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Evaluating organic acids as alternative leaching reagents for metal recovery from lithium ion batteries

B. Musariri, G. Akdogan and C. Dorfling

Fakulteit Ingenieurswese
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Faculty of Engineering

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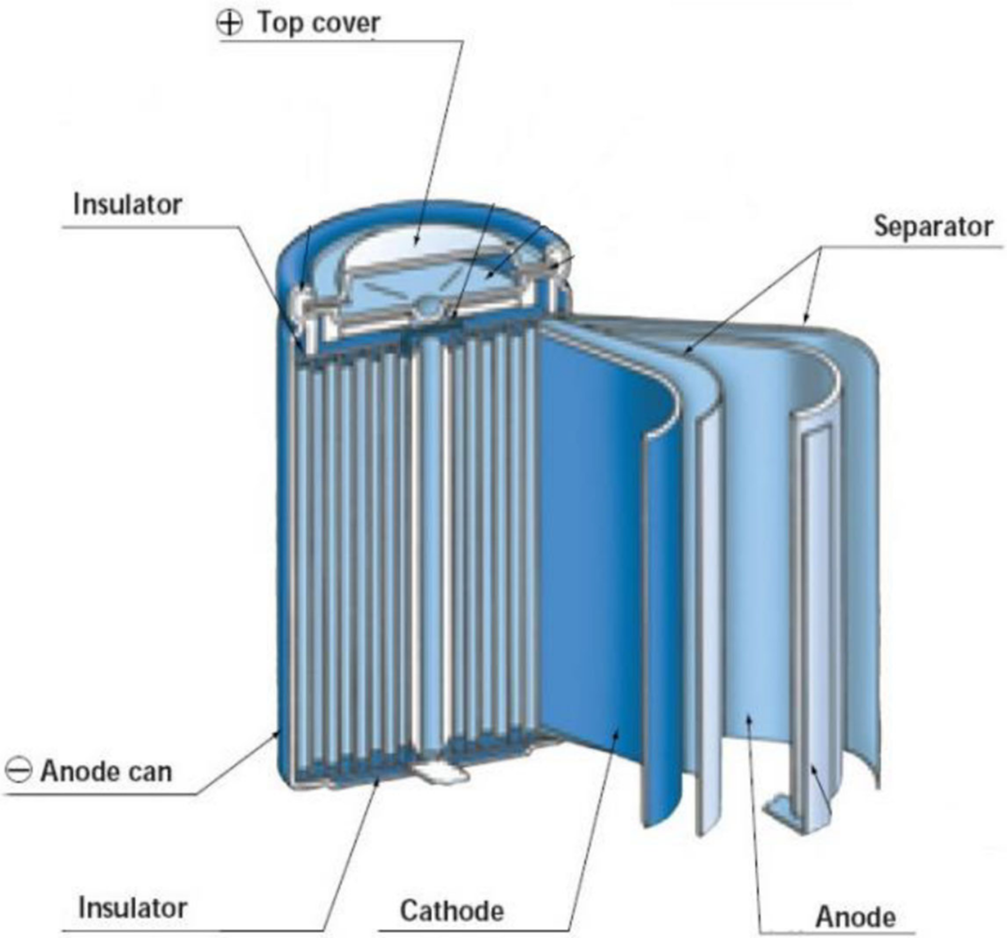
Introduction: Background

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

Background

- A lithium-ion battery consists of a cathode, an anode, organic binder, electrolyte and a separator.
- Anode - Cu foil coated with graphite.
- Cathode - Al foil coated with cathodic material.
- $LiCoO_2$, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ $LiMn_2O_4$ and $LiNiO_2$ are some of the most common commercially used cathodic material.
- Polymeric Polyvinylidene floride (PVDF) binder used to aggregate cathodic active powder.



Introduction: Background

- Expected rise in LIB waste in upcoming years.
- Recycling, landfilling and incineration are the most adequate methods of treating LIBs.
- In land fills heavy metals slowly leach into soil.
- Conversion of oxides to their metallic form during incineration.
- Recycling reduces pollution, and provides expensive raw materials such as Li and Co.
- Current commercial LIB recycling processes have environmental issues.
- Sustainable management of natural resources and environmental protection.
- More environmentally friendly leaching reagents.

Objectives

- Perform leaching tests to investigate the use of organic acids as leaching reagents for metal (Co, Li and Ni) recovery from LIB cathodic material, using citric and DL-malic acid as competitors.
- Compare the leaching performances of citric acid and DL-malic acid.

Experimental: Discharging and dismantling

- LIBs from scrap laptops were used.
- Batteries were discharged by immersion in 1 wt. % NaCl solution for 48 hours and air dried.
- Dismantled and separated into anodes, cathodes and plastic separators.
- Cu from the anode was recovered in its metallic form.

Experimental: Leaching of cathodes with NaOH

- Cathodes treated with 10 wt. % NaOH solution at 25℃ and S/L ratio of 1:10 for 2 hours.
- The aim was to selectively dissolve Al at the cathode and leave behind the cathodic material as a residue.
- After washing and filtration, residue was dried at 60℃ for 24 hours before being ground to a particle size less than 106μm.
- Sample was split into smaller quantities which were used for characterisation and as feed to the leaching tests.

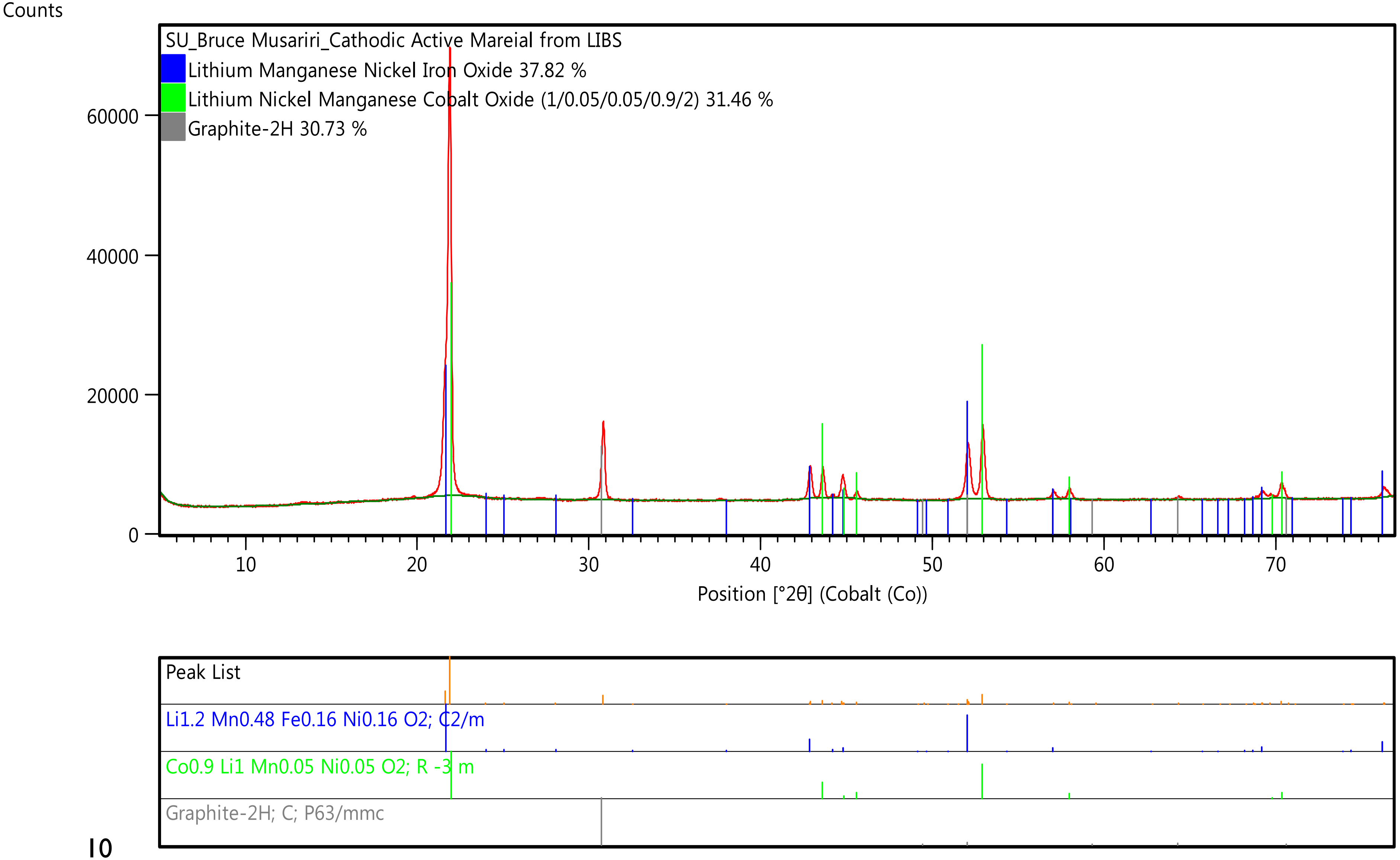
Experimental: Characterization

- Aqua regia digestion performed to determine the average metal content in the cathodic material.
- X-ray Diffraction (XRD).
- Scanning Electron Microscopy (SEM)

Results: Characterisation – aqua regia

Metal	Metal phase (%)	Cathodic material (g/kg)
Al	1.50±0.0	6.75 ± 0.47
Co	29.28±0.48	131.45 ± 3.32
Cu	0.11±0.001	0.48 ± 0.03
Li	9.89±0.40	44.41± 2.56
Mn	24.77±0.57	111.30 ± 5.93
Ni	34.45±0.41	154.70 ± 6.19

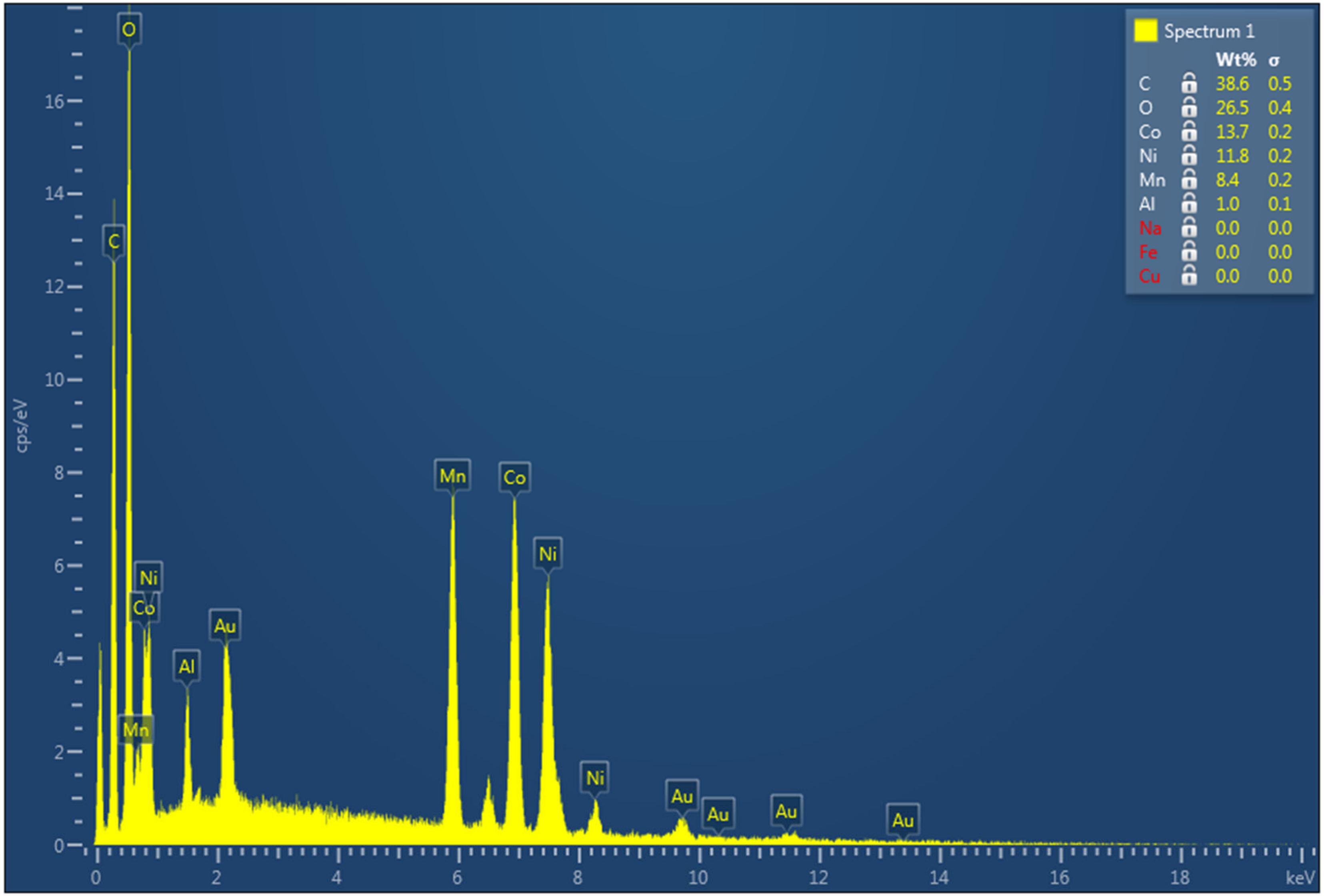
Results: Characterisation - XRD analysis



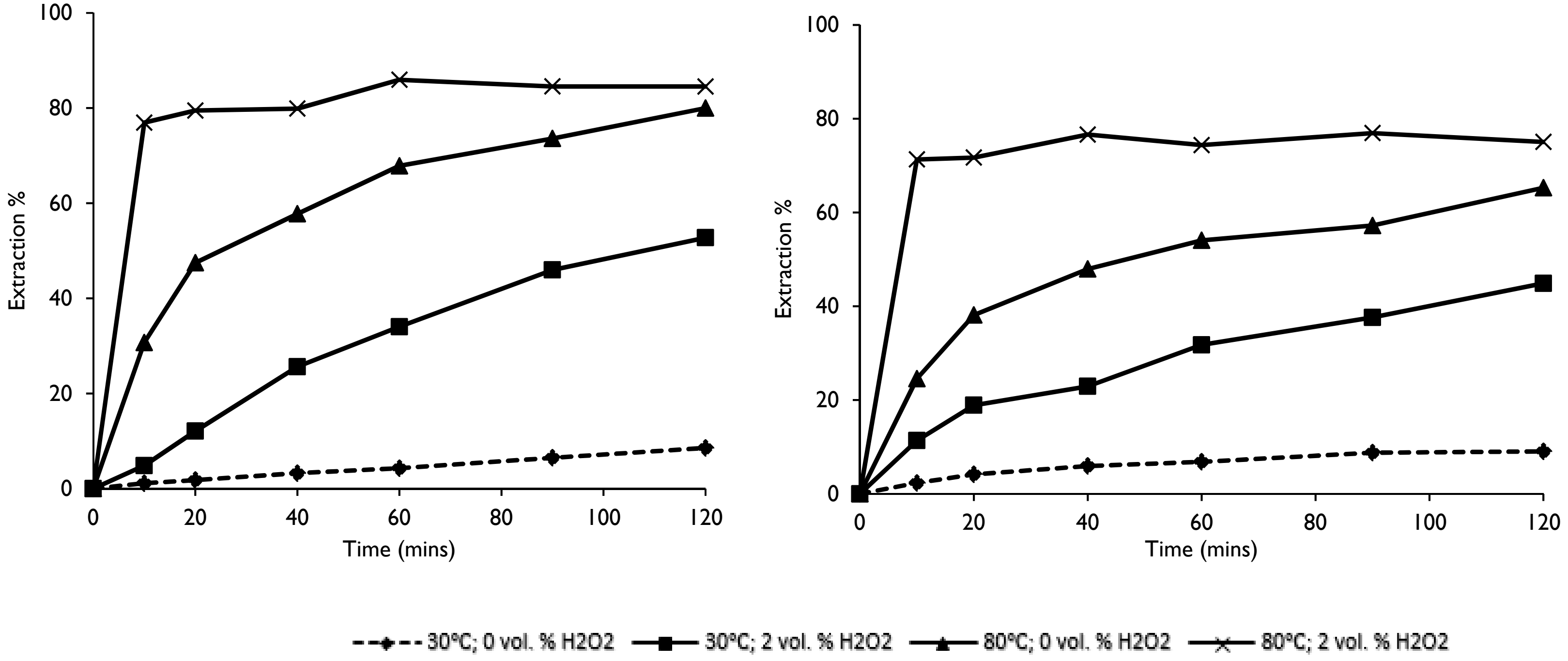
Results: Characterisation – EDS Quantitative

	Wt. %									
Test	**C**	**O**	**Na**	**Al**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**total**
1	38.60	26.48	0	1.04	8.41	0	13.71	11.76	0	100
2	38.1	27.4	0	1.13	8.66	0	12.27	12.44	0	100
3	40.47	28.85	0	1	7.73	0	10.95	11	0	100
4	39.24	27.54	0.36	1.12	8.06	0	11.97	11.71	0	100
5	38.91	27.03	0	1.04	8.09	0	12.71	11.78	0.44	100
Average	39.06	27.46	0.07	1.066	8.19	0	12.32	11.73	0.088	100

Results: Characterisation – EDS spectrum, Test 1



Results: Effect of H_2O_2 addition



- Effect of H_2O_2 addition on Co leaching with 1M citric and DL-malic acid at 20 g/L pulp density.
- For both acids, the inclusion of H_2O_2 results in faster leaching kinetics, at both high and low temperature.

Results: The role of H_2O_2

- There is a strong ionic bond between Co^{3+} and oxygen in $LiNi_{0.05}Mn_{0.05}Co_{0.9}O_2$ and its dissolution involves the reduction of Co^{3+} in the solid state to the more soluble Co^{2+}
- H_2O_2 acts as a reductant and reduces Co^{3+} to Co^{2+} according to the half reactions represented by Equations 1 and 2 (Skoog *et al., 2013)*
- $H_2O_{2(l)} + 2H^+_{(aq)} + 2e^- \leftrightarrow 2H_2O_{(l)}$ $\quad E^\theta = +1.78$ V $\quad$ [1]
- $Co^{3+}_{(aq)} + e^- \leftrightarrow Co^{2+}_{(aq)}$ $\quad E^\theta = +1.80$ V $\quad$ [2]
- Equation 1 shows H_2O_2 acting as a reductant in an acid solution.
- Equation 2 represents the reaction for the reduction of Co^{3+} to Co^{2+}.
- This breaks the Co and oxygen bond in the oxide phase, resulting in the dissolution process progressing faster.

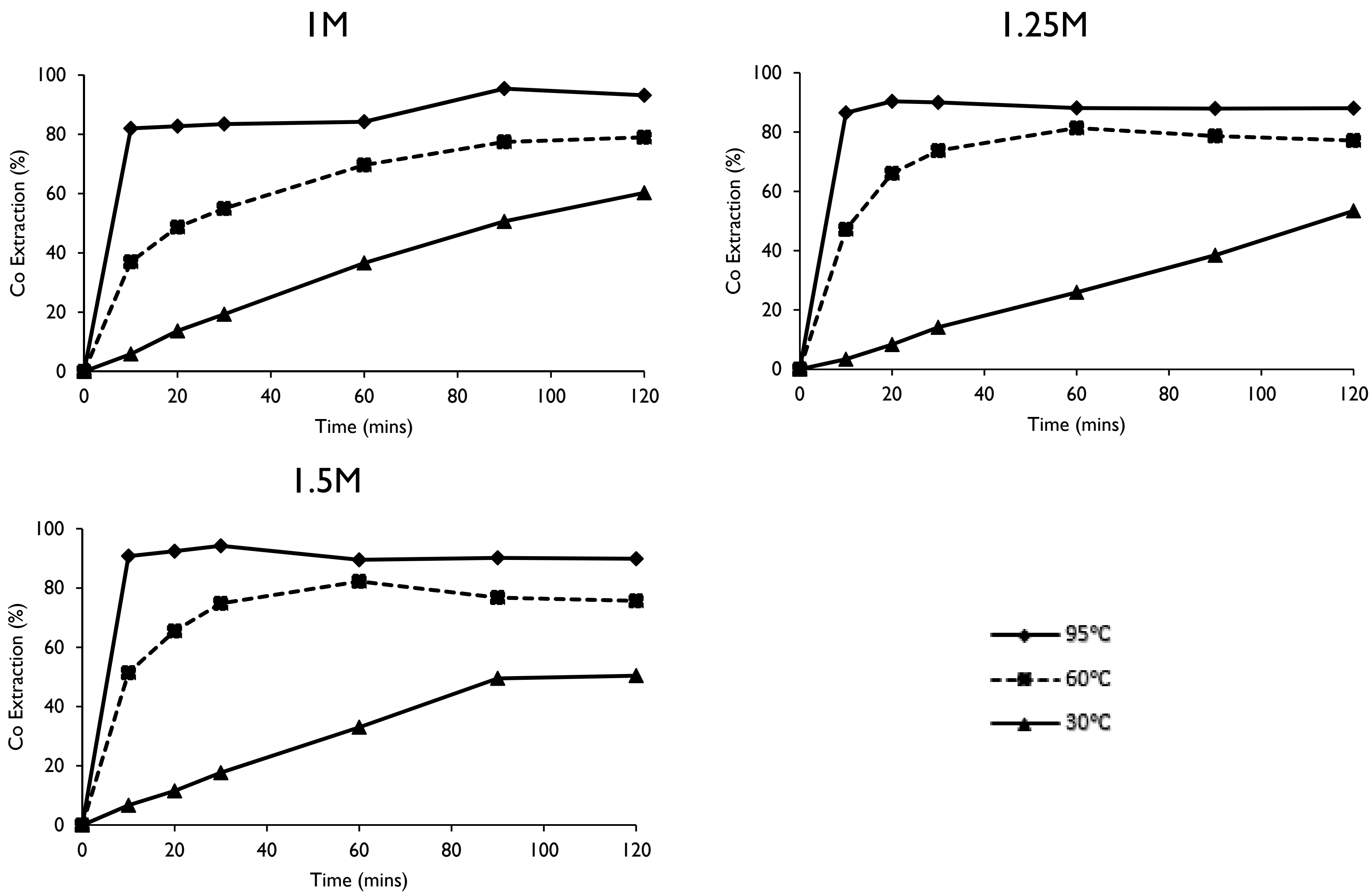
Experimental: Full factorial experimental design for acid leaching tests

Variable	**Set point**		
Acid concentration (M)	1	1.25	1.5
Temperature (°C)	30	60	95

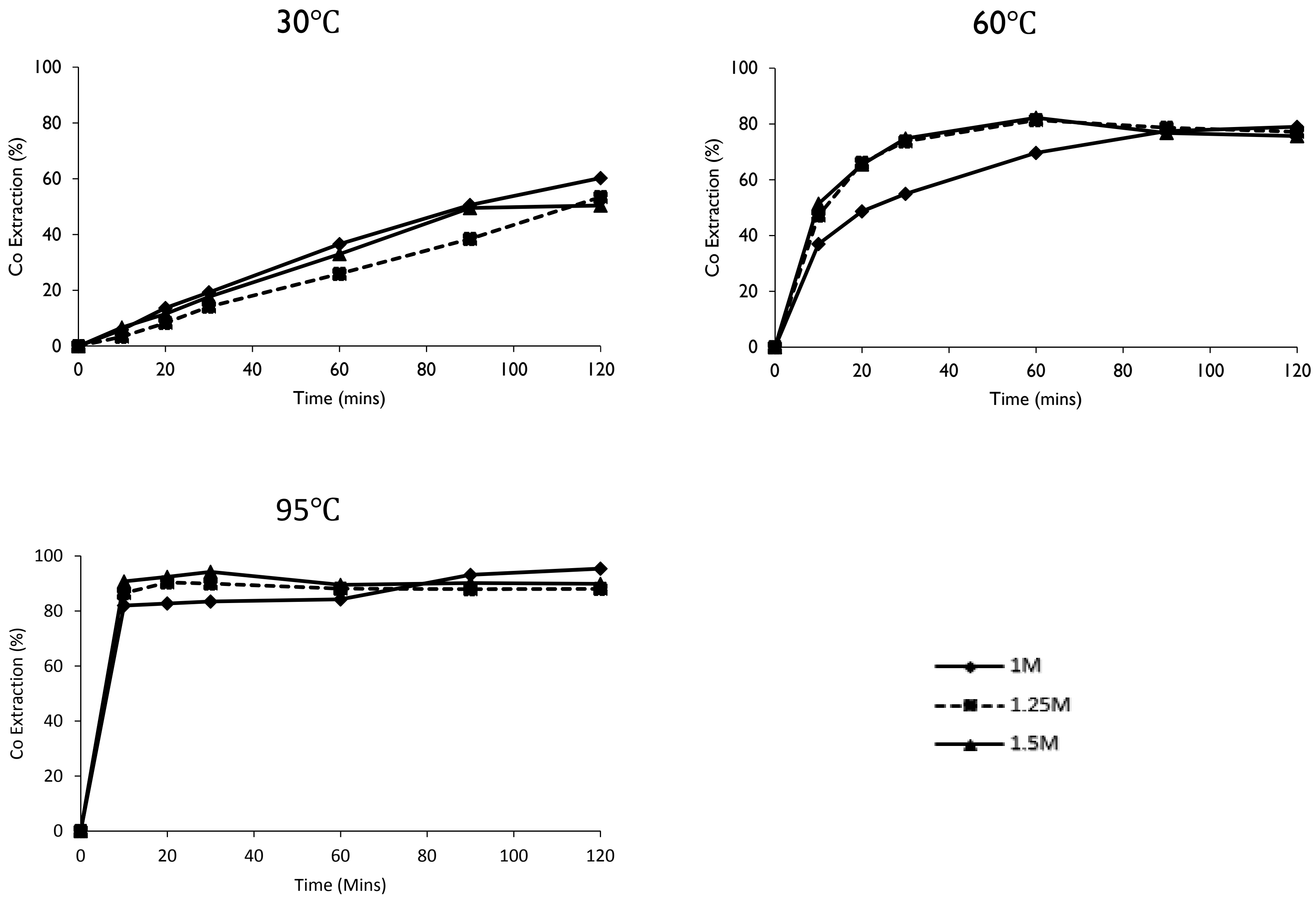
Experimental: Parameters kept constant during acid leaching tests

Parameter	Set point
H_2O_2 concentration	2% v/v
Pulp density	20g/L
Leaching time	120 mins
Agitation speed	750 rpm

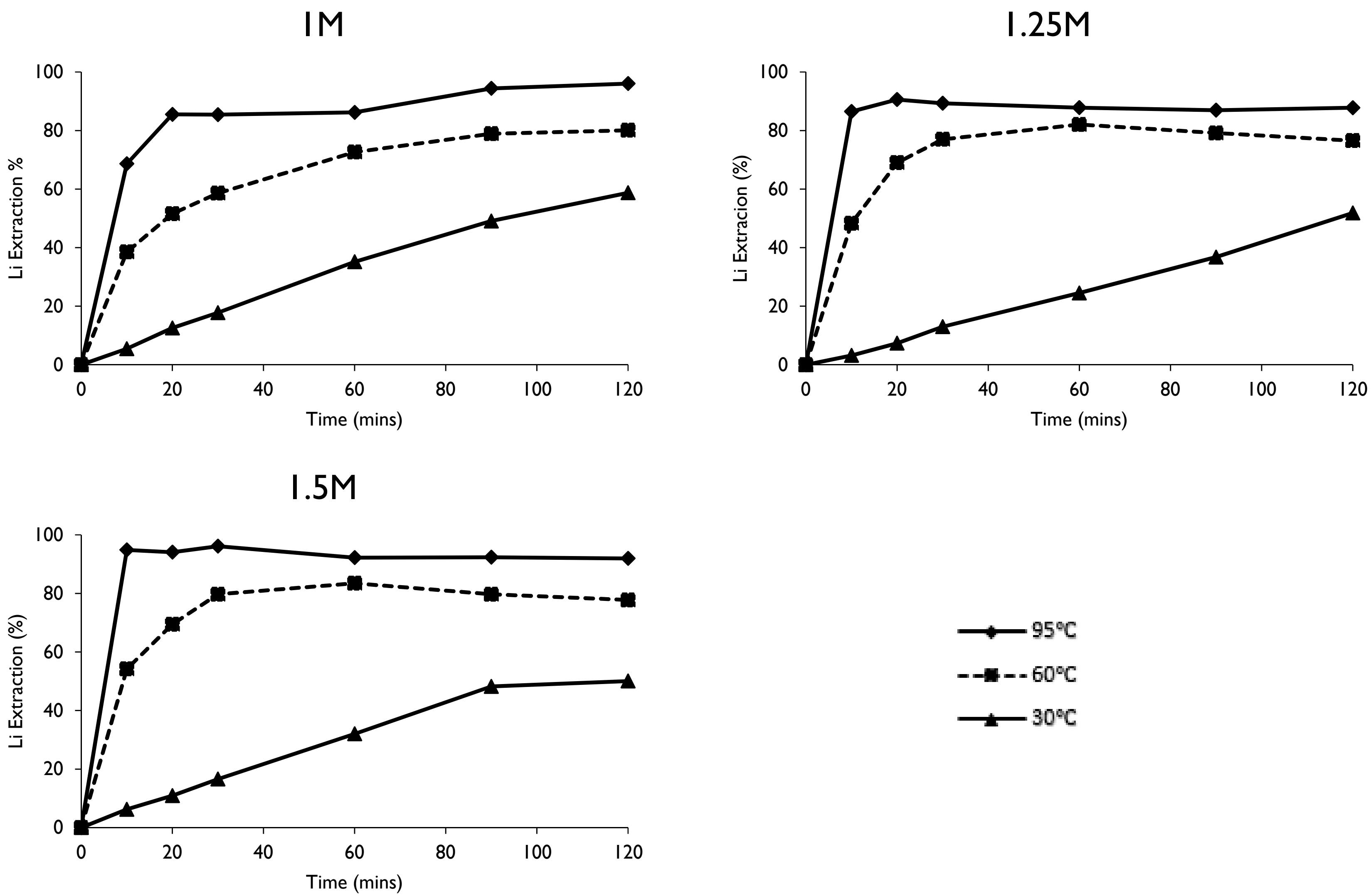
Results: Citric acid leaching - Co



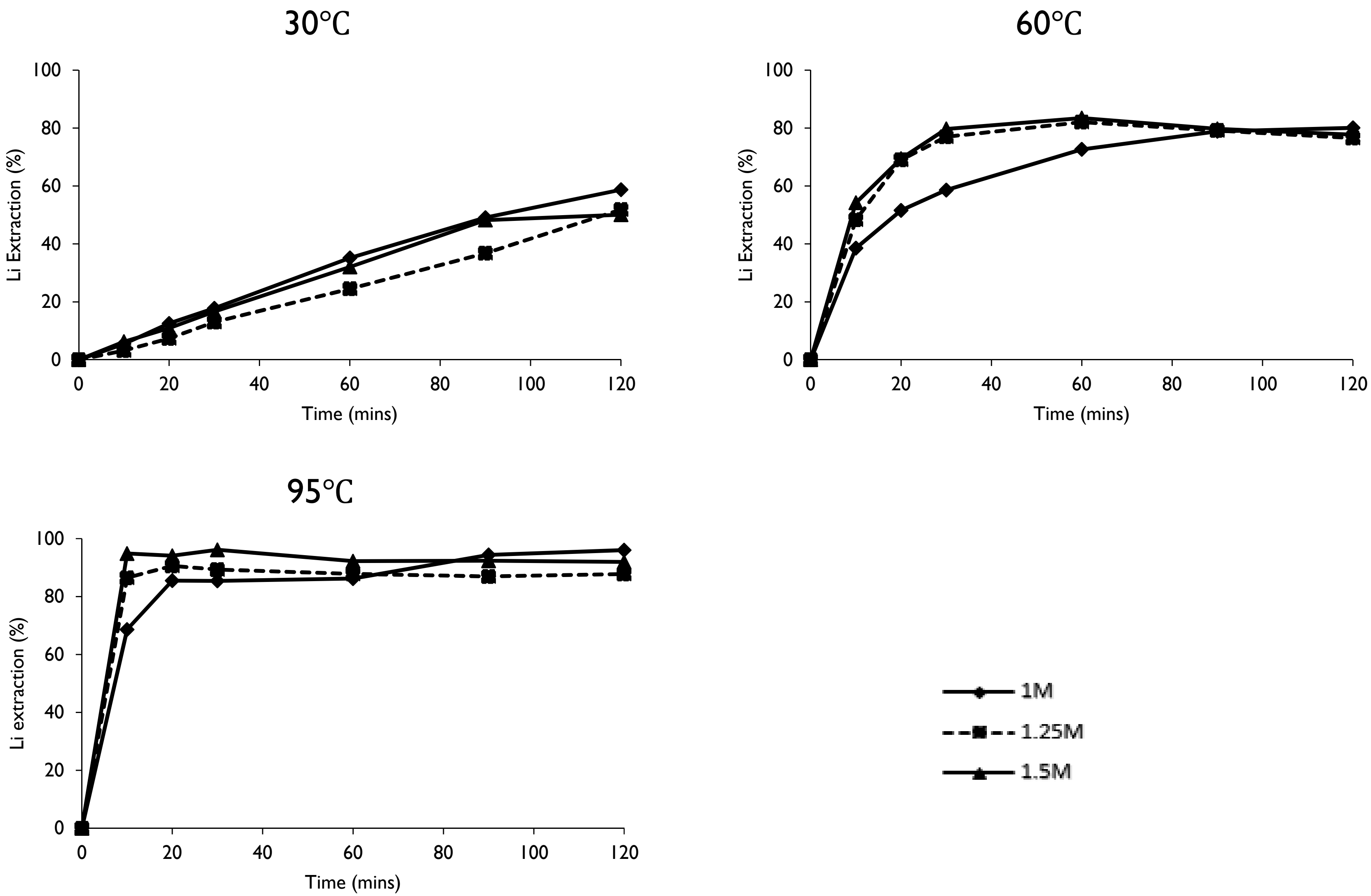
Results: Citric acid leaching - Co



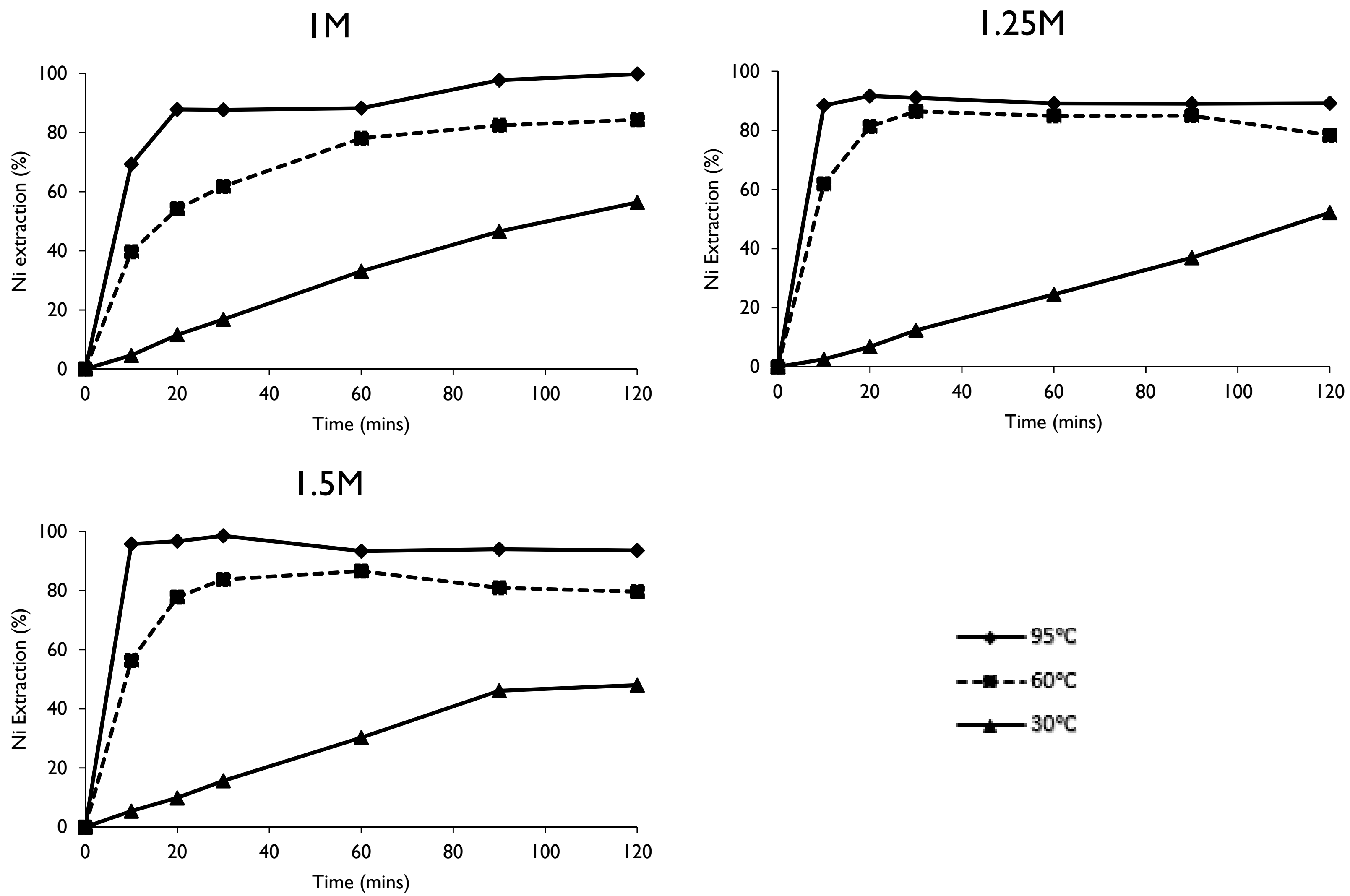
Results: Citric acid leaching - Li



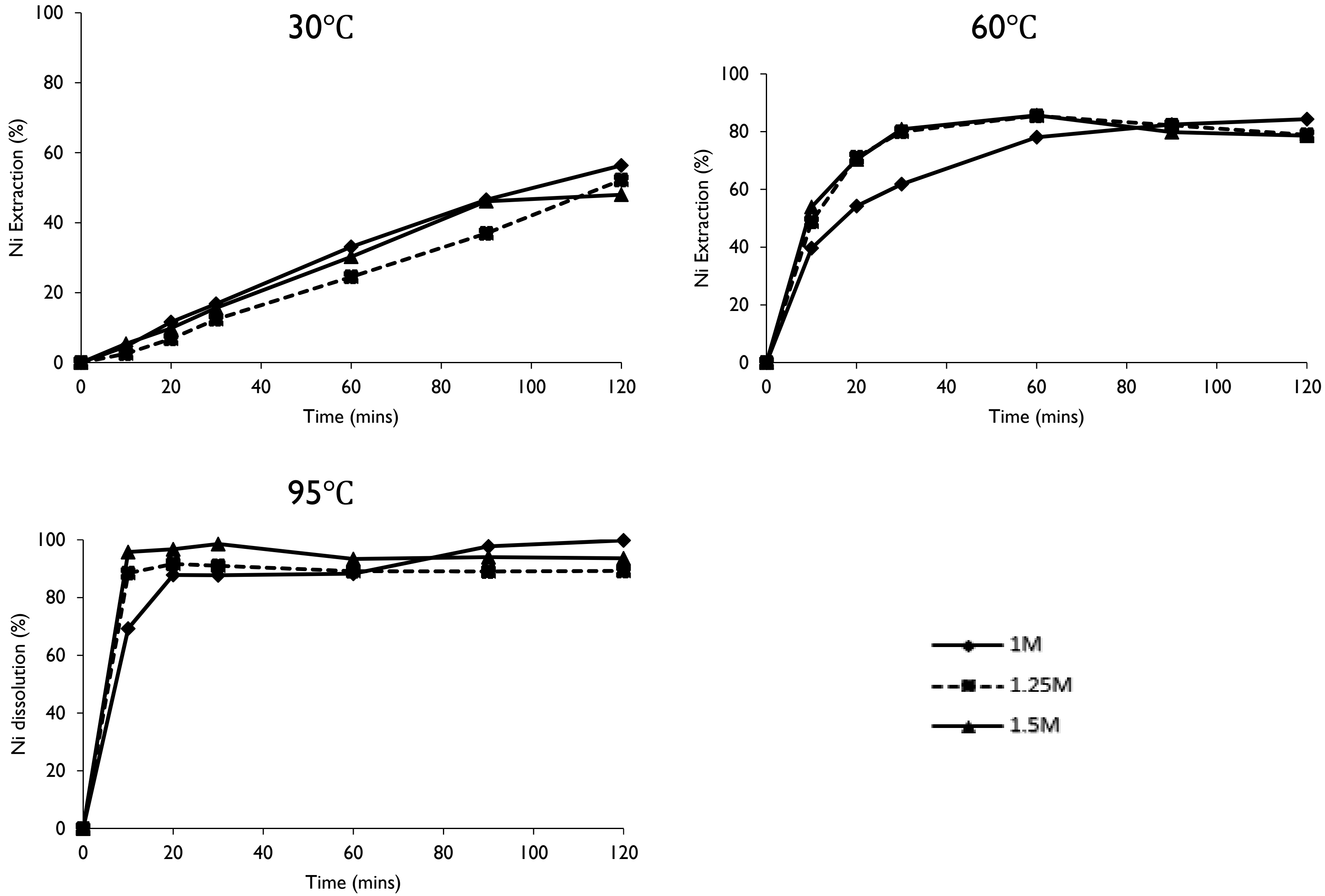
Results: Citric acid leaching - Li



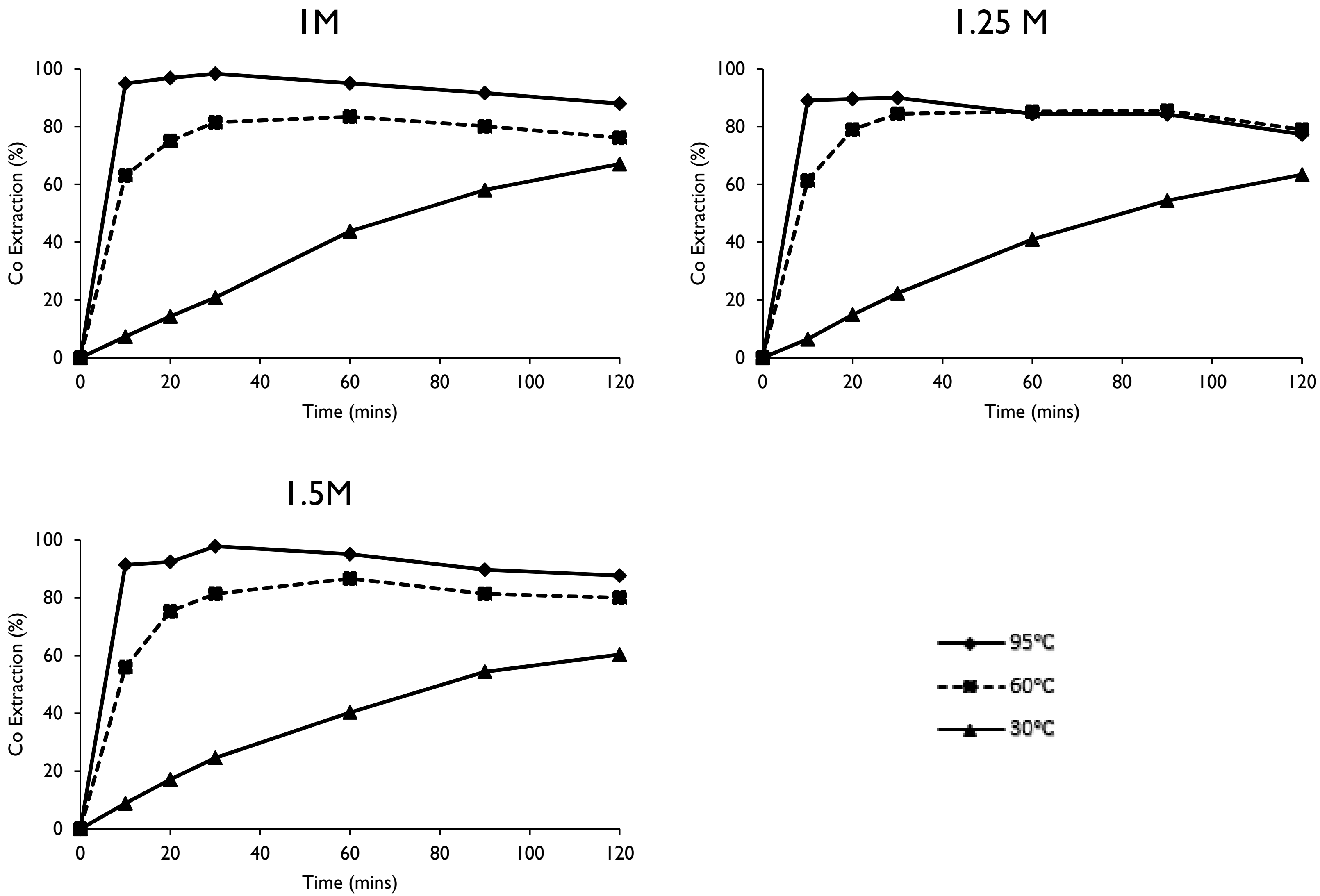
Results: Citric acid leaching - Ni



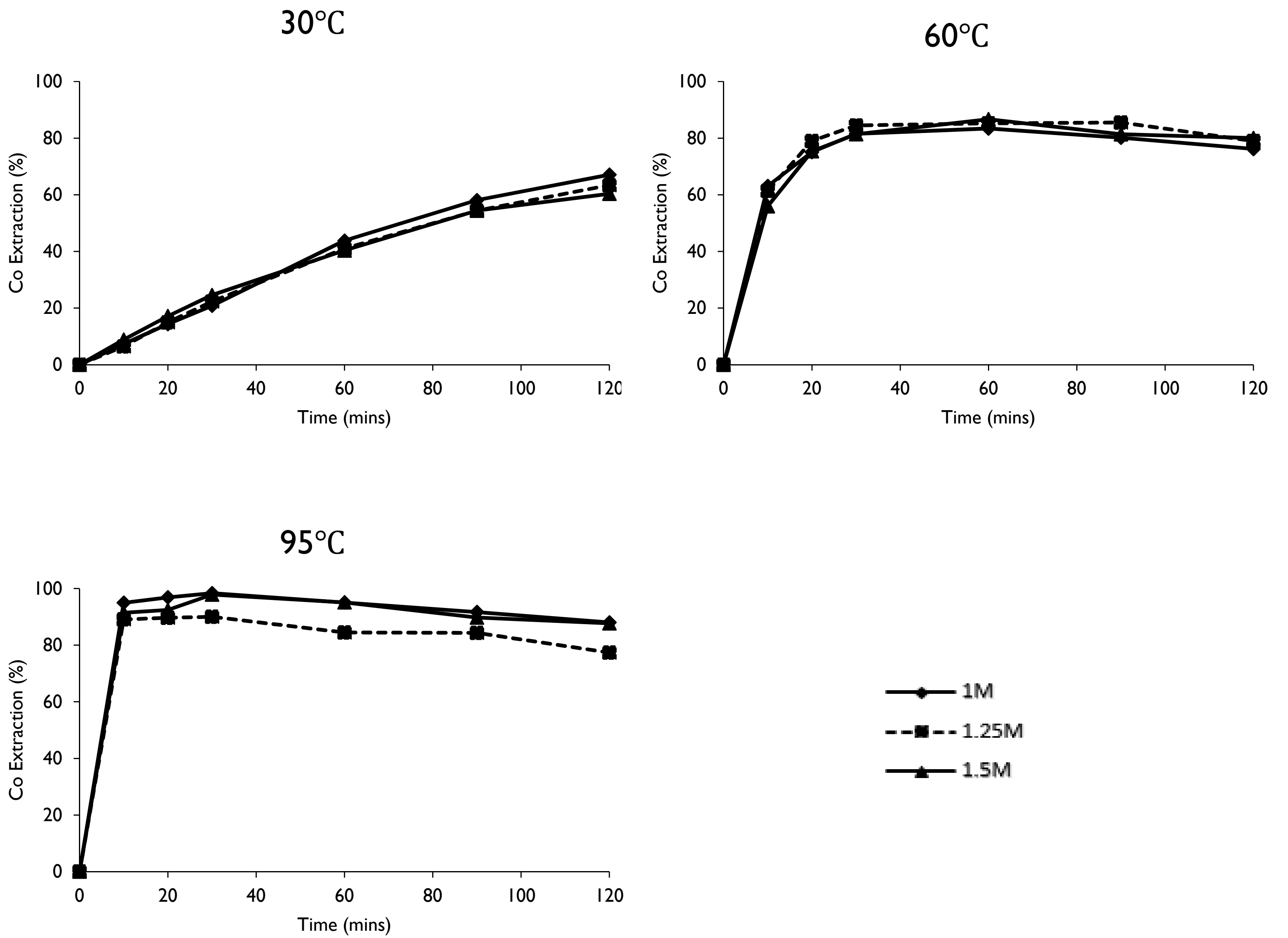
Results: Citric acid leaching - Ni



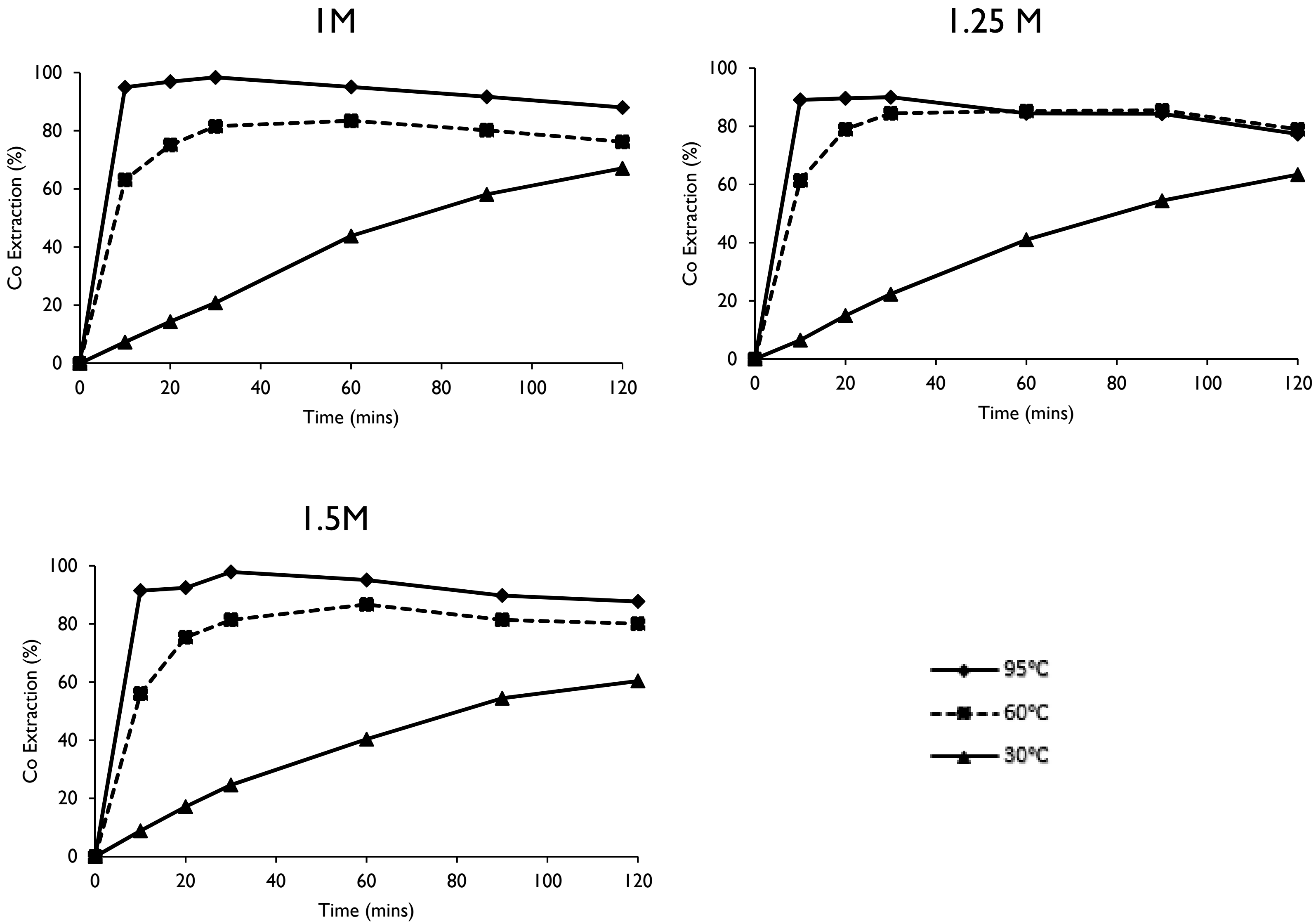
Results: DL-malic acid leaching - Co



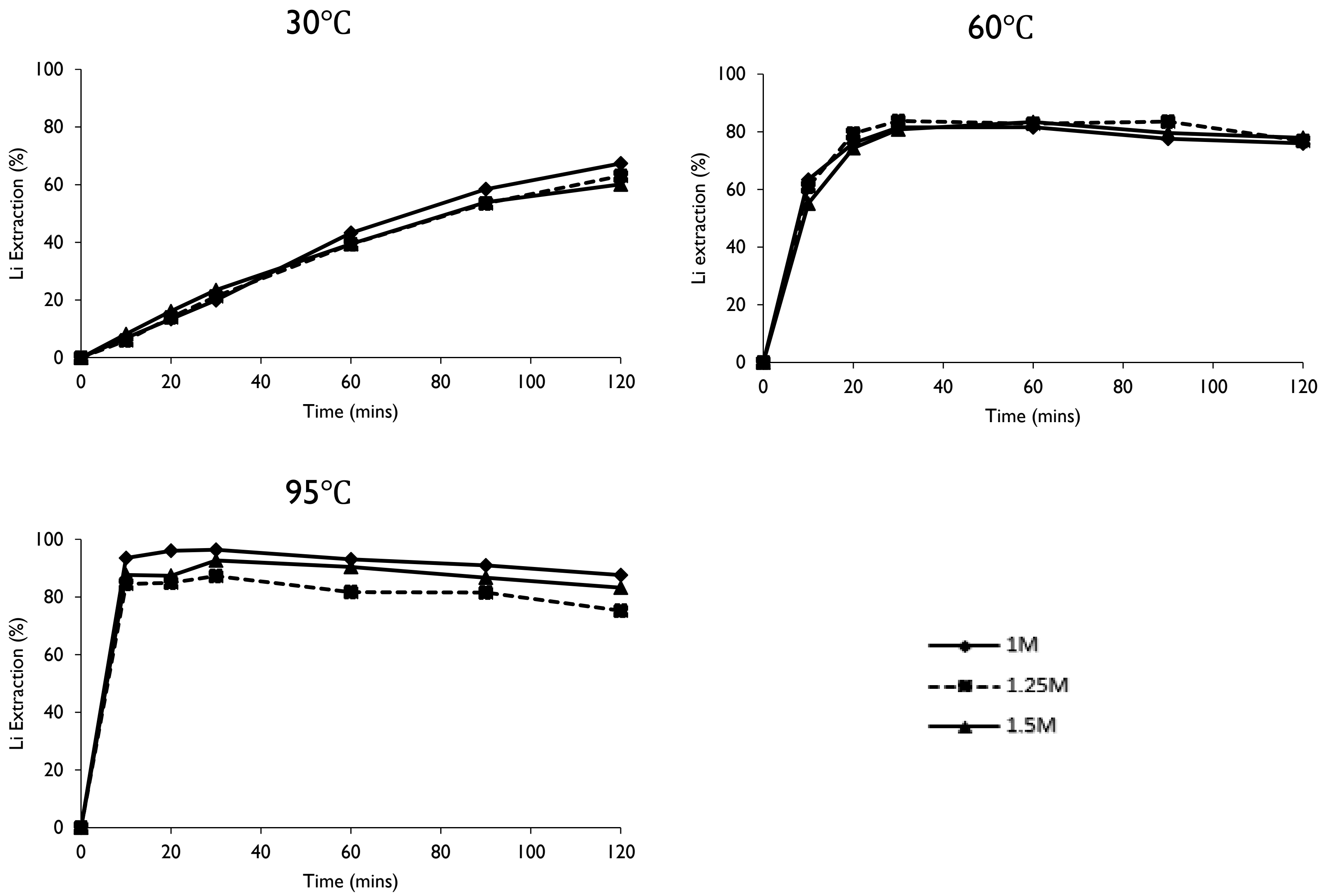
Results: DL-malic acid leaching - Co



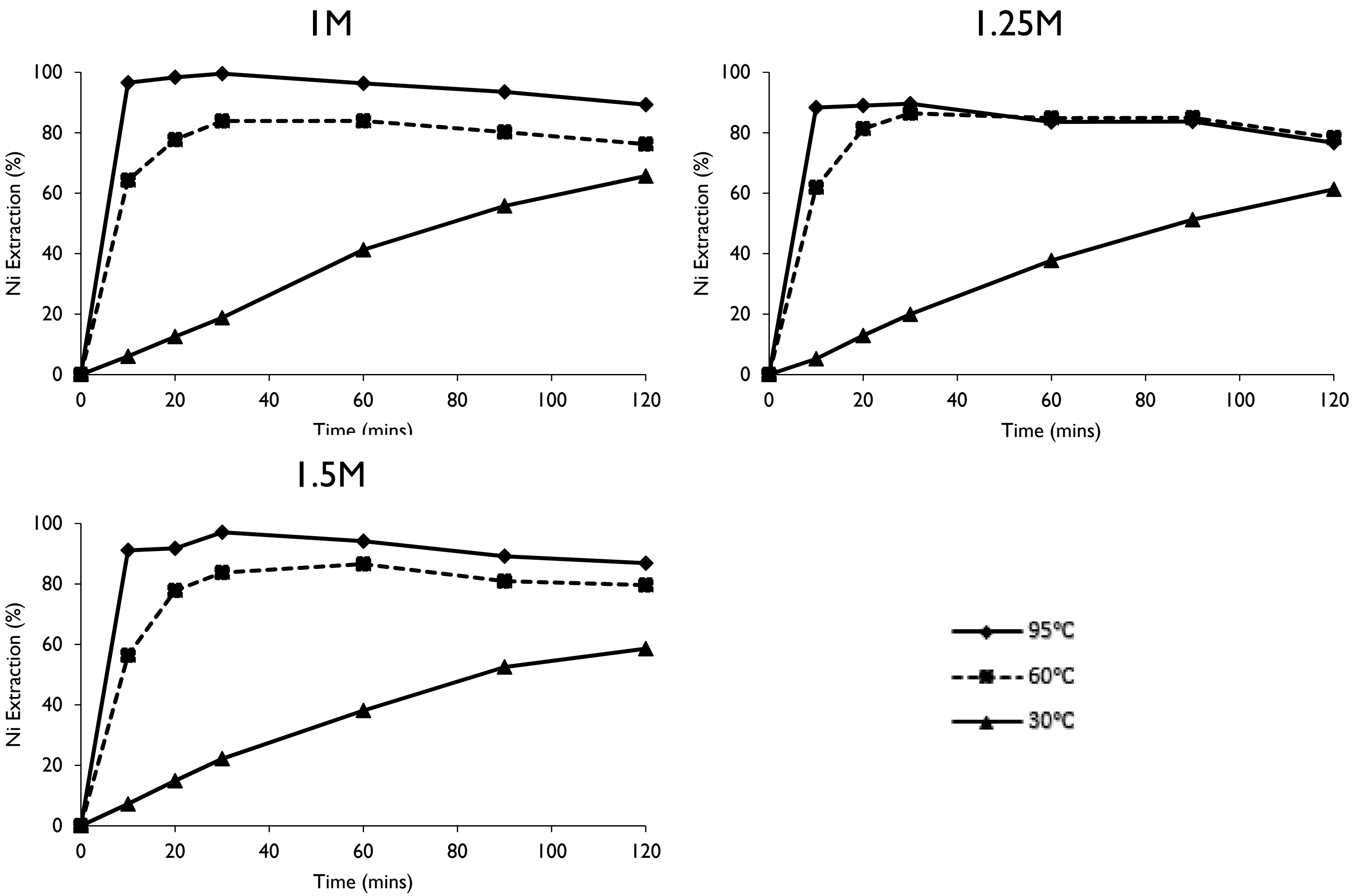
Results: DL-malic acid leaching - Li



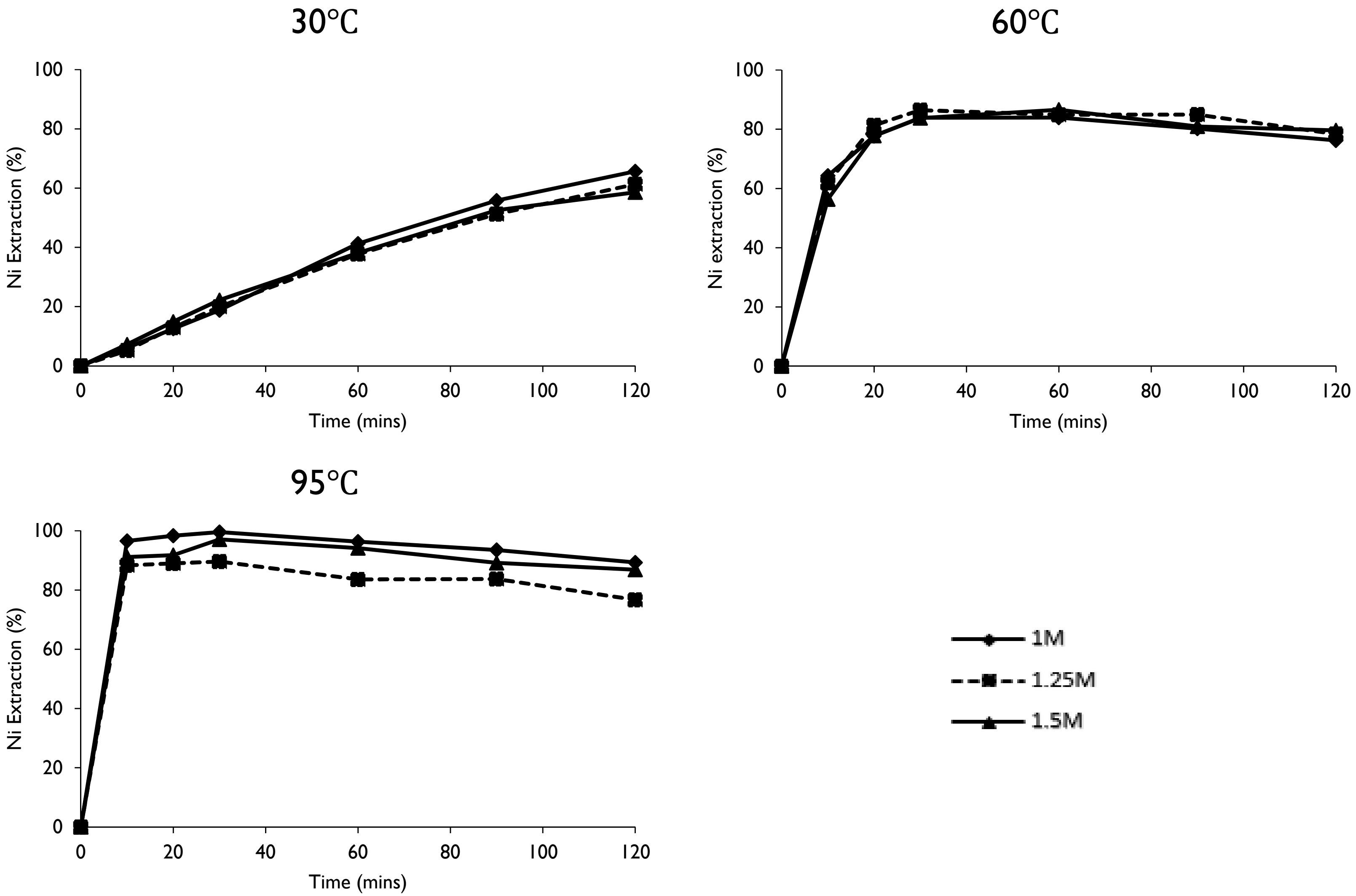
Results: DL-malic acid leaching - Li



Results: DL-malic acid leaching - Ni



Results: DL-malic acid leaching - Ni



Conclusions

- It is possible to recover 95% Co, 96% Li and 99% Ni within 30 minutes using 1.5M citric acid, in the presence of 2% v/v H_2O_2, at 95℃ and 20 g/L pulp density.
- 99% Co, 96% Li and 99% Ni can be extracted within 30 minutes using 1M DL-malic acid, with 2% v/v H_2O_2, at 95℃ and 20 g/L pulp density.
- Organic acids are good leaching reagents for metal recovery from LIB cathodic material.
- The performances of citric and DL-malic acid with regard to Li and Ni are similar, however, there appears to be more Co dissolution with DL-malic acid (99%).

Acknowledgements

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