BRIEFING NOTE

July 2020

THE DEVELOPMENT OF AN INTEGRATED PROCESS FLOWSHEET FOR THE SEQUENTIAL EXTRACTION & RECOVERY OF VALUABLE METALS FROM WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT (WEEE)

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KEY FINDINGS

This project explored the potential of staged hybrid chemical and biological technologies in the extraction and recovery of metals from waste electrical and electronic equipment (WEEE). Studies were concentrated on developing key kinetics of complementary chemical leaching reactions and microbial ferric iron regeneration mechanisms in bioleaching systems to maximise the extraction of valuable metals from printed circuit boards (PCBs). Abiotic leaching of pure metals in acidic environments was very fast when ferric iron was used as the primary oxidant. Given these rapid kinetics and the stoichiometric requirements, a significant economic investment was needed to continually supply the necessary reagents to sustain such a process. Biologically facilitated systems alleviated this economic burden as acidophilic microorganisms regenerate the ferric iron oxidant needed to promote the dissolution of metals from PCBs. Reactor design and the mode of operation was essential in realising the benefits of bioleaching since acidophilic microorganisms were susceptible to inhibition as metals accumulated in the reaction environment. Enhanced extraction rates were achieved when microbial and chemical reaction mechanisms were separated into two-staged reactor configurations with reactors in series providing the greatest improvement in performance as inhibitory effects were alleviated. Integrated flowsheet analysis showed that this approach minimized the large volume of effluent generated during chemical leaching. This lessened the process dependence on replenishing resources and resulted in lower overall operating costs compared to traditional hydrometallurgical approaches.

INTRODUCTION

Electronic waste (e-waste) is currently the fastest growing waste in the industrialised world (Blade et al., 2017). With increasing demand, decreasing lifespan and rapid growth in digital technology, several million tonnes of e-waste is generated annually. Currently, waste electronic and electrical equipment (WEEE) is either discarded to landfill sites or it is incinerated. However, these methods are potentially hazardous leading to widespread pollution and health complications to communities within the dump epicenter (Bourguignon, 2015).

An integral part of WEEE is the printed circuit board (PCB). These electrical components consist of precious and base metals that are typically higher and more accessible than corresponding virgin ores (Baxter, 2016). Currently, this valuable revenue stream is being lost due to ineffective recycling techniques - the bulk of which is being recycled using crude and unregulated methods. Currently, much of the high-value components of the generated e-waste is exported, transferring beneficiation to more affluent countries (Schwarzer et al., 2005). To benefit from this resource, full value recovery should occur within the economy generating it. Handling the bulk e-waste load, presents a large financial return if handled appropriately. Opportunities arise if wealth generation is transitioned from linear economies to circular economies to reduce waste burden and enhance resource productivity.

Presently, formal e-waste processing is predominantly by pyrometallurgical methods (Khaliq et al., 2014). A practice that releases significant pollutants that requires extensive emission control systems to protect both the environment and surrounding inhabitants. Metal recovery technologies that have low energy requirements, are less capital intensive, low in pollution and is flexible enough to recover metals from a variety of advancing electronic devices is preferred. Both hydrometallurgical, and especially biohydrometallurgical, processes are promising alternatives that are less energy and environmentally onerous processes (Priya and Hait, 2017). Unlike chemically induced hydrometallurgical processes, costs associated with continual reagent supplementation to sustain the leaching process are alleviated in biohydrometallurgy (Adhapure et al., 2014). In this process, acidiphilic microorganisms are used to regenerate oxidising agents (ferric iron from ferrous iron) to facilitate the perpetual leaching of metals. High levels of dissociated metals that accumulate in the reactions, however, are known to inhibit microbial activity and consequently adversely impact process performance (Rawlings, 2005). Process configuration and microbial adaptation are therefore key aspects in overcoming process limitations. In this study, an integrated approach to e-waste management was considered to extract maximum value from e-waste using complementary technologies to enhance resource recovery using microbially assisted processes to reclaim metals of value from PCBs.

METHODS

Experimental studies focussed on elucidating the participating chemical and microbial oxidation kinetics in the metal beneficiation process. Chemical leaching reactions were performed at 37°C, consistent with mesophilic microbial oxidation conditions. Kinetic studies were performed in shake flasks at 37°C and 120 rpm. The pH, redox potential, ferric and total iron concentration were frequently measured as a means to evaluate the extent of reaction. Microbial oxidation kinetic experiments were performed in batch multiwell plates (MWPs) using Greiner Bio-one CELLSTAR® 12 Well Suspension Culture Plates (4 ml volume per well). The effect of select metals associated with PCBs on ferrous oxidation activity was investigated. Metals of interest included Cu^{2+}, Ni^{2+} and Zn^{2+}. Each well was charged with nutrient medium, 5 g/L ferrous and ferric iron, the designated volume of the metal stock solution inoculated with a mixed mesophilic cell culture dominated by *Leptospirilum ferriphilum* ($1x10^7$ cells/ml) such that a 3 ml total working volume was achieved. Each MWP was fitted with an AeraSeal™ film and placed in a humidified container to mitigate evaporative losses. The MWPs were incubated in a shaking incubator at 37°C and agitated at 120 rpm. A process flowsheeting approach was adopted to evaluate the techno-economic feasibility of the bio-assisted technologies.

RESULTS

Few studies report reaction kinetics for metal extraction from e-waste (Lambert et al., 2015). The influence of excess metals in solution on extraction and microbial oxidation rates are therefore not completely understood. Understanding the rates of microbial regeneration of the leaching reagent under these increasingly metal-rich environments, was essential at maintaining a favourable microbial growth environment and hence sustained metal extraction reactions.

Chemical leach kinetics of major metals associated with PCBs, together with microbial oxidation kinetics in the presence and absence of inhibition, were quantified as a means to inform the design of metal beneficiation processes in either single or multi-stage reactor systems. Process development and reactor design was contingent on decoupling relevant bioleaching kinetics. A significant part of the study focused on determining the optimum operating conditions required to achieve maximum specific microbial oxidation rates for select reactor configurations. Microbial adaptation was used to counter microbial inhibition and enhance ferrous iron oxidation to regenerate the primary oxidant, ferric iron, in metal extraction mechanisms.

In the chemical leaching study, copper, zinc and nickel were chosen as the metals of interest. These were selected based on abundance and their potential to influence microbial activity at low concentrations. A synergistic interaction between the participating oxidants, confirmed that that the leaching kinetics are dependent on the change in the oxidative-reductive potential of the ferric (C_{Fe3+}) to ferrous (C_{Fe2+}) iron concentration ratio to an order near $n = 1$ with the temperature dependent rate constant for copper was found to be $k = 0.082$ g L^{-1} min^{-1} at 37°C.

The impact of the metal cations of interest on the ferrous oxidation activity of a *Leptospirilum ferriphilum* dominated mixed mesophilic culture was individually investigated at metal concentrations typical of PCB composition. It was clear that the net generation of ferric iron was impeded when the bioleaching culture was exposed to increasing metal concentrations. It was further evident that Cu^{2+} elicited the most significant inhibitory effect on the microbial culture, resulting in negligible ferrous iron oxidation and complete microbial arrest once critical concentrations were exceeded. At these concentrations, metals were above tolerable limits causing cell death.

To overcome these limitations, the separation of the biological turnover of ferrous iron to the primary oxidant ferric iron from the chemical leaching of the PCBs was considered. This was assessed by developing mathematical models for multiple reactor types and in staged configurations. The consequence of cationic build-up was incorporated in these models and means to alleviate these were explored through inter-stage recovery and recycle (Figure 1). Arrangement and design of these reactor systems were evaluated by identifying the optimal trade-off between cost, energy and performance for the bioleaching of base metals from waste PCBs. Hybrid (bio)hydrometallurgical reaction systems in which continuous flow reactors in separate and staged biological and chemical oxidation reactors exhibited the greatest overall performance for the extraction of metals from PCBs.

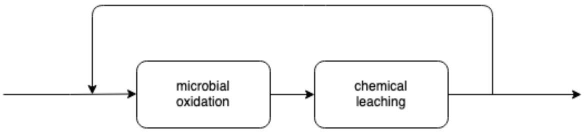

***Figure 1**: Staged microbial ferrous oxidation with acid-ferric iron leaching to recover metals of value from PCBs*

A cost-effective method for the selective recovery of metals was considered using chitin and chitosan from Black Soldier Fly (BSF) larvae shells from the multi-metal pregnant leach solution, downstream of the e-waste bioleaching unit operations. The polymer production methods were found to impact the performance of the biosorbents. Under optimised conditions using single and model bimetallic solutions, chitin proved to be effective in selectively recovering ferrous and ferric iron over other base metals such as copper, whilst chitosan demonstrated preference for copper over iron and aluminium. Adsorption of the metals onto chitin and chitosan were spontaneous on both polymers, favouring chemisorption with surface complexation.

Reducing energy requirements upstream to metal extraction further improved the techno-economic feasibility of the microbially facilitated hybrid process. Irrespective of the approach, upstream processes between technologies were mostly indistinguishable. Collection and pre-processing steps entailed similar costs as if operated in a single operation. By reducing energy intensive comminution operations such as crushing or milling a significant decrease in the contribution of the utility costs to the total operational costs could be realized by up to *ca*. 15.0%.

CONCLUSIONS

Techno-economically, this hybrid approach minimises fresh feed requirements and the quantity of discharge effluent that must be treated, thereby reducing the energy footprint needed for additional treatment of waste streams. It is clear from experimental outcomes, reaction modelling and literature-based analyses, a staged microbially facillitated process is the route with the greatest potential to reduce overall costs and to achieve the greatest financial return with reduced environmental burden when recovering metals from PCBs.

Acknowledgements: The authors acknowledge the funding received from the Department of Science and Technology (DST) through the Waste RDI Roadmap and Plastics SA. Further funding and support through the DST-NRF SARChI chair in Bioprocess Engineering (UID 64788), is gratefully acknowledged.

Disclaimer: The content and views included in this Briefing Note are based on independent analysis and do not necessarily reflect the position of the Department of Science and Technology or the CSIR.

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This Briefing Note is produced as part of the Waste RDI Roadmap Briefing Note Series,
an initiative of the Department of Science and Innovation managed by the CSIR.
The Note stems from the findings of a grant project funded under the Roadmap, entitled
"The development of an integrated process flowsheet for the sequential extraction and recovery of valuable metals from waste electrical and electronic equipment (WEEE)".

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