Atomic Absorption Spectrometer for Assessing the Inorganic Contaminants in Processed E Waste

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Abstract—E–waste handling appears to be national agenda towards hazardous waste management. The annual e–waste generation in India is approximated to be 4.1 million metric tonnes. In India, Bengaluru, Karnataka is popularly called as Silicon Valley of India as it hosts many software industries. The annual generation of e–waste at Bengaluru is 9,118.74 metric tonnes and expected to escalate at a rate of 2.25 tonnes/year. It is understood that e–waste comprises of obsolete electrical and electronic items. They are collected and transported to e–waste handling units. At the handling unit, they are segregated, dismantled and separated into plastic and metal items manually. Worn out copper cables, wires and printed circuit boards (PCBs) are shredded and pulverized to extract the metals. This results in generation of processed e–wastes such as Floor dust, Pulverized Epoxy Powder, PVC Cable Granule and PCB metal powder. These processed e–wastes contain inorganic and organic contaminants and it requires safe handling and disposal. Inorganic contaminants such as metals are expected to be higher in the processed e–wastes which needs to be examined for their levels. The present study attempts to investigate metals such as Copper (Cu), Zinc (Zn), Iron (Fe), Lead (Pb), Cadmium (Cd), Chromium (Cr), Nickel (Ni) and Lithium (Li) in the processed e–wastes. As the processed e–wastes are expected to contain good metal residues, their levels are compared with statutory limits to comment on their toxicity. Further, existing methods of metal recovery are discussed along with their impact on environment upon disposal.

Index Terms—E–waste, Inorganic Contaminants, Metal Recovery, Environmental Hazard

I. INTRODUCTION

E–WASTES are a result of the outdated and unserviceable electronic and electrical items which are generated in an extremely high quantity [1]. Globally, 20 million tonnes of e–wastes are added which goes untreated. Among the nations, China ranks first in generation of E–waste at a rate of 6 million tonnes per year[2]. Currently, in India about 4.1 million tonnes of e–waste are generated and it is expected to reach 8 million tonnes by 2025 [3]. Although a disproportionate generation of e–waste is seen among the various states of India, at Bengaluru, Karnataka about 9118.74 tonnes/annum of e–waste are generated and handled at various e–waste handling sites (IRGSSA, 2005).

The present E–waste handling methods include the collection, segregation, dismantling and disposal. Most of these methods are manual, crude and primitive due to the expensive high–tech recovery process [4]. It was observed that at an e–waste handling site the electrical components are initially segregated into metal and non–metallic components. The electrical equipment is wrenched and broken into smaller pieces. The circuit boards are chopped and attempted for precious metal recovery. The worn out wires are stripped from their plastic insulation. The obsolete batteries are safely shifted to State Storage Transport and Disposal facility established by the State Pollution Control Board (SPCB). It is understood that in the process of handling, four types of processed e–wastes namely, Floor dust, Pulverized Epoxy Powder, PVC Cable granule and PCB Metal. powder are generated. They contain appreciable levels of metal residues which go un–covered. Further, if these e–wastes are discharged to environment without a proper treatment, it can cause a hazard to the environment. Thus, in the present study, we aim to investigate metals such as Cu, Zn, Fe, Pb, Cd, Cr, Ni and Li in the processed e–wastes collected from two different e–waste handling units. Further, we also attempt to discuss the various metal recovery methods available, their limitations and the impact on processed e–wastes upon disposal.

II. EXISTING METHODS

Flame Photometry and ICP (Inductive Couple Plasma) shows there significance as an atomic optical emission spec–troscopy technique that uses the flame as source of atoms excitation. Graphite furnace methods extended the range of usefulness atomic absorption It can not measure the con–centration of metal ion with high accuracy. ICP is highly sensitive method used to analyse trace amounts of hazardous metals. The major disadvantage is the high capital cost of the instrumentation and lighter elements are prone to interferences. GFAAS (Graphite Furnace Atomic Absorption Spectrometer) used for extraction and determination of trace and ul–tratrace impurities from edible oils via an ultrasound–assisted extraction using tetramethylammonium hydroxide (TMAH) and ethylenediaminetetraacetic acid (EDTA) at pH 12 for the extraction of elements (Pb, Cu, Fe, Mn, Cd, Cr, Zn) from edible oils extracted from various seeds (i.e. mustard oil, sun ower oil, sesame oil, ground nut oil, coconut oil, rice bran oil and corn oil). The extracted trace or toxic elements observed to be present at parts per billion levels. Use of EDTA has enabled the pre–concentration of impurities also and subsequently improved the detection limits.
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Combination of TMAH and EDTA of the proposed method resulted in better detection limits for the rapid determination of impurities in edible oils. The achieved detection limits were better than those obtained with the microwave digestion. This method is a simple and rapid alternative method for the determination of ultratrace impurities in edible oils.

Absorption Tubes uses a Metal furnace atomic absorption spectrometry to determine the trace amounts of Cr, Zn, Cd, and Pb. It results in enhancement of the atomic absorbance of the metals. The roof-type absorption tube was effective for Cr, Zn, Cd, and Pb, as their absorbance intensities increased by 31-66% compared to those measured by the system without the absorption tube. Meanwhile, the tube-type absorption tube was effective in the determination of low boiling point metals, and the absorbance intensities obtained for Cd and Zn were double of those measured without the absorption tube. The proposed method was successfully applied in the determination of Zn in tap water.

III. METHODOLOGY

A. Study Site
Dobaspet Industrial Area, Bengaluru Rural District, Karnataka (12.991 N; 77.7094E) is one of the major industrial area (1225 acres) established by Karnataka Industrial Area Development Board (KIAB), Govt. of Karnataka (Fig 1). There are 38 e-waste recycling units approved by SPCB at Karnataka and two major e-waste handling units located at this industrial area are selected. The current capacity of these units is to handle 6-8 tonnes/day. It has an integrated production line for recycling the worn-out cables and waste wires. The metal components from e-waste and scrap items are supplied to local smelters for recycling and recovery of metals. In these processing units, the electronic waste gadgets are initially dismantled manually to separate the metallic components from plastic. The metal parts of the electronic items such as screws, copper wires and PCBs are chopped to fine powder for metal recovery.

B. Sample Collection
Altogether 40 samples of floor dust, pulverized epoxy powder and PVC cable granule, PCB metal powder were collected from Site I and II, respectively. At study site -I, the floor dust was swept manually with a plastic sterile brush from the dismantling area and the pulverized epoxy powder generated from the cable-shredding machine are collected, stored in pre-cleaned polythene bags and transported to the laboratory. From the other study site -II, PVC cable granule and PCB metal powder are collected from the shredding machines. At the laboratory, they were grounded and sieved to obtain a fine powder and subjected to acid digestion for analysis of metals.

C. Sample Digestion and Analysis
The procedure for digestion of samples was followed as per Jayakumar and Muralidharan (2015) with slight modifications.

Fig. 1. Map of Bengaluru Rural District, KARNATAKA

Briefly, about 1 g of the sample was weighed, digested using Microwave Digestion System (Milestone, MLS 1200) in 10 mL HNO3 (69 GR-Merck) for 10 min, 1 mL HClO4 (70% GR-Merck) for 5 min and 10 mL H2O2 (30% GR-Merck) for 10 min at 250 W magnetron power settings and analysed for metals such as Cu, Zn, Fe, Pb, Cd, Cr, Ni and Li using a double beam Atomic Absorption Spectrometer (Perkin Elmer, Model AA800). Standards for metals manufactured by Merck, India (99.9% pure) were used to calibrate the instrument. To validate calibration during measurements, for every ten samples, blank and calibration standards were read thrice and relative standard deviation was computed. While the detection limit for Cu, Cr, Fe, Ni and Li was 0.002 ppm, the same for Cd, Pb and Zn was 0.001, 0.03 and 0.02 ppm respectively.

The quantification limits of metals were three times the detection limit. Recovery rates for Cu, Cd, Pb, Zn, Cr and Ni were 86, 88, 85, 90, 87 and 89%, respectively. Li and Fe had recovery rate in the range of 90-95%. The results were not corrected for percent recovery and expressed in g/g (mean S.E).

D. Statistical Analysis
The data was examined statistically using SPSS Software Ver.17. Ensuring normal distribution of data through Shapiro- Wilk test, parametric tests such as Single Factor analysis (ANOVA) was used to identify the variation in metals among the different e-wastes at 95% significance levels.

IV. RESULTS AND DISCUSSION

A. Variation in Metal levels among the different types of processed e-wastes collected from two sites
The levels detected in all the processed e-wastes were high. Floor dust measured the highest levels of levels of Zn and Fe and lowest for Li. The levels recorded in PVC cable granule, and PCB metal powder collected from site II were the lowest for Zn and Fe, respectively with significant mean differences (MD = 248214.01; F =1511.06 df =6,63; p=0.000). Zn concentration also varied among the e-wastes significantly (F = 23.82; df = 6, 63 p= 0.000).
However, the mean differences between floor dust and PCB metal powder (MD=1031.03; p=0.093) are not significant. The levels of Fe recorded in the different e-wastes were appreciable. The mean differences found to be significant among the e-wastes (F=37.35; df = 6,63; p=0.000) except PVC cable granule (MD=2826.82; p=0.374) collected from site II.

Pulverized epoxy powder recorded the lowest level for all the metals. Non-essential toxic metals such as Pb, Ni, Cd, Cr and Li were found to be appreciably detected in all the e-waste samples. PVC cable granule and PCB metal powder had the highest levels of Cu, Pb, Cr and Cd, Ni, respectively. Significant differences in mean Ni levels could be observed among the e-wastes (F = 578.26; df = 6,63; p=0.000). Differences in mean Cr (F=25.491; df = 6,63; p=0.000) and Li (F= 358.239; df = 6,63; p=0.000) levels among e-wastes could be observed and they appear significant.

Pulverized epoxy powder is generated through fine shredding of wires, which are initially stripped from its insulation. Further, when PCBs are chopped to specific dimensions and shredded to recover metals, it also produces fine pulverized powder. This mixture is referred as pulverized epoxy powder. The worn-out copper cables contain plastic wrappings, muti- lated soldered edges, wall paint spillages and corroded green colour exudes which contributes for the metal levels.

Floor dust is a type of processed e-waste generated, when obsolete electronic items undergo segregation and dismantling at handling site. It contains the external dust adhered to the electronic items during transportation or the dust already present during disposal, transudes from the worn-out batteries, scrap paint remnants, broken glass coverings, metal screws and nuts. Hence, the high level of metals in the floor dust is attributed to the mixture of the electronic oddments.

The significant high levels of Cu and Ni in the PCB metal powder may be due to blemished soldering, mutilated PCBs and Ni shreds from the paint coatings of the plastic laces of the metal wires, which are expelled during the process of shredding the PCBs, stripping and pulverizing of wires. PCBs are the major components of e-waste (about 85%) and they contain both non-metallic (plastics, epoxy, resins, and glasses) and metal (copper, iron, lead, and nickel) components. They are mainly chipped out from mobile phones, computers, television sets and other domestic household and industrial appliances to recover metals. It is needless to mention that lead is widely used as a soldering agent in cables and wires. Hence, the PVC cable granulated powder contains high levels of Pb. Cd is used to prevent corrosion and mixed in paints.

Earlier it is widely used in batteries and solar panels. Further, it is also used to stabilize plastic. Hence, the corroded electronic oddments release Cd during their handling and processing.

PVC cable granule contained highest levels of Cr and it is accounted through the plastic insulation and metal present in the PVC cable. The metal concentrations reported in the present study were far lesser than the values reported in studies conducted on printed circuit boards of mobile phones and other electrical waste components. In a study conducted on worn- out printed circuit boards of different discarded mobile phones at Nigeria [5] to determine metals showed very high levels of Cu (25000 92300 mg/kg), Pb (20100 8400 mg/kg) and Cd (21003300 mg/kg). [6] characterized and quantified metals such as Pb (600000200 mg/kg), Ni (50.034.0 mg/kg), Cr (65.440 mg/kg), Cu (6.815.0 mg/kg), Cd (9630 mg/kg), Pb (2100000200 mg/kg), Ni (360 mg/kg), Cu (5150 mg/kg) and Zn (1360 mg/kg). The values for metals such as Cd, Cu, Ni and Zn in floor dust are comparable with the indoor dust of e-waste workshop and found to be at least 1.5 times lower. However, the levels are supposed to cause adverse health consequences to handlers upon chronic exposure.

A study on metals on the indoor dust of e-waste workshop [8] reported high values of Pb (9630 mg/kg), Cd (10.8 mg/kg), Ni (360 mg/kg), Cu (5150 mg/kg) and Zn (1360 mg/kg). The values for metals such as Cd, Cu, Ni and Zn in floor dust are comparable with the indoor dust of e-waste workshop and found to be at least 1.5 times lower. However, the levels are supposed to cause adverse health consequences to handlers upon chronic exposure.

### Table I: Metal Levels In The Different Processed E-Wastes Collected From Two Handling Sites (X 10-3mean Sd G/G)

| Study Site | E-waste | Cu   | Zn   | Fe   | Pb   | Cd   | Cr   | Ni   | Li   |
|-----------|---------|------|------|------|------|------|------|------|------|
| I         | Pulverized | 1.10 | 0.40 | 4.22 | 0.34 | 7.43 | 6.29 | 0.53 | 0.03 |
|           | Epoxy Powder | ±0.75 | ±0.20 | ±1.18 | ±0.40 | ±1.51 | ±3.46 | ±0.17 | ±0.05 |
| I         | Floor dust | 4.17 | 1.16 | 11.61 | 0.29 | 5.47 | 39.61 | 0.35 | 0.028 |
|           | ±2.73 | ±2.60 | ±3.5 | ±1.41 | ±2.97 | ±18.28 | ±0.07 | ±0.12 |
| II        | PVC Cable granule | 59.16 | 0.57 | 8.31 | 4.56 | 90.39 | 46.09 | 0.09 | 0.014 |
|           | ±13.28 | ±0.08 | ±2.22 | ±0.15 | ±1.57 | ±21.08 | ±0.01 | ±0.27 |
| II        | PCB Metal | 0.60 | 3.14 | 3.36 | 3.56 | 96.85 | 10.82 | 1.83 | 0.03 |
|           | Powder | ±0.02 | ±0.54 | ±2.21 | ±0.55 | ±10.97 | ±0.45 | ±0.14 | ±0.39 |

B. Metal recovery methods available

It is understood that e-wastes contain 40-50 times more precious metals like gold (Au) than natural ores, which may be recovered to minimize the
metal extraction from the ores. By and large, recovery of metals from e-wastes in developing countries is still practiced using pyrometallurgical or hydrometallurgical methods [9]. In pyrometallurgical process, high temperature is applied (≥2500°C) to recover metals which demands high energy to operate. Non-ferrous metals from the e-waste scrap are primarily removed through pyrometallurgical methods [10]. However, hydrometallurgical methods are pop-ularly used to separate precious metals owing to their better recovery rates and found to be economical. Hydrometallurgical methods involve acids and solvents to leach the metal from the waste [11]. The waste acids and solvents carry trace quantities of metals and other contaminants which pose a threat to the environment. To overcome this challenge, bio-hydrometallurgy–cal techniques employing microorganisms such as bacteria and fungi [12] were used to leach metals from e-waste. This has the dual benefits of less industrial production of strong acids to leach metals and better treatment on the weak organic acids produced by the microbial cultures. Nevertheless, the toxic influence of metals on the growth medium and high lag phase in reaction were found to be the drawbacks in bioleaching [13].

There are studies illustrating the economic feasibility of recovering metals from e-waste scraps through electrochemical process. A significantly lower capital investment of 2.9kg e-waste per dollar can be achieved with the electrochemical process and comparatively less with black Cu smelting process (1.3kg per dollar) [14]. Ball milling techniques showed a fast leaching and quick recovery of metals. Nevertheless, the above-mentioned methods may release residues containing metals to the soil. Thus, eco-friendly, feasible and cost-effective recovery tech-nologies are not available in the developing countries to recover metals from soil contaminated with e-wastes where integrated e-waste management systems are yet to be estab-lished [15].

C. Efficiency
E-waste contains a complex mixture of metals at varying concentration. Atomic Absorption Spectrometer could detect the metals with good precision and accuracy. Individual metal concentrations could be analysed in the e-waste and it has at-tempted to eliminate the interference of other metals. Thus we observe Atomic Absorption Spectrometer to be on appropriate technique to analyze metals in e-waste.

V. CONCLUSIONS
This study has identified significant variation in levels of metals between different types of processed e-wastes. Although both the wastes had high levels of metals, pulverized epoxy powder had higher levels of toxic metals such as Cd, Pb and Ni than floor dust. In comparison with the values reported in literature and statutory limits, the levels are far lesser. However, the risk of metal toxicity in disposing these e-wastes cannot be ignored owing to their high volume being contin-uously generated. In India, primitive methods of incineration and land fill techniques are still practiced which has resulted in the contamination of soil, water and plant in Mandoli Industrial area, Delhi [16]. The present e-wastes generated appear to contain good levels of valuable metals such as Cu, Fe and Zn, which may be recovered through the available hydrometallurgical, pyro metallurgical and bio leaching process. Further, vermin remediation may also be attempted to recover the metals. Earthworms are proven to be potent indicators of soil contamination owing to their sedentary, continuous interaction with soil, ability to bioaccumulate and tolerate the stress produced by the contaminants elevate their role in bioremediation (vermi remediation) of contaminated soil (especially with heavy metals) [17]. Thus, this study has characterized the metal contents in the wastes generated during the handling and processing of e-waste and now gives us a challenge to take appropriate actions to reduce the waste and recover the valuable metals thereby practicing sound environmental waste management.

REFERENCES
1. Pariatamby A and Victor D, Policy trends of e-waste management in Asia. Journal of Material Cycles and Waste Management, Volume 413, number 4, 2013, pp. 411–419.
2. Chen A, Dietrich KN and Ho S, Developmental Neuro toxins in E-Waste: An Emerging Health Concern”. Environ Health Perspect, Volume 119, 2011, pp. 431-438.
3. Jayaprada A, Scenario of E-waste in India and application of new recycling approaches for e-waste management. Journal of Chemical and Pharmaceutical Research, Volume7/ Issue 3, 2015, pp.232-238.
4. Zheng J, Xi L, Yuan JG, He LY, Zhou YH, Luo Y, Chen SJ, Mai BX and Yang ZY. Heavy metals in hair of residents in an e-waste recycling area, South China: Contents and assessment of bodily state’, Arch. Environ. Contam. Toxicol, Volume61/ 2011, pp. 696-703.
5. Nnorom I C, Osibanjo O: Determination of metals in printed wiring boards of waste mobile phones. Toxicological & Environmental Chemistry, Volume 93/ Number 8, 2011, pp.1557-1571.
6. Ogundiran M B, Buluku TG, Babayemi JO , Osibanjo O. Waste rechargeable electric lamps: characterisation and recovery of lead from their lead-acid batteries, J Mater Cycles Waste Manag, Volume19, 2017, pp. 163–171.
7. Divya B, Harish S, Ramaswamy K, Kishorebabu M, Raju N, Govindaraju R, Rambabu U, Monnirathnam N. R. Estimation of Cd, Pb and flame retardants in electric mosquito bat using EDXRF, ICP-OES, AAS and GC–MS, Int. J. Environ. Sci. Technol, 2017.
8. Xu F, Liu Y, Wang J, Zhang G, Zhang W, Liu L, Wang J, Pan B, Kuangfei Lin K. Characterization of heavy metals and brominated flame retardants in the indoor and outdoor dust of e-waste workshops: implication for on-site human exposure, Environ Sci Pollut Res, Volume22, 2015, pp. 5469–5480.
9. Muammer Kaya. Recovery of metals and nonmetals from electronic waste by physical and chemical recycling process, Waste Management, Volume 57, 2016, pp.64-90.
10. Anshu Priya, Subrat Hai. Extraction of metals from high grade waste printed circuit board by conventional and hybrid bioleaching using Acidithiobacillus ferrooxidans, Hydrometallurgy, Volume 177, 2018, pp. 132-139.
11. Hyunju Lee, Brajendra Mishra. Selective recovery and separation of copper and iron from fine materials of electronic waste processing, Minerals Engineering Volume/ 121, 2018, pp. 1-7.
12. Singh M, Thind PS, John S. Health risk assessment of the workers exposed to the heavy metals in e-waste recycling sites of Chandigarh and Ludhiana, Punjab, India, Chemosphere, Volume/ 203, 2018, pp.426-433.
13. Wang S, Zheng Y, Yan W, Chen L, Dummi Mahadevan G, Zhao F. Enhanced bioleaching efficiency of metals from E-wastes driven by biochar, Journal of Hazardous Materials, Volume/320, 2016, pp. 393-400.
14. Luis A, Diaz-Teddi E, Lister. Economic evaluation of an electrochemical process for the recovery of metals from electronic waste, Waste Management, Volume/74,2018, pp. 384-392.
15. Mahdi Ikhlayel. An integrated approach to establish e-waste management systems for developing countries. Journal of Cleaner Production, Volume 170, 2018, pp. 119-130.

16. Pradhan JK, Kumar S. Informal e-waste recycling: environmental risk assessment of heavy metal contamination in Mandoli industrial area, Delhi. India Environ Sci Pollut Res, Volume 21, 2014, pp. 7913–7928.

17. Zheng K, Liu Z, Li Y, Cui Y, Li M. Toxicological responses of earthworm (Eisenia fetida) exposed to metal-contaminated soils. Environ Sci. Pollut Res, Volume 20 2013, pp. 8382-90.

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