INTEGRATED GREEN TECHNOLOGIES FOR METAL RECOVERY FROM ELECTRONIC WASTE: FOCUS ON DEEP EUTECTIC SOLVENTS (DES) LEACHING

SNIGDHA MISHRA

DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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Integrated Green Technologies for Metal Recovery from Electronic Waste: Focus on Deep Eutectic Solvents (DES) Leaching

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SNIGDHA MISHRA

DEPARTMENT OF CHEMICAL ENGINEERING

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Certificate

This is to certify that the thesis entitled "**Integrated Green Technologies for Metal Recovery from Electronic Waste: Focus on Deep Eutectic Solvents (DES) Leaching**" submitted by **Ms. Snigdha Mishra** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy**, is a record of the original bonafide research work carried out by her. She has worked under my supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of this thesis. The results contained in this thesis have not been submitted in part or full to any University or Institute for the award of any degree or diploma.

Prof. K. K. Pant

Supervisor

Department of Chemical Engineering

Indian Institute of Technology Delhi

Prof. Vikram Singh

Co-supervisor

Department of Chemical Engineering

Indian Institute of Technology Delhi

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ABSTRACT

Electronic waste (e-waste) is a trivialized resource that can be explored for the plethora of economic opportunities they offer. E-waste is a rich source of precious metals (platinum, gold, silver), base metals (aluminum, iron, copper), heavy (zinc, mercury, chromium, lead), and rare earth metals (tantalum, platinum groups). The use of e-waste as a rich secondary source of metals can significantly bridge the huge gap between demand and supply for several scarce metals, e.g., tin, silver, gold, platinum, lithium, etc. Nevertheless, the recycling rate of e-waste is quite low and mostly concentrated in unregulated informal sectors, usually open dumping or burning. Additionally, e-waste consists of toxic additives or hazardous substances like mercury, brominated flame retardants (BFR), etc., which if left untreated pose serious damage to the ecosystem. Thus, e-waste recycling provides an opportunity for resource recovery and minimization of its impact on the environment if left untreated.

In the present study, attempts have been made for the development of integrated green and sustainable technology for metal recovery and the generation of valuable products from e-waste. Different types of Waste printed circuit boards (WPCB) of mobile phones were collected from the local market and were used as a source of e-waste. Initially, the metallic fraction from WPCB was recovered using subcritical to supercritical methanol treatment. The obtained products were compared with pyrolysis products. Experiments were conducted in the temperature range of 150 °C to 300 °C at an autogenous pressure. At optimized conditions 300 °C temperature, 1:20 (g/ml) of solid: liquid ratio, 3 h liquid products had no bromine content as compared to pyrolysis product. The metallic fraction was enriched and had a similar metallic composition as that of pyrolyzed solid products.

Further, a range of green choline chloride deep eutectic solvents with variation of HBDs to alcohols, urea, carboxylic acids were synthesized and tested for metal extraction application. Initially, detailed investigation of DESs structures and their physiochemical properties were conducted via various analytical techniques and theoretical calculations. Metal oxides dissolution in range of DESs were tested and selective metal leaching solvents were shortlisted for further process optimization. Carboxylic acid-choline chloride DESs, particularly FA-ChCl (Formic Acid-Choline chloride) were observed to have greater than ~90 % extraction of copper, tin, iron, nickel while urea-choline chloride had selective and above ~90 % zinc extraction from WPCBs. Neat organic acids were further tested for process optimization. It was observed that

oxalic acid had selective extraction (>92 %) of tin from e-waste under optimum condition. The major disadvantage observed in using DES system was its slow kinetics. Henceforth, Sulfonic acids which had lower pH than carboxylic acid were mixed with choline chloride for DES preparation and metal extraction: Methyl sulfonic acid-Choline chloride (MSA-ChCl) and p-toluenesulfonic acid-Choline chloride DESs. The best performing MSA-ChCl DES was selected for metal extraction from PCB. Various process parameters like S/L ratio, stirring speed, time, temperature was optimized for metal leaching. Ultimately at the end cementation metal was added in both DES for individual recovery of metal.

Based on the experimental results it can be concluded that supercritical methanol is an efficient approach for generating valuable products from e-waste plastic. For metal recovery, green deep eutectic solvents were potential leaching agents to extract metals and cementation can be effectively used to harness selective metal recovery. To conclude, it is recommended that greener alternatives to conventional technology have potential to replace some conventional harmful agents in metal leaching process.

संक्षिप्त विवरण

इलेक्ट्रॉनिक कचरा (ई-कचरा) एक ऐसा उपेक्षित संसाधन है जिसमे ढेर सारे आर्थिक अवसर छुपे हुए हैं। ई-कचरा बहुमूल्य धातुओं (प्लैटिनम, सोना, चांदी), आधार धातुओं (एल्यूमीनियम, लोहा, तांबा), भारी धातुओं (जस्ता, पारा, क्रोमियम, सीसा) और दुर्लभ पृथ्वी धातुओं (टैंटलम, प्लैटिनम समूह) का एक समृद्ध स्रोत है। धातुओं के एक समृद्ध द्वितीयक स्रोत के रूप में ई-कचरे का उपयोग टिन, चांदी, सोना, प्लैटिनम, लिथियम आदि जैसे कई दुर्लभ धातुओं की मांग और आपूर्ति के बीच के बड़े अंतर को पाट सकता है।

हालांकि, ई-कचरे की पुनर्चक्रण दर काफी कम है और ज्यादातर अनियमित अनौपचारिक क्षेत्रों, जैसे खुले में फेंकने या जलाने पर केंद्रित है। इसके अतिरिक्त, ई-कचरे में जहरीले योजक या खतरनाक पदार्थ जैसे पारा, ब्रोमिनेटेड फ्लेम रिटार्डेंट (बीएफआर) आदि होते हैं, जिन्हें यदि अनुपचारित छोड़ दिया जाए तो पारिस्थितिकी तंत्र को गंभीर नुकसान पहुंचाते हैं। इस प्रकार, ई-कचरा पुनर्चक्रण संसाधन पुनर्प्राप्ति और पर्यावरण पर इसके प्रभाव को कम करने का अवसर प्रदान करता है, बशर्ते इसे अनुपचारित न छोड़ा जाए।

इस अध्ययन में, धातु पुनर्प्राप्ति और ई-कचरे से मूल्यवान उत्पादों के निर्माण के लिए एकीकृत हरित और टिकाऊ प्रौद्योगिकी के विकास का प्रयास किया गया है। मोबाइल फोन के विभिन्न प्रकार के **खराब मुद्रित सर्किट बोर्ड** (डब्ल्यूपीसीबी) स्थानीय बाजार से एकत्र किए गए और ई-कचरे के स्रोत के रूप में उपयोग किए गए। प्रारंभ में, सबक्रिटिकलसे लेकर सुपरक्रिटिकल मेथनॉल उपचार का उपयोग करके डब्ल्यूपीसीबी से धातु अंश प्राप्त किया गया था। प्राप्त उत्पादों की तुलना पायरोलिसिस उत्पादों से की गई। परीक्षण 150 °C से 300 °C के तापमान सीमा में स्वायत्त दाब पर किए गए। अनुकूलित परिस्थितियों में 300 °C तापमान, 1:20 (ग्राम/मिलीलीटर) ठोस: तरल अनुपात पर, 3 घंटे के तरल उत्पादों में पायरोलिसिस उत्पाद की तुलना में ब्रोमिन की मात्रा नहीं थी। धातु अंश समृद्ध था और पायरोलाइज्ड ठोस उत्पादों के समान धातु संरचना थी। इसके अलावा, विभिन्न विविध हाइड्रोजन बांड दाता (एचबीडी) के साथ कोलीन क्लोराइड आधारित गहरे यूनेक्टिक विलायकों (डीईएस) का संश्लेषण किया गया जिनमें अल्कोहल, यूरिया, कार्बोक्जिलिक एसिड शामिल हैं और धातु निष्कर्षण अनुप्रयोग के लिए परीक्षण किया गया। प्रारंभ में, विभिन्न विश्लेषणात्मक तकनीकों और सैद्धांतिक गणनाओं के माध्यम से डीईएस संरचनाओं और उनके भौतिक-रासायनिक गुणों की विस्तृत जांच की गई। डीईएस की श्रेणी में धातु ऑक्साइडों के विघटन का परीक्षण किया गया और आगे की प्रक्रिया के अनुकूलन के लिए चुनिंदा धातु निक्षालन विलायकों को चुना गया। कार्बोक्जिलिक एसिड-कोलीन क्लोराइड डीईएस, विशेष रूप से एफए-सीएचसीएल (फॉर्मिक एसिड-कोलीन क्लोराइड) तांबा, टिन, लोहा, निकल के 90% से अधिक निष्कर्षण के लिए प्रभावी पाए गए, जबकि यूरिया-कोलीन क्लोराइड

का उपयोग जस्ता के चुनिंदा और 90% से अधिक निष्कर्षण के लिए किया गया। प्रक्रिया अनुकूलन के लिए शुद्ध कार्बनिक अम्लों का परीक्षण किया गया। यह पाया गया कि ऑक्सालिक एसिड इष्टतम परिस्थितियों में ई-कचरे से टिन का चुनिंदा निष्कर्षण (>92%) करता है। डीईएस प्रणाली का उपयोग करने में पाया गया मुख्य नुकसान इसकी धीमी गतिशीलता थी। इसलिए, कार्बोक्सिलिक एसिड से कम pH वाले सल्फोनिक एसिड को डीईएस बनाने और धातु निष्कर्षण के लिए कोलीन क्लोराइड के साथ मिलाया गया: मेथिल सल्फोनिक एसिड-कोलीन क्लोराइड (एमएसए-सीएचसीएल) और पैरा-टोल्यूएनेसल्फोनिक एसिड-कोलीन क्लोराइड आधारित डीईएस। पीसीबी से धातु निष्कर्षण के लिए सबसे अच्छा प्रदर्शन करने वाले एमएसए-सीएचसीएल डीईएस को चुना गया। धातु के निष्कर्षण (लीचिंग) को अनुकूलित करने के लिए विभिन्न प्रक्रिया मापदंडों जैसे ठोस-तरल अनुपात (एस/एल अनुपात), हलचल गति, समय और तापमान को बनाया गया। अंत में, दोनों डीईएस में अलग-अलग धातुओं को पुनर्प्राप्त करने के लिए सीमेंटेशन धातु को मिलाया गया।

प्रयोगात्मक परिणामों के आधार पर यह निष्कर्ष निकाला जा सकता है कि सुपरक्रिटिकल मेथनॉल ई-कचरे के प्लास्टिक से मूल्यवान उत्पाद प्राप्त करने के लिए एक कुशल तरीका है। धातुओं को पुनर्प्राप्त करने के लिए हरित गहरे यूनेक्टिक विलायक (डीईएस) धातुओं के निष्कर्षण के लिए संभावित निक्षालन एजेंट हैं और चुनिंदा धातु पुनर्प्राप्ति के लिए सीमेंटेशन का प्रभावी ढंग से उपयोग किया जा सकता है। अंत में, यह अनुशंसा की जाती है कि पारंपरिक तकनीक के हरित विकल्पों में धातु निष्कर्षण प्रक्रिया में कुछ पारंपरिक हानिकारक एजेंटों को बदलने की क्षमता है।

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