperature. It is capable of processing large amounts of waste but is the most energy-intensive and has difficulty producing high purity materials. It is perhaps the least environmentally benign. There is also a substantial loss of valuable metals in the slag [18].

Bio metallurgy is an emerging technology that involves the uses of micro-organisms to solubilize the metals. It is considered a green method, but it suffers from extremely slow kinetics and time-consuming processes [20–22].

Hydrometallurgy uses solution chemistry for leaching, purification, and metal recovery. It offers a high recovery rate, high purity products, low energy consumption, and no gas emissions [23]. The only identified drawback is wastewater generation, and there has been significant improvement in recent years [24].

The preliminary stage of hydrometallurgy involves chemical dissolution of the target metals from “black mass” (crushed, shredded, and processed spent battery cells). This is not always selective, thereby resulting in generation of mixed metal leach solutions which are too complex for simple ion-exchange and precipitation methods to process. Various acid lixiviants, chloride media [25–28], nitrate media [16,29], sulphate media [30–32], and mixed organic and inorganic acids [33], have all been studied for leaching of critical metals from end-of-life battery materials. Some studies reported combining pyro- and hydrometallurgy in which samples are roasted, followed by water and sulfuric acid leaching, respectively [34–36]. Sulfuric acid leaching produced a mixed metals solution that required further separation and purification [37].

In this paper, liquid–liquid extraction is examined because it is a proven separation and purification method for aqueous metals that is cost effective, environmentally friendly, and yet can handle large feeds and yields high purity products. Solvent extraction of critical metals from spent lithium-ion batteries leached using different extractants and diluents have been reported in the literature, although most studies were performed using only two or three metals of interest [13,27,38–40].

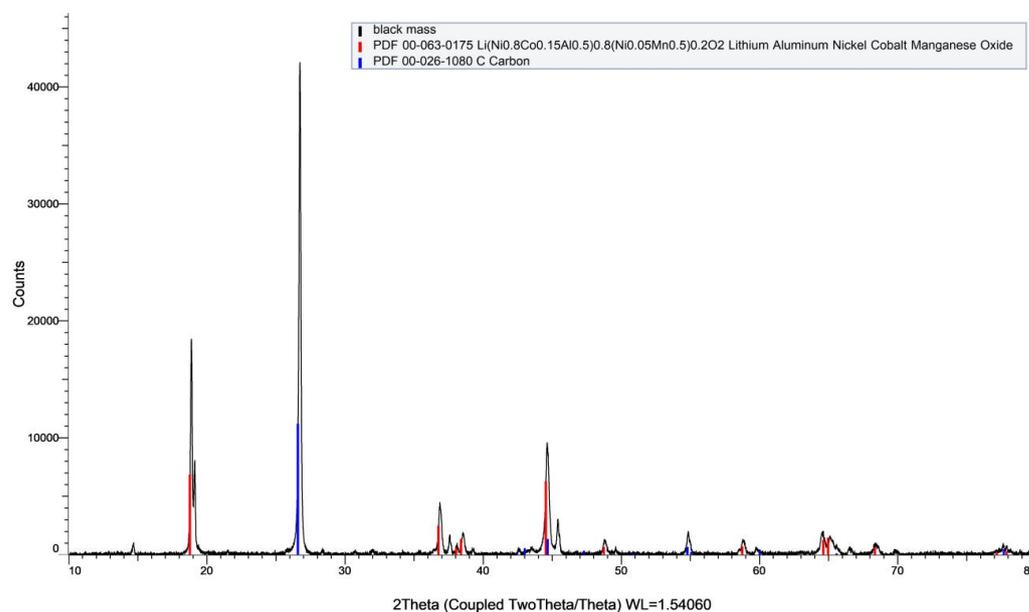
Since these are ideal cases when dealing with mixed end-of-life batteries, more work is needed to complement further study reported on the extraction of critical metals from metal impurities, which can behave differently with extractants. Moreover, separation of  $\text{Co}^{2+}$  from solution that contains  $\text{Mn}^{2+}$  and  $\text{Al}^{3+}$  is known to be complicated in practice, and it is reported to be advisable to remove them prior to critical metals separation [37]. Therefore, this paper focuses on the sequential extraction of  $\text{Mn}^{2+}$  and then subsequent metal

impurities ( $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ) from a sulfate leached liquor of spent lithium-ion batteries to produce raffinates rich in  $\text{Li}^+$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$ . The study also examines the performance of different diluents and proposed flowsheets for the extraction and stripping steps.

## 2. Experimental

### 2.1. Materials

Black mass samples were collected from an authorized supplier of waste materials. The black mass was dried and ground into powder using a mortar and pestle. The ground sample was characterized with XRD for mineralogical phase identification of the metals, as presented in Figure 1. After digestion of the powdered sample with aqua regia (1  $\text{HNO}_3$ :3  $\text{HCl}$ ), the metal contents in the digest solution were analyzed using ICP-OES (Agilent 5110), as presented in Table 1. A simulated solution matching the exact concentration of metals in the digested solution was prepared using analytical grade metal sulfate salts (Aldrich, 99% purity). At the same time, real mixed metal leach liquor was generated via acid leaching of the black mass. The extractants di-2-ethylhexylphosphate (D2EPHA) and dialkyl phosphinic acid (Cyanex-272) were supplied by CYTEC Solvay, Princeton, NJ, USA. The diluents used for the extraction (kerosene, toluene, Exxal-10, and dichloromethane) were purchased from Fischer chemical.



**Figure 1.** XRD microgram of powdered black mass showing the major peaks as graphite and oxides of lithium, aluminum, nickel, cobalt, and manganese.

**Table 1.** Metal content of powdered black mass.

Metal	Ni	Co	Li	Mn	Cu	Al	Fe
Conc. (g/L × 100)	1.21	0.89	0.31	0.57	0.101	0.102	0.14

### 2.2. Leaching Procedure

Acid leaching with homogenized black mass was carried out using different concentrations of sulfuric acid ( $\text{H}_2\text{SO}_4$ ). The leaching experiments were carried out using three-necked glass reactors on a temperature and speed controlled hot-plate under magnetic stirring at 100 rpm, and a thermometer was coupled to the reactor. The effects of  $\text{H}_2\text{SO}_4$  concentration on the leaching efficiency of metals were studied when the solid/liquid ratio (S/L), temperature, and time were kept constant. The metal content in the pregnant leach

liquor was determined using ICP-OES (Agilent 10), and the percentage extraction of each metal was calculated according to Equation (1) reported elsewhere [41].

$$\text{Leaching (\%)} = (1000 \times C_m) / (P \times X_m) \quad (1)$$

where  $C_m$  = concentration of metals in the leached solution in grams per litre (g/L).

$P$  = Pulp density of black mass to lixiviant (%), i.e., g/100 mL.

$X_m$  = Metal content in the black mass (%).

### 2.3. Liquid–Liquid Extraction Procedure

Batch experiments first focused on extraction of metal impurities ( $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ ) from the leach solution to produce solutions containing only  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Li}^+$ . Initial experiments were conducted using D2EPHA and Cyanex-272 as extractants in kerosene at varying pH values. Further experiments were conducted with D2EPHA, which showed a higher affinity towards the metal impurities and left the critical metals ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Li}^+$ ) in the raffinate. Extractions were performed by mixing an equal amount of organic (O) and aqueous (A) in a 100 mL graduated plastic vial. After mixing long enough to attain equilibrium (20 min), the two phases were separated using a separatory funnel, and the aqueous phase was collected for metal analyses. The metal concentration in the aqueous solution was measured by ICP-OES, and the extraction efficiency (E%) as a function of pH, concentration of the extractant, and the ratio of organic to aqueous solution was calculated using Equation (2).

The performance of D2EPHA in different diluents was also investigated. The spent organic extractant was stripped using different strippants. The stripping efficiency (S%), distribution ratio (D), and separation factor ( $S_f$ ), were calculated based on Equations (3)–(5)

$$E\% = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

$$S\% = \left( \frac{C_{st}}{C_i - C_e} \right) \times \left( \frac{V_s}{V_{st}} \right) \times 100 \quad (3)$$

$$D = \left( \frac{C_i - C_e}{C_e} \right) \quad (4)$$

$$S_f = \frac{D_{im}}{D_{om}} \quad (5)$$

where  $C_i$  (g/L) is the initial concentration of metal in the aqueous phase,  $C_e$  (g/L) is the equilibrium concentration in aqueous phase,  $C_{st}$  is the concentration of metal in the stripping solution,  $V_s$  is the volume of strippant,  $V_{st}$  is the volume of the stripping solution,  $D_{im}$  is the distribution ratio of interested metal, and  $D_{om}$  is the distribution ratio of other metals. Based on optimized results obtained using a simulated solution, further extraction was performed with real leached liquor using D2EPHA in kerosene.

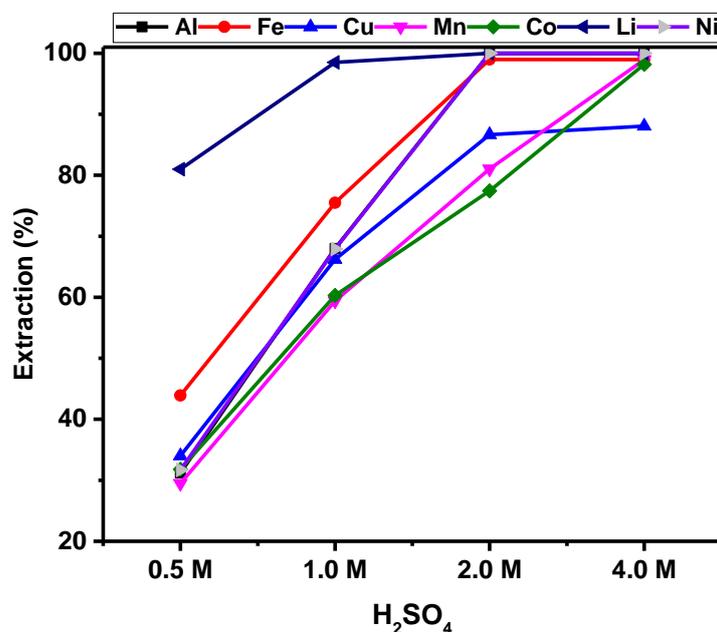
## 3. Results

### 3.1. Leaching

In the hydrometallurgy process, leaching is a primary step of the utmost importance that involves the dissolution of soluble metals from ore or materials, while the insoluble parts known as residue are used for other purposes. In this study, the black mass obtained from the industry was directly leached with sulfuric acid without treatment or addition of oxidant.

The results obtained show that the leaching efficiency of metals increased with increases in the concentration of  $\text{H}_2\text{SO}_4$  from 0.5 to 4.0 M (Figure 2). It is shown that 81%  $\text{Li}^+$  was leached out of the sample, when the leaching efficiency of other metals is <40% using a mild acid (0.5 M  $\text{H}_2\text{SO}_4$ ). This is an indication that selective leaching of Li from

other metals is achievable with this black mass. High leaching efficiency of  $\text{Li}^+$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Al}^{3+}$  was achieved using 4.0 M of  $\text{H}_2\text{SO}_4$  without the use of an oxidant or reagent. Similar results were reported in the literature [32,42,43]. This is because metals in this specific black mass exist in their oxide form (Figure 1), thereby allowing a facile reaction with sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and producing a pregnant leach liquor of nickel, manganese, cobalt, and lithium sulfates [42].



**Figure 2.** Leaching studies of metals in black mass using different  $\text{H}_2\text{SO}_4$  concentrations (pulp density-20 g/L, leaching temperature 90 °C, leaching time-120 min, stirring speed-100 rpm).

Based on the weight difference of the residue after leaching, and the black mass before digestion, it is estimated that 53.5 and 59% of the black mass was dissolved in 2.0 and 4.0 M of  $\text{H}_2\text{SO}_4$ , respectively.

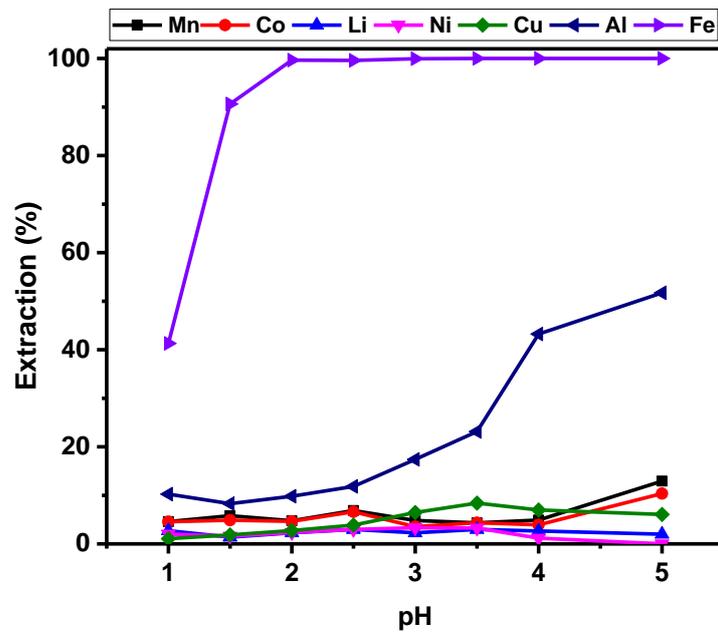
### 3.2. Liquid Liquid Extraction

#### 3.2.1. pH Studies

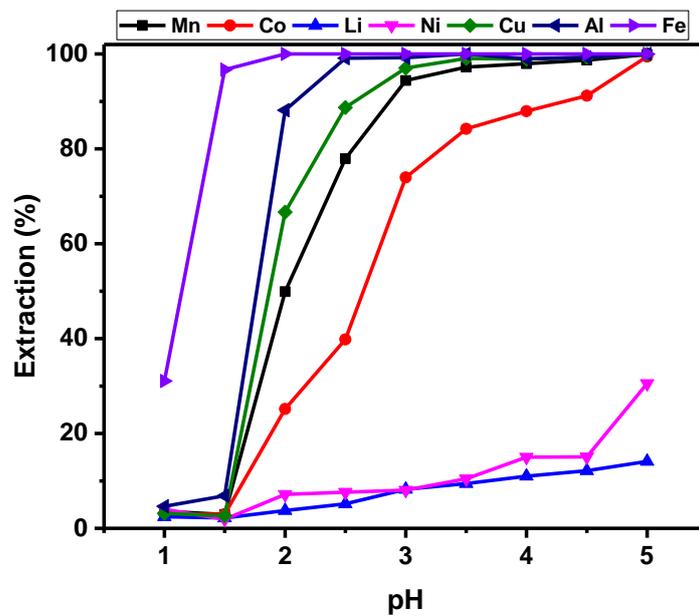
One of the most important variables is pH, which directly affects the solvation, stability, and the oxidation state of metal ions in the solution. More importantly, pH affects the performance, charge, and selectivity of the extractants. The selectivity of D2EPHA and Cyanex-272 using mixed metal sulfate solutions at different pH was studied, and the results are presented in Figure 3. Extractions at pH 2.0 using Cyanex-272, Na-Cyanex-272, and D2EPHA removed all  $\text{Fe}^{3+}$  (100%). It is interesting to note that  $\text{Al}^{3+}$  (40%) was partially removed using 20% v/v Cyanex-272 at pH 4, but more  $\text{Al}^{3+}$  (49.8%) was removed when the pH was increased to 5.0 (Figure 3a). With 20% Na-Cyanex-272, the extraction efficiency increased as the pH increased from 1 to 5. The extraction of  $\text{Al}^{3+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Mn}^{2+}$  were higher compared to  $\text{Co}^{2+}$  while co-extraction of  $\text{Ni}^{2+}$  and  $\text{Li}^+$  was extremely low but increased as pH increased from 2.5. Further experiment was performed with 40% v/v D2EPHA at pH 2.5 and the results showed that  $\text{Mn}^{2+}$  (85%),  $\text{Al}^{3+}$  (98%),  $\text{Fe}^{3+}$  (100%) and  $\text{Cu}^{2+}$  (43%) were extracted at pH 2.5. Interestingly, only small amounts (<5.0%) of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Li}^+$  were trapped or co-extracted (Figure 3c).

In summary, the results with Na-Cyanex-272 show that selectivity towards the metals of interest ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Li}^+$ ) is difficult to achieve starting from a real-world mixed metal system. Extraction of  $\text{Fe}^{3+}$  from leach solutions with Cyanex-272 prior to D2EPHA extraction (for  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{Cu}^{2+}$ ) would be viable for this mixed metal solution. As reported in the literature, extraction of metals of interest co-existing with impurities has been problematic [44]. For instance,  $\text{Al}^{3+}$  was difficult to strip as it remained with  $\text{Co}^{2+}$

in the product; similar results were found with  $Mn^{2+}$  [44,45]. Therefore, these elements must be removed before separation of  $Co^{2+}$ ,  $Ni^{2+}$ , and  $Li^+$ . Precipitation is not viable due to additional steps, equipment, and cost, as well as possible losses of the valuable metals. The economical and best approach is to selectively remove the impurities by alternate extractants, since they can be reused. Therefore, we studied other parameters using D2EPHA for the extraction of  $Mn^{2+}$ ,  $Al^{3+}$ ,  $Fe^{3+}$ , and  $Cu^{2+}$  to produce a raffinate rich in  $Ni^{2+}$ ,  $Co^{2+}$ , and  $Li^+$ .

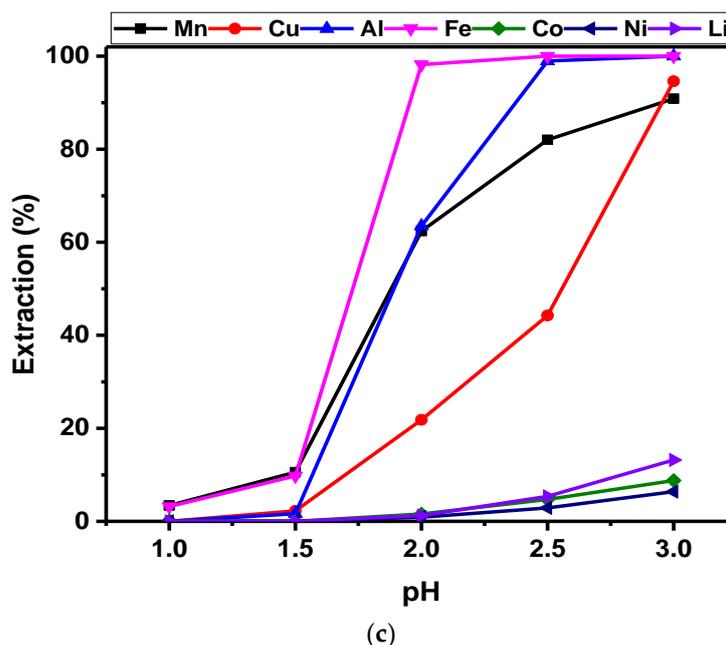


(a)



(b)

Figure 3. Cont.



**Figure 3.** pH studies for the extraction of metals by extractants in kerosene. (a) 20% *v/v* Cyanex-272, (b) 20% *v/v* Na-Cyanex-272, (c) 40% *v/v* D2EHPA. Conditions: 100 g black mass sulfate leachate (containing Ni-0.72, Co-0.60, Mn-0.31, Li-0.15, Cu-0.101, Al-0.075, and Fe-0.055 g/L), 25 °C, mixed 20 min, centrifugation-1000 rpm, saponification of Cyanex-0.02 g NaOH).

### 3.2.2. Diluent's Efficiency

The choice of diluent is very important in solvent extraction as it dramatically affects the extraction performance. However, in liquid–liquid extraction, diluents should have some specific quality before they can be used in conjunction with an extractant, and such properties include good selectivity, inflammability, solubility, good resistance to degradation, non-toxicity, and being commercially available, among others [46]. Here, we show interesting effects of the diluent on the separation efficiencies using D2EHPA in kerosene, toluene, Exxal-10, and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>), as potential diluents.

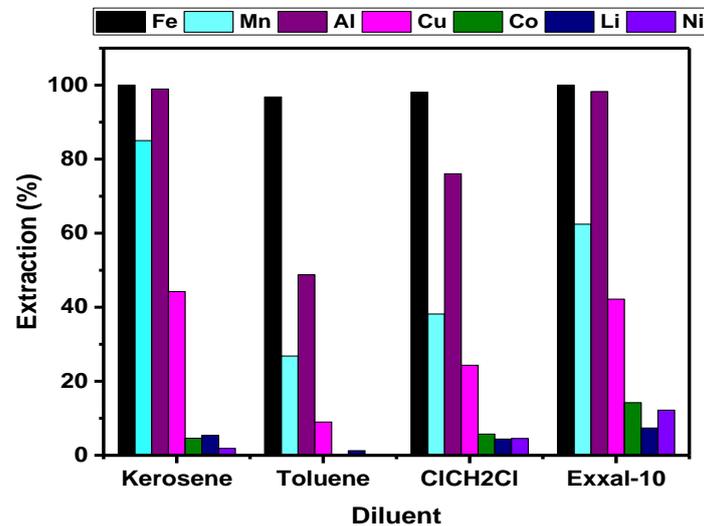
The results presented in Figure 4 show that metal extractability by D2EHPA is better in kerosene and Exxal-10 compared to dichloromethane and toluene. Quantitative extraction of Fe<sup>3+</sup> was seen using D2EHPA in kerosene, while only a slight decrease in Fe<sup>3+</sup> extraction (~98%) was seen using D2EHPA in toluene, dichloromethane, and Exxal-10. There was lower extraction efficiency of Mn<sup>2+</sup>, Al<sup>3+</sup>, and Cu<sup>2+</sup> using D2EHPA in toluene, dichloromethane, and Exxal-10. In summary, the order of extraction efficiency is Kerosene > Exxal-10 > CH<sub>2</sub>Cl<sub>2</sub> > toluene.

This behavior is due to the different physicochemical properties (polarity index, dipole moment, viscosity, density, and solubility parameters exhibited by the diluents [47–50] and is supported by several authors that have made use of kerosene as a diluent in the solvent extraction of metals [51,52].

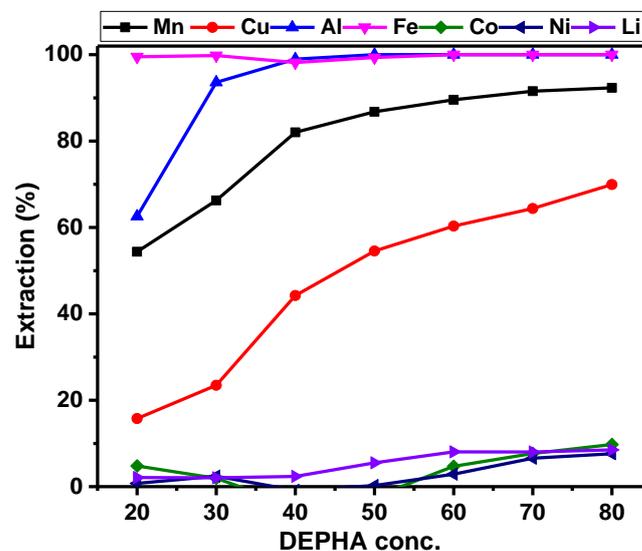
### 3.2.3. Extractant Concentration

The D2EHPA concentration varied from 20 to 80% *v/v*, and extraction was performed at pH 2.5, with other conditions kept constant. The results of these experiments are presented in Figure 5, showing that recovery efficiency of Al<sup>3+</sup>, Mn<sup>2+</sup>, and Cu<sup>2+</sup> increased as the concentration of D2EHPA increased. It was observed that 100% Fe<sup>3+</sup> removal is possible at 20% *v/v* D2EHPA, while higher extraction efficiency for Al<sup>3+</sup>, Mn<sup>2+</sup>, and Cu<sup>2+</sup> was noticed when the concentration reached 40% *v/v*. However, only a slight increase in the extraction efficiency was noticed when the concentration was further increased. Most importantly, unwanted co-extraction of Co<sup>2+</sup>, Ni<sup>2+</sup>, and Li<sup>+</sup> also slowly increased when

the D2EPHA concentration reached 60% *v/v* and above. Based on these results, a second extraction stage with D2EPHA using 40% *v/v* D2EPHA at pH 2.5 would ensure that the remaining  $\text{Cu}^{2+}$  and  $\text{Mn}^{2+}$  are extracted, leaving behind a solution that is rich in  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Li}^+$ .



**Figure 4.** The effect of diluents on the extraction efficiency of metals from sulfate simulated solutions. Condition: 40% *v/v*, pH 2.5, 25 °C, 20 min, O:A 1:1, initial metal content: Ni-0.74 g/L, Mn-0.3 g/L, Co-0.6 g/L, Li-0.152 g/L, Cu-0.11 g/L, 0.055 g/L Al, and 0.020 g/L Fe.

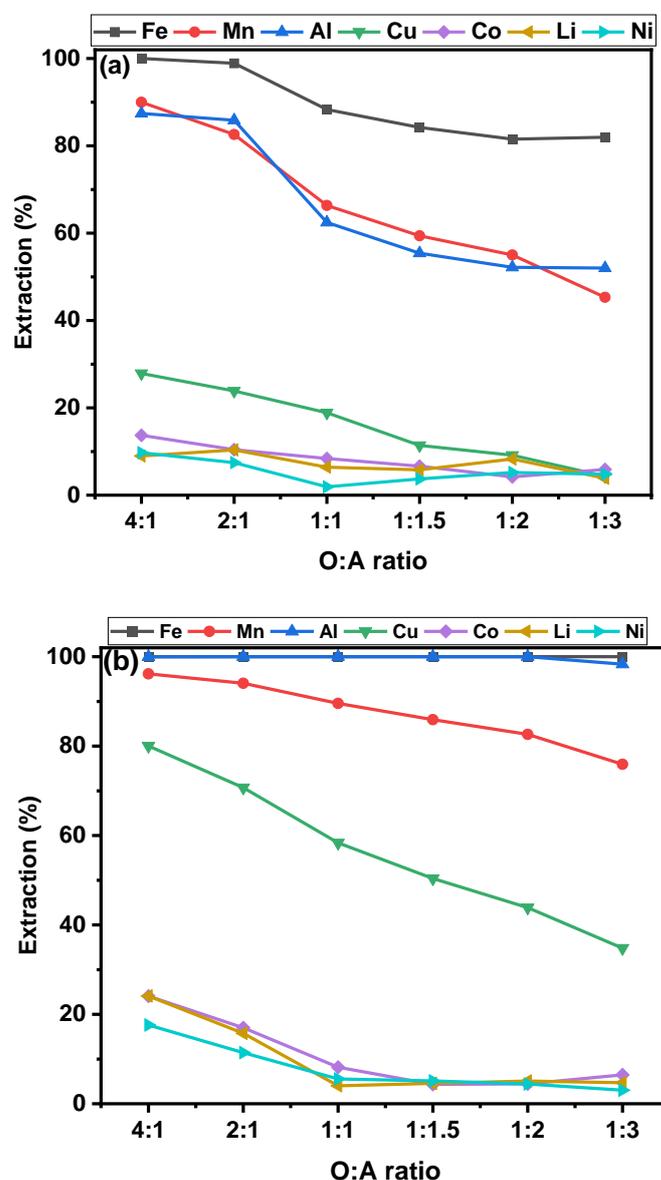


**Figure 5.** Plot of extractant concentration for the extraction of metals. Condition: sulfate simulated solution (Ni-0.72, Co-0.60, Mn-0.31, Li-0.15, Cu-0.101, Al-0.075, and Fe-0.055 g/L, condition: 25 °C, 20 min, centrifugation-1000 rpm).

### 3.2.4. Extractant Ratio

The ratio of organic to aqueous phase is important to obtain the optimum extraction efficiency. Here, the organic phase volume is kept constant while the aqueous phase was varied, and metal extraction efficiencies are presented in Figure 6. Based on the plots of different concentration of organic extractant, it was shown that extraction efficiency of  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ , and  $\text{Cu}^{2+}$  all proportionally decreased with increased aqueous volume. Thus, using 20% *v/v* D2EPHA in kerosene, the optimum O:A ratio is 1:1. When the organic ratio was higher, at 4:1 and 2:1, higher percentages of desired  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Li}^+$  were co-extracted. Lower ratios of O:A showed lower extraction of  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Li}^+$ . The

extraction efficiency of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  was 100% and remained unchanged with an increase in the O:A ratio and when the extractant concentration was increased from 20 to 40% *v/v*. It was also observed that extraction efficiency of  $\text{Mn}^{2+}$  and  $\text{Cu}^{2+}$  decreased proportionately as the O:A ratio increased. Notably,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Li}^{+}$  were only significantly co-extracted using low O:A ratios and 40% *v/v* of D2EPHA to kerosene.



**Figure 6.** Variation in the organic and aqueous ratio. (a) 20% *v/v* D2EPHA, and (b) 40% *v/v* D2EPHA; Conditions: sulfate simulated solution (Ni-0.72, Co-0.60, Mn-0.31, Li-0.15, Cu-0.101, Al-0.075, and Fe-0.055 g/L, condition: 25 °C, 20 min, centrifugation-1000 rpm).

### 3.2.5. Separation Factor

This is a measure of the degree of selective separation of the metal(s) of interest over other metals using a specific extractant. The results of these experiments show that D2EPHA has a strong selectivity towards  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{Cu}^{2+}$ , and the selectivity is much higher than that for  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Li}^{+}$  at the varying solution pH studied. Table 2 shows that  $\text{Mn}^{2+}$  has a higher separation factor relative to all metals except  $\text{Fe}^{3+}$  at a pH of 2.0. Increasing the pH of the solution beyond 2.0 resulted in a higher separation factor of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  over  $\text{Mn}^{2+}$ . The best overall separation factor was obtained at pH 2.0, as recovery efficiency and selectivity of D2EPHA towards  $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{Cu}^{2+}$

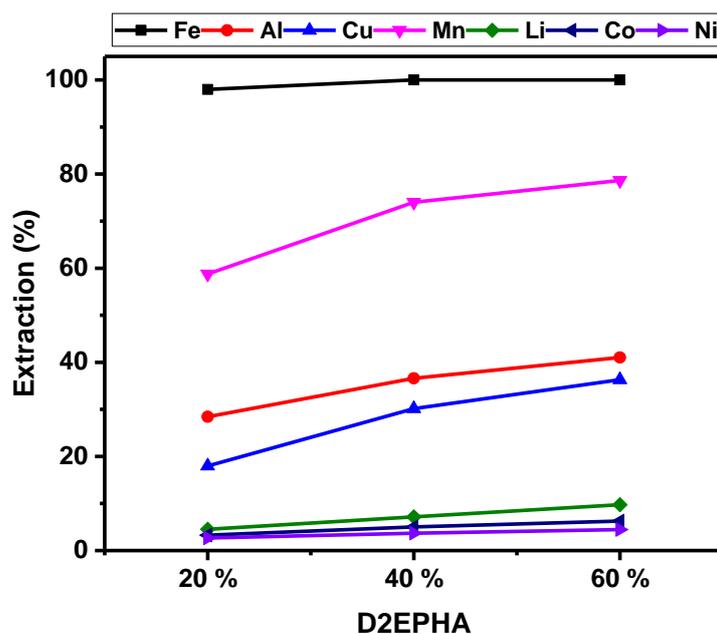
is higher. Therefore, the raffinate would be rich in  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Li}^+$ , which may be further separated with other systems. In summary, the order of extraction efficiency of metals studied is  $\text{Fe}^{3+} > \text{Mn}^{2+} > \text{Al}^{3+} \gg \text{Cu}^{2+} \gg \gg \gg \text{Co}^{2+} \sim \text{Li}^{2+} \sim \text{Ni}^{2+}$  based on the results presented in Table 2.

**Table 2.** Separation factor of metals using 40% v/v D2EPHA in kerosene at 25 °C in 20 min.

pH	2.0	2.5	3.0
Mn/Co	24	95	52
Mn/Ni	31	252	146
Mn/Li	80	389	65
Mn/Cu	6	6	6
Al/Mn	1	21	452
Fe/Mn	1376	252	1074

### 3.3. Extraction Using Real Leached Liquor

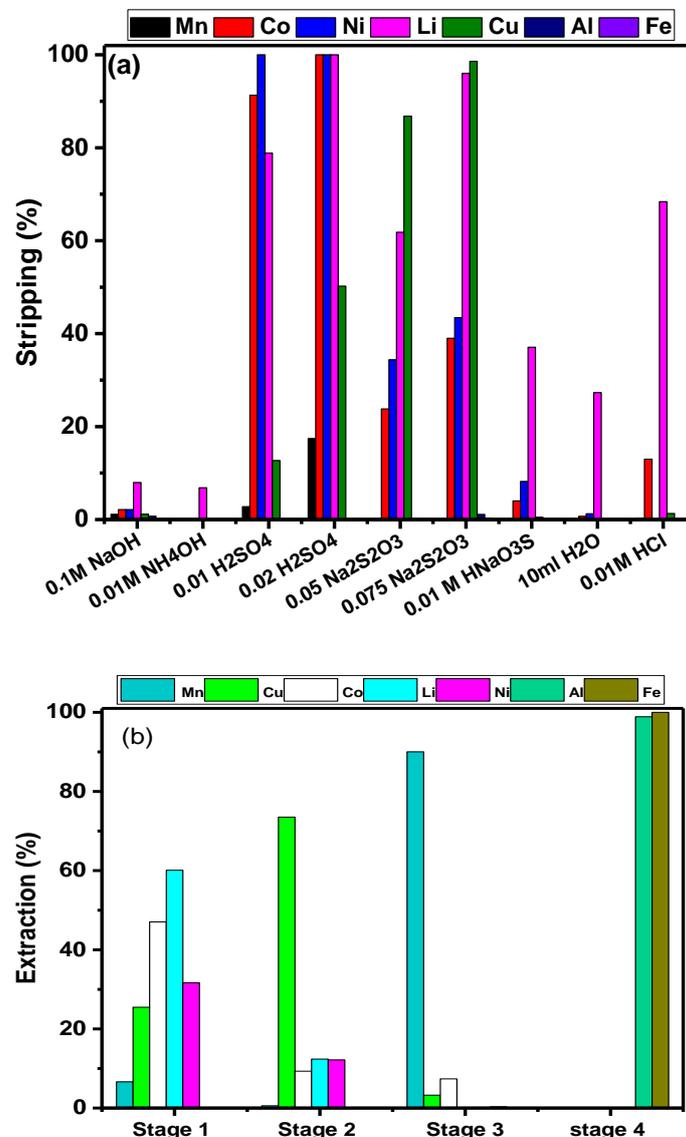
The performance of D2EPHA in kerosene for the extraction of manganese and metal impurities from rich Ni, Co, and Li sulfate leached liquor was studied. This is important because real liquor contains other trace impurities which might directly interfere with the reaction, thereby affecting extraction efficiency. However, the extraction experiment was performed using the optimized condition obtained from the extraction with the simulated solution. The results presented in Figure 7 show that the extraction efficiency using D2EPHA in kerosene for the real leached liquor and the simulated solution (Figure 5) is the same; it increases with increases in the concentration of D2EPHA from 20 to 40% v/v. The optimum concentration is 40% v/v, as a further increase in the concentration to 60% v/v resulted in a slight increase in the co-extraction of critical metals ( $\text{Co}^{2+}$ ,  $\text{Li}^{2+}$ , and  $\text{Ni}^{2+}$ ). At the optimum condition, extraction efficiency of  $\text{Mn}^{2+}$  from the simulated solution was 81.5%, whereas 78.6% was extracted from real leached liquor. A similar trend was observed with  $\text{Al}^{3+}$ , and this is because the concentration of metals Mn and Al were higher in the leached liquor. Almost the same extraction efficiencies of  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  were obtained from both the simulated and real leached liquor, and  $\text{Li}^+$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$  remained in the raffinate.



**Figure 7.** Extraction efficiency of metals from 2.0 M sulfate leached liquor [condition: Ni-1.47, Co-0.98, Mn-0.57, Li-0.43, Cu-0.98, Al-0.107, and Fe-0.045 g/L, 25 °C, 20 min, centrifugation-1000 rpm].

### 3.4. Stripping

From an economic perspective, stripping metals from extractant is an important aspect to maximize the extractant. In our study, selective stripping of metals from the loaded extractant is critical to produce a concentrated metal solution needed in the crystallization of a metal salt or to serve as a good electrolyte to produce a quality cathode metal. The stripping of metals loaded into D2EPHA obtained using simulated mixed metals solution was carried out. Different reagents were tested as strippants, with the objective of selectively recovering  $\text{Mn}^{2+}$  as a concentrated  $\text{MnSO}_4$  solution. As shown in the results presented in Figure 8, NaOH and  $\text{NH}_4\text{OH}$  were noticed to be unsuitable for the stripping of metals from D2EPHA. Meanwhile, highly diluted acid performed excellently for the removal of trace  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Li}^{2+}$  that was trapped or co-extracted unto D2EPHA. Interestingly, using 0.01M of  $\text{H}_2\text{SO}_4$ , although most (>80%) of the  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Li}^{2+}$  were stripped, a small amount (<5.0%) of  $\text{Mn}^{2+}$  was also stripped. When the acid concentration was increased to 0.02 M,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Li}^{2+}$  were stripped quantitatively, but  $\text{Mn}^{2+}$  (20%) and  $\text{Cu}^{2+}$  (51%) were also stripped out.



**Figure 8.** Stripping profile. (a) Conditions: O: A-1:1, 20% v/v D2EPHA, temperature-25 °C, time-20 min; (b) stepwise stripping-stage 1: 0.01M  $\text{H}_2\text{SO}_4$ , stage 2: 0.75 M  $\text{Na}_2\text{S}_2\text{O}_3$ , stage 3: 0.5 M  $\text{H}_2\text{SO}_4$ , stage 4: 1.0 M  $\text{C}_2\text{H}_2\text{O}_4$ ; conditions: O: A-1:1, 40% v/v D2EPHA, temperature-25 °C, time-20 min.

When the stripping solution was changed to 0.05 M sodium thiosulfate ( $\text{Na}_2\text{S}_2\text{O}_3$ ),  $\text{Cu}^{2+}$  (86%),  $\text{Li}^+$  (62%),  $\text{Ni}$  (53%), and  $\text{Co}^{2+}$  (24%) were stripped from D2EPHA. When the concentration of  $\text{Na}_2\text{S}_2\text{O}_3$  was increased to 0.075 M, it was found that  $\text{Cu}^{2+}$  (98.5%),  $\text{Li}^+$  (96%),  $\text{Ni}^{2+}$  (44%), and  $\text{Co}^{2+}$  (39%) were also stripped from D2EPHA. This result shows that thiosulphate solution is a good strippant to remove  $\text{Cu}^{2+}$  and other impurities from D2EPHA. Lastly,  $\text{Li}^+$  (40%) was stripped using 0.01 M sodium bisulfite ( $\text{HNaO}_3\text{S}$ ) while traces of  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Li}^+$  (34%) were removed with  $\text{H}_2\text{O}$  without the presence of any metals; and  $\text{Li}^+$  (71%) and  $\text{Co}^{2+}$  (15%) were stripped with 0.01 M HCl. In general, it was observed that  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  remained in the D2EPHA. This recalcitrant stripping of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  from D2EPHA has been reported [53,54]. However, the stripping of metals from higher concentrated extractant (40% v/v D2EPHA) was investigated (Figure 8b). The stripping results are presented in Figure 8b. In the first stage, 0.01 M  $\text{H}_2\text{SO}_4$  was used to remove trapped or trace co-extracted metals ( $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Li}^+$ ). It is shown that a significant amount of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Li}^+$  were stripped with trace  $\text{Mn}^{2+}$ . However, further stripping was performed using 0.075 M  $\text{Na}_2\text{S}_2\text{O}_3$  and the remaining  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Li}$  was selectively stripped without  $\text{Mn}^{2+}$ . Thus, recoverable impurities were totally stripped from D2EPHA in two stages, retained  $\text{Mn}^{2+}$  was selectively stripped as  $\text{MnSO}_4$  (92.1%) using 0.5 M  $\text{H}_2\text{SO}_4$ , and the  $\text{MnSO}_4$  solution is suitable for concentration and crystallized as  $\text{MnSO}_4$  salt. The remnant impurities ( $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ ) were finally stripped with 1.0 M oxalic acid, and D2EPHA was fully reconditioned for reuse.

3.5. Conceptual Flow Sheet

Based on the optimized parameters, the steps for the extraction of metal impurities from sulphate leached liquor of a black mass using D2EPHA in kerosene are summarized in the flow sheet below (Figure 9). The aqueous phase (simulated leach liquor) was pumped through a solvent extractor compartment loaded with a proportion of organic phase (D2EPHA in kerosene). Next, the loaded extractant was washed with dilute  $\text{H}_2\text{SO}_4$ , and trapped or co-extracted  $\text{Co}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Ni}^{2+}$ , and  $\text{Cu}^{2+}$  were washed out. In the next stage,  $\text{Cu}^{2+}$  was completely stripped with other impurities. In the third stage,  $\text{Mn}^{2+}$  retained in the extractant was stripped using concentrated  $\text{H}_2\text{SO}_4$ , leaving behind  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ , which were finally stripped using an oxalic acid solution. The spent extractant was reconditioned with  $\text{H}_2\text{O}$  and may be reused repeatedly.

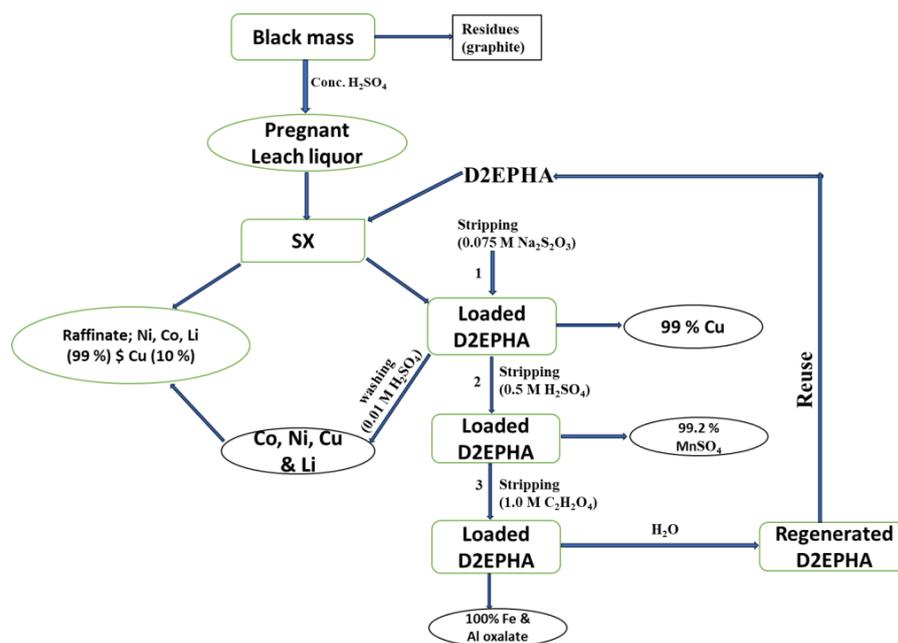


Figure 9. Proposed flow sheet for the extraction of metal impurities from sulphate leached liquor of black mass and concentration of critical metals rich liquor.

#### 4. Conclusions

The extraction performance of D2EHPA, Cyanex-272, and Na-Cyanex-272 was first compared to determine the most selective extractant to remove metal impurities from a simulated critical metals leach solution. D2EHPA was preferred, and sequential extraction of metal impurities ( $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Cu}^{2+}$ ) from critical metals ( $\text{Co}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Ni}^{2+}$ , and  $\text{Mn}^{2+}$ ) using different diluents was achieved. The extraction efficiencies of metal impurities were highest using D2EHPA in kerosene. Exxal-10 also showed high extraction efficiency, except that significant amounts of  $\text{Co}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Ni}^{2+}$ , and  $\text{Mn}^{2+}$  were also co-extracted. The extraction efficiencies decreased with increases in O:A ratios from 1:1 to 1:3. Four stages of stripping were conducted, and selective stripping of  $\text{Mn}^{2+}$  as  $\text{MnSO}_4$  was accomplished after co-extracted metal impurities ( $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ , and  $\text{Cu}^{2+}$ ) were removed. The extractant was regenerated when the recalcitrant  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  were finally stripped from D2EHPA using oxalic acid. A proposed flow sheet for the sequential extraction of metal impurities from critical metals rich solution was developed.

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