

**DEVELOPMENT OF A GREEN PROCESS FOR THE
RECOVERY OF METALS FROM WASTE
ELECTRONICS AND CONVERSION OF E-WASTE
PLASTIC INTO OIL (CHEMICALS)**

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Development of a Green Process for the Recovery of Metals from Waste Electronics and Conversion of E-Waste Plastic into Oil (Chemicals)

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*Dedicated to my
parents and family*

Certificate

This is to certify that the thesis entitled "Development of a Green Process for the Recovery of Metals from Waste Electronics and Conversion of E-Waste Plastic into Oil (Chemicals)," being submitted by Ms. Amrita Preetam to the Indian Institute of Technology Delhi for the award of "Doctor of Philosophy" is a record of bonafide research work carried out by her. She has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis. To the best of our knowledge, the results contained in this thesis have not been submitted in part or full to any other university or institute for the award of any degree or diploma.

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Abstract

Electrical and electronic equipment (EEE) has become an indispensable part of our day-to-day life. Waste Electrical and Electronic Equipment (WEEE), commonly known as electronic waste (e-waste), is swiftly increasing at an annual rate of 3-5%. As per the global e-waste monitor report, the e-waste generated in 2019 was around 53.6 million metric tons (Mt). It is assumed that the increase will be by 74Mt by 2030. In 2019, only 9.3 MMT, i.e., 17.4 % of the total e-waste produced, was recycled by the formal sector. The fate of around 82.6 % of e-waste is unknown: it was either landfilled or treated by the informal sector. The increasing improper disposal of e-waste is causing a ruinous effect on our environment and harming the health of animals and humans. E-waste is a heterogeneous composition of several base metals (Cu, Pb, Zn, Ni, etc.), precious metals (Au, Ag, etc.), polymers, ceramics, etc. Recycling e-waste in a systematic way can save the total energy related to virgin mining. Hence, e-waste is assessed as a secondary resource, and the recovery of metals from them is commonly called "Urban Mining." Apart from metals, plastics are an essential component of e-waste, which shares approx. 30% of the entire amount of e-waste generated and can be converted into liquid products (oil) in the form of valuable chemicals or fuel.

Therefore, in the present study, attainment has been made for the complete utilization of e-waste to recover materials in a sustainable form with minimal discharge. For overall e-waste plastic conversion, we have taken waste computer casing plastics (WCCP). For metallic fraction recovery, we have used waste random access memory (WRAM) as a feedstock for our work. WRAM is considered as a rich source of base metals such as tin, nickel, zinc, lead and precious metals such as gold, copper, silver etc., along with it also includes several high-grade polymers. Initially, the feed preparation was performed by dismantling, crushing, and grinding

the feed. Afterward, the WCCP is treated using subcritical-supercritical acetone (SCA) technology to convert the e-waste plastic into oil. The optimum condition was 300°C, in 120min, 0.05 S/L(g/ml) ratio and 0.5g of NaOH. The highest oil yield achieved was 87.89%, with a heating value of 36.7 MJ/kg. GC-MS results disclosed that the liquid product (oil) comprises single- and duplicate-ringed aromatic and oxygen-containing compounds. Isophorone is the significant component of the liquid product obtained. In another study, the WRAM is pre-treated with subcritical-supercritical (SCF) technology with different solvents such as subcritical-supercritical methanol (SCM), subcritical-supercritical ethanol (SCE) to enrich the metallic fraction and to convert the organic fraction into oil. Ethanol is found to be promising and appropriate as compared to methanol in terms of effective results, affordability, and sustainability. The optimum condition obtained using the SCE study is 250°C, in 120min, 0.02(g/ml), and 0.5g of NaOH. After the SCF treatment, more than 90% of the solvent used is recycled through a rotary evaporator, which helps to make the process close-loop and near zero discharge. Afterwards, the pre-treated WRAM (waste random access memory) is treated with acetic acid as a chelating agent for the recovery of base metals (Cu, Pb, Zn, Ni) with extraction efficiency of Cu, 83.7% of Ni, 79.3% of Zn, and 88.8% of Pb respectively at an optimum condition of 1.2 M of CH₃COOH concentration, 10% of H₂O₂ concentration, 55°C, 1:20 S/L ratio, 350 agitation speed, and 5 h of reaction time. Subsequently, the kinetic study revealed that the diffusion-controlled mechanism governs the metal extraction. The calculated activation energy for Cu, Pb, Zn, and Ni are 11.3, 12.6, 17.6, and 13.3 kJ/mol, respectively. Furthermore, the metal-leached salt recovered from the leached solution was thoroughly characterized. It was observed that the leached salt could be comparable with standard copper acetate, revealing the acetic acid's ligation property. Selective recovery of Cu with 92.7 wt.% recovery was attained using the electrodeposition technique.

The solid residue left in the base metal leaching study is used as a feedstock in the next study to recover precious metals (Au, Ag) using thiourea as a leaching agent. The optimum condition for this study is 24 g/L thiourea, 0.6% of Fe^{3+} , and 0.5 mol/L sulfuric acid for pH adjustment (pH=2) at 30 °C in a 40 mL solution. The extraction efficiency of 87.5%, 65%, 34.28%, and 79.7% for Au, Ag, Ni, and Cu, respectively, is obtained from this study. Selective recovery of gold from e-waste is a significant challenge due to its heterogeneous nature and existing inappropriate recovering processes. Considering these issues, in this study, we have synthesized a porous nanonet polymer (Por-net) through a one-pot Friedel Craft polymerization method containing multiple functional groups, i.e., porphyrin and triphenylamine, within a single framework material. Around 1250 mg g⁻¹ capacity of Au was recovered under realistic experimental conditions. Moreover, the adsorption isotherm and kinetics study revealed the Langmuir model and pseudo-second-order kinetic fittings for the Au adsorption on Por-net. The Por-net showed excellent desorption efficiency, recyclability, selectivity, and chemical stability. At last, the economic feasibility of Por-net for the purpose of recovering gold from e-waste is also explored.

The overall process revealed an integrated approach for treating e-waste plastic and recovering metals (base and precious metals). Therefore, the work represents a greener and feasible approach in promoting sustainable development, circular economy, responsible waste management, resource generation, waste minimization, and e-waste management.

सारांश

विद्युत और इलेक्ट्रॉनिक उपकरण (EEE) हमारे दैनिक जीवन का एक अनिवार्य हिस्सा बन गए हैं। अपशिष्ट विद्युत और इलेक्ट्रॉनिक उपकरण (WEEE), जिसे आमतौर पर इलेक्ट्रॉनिक कचरा (ई-कचरा) कहा जाता है, वार्षिक 3-5% की दर से तेजी से बढ़ रहा है। वैश्विक ई-कचरा मॉनिटर रिपोर्ट के अनुसार, 2019 में उत्पन्न ई-कचरा लगभग 53.6 मिलियन मीट्रिक टन (MMT) था। अनुमान है कि 2030 तक यह बढ़कर 74 मिलियन टन हो जाएगा। 2019 में, केवल 9.3 MMT अर्थात् कुल उत्पन्न ई-कचरे का 17.4% औपचारिक क्षेत्र द्वारा पुनर्नवीनीकरण किया गया था। लगभग 82.6% ई-कचरे का भाग्य अज्ञात है: इसे या तो लैंडफिल किया गया या अनौपचारिक क्षेत्र द्वारा उपचारित किया गया। ई-कचरे का बढ़ता अनुचित निपटान हमारे पर्यावरण पर विनाशकारी प्रभाव डाल रहा है और पशुओं और मनुष्यों के स्वास्थ्य को नुकसान पहुंचा रहा है। ई-कचरा कई आधार धातुओं (जैसे Cu, Pb, Zn, Ni आदि), कीमती धातुओं (जैसे Au, Ag आदि), पॉलिमर, सिरेमिक आदि का विषम मिश्रण है। ई-कचरे को व्यवस्थित तरीके से पुनर्नवीनीकरण करने से कच्चे खनन से संबंधित कुल ऊर्जा की बचत हो सकती है। इसलिए, ई-कचरे को एक द्वितीयक संसाधन के रूप में आंका गया है और उनसे धातुओं की वसूली को सामान्यतः "शहरी खनन" कहा जाता है। धातुओं के अलावा, प्लास्टिक ई-कचरे का एक आवश्यक घटक है, जो उत्पन्न कुल ई-कचरे का लगभग 30% हिस्सा है और इसे मूल्यवान रसायनों या ईंधन के रूप में तरल उत्पादों (तेल) में परिवर्तित किया जा सकता है।

इसलिए, वर्तमान अध्ययन में न्यूनतम डिस्चार्ज के साथ सामर्थ्यपूर्ण रूप से सामग्री की वसूली के लिए ई-कचरे का पूरा उपयोग करने का प्रयास किया गया है। समग्र ई-कचरे के प्लास्टिक के परिवर्तन के लिए हमने कंप्यूटर केसिंग प्लास्टिक्स (WCCP) का उपयोग किया है। धातु अंश की वसूली के लिए हमने अपने कार्य के लिए वेस्ट रैंडम एक्सेस मेमोरी (WRAM) का उपयोग किया है। प्रारंभ में, फीड तैयारी को विघटन, क्रशिंग और ग्राइंडिंग करके किया गया था। इसके बाद, WCCP को सबक्रिटिकल-सुपरक्रिटिकल एसीटोन (SCA) तकनीक का उपयोग करके ई-कचरे के प्लास्टिक को तेल में परिवर्तित करने के लिए उपचारित किया गया। अनुकूलतम स्थिति 300°C, 120 मिनट, 0.05 S/L (g/ml) अनुपात और 0.5g NaOH थी। सबसे अधिक तेल की उपज 87.89% थी, जिसका हीटिंग मान 36.7 MJ/kg था। GC-MS परिणामों से पता चला कि तरल उत्पाद (तेल) में एकल और डुप्लिकेट-रिंगड एरोमैटिक और ऑक्सीजन युक्त यौगिक शामिल हैं। प्राप्त तरल उत्पाद का प्रमुख घटक इसोफोरोन है।

एक अन्य अध्ययन में, WRAM को विभिन्न सॉल्वेंट्स जैसे सबक्रिटिकल-सुपरक्रिटिकल मेथनॉल (SCM), सबक्रिटिकल-सुपरक्रिटिकल एथेनॉल (SCE) के साथ पूर्व-उपचारित किया गया है ताकि धातु अंश को समृद्ध किया जा सके और जैविक अंश को तेल में परिवर्तित किया जा सके। मेथनॉल की तुलना में एथेनॉल को प्रभावी परिणामों, सामर्थ्यता और स्थिरता के मामले में उपयुक्त पाया गया है। SCE अध्ययन का अनुकूलतम स्थिति 250°C, 120 मिनट, 0.02(g/ml) और 0.5g NaOH थी। SCF उपचार के बाद उपयोग किए गए सॉल्वेंट का 90% से अधिक एक रोटरी एवापोरेटर के माध्यम से पुनर्नवीनीकरण किया गया है, जिससे प्रक्रिया को क्लोज-लूप और निकट शून्य डिस्चार्ज बनाया गया है। इसके बाद, पूर्व-उपचारित WRAM को धातु अंश की वसूली के लिए एसीटिक एसिड का उपयोग किया गया है। Cu की 83.7%, Ni

की 79.3%, Zn की 88.8% और Pb की 88.8% वसूली की गई है। अनुकूलतम स्थिति 1.2 M CH₃COOH की सांद्रता, 10% H₂O₂ की सांद्रता, 55°C, 1:20 S/L अनुपात, 350 गतिशीलता गति और 5 घंटे की प्रतिक्रिया समय है। इसके बाद, धातु अंश की निकासी के लिए विद्युत जमावट तकनीक का उपयोग किया गया है, जिसमें Cu की 92.7 wt.% की वसूली प्राप्त की गई है।

धातु निकासी अध्ययन में छोड़े गए ठोस अवशेष का उपयोग अगले अध्ययन में किया गया है, जिसमें कीमती धातुओं (Au, Ag) की वसूली के लिए थायूरिया का उपयोग किया गया है। इस अध्ययन के लिए अनुकूलतम स्थिति 24 g/L थायूरिया, 0.6% Fe³⁺ और 0.5 mol/L सल्फ्यूरिक एसिड (pH=2) 30°C में 40 mL समाधान है। इस अध्ययन से Au, Ag, Ni और Cu की क्रमशः 87.5%, 65%, 34.28% और 79.7% की निकासी क्षमता प्राप्त की गई है। ई-कचरे से सोने की चयनात्मक वसूली एक महत्वपूर्ण चुनौती है, क्योंकि इसकी विषम प्रकृति और मौजूदा अनुचित वसूली प्रक्रियाएं हैं। इन मुद्दों को ध्यान में रखते हुए, इस अध्ययन में हमने एक एकल फ्रेमवर्क सामग्री के भीतर कई कार्यात्मक समूहों, अर्थात् पॉर्फिरिन और ट्राइफेनिलैमाइन युक्त एक एकल-पॉट फ्राइडल क्राफ्ट पॉलीमराइजेशन विधि के माध्यम से एक पोरस नैनोनेट पॉलीमर (पोर-नेट) का संश्लेषण किया है। वास्तविक प्रयोगात्मक स्थितियों में लगभग 1250 mg g⁻¹ Au की वसूली की गई है। इसके अलावा, सोखना समकालन और किनेटिक्स अध्ययन ने पोर-नेट पर Au के सोखने के लिए लैंगमुइर मॉडल और छद्म-द्वितीय क्रम के किनेटिक फिटिंग का खुलासा किया है। पोर-नेट ने उत्कृष्ट desorption दक्षता, पुनरावृत्ति, चयनात्मकता और रासायनिक स्थिरता दिखाई है। अंत में, ई-कचरे से सोने की वसूली के उद्देश्य के लिए पोर-नेट की आर्थिक व्यवहार्यता की भी खोज की गई है।

समग्र प्रक्रिया ने ई-कचरे के प्लास्टिक और धातुओं (आधार और कीमती धातुओं) की वसूली के लिए एकीकृत दृष्टिकोण का खुलासा किया है। इसलिए, यह कार्य स्थायी विकास, सर्कुलर अर्थव्यवस्था, जिम्मेदार अपशिष्ट प्रबंधन, संसाधन उत्पन्न, अपशिष्ट न्यूनीकरण और ई-कचरा प्रबंधन को बढ़ावा देने में एक हरित और व्यावहारिक दृष्टिकोण का प्रतिनिधित्व करता है।

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