Development of an environmentally friendly metal extraction process from lithium-ion batteries

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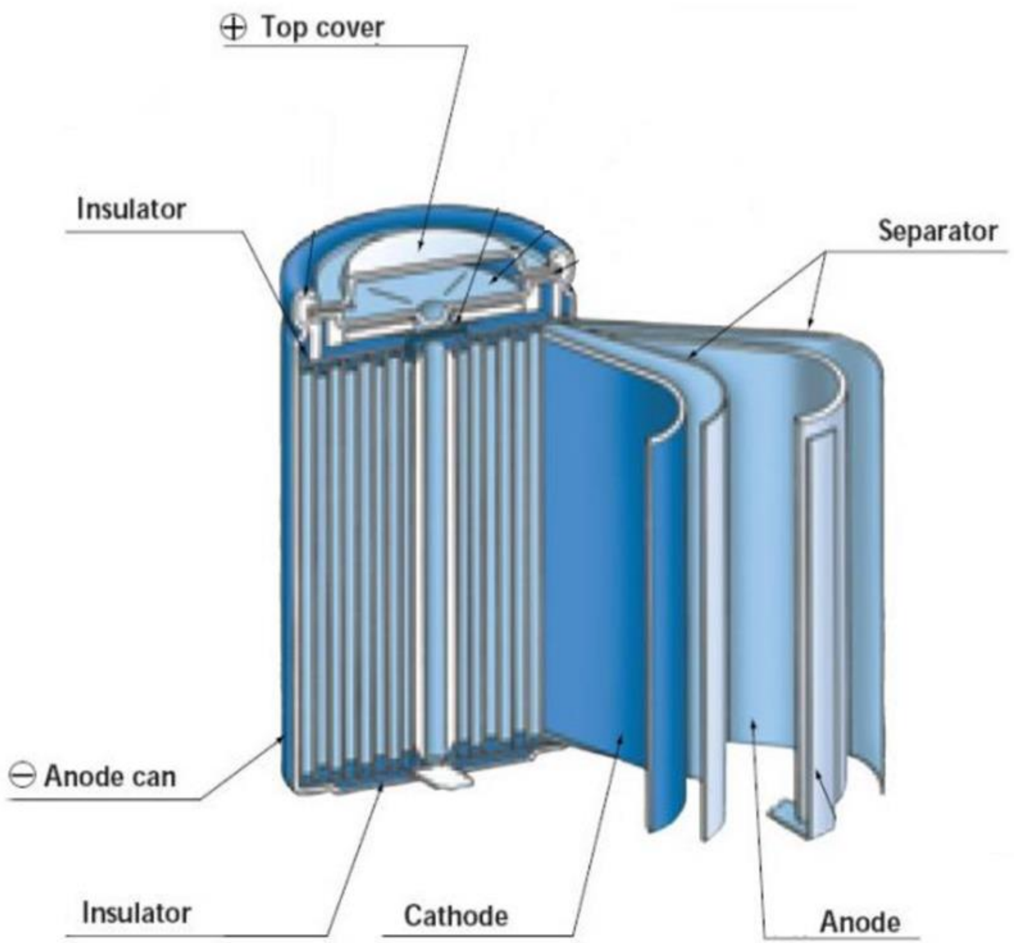
Introduction: Use of LIBs

- Lithium ion batteries widely used in electronic devices e.g cell-phones, laptops as well as in electric cars

Introduction: Schematic of LIB



Introduction: Main features of a LIB

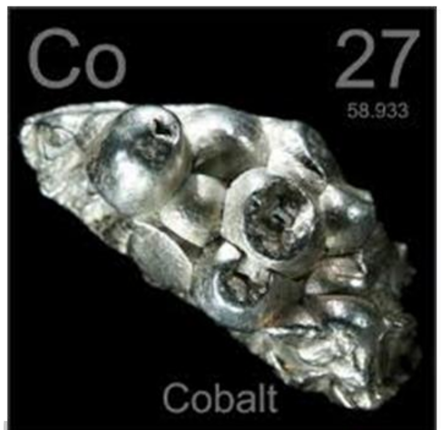
- A lithium-ion battery consists of a cathode, an anode, organic binder, electrolyte and a separator.
- Anode - thin Cu sheet coated with graphite
- Cathode - thin Al sheet coated with active material
- Usually $LiCoO_2$, $LiMn_2O_4$ and $LiNiO_2$ coat the cathode
- Polymeric Polyvinylidene floride (PVDF) binder used to aggregate cathodic active powder.

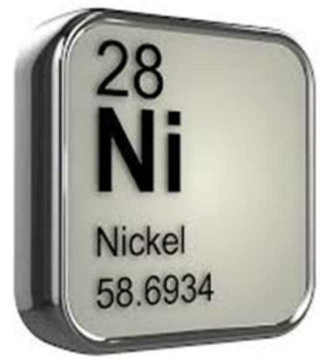
Introduction: Treatment of waste LIBs

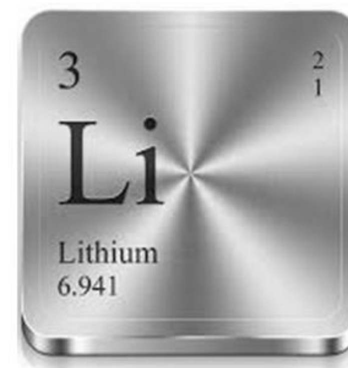
- There is an expected rise in LIB waste in upcoming years due to the high volumes of consumer electronics.

Introduction: Problem statement

- For the sustainable management of natural resources and to reduce environmental pollution, a simple and environmentally benign process for metal recovery from LIBs must be developed to recover as much value as possible.







Introduction: Objectives

- Evaluate the technical feasibility of using organic acids [citric and DL-malic acid] as lixiviants for Co, Li and Ni recovery from LIBs.
- Select the most suitable organic acid between citric and DL-malic acid with regard to both cost and leaching performance.

Experimental: Discharging and dismantling

- LIBs dismantled to individual cell level - plastic casings removed.
- Batteries discharged by immersion in 1 wt. % NaCl solution for 48 hours and air dried.
- Further dismantling and removal of steel casings.
- Anodes and cathodes separated

Experimental: Leaching of cathodes with NaOH

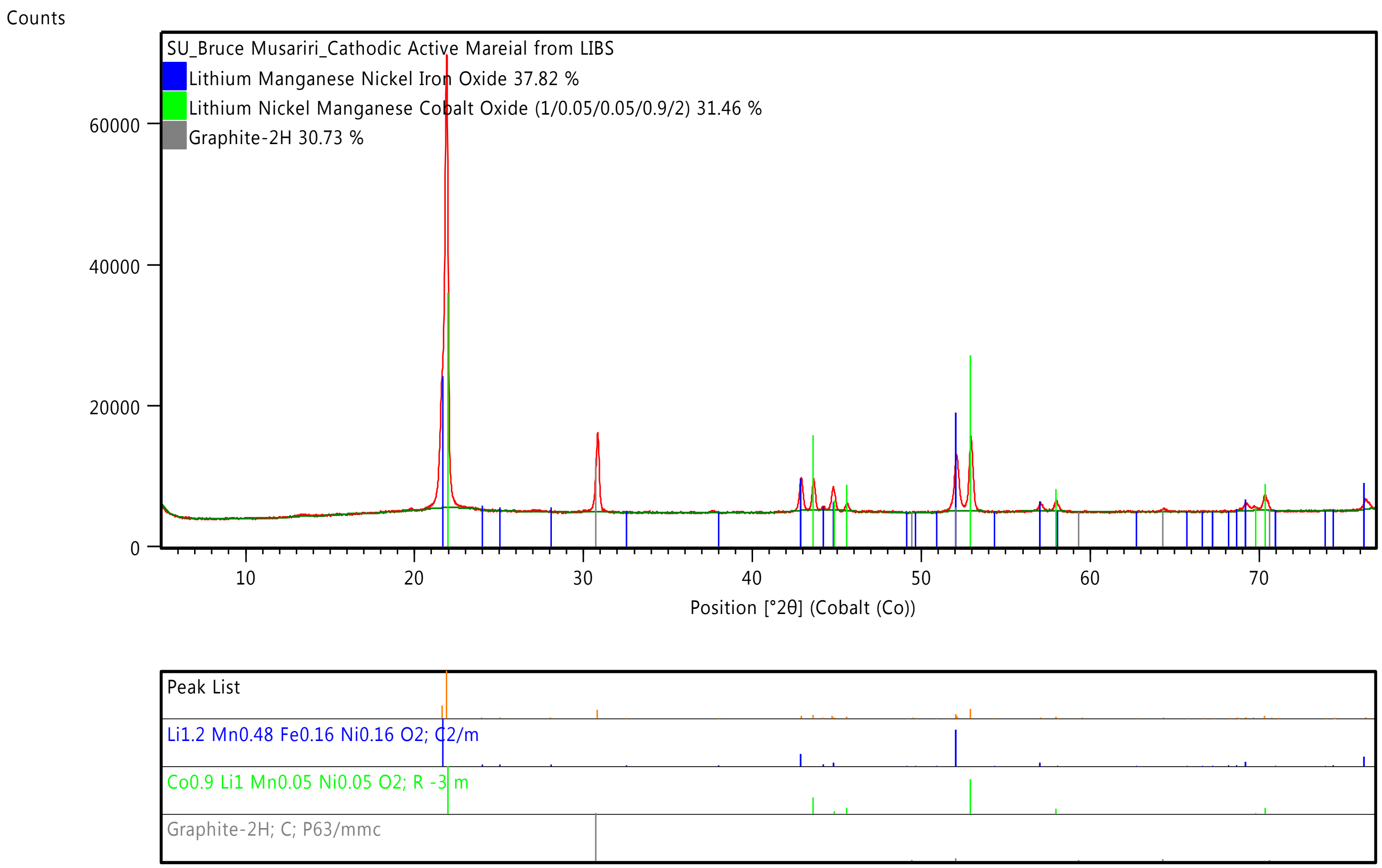
- Cathodes treated with 10 wt. % NaOH solution at 25℃ and 100g/L pulp density for 2h.
- After filtration, residue dried at 60℃ for 24h and ground to a particle size less than 106μm.
- Material split into smaller samples which were used as feed to the leaching tests

Experimental: Characterization - Aqua regia

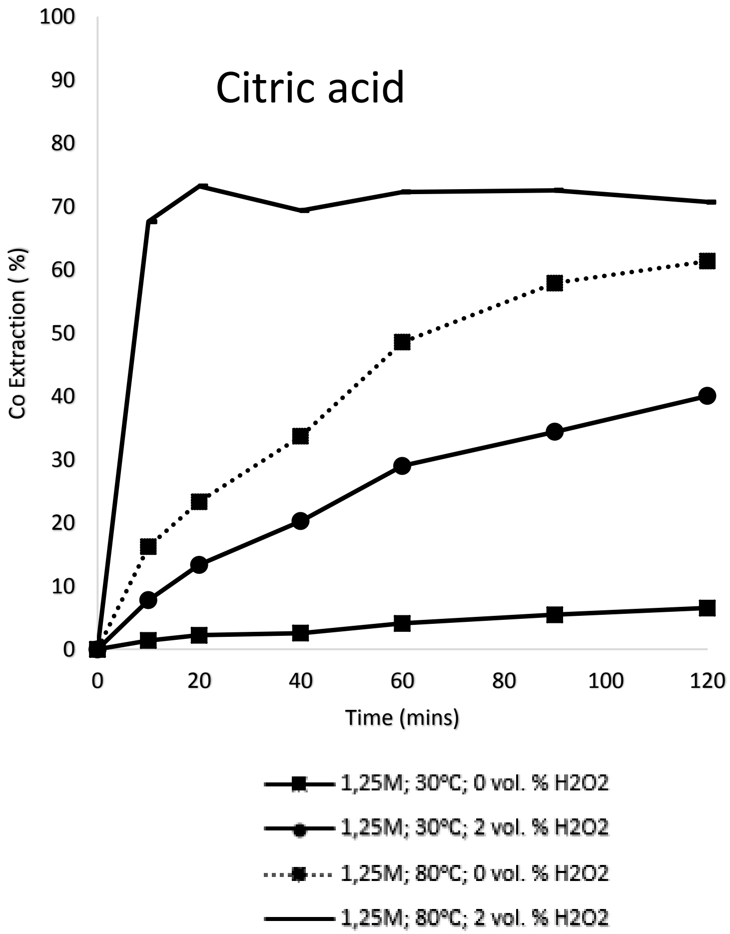
Al [wt. %]	Co [wt. %]	Cu [wt. %]	Li [wt. %]	Mn [wt. %]	Ni [wt. %]
1.38±0.10	26.94±0.68	0.09±0.006	9.10±0.52	22.81±1.22	31.71±1.27

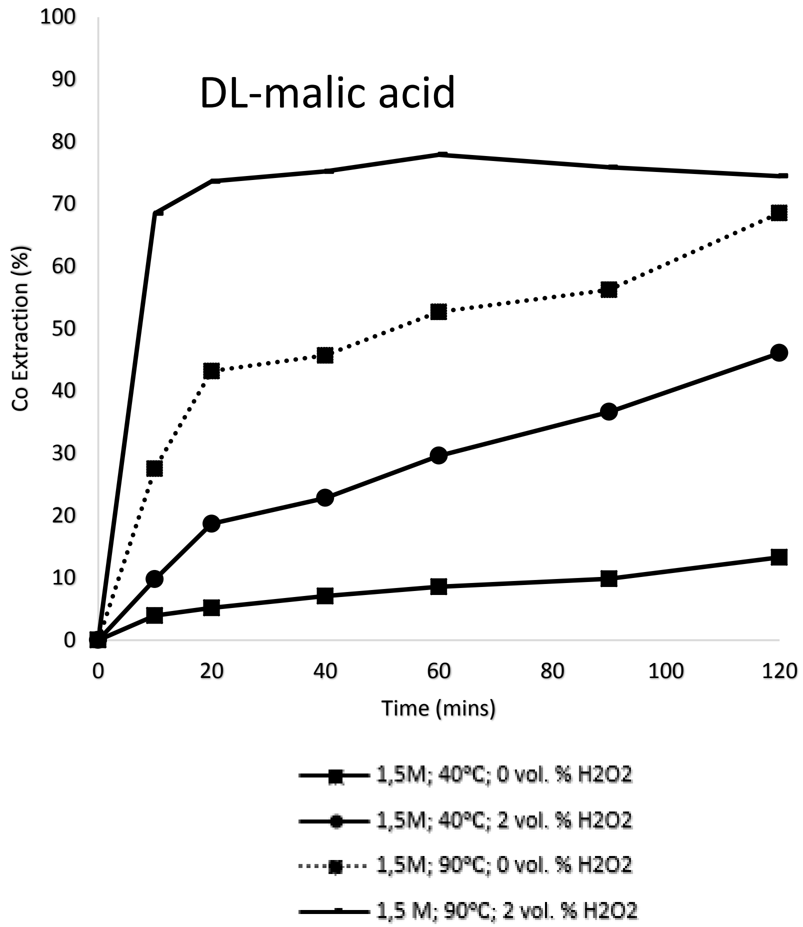
- Composition of cathodic active material determined using ICP-OES after aqua regia digestion

Experimental: Characterization - XRD



Experimental: Initial tests on H_2O_2 addition





Experimental: Citric acid leaching mechanism

Without $\mathbf{H_2O_2}$

- $20LiNi_{0.05}Mn_{0.05}Co_{0.9}O_{2(s)} + 10C_6H_8O_{7(aq)} \rightarrow 5Co_3O_{4(s)} + 20Li^+_{(aq)} + Ni^{2+}_{(aq)} + 3Co^{2+}_{(aq)} + Mn^{2+}_{(aq)} + 10C_6H_5O_7{}^{3-}_{(aq)} + 15H_2O_{(l)} + \frac{5}{2}O_{2(g)}$ [1]
- $Co_3O_{4(s)} + 2C_6H_8O_{7(aq)} \rightarrow Co_3(C_6H_5O_7)_{2(aq)} + 3H_2O_{(l)} + \frac{1}{2}O_{2(g)}$ [2]

With $\mathbf{H_2O_2}$

$\mathbf{Co^{3+}}$ reduced to the more soluble $\mathbf{Co^{2+}}$

- $20LiNi_{0.05}Mn_{0.05}Co_{0.9}O_{2(s)} + 20C_6H_8O_{7(aq)} + 20H_2O_{2(l)} \rightarrow 5Co_3O_{4(s)} + 20Li^+_{(aq)} + Ni^{2+}_{(aq)} + 3Co^{2+}_{(aq)} + Mn^{2+}_{(aq)} + 20C_6H_5O_7{}^{3-}_{(aq)} + 50H_2O_{(l)} + 10O_{2(g)}$ [3]

Experimental: DL-Malic acid leaching mechanism

Without $\mathbf{H_2O_2}$

- $20LiNi_{0.05}Mn_{0.05}Co_{0.9}O_{2(s)} + 15C_4H_6O_{5(aq)} \rightarrow 5Co_3O_{4(s)} + 20Li^{+}{}_{(aq)} + Ni^{2+}{}_{(aq)} + 3Co^{2+}{}_{(aq)} + Mn^{2+}{}_{(aq)} + 15C_4H_4O_5{}^{2-}{}_{(aq)} + 15H_2O_{(l)} + \frac{5}{2}O_{2(g)}$ [4]
- $Co_3O_{4(s)} + 3C_4H_6O_{5(aq)} \rightarrow 3CoC_4H_4O_{5(aq)} + 3H_2O_{(l)} + \frac{1}{2}O_{2(g)}$ [5

With $\mathbf{H_2O_2}$

$\mathbf{Co^{3+}}$ reduced to the more soluble $\mathbf{Co^{2+}}$

- $20LiNi_{0.05}Mn_{0.05}Co_{0.9}O_{2(s)} + 20C_4H_6O_{5(aq)} + 20H_2O_{2(l)} \rightarrow 5Co_3O_{4(s)} + 20Li^{+}{}_{(aq)} + Ni^{2+}{}_{(aq)} + 3Co^{2+}{}_{(aq)} + Mn^{2+}{}_{(aq)} + 20C_4H_4O_5{}^{2-}{}_{(aq)} + 50H_2O_{(l)} + 10O_{2(g)}$ [6]

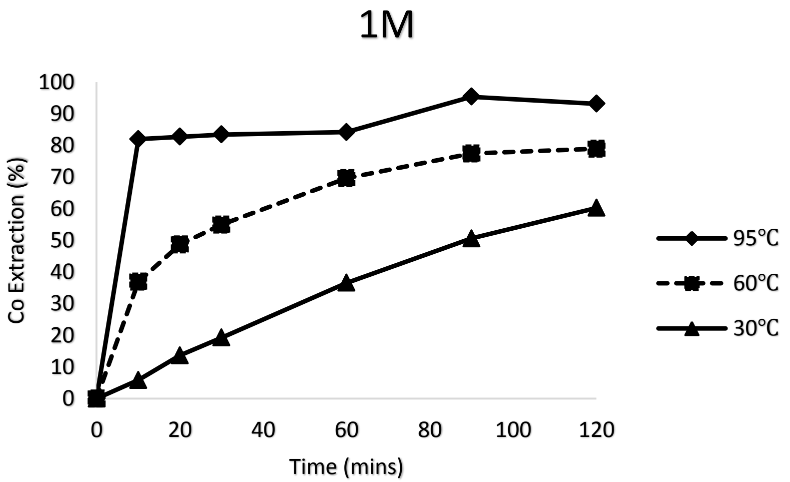
Experimental: Full factorial design - Leaching

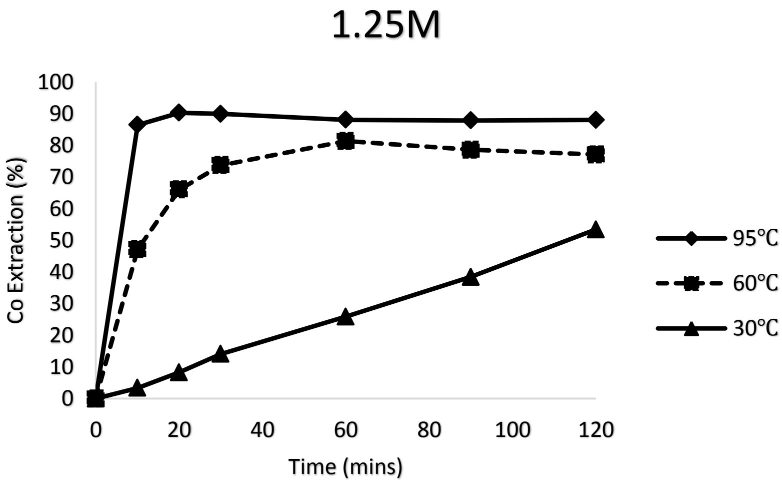
Variable	Set point		
Acid concentration (M)	1	1.25	1.5
Temperature (℃)	30	60	95

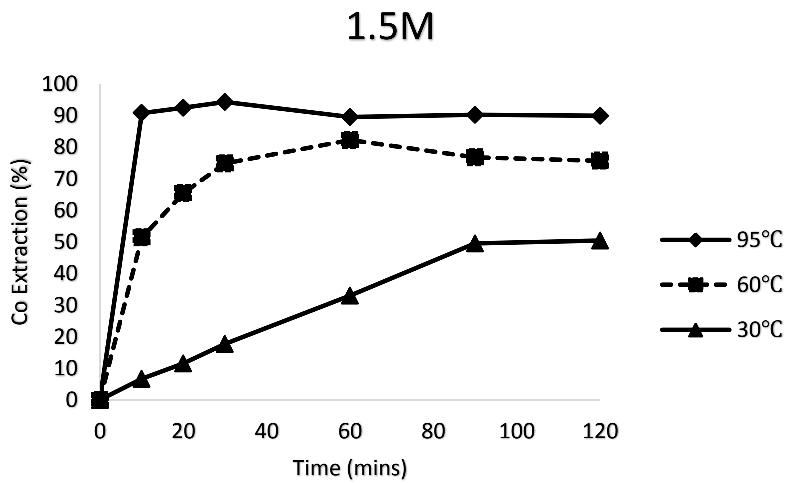
Parameters kept constant

Parameter	**Set point**
Hydrogen peroxide concentration	2 vol. %
Pulp density	20g/L
Leaching time	120 mins
Agitation speed	750 rpm

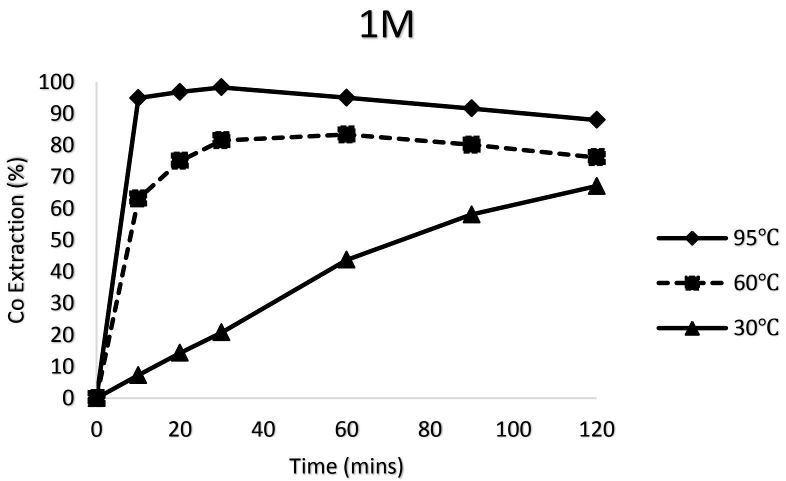
Experimental: Citric acid leaching results

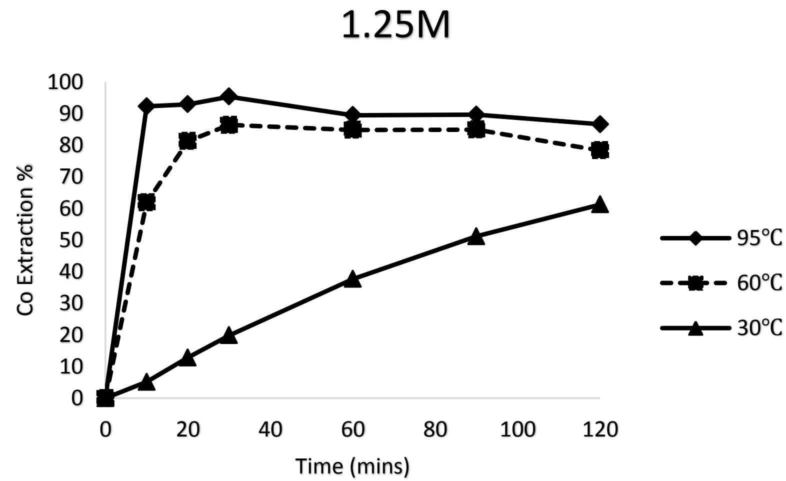


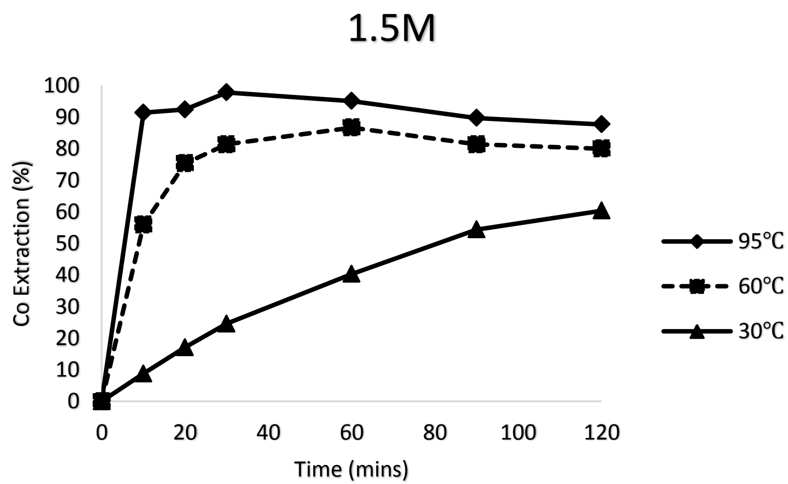




Experimental: DL-malic acid leaching results







Experimental: Optimum leaching conditions

- 95% Co, 96% Li and 99% Ni recoveries at conditions: 1M citric acid, 2% v/v H_2O_2, 95℃ and 20 g/L pulp density.
- 98% Co, 96% Li and 99% Ni recoveries at conditions: 1M DL-malic acid, 2% v/v H_2O_2, 95℃ and 20 g/L pulp density

Citric acid vs DL-malic acid

Acid	Price
Citric acid	USD 700-900/Metric Ton
DL-malic acid	USD 1800-2500/Metric Ton

Conclusions and next step

- Organic acids are effective leaching agents for Co, Li and Ni recovery from LIBs, yielding over 95% metal recoveries.
- Leaching performances of Citric and DL-Malic acid are generally similar, but citric acid is cheaper and therefore, a more suitable lixiviant.

Next step

- Devepment of a process fro metal recovery from solution and separation into individual streams.
- More tests with higher pulp densities, to make the process more economically feasible

Thank you for your attention

Any questions

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