Development of Green Integrated Technology for Critical Material Recovery from End-of-Life Lithium-Ion Batteries

Shally Gupta

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Shally Gupta

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This thesis is dedicated to

my beloved GRANDPARENTS

(My Grandmother – Maya Goyal & My Grandfather – Darshan Lal Goyal)

You are no longer here but your dreams remain the foundation of this achievement.

"Though unseen, your love remains; though unheard, your blessings endure"

Supervisor Certification

This is to certify that the thesis entitled "**Development of Green Integrated Technology for Critical Material Recovery from End-of-Life Lithium-Ion Batteries**" submitted by **Ms. Shally Gupta** to the Indian Institute of Technology Delhi and The University of Queensland for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her. **Ms. Shally Gupta** has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which, to our knowledge, has reached the requisite standard. The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

Prof. Kamal Kishore Pant
Department of Chemical Engineering
Indian Institute of Technology Delhi
Hauz Khas New Delhi, India - 110016

Prof. Glen Corder
Sustainable Minerals Institute
The University of Queensland
St. Lucia, Brisbane, Australia - 4076

Prof. Anil Verma
(Co-supervisor)
Department of Chemical Engineering
Indian Institute of Technology Delhi
Hauz Khas New Delhi, India - 110016

Abstract

The global transition towards a carbon-neutral society has intensified the consumption of lithium-ion batteries (LIBs) in energy storage and mobility systems. The exponential surge in LIB utilization and rapid accumulation of end-of-life (EoL) LIBs is raising concerns about resource scarcity and waste management. EoL LIBs are increasingly recognized as a key secondary source of strategically critical metals such as Li, Co, Ni, Mn, Cu, and Al; their recycling for the recovery of these metals is termed “urban mining”. Recycling offers considerable potential for resource recovery and integration into the circular economy. Conventionally, hydrometallurgy processes dominate commercial recycling practices. However, the use of corrosive lixiviants, inadequate selectivity and recyclability of reagents, poorly optimized metal separation steps, and low recovery efficiency for Li are critical limitations associated with these recovery routes. Therefore, the development of a sustainable and energy-efficient recycling process for EoL LIBs waste management has become essential in the transition toward a circular energy economy.

To address these challenges, this research focused on the implementation of chelating agents and deep eutectic solvents (DESs) as next-generation green lixiviants. Efforts have been made to develop an environmentally benign closed loop for the recovery of critical materials from EoL LIBs. For this purpose, different types of spent batteries collected from a waste recycling plant were thoroughly characterized to understand the chemistry of the electrode materials and then used as raw materials for the process.

In the first study, an aminopolycarboxylic chelator, ethylenediaminetetraacetic acid (EDTA), was used as a lixiviant for the extraction of the metals Li, Co, and Cu from industrial black mass EoL LIBs. Through systematic optimization of reaction parameters, including EDTA concentration, temperature, pulp density, pH, and reaction time, maximum recoveries of ~94% Co, 96% Li, and 97% Cu were achieved under the optimal conditions of 0.8 M EDTA, 90 °C,

pH = 10, and 4 h. Kinetic modeling using the shrinking core model demonstrated interfacial chemical reaction control, with evaluated activation energies of 51.9, 41.0, and 42.3 kJ mol^{-1} for Co, Li, and Cu, respectively. Notably, EDTA was successfully recovered and reused, and a selective downstream precipitation sequence enabled complete metal separation, confirming the feasibility of a closed-loop EDTA-based recycling process.

Further, a green DES of ethylene glycol and tartaric acid was synthesized and tested for the extraction of Li, Ni, Co, and Mn from the cathode active material of EoL LIBs. Response surface methodology was employed to identify the optimal process parameters (118 °C, 17 min, 42 g/L, MR 3:1), yielding high extraction efficiencies of ~99% Li, 96% Ni, 95% Co, and 98% Mn. The mechanistic analysis highlighted the synergistic functions of DES constituents. A highly selective downstream separation protocol ensured an overall metal recovery of ~99%, wherein one-step, selective separation of Li and transition metals was achieved by using water as an anti-solvent. Both DES and recovered products were efficiently reused, validating the potential for industrial-scale implementation.

After metal recovery, the spent anode was recycled via an integrated process of DES leaching and thermal treatment. A novel methanesulfonic acid-based DES was used for regenerating spent graphite from EoL LIB anodes. The optimized system enabled ~99% extraction of residual Li and Cu and removed organic contaminants through hydrogen-bond-driven dissolution. Combined DES and thermal treatment facilitated in situ sulfur doping and restoration of the layered graphite structure. The regenerated graphite achieved a high specific capacity of 343.1 mAh g^{-1} at 0.2 C and retained 90.3% of its capacity even after 500 cycles, demonstrating significantly enhanced electrochemical performance.

Overall, these solvents exhibit strong metal-complexation behaviour, low toxicity, and excellent recyclability, operating under mild conditions without producing hazardous by-products. The DES-based processes developed in this work offer a comprehensive, green, and

scalable closed-loop recycling solution for recovering high-value metals and regenerating high-performance graphite from EoL LIBs. The incorporation of DES as a lixiviant into hydrometallurgical processes not only minimizes secondary waste but also significantly enhances the environmental sustainability of recycling operations, as endorsed by life cycle and environmental impact analyses.

Abstract in Hindi

कार्बन-न्यूट्रल समाज की ओर वैश्विक बदलाव ने ऊर्जा संचयन और गतिशीलता प्रणाली में लिथियम-आयन बैटरी (LIBs) की खपत को बढ़ा दिया है। LIB के इस्तेमाल में तेज़ी से बढ़ोतरी और अपशिष्ट (EoL) LIBs के तेज़ी से जमा होने से संसाधनों की कमी और कचरा प्रबंधन के बारे में चिंताएँ बढ़ रही हैं। EoL LIBs को Li, Co, Ni, Mn, Cu, और Al जैसी रणनीतिक रूप से महत्वपूर्ण धातुओं के एक प्रमुख माध्यमिक स्रोत के रूप में पहचाना जा रहा है; इन धातुओं की रिकवरी के लिए उनकी पुनर्चक्रण को "अर्बन माइनिंग" कहा जाता है। पुनर्चक्रण, संसाधन रिकवरी और सर्कुलर अर्थव्यवस्था में एकीकरण के लिए काफी संभावनाएँ प्रदान करती है। पारंपरिक रूप से, हाइड्रोमेटलर्जी प्रक्रियाएँ व्यावसायिक पुनर्चक्रण तरीकों पर हावी हैं। हालाँकि, संक्षारक लीचिंग एजेंटों का उपयोग, अभिकर्मकों की अपर्याप्त चयनात्मकता और पुनर्चक्रण क्षमता, जटिल तरीके से अनुकूलित धातु पृथक्करण चरण, और Li के लिए कम रिकवरी दक्षता, इन रिकवरी मार्गों से जुड़ी महत्वपूर्ण सीमाएँ हैं। इसलिए, सर्कुलर ऊर्जा अर्थव्यवस्था की ओर बदलाव में EoL LIBs कचरा प्रबंधन के लिए एक स्थायी और ऊर्जा-कुशल पुनर्चक्रण प्रक्रिया का विकास आवश्यक हो गया है।

इन चुनौतियों से निपटने के लिए, इस शोध में अगली पीढ़ी के हरित लीचिंग एजेंटों के रूप में चेलेटिंग एजेंटों और डीप यूटेक्टिक सॉल्वैंट्स (DESs) के कार्यान्वयन पर ध्यान केंद्रित किया गया। EoL LIBs से महत्वपूर्ण सामग्रियों की रिकवरी के लिए पर्यावरण के अनुकूल बंद लूप प्रक्रिया विकसित करने के प्रयास किए गए हैं। इस उद्देश्य के लिए, एक कचरा रीसाइक्लिंग प्लांट से एकत्र की गई विभिन्न प्रकार की खराब बैटरियों की इलेक्ट्रोड सामग्री की केमिस्ट्री को समझने के लिए अच्छी तरह से विश्लेषण किया गया और फिर उन्हें प्रक्रिया के लिए कच्चे माल के रूप में इस्तेमाल किया गया।

पहले अध्ययन में, एक एमिनोपॉलीकार्बोक्सिलिक चेलेटर, एथिलीनडायमिनेटेट्राएसिटिक एसिड (EDTA), का उपयोग औद्योगिक ब्लैक मास EoL LIBs से Li, Co, और Cu धातुओं के निष्कर्षण के लिए एक लीचिंग एजेंट के रूप में किया गया था। EDTA सांद्रता, तापमान, पल्प घनत्व, pH, और प्रतिक्रिया समय सहित प्रतिक्रिया मापदंडों के व्यवस्थित अनुकूलन के माध्यम से, 0.8 M EDTA, 90 °C, pH = 10, और 4 घंटे की इष्टतम स्थितियों के तहत ~94% Co, 96% Li, और 97% Cu की अधिकतम रिकवरी प्राप्त की गई। Shrinking कोर मॉडल का उपयोग करके काइनेटिक मॉडलिंग ने इंटरफेशियल रासायनिक प्रतिक्रिया नियंत्रण का प्रदर्शन किया, जिसमें Co, Li, और Cu के लिए क्रमशः 51.9, 41.0, और 42.3 kJ

mol-1 की सक्रियण ऊर्जा का मूल्यांकन किया गया। खास बात यह है कि EDTA को सफलतापूर्वक रिकवर और दोबारा इस्तेमाल किया गया, और एक चयनात्मक डाउनस्ट्रीम प्रेसिपिटेशन अनुक्रम ने मेटल को पूरी तरह से अलग करने में मदद की, जिससे क्लोज्ड-लूप EDTA-आधारित पुनर्चक्रण प्रक्रिया की व्यवहार्यता की पुष्टि हुई।

इसके अलावा, एथिलीन ग्लाइकोल और टार्टरिक एसिड का एक ग्रीन DES सिंथेसाइज किया गया और EoL LIBs के कैथोड एक्टिव मटीरियल से Li, Ni, Co, और Mn निकालने के लिए इसका परीक्षण किया गया। सबसे अच्छे प्रोसेस पैरामीटर (118 °C, 17 मिनट, 42 g/L, MR 3:1) की पहचान करने के लिए रिस्पॉन्स सरफेस मेथोडोलॉजी का इस्तेमाल किया गया, जिससे ~99% Li, 96% Ni, 95% Co, और 98% Mn की उच्च निष्कर्षण दक्षता मिली। मैकेनिस्टिक एनालिसिस ने DES घटकों के तालमेल वाले कार्यों पर प्रकाश डाला। एक अत्यधिक सेलेक्टिव डाउनस्ट्रीम सेपरेशन प्रोटोकॉल ने ~99% की कुल मेटल रिकवरी सुनिश्चित की, जिसमें पानी को एंटी-सॉल्वेंट के रूप में इस्तेमाल करके Li और ट्रांजिशन मेटल्स का एक-चरणीय, चयनात्मक पृथक्करण हासिल किया गया। DES और रिकवर किए गए दोनों उत्पादों का कुशलतापूर्वक दोबारा इस्तेमाल किया गया, जिससे औद्योगिक पैमाने पर लागू करने की क्षमता साबित हुई।

मेटल रिकवरी के बाद, इस्तेमाल किए गए एनोड को DES लीचिंग और थर्मल ट्रीटमेंट की एक एकीकरण प्रक्रिया के माध्यम से पुनर्चक्रण किया गया। EoL LIB एनोड से इस्तेमाल किए गए ग्रेफाइट को रीजेनरेट करने के लिए एक नया मेथेनसल्फोनिक एसिड-आधारित DES प्रयोग किया गया । ऑप्टिमाइज्ड सिस्टम ने अवशिष्ट Li और Cu का ~99% एक्सट्रैक्शन सक्षम किया और हाइड्रोजन-बॉन्ड-संचालित विघटन के माध्यम से ऑर्गेनिक दूषित पदार्थों को हटा दिया। संयुक्त DES और थर्मल ट्रीटमेंट ने in-situ सल्फर डोपिंग और लेयर्ड ग्रेफाइट संरचना की बहाली में सुविधा प्रदान की। रीजेनरेटेड ग्रेफाइट ने 0.2 C पर 343.1 mAh g-1 की उच्च विशिष्ट क्षमता हासिल की और 500 चक्रों के बाद भी अपनी 90.3% क्षमता बनाए रखी, जो काफी बेहतर इलेक्ट्रोकेमिकल प्रदर्शन को दर्शाता है।

कुल मिलाकर, ये सॉल्वैंट्स मजबूत मेटल-कॉम्प्लेक्सेशन व्यवहार, कम विषाक्तता और उत्कृष्ट पुनर्चक्रण क्षमता प्रदर्शित करते हैं, जो खतरनाक उप-उत्पादों का उत्पादन किए बिना हल्की परिस्थितियों में काम करते हैं। इस काम में विकसित DES-आधारित प्रक्रियाएं उच्च-मूल्य वाली धातुओं को रिकवर करने और EoL LIBs से उच्च-प्रदर्शन वाले ग्रेफाइट को रीजेनरेट करने के लिए एक व्यापक, हरित और स्केलेबल क्लोज्ड-लूप रीसाइक्लिंग समाधान प्रदान करती हैं। हाइड्रोमेटलर्जिकल प्रक्रियाओं में लिक्सिविएंट के

रूप में DES को शामिल करने से न केवल माध्यमिक कचरा कम होता है, बल्कि पुनर्चक्रण संचालन की पर्यावरणीय स्थिरता में भी काफी वृद्धि होती है, जैसा कि जीवन चक्र और पर्यावरणीय प्रभाव विश्लेषण द्वारा समर्थित है।

Declaration by Author

This thesis is composed of my original work and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly authored works that I have included in my thesis.

I have clearly stated the contribution of others to my thesis as a whole, including statistical assistance, survey design, data analysis, significant technical procedures, professional editorial advice, financial support and any other original research work used or reported in my thesis. The content of my thesis is the result of work I have carried out since the commencement of my higher degree by research candidature and does not include a substantial part of work that has been submitted to qualify for the award of any other degree or diploma in any university or other tertiary institution. I have clearly stated which parts of my thesis, if any, have been submitted to qualify for another award.

I acknowledge that an electronic copy of my thesis must be lodged with the University Library and, subject to the policy and procedures of The University of Queensland, the thesis be made available for research and study in accordance with the Copyright Act 1968 unless a period of embargo has been approved by the Dean of the Graduate School.

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Shally Gupta
Joint Ph.D. student UQ-IITD
IITD Entry Number: 2020QIZ8591
UQ student Number: 46572242
June 2026

Publications included in this thesis

1. **S. Gupta**, A. Tandon, K. K. Pant, G. Corder, Y. Sharma, Unveiling green solvent and thermal treatment-based integrated process for in situ S-doping and regeneration of anode graphite from end-of-life lithium-ion batteries, *Chemical Engineering Journal* 518 (2025) 164728, https://doi.org/10.1016/j.cej.2025.164728.
2. **S. Gupta**, K. K. Pant, G. Corder, A tandem approach for precipitant-free highly selective recovery of valuable metals from end-of-life lithium-ion batteries using a green deep eutectic solvent, *Journal of Cleaner Production* 461 (2024) 142624, https://doi.org/10.1016/j.jclepro.2024.142624.
3. **S. Gupta**, K. K. Pant, G. Corder, An environmentally benign closed-loop process for the selective recovery of valuable metals from industrial end-of-life lithium-ion batteries, *Chemical Engineering Journal* 446 (2022) 137397. https://doi.org/10.1016/j.cej.2022.137397.

Book Chapter

- P. R. Jadhao, **S. Gupta**, K. K. Pant, K. D. P. Nigam, Metal recovery from lithium-ion batteries using bioleaching: A greener approach in Biodegradation of Toxic and Hazardous Chemicals, *CRC Press* (2023) Taylor & Francis, https://doi.org/10.1201/9781003391487-10.

Patent

- **S. Gupta**, **K. K.** Pant, Process for recovery of lithium and transition metals from lithium-ion batteries (2024) (Indian Provisional Patent Application No.: 202311062897).

Contributions by others to the thesis

All chapters

Editorial suggestions were provided by all the supervisors, including Prof. K. K. Pant, Prof. Glen Corder, Prof. Anil Verma, and the Ph.D. committee, comprising Prof. Manoj Kumarr Ramteke, Prof. B. J. Alappat, and Dr. Artem Golev.

Chapter 4

The industrial black mass was provided by the e-waste recycling plant, Exigo, Panipat.

Chapter 6

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Statement of parts of the thesis submitted to qualify for the award of another degree

No work submitted towards another degree has been included in this thesis.

Research involving human or animal subjects

No animal or human subjects were involved in this research.

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"In research, progress is rarely loud - it grows quietly, in the spaces between failure and perseverance." - Unknown

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