



Recovery of Value from an Electronic Waste Stream using a Biological Matrix

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Abstract

Increasing reserves of electronic waste highlight this as a valuable source of metals to re-enter the manufacturing circuit while minimising its environmental burden and realising a circular economy. Base metals may be extracted by bio-assisted ferric and acid prior to precious metal extraction. Recycling of the iron fraction intensifies this process; hence recovery of ferrous ions is important in the leaching of printed circuit boards (PCBs) by acidophiles. Chitin has shown high selectivity for iron in multi-metal solutions. In this study, chitin sourced from fly larvae (*Hermetia illucens*) was able to absorb ferrous ions up to an absorption capacity of 6.03 mg/g of chitin. The results of this study show the potential for chitin sourced from fly larvae to act as a sorbent for ferrous ion recovery from leachate solutions.

Keywords: E-waste, Waste electronic and electrical equipment (WEEE), bioleaching, iron, chitin, fly larvae

Introduction

In 2017, 47 million metric tonnes of Waste electronic and electrical equipment (WEEE) was produced globally, with South Africa producing 340 metric tonnes (Baldé et al., 2017). The need to recover value from waste metal streams and to reduce their environmental impact has motivated research into metal recovery from these waste streams. WEEE has been identified as a waste stream of high value, with about 40% of printed circuit boards (PCBs) containing base, precious and platinum group metals in greater amounts than found in mined ores (Yunus & Sengupta 2016). WEEE is also classified as hazardous, due to the high amounts of metal and other compounds such as polychlorinated biphenyl and halogenated flame retardants. Pyrometallurgy is the current conventional method of processing WEEE, however, bioleaching has been proposed to be a more environmentally friendly and less energy intensive route (Kavitha 2014). Biohydrometallurgy along with hydrometallurgical routes result in the production of metal-rich leachates.

Metal recovery from leachate solutions may include but not limited to several processes such as precipitation, cementation, solvent extraction, electrowinning, ion exchange

and biosorption. Cementation of copper and iron has several drawbacks, the most limiting being its poor selectivity in multi-metal ion solutions (Panão et al. 2006). Iron recovery by precipitation with limestone was found to be inefficient due to contamination with gypsum and slow settling time of the precipitated iron (Neale et al. 2011). Solvent extraction-electrowinning (SX-EW) process for copper recovery has been found to have a high environmental impact with respect to the climate change indicators (Ayres et al. 2002). Ion exchange resins, although efficient, may be too expensive for use in recovery of metals from waste streams. The various limitations in these processes has resulted in the consideration of bio sorbents for the selective recovery of metals from multi-metal solutions. Chitin and chitosan have been distinguished as more effective bio sorbents than bacteria, fungi, algae, proteins and tannin derivatives (Cui & Zhang 2008). Fly larvae shells are a large waste product in the biological treatment of industrial food wastes to produce protein rich feeds and have been shown to contain 40 % of their weight as chitin (Gyliene et al. 2003). Chitin is the second most abundant natural polymer after cellulose and chitosan is its de-acetylated derivative (Zhou et al. 2004). Both



polymers have shown great potential for application as bio sorbents of metals in solutions (Dutta et al. 2004).

Metal absorption studies using chitin and chitosan have shown higher selectivity for iron and copper respectively, from multi-metal solutions (Gyliene et al. 2002; Rhazi et al. 2002; Zhou et al. 2004). However, the ability of these polymers to recover metals from leachate solutions has not been investigated in-depth, particularly in the application to metal-rich solutions from the acidic bio-leaching of electronic waste. Iron is a lixiviant in the mechanism for the bio-assisted ferric and acid leaching of PCBs by acidophiles (Choi et al. 2004) and recovery of ferrous ions after chemical leaching is important in a two-step bioleaching process in which Fe^{2+} is oxidised to the lixiviant Fe^{3+} microbially (Brandl et al. 2001). Although Gyliene et al. (2002) investigated the recovery of ferric ions by fly larvae shells of *Musca Domestica*, recovery of ferrous ions was not investigated. The objective of this paper is to investigate the recovery of ferrous ions from a model leachate solution using chitin sourced from fly larvae of *Hermetia illucens* and to investigate the cost of producing chitin from fly larvae as an adsorbent material for iron.

Methods

Preparation of Sorbent

Fly larvae (*Hermetia illucens*) are produced as a waste stream during the production of animal feed. The fly larvae, initially stored at -20°C , was used to produce chitin as described in Gyliene et al (2002), except for the use of room temperature conditions for the deproteinisation steps as described in Tetteh (1991). Furthermore, the decolorisation of the chitin was not performed. The major steps in the extraction of chitin involved removal of proteins and minerals in an acidic solution (demineralisation) and removal of the proteins from the fly larvae using alkali treatment (deproteinisation). In preparation, the fly larvae were first washed with water, then dried at room temperature for 24 hours and crushed to liberate the material inside the fly larvae. Demineralisation was performed using 2M HCl at ambient conditions, where 20 g crushed fly larvae were placed into 225

ml of 2M HCl for 2 hours. After the demineralisation process, the fly larvae were filtered and washed with de-ionized water until neutral pH, then dried at room temperature for 24 hours. The remaining dried demineralised fly larvae of 8 g was then crushed to sizes range between 0.150 mm and 2 mm. The dried demineralised fly larvae were then deproteinated in 200 ml of 4 % (w/v) NaOH at ambient conditions for 5 h. The small dark brown chitin particles produced were used in the ferrous iron absorption and desorption experiments.

Absorption experiments

Experiments to investigate the absorption of ferrous ion were performed under batch conditions in Erlenmeyer flasks at 31.5°C on a shaker at 120 rpm, in triplicate. Aliquots of 200 mL of the model stock solution was added to each Erlenmeyer flask. The model stock solution contained 176 mg/L Fe^{2+} to represent the average concentration in the leachate from acidic bioleaching of 1g of PCB with acidophiles (Brandl et al. 2001). Adsorption conditions were adapted from Zhou et al (2004) and the pH was set to 4 by addition of H_2SO_4 (96 %) and maintained by adjustment with NaOH or H_2SO_4 accordingly. A mass of 0.7 g chitin was loaded into the Erlenmeyer flasks. Solution samples were taken hourly until equilibrium was reached. Ferrous iron concentrations in solution were measured spectrophotometrically using the modified ferric chloride assay developed by Govender et al (2012).

Desorption experiments

The desorption experiments were carried out in 0.1 M HCl with magnetic stirring according to the method proposed in Vijayaraghavan et al (2005). The ferrous-loaded chitin was placed in 100 ml 0.1 M HCl. The metal concentration of ferrous iron eluted into solution was measured every 15 mins for the first hour and then every half an hour thereafter spectrophotometrically.

Results and discussion

Preparation of Sorbents

During the preparation of bio sorbents, it was observed that settling, decanting followed



Table 1: Yields and cost of chitin production in this study and the study by Gyliene et al. (2002)

Studies	Present study	(Gyliene et al 2002)
Chitin source	Fly larvae (<i>Hermetia illucens</i>)	Fly Larvae Shells (<i>Musca domestica</i>)
raw material used (g)	20	40
HCl used (kg)	0.0164	0.0602
NaOH used (kg)	0.008	0.024
Chitin produced (g)	2.2	24
Electricity used (kWh)	-	0.143
Yield (%)	11	60
Cost of chitin production (R/kg)	66	26

by filtration was the most efficient method of separating the fly larvae material from reagents. The settling time prior to decanting was less than 2 minutes. Crushing of the fly larvae directly after the initial washing step resulted in a mushy paste of fly larvae material and exposed the material covered by the fly larvae shells for liberation. Demineralization resulted in the liberation of material inside the fly larvae. Prolonged drying of fly larvae in an 80°C oven after washing resulted in a release of a foul odour. Therefore, drying at room temperature for 24 hours was adopted to successfully dry the fly larvae material. Table 1 shows the yield and cost of production based on operational costs only of chitin in this study in comparison to that by Gyliene et al. (2002). The yield obtained in the present study was 11%. However, the yield relative to the fly larvae shell component of the fly larvae is 46 %, estimated based on the compositions of fly larvae given in Gyliene et al. (2003) and Caruso et al. (2014). The yield in this study was low in comparison to the yield of 60% obtained by Gyliene et al. (2002), which is similar to those reported in Horowitz et al. (1957) and Tetteh (1991). In the deproteination conditions in Gyliene et al. (2002), fly larvae shells were placed in 4 % (w/v) NaOH at 60 °C for 2 hours while in this study larvae were placed in the same concentration of NaOH at room temperature for 5 hours. The prolonged deproteination in this study may have resulted in the loss of raw material, however the major factor for the difference in yield is the raw materials used. This study used fly

larvae from *Hermetia illucens* while Gyliene et al. (2002) used fly larvae shells from *Musca domestica*. Fly larvae has been shown to contain a large amount of protein and lipids of about 40 % to 60 % by dry mass (Caruso et al. 2014). Therefore, the large loss of material in this study may be attributed to the removal of the larger amounts lipids and proteins from the fly larvae.

Table 1 shows that the cost of production of chitin in this study was R 66 per kg of chitin while the cost of production in Gyliene et al. (2002) was R 26 per kg of chitin. The use of fly larvae shells in Gyliene et al. (2002) resulted in higher yields of chitin when compared to the use fly larvae in this study. This shows that regardless of larger amounts of reagents used and the use of electricity in heating the NaOH to 60°C in the deproteination conditions in Gyliene et al. (2002), the higher yield due to the use of fly larvae shells compared to fly larvae resulted in 60 % less cost of production than obtained in this study. These results indicate that yield of chitin relative to the raw material is an important parameter in the cost of production of chitin. The amount of indirect CO₂ emission produced from the use of electricity in the deproteination conditions in Gyliene et al. (2002) is 0.0061 kg of CO₂ per g chitin produced. This value is based on the emission factor of electricity in South Africa and indicates a higher environmental impact than the deproteination at ambient conditions as done in this study.

The average market value of chitin is R 200 per kg of agriculture grade chitin (Alibaba,



2018). The cost of production of chitin in this study is 3 times less than that of the average market value of agriculture grade chitin. This indicates high value addition with regards to the fly larvae.

Sorption of free metal ion

Figure 1 shows the adsorption of ferrous ions from a solution of 176 mg/L of Fe^{2+} onto 0.7 g chitin. The sorption capacity obtained in this study was 6.03 mg Fe^{2+} /g chitin (0.108 mmol Fe^{2+} /g chitin), with 4.10 mg ferrous ions being absorbed in the first 220 minutes (3.67 hours). This was equivalent to 94.8 % of sorption capacity of the 0.7 g chitin used, indicating an average sorption rate of 0.0279 mg Fe^{2+} per g chitin per minute. Similar absorption times for ferric ions were observed in Gyliene et al. (2002), and Zhou et al. (2004). The sorption capacity obtained in this study for ferrous ions was 82 % less than the 0.6 mmol Fe^{3+} /g chitin obtained by Gyliene et al. (2002) for

ferric ions. The difference in sorption capacity might be due to the difference in the metal ions being adsorbed and possible difference in degree of acetylation of the chitin.

Table 2 shows the recovery cost of iron from solution using chitin as sorbent in this study relative to ion exchange resins as reported in the literature. The absorption capacity of chitin produced in this study is less than that of the ion exchange resins, shown in Table 2 and the cost of recovery of iron was 73 %, 85 %, 474 % more than that of the ion exchange resins Purolite S957, Na-Y zeolite, Lewatit TP 207 resin respectively used in Martins et al. (2017). These preliminary results show that there is a need to reduce the cost of production of chitin or to improve the absorption capacity of the chitin produced from fly larvae for it to be competitive with ion exchange resins in the recovery of ferrous ion from solution.

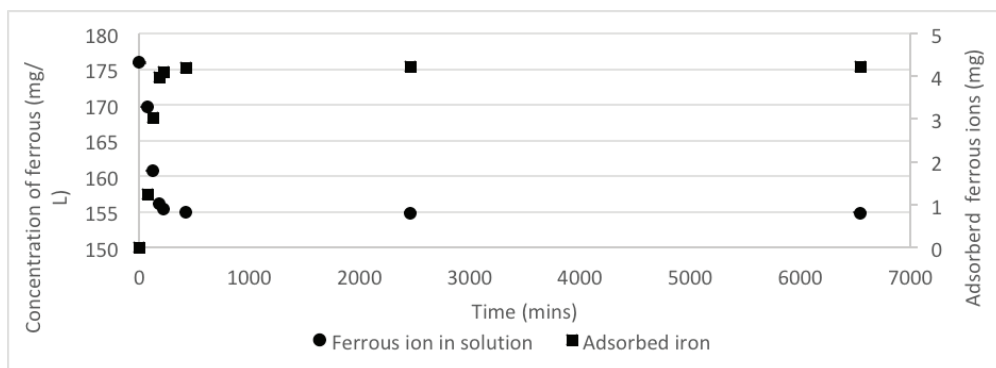


Figure 1: Adsorption of ferrous ions onto 0.7 g of chitin produced from Fly larvae (*Hermetia illucens*) from a solution of 176 mg/L ferrous ions

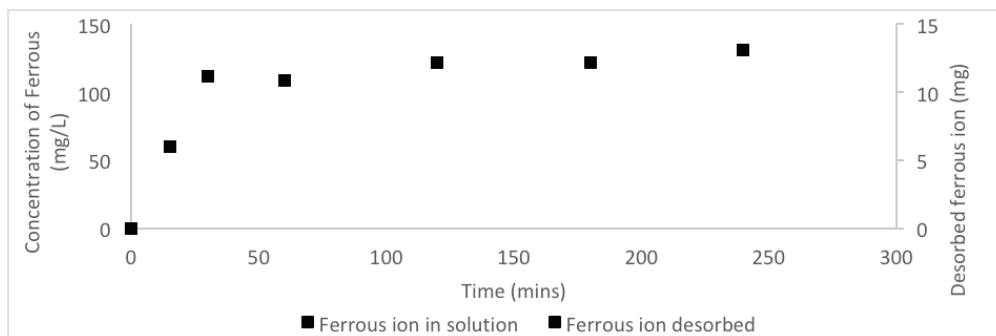


Figure 2: Desorption of ferrous ions from 2.1 g of chitin produced from Fly larvae (*Hermetia illucens*) in 0.1M HCl



Table 2: Comparison of the recovery costs of iron from solution using chitin in this study relative to ion exchange resins

Material	Cost (R/kg)	Absorption capacity (mg Iron/g)	Recovery costs (R/mg Iron)	Reference
Purolite S957	263	42.0	0.0063	(Izadi et al. 2017)
Na-Y zeolite	325	55.9	0.0059	(Kim & Keane 2002)
Chitin	66	6.03	0.0109	This study
Lewatit TP 207 resin	106	56.0	0.0019	(Martins et al., 2017)

Desorption of free metal ion

Figure 2 shows the desorption of ferrous ions from chitin. The average desorption was 6.21 mg Fe²⁺/ g chitin, compared to a loading of 6.03 mg / g chitin. In the first 30 minutes, 85.0 % of the ferrous ions adsorbed on the chitin was desorbed while the rest was desorbed after 2 hours. A desorption time of 2 h was also observed in Gyliene et al. (2002). This gives an average desorption rate of 0.0518 mg Fe²⁺ per gram of chitin per minute. The amount of ferrous ion desorbed relative to the amount adsorbed was 103 %. These results show that there was complete desorption of ferrous ions adsorbed and that desorption of ferrous ion on chitin occurs at a faster rate than adsorption.

Conclusions

This study demonstrated the preparation of chitin from the fly larvae (*Hermetia illucens*) and the ability to recovery ferrous iron using this bio sorbent. Settling, decanting followed by filtration is an efficient method of separating fly larvae from reagent solutions. Drying fly larvae after washing is an important pre-step before the crushing of fly larvae. Drying the fly larvae at room temperature is as effective as drying in the oven at 80°C. The initial crushing of the fly larvae results in the exposure of material in the fly larvae for liberation and demineralization resulted in liberation of some of the materials inside the fly larvae. The use of fly larvae as a raw material resulted in lower yields of chitin when compared to the use of fly larvae shells. The yield of chitin relative to the raw material used indicated to be an important parameter in the cost of production of chitin. The cost of production for chitin from fly larvae was three times less

than the market value of agriculture grade chitin. The chitin produced from fly larvae (*Hermetia illucens*) adsorbed ferrous ions to a loading capacity of 6.03 mg Fe²⁺/ g chitin. There is a need to reduce the cost of production of chitin or to improve the absorption capacity of the chitin produced from fly larvae (*Hermetia illucens*) to improve its ferrous ion recovery cost. This study showed that all adsorbed ferrous ions can be completely desorbed with HCl and that the desorption rate of ferrous ion from chitin is faster than the adsorption rate. This investigation shows that fly larvae (*Hermetia illucens*) has a potential to be a sorbent for ferrous ions in leachate solutions.

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References

- Alibaba (2018) Chitin products. Available: https://www.alibaba.com/trade/search?fsb=y&IndexArea=product_en&CatId=&SearchText=chitin [2018, May 14].
- Ayres RU, Ayres LW, Rade I (2002) The Life Cycle of Copper, its Co-Products and By-Products. Journal of Industrial Ecology. (24). DOI: 10.1162/108819899569458.
- Baldé CP, Forti V, Kuehr R, Stegmann P (2017) The Global E-waste Monitor 2017: Quantities, Flows, and Resources. Bonn: UNU-VIE SCYCLE. DOI: ISBN 978-92-808-4556-3.
- Brandl H, Bosshard R, Wegmann M (2001) Computer-munching microbes: Metal leaching from electronic scrap by bacteria and fungi. Process



- Metallurgy. 9(C):569–576. DOI: 10.1016/S1572-4409(99)80146-1.
- Caruso, D, Devic E, Subamia IW, Talamond P, Baras E (2013) *Technical handbook of domestication and production of diptera Black Soldier Fly (BSF) Hermetia illucens, Stratiomyidae*. D. Nastiti Murti, Ed. PT Penerbit IPB Press. Available: <https://uved-formation-aquaculture.cirad.fr/content/download/4328/32130/version/3/file/BLACK+SOLDIER+Technical+Handbook.pdf>. Choi MS, Cho KS, Kim DJDS (2004) Microbial Recovery of Copper from Printed Circuit Boards of Waste Computer by *Acidithiobacillus ferrooxidans*. Journal of Environmental Science and Health, Part A- Toxic/Hazardous Substances & Environmental Engineering. A 39(11–12):2973–2982. DOI: 10.1081/lesa-200034763.
- Dutta PK, Dutta J, Tripathi VS (2004) Chitin and chitosan: Chemistry, properties and applications. Journal of Scientific & Industrial Research. 63(January):20–31.
- Govender E, Harrison STL, Bryan CG (2012) Modification of the ferric chloride assay for the spectrophotometric determination of ferric and total iron in acidic solutions containing high concentrations of copper. Minerals Engineering. 35:46–48. DOI: 10.1016/j.mineng.2012.05.006.
- Gyliene O, Rekertas R, Šalkauskas M (2002) Removal of free and complexed heavy-metal ions by sorbents produced from fly (*Musca domestica*) larva shells. Water Research. 36(16):4128–4136. DOI: 10.1016/S0043-1354(02)00105-7.
- Gyliene O, Razmute I, Tarozaitė R, Nivinskiene O (2003) Chemical composition and sorption properties of chitosan produced from fly larva shells. Chemija (Vilnius). 14(3):121–127.
- Horowitz T, Roseman S, Blumenthal J (1957) The Preparation of Glucosamine Oligosaccharides. I. Separation. J. Am. Chem. Soc. 79:5046–5049.
- Izadi A, Mohebbi A, Amiri M, Izadi N (2017) Removal of iron ions from industrial copper raffinate and electrowinning electrolyte solutions by chemical precipitation and ion exchange. Minerals Engineering. 113(April):23–35. DOI: 10.1016/j.mineng.2017.07.018.
- Kavitha AV (2014) Extraction of precious metals from ores thereof. Journal of Chemical and Pharmaceutical Sciences. (3):147–149.
- Kim JS, Keane MA (2002) The removal of iron and cobalt from aqueous solutions by ion exchange with Na-Y zeolite: Batch, semi-batch and continuous operation. Journal of Chemical Technology and Biotechnology. 77(6):633–640. DOI: 10.1002/jctb.618.
- Lehohla P (2015) Environmental Economics Accounts Compendium. Pretoria.
- Martins PJM, Reis PM, Martins RC, Gando-Ferreira LM, Quinta-Ferreira RM (2017) Iron recovery from the Fenton’s treatment of winery effluent using an ion-exchange resin. Journal of Molecular Liquids. 242:505–511. DOI: 10.1016/j.molliq.2017.07.041.
- Neale JW, Gericke M, Ramcharan K (2011) The application of bioleaching to base metal sulfides in Southern Africa: prospects and opportunities. The Southern African Institute of Mining and Metallurgy. 367–388.
- Panão ASI, Carvalho JMR De, Correia MJN (2006) Copper Removal from Sulphuric Leaching Solutions by Cementation. Technical University of Lisbon. Available: https://fenix.tecnico.ulisboa.pt/downloadFile/395137462214/Artigo_Cementacao.pdf.
- Rhazi M, Desbrières J, Tolaimate A, Rinaudo M, Vottero P, Alagui A, El Meray M (2002) Influence of the nature of the metal ions on the complexation with chitosan. Application to the treatment of liquid waste. European Polymer Journal. 38(8):1523–1530. DOI: 10.1016/S0014-3057(02)00026-5.
- Tetteh AY (1991) Optimization studies on chitin extraction from crustacean solid wastes. McGill University. Department of Food Science and Agricultural Chemistry. 15–80.
- Vijayaraghavan K, Jegan JR, Palanivelu K, Velan M (2005) Nickel recovery from aqueous solution using crab shell particles. Adsorption Science & Technology. 23(4):303–311. DOI: 10.1260/0263617054770002.
- Yunus PA, Sengupta B (2016) E-Waste Indian Perspective and Recovery of Valuable Metals From E-Waste-A Review. *International Refereed Journal of Engineering and Science (IRJES)*. 5(4):70–80.
- Zhou D, Zhang L, Zhou J, Guo S (2004) Cellulose/chitin beads for adsorption of heavy metals in aqueous solution. Water Research. 38(11):2643–2650. DOI: 10.1016/j.watres.2004.03.026.

