ENVIRONMENTAL IMPACT ASSESSMENT AND BIOLEACHING OF METALS FROM ELECTRONIC WASTE (E-WASTE)

BY

JATINDRA KUMAR PRADHAN

JAYPEE UNIVERSITY OF INFORMATION TECHNOLOGY
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By

JATINDRA KUMAR PRADHAN

ATHESIS SUBMITTED IN FULFILLMENT OF THE REQUIREMENTS FOR

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SUPERVISOR'S CERTIFICATE

This is to certify that the thesis entitled, "**Environmental Impact Assessment and Bioleaching of Metals from Electronic Waste (e-waste)",** which is being submitted by **Jatindra Kumar Pradhan** for the award of degree of **Doctor of Philosophy** in **Biotechnology** by the Jaypee University of Information Technology at Waknaghat, is the record of candidate's own work carried out by him under my supervision. This work has not been submitted partially or wholly to any other University or Institute for the award of this or any other degree or diploma.

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DECLARATION

I Certify that

a. The work contained in this thesis is original and has been done by me under the guidance of my supervisor Dr. Sudhir Kumar.

b. The work has not been submitted to any other organization for any degree or diploma.

c. Whenever, I have used materials (data, analysis, figures or text), I have given due credit by citing them in the text of the thesis.

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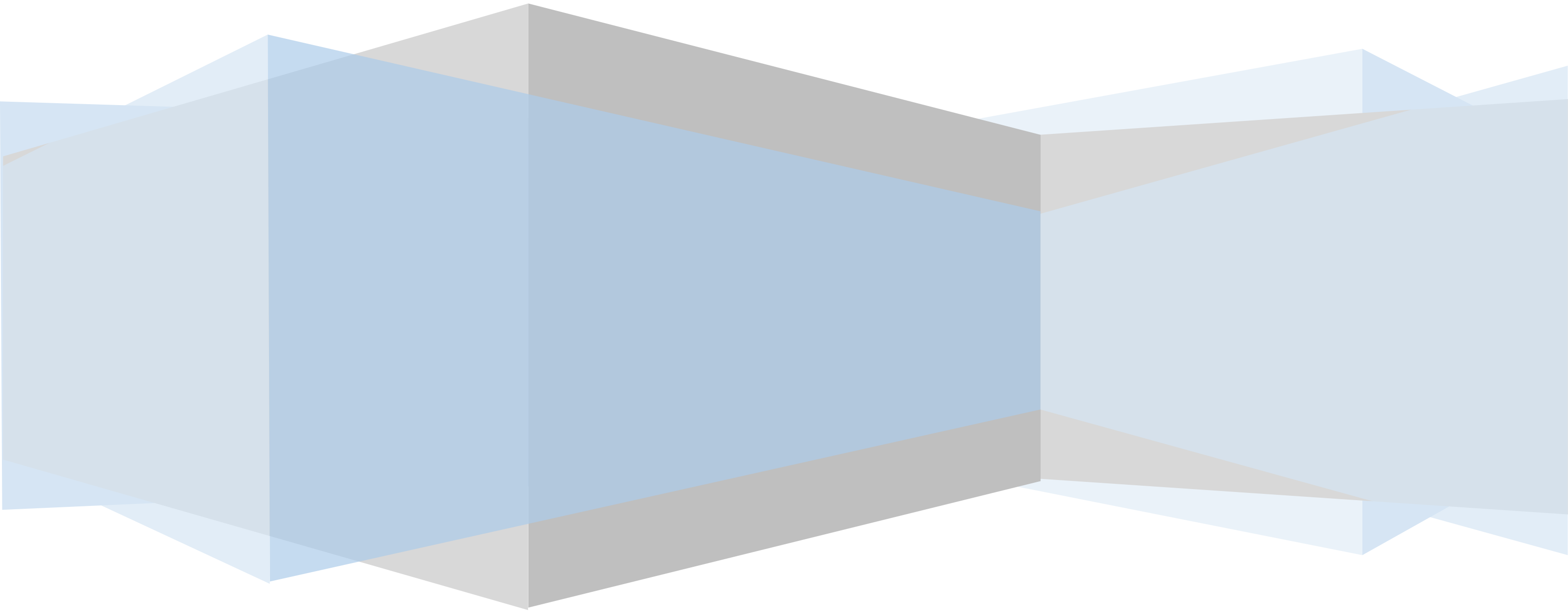

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[Jatindra Kumar Pradhan]

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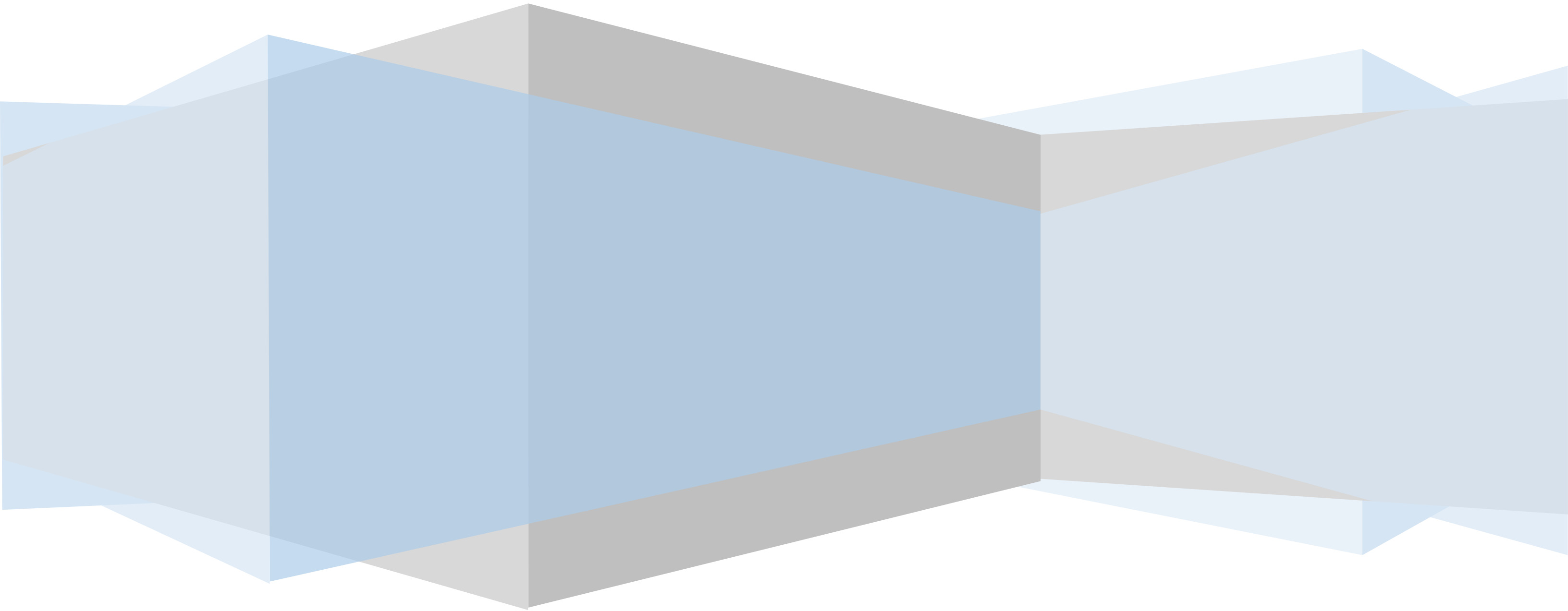

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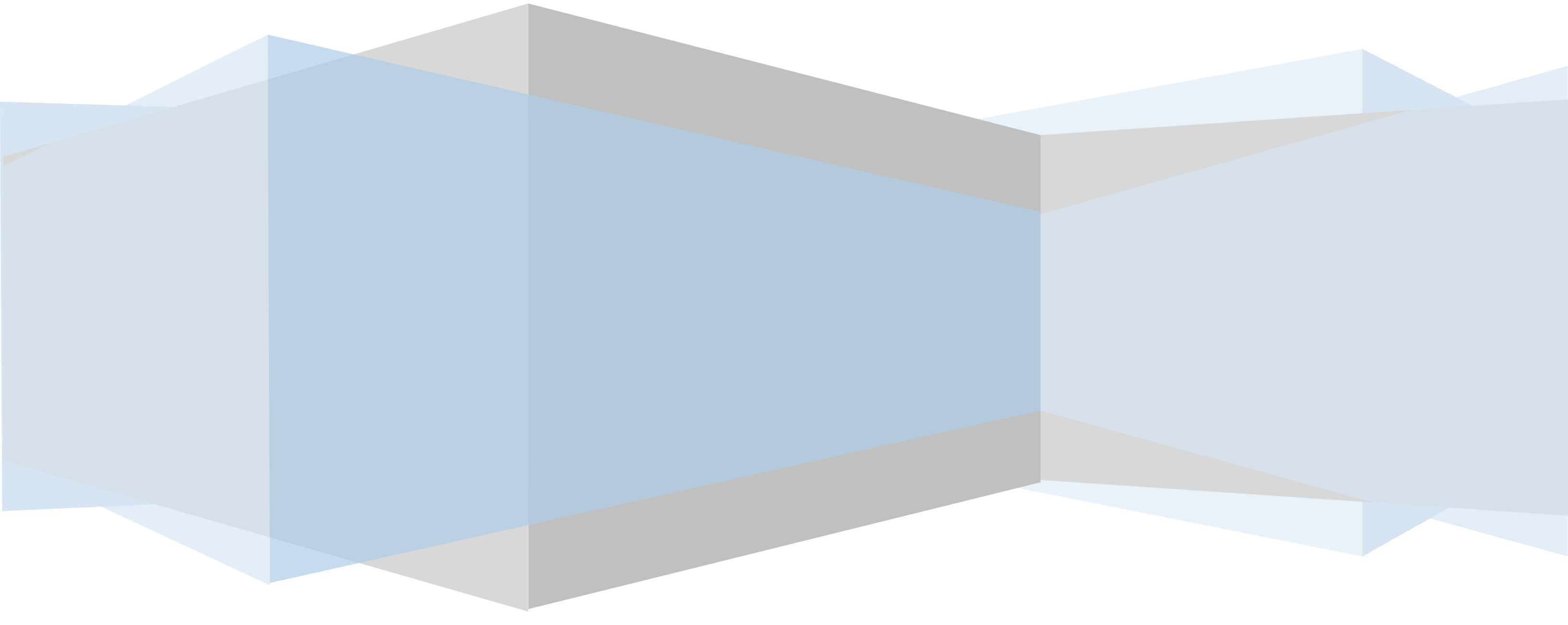

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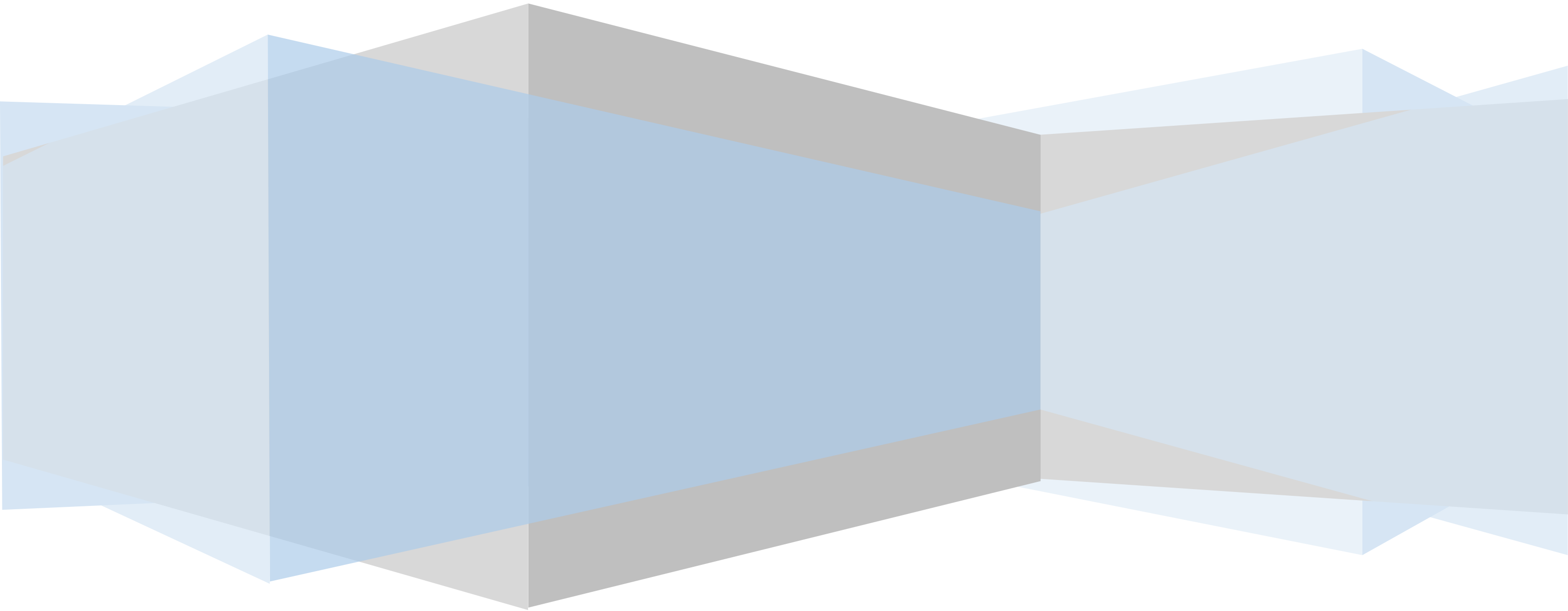

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ABBREVIATIONS

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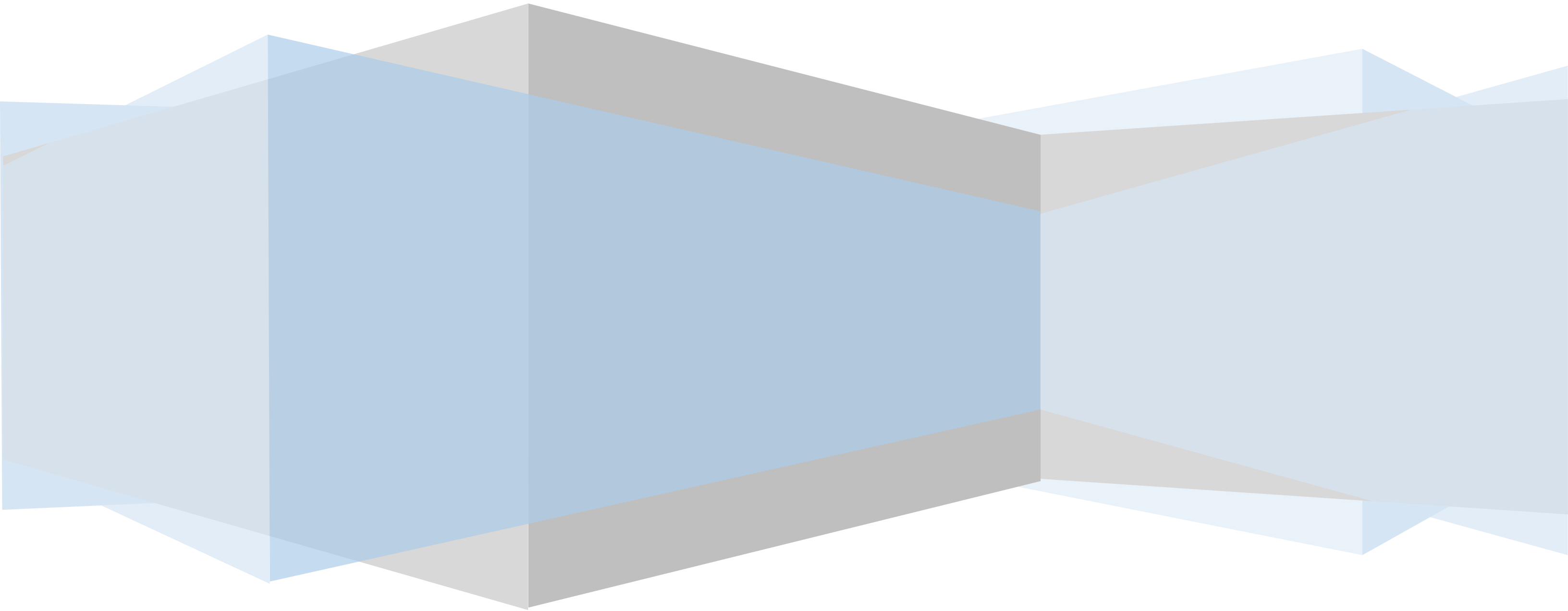

Abbreviations	Full form	Abbreviations	Full form
Ag	Silver	Pb	Lead
Al	Aluminium	PCA	Principal Component Analysis
As	Arsenic	PHA	Poly hydroxyalkanoate
ATEC	Average Toxic Element Concentration	PLI	Pollution Load Index
BLAST	Basic Local Alignment Search Tool	PPE	Personal Protective Equipment
Cd	Cadmium	Se	Selenium
CPCB	Central Pollution Control Board	TCLP	Toxicity Characteristic Leaching Procedure
CPU	Central Processing Unit	TOC	Total Organic Carbon
Cu	Copper	TSB	Two Step Bioleaching
Cr	Chromium	WEEE	Waste Electrical and Electronic Equipment
CRT	Cathode Ray Tubes		
EDXRF	Energy Dispersive X-ray Fluorescence	Au	Gold
EOL	End of Life	Pt	Platinum
EF	Enrichment Factor		
EPA	Environment Protection Agency	Zn	Zinc
Fe	Iron	Mn	Manganese
FTIR	Fourier Transform Infrared Spectroscopy	Si	Silicon
g	Gram	Be	Beryllium
HDPE	High Density Polyethylene	PC	Personal Computer
Hg	Mercury		
HCA	Hierarchial Cluster Analysis		
HPLC	High Performance Liquid Chromatography		
kg	Kilogram		
I_{geo}	Index of Geoaccumulation		
IWS	Indian Water Standard		
MDS	Multi-Dimensional Scaling		
m	Metre		
mL	Milli Litre		
µm	Micro metre		
MSW	Municipal Solid Waste		
MCAB	Mixed Culture of Acidophilic Bacteria		
Ni	Nickel		
O.D.	Optical Density		
OSB	One Step Bioleaching		

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ABSTRACT

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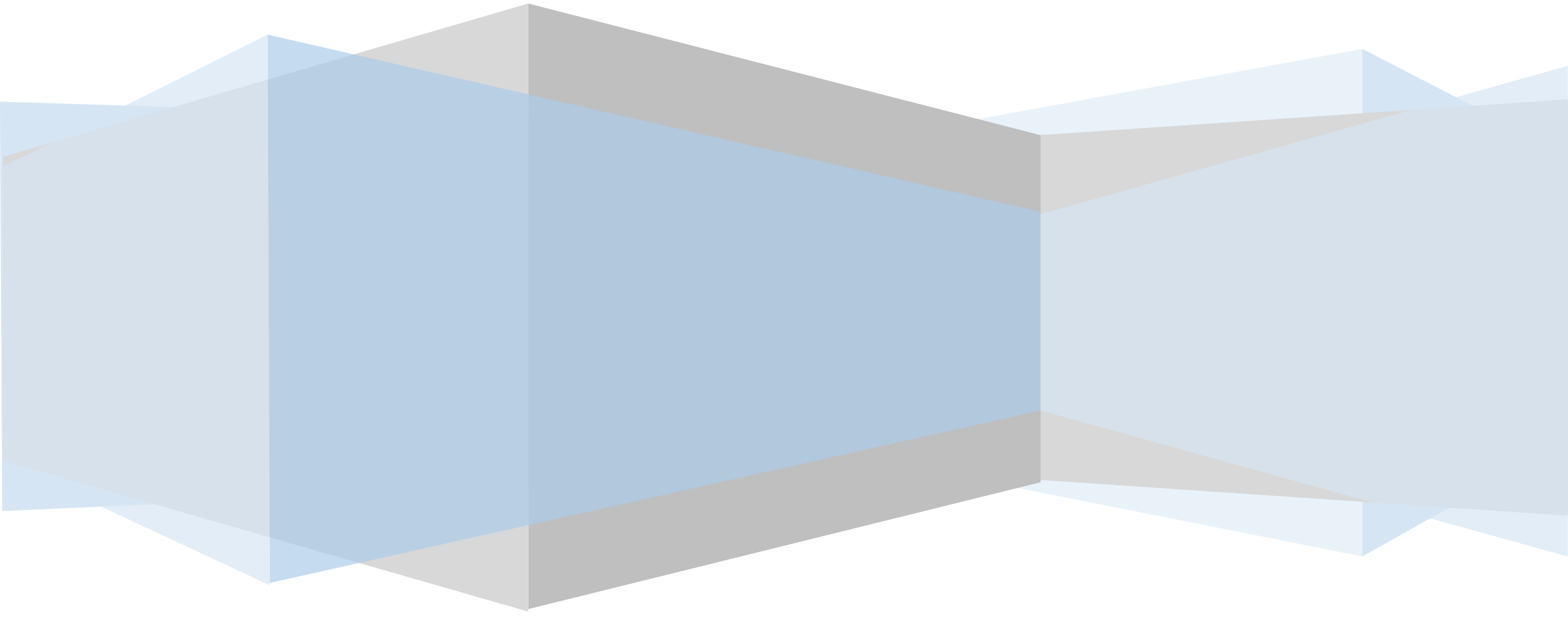

ABSTRACT

The ‘electronic industry’ is the largest and fastest growing industry in the world. The increasing “market penetration” in developing countries, “replacement market” in developed countries and “high obsolescence rate” are prominent reasons for rapid growing electronic waste (E-waste) streams. The increasing volumes of E-waste, in combination with the complex composition of these items and the resulting difficulties in treating them properly, are the cause of concern. In present scenario, gravity of the E-waste problem has increased due to the heterogeneity of the metals present, because of which the reprocessing of electronic waste is quite limited. Bioleaching is an eco-friendly approach to recover metals; uses lesser energy as compared to roasting and smelting. Metal recovery from E-waste by bioleaching process showed a good potential in present study. Both single and mixed cultures of cyanogenic bacteria were able to mobilize metals from E-waste of Printed Circuit boards (PCBs) with different efficiencies. *Chromobacterium violaceum* was capable to leach 79%, 69%, 46%, 9%, and 7% of Cu, Au, Zn, Fe, and Ag, respectively at an E-waste concentration of 1% w/v. Whereas mixture of *Chromobacterium violaceum* and *Pseudomonas aeruginosa* exhibited leaching of metals more than 83%, 73%, 49%, 13%, and 8% of total Cu, Au, Zn, Fe, and Ag, respectively. The optimum pulp density for the E-waste leaching with *Aspergillus niger* occurred at 1% (w/v) in one-step and two-step leaching process. An increase in the pulp density led to a decrease in the leaching yields. At 1% pulp density, *A. niger* leached 86%, 74%, 80%, and 50% of Al, Zn, Cu and Fe respectively in two-step bioleaching. At 5% pulp density, the bioleaching efficiency for Al, Zn, Cu and Fe decreased to 50–60%, 20-25%, 25-30% and 30-35%, respectively in both one step and two step bioleaching process. Mixed culture of acidophilic bacteria (MCAB) was used as inoculants in two step bioleaching to recover metals from metal concentrate of waste motherboards of personal computers. MCAB was able to mobilize 93% Cu, 87% Zn and 84.7% Al at 1% w/v E-waste concentration. Our survey of E-waste management in India (H.P., Chandigarh, Delhi, Meerut and Bangalore) alarms that, E-waste is a great challenge from both environment and technology point of view as its rate of growth is much higher than the rate of disposed, reuse and recycling. Socioeconomic, infrastructural, and legal reasons are the barriers of E-waste management in India. The majority of the E-waste recycling and recovery options practiced in India are rude and hazardous, causing severe environmental and occupational hazards. The impact assessment study in Mandoli industrial area of Delhi provides a snapshot of work place, environmental pollution (soil, water and plant contamination) of the industrial units and dump sites associated with the informal E-waste recycling units. Generally, Cu (6735 mg/kg) (exceeding the screening value for residential soil), Al (8822 mg/kg), Fe (4037 mg/kg), and Pb (2134 mg/kg) (exceeding the screening value for residential soil) were high in soils from recycling area as compared to village soils. From our toxicity characteristic leaching study; Pb was observed to be the most concerned heavy metal in E-waste, which was not detected in the leachate during the one year simulation study. The observation suggests that Pb may readily leach out from E-waste buried in MSW landfills, but is strongly retained by the solid waste around the E-waste through the mechanisms of adsorption and chemical complexation. In nut shell, higher metal bioleaching capabilities were achieved by using combinations of mixed cultures of cyanogenic bacterial strains. Precious metals such as gold were mobilized by cyanogenic bacteria which can be developed as an industrial application of bioleaching in alkaline conditions (biocyanidation). However, issue of heterogeneity of the electronic waste should be addressed at first hand to make the process of bioleaching cost-effective and successful at industrial scale. Precious metals were mobilized through bioleaching which might be considered as an industrial application for recycling of E-waste in the near future.

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CHAPTER 1

INTRODUCTION

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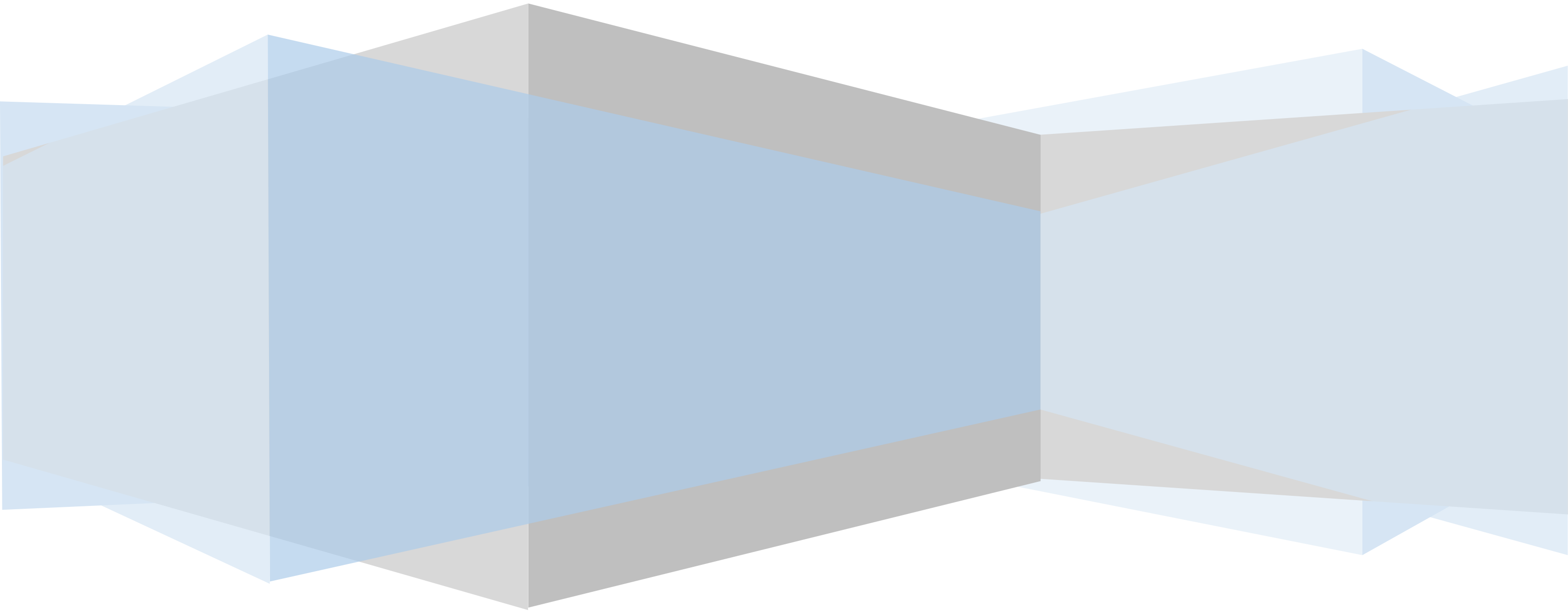

1.1 E-WASTE

Rapid technology change, a tremendous growth in the field of information technology and low initial costs have resulted in a fast-growing surplus of electrical and electronic equipment waste (WEEE) or electronic waste (e-waste) all over the world [1-4]. E-waste from electronic industry is growing at an alarming rate. E-waste lacks a standard definition. A number of countries and associations have come out with their own definitions, interpretations and usage of the term e-waste.

The e-waste management guidelines provided by Government of India defines “e-waste comprises of wastes generated from used electronic devices and house hold appliances which are not fit for their original intended use and are destined for recovery, recycling or disposal. Such wastes encompass wide range of electrical electronic devices such as computers, hand held cellular phones, personal stereos, including large household appliances including refrigerators, air conditioners etc” [5].

Internationally, the most accepted definition of e-waste is the definition as per the WEEE Directive which defines electronic waste, "e-waste" or "Waste Electrical and Electronic Equipment" ("WEEE") as the “waste material consisting of any broken or unwanted electrical or electronic appliances.” Technically, e-waste is only a subset of Waste Electrical and Electronic Equipment (WEEE). According to the Organization for Economic Cooperation and Development (OECD), any appliance using an electric power supply that has reached its end-of-life would come under WEEE (EU 2002) [6, 7]. The electrical and electronic equipment can be broadly categorized into following categories (EU 2002) [7]:

i. Large household appliances (refrigerator, freezer, washing machine, cooking appliances, etc.)
ii. Small household appliances (vacuum cleaners, watches, grinders, etc.)
iii. IT and telecommunication equipment (PCs, printers, telephones, etc.)
iv. Consumer equipment (TV, radio, video camera, amplifiers, etc.)
v. Lighting equipment (CFL, high intensity sodium lamp, etc.)
vi. Electrical and electronic tools (drills, saws, sewing machine, etc.)
vii. Toys, leisure, and sport equipment (computer/video games, electric trains, etc.)
viii. Medical devices

ix. Monitoring and control instruments (smoke detector, heating regulators, thermostat, etc.)
x. Automatic dispensers (for hot drinks, money, hot and cold bottles, etc.)

1.1.1 Components and composition of e-waste

Primary materials and components of “Electrical and Electronic Equipment” include metal, motor/compressor, cooling, plastic, insulation, glass, LCD, rubber, wiring/electrical, transformer, magnetron, textile, circuit board, fluorescent lamp, incandescent lamp, heating element, thermostat, FR/BFR-containing plastic, batteries, CFC/HCFC/HFC/HC, external electric cables, refractory ceramic fibers, radioactive substances and electrolyte capacitors. The diverse composition of these components may contain many different substances those falls under “hazardous” and “non-hazardous” categories. These consist of ferrous (38%) and non-ferrous metals (28%), plastics (19%), glass (4%), wood and plywood, printed circuit boards, concrete and ceramics, rubber and other items (11%) [8]. E-waste is a complex mixture of precious metals (Ag, Au, Pd, and Pt); base metals (Cu, Al, Ni, Sn, Zn, and Fe); heavy metals (Hg, Be, Pb, Cd, Cr (VI), As, Sb, and Bi); halogens and combustibles plastics (flame retardants) [9]. Presence of elements like Pb, Hg, As, Cd, Se, Cr and flame-retardants beyond threshold quantities in e-waste and its components drag them in to the category of hazardous waste. Besides toxic materials, e-waste also contains considerable quantities of valuables in the form of precious metals. E-waste is, therefore, both valuable as a source for secondary raw material and toxic if treated and discarded improperly [10].

A surprising 320 tons of Au and more than 7,500 tons of Ag are now used annually to make personal computers, cell phones, tablet computers and other new electronic and electrical products worldwide, adding more than $21 billion in value each year to the rich fortunes in metals eventually available through “urban mining” of e-waste [11]. Most of those valuable metals will be wasted, however; just 15% or less is recovered from e-waste today in developed and developing countries. E-waste contains precious metal “deposits” 40 to 50 times richer than ores mined from the ground [11].

1.1.2 Hazards involved with e-waste

The presence of toxic substances makes the e-waste a hazardous material. Table 1.1 provides a list of toxic materials present in the e-waste and their effects on human health. The impact of e-waste disposal on the environment and health depends on the nature of e-waste management practices followed. Uncontrolled burning, processing, and disposal can trigger serious health problems especially among those directly exposed. The conventional technologies of waste management include landfills, open-air-burning and incineration. Many of the materials found in e-waste generate hazardous toxic substances on burning that are dispersed in the atmosphere. This is particularly true for open-air burning, which releases several toxins including various carcinogens and neurotoxins, e.g. dioxins and furans into the air. The Cu in the e-waste can catalyze the production of dioxins, PBDDs, and PBDFs. The release of resultant pollutants can trigger a host of illnesses in humans. It can also result in loss of property. In landfills such leachate can contaminate ground water resources. The vaporization of volatile compounds is yet another environmental concern.

1.1.3 Global scenario and management of e-waste

Rapid technological innovations encourage the purchase and frequent upgrading of electronics products. This increase is directly linked to rise in the amount of used electronic equipments and thus the waste generated from it. E-waste is becoming an important issue in many parts of the world. Some 20 to 50 million metric tons of e-waste is generated globally every year [12]. Given the increasing quantities and economic value (due to the presence of base and precious metals) attached to these products at the end of life, recycling of e-waste is increasingly catching attention. At the same time, due to the presence of hazardous substances, unsafe handling of e-waste is also a growing matter of concern. It has been estimated that about 20 million computers enter the market every year in the USA and 12 million computers are disposed every year, and out of these, only about 10% are remanufactured or recycled [13]. The destination of un-recycled e-waste in the developed countries includes landfills, incinerators or export to developing countries. Due to concerns over environmental pollution as a result of the toxic and hazardous materials contained in e-waste, concerted efforts have been made at diverting these toxic materials from landfill. Today, a large proportion of European and North American e-waste are exported in some cases illegally to Asia, with China being one but not the only destination [14]. About 50-80% of e-waste from the industrialized countries is exported to recycling centers in developing countries such as China, India, Pakistan, Vietnam, and the Philippines because of the lower wages for labor and less functional/lenient environmental regulations in these countries [15]. Recently, e-waste trade has been increasing in African countries too [16].

Table 1.1: Materials of health concern in e-waste

Name	Use/Location	Health Effects
Plastics	Includes organics and oxides (other than silica)	PBDE-endocrine disruption and affects on fetal development; PBBs-increased risk of cancers of the digestive and lymph systems
Pb	Metal joining, radiation shield/CRT, PWB (printed wiring board)	Damage to central and peripheral nervous system, circulatory system, and kidneys; effects on endocrine system, serious adverse effects on brain development
Al	Structural, conductivity, CRT, PWB, connectors	Skin rashes, skeletal problems, and respiratory problems including asthma; linked to Alzheimer's Disease
Ga	Semiconductor/PWB	Clear evidence of carcinogenesis in experimental animals
Ni	Structural, magnetivity, CRT, PWB	Allergic reactions, asthma, chronic bronchitis, impaired lung function; reasonably anticipated to be a human carcinogen
V	Red phosphor emitter/CRT	Lung and throat irritation
Be	Thermal conductivity, PWB, connectors	Lung damage, allergic reactions, chronic beryllium disease; reasonably anticipated to be a human carcinogen
Cr	Decorative, hardener, (steel) housing	Ulcers, convulsions, liver and kidney damage, strong allergic reactions, asthmatic bronchitis, may cause DNA damage; a known human carcinogen
Cd	Battery, blue-green phosphor emitter/housing, PWB, CRT	Pulmonary damage, kidney disease, bone fragility; reasonably anticipated to be a human carcinogen
Hg	Batteries, switches/housing, PWB	Chronic brain, kidney, lung, and fetal damage; increases in blood pressure and heart rate, allergic reactions, effects on brain function and memory; a possible human carcinogen
As	Doping agents in transistors/PWB	Allergic reactions, nausea, vomiting, decreased red and white blood cell production, abnormal heart rhythm; inorganic arsenics a known human carcinogen
Si	Glass, solid state devices/CRT, PWB	Respirable size crystalline silicacan cause silicosis, emphysema, obstructive airway disease, and lymph node fibrosis; a known human carcinogen

More often the developing countries lack the infrastructure and technical capacity necessary for safe disposal of such wastes. The e-waste recycling and disposal methods in countries like India, China and Pakistan often pollute the environment with processes like open burning of plastic waste and dumping of the recycled remains in rivers [17]. Currently, the majority of e-waste in China, India and other developing countries are processed in backyards or small workshops using primary methods such as manual disassembly and open burning [18]. The appliances are stripped of their most valuable and easily extracted components such as PWB, CRTs, cables, plastics, metals condensers, and the worthless materials such as batteries, liquid crystal displays (LCDs) or wood. These fractions are processed to directly reusable components and secondary raw materials in a variety of refining and conditioning processes. The remaining parts are dumped or stockpiled directly.

1.1.4 Global initiatives for e-waste management

In the international arena several countries and group of countries have framed laws and policies to manage and regulate the adverse effects of e-waste. Countries in Europe and Japan have been the leader in formulating policies/laws/regulations for WEEE/e-waste followed by their institutionalization and implementation. In 2003, two main directives were formulated by the European Union for e-waste reduction, recycle and reuse. These are "Waste Electrical and Electronic Equipment Directive" (also known as WEEE Directive) [19] and "The Restriction of the use of certain Hazardous Substances in Electrical and Electronic Equipments" (called the RoHS Directive) [20]. These two regulatory frameworks being the source of inspiration for legislation by a number of countries across the world, aim to help reduce the overall amounts of e-waste by pushing for adoption of environmentally friendly disposal methods. WEEE directives provide a regulatory basis for collection, recovery and reuse/ recycling targets in EU. The fundamental principle of WEEE directive is "Extended Producer Responsibility", where producers are responsible for WEEE/e-waste take back. Those European countries, which are not part of EU either follow EU directive or more stringent standards based on WEEE/ e-waste management. Majority of countries have regulations similar to WEEE directives [19]. Countries like Japan have regulations focused on "Reuse, Recycling and Recovery". Other countries like Canada and Australia are developing their systems based on the similar principles of "Extended Producer Responsibility".

RoHS Directive, in effect from July 1st 2006, aims to reduce the use of hazardous substances in electronic and electrical equipments to the maximum extent possible [20]. The directive provides that new electrical and electronic equipment put on the EU market must not contain Pb, Hg, Cd, Cr, or the flame retardants PBB and PBDE beyond the prescribed limits. The products which are exempted from the requirements of the Directive include mercury in certain types of fluorescent lamps, Pb in the glass of cathode ray tubes, electronic components and fluorescent tubes, Pb in electronic ceramic parts, and Cr as an anti-corrosion of the carbon steel cooling system in absorption refrigerators.

1.1.5 Indian scenario of e-waste

The electronic industries have emerged as the fastest growing segment of Indian industries in terms of production, internal consumption, and export. Within this segment, the IT industry is a prime mover with an annual growth rate of 42.4% between 1995 and 2000 [21]. The Indian IT industry has a prominent global presence today largely due to the software sector. Promotion of the software industry and protection of the hardware industry from external competition has resulted in this skewed growth. More recently however, policy changes have led to a tremendous influx of leading multinational companies into India to set up manufacturing facilities, and research and development centers for the hardware, as well as the software sectors. Besides IT industrial growth, electronic appliances sales and purchase in individual households has also increased tremendously. In 2002 there was a 53.1% increase in the sales of domestic household appliances compared to 4 years before. The growth in personal computers (PC) ownership per capita between 1993 and 2000 was 604% compared to a world average of 181% [22]. The quantity of obsolete PCs from individual households is relatively small; however, as the population of the country is accelerating at an alarming rate and the use of computers at household level increases, it is expected to generate huge quantities of obsolete PCs in the years to come. An estimated 30,000 computers become obsolete every year from the IT industry in Bangalore alone and was attributed to an extremely high obsolescence rate of 30% per annum [23]. The global annual generation of e-waste is given in Table 1.2. It can be seen from the table that India is ranked fourth amongst the selected countries. The annual e-waste generation in India has been estimated to be 146,180 tons based on selected electrical and electronic equipment items [24]. E-waste quantity is expected to be more than 800,000 tons by this year [25]. In

India, more than 60% of its e-waste is generated from 65 cities. The top 10 cities that generate e-waste are Mumbai, Delhi, Bangalore, Chennai, Kolkata, Ahmadabad, Hyderabad, Pune, Surat and Nagpur [26].According to the study conducted by the NGO Toxic Link, the Mumbai city faces grave health and environmental risk posed by a whopping 19,000 tons of e-waste produced here apart from a good amount of same being imported clandestinely [27]. About 25,000 workers are employed at scrap-yards in Delhi alone, where 10,000 to 20,000 tons of e-waste is handled every year [28].

1.1.6 Present e-waste management system in India

In India, e-waste ends up mainly with recyclers mushroomed in large numbers on the outskirts of cities like Delhi, Mumbai, Bangalore, Chennai, etc. Most of the operations related to e-waste such as collections, segregation, dismantling, recycling, and disposals are performed manually in India. In absence of the adequate technologies and equipment, most of the techniques used for the recycling/treatments of e-waste are very raw and dangerous [29].

Recycling of e-waste is a market-driven and is a growing industry in India. The waste collectors pay consumers a positive price for their obsolete appliances. The small collectors in turn sell their collections to traders who aggregate and sort different kinds of waste and then sell it to recyclers, who recover the metals [30]. They sell secondhand parts either to computer assemblers in the grey market or to buyers directly. Furthermore, the recyclers lack proper technical knowledge in that they have adopted very raw, primitive methods of the recycling process. A majority of them do not have any awareness on aspects of Safety, Health and Environment (SHE) that makes the overall situation extremely hazardous for those who are actively associated with the primary operation process. Apparently, they cannot afford to adopt best affordable technologies and this is what makes all the difference between a process in a developed economy and in a developing (transition) economy.

Most of them work with their bare hands, extracting precious metals such as Au and Ag using very primitive chemical processes by children and women indiscriminately. Thus, the rudimentary working conditions give rise to the toxic substances that pose severe threats, not only to those who are engaged directly in the operations, but also to the surrounding environment.

Table 1.2: E-waste generation in selected nations

Country	Categories of appliances counted in E-waste	Generation (Tons per annum)	Rank	Reference
Switzerland	Office and telecommunications equipment, consumer entertainment electronics, large and small domestic appliances, refrigerators, fractions	66,042	7	[17]
Germany		1,100,000	2	[25]
UK		915,000	3	[26]
USA	Video products, audio products, computers and telecommunications equipment	2,124,400	1	[27]
Taiwan	Computers, home electrical appliances (TVs, washing machines, air conditions, refrigerator)	14,036	9	[28]
Thailand	Refrigerators, air conditioners, TVs, washing machines, computers	60,000	8	[29]
Denmark	Electronic and electrical appliances including refrigerators	118,000	5	[30]
Canada	Computer equipment and consumer electronics	67,000	6	[31]
India	Electronic and electrical appliances	146,180	4	[32]

Emitted toxic fumes, acid solutions, and hazardous ashes are some of the threats. Some of the wastes including lead are dumped along with the municipal waste and then burnt in the open air. A huge volume of unwanted components and residues are dumped in the near vicinity of the recycling sites that diffuses out to contaminate the broader area. Table 1.3 shows the risks involved in unsafe handling of e-waste [31]. First column summarizes the typical pathways for the release of some of pollutants from e-waste; second column contains in brief the details of PCB recycling an activity which has maximum risk of occupational and environmental hazards associated with it; and the third column summarizes the common processes of recycling e-waste and potential occupational and environmental hazards associated with those processes. Besides, the recycling methods adopted are only helpful in the recovery of merely a few metals viz., Cu, Au, Ag, Al, Fe, Pb, and plastics. The present technology is of no use for the recovery of other components, for instance, glass or elements like Pt, Pd, and Ni. Thus in India, the e-waste is generated in huge amounts and there is no proper management method to handle this e-waste and also people are unaware of the health hazards and pollution these e-waste generate. This could be perhaps due to (i) the low level of awareness among workers regarding the hazards of the chemicals, (ii) adopting primitive process in which they are exposed to, (iii) the minimum protection and safety measures they are obliged to take, and (iv) the lack of formal guidelines as well as a lax enforcement of existing environmental laws.

Table 1.3: Typical pathways for release of pollutants from e-waste

Heavy metals	Dioxins and furans	Acids
• Dust generated during mechanical treatment, for example, the dismantling and crushing of e-waste. • Flue gas released during thermal treatment, for example, the release of metals from compounds during the incineration of plastic. • Vaporization wherein metals are released from compounds in an acid bath	• Dioxins and furans are emitted during the thermal treatment of e-waste. • The combustion of cable insulation containing PVC in order to recycle copper wiring • The incineration of epoxy resin containing flame retardant from circuit boards in order to recycle the metal they contain	• Released in the form of vapour when metals are released from compounds. May also get distributed throughout the surrounding area in the following ways • Factory air and dust being blown into the vicinity • Leaching through waste water and seepage • Release of flue gas into the atmosphere as a result of open incineration of furnace combustion

1.1.7 Status of e-waste initiatives in India

The growing hazards of e-waste in India, as discussed above, were noticed by the government, industry, users, and NGOs and felt it necessary that the treatment of e-waste for recovery shall follow environmentally sound technologies. The Ministry of Environment of Forests (MoEF), Government of India (GOI) has initiated activities for the management of e-waste in India through the International Co-operation and Sustainable Division-II (IC and SD-II). IC and SD-II has implemented the Advisory Services in Environment Management (ASEM) project with the technical assistance of German Technical Co-operation (GTZ) [32]. This is one of the major activities launched by the ASEM programme. Apart from the initiatives under taken in ASEM project, the MoEF has been instrumental in promoting the e-waste issues, with the help of the Confederation of Indian Industries and Canadian Agency for International Development (CII-CIDA) project under the aegis of the Indo-Canada Environment Programme. In continuation, these initiatives were followed with a dialogue with EMPA and GTZ that resulted in a collaborative programme entitled "Indo-Swiss-German e-waste Initiative" [33]. The marshaled objective and scope of this initiative include: (i) Management of e-waste in an environmentally sound manner so as to reduce the risks to the society as also to abate the pollution of the environment owing to unsafe e-waste handling; (ii) development of skills to all concerned through knowledge transfer by means of seminars, workshops, campaign, etc.; and (iii) initially, selecting the existing informal recyclers as the target group for evolving methodologies to create an integrated formal category. As reported by Widmer (2006), this program has been conceived with various supports as: (1) National support for WEEE Strategy and Coordination Work Group; (2) Local and regional support, for instance, from Delhi, Bangalore, and Mumbai; (3) Industry Initiatives from Manufacturers Association of Information Technology (MAIT), E-Parisaraa Pvt. Ltd.; (4) International Support, primarily from Germany and Switzerland as also from UNEP (for Environment and E-waste in India) and from EU (for the Creation of Optimum Knowledge Bank for Efficient E-Waste Management in India) [34].

E-waste (Management and Handling) rules, 2011 notified under the Environment (P) Act, 1986 [35]. The objective of these rules is to put in place an effective mechanism to regulate the generation, collection, storage, transport, import, export, environmentally sound recycling, treatment and disposal reducing wastes destined for final disposal. These rules also have mandatory provisions like extended producer responsibility (EPR), collection system and registration of recyclers and reduction in the hazardous substances (RoHS). Still there are so many concerns and challenges associated with e-waste management in India.

1.1.8 E-waste concerns and challenges in India

i. Accurate figures are not available for rapidly increasing e-waste volumes generated domestically and by imports.
ii. Low level of awareness among manufacturers and consumers of the hazards of incorrect e-waste disposal
iii. Major portion of e-waste is processed by the informal (unorganized) sector using rudimentary techniques such as acid leaching and open-air burning, which results in severe environmental damage
iv. E-waste workers have little or no knowledge of toxins in e-waste and are exposed to health hazards
v. Inefficient recycling processes result in substantial losses of material value and resources

1.2 RECYCLING OF E-WASTE

Waste electric and electronic equipment (WEEE), or electronic waste (e-waste), has been taken into consideration not only by the government but also by the public due to their precious and hazardous material contents [36-40]. Currently, the main options for the treatment of e-waste are involved in reuse, remanufacturing, and recycling, as well as incineration and land filling. In many cases, electronic equipment which is no longer useful to the original purchaser still has value for others. In this case, equipment can be resold or donated to schools or charities without any modification. Reuse of end of life (EOL) electronic equipment has first priority on the management of e-waste since the usable lifespan of equipment is extended on a secondary market, resulting a reduction of the volume of treated waste stream. Remanufacturing is a production-batch process where used products or cores, are disassembled, cleaned, repaired or refurbished, reassembled and tested to produce new or like-new equipment's [41]. Recycling means the reprocessing in a production of the waste materials for the original purpose or for other purposes. Recycling of e-waste involves disassembly and/or destruction of the EOL equipment in order to recover materials.

The hierarchy of treatment of e-waste encourages reuse of the whole equipment first, remanufacturing, then recovery of materials by recycling techniques, and as a last resort, disposal by incineration and land filling. Recycling of e-waste is an important subject not only from the point of waste treatment but also from the recovery aspect of valuable materials. The US Environmental Protection Agency (EPA) has identified seven major benefits, such as saving in energy and reduction in pollutions when scrap iron and steel are used instead of virgin materials. Using recycled materials in place of virgin materials results in significant energy savings [37, 42].

1.2.1 Steps of recycling

Currently, recycling of e-waste can be broadly divided into three major steps [37]:

- ***Disassembly:*** selectively disassembly, targeting on singling out hazardous or valuable components for special treatment, is an indispensable process in recycling of e-waste;
- ***Upgrading:*** using mechanical processing and/or metallurgical processing to up-grade desirable materials content, i.e. preparing materials for refining process;
- ***Refining:*** in the last step, recovered materials are retreated or purified by using chemical (metallurgical) processing so as to be acceptable for their original using.

1.2.2 Existing recycling processes

1.2.2.1 Mechanical recycling of e-waste

Mechanical process and disassembly are mainly used for the pre-treatment of e-waste for upgrading the valuable materials content. Mechanical recycling of e-waste has been extensively reviewed by Cui and Forssberg in 2003 [37], and has been investigated by different researchers [43-49]. E-waste is diverse and complex, in terms of materials and components makeup as well as the original equipment's manufacturing processes. Characterization of this waste stream is of paramount importance for developing a cost-effective and environmentally friendly recycling system. Selective disassembly, targeting on singling out hazardous and/or valuable components, is an indispensable process in the practice of recycling of e-waste. Mechanical/physical processing, based on the characterization of e-waste, provides an alternative means of recovering valuable materials. Mechanical processes, such as screening, shape separation, magnetic separation, Eddy current separation, electrostatic separation, and jigging have been widely utilized in recycling industry. However, recycling of e-waste is only beginning and mechanical recycling cannot efficiently recover precious metals.

In the last refining step, recovered metals are melted or dissolved by using metallurgical techniques, including pyrometallurgical processing and hydrometallurgical processing for removal of impurities. The primary hazards of mechanical treatment methods are associated with the size reduction and separation steps. Shredding, grinding or other size reduction processes generate dusts of the components being shredded in the facility. The composition of the dusts formed during this process includes plastics, metals, ceramic, and silica (glass and silicon dust) [49]. Separation processes are associated with the same hazard of dust, as during the step shredded particles are handled. The dusts may pose an inhalation and dermal exposure hazard to workers as well as risk of environmental contamination. There is scientific evidence that hazardous substances are released during shredding. Shredding of plastics flame retarded with BFRs leads to the release of the chemicals into the ambient environment. BFRs, particularly PBDEs, were detected in the grams per kilogram concentration range in the fine dust fraction recovered in the off-gas purification system of a Swiss recycling plant engaged in mechanical treatment of e-waste [50]. This emphasizes the high potential for BFR emissions during the mechanical processing of e-waste. Takigami et al. (2006) measured concentrations of BFRs, including PBDEs, TBBPA and hexabromocyclododecane (HBCD), and polybrominated dibenzo-p-dioxins/dibenzofurans (PBDDs/Fs) in the air of a TV recycling facility [51].

1.2.2.2 Pyrolysis processes

Pyrolysis can make the separation of the organic, metallic, and glass fiber fractions of PCBs much easier and therefore make e-waste recycling more viable. When e-wastes were heated to 800℃ in an oxygen free atmosphere, the organic fraction decomposed to form volatile oils and gases, leaving behind a metal and glass fiber fraction. For example, after pyrolysis, waste computer PCBs break down into, on average, 68.9 wt% residue which contains metals, 22.7 wt% oil, and 4.7 wt% gas [52].

Metals contained in the residue could then be recovered by traditional routes, such as hydrometallurgical or hydrometallurgical processes. The organic gases can be used as either a chemical feedstock or a fuel [52, 53].

1.2.2.3 Pyrometallurgical process

Pyrometallurgical processing, including incineration, smelting in a plasma arc furnace or blast furnace, drossing, sintering, melting and reactions in a gas phase at high temperatures [54-56] has become a traditional method to recover non-ferrous metals as well as precious metals from e-waste in the past two decades. In the process, the crushed scraps are burned in a furnace or in a molten bath to remove plastics, and the refractory oxides form a slag phase together with some metal oxides. Pyrometallurgical technology is employed by many leading recycling companies, such as Boliden, Dowa, Umicore and X-Strata in their recycling systems [57]. Umicore is able to recycle seventeen metals, including seven precious metals [58]. However, pyrometallurgical treatment raises concerns regarding possible formation of brominated and chlorinated di-benzo furans and dioxins in burning processes due to the presence of halogens in the plastic parts of electronic waste [59].

1.2.2.4 Hydrometallurgical process

As discussed above, precious metals contribute the most value in electronic scraps. From an economic point of view, recovery of precious metals from e-waste is most attractive. In the past two decades, the most active research area on recovery of metals from electronic scraps is recovering precious metals by hydrometallurgical techniques [60-68]. Comparing with the pyrometallurgical processing, hydrometallurgical method is more exact, more predictable, and more easily controlled [69]. The main steps in hydrometallurgical processing consist of a series of acid or caustic leaches of solid material. The solutions are then subjected to separation and purification procedures such as precipitation of impurities, solvent extraction, adsorption and ion-exchange to isolate and concentrate the metals of interest. Consequently, the solutions are treated by electro refining process chemical reduction, or crystallization for metal recovery [70–74].

Despite the high recovery rate of acid leaching, it has many disadvantages, which prohibit its wide industrial application. For example, it requires special stainless steel and rubber-lined equipment, which increase equipment costs. Moreover, the chlorine gas produced in the reactions is highly poisonous and may cause serious health risks [75]. These processes are also expensive because more investment is necessary to set up highly efficient facilities [76], there is a high consumption of energy and they are not regarded as an economical way to extract valuable components from e-waste [77, 78].

1.2.2.5 Bio-hydrometallurgical processes

In modern recycling industry several new processes are used which are easily applicable and economical and environment friendly. Application of bio-hydrometallurgical processes to extract different metals is one of the above said new age techniques. The area of discipline in which microbes are used to extract different metals from e-waste and low grade ores, is collectively termed as bio-hydrometallurgy. Bioleaching is a part of biohydrometallurgy emerging as commercial exploitable technology applicable for metal extraction from e-waste.

Bioleaching

Bioleaching is a process in which naturally occurring microorganisms or their metabolites dissolute metals from their mineral sources. The dissolution is done by means of chemical or bacterial oxidation.

Why bioleaching?

Bioleaching processes have so many advantages over other leaching processes for recovery of metals from e-waste. Bioleaching is considered to be more environmentally benign process than other leaching processes, because it does not include noxious off-gasses or toxic effluents. Other advantages are simplicity of plant operation and maintenance, low capital and operating costs, and applicability to various metals [78-80].

Microorganisms used in bioleaching

For biochemical leaching, both autotrophic and heterotrophic bacterial and fungal species have been used for different ores and solid waste.

The bacteria belonging to the genus *Thiobacillus* are aerobic and acidophilic chemolithotrophs which play an important role in the bioleaching of metals from sulphidic minerals. They have been the most extensively studied microorganisms in terms of their physiological and biochemical characteristics. These bacteria derive their energy requirements from oxidation of iron and sulfur compounds. Ferric iron and sulphuric acid produced in the system bring about metal solubilisation. In the process both autotrophic and heterotrophic microorganisms tested for metal removal or substrate degradation are species of *Acidithiobacillus, Bacillus, Pseudomonas, Sulpholobus, Leptospirillum, Acidophillum, Cyanobacteria, Aspergillus, Penicillium, Rhizopus, Streptomyces* etc. Specifically, a consortium of microorganisms namely, *Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans, Leptospirillum ferrooxidans, Sulpholobus* sp. and thermophilic bacteria including *Sulpholobus thermosulphidoxidans* and *Sulpholobus brierleyi* are known to be involved in bioleaching.

Heterotrophic bacteria and fungi which require organic supplements for growth and energy supply may contribute to metal leaching. As in case of manganese leaching, metal solubilization may be due to enzymatic reduction of highly oxidized metal compounds [81] or is effected by the production of organic acids (e.g. lactic acid, oxalic acid, citric acid, gluconic acid) and by compounds with at least two hydrophilic reactive groups (e.g. phenol derivatives) which are excreted into culture medium and dissolve heavy metals by direct displacement of metal ions from the ore matrix by hydrogen ions and by formation of soluble metal complexes and chelates [82]. The heterotrophic microorganisms do not have any benefit from the metal leaching. Among the bacteria, members of genus *Bacillus* are most effective in metal solubilization, and in fungi the genera *Aspergillus and Penicillium* are the most important ones.

Biodiversity of bioleaching microbes have been observed according to a variety of conditions in leaching environment. There are three different kinds of microorganisms used for bioleaching studies on the basis of optimum temperature for the growth of microorganisms *i.e.* mesophiles, moderate thermophiles, and extreme thermophiles. *Aicidithiobacillus ferroxidans,* and *Acidithiobacillus thioxidans* are two important microorganisms in bioleaching processes that operate at 40ºC or less. Besides mesophilic and moderately thermophilic bacteria (*Sulfobacillus thermosulfidooxidans* and *Sb. acidophilus*), extreme thermophilic bacteria were also used for the bioleaching processes. Several studies with mesophilic microorganisms such as *Acidithiobacillus ferrooxidans* and *Leptaspirillum ferrooxidans* have shown very low Cu leaching rates [83, 84]. However when thermophilic microorganisms are used leaching rates are considerably enhanced, due to high temperatures, higher metal tolerance capacity and the metabolic characteristics of these type of microorganisms [85]. A variety of thermophilic microorganisms (especially *Sulfolobus* sp.) has been enriched and isolated from bioleaching environments [86, 87]. Temperature optima for growth and metal leaching were in the range between 65 and 85°C. Although Cu extraction from mine tailings is more efficient using thermophilic instead of mesophilic organisms, extremely thermophilic microorganisms show a higher sensitivity to Cu and to high pulp densities in agitated systems, therefore, limiting some practical applications [87].

Bioleaching mechanism

Mineralytic effects of bacteria and fungi on minerals are based mainly on three principles, namely acidolysis, complexolysis, and redoxolysis. Microorganisms are able to mobilize metals by

i. The formation of organic or inorganic acids (protons);

ii. Oxidation and reduction reactions; and

iii. The excretion of complexing agents. Sulfuric acid is the main inorganic acid found in leaching environments.

It is formed by sulfur-oxidizing microorganisms such as *Acidithiobacilli* sp. A series of organic acids are formed by bacterial (as well as fungal) metabolism resulting in organic acidolysis, complex and chelate formation [88]. A kinetic model of the coordination chemistry of mineral solubilization has been developed which describes the dissolution of oxides by the protonation of the mineral surface as well as the surface concentration of suitable complex forming ligands such as oxalate, malonate, citrate, and succinate [89]. Proton-induced and ligand-induced mineral solubilization occurs simultaneously in the presence of ligands under acidic conditions.

Types of bioleaching

The efficiency of bio-processing in variably increases with operating time, as microorganisms adapt to their environment and also bioleaching processes. Bacterial dissolution of metals is thought to involve two mechanisms: direct and indirect.

- ***In direct leaching***, bacteria attach themselves to the metal ore or solid waste. Through a biochemical reaction known as oxidation, the bacteria then change the metal ores or solid waste into soluble metals.
- ***In indirect*** leaching the bacteria need not to be in contact with the mineral surface. The bacteria only have a catalytic function because they accelerated the reoxidation of ferrous iron to ferric iron which takes place very slowly in the absence of bacteria.

Factors affecting bioleaching

Like all other life processes, the leaching of e-waste by microbes is influenced by environmental factors. The details about the different factors are described in table 1.4 (Table-1.4).

Challenges with bioleaching of e-waste

i. Due to bioleaching being a very slow process as compared to other leaching processes, this method sometimes not economical.

ii. Toxic chemicals are sometimes produced in the process. Sulfuric acid and H^+ ions that have been formed can leak into ground and surface water turning it acidic, causing environmental damage.

iii. Heterogeneity and complex character of e-waste provide toxic environment to bioleaching microorganisms

Table 1.4: Main factors affecting bioleaching

Factor	Effect	Reference
Physicochemical		
Temperature	Affects leaching rate, microbial composition and activity, affects the formation of precipitates	[90-95]
pH	Affects microbial growth and formation of precipitates	[90-94]
Oxygen reaction	Electron acceptor needed in chemical and biological oxidation, influence on microbial activity, may become limiting factor because of the low solubility in water especially at elevated temperatures	[90-95]
Microbiological		
Microbial diversity cultures	Mixed cultures tend to be more robust and efficient than pure	[91, 95, 96]
Population density	High population density tends to increase the leaching rate	[91]
Metal tolerance	High metal concentrations may be inhibit the microbial activity	[92, 93]
Adaptation ability	Adapted strains exhibit generally better leaching efficiencies, indigenous bacteria growing in particular environment and likely to be those best adapted to that environment	[91, 95-97]
Minerals		
Composition	Provides electron donor and trace elements	[90]
Particle size	Affects the available mineral/liquid contact area	[90, 91, 98]
Surface area	Leaching proportional to the increase in mineral surface area	[91]
Porosity	Cracks and pores in the particles give rise to the internal area	
Presence of other metal sulfide	Mineral having the lowest potential is generally oxidized first	[90-94]

Bioleaching of e-waste: Research status

Bioleaching has been successfully applied in recovery of metals from metallic sulfides, which are the major bearing minerals for many base and precious metals, by the use of bacterially assisted reactions [99]. The extraction of metals such as Co, Mo, Ni, Pb, and Zn from sulfidic ores by bioleaching is technically feasible [100]. However, today only Cu and Au are the metals that are industrially produced in significant proportions by this way [99]. Although, this process has been successfully applied for the leaching of metals from ores [101], data pertaining to its application for the extraction of e-waste is still scanty.

Faramarzi et al. (2004) [108] reported their preliminary investigation on the feasibility of recovery of Au from printed circuit boards by bioleaching process. Gold containing pieces (5mm X 10mm) were obtained by manually cutting printed circuit boards followed by manual sorting. Each piece contained approximately 10 mg of Au. Using *Chromobacterium violaceum,* it is demonstrated that Au can be microbially solubilized from printed circuit boards. The maximum dicyanoaurate $[Au(CN)^{2-}]$ measured corresponds to a 14.9% dissolution of the initially Au added.

Microbiological processes, applied to mobilize metals from electronic waste materials were carried out by Brandl et al. (2001) [91]. Dust collected from shredding processes of electronic scrap was used in the investigation. The leaching experiments by using a mixed culture of *Thiobacillus ferrooxidans* and *T. thiooxidans*on electronic scrap showed that the addition of elevated amounts of scrap led to an increase of the initial pH due to the alkalinity of electronic scrap. In order to reduce toxic effects on the microorganisms, a two-step process was introduced. In the first stage, biomass was produced in the absence of electronic scrap. Subsequently, electronic scrap was added in different concentrations and the cultures were incubated for an additional time period. The leaching results showed that at scrap concentrations of 5 and 10 g/L, respectively, *Thiobacilli* were able to leach more than 90% of the available Al, Cu, Ni, and Zn. At higher concentration, metal mobilization was reduced, especially for Aland Cu. Ni and Zn showed much better results with mobilization of 60% and 95%, respectively. In all cultures, Pb and Sn were not detected in the leachate. It is proposed that Pb precipitated as PbSO4, and Sn precipitated probably as SnO. That was confirmed by applying a computer program named MICROQL to model the speciation of dissolved components under the given conditions [91]. An Atomic Absorption Spectroscopy (AAS) study of this kind of precipitates formed during the bioleaching of electronic scrap by *S. thermosulfidooxidans* confirmed the presence of lead and Sn in the precipitates [97].

The feasibility for using fungi (*Aspergillus niger and P. simplicissimum*) to leach metals from electronic scrap by a two-step process was also investigated by Brandl et al. (2001) [89]. The one-step leaching experiments by fungi demonstrated that at a concentration of >10 g/L of scrap in the medium, microbial growth was inhibited. In a two-step leaching, however, concentrations of up to 100 g/L electronic scrap could be easily treated resulting in almost complete solubilization of the available Cu, Pb, Sn, and Zn. The two-step leaching process was demonstrated using a commercial gluconic acid produced by *A. niger*. The two-step process has been suggested by Brandl and coworkers [102, 103] for metal mobilization from fly ash using both bacteria and fungi with the following advantages: (a) biomass is not in direct contact with metal-containing waste and might be recycled; (b) waste material is not contaminated by microbial biomass; (c) acid formation can be optimized in the absence of waste material; (d) higher waste concentrations can be applied as compared to the one-step process resulting in increased metal yields.

To increase the solubility of Cu and improve the efficiency of this bioleaching process, addition of a complexing agent was attempted by Choi et al. (2004) [104]. When citric acid was not added, only about 37 wt% of the total leached Cu remained dissolved; however, it increased to greater than 80 wt% in the existence of citric acid. This indicates that the addition of a complexing agent like citric acid to the bioleaching solution can raise the solubility of the leached metal ions, which enables subsequent recovery processes, including solvent extraction, to be carried out more efficiently.

Bioleaching processes were used to mobilize metals from printed wire boards (PWBs) by Wang et al. (2009) [105] using the bacteria *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* isolated from an acidic mine drainage. The experimental results demonstrate that all the percentages of Cu, Pb, and Zn solubilized into the leaching solution from actual PWBs basically increased with decrease of sieve fraction of sample and decrease of PWBs concentration. The concentration of PWBs should be controlled under the range from 7.8 to 19.5 g/L. Under 7.8 g/L of the concentration of PWBs, the percentages of Cu solubilized are 99.0%, 74.9%, 99.9% at 0.5–1.0mm of sieve fraction at 9 day of leaching time by the pure culture of *A. ferrooxidans*, the pure culture of *A. thiooxidans*,and mixed culture of *A. ferrooxidans* and *A. thiooxidans,* respectively, while the percentages of Cu, Pb and Zn solubilized are all more than 88.9% at <0.35mmof the sieve fractions of sample at 5 day of leaching time by the above three kinds of cultures. Variation of pH and redox potential of leaching solution with time implied that Fe^{3+} oxidized from Fe^{2+} in the culture medium in presence of *A. ferrooxidans* caused the mobilization of metals. It is concluded that *A. ferrooxidans* and *A. thiooxidans* were able to grow in the presence of PWBs and the pure culture of *A. ferrooxidans*, and the mixed culture of *A. ferrooxidans* and *A. thiooxidans* can not only efficiently bioleach the main metal Cu but also bioleach other minor metals such as Pb and Zn as well.

Ten et al. (2003) [106] reported the bioleaching of electronic scrap material (ESM) from a local waste recycling company using *Aspergillus niger*. Bioleaching experiments were carried out using *Aspergillus niger*, at various ESM pulp densities (0.1%-2.0% w/v). Using a two-step bioleaching process, the fungus was able to grow at up to 1.0% w/v, with the optimum pulp density at 0.1% w/v, under which about35% Sn, 65% Pb, Zn, Al, and Mn and more than 70% Fe, Ni, and Cu were mobilized. It was also observed that various organic acids produced by the fungus during the leaching process paralleled the leaching of the heavy metals. Higher pulp density led to a decrease in acids produced due to the inhibitory effect of the toxic metals. The use of spent medium resulted in higher metal leaching efficiency than the two-step bioleaching at all pulp density (with the exception of Fe and Al at 0.1% w/v), due presumably to higher concentration of citric acid and lower concentration of oxalic acid in the spent medium which enhanced metals dissolution. Metals solubilization in spent medium leaching was not attributed to extracellular enzymes, but was mainly due to the action of the organic acids. Chemical leaching confirmed that citric, gluconic and oxalic acids were the responsible leaching agents in the bioleaching processes in removing heavy metals from the ESM. Compared with chemical leaching at 0.1% w/v, *A. niger* achieved similar leaching efficiency for Al, and was more efficient in the extraction of Fe, Sn and Au.

A bacterial strain (*Chromobacterium violaceum*) as well as two fungal species (*Pleurotus ostreatus*, *Boletus satanas*) were cultivated under cyanide-forming conditions (glycine-rich growth media) in the presence of metal-containing solids such as nickel powder, platinum wire, automobile catalytic converter, or electronic scrap by Brandl et al. (2003) [107]. All three organisms were able to mobilize Ni from fine-grained nickel powder.

Cu and Pt cyanide were detected during the treatment of spent automobile catalytic converters by *C. violaceum*. From highly complex metal containing wastes (e.g. electronic scrap), however, metal mobilization as cyanide complexes by cyanogenic microorganisms was hardly detectable in spite of the high metal content. The reason is probably the presence of compounds consuming or adsorbing cyanide. There are so many metals and metalloids such as Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Mo, Tc, Ru, Rh, Pd, Ag, Cd, W, Re, Os, Ir, Pt, Au, Hg, Tl, Po, and U that form well-defined cyanides complexes with cyanide, which often show very good water solubility and exhibit high chemical stability [108]. Cyanide synthesis by bacteria is restricted to the proteobacteria *C. violaceum* and to fluorescent pseudomonades (*P. aeruginosa* and *P. fluorescens*) as well as certain fungi (*Marasmiusoreades* and *Clitocybe*sp.) [109]. Glycine is the immediate metabolic precursor for cyanide biosynthesis in proteobacteria and pseudomonades has been proved by *in vivo* studies [110, 111].

Brandl et al. (2008) [112] reported that Cyanogenic *Chromobacterium violaceum*, *Pseudomonas fluorescens*, and *P. plecoglossicida* were able to mobilize Ag, Au, and Pt when grown in the presence of various metal-containing solids such as gold-containing electronic scrap, silver-containing jewelry waste, or platinum-containing automobile catalytic converters. Five percent of Ag was microbially mobilized from powdered jewelry waste as dicyanoargentate after one day, although complete dissolution was obtained when non-biological cyanide leaching was applied. Dicyanoargentate inhibited growth at concentrations of N_20 mg/L. Au was bacterially solubilized from shredded printed circuit boards. Maximum dicyanoaurate concentration corresponded to 68.5% dissolution of the total Au added. Additionally, cyanide-complexed Cu was detected during treatment of electronic scrap due to its high Cu content of approximately 100 g/kg scrap. However, only small amounts of Pt (0.2%) were mobilized from spent automobile catalytic converter after 10 days probably due to passivation of the surface by an oxide film. In summary, all findings demonstrate the potential of microbial mobilization of metals as cyanide complex from solid materials and represent a novel type of microbial metal mobilization (termed “biocyanidation”) which might find industrial application.

Zhu et al. (2011) [113] studied the bioleaching of metal concentrates of waste printed circuit boards (PCBs) by mixed culture of acidophilic bacteria. In this study, the effects of initial pH, initial Fe(II) concentration, metal concentrate dosage, particle size, and inoculation quantity on the bioleaching were investigated so as to determine the optimum conditions and evaluate the feasibility of bioleaching of metal concentrates of PCBs by mixed culture of acidophilic bacteria (MCAB). The results showed that the initial pH and Fe(II) concentration played an important role in Cu extraction and precipitate formation. Under the optimized conditions of initial pH 2.00, 12g/L initial Fe(II), 12g/L metal concentrate dosage, 10% inoculation quantity, and 60-80 mesh particle size, 96.8% the Cu leaching efficiency was achieved in 45h, Al and Zn 88.2% and 91.6% in 98h, respectively. All findings demonstrated that metals could be efficiently leached from metal concentrates of waste PCBs by using the MCAB, and the leaching period was shorten from about 8 days to 45h.

2.3. OUR WORK AND OBJECTIVES

The present work is thus originated keeping in view the emergency and importance of e-waste management in India. Informal and rudimentary ways of recycling of e-waste cause environmental problems and human health implications. So there are extensive studies required on survey and impact assessment of e-waste from generation to post recycling process. It is a vital step to develop bioleaching strategy for recycling of e-waste due to its efficiency, environmental friendly and cost effective traits. Based on the generation, utilization, management and recycling problems of e-waste in India, following objectives were laid down to provide appropriate knowledge and solutions to the above said problems.

1. Survey and impact assessment of e-waste contaminated sites (soil, water and local vegetation profile for its heavy metal constituents along with detailed study of industrial scale operations)
2. TCLP (Toxicity characteristic leaching procedure) studies to simulate the actual landfill conditions
3. Bioleaching studies of metal contained e-waste
    - i) Bioleaching studies by cyanogenic bacterial species
    - ii) Bioleaching studies by thermophilic bacteria
    - iii) Bioleaching studies by acidophilic bacteria
    - iv) Fungal bioleaching studies

To clearly and coherently demonstrate the aim, results and conclusion of each objective are arranged as a separate section in a publishing format.

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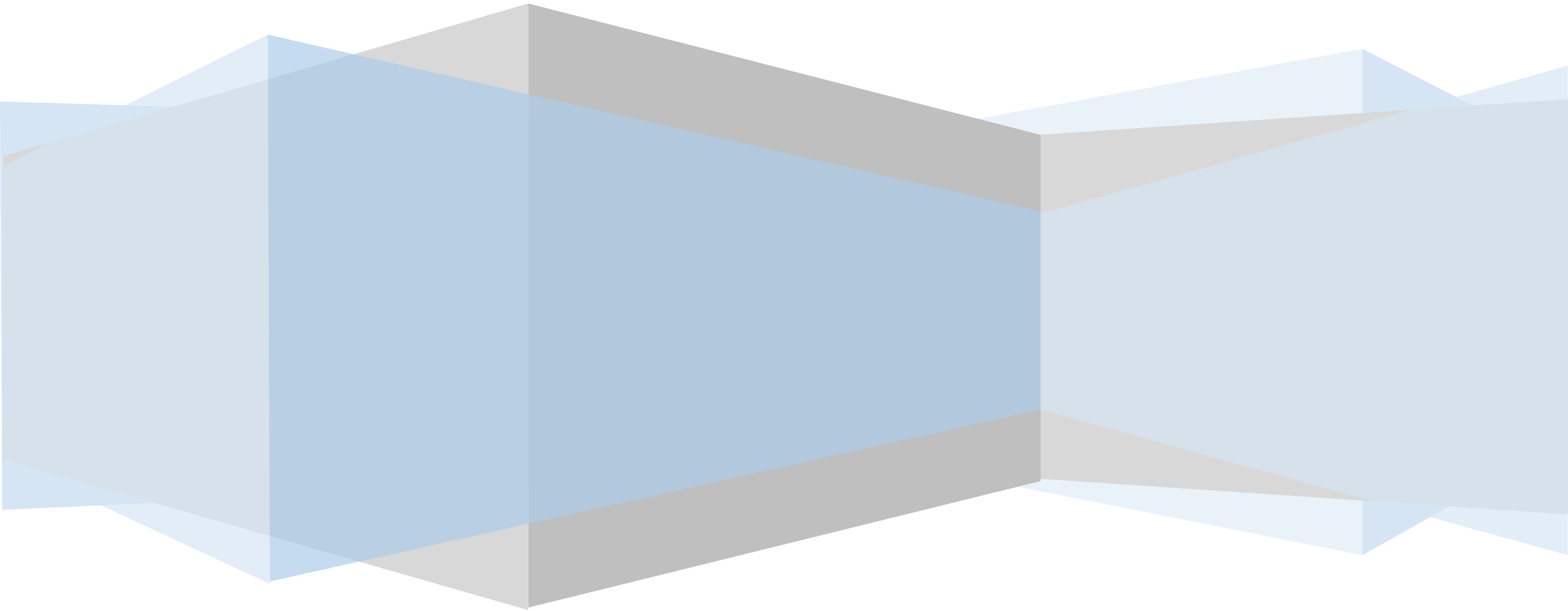
CHAPTER 2

SURVEY AND IMPACT ASSESSMENT OF E-WASTE CONTAMINATED SITES (SOIL, WATER & LOCAL VEGETATION PROFILE FOR ITS HEAVY METAL CONSTITUENTS ALONG WITH DETAILED STUDY OF INDUSTRIAL SCALE OPERATIONS)

JATINDRA KUMAR PRADHAN



2.1 INTRODUCTION

Waste electrical and electronic equipment or WEEE or e-waste is one of the fastest growing waste streams in the world. In the developed countries, on an average it constitutes 1% of the total solid waste. In developing countries, it accounts for 0.01% to 1% of the total municipal solid waste generation, with annual generation per capita being less than 1.0 kg. However, it is growing at an exponential pace in these countries. The increasing 'market penetration' in developing countries, 'replacement market' in developed countries, and high obsolescence rate' make e-waste as one of the fastest growing stream. Composition of e-waste is very diverse and differs in products across different categories. E-waste contains more than 1000 different substances, which fall under 'hazardous' and 'non-hazardous' categories.

Many countries across the world are currently facing with the problem of e-waste. Due to huge population and the changing consumption patterns, India is generating huge volume of e-waste, which moves into informal waste trade and recycling processes, making e-waste disposal unique in character. The recycling of e-waste may prove to be a highly lucrative business, as valuable metals like Au, Cu, and Pb are recovered from this waste, and therefore, more and more people are engaging in this trade in India. The processing of this waste in India is largely carried out in an informal backyard set-up, which is unregulated and does not follow the prescribed environmental norms for handling hazardous substances. The operations are generally rudimentary in nature, causing extensive damage to both the environment and human health. The growth pattern of e-waste is closely linked to the authorities, communities, and policy-makers in the country. E-waste is borne not only out of quantity but also out of the toxicity of the ingredients found in such waste.

Keeping in mind, the complications associated with the e-waste generation, reuse, recycling and final disposal, a survey and impact assessment of e-waste of different cities in India was carried out following uniform approach and methodology. The goal of this study was the qualitative and quantitative analysis of existing e-waste recycling systems in India. The subtasks of this study are mentioned as under:

- Identification and location of e-waste disposal sites and recycling facilities in Himachal Pradesh, Chandigarh, Meerut, Delhi, and Bangalore and selection of representative sites for impact assessment study (Figure 2.1).

- Study of occupational health of workers at handling and recycling e-waste facilities.
- Analysis of surface soil, groundwater and local vegetation near the recycling sites for any possible heavy metal contamination.

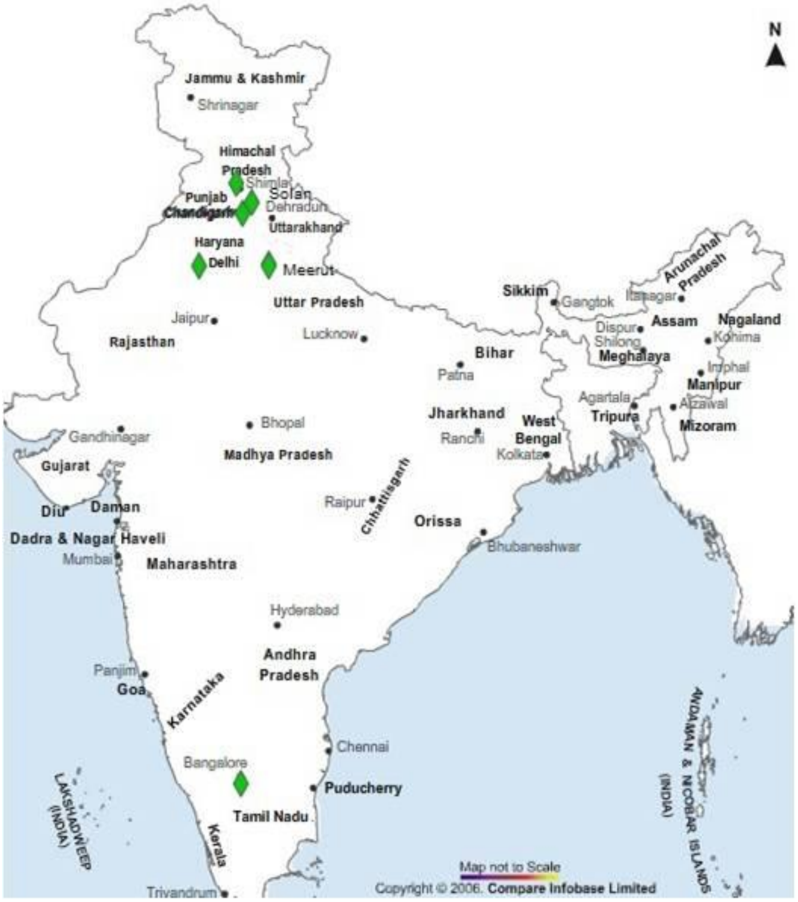


Figure 2.1: Survey locations (marked as ◆) in Indian political map

2.2 MATERIALS AND METHODS

2.2.1 Survey and study of occupational health at e-waste recycling facilities

For the study, the tracer item chosen was the personal computer (PC). A tracer item in this context stands for an electrical or electronic item which is surveyed along its whole life span, from cradle to grave. Reliable statistics of measurable recycling practiced, and the high dynamics in the information technology sector were reasons for the decision to use the PC as a tracer.

The assessment strategy followed a certain order: Stakeholders of the e-waste recycling stream were identified including consumers, traders, repair shops, scrap dealers and dismantlers. Qualitative research involved semi-structured in-depth interviews with the formal and informal e-waste recyclers. One-to-one interviews were conducted with the representatives of these organizations, consumers, traders, repair shops, scrap dealers and dismantlers to gather information with respect to following areas:

- Detailed understanding of each stage: Sourcing, Logistics, Processing of e-waste
- Current handling capacities
- Status of technology being used currently
- Challenges faced: at technical level

Our study included the survey of sources of e-waste generation, stockpiling, collection, handling, brokering, and processing. E-waste generation by production of accessory items was also studied.

Generation and stockpiling: Different “economic actors” purchase, use and then stockpile or discard e-waste. These range from manufacturers such as multinational companies (MNC’s) to large and small businesses, households, institutions and non-profit organizations.

Collection: There is a wide variety of possible collection alternatives for e-waste. A variety of entities are providing these services including electronic industries, private or non-profit recycling services, and the public sector through the solid waste management and recycling infrastructure.

Handling and brokering**:** E-waste is consolidated and made ready for processing. It also includes sorting to determine what equipment can be refurbished or reused as a whole unit and what equipment must be dissembled for commodity processing.

Processing**:** It includes e-waste usage as feedstock for new production or refurbishing. Outputs from dismantling activities include scrap commodities such as glass, plastics and metals, which are primary elements of electronic hardware.

Production**:** Processed commodities or refurbished items return as new products for sale and consumption by end users. There are many different players and industries involved at this step.

Survey and impact assessment on e-waste management in India was studied giving emphasis on the urgency of micro level intervention to tackle the potential problem of e-waste in India. In the above context, survey for e-waste contaminated sites was conducted in following regions.

a) Himachal Pradesh (Shimla, Baddi and Nalagarh)
b) Chandigarh
c) Meerut
d) Bangalore (E-Parisaraa Pvt. Ltd. and Ash Recyclers – Both are formal e-waste recycling companies)
e) Delhi (Turkman Gate, Shastri Park, Old Seelampur, Loni, Mandoli, Mayapuri and Nehru Place)

There were two types of questionnaire prepared; one was for IT companies and another for consumers, traders, repair shops, scrap dealers and dismantlers. The questionnaires are given below.

Questionnaire for IT companies

Q1: Demographic information

Type of organization

a) Multinational Corporations
b) Public Limited Companies
c) Small-Scale Industries
d) Industry sector
e) Manufacturing
f) IT services
g) Constructions
h) Retail
i) Wholesale/ Distribution
j) Education / Cultural services
k) Trading
l) Others

Q2: Number of computers owned

a) 1-50 computers
b) 51-200 computers
c) 201-500 computers
d) 500+ computers

Q3: Number of computers owned and/or leased

- a) Owned
- b) Leased
- c) Both

Q4: Number of Computers upgraded and/or replaced since the last 5-10 years

- a) Upgraded
- b) Replaced
- c) Both

Q5: Frequency of replacement

- a) 6 months-1yr
- b) 1-2 yrs.
- c) 2-3 yrs.
- d) 3+ yrs.

Q6: Outcome for IT equipment replaced

- a) Sent for repair
- b) Sold for reuse
- c) Donated for reuse
- d) Sent to disposal company for recycling
- e) Sent to e-waste dumping site
- f) Others

Q7: Responsible team person appointed for e-waste disposal and management

- a) IT disposal team
- b) Environmental wing
- c) Community affairs section

Q8: Does any Purchasing policy exist to account for the environment and recycling of e-waste

- a) Policy exists
- b) Policy does not exist
- c) Does not Know

Q9: Reasons for replacing IT equipment

- a) Need faster computers
- b) Run out of hard drive space

c) Need to upgrade software
d) Updated computer prices are affordable
e) Tax saving
f) Budget will be reduced if does not used
g) Others

Q10: Is the company aware of what happened to their IT equipment after disposal?

a) Yes
b) No
c) Don't know

Q11: If aware, specify what happens to End of Life (EOL) computers and other electronic items.

a) Put back to community use
b) Commercial recycling
c) Sent to landfills
d) Others

Q12: Mechanisms to check what has happened to redundant computers

a) Mechanisms exist
b) Mechanisms don't exist
c) Don't know if mechanisms exist

Q13: Are there any government programs or initiatives that have been put in place regarding safe disposal of e-waste and its recycling (e.g. Recycler responsibility; supplier take back initiatives)?

a) Yes
b) No
c) Don't know

Q14: If yes, please specify the programs in a few words.

Q15: If you were to dispose-off the unused equipment, what administrative and technical processes do you follow?

Q16: Are there any servicing, leasing, repair or disposal deals involved?

a) Yes
b) No

c) Don’t know

Q17: If yes, please specify this process in brief.

Questionnaire for consumers, traders, repair shops, scrap dealers and dismantlers

Q1: What are the sources of e-waste generation?

Q2: What is the quantity of e-waste handled annually?

Q3: Who is the seller or purchaser of the e- waste?

Q4: Type of your business activity

Q5: Purpose of e-waste processing operation, if any

a) Source destruction
b) De-manufacturing for recovery of precious metals (Au, Ag etc.)
c) Liberation/separation of certain waste for reclamation/recycling

Q6: What types of technology are used for e-waste recycling?

Q7: After recovery of metals, where the leftover is disposed?

Q8: Description of the waste (If you have more than one, tick multiple options)

a) CPUs
b) CRTs (Monitors)
c) Key boards
d) Printers
e) Hard drivers
f) Circuit boards
g) Main frames
h) Audio/video equipment
i) Telephones (Cell, Mobiles, Land line unit etc.)
j) CD/floppy discs
k) TVs
l) Refrigerator
m) Others

Q9: Unprocessed e-waste specification (Refrigerators, televisions, washing machine etc.) as received

a) Maximum individual size from………inch up to……….inch.
b) Oversize components to………..inch ……..% maximum

c) Gross average weight………..kg

Q10: Non-hazardous composition of waste

a) Plastic types…………… %
b) Ferrous type…………… %
c) Non-ferrous type………. %
d) Glass, etc………………. %
e) Others …………………. %
f) Don't know

Q11: Hazardous composition of wastes

a) Lead……………..%
b) Cadmium………...%
c) Nickel………….....%
d) Zinc………………%
e) PVC………………%
f) Arsenic……………%
g) Aluminium……… %
h) Silver……………..%
i) Mercury…………..%
j) Iron……………….%
k) Barium……………%
l) Others……………. %
m) Don't know

Q12: Do you observe the hazardous waste management rules and export import issues?

a) Yes
b) No
c) Don't know the rules

Q13: If yes, which of the following do you observe?

a) Guidelines for management of hazardous wastes-Ministry of Environment and Forestry (MoEF) 2011
b) Guidelines for setting up to operating facilities
c) Hazardous waste landfill rules 2000

d) Code of practice for environmentally sound management of lead acid batteries, zinc ash/skimming and waste oil-Central Pollution Control Board (CPCB) June 2000
e) Central pollution control board constituted under the water (prevention and control of pollution) Act, 1974.
f) State pollution control board constituted under the water (prevention and control of pollution) Act, 1974.

Q14: Is the e-waste trade economically efficient for you?

a) Yes
b) No
c) Adjustable

Q15: Are you aware about toxic elements present in e-waste?

a) Yes
b) No

Q16: If yes, what preventive measures did you adapt?

Q17: Do you see any polluted air and water discharge during e-waste recycling?

a) Yes
b) No

Q18: If yes, what are the common health issues observed in your locality?

Q19: What is the approximate net profit from e-waste processing at your end?

Q20: Do you know or have linkage with any large establishment for e-waste recycling?

2.2.2 Impact assessment of e-waste contaminated sites (Soil, Plant and Water)

2.2.2.1 Study area

The study area is situated in Mandoli industrial area, Mandoli, Seemapuri, North East Delhi, India having geographical coordinates 28° 42' 16.6176" North and 77° 19' 5.10096" East. We found that the active uncontrolled processing of e-waste has left open incineration sites scattered among agricultural fields, and electronic debris dumped around the industries. A preliminary survey of contaminant levels in Mandoli industrial area was conducted for heavy metal impact assessment due to informal e-waste recycling. The location of Mandoli industrial area in the map of Delhi is depicted in Figure 2.2.

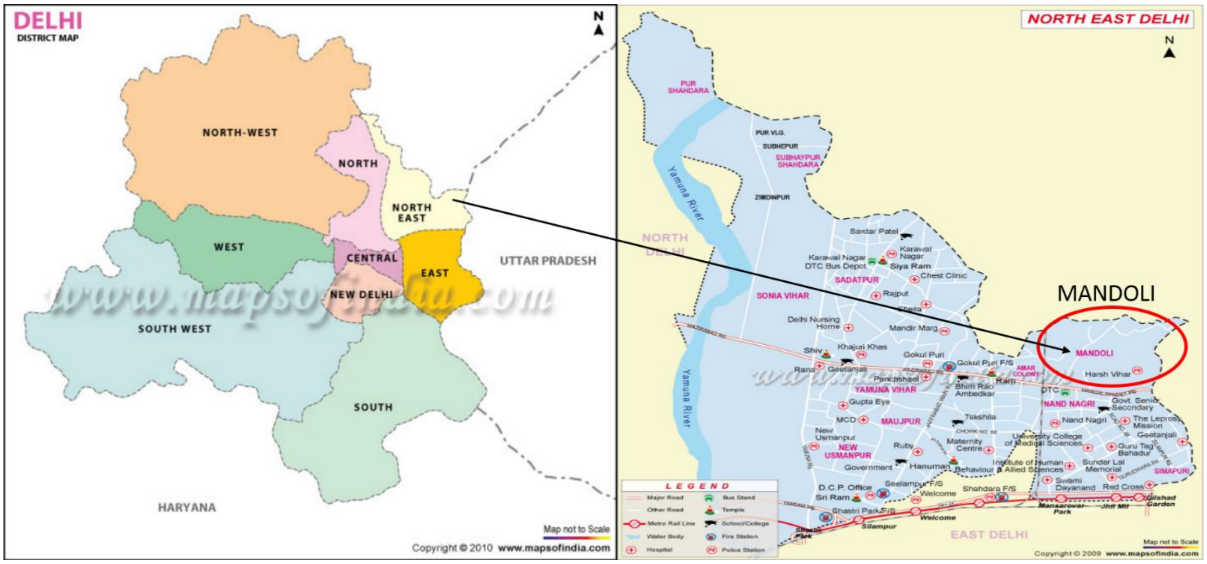


Figure 2.2: Location of sample collection areas in the vicinity of Mandoli

2.2.2.2 Soil, plant and water sampling

The selection methods for sampling sites varied within small limits because of difficult sampling conditions in the study area. Difficult sampling conditions include restricted entry to industries for sampling and surveying. Beside these problems, Workers were hesitant to disclose the information regarding collection, processing and disposal of e-waste. A total five sites (Table 2.1) were selected for this study, based on the preliminary survey of Mandoli industrial area. A random sampling technique was followed for sampling of soil and plants. Samples were collected from the different sections of the same area. Four samples were collected and homogenised for making a model sample for one area. The soil samples of top soils (0-15cm) from every area were collected manually. Like soil samples, the plant materials (herbs) were also collected as a whole plant system which includes root, shoot, and all other parts of plant. Water samples were collected from two bore wells. The samples were carried out to laboratory in aseptic condition. All of the samples were put in polythene zip-bags and transported to the laboratory and stored at -20ºC for further analysis. The fresh plant samples were washed with tap water, rinsed with distilled water, and the fresh weight was recorded. Soil and plant samples were then freeze-dried, and the dry weight of plant samples was measured. After drying, the soil was passed through a 2 mm sieve. The subsamples of the plant and soil were ground with mortar pastel, and used for metal analysis.

Table 2.1: Description of sampling locations

Sampling locations in Mandoli industrial area, Delhi	Soil	Plant	Water
E-waste recycling site (from inside the recycling unit)	S1		W1
E-waste dumping site	S2	P1	
Arable land, an area 50 m distance from e-waste recycling site	S3	P2	
Arable land, an area 100 m distance from e-waste recycling site	S4	P3	
Arable land (adjacent village), an area 500 m distance from e-waste recycling site	S5	P4	W2

2.2.2.3 Analysis of soil

All dried soil samples were ignited (1.00 + 0.05g) in a porcelain crucible at 400 °C in muffle furnace for 4-5h. Then the ignited samples were transferred to a 100 mL Teflon beaker and treated the sample with 10 mL of 1:1 H_2O and HCl for one hour at 60-80°C. Supernatants were decanted which contained most of the alkaline earth metals, into a 250 mL volumetric flask and retained. The residues were dissolved by adding 10 mL of HF and 10 mL of HCl and evaporating to dryness and this step was repeated once. Finally, 5 mL of HCL added and evaporated to dryness, and dissolved the residue in 5 mL HCl. The solution was transferred to a 250-mL volumetric flask, combining it with the acid extract for high alkaline earth samples, and diluted with de-ionized water to volume so that the final acid volume was approximately 5% (v/v) HCl. The diluted solutions were filtered through glass fiber filter (0.45 µm) before metal determination using atomic absorption spectrometer (PerkinElmer AAnalyst 400 Spectrometer) [114].

2.2.2.4 Analysis of plant

Common grass named as *Cynodon dactylon* was collected as plant sample. Ground dried plant samples (1.0g + 0.05g) placed it in a small beaker. Concentrated HNO_3 (10 mL) was added and allowed to stand overnight. The mixture was heated carefully on a hot plate until the production of red NO_2 fumes had ceased. The beaker was cooled followed by addition of small amount (2-4 mL) of 70% $HClO_4$. It was heated again and allowed to evaporate to a small volume. The extracted samples were transferred to a 50 mL flask and diluted to 100 mL volume with de-ionized water. The diluted solutions were filtered through glass fiber filter (0.45 µm) before metal determination using atomic absorption spectrometer (PerkinElmer AAnalyst 400 Spectrometer) [115].

2.2.2.5 Analysis of water

Water samples were filtered through a 0.45 µm micro-pore membrane filter before metal determination using atomic absorption spectrometer (PerkinElmer AAnalyst 400 Spectrometer). This was done to avoid clogging of the burner capillary [116].

The soil, plant and water samples were analyzed using atomic absorption spectrometer (PerkinElmer AAnalyst 400 Spectrometer) for thirteen metal elements (Ag, Al, As, Cd, Co, Cu, Cr, Fe, Hg, Ni, Pb, Se, and Zn). The major criteria for selecting metals for investigation are shown in Table 2.2.

2.2.2.6 Data analysis

Contents of 13 metal elements were compiled to form a multi-element database using SPSS. Statistical analysis including descriptive analysis, ANOVA, factor analysis (principal component analysis), multidimensional scaling, hierarchical cluster analysis, and Pearson correlation analysis were performed using SPSS 17.0.

Analysis of variance (ANOVA) was performed and the mean of the results were compared by Duncan’s multiple range tests at 5% significance level. ANOVA was used to assess the significant impacts of land uses on the accumulation of heavy metals in Mandoli industrial area soil. Prior to further statistical analysis, the data were Z-score normalized to create uniformity in the units of variables [117]. Principal component analysis (PCA) decomposes multivariate data into a set of abstract eigenvectors and an associated set of abstract Eigen values [118-120]. Each Eigen value presents a portion of the total variation in the data, and each eigenvector is a linear combination of the original variables. PCA has been applied in this study to reveal structure in data, which helps in finding relationship between sampling areas and elements. Factor analysis classified elements based on the close relationships between them, while multidimensional scaling (MDS) and cluster analysis (CA) were used to distinguish visually the similarities or the differences in-between elements by a derived stimulus configuration and a cluster tree, respectively. Derived stimulus configuration was obtained using Euclidean distance model, while a cluster tree was obtained based on Pearson's correlation coefficient. In hierarchical CA, clustering leads to a tree-like structure called dendrogram [119], which provides information about the number of classes in a dataset. The Ward's method is used to carry out for CA analysis [121].

Table 2.2: Examples of toxic heavy metals in e-waste

Element	Electronic components (partial list)	References
Ag	Printed circuit boards	[122]
Al	Capacitors	[123]
As	Light-emitting diodes (LEDs), small quantities in the form of gallium arsenide within light emitting diodes	[124]
Cd	Switches and solder joints; Cadmium compounds in rechargeable batteries; UV stabilizers in older PVC cables and 'phosphor' coatings in CRTs; printer inks and toners in photocopying-machines (printer drums)	[125]
Cu	Printed circuit boards; wires and cables.	[126]
Cr	Magnetic tapes; floppy disks; additives in plastics-like pigments.	[127]
Fe	Printed circuit boards	[123]
Hg	Fluorescent lamps; CCFL (cold cathode fluorescent lamps) in LCDs; relays; float, pressure, tilt and temperature switches	[128]
Ni	Ni-Cd batteries; Ni-Mn batteries; electron guns of cathode ray tubes.	[124]
Pb	Solders (as an alloy with tin); lead oxide in the glass of cathode ray tubes (televisions and monitors); lead–acid batteries. These compounds are used as stabilizers in some PVC cables and other products.	[125]
Se	Older photocopying-machines (photo drums)	[129]
Zn	'Phosphor' coatings in older cathode ray tubes; additives in plastics.	[124]

2.2.2.7 Soil contamination assessment

Index of geoaccumulation

The index of geoaccumulation (I_{geo}) enables the assessment of contamination by comparing current and preindustrial concentrations. Originally used with bottom sediments [130], it can also be applied to the assessment of soil contamination. It is computed using the following equation:

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n}$$

where C_n is the total concentration of element n in the surface layer of the soil tested and B_n is the concentration of element n in Earth's crust [131, 132]. A factor of 1.5 is used to represent possible variations in the base level of the metal measured in the environment and as a factor of correction for any anthropogenic influence in the calculation. We decided to focus on the comparison between the concentrations obtained and the concentrations of elements in the Earth's crust, because soil is a part of the surface layer of the Earth's crust and its chemical composition is related to the one of the crust. Muller (1981) [133] has distinguished six classes of the geoaccumulation index (Table 2.3). Class 6 is an open class and comprises all values of the geoacuumulation index higher than class 5.

Enrichment factor (EF)

Enrichment factor (EF) is defined for soil as the ratio of relative concentration of an element in a sample to the relative concentration of the same element in a reference soil. It provides a comparison between the compositions of two soils. Since different procedures are involved in sample pretreatment and digestion, the use of relative concentrations ensure a proper comparison. The reference soil can be any soil without any contaminant. Similarly to I_{geo}, the reference environment adopted by us was the average concentrations of elements in the Earth's crust [131, 132]. This aimed to enable a comparison of the two factors I_{geo} and EF. A reference element is the one characterized by low occurrence variability. The most common reference elements are Sc, Mn, Ti, Al and Fe [134-138]. In our study, we used Al to be the marker element of the soil. Eventually, the value of the enrichment factor was calculated using the modified formula based on the equation suggested by Buat-Menard and Chesselet (1979) [139] and Daud et al. (2009) [140].

$$EF = \left[\frac{C_n(Sample)}{C_{ref}(Sample)}\right] \Big/ \left[\frac{B_n(Background)}{B_{ref}(Background)}\right]$$

where C_n(sample) is the content of the examined element in the examined environment, C_{ref} (sample) is the content of the reference element in the examined environment, B_n

(background) is the content of the examined element in the reference environment and B_{ref} (background) is the content of the reference element in the reference environment. Five contamination categories are recognized on the basis of the enrichment factor [130] mentioned in Table 2.4.

Table 2.3: Six classes of the geoaccumulation index

Class	Value	Soil quality
0	$I_{geo} \leq 0$	Practically uncontaminated
1	$0 < I_{geo} < 1$	Uncontaminated to moderately contaminated
2	$1 < I_{geo} < 2$	Moderately contaminated
3	$2 < I_{geo} < 3$	Moderately to heavily contaminated
4	$3 < I_{geo} < 4$	Heavily contaminated
5	$4 < I_{geo} < 5$	Heavily to extremely contaminated
6	$5 < I_{geo}$	Extremely contaminated

Table 2.4: Contamination categorized recognize on the basis of the enrichment factor

Enrichment factor	Category
EF < 2	Deficiency to minimal enrichment
EF = 2-5	Moderate enrichment
EF = 5-20	Significant enrichment
EF = 20-40	Very high enrichment
EF > 40	Extremely high enrichment

Contamination factor and degree of contamination

The assessment of soil contamination was also carried out using the contamination factor and degree. The contamination factor was calculated using the equation described by Hakanson (1980) [141]:

$$C_f^i = \frac{C_{0-1}^i}{C_n^i}$$

where C_{0-1}^i is the mean content of metals from at least five sampling sites and C_n^i is the preindustrial concentration of individual metal. In our work, we applied a modification of this factor which used the concentration of elements in the Earth's crust as a reference value, similarly to the other factors. Hakanson (1980) [141] defines four categories of contamination factor (Table 2.5).

Table 2.5: Categories of contamination factors

Contamination factor	Category
$C_f^i < 1$	Low contamination factor indicating low contamination
$1 \le C_f^i < 3$	Moderate contamination factor
$3 \le C_f^i < 6$	Considerable contamination factor
$6 \le C_f^i$	Very high contamination factor

The C_{0-1}^i is a single-element index. The sum of contamination factors for all elements examined represents the contamination degree (C_{deg}) of the environment and four classes are recognized (Table 2.6) [141].

Table 2.6: Classes of contamination degree

Contamination degree	Category
$C_{deg} < 8$	Low degree of contamination
$8 \le C_{deg} < 16$	Moderate degree of contamination
$16 \le C_{deg} < 32$	Considerable degree of contamination
$32 \le C_{deg}$	Very high degree of contamination

Pollution load index (PLI)

Pollution load index (PLI), also known as integrated pollution index, is used to assess the level of pollution at a site for a selected number of elements [140]. The element selection depends upon the nature of the study. PLI is a geometric mean of the relative concentrations, called concentration factors (contamination factors), of selected elements. PLI is calculated as:

$$PLI = \sqrt[n]{\prod_{i=1}^{n} C_f^i}$$

where n is the number of selected elements. Since a reference site has PLI = 1, therefore a site is said to be polluted if PLI > 1. The higher the value of PLI, the more polluted a site would be.

Average toxic element concentration (ATEC)

Both EF and PLI are relative measures; EF gives idea about the enrichment of different elements in a soil relative to a reference soil. PLI is also based on relative concentrations that stipulate idea about pollution level of a site relative to a reference site. Both EF and PLI change with variation in the reference data. In literature, there is no single source of reference data; some researchers used Mason’s data [142] and others employed local data [143]. To remove the relative nature of EF and PLI, we introduce, here, a new measure of pollution level assessment [144]. It is “average toxic element concentration” (ATEC), which is an absolute measure and provides average concentration of toxic elements. ATEC is defined as

$$ATEC = \sqrt[n]{\prod_{i=1}^{n} C_n}$$

Where C_n is the total concentration of element n in the surface layer of the soil tested. The lower the ATEC, the smaller will be pollution level and better will be the soil. ATEC for world average concentration of soil [131, 132] is 12.44 showing no pollution; all values higher than this value will indicate some level of pollution. In terms of pollution level, ATEC value of more than 124.4, a ten times higher value, can be associated with high level of pollution.

2.3 RESULTS AND DISCUSSIONS

2.3.1 Identification and location of e-waste disposal sites and recycling facilities in Himachal Pradesh, Chandigarh, Meerut, Delhi, and Bangalore and selection of representative sites for impact assessment study

2.3.1.1 Rationale of selecting these cities for survey and impact assessment studies

Jaypee University of Information Technology is equidistance (24 km to either side) from the capital and most populated city oh Himachal Pradesh (H.P.) i.e. Shimla and industrial hub of H.P. i.e. Solan. So we were keen to assess the e-waste problem of our area. From previous literature, we found that Delhi is the biggest e-waste hub which represents the northern part of India [145]. Delhi collects e-waste from northern Indian cities e.g. Chandigarh, Meerut, and other parts of India like Bangalore and also imports from developed countries. We selected Shimla, Solan, Chandigarh, Meerut, Delhi, and Bangalore for our study. Bangalore was selected as it is the largest and fastest growing IT city of India.

2.3.1.2 E-waste scenario from the perspective of Himachal Pradesh (H.P.)

Shimla, the capital city of H.P., Baddi and Nalagarh (Industrial belt of District Solan of H.P.) was selected for studying the e-waste generation and management in Himachal Pradesh. The sources of e-waste were educational institutes, individual households, government offices, and computer manufacturing units. Baddi and Nalagarh have many computer manufacturing and packaging units like, Lenovo, Intex, Spice and eSYS technologies. Here the e-waste is managed by following the 3R (Reuse, Resale and Recycle) process. The obsolescence rate of personal computers was found to be close to 7 years after analysing the data collected form scrap dealers and consumer behaviour. Shivalik Solid Waste Management Limited, which is situated at Nalagarh is the only engineered solid waste land filling site of Himachal Pradesh built in March, 2007 as a public private joint venture. Unfortunately, no single company permanently tie up with this landfilling organization to safe disposal of their solid waste including e-waste. E-waste recycling processes included segregation and it’s dismantling and reuse in the local markets with scrap dealers. The remaining e-waste is sent to either Delhi or Chandigarh for improved recycling. As of now, there are no formal recycling units in Himachal Pradesh for recovery of metals from e-waste. Beside this, there is little awareness among public regarding e-waste.

2.3.1.3 E-waste scenario from the perspective of Chandigarh

Chandigarh is a city in India that serves as the capital of two states, Punjab and Haryana, and is union territory of India. The city boasts a high standard of living with the highest per capita income in the country and tops the list of Indian states and union territories with a Human Development Index (HDI) of 0.987 (2011 census). Chandigarh houses many prominent institutes of higher learning, such as IMTECH (Institute for Microbial Technology), CSIO (Central Scientific Instruments Organization), PGIMER (Postgraduate Institute for Medical Education and Research), Panjab University, National Institute of Pharmaceutical Education and Research (NIPER), University Institute of Engineering and Technology (UIET) and many more. Apart from these, many colleges and schools exist in Chandigarh which are well equipped with many electrical appliances and computers.

The study involved primary research and expert interviews of the vendors and both formal and informal recyclers in industrial areas of Chandigarh (Phase-I and II), sector-23, 45 (Burail), Rajiv Gandhi IT Park and sector-47. As per our survey in March, 2009, around 94% of the organizations did not have any policy on disposal of obsolete IT products and e-waste (Figure 2.3) and to our surprise most of the business organizations were not aware about e-waste.

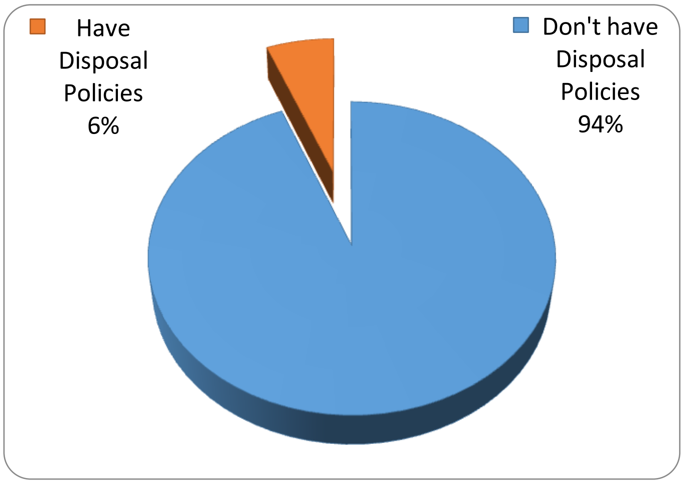


Figure 2.3: Percentage of disposal policy on obsolete IT products in Chandigarh

Obsolescence rate analysis was carried out assuming an average life for each item based on market trends and consumer behavior. The obsolescence rate for personal computers was 5-7 years in Chandigarh region. There were no formal recycling units to recover metals from e-waste. At present, e-waste is managed with the help of local scrap dealers following segregation, dismantling and refurbishment. The unused dismantled parts are sent to Delhi and Amritsar for advanced recycling process. The major processes used for recycling/reusing of PCs in Chandigarh region are mentioned in Table 2.7.

Table 2.7: Major dismantling processes followed in Chandigarh for obsolete PCs

Processing components	Process details	Processing	Remarks
Cathode ray tube (CRT), Computer casing, Printed circuit boards (PCBs), Printed wire boards (PWBs), Integrated circuits (ICs), Yoke copper, Rare earth core and Gold from pin and comb	Dismantling of Monitor and extraction of components	Yes	In local market
	Re-gunning of CRTs	No	Sent to Delhi market
	IC's Extraction from PWB	Yes	Reselling and reuse in local market
	Acid Bath for PWB	No	Sent to Delhi market
	Surface Heating of PWB and Extraction of components	No	Sent to Delhi market
	Wire PVC and Copper	Yes	Reselling and reuse in local market
	Plastic Shredding	No	Sent to Delhi market
	Gold Extractions from pins and Comb	No	Sent to Amritsar and Delhi market
	Yoke core and copper extraction from wire	No	Sent to Delhi market
	Metallic Core of Transformer and Copper	Yes	Reselling and reuse in local market
	Rare Earth Core of Transformer and Copper	Yes	Reselling and reuse in local market
	Rare Earth Core of Static Transformer	Yes	Reselling and reuse in local market

E-waste trade value chain in Chandigarh has been established by studying the conventional trade value chain (Figure 2.4). Many different ‘economic actors’ purchase, use and then stockpile or discard e-waste. These range from MNCs to large and small business, households, institutions and non-profit organizations. Mostly the scrap dealers collect e-waste as per weight with minimal rate. The price of CPU of PCs was within the range of ₹20-25/kg where as the price of PC monitors range from ₹70-400 per piece. The next trade link in the cycle is the handling and brokering services (refurbishment and sale). Here the e-waste is consolidated and/or sorted to determine what equipment can be refurbished or reused as whole units and what equipment must be disassembled for commodity processing. The final step in this cycle is to turn the processed commodities or refurbished whole electronics back into new products for sale and consumption by end users. The conventional trade value chain follows three levels of hierarchy i.e. preliminary, secondary, and tertiary e-waste generators. The input to the first level comes from the formal organized markets like IT parks, government and private offices, households, and organized markets, where e-waste from domestic consumers comes either in exchange schemes or as discarded items. Therefore, the major stakeholders are scrap dealers/dismantlers who purchase e-waste from the first level in bulk quantities. They have limited capacity of dismantling and are involved in trading of e-waste with next level of dismantlers/scrap dealers. The market between the first and second level is semi-organized (i.e. partly formal) while the market between the second and third levels is completely informal. The tertiary e-waste generators are the recyclers who extract metals, plastics and glasses in uncontrolled environments. The major stakeholders between the first and second levels are scrap dealers/dismantlers who purchase e-waste from first level scrap dealers/traders and are involved in real dismantling of e-waste. The major stakeholders between the second and third levels are electronic item extractors, glass and plastic extractors who sell the product to metal extractors and end users. Preliminary results show that there were no organized metal extractors in Chandigarh region. Dismantling of the e-waste was rudimentary while the major quantities of e-waste transported to Delhi or Amritsar for metal extraction.

From this study we found, approximately 1, 00,000 computers exist in Chandigarh city. With the setting up of Rajiv Gandhi Technology Park having MNCs like Infosys, IBM etc., Chandigarh will be a technology hub of the region adding more electronic equipment’s.

Moreover increase in population along with literacy rate, dependency on computer will further increase in this city. The study also revealed that the dependency on computers will be doubled within 1-2 years. With respect to dependency on computers the number of computer will increase 2-3 times more in household and business. Easy availability and affordable prices of electronic items like world's cheapest laptop developed in India will increase redundancy of the electronic items giving more e-waste to the environment. Assuming an average computers weight about 27 kg [146] the study revealed that, a total of 35 metric tons of e-waste will generate after four years. Currently e-waste recycling, especially processing, remains concentrated in the informal sector in Chandigarh due to lack of proper enforcement of e-waste or hazardous waste law and processing technologies.

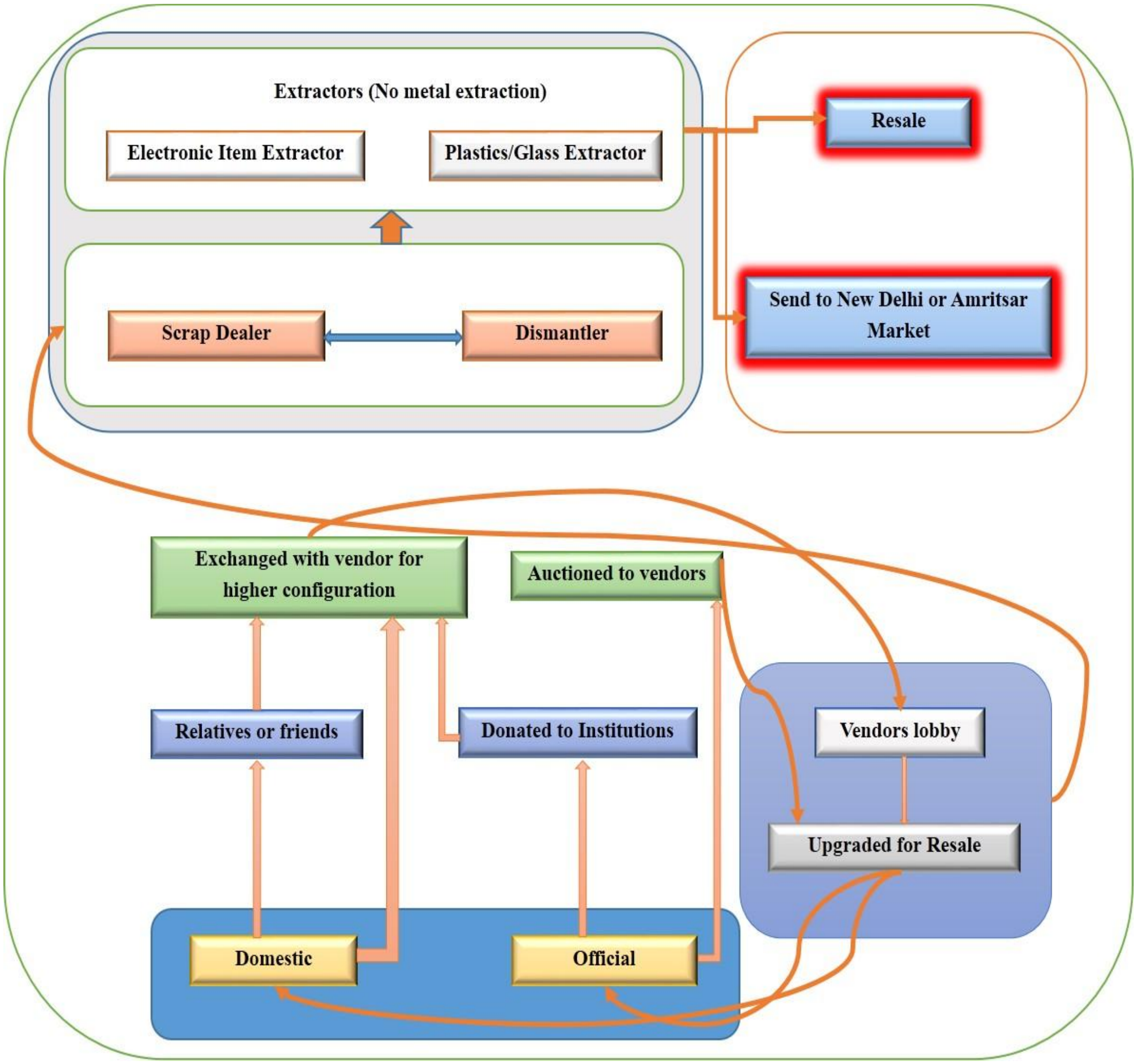


Figure 2.4: E-waste trade value chain in Chandigarh region

2.3.1.4 E-waste scenario from the perspective of Meerut

Meerut is the 16th largest metropolitan area in India and the 25th largest city in India. Meerut is the fastest developing city of Uttar Pradesh after Noida and Ghaziabad. The main sources of e-waste are the educational institutes besides the IT companies because the establishments of IT companies are in infancy in Meerut. Computer dismantling and resale occur in "Jailchungi" and "Shastri Nagar" market in Meerut. Here computers, monitors and other collected electronics are consolidated and/or sorted to determine what equipment can be refurbished or reused as whole units and what equipment must be disassembled for commodity processing. The scrap dealers collect these e-wastes as per weight. It was noted that, the price for Black and White monitor was just ₹200 whereas for color monitor it was ₹400. The astonished thing was the CPU rate, which was ₹20/kg whereas the key boards and optical mouse were just for ₹10. It was observed that, trend of resale of old computer parts was similar to Chandigarh market. At present, e-waste is segregated, dismantled and reused in the local markets with scrap dealers and a part of it is sent to Delhi (Seelampur and Mandoli). There was no government recognized recycling unit established for recycling of e-waste in Meerut. After 4 to 5 years, it may be a future e-waste port for India due to a fully established industrial area with IT companies.

2.3.1.5 E-waste scenario from the perspective of Bangalore

A field study and an interview process with members from formal recyclers produced a model. The survey results are presented first, followed by the model calculations and material flow analysis. Bangalore is generating around 12,000 tons of e-waste (from computers and peripherals) per year. This estimate is based on information received from recyclers in Bangalore and from the fact that 30% of all equipment in IT industry became obsolete every year and end up as e-waste. Two government authorized recyclers (E-Parisaraa Pvt. Ltd. and Ash Recyclers) have established good infrastructural facilities in the field of e-waste recycling in Bangalore and we analyzed their working model. E-Parisaraa is India's first e-waste recycling company approved by both Central Pollution Control Board and Karnataka State Pollution Control Board, located in Dobaspet Industrial Area near Bangalore, Dobaspet Industrial area is already earmarked for hazardous waste management by Government of Karnataka. The initiative is to aim at reducing the accumulation of used and discarded electronic and electrical equipment's, which mostly end up in landfill or partially recycled in a unhygienic conditions by backyard recyclers and then partly thrown into waste streams damaging the environment. The objective of the E-Parisaraa is to create an opportunity to transfer waste into socially and industrially beneficial raw materials like valuable metals, plastics and glass using simple, cost efficient, home grown, environmentally friendly technologies suitable to Indian conditions.

Ash Recyclers, was established in 1981 as Ash Scrap Dealer, which is determined to provide a safe and sustainable e-waste management and recycling that meets the global standards. Ash recyclers have a well-established standard methodologies and documented procedures for Reduce, Reuse and Recycling of electronic waste complying with WEEE Regulations. The model (Figure 2.5 and 2.6) shows a chain of processes for the tracer item PC. The system is divided into two sections: pre- and post-recycling processes. Five percent of the items produced are rejected and go directly into the “Recycling” process. The field assessment of this study revealed the existence of a vital refurbishing and upgrading industry, dealing exclusively with used personal computers. The “Repair” to “Traders” processes includes the upgrading of PCs with faster processors, increase in hard disc memory or other replacements. The reuse of components (flow from “Reuse” to “Traders”) depicts the recycling of components- such as IC processing chips, memory cards, capacitors or other individual components- which enter the market by being sold after having their functionality checked. Figure 2.5 shows the material flow of the pre-recycling processes whereas Figure 2.6 shows the post-recycling processes. In Figure 2.5, the process “Recycling” links the two sections of the system and at the same time symbolizes a “point of no return”. After entering the “Recycling” process, no items, components or materials even return directly to the pre-recycling processes.

The post recycling process adopted is simple and having minimum landfill options and without incineration. In general, mechanical and recovery operations are being carried out. Mechanical operations include: manual dismantling, segregation, pulverizing and density separation in an eco-friendly manner, while recovery operations are carried out for metals, glass, and plastics separately.

E-waste management at organizational level

Bharat Electronics Ltd., (BEL) set-up to meet the specialized electronic needs of the Indian defense services, has been the first public sector company to initiate e-waste management. The public sector companies have recently initiated a program to manage e-waste. E-waste is segregated into four categories namely-

- Computer and Computer peripherals
- PCBs (printed circuit boards) and electronic components
- Electrical wires/cables, cut wires
- All other electronic equipment

The segregated waste is recycled at authorized e-waste recycling facilities in Bangalore. As per government regulations, tenders are called for the sale of this e-waste. Earlier all scrap dealers were invited to take part in the tender. In the present situation the tender is restricted to only Govt. authorized e-waste recyclers. In addition to the public sector, large private companies including the MNCs are also involved in auctions to dispose their e-waste.

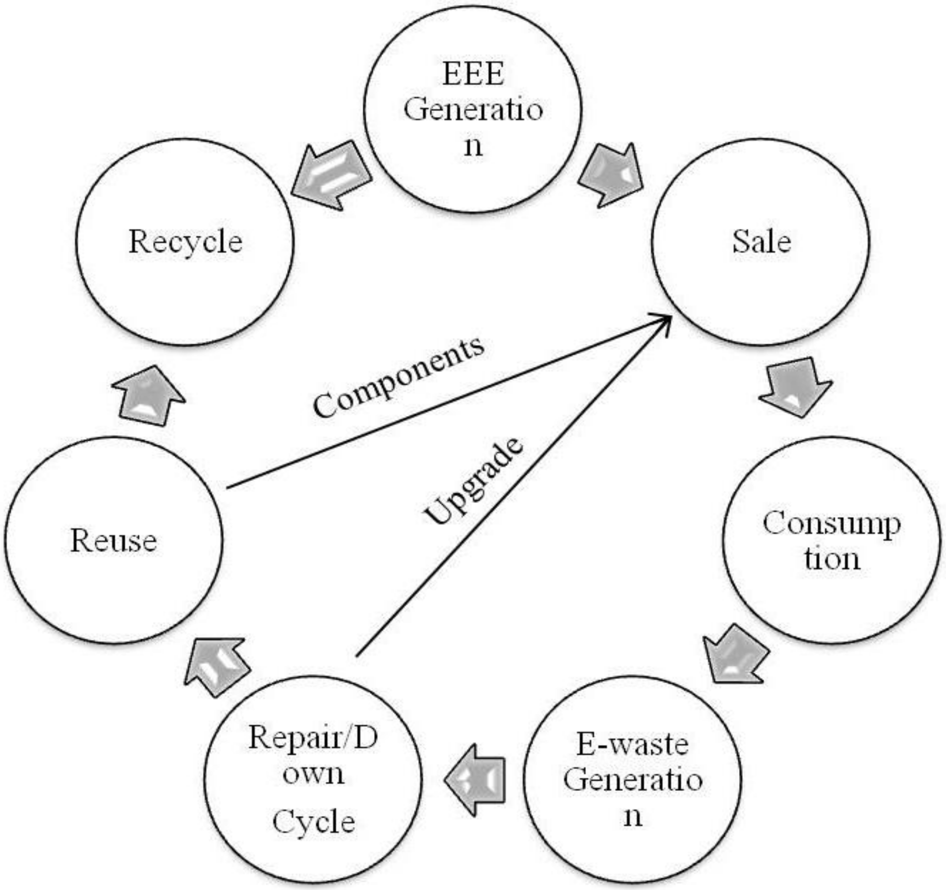


Figure 2.5: Material flow of the pre-recycling processes of the tracer item personal computer within the system border Bangalore

Role and status of stakeholders' involvement

Bangalore has emerged as a key city, which has identified the different stakeholders and is making demands to ensure that attention is given to e-waste and its proper management and disposal. Currently three main stakeholders have been identified. Namely

- The Government- agencies associated with e-waste that include Karnataka State Pollution Control Board (KSPCB), Greater Bangalore Municipal Corporation (GBMC), Department of Information Technology, Government of Karnataka
- The Generators (mainly producers and consumers)
- The Recyclers (Both formal and informal recyclers)

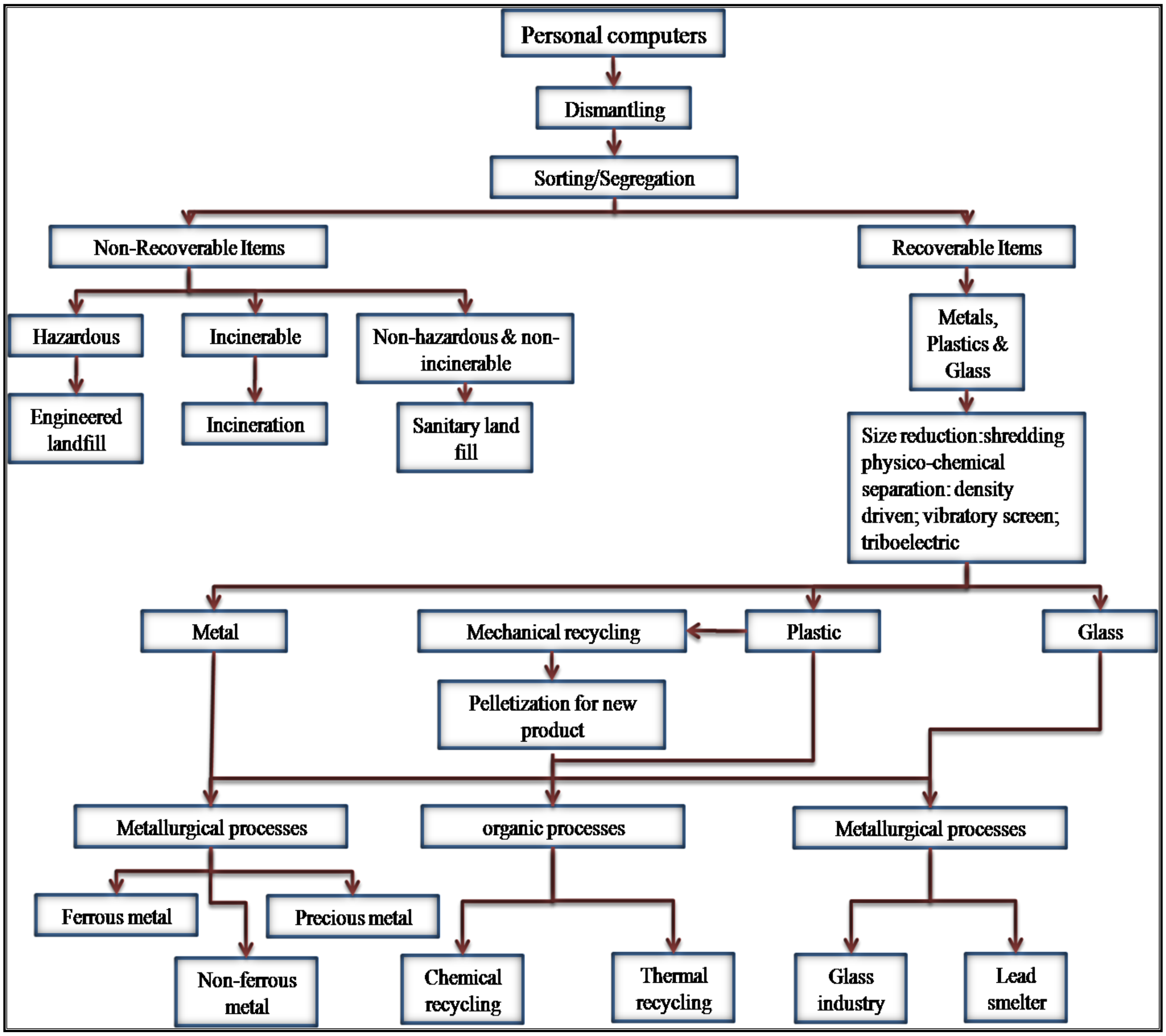


Figure 2.6: Post recycling processes for the tracer item personal computer in Bangalore

- ***Government agencies***

The Karnataka State pollution Control Board (KSPCB) has the responsibility for enforcement of the rules and legislation. Discussions with the department made it clear that the hazardous waste rules are currently sufficient to address the safe disposal and recycling of e-waste. The industries are bound to dispose of the e-waste to a proper recycler who is authorized by the KSPCB or to find a proper land fill. None of the legislations objects to sale of e-waste to authorized bodies but selling it to scrap dealers that do not have an authorization from the KSPCB is against the law. Bangalore has three authorized e-waste recycling units. A tracking system is also on place whereby waste disposed through the authorized vendors is documented under the hazardous waste rules. KSPCB has also made it mandatory for all new establishments seeking Consent for Establishment (CFE) to comply with e-waste regulations. Most of the IT companies in Bangalore are now aware about the regulations regarding safe disposal of e-waste.

- ***Generators***

The corporate sector and government institutions contribute largely to e-waste in the form of IT equipment. In addition educational institutions and households are also significant contributors. Within the corporate sector the hardware companies have been looked at with special interest since they are required to take responsibility for the generation of e-waste. E-waste is also generated from the small and medium scale enterprises (SMEs) that manufacture electronic/electrical components. In Karnataka there are 2,000 SMEs engaged in various different manufacturing activities including manufacture of components for the electrical and electronics industry. It is also noted that SMEs generate e-waste not just from manufacturing but also contribute through extensive use of electronic equipment. If the service sector is included then the potential for generation of e-waste is huge. Most IT companies and related units in Bangalore have introduced well defined e-waste management systems including identification, segregation and safe disposal of e-waste.

- ***Recyclers***

There are two types of recyclers in Bangalore that play important role for managing the e-waste; (a) formal recyclers, (b) informal recyclers. Out of the two, the formal recyclers handle maximum e-waste recycling (E-Parisaraa Pvt. Ltd. and Ash Recyclers). E-Parisaraa Pvt. Ltd. is an enterprise solution to e-waste recycling technology in the country and was the first authorized e-waste recycler in Bangalore. In the current situation in the city, E-Parisaraa has made considerable inroads and is now a credible e-waste recycler with many big names as its customers. This included HP, IBM, GE, Intel, Motorola, ABB, Philips, Sony, WeP and SBI etc. The facilities have initiated occupational health and safety measures for all its employees with an annual turnover of 550 tons of e-waste. It entered into a contract with various companies and purchases the waste directly from them at the rate ₹8-10/kg. E-Parisaraa also acquires an export license and sending a consignment of e-waste to 'Umicore Precious Metal Refining' in Brussels, Belgium and in certain other overseas industries for pyrometallurgical and hydrometallurgical recycling. Ash Recyclers is a Bangalore based environmentally conscious e-waste recycling organization, which received authorization from the KSPCB at around the same time as E-Parisaraa in 2005. Its solution consists of creating a mix of reuse and recycling of e-waste to have a zero environmental impact and maximize value from the process of e-waste disposal. It is known to encourage second hand sale through retrieval of working components and refurbishing of old equipment through manual sorting of reusable components, company also dismantles e-waste to recover useful materials for secondary use.

Material Recovery from e-waste

As an example of the case study from our field data, Figure 2.7 shows the material recovery from one ton e-waste at E-Parisaraa Pvt. Ltd., Bangalore. Glass is 20% by weight; plastics are 23% by weight followed by metals 57%. Metals are recovered from printed circuit boards, cables, non-ferrous metals and ferrous metals. Out of one ton computer waste, 99% is used for recovery of precious metals and another 1% for safe land filling. There is no statistical data for recovery of metals by informal recyclers.

Status of technology, challenges and innovative options

It was found that current recycling operations of these companies are limited only to preprocessing of e-waste material. The processes used are a combination of manual and mechanical processes, in which manual processes forms a large part. It was also noticed that formal recyclers have a permission to establish a recycling plant and consent to export metals to approved smelters globally.

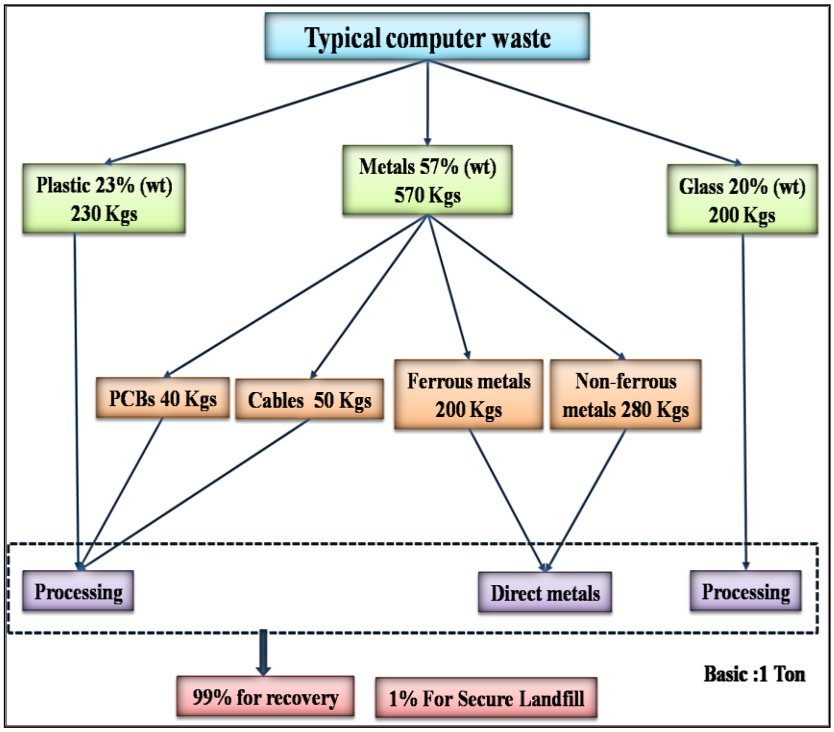


Figure 2.7: Computer composition based on the research on material recovery from e-waste conducted at E-Parisaraa Pvt. Ltd.

The companies use thermal shock techniques for separation process followed by feeding the e-waste into the shredders signaling the start of mechanical stage. The shredder materials, laden with precious metals, are then sent to smelting refineries for extraction of these metals. The technology being used for e-waste recycling in Bangalore is the shredding/pulverizing technology followed by pyrometallurgical and hydrometallurgical process. There is a need to develop a cost effective technology for extraction of precious metals and for safe disposal of hazardous metals.

From the result it was found that, the refurbishing and upgrading of personal computers constitute one of the key drivers of the pre-recycling processes. However the material flow is only based on the market values of the upgraded or refurbished items. This scheme comprises one of the most effective mechanisms to: (i) create additional value and (ii) to prevent an accelerated flow rate through the whole system. The incentive is the increasing need for low cost personal computers among the ever-increasing group in the Indian population that uses computers. The market demand creates jobs and business in a second hand industry and at the same time decrease the overwhelming load of e-waste.

2.3.1.6 E-waste scenario from the perspective of Delhi

Delhi, the capital city of India, is the hub for e-waste recycling activities. There being no authorized formal recycler in Delhi, dismantling and recovery of precious materials from e-waste is carried out by the informal sector. We surveyed the major locations in Delhi (Turkman Gate, Mayapuri, Old Seelampur, Shastri Park and Mandoli industrial area) and details are enumerated below.

Turkman Gate

Turkman Gate is one of the biggest scrap markets in Delhi known for handling e-waste. Turkman Gate is the area where e-waste comes in large quantity especially computer waste. There are some formal and informal collection systems for e-waste in scrap trading. The response for structured discussions was not encouraging in this grey market for e-waste. A few respondents shared some information while others were hesitant to respond. These scrap dealers collect e-waste from closed factories, running factories, government and private offices. From informal sources, it was learnt that scrap dealers collect 600-700 kg e-waste around each week. Dissembling processes are being carried out in closed units of this area.

Mayapuri

Mayapuri scrap market is known for handling e-waste and scrap of automobile sector. The e-waste comprise of electrical components like heaters, geysers, electrical motors, compressors, fridge, air conditioners, etc. and electronic components like computers, printers, electronic type writers, tape recorders, fax machines, telephones, televisions etc. They do not have any conceptual separation for the scrap material as they treat all scrap as a unified one. The frequency of e-waste collection is random. Collection frequency depends on the quantity of scrap available in the market. These scrap dealers have been operating from last 15-25 years in the e-waste area. Their shift to handle various type of scrap is natural as per the latest trends in technology which brings new electronic and electrical items. The response regarding mobile phones recycling was not encouraging at all. They prefer computer waste than mobile phone waste as they get better profit margin and good recoverable items from computer waste.

Old Seelampur

Old Seelampur is one of the biggest retail markets of electronic and electrical scrap trading. During our visit for structured discussions, it was felt that scrap dealers were trying to conceal the information and had some fear in their minds. They collect all type of scrap especially computers, printers, or other accessories like hard disk, compact disc Rom, monitor, mother board, other circuit boards and switched-mode power supply etc. Collection of e-waste is done through all possible sources like repair shops, service centres, through their own scrap collectors or daily scrap hawkers. The other sources of e-waste collection are also from other states through the scrap traders. Whenever companies want their scrap material to be cleared off, they just call these scrap dealers and the deal is fixed after inspecting the scrap. Old Seelampur acquires about 15-20 trucks of e-waste, amounting to about 1.0-2.0 tons of e-waste every day. The shops are generally located in the residential buildings. Approximately, 150-250 shopkeepers are engaged in this business, with two or three people working in each shop. After collecting e-waste, they either simply sell it in bulk with some profit margin. Alternatively, the parts, which fetch them a good profit, are separated and sold with higher margin. They concealed information regarding their e-waste processing technologies and facilities. These scrap dealers have been working in this area from last 10-20 years. These scrap dealers / junk dealers do not carry any concern about environment and safe handling of e-waste. Besides trade in scrap, they also dismantle the e-waste in concealed locations. Especially extracting copper by open air burning of printed circuit boards.

Previous visits by various groups to these e-waste processing units revealed the practices of scrap dealers very critically. This made them sceptical and it was really hard to get the requisite information from them amicably. They revealed that some photographs and video shootings were taken and shown publicly by previous visitors depicting the mishandling of e-waste by them with adverse environmental consequences and health hazard to workers engaged in these activities. Exposure of their practices through media and other green advocacy groups made their life difficult and worrisome. Another fear that haunts them is the sealing drive by Municipal Corporation of Delhi (MCD). The sealing drive is a campaign by the Municipal Corporation of Delhi (MCD) to close (and thus "seal" the locks of) a number of illegal commercial establishments in Delhi, India which are running in residential areas without authorization. These fears made them more sensitive and less responsive to the queries by study team.

Shastri Park

Shastri Park is known for trading and dissembling of e-waste especially computers. Generally, e-waste material like computers and other equipment come from Old Seelampur for dismantling and further processing. The response of scrap dealers from Shastri Park was almost similar to scrap dealers of Old Seelampur. Shastri Park has 10-15 shops involved mostly in dismantling and disassembling operations. The scrap dealers buy old computers for ₹300-500 each from the household. During dissembling process, breaking and separation of each and every part of computer and its accessories like mother board, monitor, printer, hard disk, floppy disk, compact disk Rom, switched-mode power supply, etc. is carried out. The sellable carried out in Muradabad and Loni in Uttar Pradesh as this process is legally prohibited in Delhi due to Pollution Control Norms. It was revealed that extraction processes are being carried out informally within the closed house premises during night only. Generally, most of the customers include repair shop mechanics.

Recyclers (Mandoli industrial area)

There is no authorized recycling facility for e-waste in Delhi and its vicinity. Recycling is mainly carried out informally in Mandoli industrial area (Delhi). This area consists of around 50-80 small PC recycling units, cable recycling units, and battery recycling units. The PC recycling units are mainly engaged in the extraction of Cu and its compounds. Here is the brief operation:-

The printed circuit boards are first dipped in a caustic soda solution and the colour of the board is scrapped off with brush. The plates are then submerged into a plastic drum containing acid solution (H_2SO_4:HNO_3:H_2O_2 in the ratio 2:1:1). The metal sludge thus formed is allowed to settle at the bottom of the drum. The metals, which precipitate during this process, are separated from supernatant by decanting the acid water. The metal sludge is then spread over plastic sheets and allowed to dry in the sun. The dried metal precipitate is powdered and sold in the local market as well as in other places like Ludhiana, Amritsar, Meerut and is used for the production of metal sheets and other components. The complete set of the extraction process is carried out by both men as well as women, who generally work without proper protection arrangements in an unsafe environment. Apart from the copper compounds, certain precious metals like Au and Ag are also extracted in the process. Gold is generally recovered from gold plated pins. These gold pins are sold to goldsmiths for

₹2500-4500 per kg in Meerut. Beside these extraction processes, Cu is also extracted from transformers by open burning. We noticed that there is no scientific process for recovering metals from e-waste and the effluent (acid water) is discarded without any pre-treatment in nearby area. Photographic evidence could not be furnished as recyclers/dismantlers did not allow getting inside the recycling/dismantling premises. The resistance from these recyclers/dismantlers made the structured discussions difficult. However, some indicative information was gathered. There is no provision of protective measures for workers in the recycling/dismantling areas. All the work is done by bare hands and only with the help of traditional equipment like screwdrivers, hammers etc. The chemicals like H_2SO_4, HNO_3, HCl etc. are being used for extraction of the metals. Figure 2.8 shows some photographs from Mandoli industrial area (e-waste recycling area) which were taken during our visit.

Comparative analysis of e-waste management in different cities

From our data regarding e-waste management, we analyzed its source, obsolescence rate and price of end of life (EOL) personal computers (PCs). Common sources of e-waste are educational institutes, households, information and communication technology (ICT) industry and imported computers. Out of these, ICT industry plays an important role in production of e-waste. We did not find any formal recycling units in Himachal Pradesh (HP), Chandigarh, Meerut and Delhi and the e-waste generated from these cities were recycled by informal sectors. But Bangalore, adapts formal recycling of e-waste. We compared the obsolescence rate of PCs among the areas studied. We found the obsolescence rate of PCs was same for Himachal Pradesh, Chandigarh and Meerut. In Delhi, it was 5 to 7 years. But in case of Bangalore, the obsolescence rate was higher (3-5 yrs). This is because the Bangalore being the IT hub of India and IT industry requires quick up-gradation of software and hardware. Moreover KSPCB has also implemented e-waste regulations to every IT company to discard their IT equipment in every 3 years. They follow it strictly and recycle their e-waste through formal recyclers. Table 2.8 represents the source of e-waste, dismantle/resale areas, recycling areas and obsolete rate of PC in different cities of India. There is no difference in price of EOL PCs in Chandigarh, Meerut, HP and Delhi. The scrap dealers collect PCs as metal scrap not as e-waste. There was no organized way to collect this waste. We could not identify any government authorized dealers to collect the e-waste. The prices mentioned in Table 2.9 might vary and were average price for EOL PCs. In Bangalore, the

IT companies declare tenders for disposing their e-waste and only formal recyclers make a bid to get it. So, we found there is a structured way to collect and recycle this waste in Bangalore.

Table 2.8: Source, resale and recycling areas of e-waste in different cities of India

City	Source of e-waste	Dismantle/Resale	Recycling	Obsolescence rate in years for PC
Solan	Computer manufacturer industries, Educational institutes, Households	Nalagarh Baddi	Chandigarh Delhi	7
Chandigarh	ICT companies, Educational institutes, Households	Scrap Market Phase-I, Industrial area	Mandoli (Delhi) Amritsar	7
Meerut	Educational institutes, ICT companies, Households	Jailchungi Shastrinagar	Old Seelampur (Delhi)	7
Delhi	Computer manufacturer industries, Educational institutes, ICT companies, Imported computers, Households	Mandoli Turkman Gate Shastri Park Old Seelampur	Old Seelampur Mandoli Ferozabad Moradabad Mayapuri	5-7
Bangalore	ICT companies, Educational institutes, Households	ASH Recyclers E-Parisaraa Pvt. Ltd. (Govt. Authorized)	ASH Recyclers E-Parisaraa Pvt. Ltd.(Govt. Authorized)	3-5

Figure 2.8: Mandoli e-waste recycling area in Delhi (a) storage CRTs, (b) an area used for extraction of copper wires from transformer, (c) and (d) dumping of PWB after metal extraction, (e) premises of a recycling unit and (f) degradation of soil on the rear side of a recycling unit

Table 2.9: Comparative Price of EOL PCs

Computer parts	Baddi & Shimla	Chandigarh	Meerut	Delhi	Bangalore
B &W monitor	₹200	₹70	₹200	₹70	PC – ₹8.25/kg
Color monitor	₹400	₹400	₹400	₹300	
CPU	₹20/kg	₹20-25/kg	₹20/kg	₹15-20/kg	
Keyboards	₹10/Piece	₹10-15/Piece	₹10/Piece	₹10-15/Piece	

A flow chart (Figure 2.9) was prepared for e-waste trade cycle for all cities of India. This flow chart explains the common trends for recycling of PCs. These results indicate that, maximum out dated PCs are exchanged with vendors rather than disposed through formal recyclers or donated to their friends/relatives. The out dated PCs and its parts are resoled/reused in various sectors before going for recycling. Over all, the e-waste is recycled through reuse and resale in India.

Figure 2.9: E-waste trade cycle for all surveyed cities of India

2.3.2 Study of occupational health at recycling facilities

2.3.2.1 Health impact assessment of workers working in recycling units in Mandoli industrial area, Delhi

Mandoli industrial area is one of the major informal e-waste recycling sites in India, including mid-scale and household-sized workshops. Their operations involved: (1) manually classification and dismantling of e-waste; (2) shredding; (3) separation of e-waste (scrap or components, such as printers, mobile phones or printed circuit boards); (4) manual separation and solder recovery for mounted printed circuit board; (5) usage of acids to extract materials (precious metals) from e-waste; and (7) shredding and heat-extruding processing of scrap plastic. Because of informal and substandard processing this site is contaminated with heavy metal dust, effluents and untreated residues. Open-storage of e-waste has been found at these sites along with incineration of e-waste. Contamination from particulate and gaseous emissions containing heavy metals, dioxins, PHAs, acids and other compounds from such incinerators, as well as fly ash and residue disposal, are of great concern [147]. Additionally, the low combustion temperature and locally oxygen-starved conditions associated with open burning may result in incomplete combustion and increased pollutant emissions [148].

All categories of people including children, women and old aged persons were working in recycling units without using any protections like masks, gloves, safety glasses. These units hardly abide by regulations providing the framework for controlling open burning and dumping of e-wastes and residues to minimize the risk of environmental pollution. Amid the e-waste recycling activities, agricultural operations, such as raising seasonal vegetables, were seen near the recycling area.

The extraction of the metals in the recycling units, as explained, is highly generic and rudimentary in nature. Mostly workers work in closed dingy areas. At many occasions, they handle acid, caustic solution by bare hands while being barefooted. However, when preparing the acid solution, occasionally they use rubber gloves. They hardly use mask or goggles. The extraction of Cu metal from the wires is done in small rooms with insufficient ventilation. The workers in Mandoli e-waste recycling units are thus exposed to several toxic elements. They work for 8-10 hours daily. In each of the recycling units, about six to eight men and women in the age group of 25-30 years were employed. The workers stay inside the industrial area. Children of these workers also have been seen in the recycling units, and thus exposed to toxic materials. Usually, they take meals inside the units working along with toxic and hazardous materials. Thus, not only the workers but also their children are vulnerable to the toxic and hazardous metals and materials that ultimately affect their health. The acid fumes and the toxic gases may affect workers, especially their hands, eyes, and lungs, as these are the most vulnerable body parts. During our impact assessment survey, we tried to discuss about their health problems and also about the efficiency and implications of the processes followed for recovering metals and materials from e-waste. The workers were hesitant to respond about the operations of e-waste recycling units. They did not disclose their personal information in the fear of their owner and publicity. A snapshot of recycling units and their surroundings is given in Figure 2.10.

Figure 2.10: Snapshot of Mandoli e-waste recycling units and their surroundings (a) drums containing acids (b) lodging of liquid residues (acids, water), (c) backside of recycling unit, (d) a drain having acid water and residues in front of a recycling unit

Challenges: Health and the environment

- ⊗ Informal collectors were open to a range of threats, including health hazards
- ⊗ Environmentally unfriendly recycling activities were found. Health and safety precautions for workers were also not always adhered to.
- ⊗ Potentially hazardous e-waste was disposed in landfills.

As outlined, the collection, refurbishment/repair and recycling of e-waste occurs in both the formal and informal sectors. Each of these sectors offers different views of the occupational health and impact of e-waste in the country.

Formal sector

There was a mix of formal and casual employment of workers at the recycling facilities visited in our study. At E-Parisaraa Pvt. Ltd. and ASH Recyclers, workers, who were considered semi-skilled, offered a course in English, and received on-site training for e-waste recycling. Many women were employed for less technical or physical tasks, including administrative or cleaning duties, and for activities that required repetitive labor, including cleaning of equipment and sorting waste on conveyor belts. Health and safety regulations were followed at most of the sites visited. E.g. there was a strict enforcement of the use of Personal Protective Equipment (PPE) while using dust extractors on grinders. The following measures of hazardous e-waste management for workers were observed:

- ⊕ Protection against noise (e.g. wearing ear-muffs on sites where large quantities of e-waste shifted with heavy machinery for refurbishment processes).
- ⊕ Protection for eyes (e.g. wearing safety glasses where e-waste is moved and smashed in large quantities).
- ⊕ The protected use of cleaning agents (in refurbishment processes)

Informal sector

E-waste is unlikely to be a primary waste stream for informal collectors, who will typically work with a range of recyclable items (e.g. cardboard, glass, any kinds of scrap metal, as well as old electronics). We collected this data from a so called recycler of Meerut and a Delhi based NGO named as Toxics Link. Table 2.10 shows the common processes of recycling of e-waste and their potential occupational and environmental hazard association. While the informal sector in India offers critical income generating opportunities for people, when it comes to e-waste, negative social impacts exist.

Environmental problematic practices by the informal recyclers generally include:

- ⊗ A lack of basic safety equipment
- ⊗ A lack of basic safety information about e-waste
- ⊗ The mechanical shredding of monitors and white goods such as refrigerators, washing machines, air conditioners, and PCs etc.
- ⊗ The stockpiling of hazardous fraction.
- ⊗ Passing hazardous fraction on to other recyclers, without proper knowledge of how to dispose it off safely.
- ⊗ Land filling of potentially harmful plastics.
- ⊗ Unsafe disposal of batteries in, some instances.
- ⊗ Premises that are not properly contained to prevent run-off of contaminated water
- ⊗ E-waste exposed to rain is a cause of leaching of metals.
- ⊗ Many recyclers do not treat effluents/leachates, or test land filled fraction for toxicity.
- ⊗ On-site incineration of e-waste.

Table 2.10: Potential occupational and environmental hazard associated with recycling of e-waste

Computer components	Common process of recycling	Potential occupational hazard	Potential environmental hazard
CRT	Breaking, removal of copper yoke, recycling of glass	Silicosis, inhalation or direct contact with phosphor containing cadmium and other metals such as Pb, Hg	Release of lead, mercury, barium, toxic phosphor, and other heavy metals into water and soil
PCBs	De-soldering and removing of computer chips	Inhalation of tin, lead, dioxin, beryllium, cadmium, mercury	Air emission of metals and dioxin
Chips and other related components	Chemical processing using nitric acid and hydrochloric acid	Corrosive injury to eye and skin, inhalation of acid fumes and harmful gases such as chlorine and sulphur dioxide	Hydrocarbons, heavy metals, halogenated substances, acids in water and soil, and air emission
Wires and cables	Burning to recover metal wire	Inhalation of brominated and chlorinated dioxin, PAHs	Emission of brominated and chlorinated dioxin, PAHs
Secondary steel, copper, and precious metal smelting	Furnace to recover steel and copper	Heat injury, inhalation of dioxins and heavy metals	Emission of dioxins and heavy metals

2.3.3 Analysis of surface soil, groundwater and local vegetation near the recycling sites

2.3.3.1 Heavy metal contents in surface soils

Mean and standard error comparisons of each heavy metal from S1, S2, S3, S4 and S5 sites based on Duncan’s test are presented in Table 2.11. Generally, Al and Cu were high in all the soils. On the contrary, Hg was not detected in any of the soils from S2, S3 and S4. Higher concentrations of Cu, Zn, Fe, Pb, and Cr were observed in soils from S1 and S2 than in S3, S4, and S5. The variability in the distribution of metals was evaluated with ANOVA, which revealed significant variation in concentration pattern of 13 metals (Table 2.12). Ag, Cd, and Hg concentrations were higher in soils from recycling units compared to village soil. The high heavy metal concentrations in the studied sites resulted from continuous dispersal downstream from the e-waste recycling operations like waste waters of the acid digestion [44]. Furthermore, concentrations of most of these elements were higher in S1 and S2 than S5 site i.e. soils from recycling units than agricultural land of adjoining village, showing that the crude methods of recycling may add higher levels of these elements to the environment. Elevated levels of heavy metals derived from e-waste contribute to pollution of the ambient environment. Our data were comparable to concentrations of heavy metals in soils reported earlier near and at the open-burning sites in the e-waste recycling area of Mandoli industrial area [31]. Concentrations of heavy metals in soils from Mandoli industrial area, Delhi is compared with data in literature: (1) soils/dusts polluted by dumping waste, effusion, or incineration residues, (2) soils/field surrounding small family run workshops involving e-waste recycling activities, and (3) soils from abandoned family-run workshops involving e-waste recycling activities (Table 2.13). Trends obtained in our study were comparable to Guiyu e-waste processing site in China [149]. US Environmental Protection Agency (EPA) has published soil-screening values for some trace elements for residential and industrial-outdoor area. In the present study, soil samples from S1 and S2 had concentrations over the screening values for residential soils for Cu, As and Pb. For Pb and As, soil samples collected from the e-waste recycling area (S1 and S2) exceeded the industrial outdoor screening value. These results indicate that soil contamination by heavy metals from e-waste recycling may lead to human exposure to the heavy metals.

Table 2.11: Duncan's test for mean comparisons (Standard error) of heavy metal concentrations in soil samples collected from Mandoli industrial area, Delhi.

Elements (mg/kg) (SE)	S1	S2	S3	S4	S5
Ag	12.38^{a}(1.22)	10.75^{a}(1.42)	0.46^{a}(0.05)	0.29^{a}(0.03)	0.28^{a}(0.06)
Al	8822.14^{h}(16.61)	14142.58^{g}(21.80)	6476.44^{e}(17.12)	6538.78^{e}(23.82)	6432^{e}(25.51)
As	12.85^{a}(1.86)	17.08^{a}(1.54)	3.75^{a}(0.74)	0.00^{a}(0.00)	0.00^{a}(0.00)
Cd	1.14^{a}(0.13)	1.29^{a}(0.17)	0.70^{a}(0.05)	0.06^{a}(0.02)	0.04^{a}(0.01)
Co	13.25^{a}(2.12)	12.43^{a}(1.10)	4.94^{a}(0.98)	2.32^{a}(0.31)	2.56^{a}(0.19)
Cu	6734.86^{g}(24.51)	4291.61^{f}(11.31)	76.98^{c}(3.40)	65.32^{c}(2.69)	63.45^{c}(1.89)
Cr	83.57^{b}(2.69)	115.5^{b}(5.44)	34.79^{b}(1.26)	22^{ab}(2.00)	16.35^{ab}(1.39)
Fe	4037.41^{f}(22.70)	4129.79^{e}(18.31)	2952.25^{d}(12.46)	1329.48^{d}(23.15)	1134.66^{d}(16.84)
Hg	0.07^{a}(0.02)	0.08^{a}(0.03)	0.00^{a}(0.00)	0.00^{a}(0.00)	0.00^{a}(0.00)
Ni	146.5^{c}(2.70)	126.46^{b}(3.60)	44.67^{b}(1.99)	35.11^{b}(1.52)	35.74^{b}(1.41)
Pb	2133.98^{e}(18.69)	2645.31^{d}(14.81)	40.28^{b}(4.23)	29.61^{ab}(2.98)	27.94^{ab}(3.59)
Se	12.34^{a}(1.02)	12.67^{a}(2.05)	4.58^{a}(0.60)	4.23^{a}(0.57)	4.57^{a}(0.71)
Zn	416.31^{d}(6.66)	776.84^{c}(7.94)	90.28^{c}(4.22)	68.36^{c}(2.01)	62.47^{c}(4.15)

Significant level at $P \leq 0.05$

Table 2.12: One-way ANOVA for the metals analysed from soil samples collected from Mandoli industrial area

Element	Ag	Al	As	Cd	Co	Cu	Cr	Fe	Hg	Ni	Pb	Se	Zn
F	54.20	24398.80	47.68	35.18	21.04	64177.41	210.10	5717.47	4.64	515.54	13965.61	15.09	54.20
P	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.022	0.000	0.000	0.000	0.000

Table 2.13: Metal concentration (mg/kg) in soils from Mandoli industrial area, Delhi and other studies

Sites	Ag	Al	As	Cd	Co	Cu	Cr	Fe	Hg	Ni	Pb	Se	Zn	Reference
S1	12.38	8822.14	12.85	1.14	13.25	6734.86	83.57	4037.41	0.07	146.5	2133.98	12.34	416.31	This study
S2	10.75	14142.58	17.08	1.29	12.43	4291.61	115.5	4129.79	0.075	126.46	2645.31	12.67	776.84	This study
S3	0.46	6476.44	3.75	0.7	4.94	76.98	34.79	2952.25	0	44.67	40.28	4.58	90.28	This study
S4	0.29	6538.78	0	0.06	2.32	65.32	22	1329.48	0	35.11	29.61	4.23	68.36	This study
S5	0.28	6432	0	0.04	2.56	63.45	16.35	1134.66	0	35.74	27.94	4.57	62.47	This study
E-waste recycling site in slum in Bangalore, India	2.2-320			0.385-38.9	5.2-42	61.7-4790	46-160		0.09-59		90.4-2850		126-2530	[150]
E-waste recycling facility in Bangalore, India	1.3-8.7			0.301-0.906	12.0-16	154-2190	50-62		<0.05		79.1-262		119-499	[150]
Control site in Bangalore, India	0.24-0.53			0.082-0.296	4.9-17	10-40.4	38-190		<0.05		12.6-35.6		30.3-59.8	[150]
Guiyu Soil of abandoned sites using acid processing, China			26.03	1.21		4800	2600		0.21	480	150		330	[151]
Guiyu Residue from waste open burning site, China			52.1	10.02		12700	320		0.19	1100	480		3500	[151]
Area near the open burning site of e-waste in Guiyu, China				24.2		7814	307			403.6	3947		2922	[149]
Dust inside PCB processing, India			<200	<5		2670	<20		<10	14	375000		21	[125]
Residential	390	77000	0.39	70	23	3100	210	55000	23	1500	400	390	23000	[152]
Industrial-outdoor worker	5100	990000	1.6	800	300	41000	500	720000	310	20000	800	510	310000	[152]

Hierarchical cluster analysis (HCA)

Based on the HCA results, the soil sampling sites were classified into three clusters using a criteria value of rescaled distance between 0 and 10 (Fig.ure 2.11). There were two sites (S4 and S5) in cluster I, S3 in cluster II, and two sites (S1 and S2) in cluster III, respectively. The mean concentrations of heavy metals in cluster III were higher than those in cluster I and II (Table 2.11). Notably, the two sampling sites in cluster III were from e-waste recycling sites, while other three sampling sites in cluster I and II were away from the e-waste recycling sites. The location of Mandoli industrial area appeared to be affected by the heavy metal concentrations in the surface soils greatly due to the informal recycling of e-waste. The cluster analysis was performed to investigate the relationship among the 13 metal elements analysed from soil samples (Figure 2.12). The 13 elements can be classified to one group. The relationship of elements in the one group was hard to explain, and the association among elements were complicated. So the elements were further classified into six clusters i.e. Hg to Pb in cluster I; As and Cr in cluster II; Ag to Co, in cluster III; Cu in cluster IV; Cd and Fe in cluster V; Al and Zn in cluster VI respectively using a criteria value of rescaled distance between 0 and 10 (Figure 2.12).

From this analysis, it seemed that the location of the sampling sites were a very important factor in determining the soil heavy metal concentrations since the samples collected from inside the e-waste recycling sites (S1 and S2) had a much greater accumulation of heavy metals which form one cluster. It was very difficult to describe the heavy metals grouping as e-waste is complex in nature and their mode of interaction with soil systems after recycling of e-waste. To clarify these problems, factor analysis (principal component analysis) was carried out.

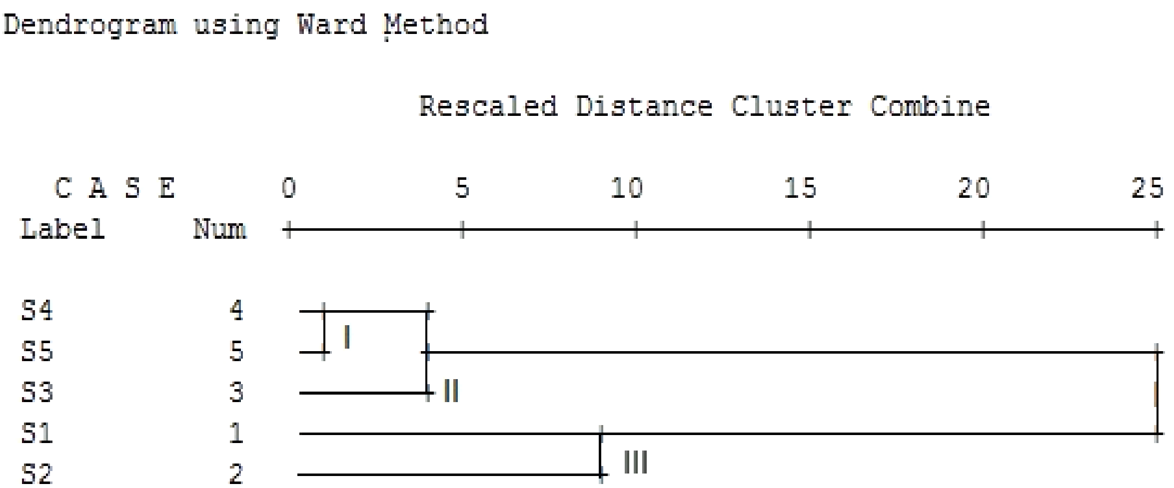


Figure 2.11: Cluster tree of soil sampling sites using cluster analysis

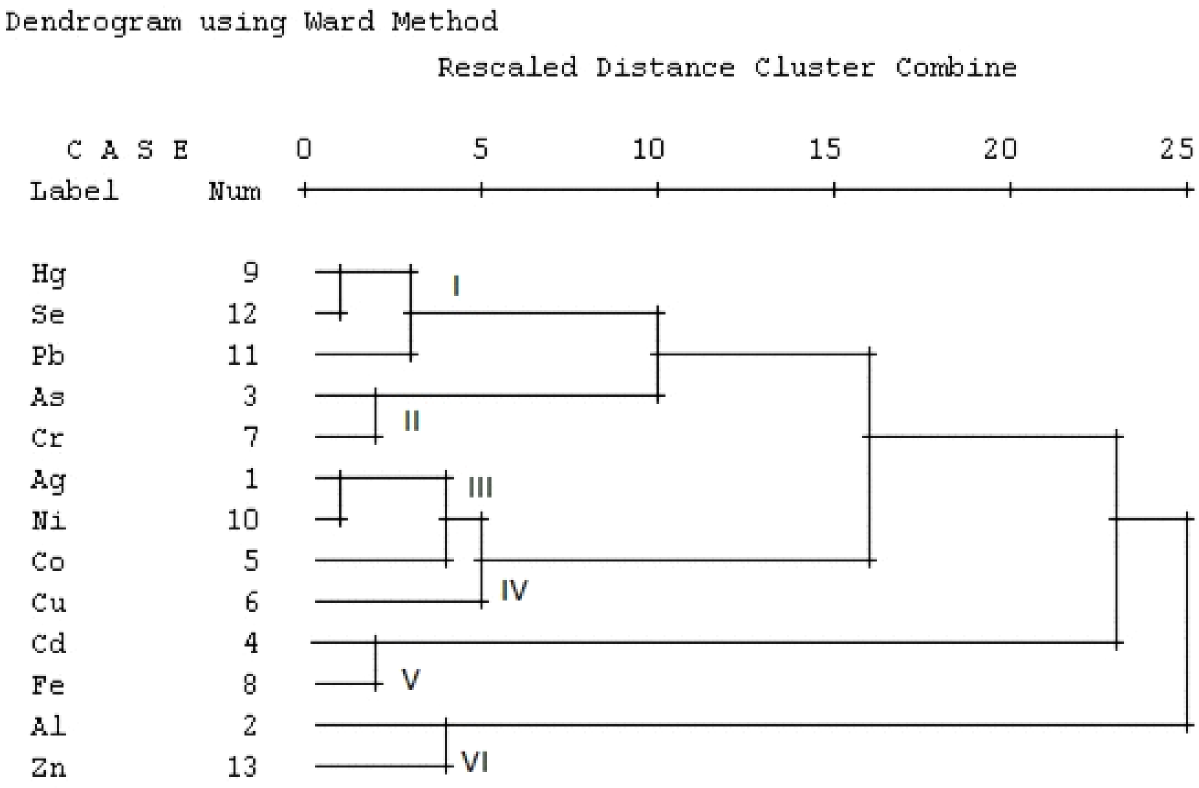


Figure 2.12: Cluster tree of elements from soil samples using cluster analysis

Principal component analysis

The data matrix of 5 X 13 (5 sampling sites and 13 elements) was used for PCA analyses. PCA was used to know the relationship among sampling sites based on the heavy metal content. The principal components with Eigen values larger than 1 were extracted with the loading rotated for the maximum variance. A total of two principal components (PC) were extracted, accounting for 98.995% of the total variance (Table 2.14). High loading of PC1 corresponded to S2, S3, S4 and S5, while S1 was low loadings to PC1 (Table 2.15) and accounted for about 72.156% of the total variance (Table 2.14). PC2 accounted for 26.839% of the total variance (Table 2.14) and showed high loadings on S1 (Table 2.15). This study selected absolute factor loadings of over 0.7 to evaluate the relationship among soil sampling sites. Figure 2.13 shows scores plot of PC1 versus PC2 indicating S4 and S5 sites were placed in one point, S1, S2 and S3 placed on separate points on the basis of rotated components values. It once again describes that, the relationship among the sampling sites based on their heavy metal content which was comparable with HCA analysis. It also describes that, due to informal recycling of e-waste the heavy metals were more deposited at sites S1 and S2, whereas S3, S4 and S5, having no informal recycling facility exhibited very less heavy metal contents and form separate groups.

Table 2.14: Total variance explained for the soil sampling sites

Component	Initial Eigen values			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.608	72.156	72.156	3.608	72.156	72.156
2	1.342	26.839	98.995	1.342	26.839	98.995
3	0.045	0.900	99.895			
4	0.005	0.105	100.000			

Table 2.15: Principal component loadings after rotation for the maximum variance in the soil sampling sites

Sites	Components	
	PC1	PC2
S4	**0.897**	0.438
S5	**0.897**	0.434
S3	**0.869**	0.462
S2	**0.714**	0.696
S1	0.413	**0.910**

Absolute factor loadings of above 0.7 are shown in bold

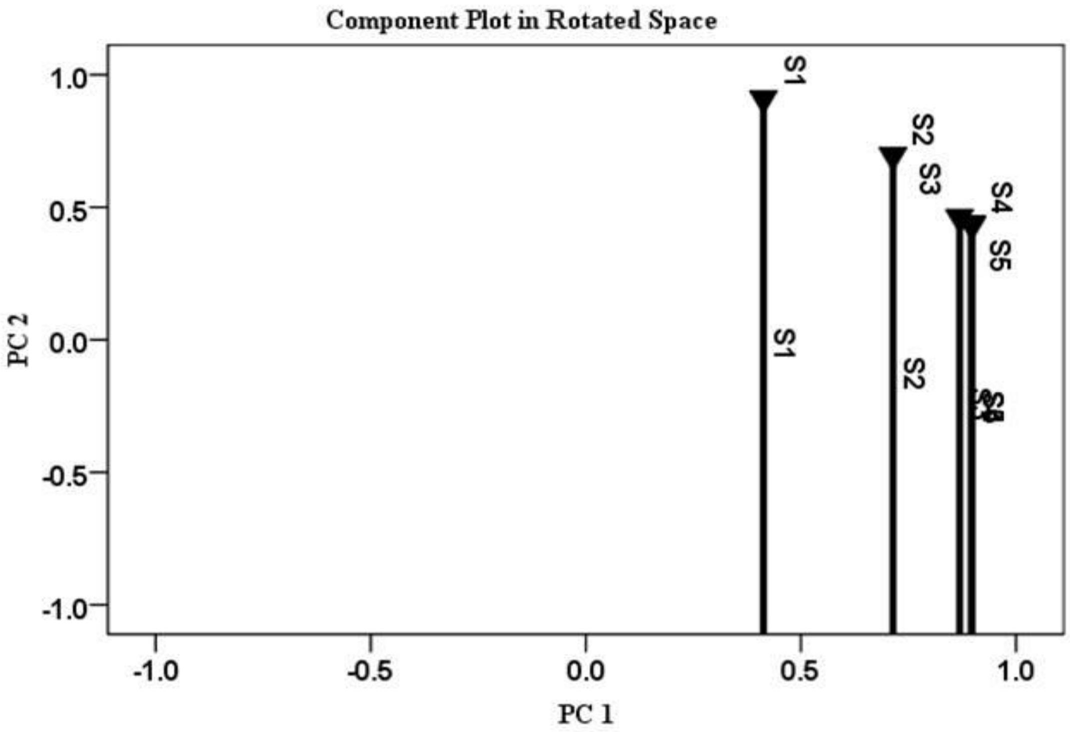


Figure 2.13: Score plot for different soil sampling sites, PC1 vs. PC2

PCA was also calculated among the thirteen heavy metals analyzed in soil samples. The Eigen values (> 1.0) of the first two components, percentage of variance and cumulative percentage of variance determined by factor analysis are presented in Table 2.16. It revealed that the Eigen values of each of two components, which exceeded 1, explained 97.224% of total variance in the data set abstracted from Mandoli industrial area. Table 2.17 presented the loading of the varimax-rotated factor matrix for the two principal components belonging metal elements. PC1, which comprised high loadings on As, Pb, Se, Hg, Co, Cr, Ag, Ni, and Zn, accounted for 76.979% of total variance (Table 2.17). High loading of PC2 corresponded to Cd, Fe, Cu, and Al and low loadings on As, Pb, Se, Hg, Co, Cr, Ag, Ni, and Zn, accounted for 20.245% of total variance. Figure 2.14 shows the score plot for heavy metals based on loading for varimax rotated factor matrix. The results were explained that, the heavy metals were formed two broad groups. But, these results also comparable to cluster analysis of elements (Figure 2.12). To explain the actual relationship among soil sampling sites and heavy metal elements, further multidimensional scaling was analyzed.

Table 2.16: Total variance explained for the heavy metals in different soil sampling sites

Component	Initial Eigen values			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	10.007	76.979	76.979	10.007	76.979	76.979
2	2.632	20.245	97.224	2.632	20.254	97.224
3	0.357	2.746	99.970			
4	0.004	0.031	100.000			

Table 2.17: Principal component loadings after rotation for the maximum variance in the heavy metals in soil samples

Elements	Components	
	PC1	PC2
As	**0.935**	0.325
Pb	**0.883**	0.465
Se	**0.859**	0.497
Hg	**0.848**	0.526
Co	**0.794**	0.596
Cr	**0.781**	0.611
Ag	**0.755**	0.539
Ni	**0.725**	0.602
Zn	**0.720**	0.683
Cd	0.340	**0.937**
Fe	0.508	**0.859**
Cu	0.638	**0.768**
Al	0.693	**0.717**

Absolute factor loadings of above 0.7 are shown in bold

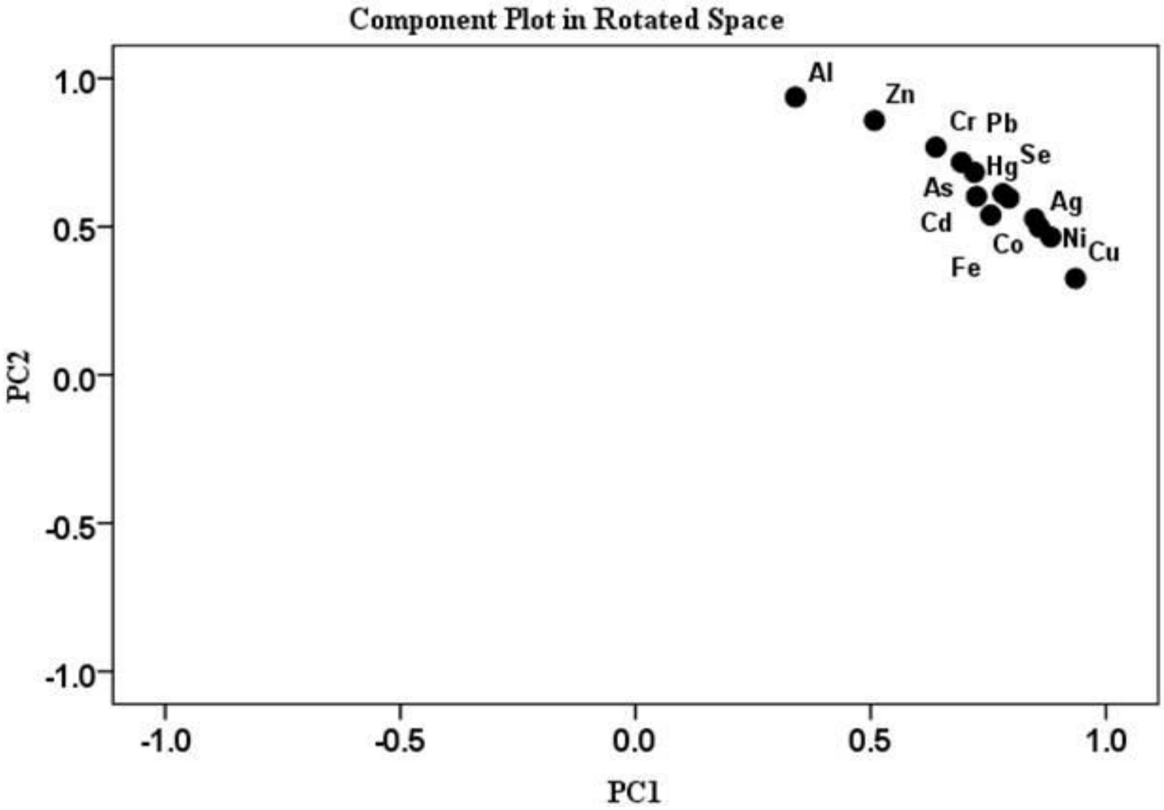


Figure 2.14: Score plot for different elements in soil samples, PC1 vs. PC2

Multidimensional scaling (MDS)

Multidimensional scaling (MDS) using Euclidean distance model was applied to further verify the classifying results above i.e. among the sampling sites (Figure 2.15) and among the heavy metal elements (Figure 2.16). The analysis of scatter plot of linear fit suggested the multidimensional scaling in this study was quit valid for the sampling sites (Figure 2.17) and among heavy metals in soil samples (Figure 2.18). The multidimensional scaling for the sampling sites showed that four groups, soil sampling sites S4 and S5 in group I, S2 in group II, S1 in group III and S3 in group IV which was consistent with the results of cluster and factor analysis. The heavy metals scattered through four groups i.e. Al, Zn and Pb in group I; Hg, Se, Ag, Ni, and Cu in group II; Co, Cd, and Fe in group III; and As, Cr in group IV. While the results were compared with cluster and factor analysis and it was similar with the dendrogram and PC values after rotation.

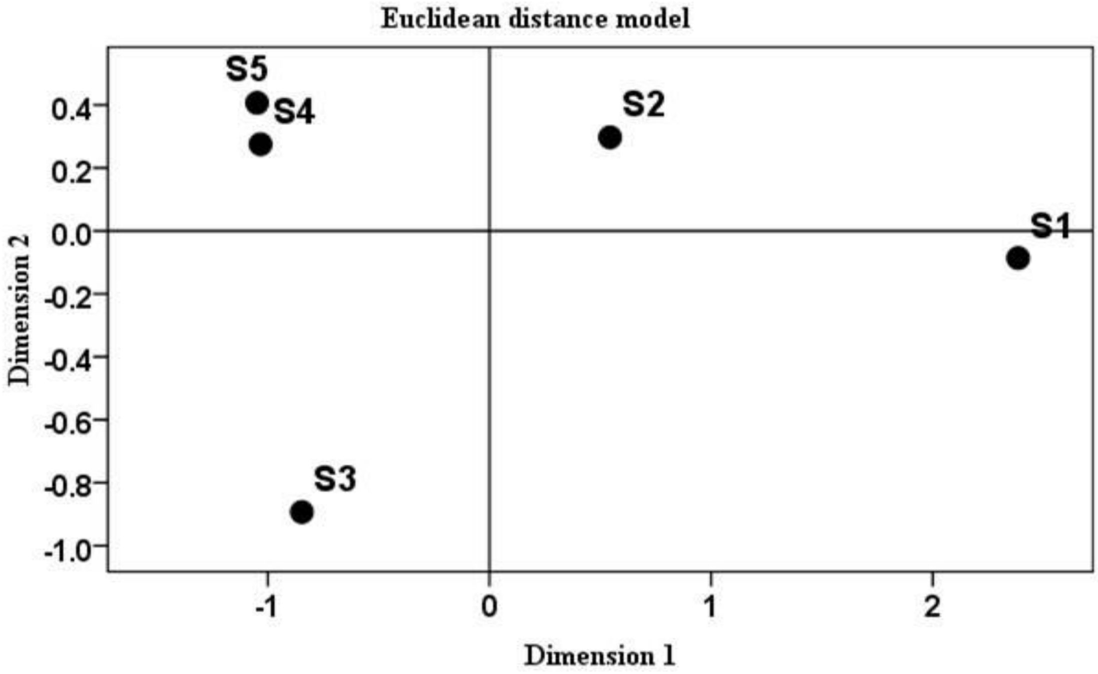


Figure 2.15: Multidimensional scaling of different soil sampling sites based on heavy metal concentration

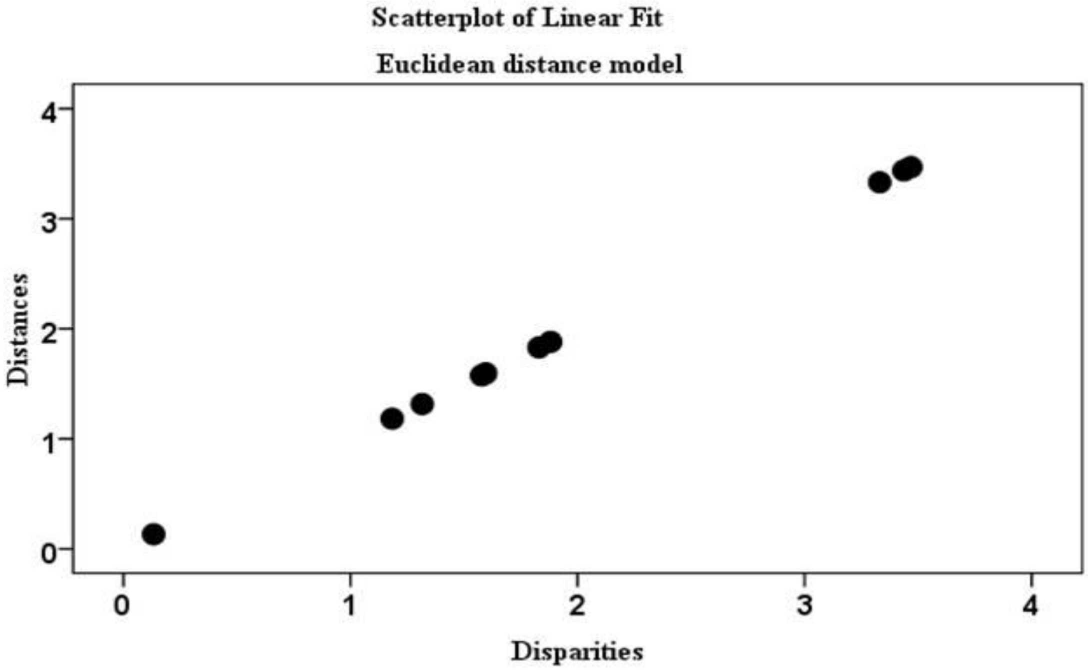


Figure 2.16: Scatter plot of linear fit for MDS analysis of soil sampling sites

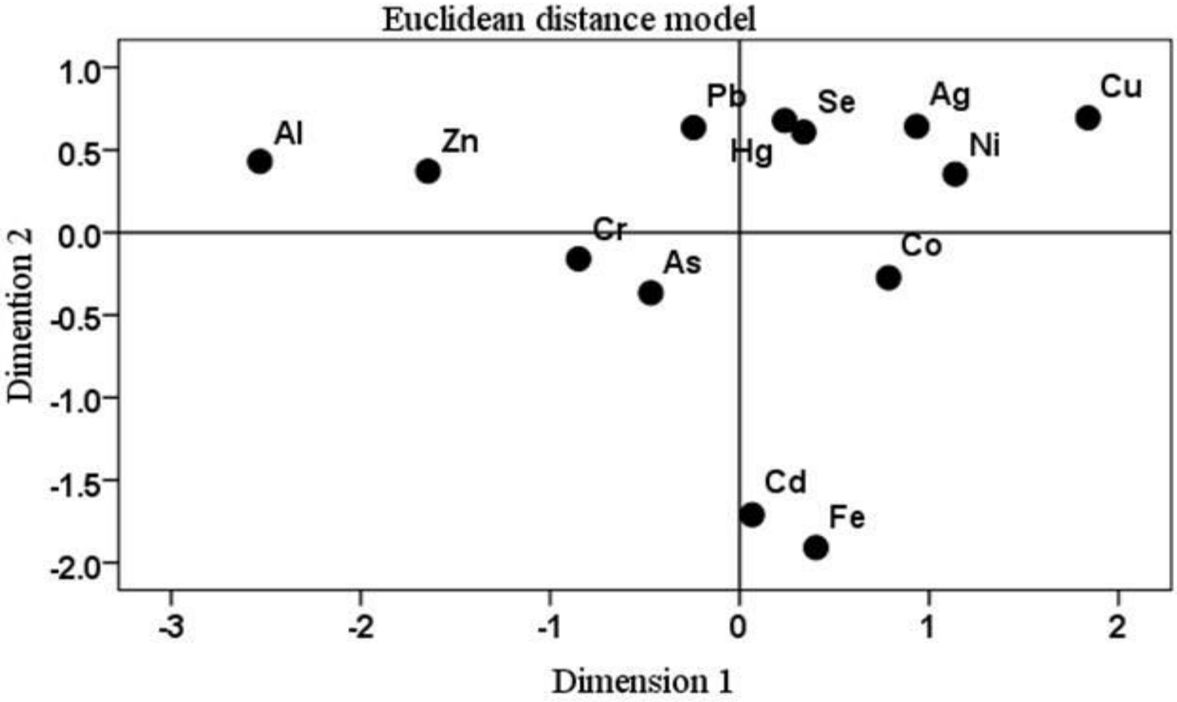


Figure 2.17: Multidimensional scaling of heavy metal concentrations of soil samples

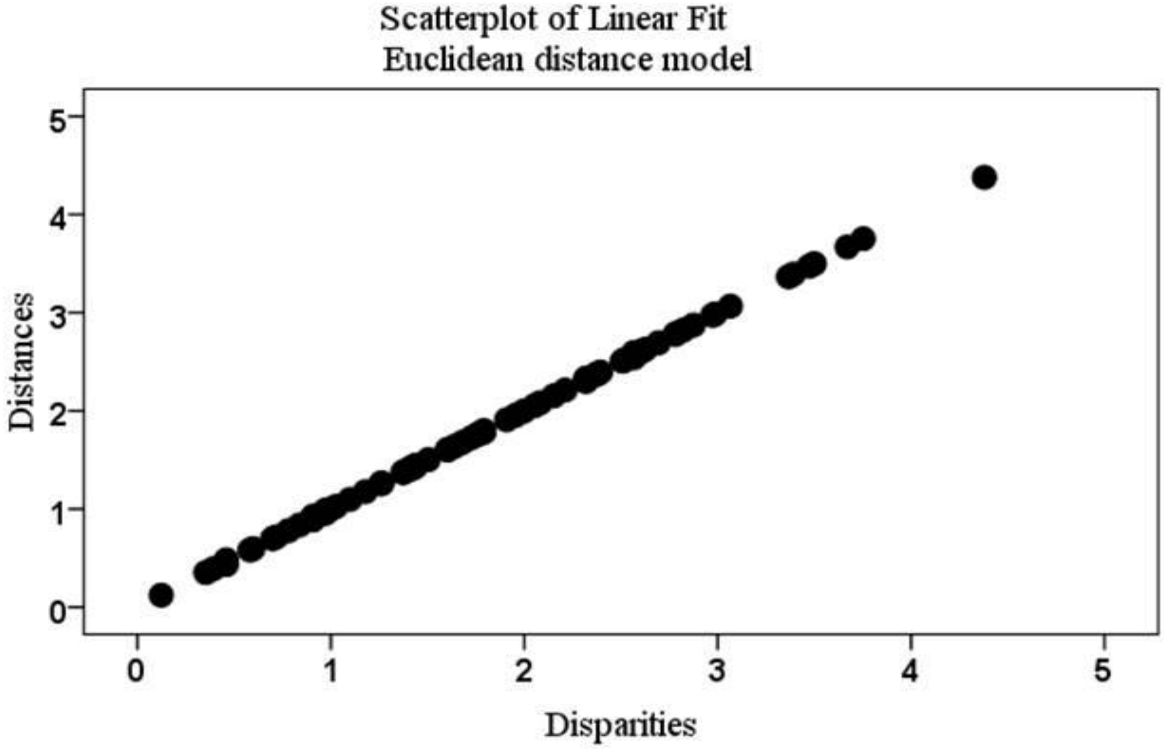


Figure 2.18: Scatter plot of linear fit for MDS analysis of heavy metal concentrations of soil samples

Index of geoaccumulation (I_{geo})

The results of the I_{geo} were used to measure the soil quality for Mandoli industrial area according to the classification proposed by Muller (1981) (Table 2.3) (Figure 2.19) [130]. According to this, S1 and S2 sampling sites were extremely polluted by Ag, Cu, Pb, and Se, while moderately to heavily pollute by As, Cd, and Zn. These metals are the main source of e-waste. In case of S3, S4 and S5 only Ag and Se showed heavily to extremely polluted where as other elements exhibited no pollution. This might be due to the absence of informal recycling units and horizontal spread of metal pollutants in these areas.

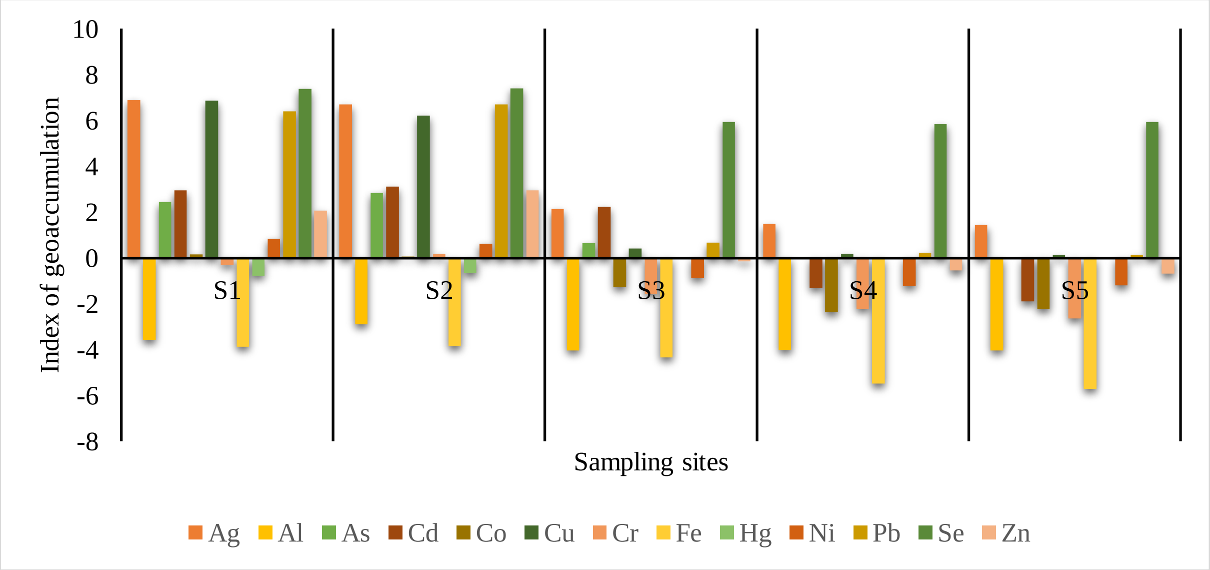


Figure 2.19: Index of geoacuumulation (**I_{geo}**) for the metals analyzed in the Mandoli industrial area for this study

Enrichment factor (EF)

Calculated EFs using Earth's crust average concentration of soil exhibited that, most of the elements including Ag, As, Cd, Co, Cu, Cr, Fe, Hg, Ni, Pb, Se and Zn had EF greater than 1 (Table 2.18). The EFs for As and Hg were less than one i.e. zero for S4, S5 and S3, S4, and S5, respectively as these elements were not detected in soil samples of these sites. S1 and S2 sites exhibited extremely high enrichment of Ag, As, Cd, Cu, Pb, Se and Zn, while these also showed significant enrichment of Co, Cr, Hg, and Ni. S4 and S5 sites explained the significant enrichment of all elements except Ag and Se which EFs showed extremely high enrichment. The EF for all elements in case of S3 was intermediate between S1, S2 and S4, S5. A comparison among different sampling sites of Mandoli industrial area based on EFs of elements shows that S1 and S2 have almost similar EFs, and S4 and S5 also have similar EFs except for As and Hg, which were higher in soils of S1 and S2. The calculated EFs explained the heavy metals were extremely high enrichment in soils of informal e-waste recycling sites as compared to soils collected from residential sites. These results explained the heavy metals occurrence in surface soils due to e-waste recycling processes.

Table 2.18: Enrichment factor of soils from Mandoli industrial area, Delhi

Element	S1	S2	S3	S4	S5
EF-Ag	1423.33	770.97	72.14	44.98	44.15
EF-As	64.63	53.59	25.73	0.00	0.00
EF-Cd	91.75	64.76	76.85	6.51	4.42
EF-Co	13.33	7.80	6.78	3.15	3.53
EF-Cu	1389.79	552.44	21.67	18.19	17.96
EF-Cr	9.75	8.40	5.54	3.46	2.62
EF-Fe	0.81	0.52	0.81	0.36	0.31
EF-Hg	7.04	4.71	0.00	0.00	0.00
EF-Ni	21.44	11.54	8.92	6.93	7.17
EF-Pb	1010.24	781.19	26.01	18.91	18.14
EF-Se	1986.23	1272.14	1005.59	918.61	1008.92
EF-Zn	50.01	58.21	14.79	11.08	10.29

Contamination factor

Table 2.19 shows the contamination factor and contamination degree of soil from Mandoli industrial area. Soils of S1 and S2 were very high contaminated $(6 \le C_f^i)$ with Ag, As, Cd, Cu, Pb, Se, and Zn whereas moderately contaminated $(1 \le C_f^i < 3)$ with Co, Cr, Hg and Ni. In case of S4 and S5 the soils exhibited low contamination factor $(C_f^i < 1)$ with Al, As, Cd, Co, Cr, Fe, Hg, and Ni and moderately contaminated with Cu, Pb, and Zn. Soil samples of S3 explained highly contaminated with Ag, Cd, and Se and the other elements exhibited low contamination factor including low contamination to moderately contamination. This data again confirms that soils collected from recycling units (S1) and dumping site (S2) acts as a sink for heavy metals and that the residential area (S4, S5) low contaminated with toxic elements. The sources of contamination that exist within Mandoli industrial area (S1 and S2) are:

- Informal recycling of e-waste like acid bath and open air burning
- Dumping of e-waste, randomly throughout the area
- Untreated industrial effluents discharged into nearby drainage

The contamination factor described above is a single element index. The sum of contamination factors for all elements examined represents the contamination degree (C_{deg}) of the environment. The sum of contamination factors for all metals examined is listed in Table 2.19 (last row) which shows that the degree of contamination in soil of study area is very high. In case of S1 and S2 all the elements contribute for the very high degree of contamination whereas only two elements (Ag and Se) contributed to S4 and S5 for very high degree of contamination. So, from these results, it was observed that S1 and S2 exhibited very high contamination as compared to S3, S4 and S5.

Table 2.19: Contamination factor of soil from Mandoli industrial area

Element	S1	S2	S3	S4	S5
Ag	176.86	153.57	6.57	4.14	4.00
Al	0.12	0.20	0.09	0.09	0.09
As	8.03	10.68	2.34	0.00	0.00
Cd	11.40	12.90	7.00	0.60	0.40
Co	1.66	1.55	0.62	0.29	0.32
Cu	172.69	110.04	1.97	1.67	1.63
Cr	1.21	1.67	0.50	0.32	0.24
Fe	0.10	0.10	0.07	0.03	0.03
Hg	0.88	0.94	0.00	0.00	0.00
Ni	2.66	2.30	0.81	0.64	0.65
Pb	125.53	155.61	2.37	1.74	1.64
Se	246.80	253.40	91.60	84.60	91.40
Zn	6.21	11.59	1.35	1.02	0.93
C_{deg}	754.15	714.56	115.30	95.15	101.33

Pollution load index (PLI)

PLI was calculated for every sampling site using 13 elements and it was assumed that these elements were usually observed in different pollution source profiles. Just like EFs, the PLIs were also calculated by using Earth's crust average elements data. If PLI value will be more than 1, then it will be said that polluted. Since PLI is the ratio of two geometric means, it generates similar patterns, if sorted from highest to lowest by using Earth's crust reference concentrations. This pattern for highly polluted to least contaminated site is as S2 > S1 > S3 > S4 > S5. From the PLI data (Table 2.20), it was observed that there was no pollution in S4 and S5 but S1 and S2 exhibited very high pollution.

Table 2.20: PLI and ATEC of soils from Mandoli industrial area

	S1	S2	S3	S4	S5
PLI	6.42	7.13	1.47	0.82	0.76
ATEC	79.91	88.70	21.63	9.72	11.51

Average toxic element concentration (ATEC)

The results (Table 2.20) show the pattern with ATEC given in parentheses S2 > S1 > S3 > S5 > S4. This pattern indicates that the soil samples from recycling units show higher ATEC than those from residential areas. Moreover, ATEC values for S1, S2, and S3 are higher than the reference value of 12.44. The main reason for all higher values is the presence of Ag, As, Cd, Cu, Pb, Se, and Zn in higher concentration.

2.3.3.2 Heavy metal concentrations in plants

The concentrations of heavy metals (mg/kg, dry weight basis) were detected in the common grass *Cynodon dactylon* in and around Mandoli industrial area (P1, P2, P3, and P4) and are presented with standard error in Table 2.21 based on Duncan's test. The variability in the distribution of metals was evaluated with ANOVA, which revealed significant differences for the cases of all elements (Table 2.22). The heavy metals concentrations data explained the plant samples from dumping site of e-waste recycling units contained higher amount of heavy metals than that of plant samples collected from residential site. As, Cr, Hg and Se were not observed in all plant samples (P1, P2, P3 and P4). As shown in Table 7, the e-waste recycling sites had the highest amounts of metals in soils which could provide a partial explanation of why the highest average concentrations of metals observed in the plant samples found there. Another major factor contributing to high metal accumulation in the plant samples could probably be ascribed to atmospheric deposition. Due to incineration of e-waste, heavy smoke containing various kinds of heavy metals, metalloids, and organic pollutants would have been discharged into the air, contaminating surrounding plants species.

Table 2.21: Duncan's test for mean comparisons of heavy metal concentrations in plant samples collected from Mandoli industrial area, Delhi.

Elements	Sites			
(mg/kg) (SE)	P1	P2	P3	P4
Ag	0.054^{a}(0.012)	0.003^{a}(0.001)	0.0028^{a}(0.001)	0.003^{a}(0.00)
As	0.00^{a}(0.00)	0.00^{a}(0.00)	0.00^{a}(0.00)	0.00^{a}(0.00)
Cd	0.049^{a}(0.005)	0.023^{a}(0.086)	0.0036^{a}(0.001)	0.0031^{a}(0.002)
Co	0.0045^{a}(0.001)	0.0023^{a}(0.001)	0.0026^{a}(0.00)	0.002^{a}(0.001)
Cu	23.07^{b}(0.831)	11.43^{b}(0.536)	11.24^{b}(0.588)	11.08^{b}(0.574)
Cr	0.00^{a}(0.00)	0.00^{a}(0.00)	0.00^{a}(0.00)	0.00^{a}(0.00)
Fe	106.37^{d}(2.696)	89.49^{d}(3.048)	90.32^{d}(1.887)	88.47^{d}(3.747)
Hg	0.00^{a}(0.00)	0.00^{a}(0.00)	0.00^{a}(0.00)	0.00^{a}(0.00)
Ni	2.36^{a}(0.912)	0.76^{a}(0.254)	0.59^{a}(0.155)	0.61^{a}(0.196)
Pb	0.76^{a}(0.294)	0.005^{a}(0.001)	0.007^{a}(0.002)	0.006^{a}(0.002)
Se	0.002^{a}(0.001)	0.00^{a}(0.00)	0.00^{a}(0.00)	0.00^{a}(0.00)
Zn	78.18^{c}(2.055)	67.67^{c}(2.378)	68.48^{c}(1.599)	68.44^{c}(3.071)

Significant level at $P \leq 0.05$

Table 2.22: One-way ANOVA for the metals analysed in plant samples at the 4 sampling sites in Mandoli industrial area, Delhi

Element	**Ag**	**As**	**Cd**	**Co**	**Cu**	**Cr**	**Fe**	**Hg**	**Ni**	**Pb**	**Se**	**Zn**
F	17.672	16.530	1011.333	84.363	8.472	3.062	6.614	12.000	4.582	17.672	16.530	1011.333
P	0.001	0.001	0.000	0.000	0.005	0.091	0.015	0.002	0.038	0.001	0.001	0.000

Hierarchical cluster analysis (HCA)

Based on the HCA results, the plant sampling sites were classified into three clusters (Figure 2.20). There were two sites (P2 and P3) in cluster I, P4 in cluster II, and P1 in cluster III respectively. The mean concentrations of heavy metals in cluster III were higher than those in cluster I and II (Table 2.21). Cluster III having the P1 area showed maximum heavy metals in plant samples located at the dumping site of e-waste recycling area. The areas in cluster II and III are away from the e-waste recycling units. Due to heavy metal contamination in the soils of P1 area, the plants might be accumulated more heavy metals as compared to others.

The cluster analysis was performed to investigate the relationship among the 12 metal elements analysed from plant samples (Figure 2.21). Out of 12 elements, only 7 elements were observed in plant samples. The 7 elements can be classified to one group. The relationship of elements in the one group was hard to explain, and the association among elements were complicated. So the elements were further classified into 4 clusters i.e. Ag, Pb, and Cu in cluster I; Zn in cluster II; Fe and Ni in cluster III; and Cd in cluster IV respectively using a criteria value of rescaled distance between 0 and 5 (Figure 2.21).

From this analysis, it seemed that the soil quality was a very important factor in determining the plant heavy metal concentrations. The plant samples collected from dumping site of e-waste recycling area (P1) had a much greater accumulation of heavy metals which form one cluster. It was very difficult to describe the heavy metals grouping as e-waste is complex in nature and their mode of interaction with soil systems after recycling of e-waste. To clarify these problems, factor analysis (principal component analysis) was carried out.

Principal component analysis

The matrix used for PCA contained data matrix of size (4 X 7) i.e. 4 sampling sites and 7 elements. The principal components with Eigen values greater than 1 were extracted with the loading rotated for the maximum variance. A total of two principal components (PC) were extracted, accounting for 99.875% of the total variance (Table 2.23). This study selected absolute factor loadings of over 0.7 to evaluate the relationship among plant sampling sites. High loading of PC1 corresponded to P1, P2, and P3, while P4 was low loadings to PC1 and accounted for about 74.675% of the total variance. PC2 accounted for 25.2% of the total variance and showed high loadings on P2, P3, and P4 and low loadings on P1 (Table 2.23).

Figure 2.22 shows scores plot of PC1 versus PC2 indicating P2 and P3 sites were placed on one point, whereas, P1 and P4 placed on separate points on the basis of rotated components values. It once again describes that, the relationship among the sampling sites based on their heavy metal content was comparable with cluster analysis. It also describes that, due to informal recycling the heavy metals were deposited at P1 sampling site soils, whereas other sites (P2, P3, and P4) showing reduced heavy metal content forms separate groups.

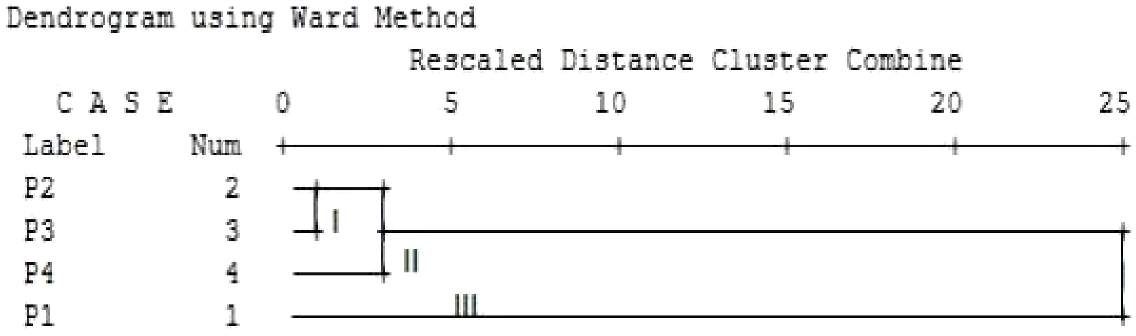


Figure 2.20: Cluster tree of plant sampling sites using cluster analysis

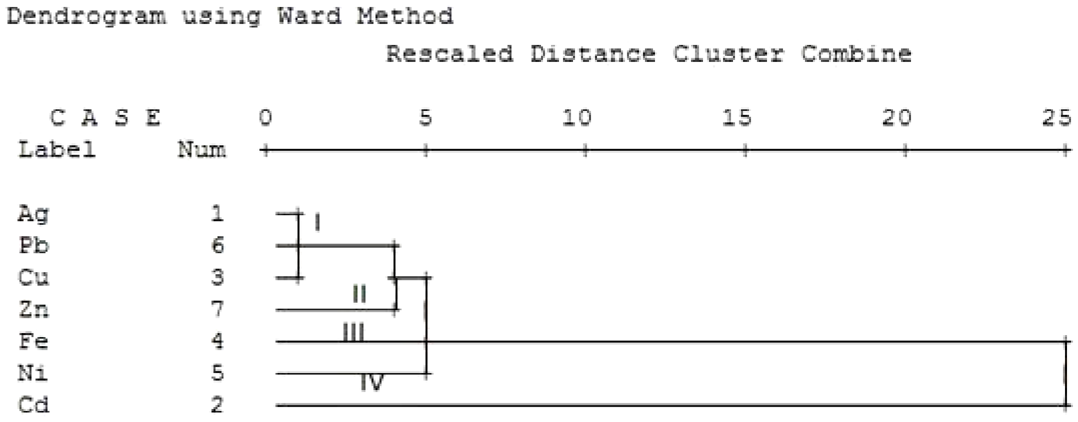


Figure 2.21: Cluster tree of elements from plant samples using cluster analysis

Table 2.23: Total variance explained for the plant sampling sites

Component	Initial Eigen values			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	2.987	74.675	74.675	2.987	74.675	74.675
2	1.008	25.200	99.875	1.008	25.200	99.875
3	0.004	0.100	99.975			
4	0.001	0.025	100.000			

Table 2.24: Principal component loadings after rotation for the maximum variance in the plant sampling sites

Sites	Components	
	PC1	PC2
P1	**0.751**	0.660
P3	**0.712**	**0.701**
P4	0.661	**0.750**
P2	**0.706**	**0.707**

Absolute factor loadings of above 0.7 are shown in bold

PCA was calculated among the heavy metals content in plant samples. It revealed that the Eigen values of each of two components, which exceed 1, explained 99.886% of total variance in the data set abstracted from Mandoli industrial area (Table 2.25). Table 2.26 presented the loadings of the varimax-rotated factor matrix for the two principal components belonging to Mandoli industrial area. PC1, which comprised high loadings on Pb, Ag, Fe, Cu, Ni, and Zn, accounted for 83.186% of total variance. High loading of PC2 corresponded to Cd, and accounted for 16.7% of total variance. Figure 2.23 shows the score plot for heavy metals in plant samples based on loading for varimax rotated factor matrix. From this result it was observed that, the heavy metals were formed four broad groups. But, these results also comparable to cluster analysis of elements based on Pearson’s correlation coefficient.

Table 2.25: Total variance explained for the heavy metals in different plant sampling sites

Component	Initial Eigen values			Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	5.823	83.186	83.186	5.823	83.186	83.186
2	1.169	16.700	99.886	1.169	16.700	99.886
3	0.008	0.114	100.000			

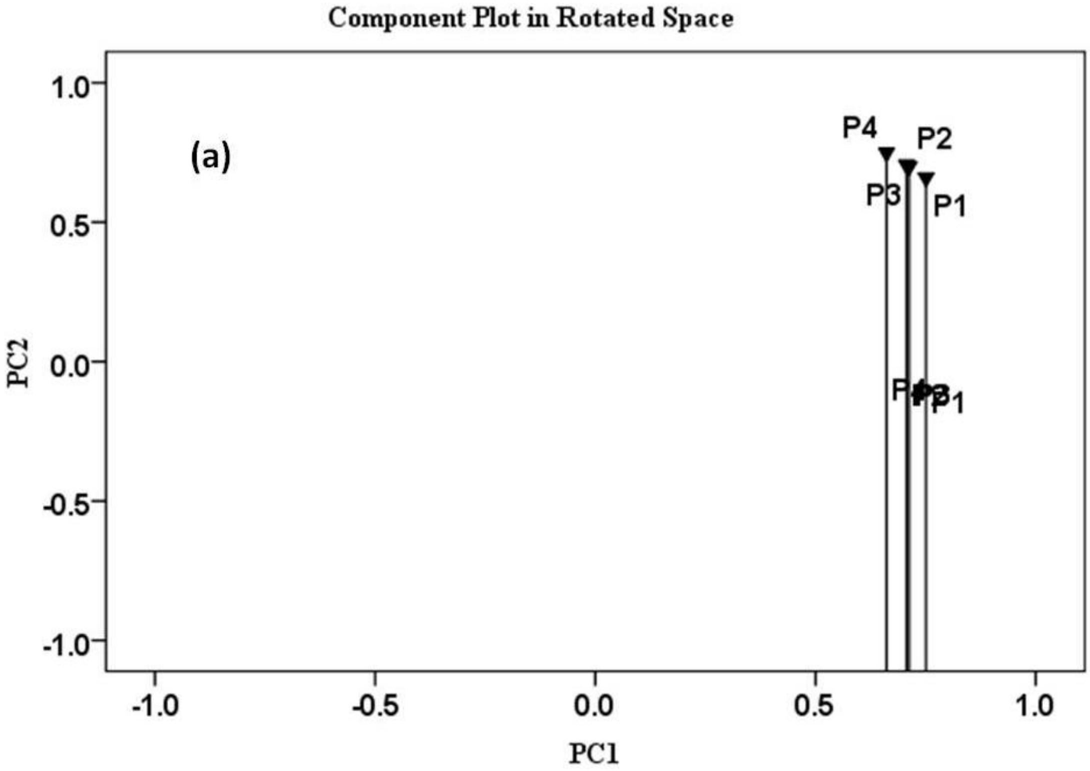


Figure 2.22: Score plot for different plant sampling sites, PC1 vs. PC2

Table 2.26: Principal component loadings after rotation for the maximum variance in the heavy metals of plant samples

Elements	Components	
	PC1	PC2
Zn	**0.875**	0.484
Pb	**0.838**	0.546
Ag	**0.836**	0.549
Fe	**0.833**	0.549
Cu	**0.825**	0.565
Ni	**0.785**	0.619
Cd	0.522	**0.853**

Absolute factor loadings of above 0.7 are shown in bold.

Multidimensional scaling (MDS)

The multidimensional scaling for the plant sampling sites showed four groups as P3 site in group I; P2 site in group II; P1site in group III; and P4 site in group IV which was consistent with the results of HCA and PCA (Figure 2.24). The heavy metals scattered through four groups i.e. Zn in group I; Ag, Cd, Pb, and Ni group II; Cu in group III; and Fe in group IV. In case of MDS analysis among the metal concentrations in plant samples (Fig.ure 2.25); the results were comparable with the results of HCA in dendrogram and PCA. The analysis of scatter plot of linear fit suggested the multidimensional scaling in this study was quit valid for the sampling sites (Figure 2.26) and heavy metal contents in plant samples (Figure 2.27).

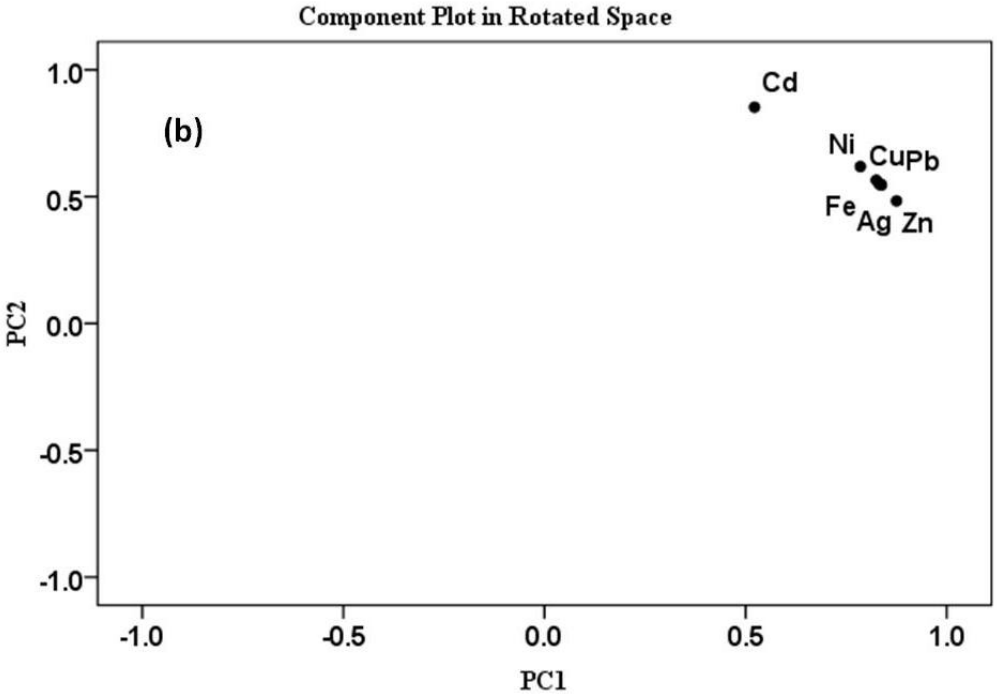


Figure 2.23: Score plot for different elements in plant samples, PC1 vs. PC2

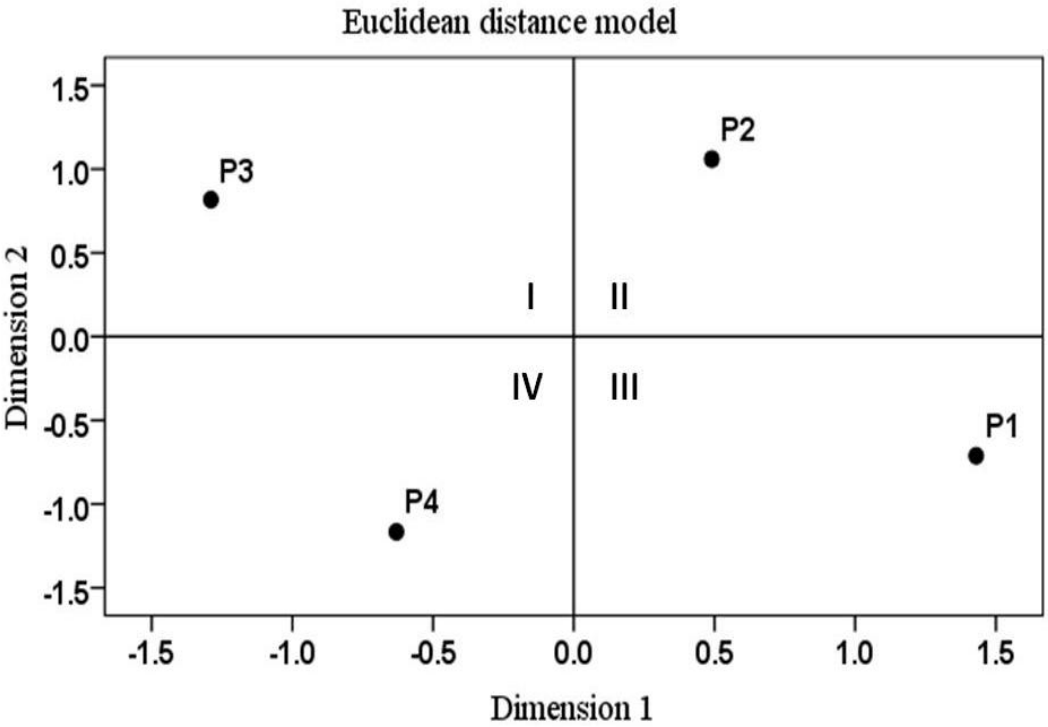


Figure 2.24: Multidimensional scaling of different plant sampling sites based on heavy metal concentration

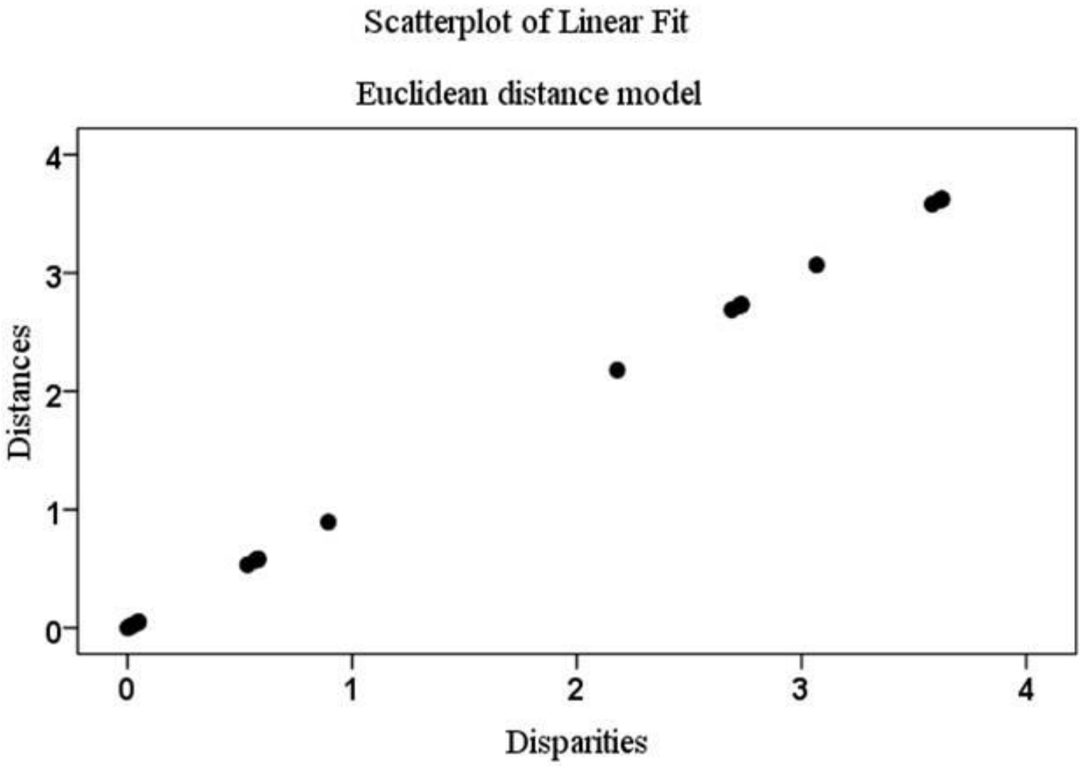


Figure 2.25: Scatter plot of linear fit for MDS analysis of plant sampling sites

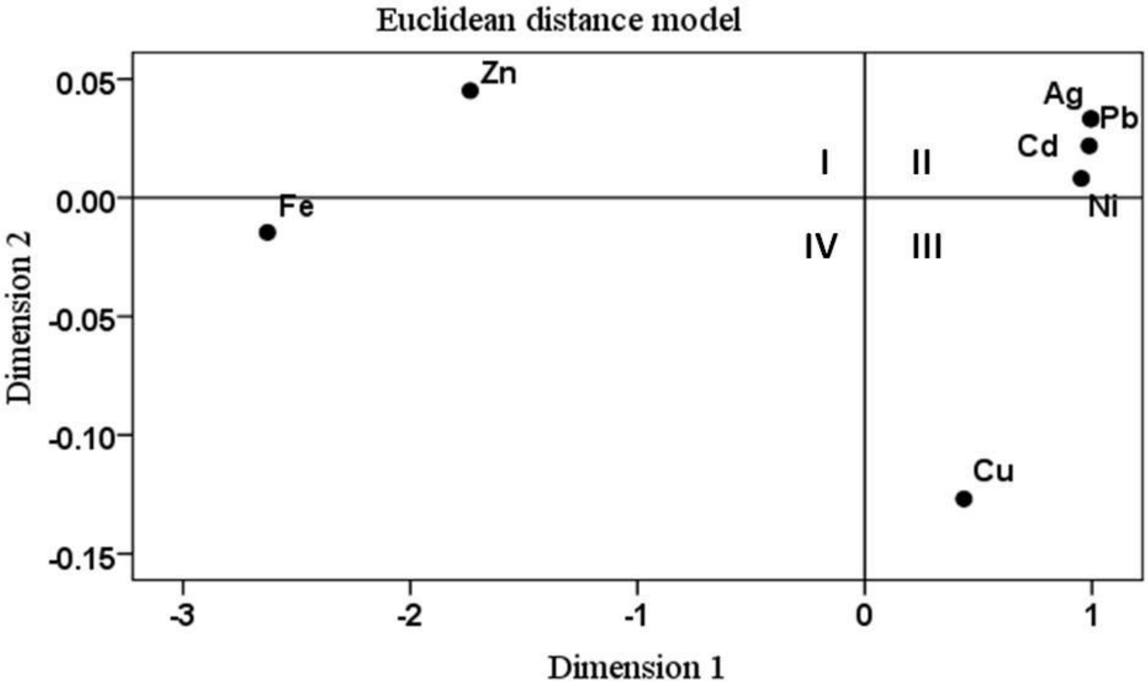


Figure 2.26: Multidimensional scaling of heavy metal concentrations of plant samples

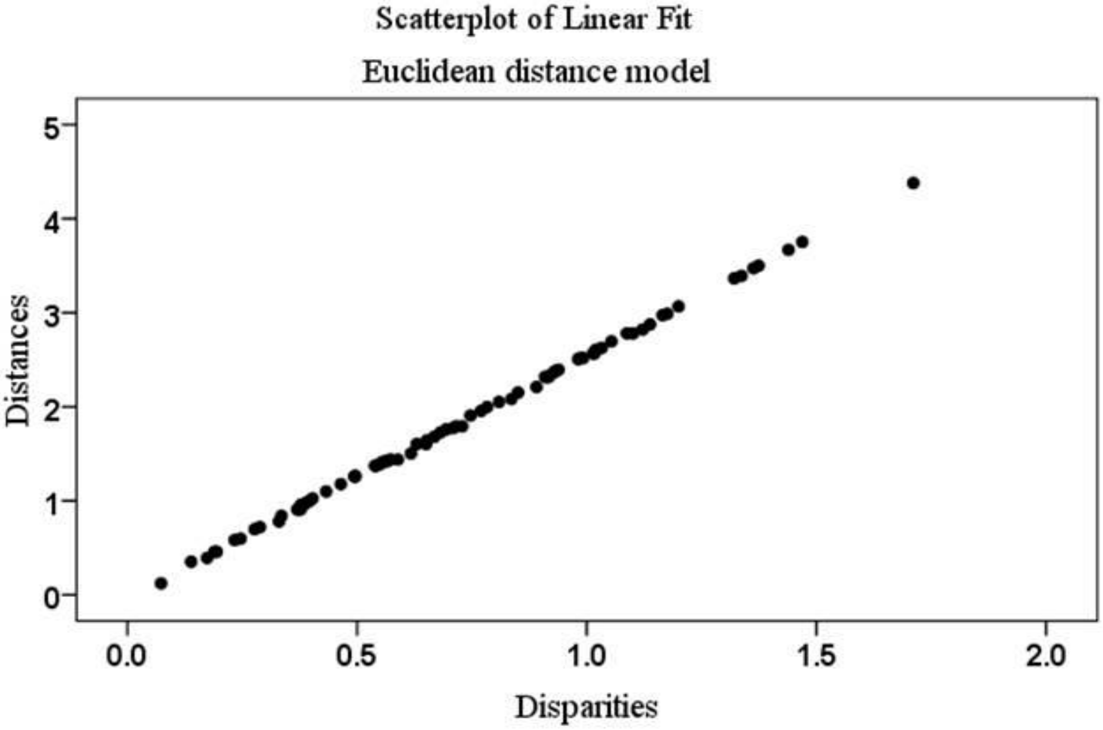


Figure 2.27: Scatter plot of linear fit for MDS analysis of heavy metal concentrations of plant samples

2.3.3.3 Heavy metal concentrations in water

The only source of water for people living in Mandoli industrial area is the groundwater which is supplemented by bore wells. With more and more industries mushrooming in the area, the residents are facing scarcity of fresh drinking water. The pH of water was slightly acidic i.e. 6.23 which is below the desired limit of 6.5-8.5. Mean and standard error comparisons of each heavy metal from W1 and W2 samples based on Duncan's test are presented in Table 2.27. The variability in the distribution of metals was evaluated with ANOVA, which revealed significant differences at p<0.05. The results indicated that, the heavy metal concentration in water sample (W1) from Mandoli industrial area is higher than the W2 (residential site). The resulted data was also compared with Indian Water Standard (IWS), 2012. All the heavy metal concentrations were within the permissible limit of IWS except Cu and Fe. The intensive uncontrolled processing of e-waste may result in the release of large amounts of heavy metals in the local environment, and a cause of high concentrations of metals to be present in the surrounding soils, plants and water.

Table 2.27: Duncan's test for mean comparisons of heavy metal concentrations of water samples collected from Mandoli industrial area, Delhi.

Elements (mg/L) (SE)	W1	W2	Permissible limit (IWS 2012)
Ag	0.03^{a}(0.005)	0.008^{a}(0.001)	0.10
Al	0.024^{a}(0.005)	0.027^{a}(0.011)	0.03
As	0.008^{a}(0.001)	0.0076^{a}(0.001)	0.01
Cd	0.001^{a}(0.00)	0.001^{a}(0.00)	0.003
Co	0.001^{a}(0.00)	0.001^{a}(0.00)	NA
Cu	0.067^{a}(0.011)	0.05^{a}(0.011)	0.05
Cr	0.01^{a}(0.00)	0.009^{a}(0.002)	0.05
Fe	0.46^{b}(0.115)	0.32^{b}(0.069)	0.30
Hg	0.00^{a}(0.00)	0.00^{a}(0.00)	0.001
Ni	0.005^{a}(0.001)	0.003^{a}(0.00)	0.02
Pb	0.009^{a}(0.002)	0.004^{a}(0.001)	0.01
Se	0.01^{a}(0.001)	0.009^{a}(0.003)	0.01
Zn	1.89^{c}(0.173)	1.46^{c}(0.057)	5.00

*NA: not available. The data presented in this table presents mean of those obtained from duplicate experiments at significant level ($P <$ 0.05) based on one-way ANOVA analysis.

2.4 CONCLUSIONS

- E-waste is a great challenge from both environment and technology point of view as its rate of growth is much higher than the rate of disposed, reuse and recycles. Socioeconomic, infrastructural, and legal reasons are the barriers of e-waste management in India. The majority of the e-waste recycling and recovery options practiced in India are rude and hazardous, causing severe environmental and occupational hazards. There is an urgent need to focus more on treatment systems involving recycling and recovery options for better e-waste treatment and management. E-waste may be measured as a ‘secondary ore’ or ‘artificial ore’ for the concentrations of precious metals richer than natural ores, which makes their recycling important from both economic and environmental perspectives. For the environmentally safe treatment and recycling of e-waste, the high initial investment is required for setting facility fitted with technologically advanced equipment and processes. There is a need of further research and consideration on policy as well as technical level to answer how to successfully manage the e-waste problems with the current e-waste system in India.
- The study in Mandoli industrial area has provided a snapshot of work place, environmental pollution (soil, water and plant contamination) of the industrial units and dump sites associated with the e-waste recycling units. The investigation soil samples from Mandoli industrial area revealed a clear accumulation of Cu, Al, Fe, and Pb were high village soils. The application of the index enrichment factor and contamination factor enabled us to find elevated contents of toxic metals in the soils collected from e-waste recycling areas-Ag, Cu, Pb, Se, As, Zn and Cd. Pollution assessment using PLI based on 13 elements reveals soils of e-waste recycling areas (S1, S2) highly polluted and soils away from e-waste recycling area (S4, S5) least polluted. The application of PCA, CA and MDS recognized four distinct groups of soils. The first group contains S4 and S5 is related with less concentration of toxic metals, which most probably due to absence of e-waste recycling units in these areas. The second and third group comprises S1 and S2 identified with high level of toxic metals due to presence of e-waste recycling units. It was observed that the plants (common grass) from discarded area of e-waste recycling units contain higher amount of heavy metals as compared to the grass samples of the adjoining village. Whereas, As, Cr, Hg and Se were not observed in the plant samples.

According to the statistical analysis (PCA, CA and MDS), based on heavy metals content the plant samples recognized four distinct groups. The plant samples collected from Mandoli industrial area (P1) shows high toxic metals contents as compared to the residential areas. It should be noted that due to high concentration of heavy metals in soils indispensable increases the heavy metals concentration in plants. These elevated amounts may enter the food chain and thus pose a hazard to human and animal health. Heavy metal concentration in water sample from industrial area is higher than the village waster sample. The resulted data was also compared with Indian Water Standard (IWS)-2009 [216] and it was observed that heavy metal concentrations are less than the desired limit of IWS except Cu and Fe. But the elevated content of toxic metals in soils if Industrial areas may also cause an increase in their content in ground waters as a result of leaching. The high heavy metal concentrations in the studied area resulted from the crude methods of recycling which, may add to the higher levels of these elements to the environment.

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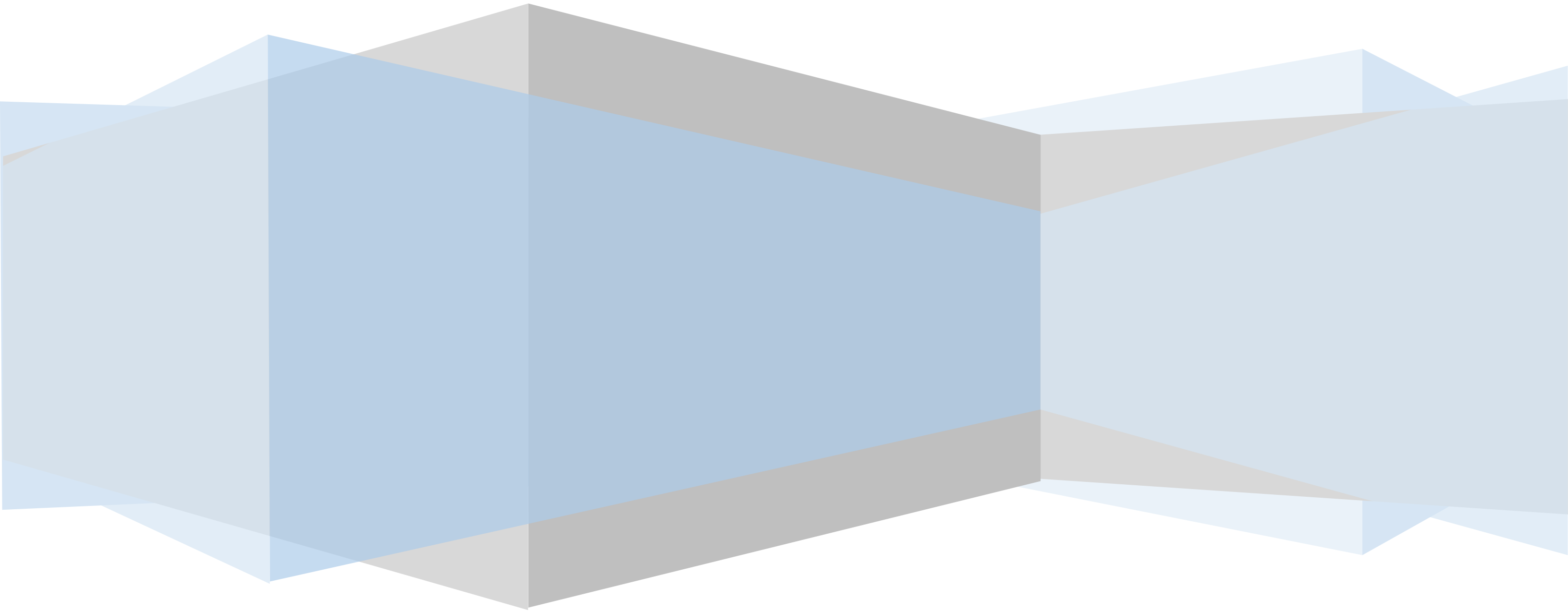
CHAPTER 3

TCLP (TOXICITY CHARACTERISTIC LEACHING PROCEDURE) STUDIES TO SIMULATE THE ACTUAL LANDFILL CONDITIONS

JATINDRA KUMAR PRADHAN



3.1 INDTRODUCTION

E-waste represents a growing segment of the solid waste stream. The management of e-waste upon disposal has become a major issue of concern for environmental regulators in the solid waste arena. Both the magnitude of the waste stream and the potential environmental impacts associated with the toxic chemicals found in e-waste are cause of concern. If the e-waste components corrode and the heavy metals become mobile, they will travel with the leachate and eventually enter the environment. The study of the leaching of the toxic substances from e-waste in landfill scenarios is important for assessing their potential long term environmental impact. The toxic chemicals commonly used in electronic devices include metals and metalloids (e.g. As, Cd, Cr, Cu, Pb, and Hg) and organic chemicals such as brominated flame retardants (BFRs). Lead is one of the heavy metal with known toxic properties that is found in large amounts in many electronic devices [153]. Electronic devices, along with lead-acid batteries, are the major contributors of Pb in the municipal solid waste stream [154]. The possible effects of Pb on human health and the environment are well-documented [155-157]. The environmental and health effects of discarded obsolete e-waste have become a global issue in recent years [158]. Toxicants laced in e-waste can enter the environment and become available to humans and other living creatures through leaching and transport with water, air, and soil. While a variety of recycling mandates and product material restrictions exist, e-waste continues to find its way to landfill either directly or from incinerate ash. According to US Environmental Protection Agency, 4.6 million tons of e-wastes were landfilled in the US in the year 2000. Additionally, it is estimated that 1 billion pounds of Pb will enter the environment in the next ten years as a result of e-waste alone. With the advent of the Restriction of Hazardous Substances (RoHS) directive and similar regulations following in Asia and in the United States, there is a pressing need to implement reliable tests of the hazardous material like e-waste. There have been studies on the leaching of heavy metals from computer components and other electronic devices using the U.S. Environmental Protection Agency (EPA) standard toxicity characteristic leaching procedure (TCLP) [158].

The TCLP is designed to simulate the possible worse case leaching scenario that might occur when a solid waste is co-disposed in a MSW landfill. Limitations to the TCLP have been also identified [159-162], but the procedure remains the testing requirement that waste generators must follow. Generally, leaching tests have been developed to characterize both the total content and environmental mobility of substances in a landfill or under similar disposal circumstances. The data generated from the tests yield (or may lead to) the following types of information:

- Classification status (Hazardous Vs. Nonhazardous)
- Biological mobility (including migration rates) of substances under specified conditions
- The effectiveness of material treatment or alterations aimed at reducing the toxicity of a given material
- Identification of the optimum disposal environment for hazardous substance mobility reduction

Figure 3.1 shows the typical steps in the leaching test procedure (TCLP). Table 3.1 shows the maximum regulatory limit for various metals as per TCLP.

Table 3.1: Maximum concentration of contaminants for toxicity characteristic

TCLP Parameter	Regulatory Limit (Maximum) (mg/L)	EPA Hazardous Waste Number
As	5.00	D004
Ba	100.00	D005
Cd	1.00	D006
Cr	5.00	D007
Pb	5.00	D008
Hg	0.20	D009
Se	1.00	D010
Ag	5.00	D011

The study presented in this chapter was conducted in support of an effort to determine the likely toxicity status of a number of different types of discarded electronic equipment [161]. Electronic devices (PCs) were disassembled into primary components before leaching, but they were not size reduced as commonly found in standard TCLP. It was hypothesized that (1) disassembled devices would be more representative of the condition when disposed in a landfill and (2) leaching concentrations for disassembled devices would be conservative (i.e., size reduced devices would leach more than disassembled devices). In this experiment, mixture of PC parts in municipality solid waste was examined as a test case. To provide additional information on this issue one of the main objectives of this study was to examine the leaching of toxic heavy metals from e-waste in landfills using a column simulation test. It is anticipated that this and similar studies will provide insight into how the e-waste impacts the landfill leachate under real-life landfill conditions.

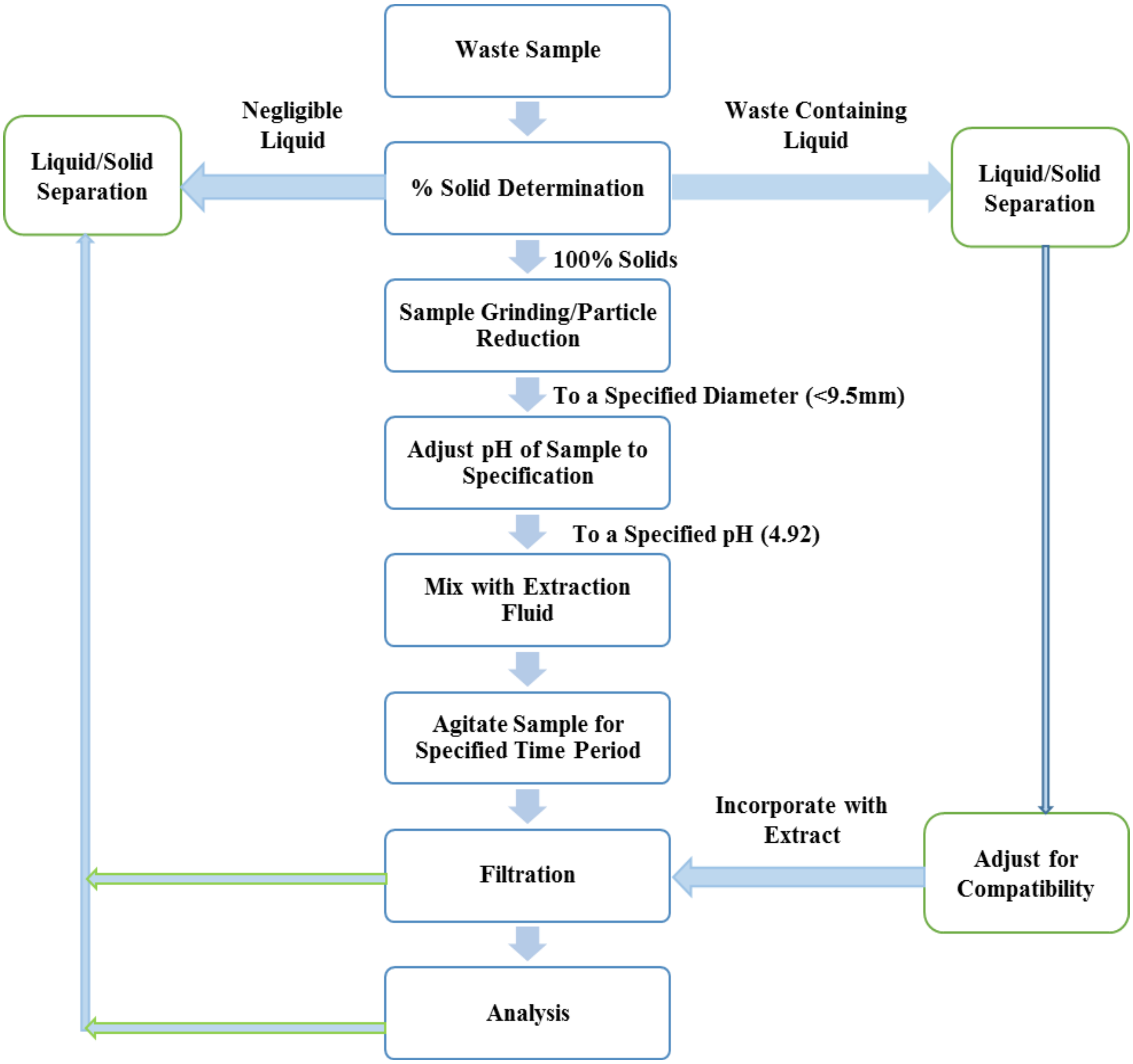


Figure 3.1: Typical TCLP flow chart

3.2 MATERIALS AND METHODS

3.2.1 E-waste components

The e-waste components used in the simulation study included CRTs from PCs and a variety of PC components. The PC components included motherboards, expansion cards, memory cards, printed wire boards, hard disc drives, compact disc drives, and power supply units taken from desktop PCs with Pentium II and III central processing units. While most of the PC components were used without size reduction, the motherboards were cut into three to four pieces so that the maximum size in the longest side of all the components did not exceed 0.2 m. The compositions and amounts of the PC components packed in the columns are given in Figure 3.2.

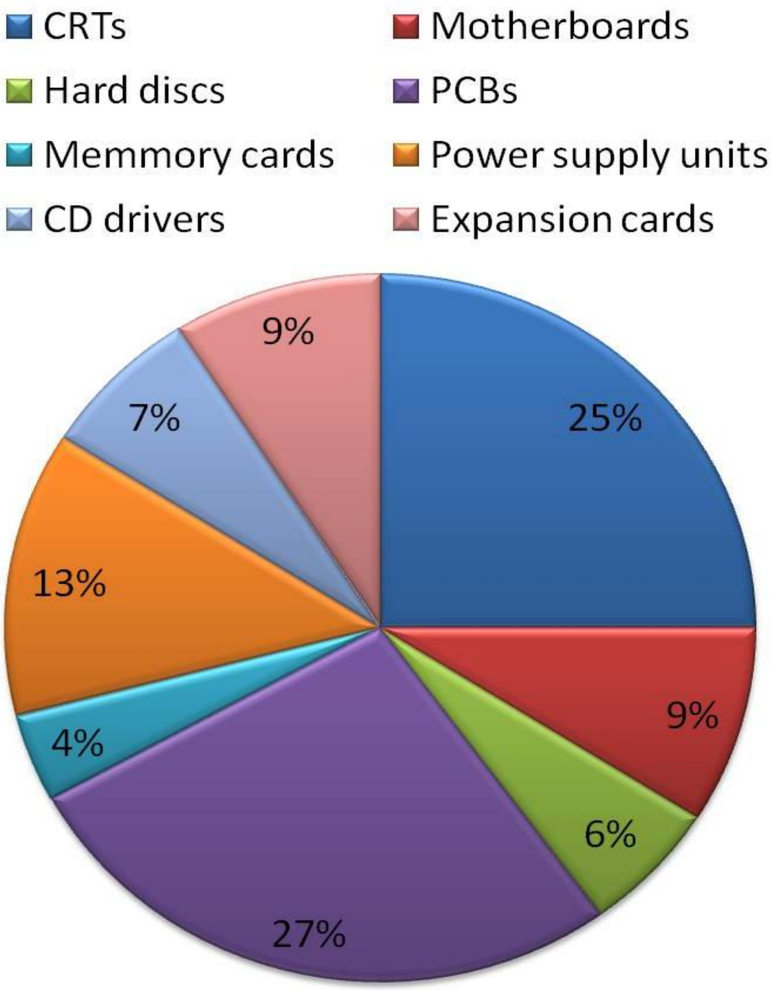


Figure 3.2: Physical composition of PC-components placed in columns for landfill simulation studies

3.2.2 Municipality solid waste (MSW)

The physical composition of the MSW used for the study is presented in Figure 3.3. MSW was collected from JUIT waste dumping site near field hostel. To achieve a relatively homogenous mixture, the large items such as plastics, and cardboards items were reduced to a maximum size of 0.15 m in the longest direction. The composition study revealed that the MSW from JUIT campus contained biodegradable organic components i.e., around 55% is yard waste, plastics and papers contributed individually around 17 and 15%, respectively.

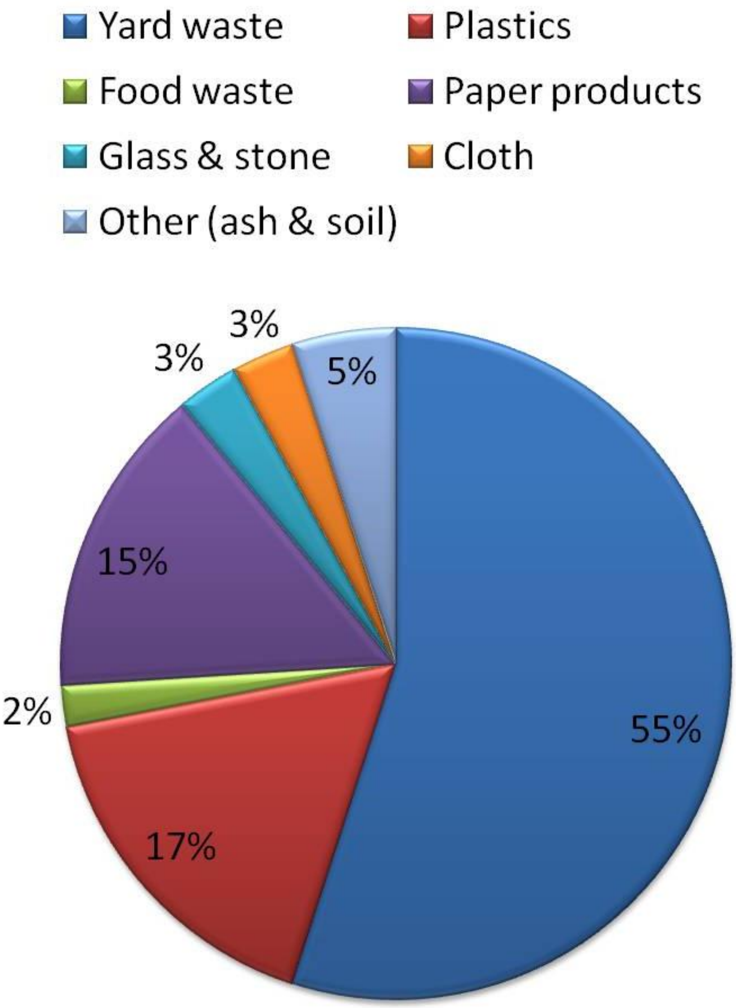


Figure 3.3: Physical composition of municipality solid waste placed in columns for landfill simulation studies

3.2.3 Preparation of landfill simulation columns for TCLP studies

The internal design of columns illustrated in Figure 3.4. Four sanitary landfill simulation columns were set up (Figure 3.5).The columns were made up of high-density polyethylene (HDPE) with inner diameter of 0.5 m and an overall height of 2.0 m. Each column consisted of a sloped bottom for leachate drainage and sample collection. Column 1 contained 0.1 m thick coarse gravel drainage layer and nonwoven geotextile placed above the bottom line. Above the geotextile layer, MSW was compacted to a density of about 600 kg/m^3. A 0.05 m layer of gravel sandwiched by nonwoven geotextile was placed above the MSW layer to permit landfill gas release. Above the geotextile layer; mildly compacted soil was placed to simulate an earth cover and to allow a uniform infiltration of water into the columns. Column 2 contained MSW and e-waste (15% of total MSW) whereas column 4 also contained both MSW and e-waste (15% of total MSW), but with an additional bottom line with soil (0.1 m) placed above the thick coarse gravel drainage layer. Appropriate controls (column 1 and column 3) were maintained without e-waste. Tap water (pH ranging from 7.5 to 8.0) was added to the top of each column on a weekly basis to simulate precipitation events as per standard methods. A sample of the leachate from each column was collected every fortnight for analysis. The operation and monitoring continued for over one year. Analysis of soil samples of the columns carried out at the end of the one year test period.

3.2.4 Analysis of leachate

The fortnightly collected leachate samples from the four columns were analyzed for pH, total organic carbon (TOC) [163], and 11 elements (Ag, Al, As, Cd, Cr, Cu, Fe, Ni, Pb, Se and Zn) which could exist in the CRTs and PC components. All pH measurements were made using pH meter (Eutech pH 510). The pH probe and meter were calibrated with standard buffer solutions (4.0, 7.0 and 10.0) with a three point calibration. TOC was measured as water soluble organic carbon by titration method. All 11 elements in the leachate samples were analyzed using atomic absorption spectrometer (PerkinElmer 400 AAnalyst Spectrometer). The leachate samples were acid-digested according to USEPA Method 3010A [164] to ensure that all the metals absorbed or contained in suspended particles in the leachate were dissolved in the solution. The solids were removed from the digested samples using Whatman No. 41 quantitative filter paper.

3.2.5 Analysis of soil samples in the columns

At the end of the one-year test period, water addition was stopped and the columns were left undisturbed for one month. Then the columns were dismantled and the material was removed layer by layer. After removing the compacted MSW and e-waste layer, the e-waste was taken out and inspected visually for physical changes. Soil samples of the bottom line layer were collected from Columns 3, and 4. Soil samples from upper layer were collected from all columns. Three samples with a weight of about 50.0 g per sample were taken from each of the columns at different spots over the sampled layers. The inert and/or non-crushable materials such as plastics, glass, metals, and rubber were avoided in the sampling. The samples were oven-dried at 100ºC, and then crushed to pass through a sieve with 2 mm openings. One gram of the dried and sieved sample was acid-digested according to USEPA method 3050B [165]. After digestion, the soils were removed by filtration through a Whatman No. 41 quantitative filter paper and the filtrate was diluted to 100 mL by de-ionized water for analysis using atomic absorption spectrometer (PerkinElmer 400 AAnalyst Spectrometer).

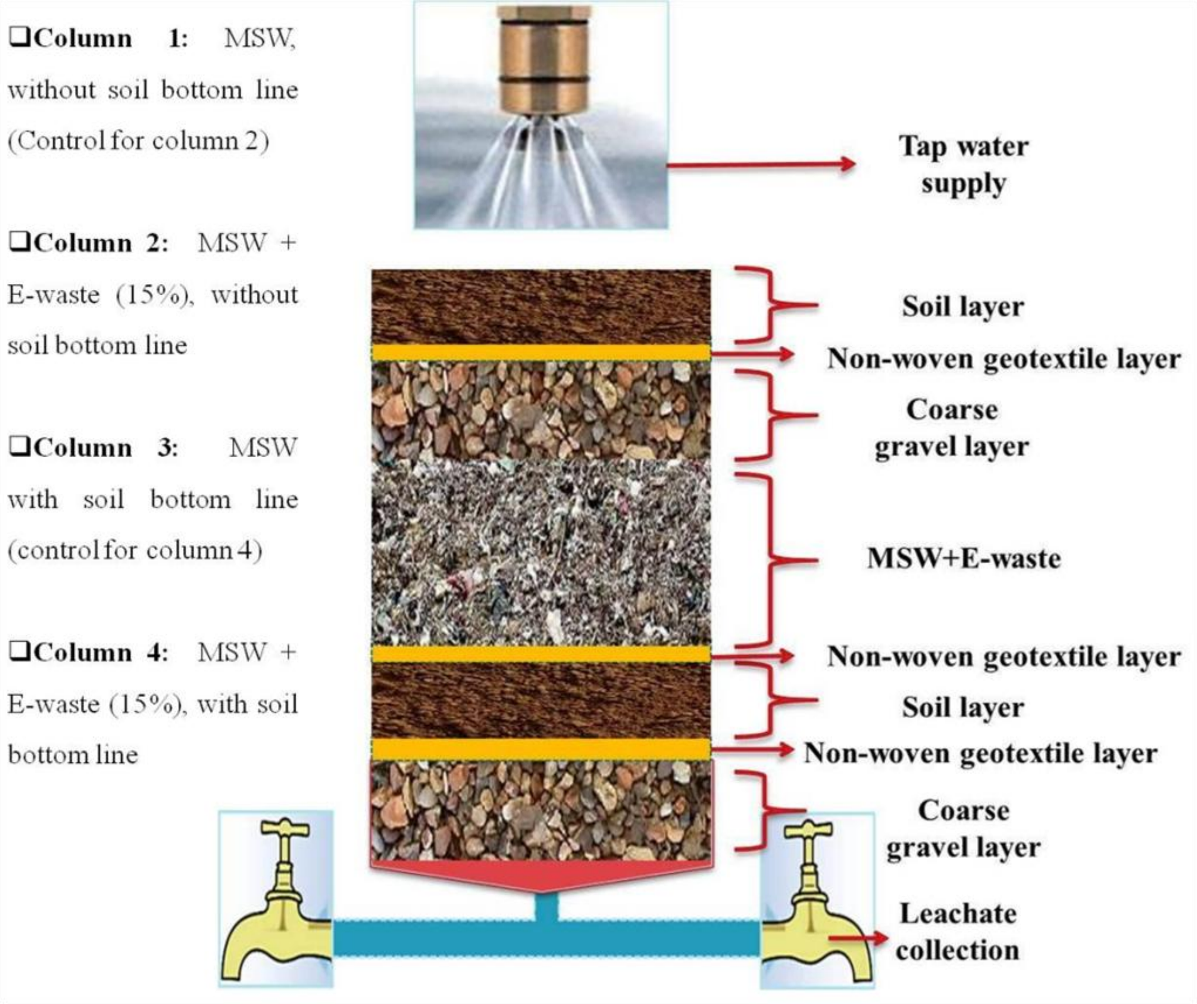


Figure 3.4: Internal design of landfill simulation columns for TCLP studies

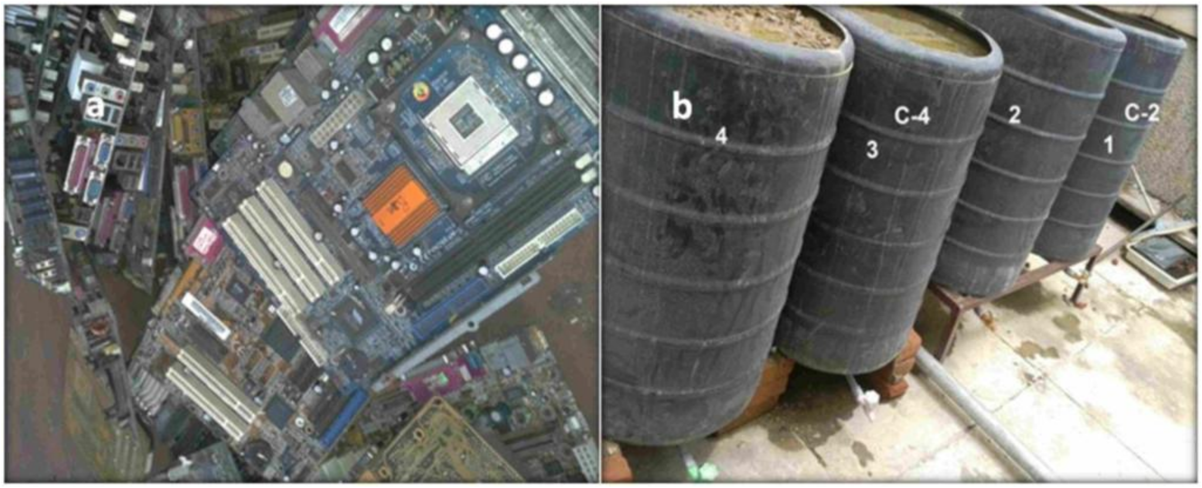


Figure 3.5: (a) E-waste used in column leaching, (b) Column leaching procedure adaptation to determine the actual hazardous metal leaching to land system

3.3 RESULTS AND DISCUSSION

3.3.1 Leachate generation and variation

The variations of the cumulative volume of the leachate with time for all the four columns were very close in both quantity and pattern. The variations for the corresponding data among the four columns were less than 5%. On the average, the total volume of leachate generated in the operation period was about 45% of the total water added into the columns. Nearly 55% of the water added to the columns was lost through evapotranspiration.

3.3.2 Leachate analysis results

The pH, and TOC profiles of the leachate from all four columns showed the same pattern and close values. The variations for the corresponding pH among the four columns were less than 5%, and the variations for the corresponding TOC values among the four columns were less than 10%. The pH showed a slight increasing trend from the beginning value of 7.4 to the ending value of 7.79 with minor fluctuations in this range (Figure 3.6a). The TOC value increased rapidly at the beginning stage and reached a peak (874.49 mg/L) in about three months then started decreasing (Figure 3.6b). After seven months, the TOC stabilized at 106 ± 5 mg/L and remained relatively constant throughout the remaining period of the study. The increase of TOC in the leachate reflected an initial stage of the biodegradation of the organic matters presented in MSW. After the peak was reached, the degradation slowed down and became fairly stable after 7 months.

Figure 3.7 (a-f) shows the concentrations of the detected elements over the 1-year leaching test period in landfill simulation columns for e-waste (Mixture of PC parts). Only six metals Fe, Zn, Al, Cu, Ni, and Cr were detected in the leachates out of the 11 elements analyzed. Among the six detected metals, only Cr is on the EPA list (D-list) of the toxicity characteristic substances for TCLP [166]. Fe was detectable with the highest concentration being 6.35 mg/L. Most of the elements exhibited a concentration decrease with time after an initial surge while Al and Ni concentration fluctuated significantly over the entire monitoring period. It was observed that, column 1 and 3 showed very low metal concentration in their leachates. This was probably due to absence of e-waste in column 1 and 3. Column 2 exhibited maximum concentration of metals in leachates, whereas column 4 showed low metal concentration in leachate as compared to column 2. Column 4 contained soil layer above gravel drainage layer and there might be deposition of metals in soil layer. Surprisingly, Pb the most leachable heavy metal under the TCLP test conditions was not detected in the leachate from any of the columns.

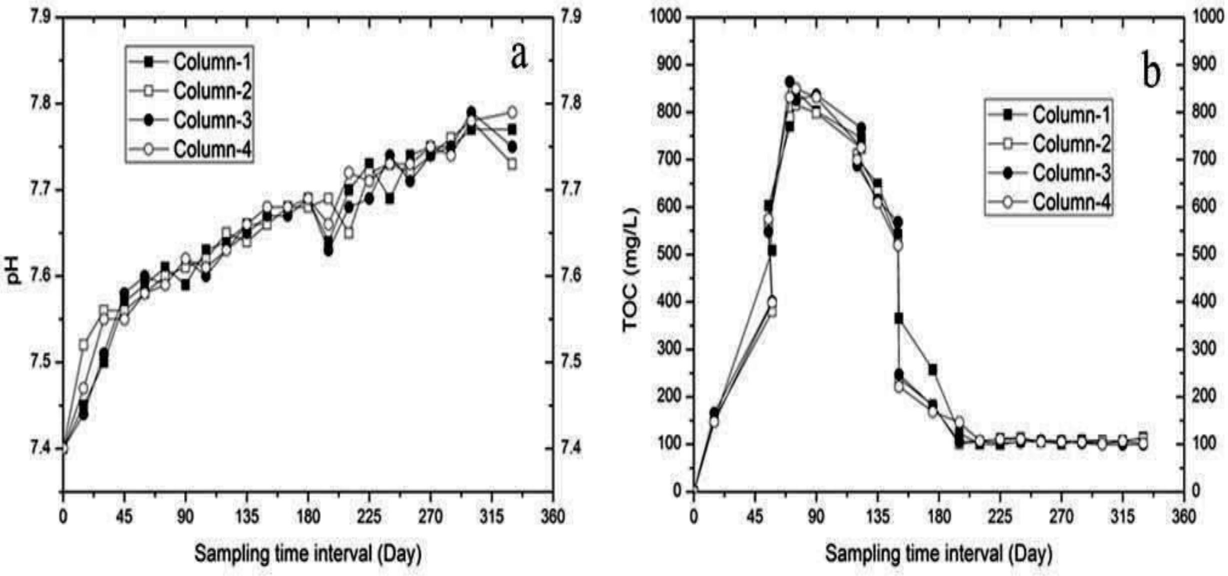


Figure 3.6: (a) pH variation in different columns throughout the experimental period; (b) TOC variation in different columns throughout the experimental period

With respect to the presence of toxic elements or compounds, electronic devices and their components are known to contain small amounts of chemicals that can exert negative impacts on human health and the environment. These chemicals like Pb are usually integral to the operation of the device and are selected because of valued material properties. Pb is found in most electronic items (CRTs or PWBs). Approximately 6.3% (w/w) of a typical computer is Pb, majority of which is attributed to the CRT [167]. Sn/Pb solder (63% Sn and 37% Pb) is the most common solder alloy used in the PWBs of electronics [168]. The U.S. EPA estimated Pb to comprise 4% (w/w) of all discarded electronics [169]. For CRT, highest concentration of Pb reported was from the TCLP standard method i.e. 413mg/L and for PWB it was 162 mg/L [158]. The levels of concentration of Pb after TCLP standard method for these PC components are much higher than that of EPA list (D list). Finally, it is noted that this research does not attempt to interpret the TCLP results with respect to environmental impacts, such as impact on leachate quality at landfills. The ability of the TCLP to simulate actual landfill environments is currently a topic of debate in the profession. For example, the authors found that heterogeneous e-waste leach much less metals when exposed to typical landfill condition compared to when exposed to TCLP solution [158]. Different redox conditions that occur in landfills in comparison to the TCLP may not also influence Pb mobility.

3.3.3 Results of soil samples in the columns

All upper layer soil and bottom layer soils were analysed before and after monitoring period for metal content. It was observed that the metal content in upper soils before and after monitoring period was approximately same with a maximum variation of 2%. In case of column 3, which was served as control having soil layer at bottom line, the heavy metal content in both upper and lower layer was approximately same. That means there was no leaching of metals occurred as it contained only MSW without any metallic components. The comparison between upper and lower layer soil samples of column 4 showed around 12% variation in heavy metal content (Figure 3.8). It implies there was very less deposition in lower soil layer. The leachable metals mostly drained out by leachate, which are below the regulatory limit of TCLP (USEPA) from e-waste.

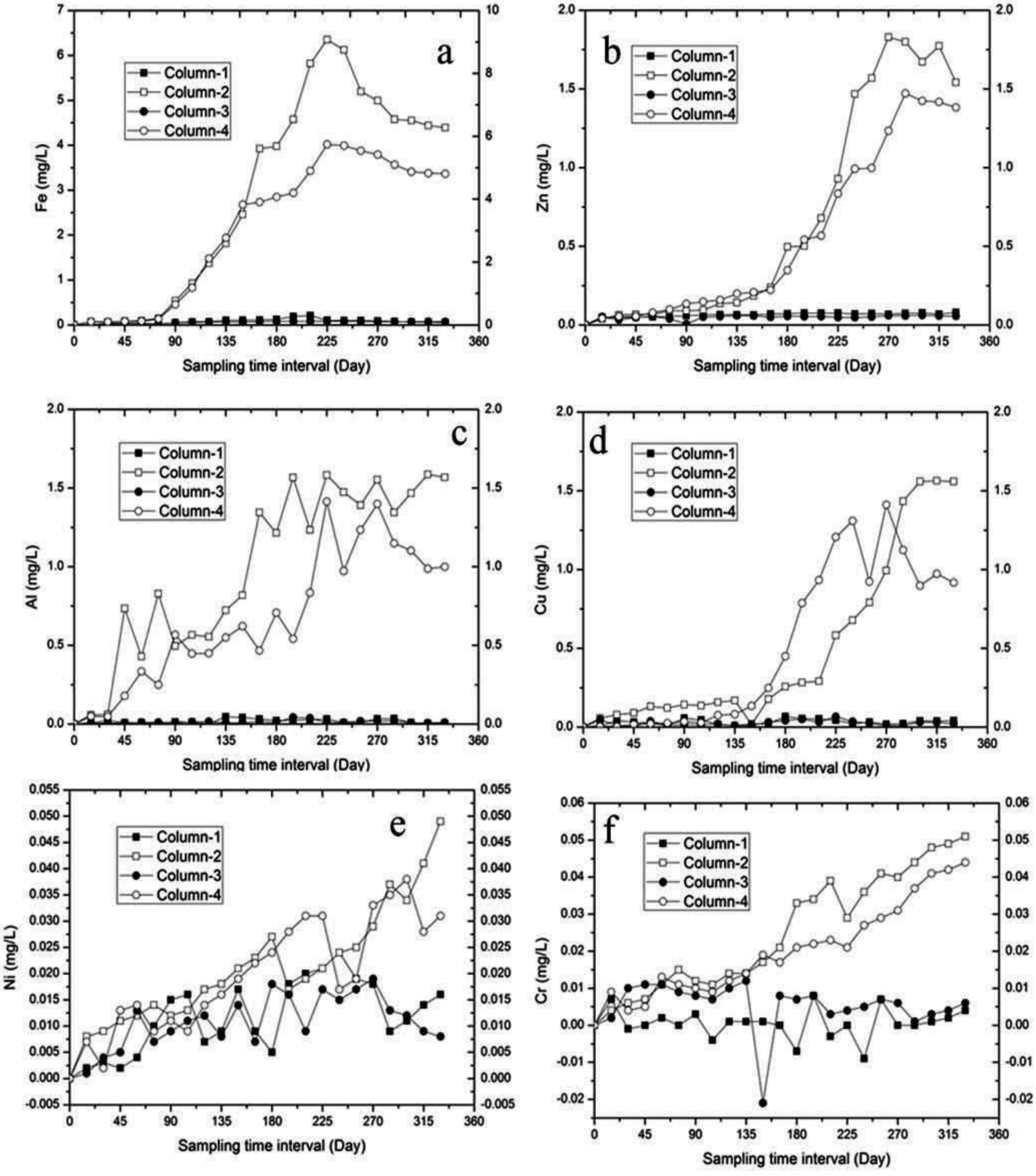


Figure 3.7: Variation of metals in different columns (column 1 and 3were control conditions for column 3 and 4) throughout the experimental period (a) Fe; (b) Zn; (c) Al; (d) Cu; (e) Ni and (f) Cr

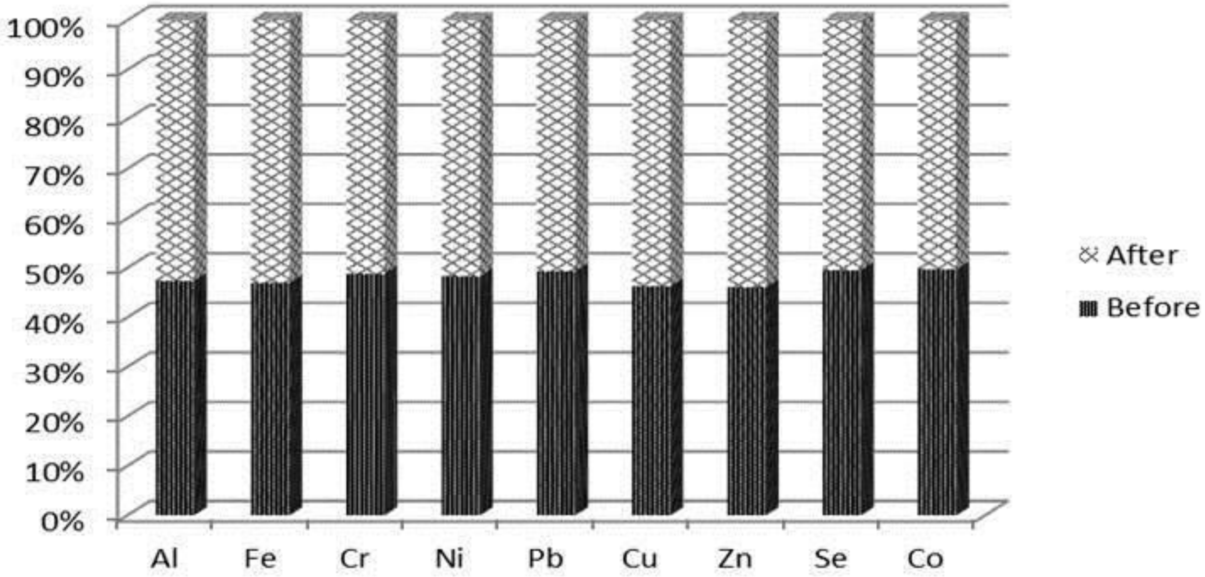


Figure 3.8: Comparison of heavy metal concentration in soils before and after monitoring period (Column 4)

3.4 CONCLUSIONS

Though the TCLP provided practical leaching data, caution must be exercised when applying the TCLP too broadly. The TCLP was designed to serve as a rapid, laboratory-scale test to determine whether a solid waste should be designated as 'hazardous' because of the leaching of selected toxic elements. The method was established to simulate possible worst-case leaching conditions that may occur in a sanitary landfill; it was not designed to predict concentrations in leachates collected from landfills [158, 169]. Researchers [170, 171] have found that certain metals may leach greater amounts in MSW leachate compared with the TCLP extracting solution. It was found that Pb leaching is lower in a typical landfill leachate compared with the TCLP [158]. Relevant tests in future studies may include leaching various e-waste components in actual MSW landfill leachates and under other severe conditions. In TCLP study Pb, the most concerned heavy metal in e-waste can be leached easily using standard EPA3011 method, but in our study it was not detected in the leachate during the one year landfill simulation study. This outcome suggests that Pb is strongly retained by the solid waste around the e-waste through the mechanisms of adsorption and chemical complexation. This does not necessarily mean that Pb can be permanently immobilized in the solid waste.

With the change of conditions and the transport of moisture, Pb may migrate and eventually reach the bottom of the landfill polluting groundwater. Efforts to divert e-waste from landfills are necessary for the protection of the environment in a long run. Besides this, concentration of other metals (Al, Fe, Cu, Zn, Ni and Cr) examined was found to be below the regulatory level of TCLP standard values (Table 3.1). Besides that, in a case of standard TCLP test, the e-waste used is of size up-to 9.5mm. In case of landfill of MSW with e-waste, size of e-waste is it is very difficult to reduce the size of e-waste before processing. So, previous studies also hypothesized that smaller particle size of e-waste (with increased surface area) results in greater leachate concentrations [172]. The findings suggest that the obsolete PCs disposed of in landfills or discarded in the environment will be releasing the toxic heavy metal Pb continuously for a longtime when subjected to landfill leachate or rain. Recycling obsolete PCs and recovery of materials from the PCs are highly important for the protection of the environment and human health. Exporting e-waste to countries or regions where open-air, primitive means are used to process the obsolete products [173] should be prohibited.

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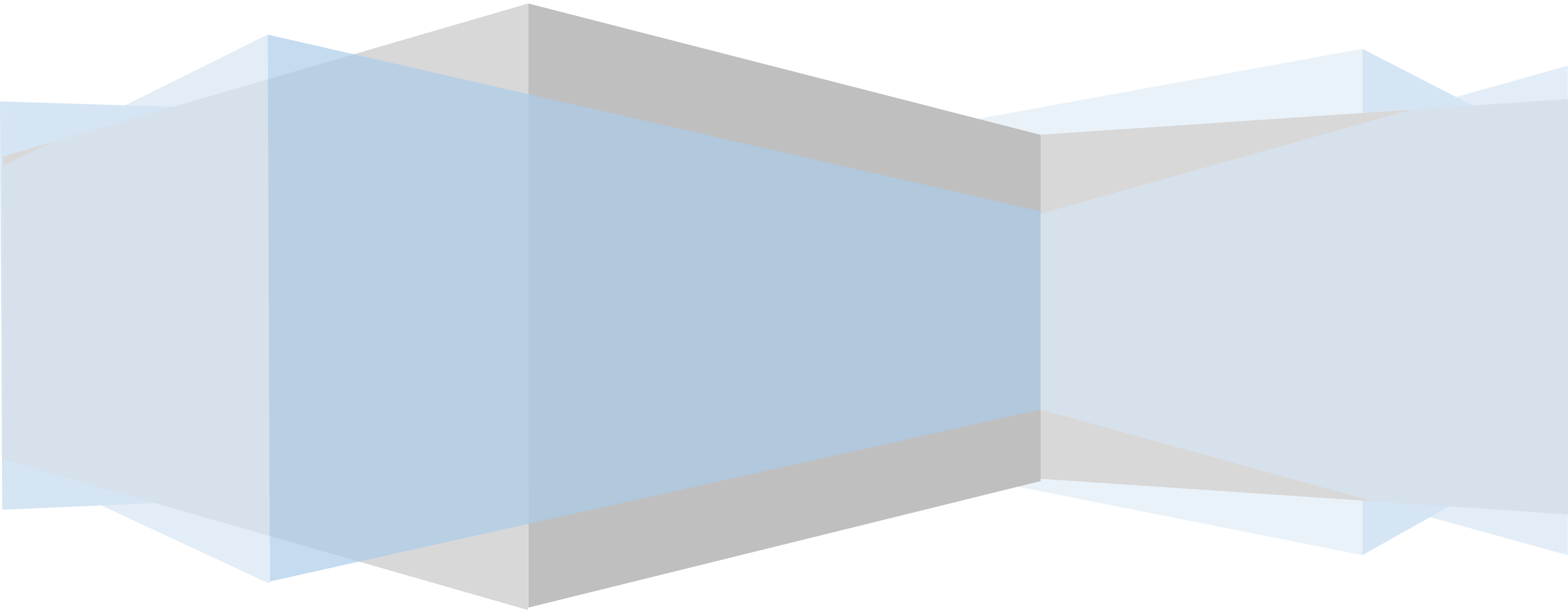
CHAPTER 4

BIOLEACHING STUDIES OF METAL CONTAINED E-WASTE

JATINDRA KUMAR PRADHAN



4.1 INTRODUCTION

Electric and electronic products continue to revolutionize communication, entertainment, transportation, education and health care around the world. There is no sign that this revolution will abate soon. Technical innovation will continue to be a cornerstone of social progress and advanced electronics are leading the way [174]. Studies by Bertram et al. (2002) [175], Jirang et al. (2008) [176] affirm that wastes from electrical and electronic equipment (WEEE) are the fastest growing waste category; this finding emphasizes the need for their efficient recycling strategies. Recycling of e-waste is an important subject not only from the point of waste treatment but also from the recovery aspect of valuable materials. However, recycling of e-waste is still quite limited due to the heterogeneity of the materials present in the products and the complexity of the production of this equipment [177]. Most of the e-waste is a complex mixture of precious metals (Ag, Au, and Pt); base metals (Cu, Al, Ni, Si, Zn and Fe); toxic metals (Hg, Be, Cd, Cr (VI), As, Sb and Bi) along with halogens and combustible substances such as plastics and flame retardants [178, 179]. Mechanical and pyrometallurgical recycling of e-waste has been investigated by different researchers [180-182]. But such processes requiring high consumption of energy cannot efficiently recover precious metals and contain halogenated flame retardants in the smelter feed that can lead to the formation of dioxins and furans. Traditional smelters designed for the treatment of mining concentrates or simple copper scrap encounter some challenges for e-waste treatment. However, state-of-the-art smelters are highly dependent on investments [183, 184].

Bioleaching approaches are generally considered a ‘green technology’ with low-cost and low-energy requirement. Microbial bioleaching is based on the natural ability of microorganisms to transform solid compounds to soluble and extractable form. This may involve enzymatic oxidation or reduction of the solid compound, or an attack on the solid compound by metabolic products [185]. Three main groups of microorganisms have been used for bioleaching process; these are autotrophic bacteria (e.g. *Thiobacillus* sp.), heterotrophic bacteria (e.g. *Pseudomonas* sp., *Bacillus* sp.) and heterotrophic fungi (e.g. *Aspergillus* sp., *Penicillium* sp.) [186]. The use of chemolithoautotrophic bacteria is advantageous because no organic carbon source is needed for their growth. On the other hand, heterotrophic bacteria and fungi can be used with higher pH (i.e. alkaline and acid consuming materials) [186]. The efficiency of recovery of metals can be increased, as revealed in Cu and Au mining where low grade ores are biologically treated to obtain metal values, which are not accessible by conventional treatments (mechanical and thermal) [187]. Besides mesophilic and moderately thermophilic bacteria, extreme thermophilic bacteria were also used for the bioleaching processes. Several studies with mesophilic microorganisms such as *Acidithiobacillus ferrooxidans* and *Leptaspirillum ferrooxidans*, have shown very low Cu leaching rates [83, 84]. However when thermophilic microorganisms are used leaching rates are considerably enhanced, due to high temperatures, higher metal tolerance capacity and the metabolic characteristics of these type of microorganisms [85]. A variety of thermophilic microorganisms (especially *Sulfolobus* sp.) has been enriched and isolated from bioleaching environments [86, 87]. Temperature optima for growth and metal leaching were in the range between 65 and 85°C. Although Cu extraction from mine tailings is more efficient using thermophilic instead of mesophilic organisms, extremely thermophilic microorganisms show a higher sensitivity to Cu and to high pulp densities in agitated systems limiting, therefore, some practical applications [87].

Though, this process has been successfully applied for the leaching of metals from ores [188], data pertaining to its application for the extraction of e-waste is still scanty. A few studies have been undertaken for the extraction of metals from e-waste/printed circuit boards with mesophilic chemolithotrophic bacteria (*Acidithiobacillus ferroxidans* and *Acidithiobacillus thioxidans*) [89, 104, 113], acidophilic moderately thermophilic bacteria (*Sulfobacillus thermosulfidooxidance* and *Thermoplasma acidophilum*) [189, 190] and cyanogenic bacteria (*Chromobacterium violaceum* and *Pseudomonas fluorescens*) [110, 111]. There are so many metals and metalloids such as Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Mo,Tc, Ru, Rh, Pd, Ag, Cd, W, Re, Os, Ir, Pt, Au, Hg, Tl, Po, and U that form well-defined cyanides complexes, which often show very good water solubility and exhibit high chemical stability [191]. Cyanide synthesis by bacteria is restricted to the proteobacteria *Chromobacterium violaceum* and to fluorescent pseudomonades (*P. aeruginosa* and *P. fluorescens*) as well as to certain fungi (*Marasmiusoreades*, and *Clitocybe* sp.) [111]. *Acidithiobacillus ferroxidans* and *Acidithiobacillus thioxidans* are the two acidophilic bacterial species most widely used in bioleaching process. But recently, the synergetic effect during bioleaching process has been noticed via mixed bacterial leaching. It was observed that the acidophilic heterotrophs could promote the growth of the mineral oxidizers by consuming organic excretion produced by these mineral oxidizers and thus improve the bioleaching efficiency [189, 191, 192]. The bioleaching approach of non sulfidic low-grade ores or mine tailings by using *Aspergillus niger* has also been intensively studied [193, 194]. The bioleaching of industrial waste materials (e.g., electronic scrap, municipal solid waste, fly ash, and spent catalyst) [195, 196] for detoxifying these materials has been considered more economical and ‘‘environmentally friendly”, as compared to traditional metals extraction methods (pyrometallurgical and hydrometallurgical) [197].

The present work is thus originated keeping in view the importance of recycling of e-waste. It is a vital step to develop bioleaching strategy for recycling of e-waste due to its efficiency, environmental friendly and cost effective traits. Based on the problems associated with e-waste during recycling following objectives were laid down to provide appropriate knowledge and solutions to the above said problems. Table 4.1 illustrates the list of microorganisms used for our bioleaching studies.

1. Bioleaching studies by cyanogenic bacterial species
2. Bioleaching studies by thermophilic bacteria
3. Bioleaching studies by acidophilic bacteria
4. Fungal bioleaching studies

Table 4.1: List of microorganisms used for bioleaching studies

Bacterial and Fungal Strains used for bioleaching studies						
Strains	*Pseudomonas fluorescens*	*Pseudomonas aeruginosa*	*Chromobacterium violaceum*	Thermophilic bacteria	Acidophilic bacteria	*Aspergillus niger*
Procurement	IMTC-CHD (MTCC-103)	Airborne microorganism isolated by our research group [198]	IMTC-CHD (MTCC-2656)	Isolated form hot spring water from Siachen (J&K)	IMMT (CSIR) BBSR	IMTC-CHD (MTCC-961)
Growth medium	Luria Bertani			Minimal media (M9)	$9K^+$	Sucrose media
Growth conditions	Aerobic pH-7.2 Temp-30ºC			Aerobic pH-7.4 Temp-60ºC	Aerobic pH-1.96 Temp-35ºC	Aerobic pH-7.2 Temp-30ºC
Types of biogenic acid produce	HCN forming bacteria (Cyanogenic)			Not Identified	Sulphuric acid	Organic acids

4.1.1 Bioleaching studies by cyanogenic bacterial species

4.1.1.1 Materials and Methods

Procurement and metal content analysis of e-waste

E-waste, in the form of ground powder of printed circuit boards of personal computers, was obtained from a Bangalore based e-waste recycling unit known as E-Parisaraa (India). Before its transportation to laboratory, no physical/mechanical separation process was used. For experimental use, the ground e-waste was further ground to fine powder (37 µm to 149 µm particle size). The e-waste sample was analyzed for metal analysis content by chemical leaching method [189]. 1.0 g of e-waste sample was dissolved in 100 mL of aqua-regia (HNO_3: HCl = 1:3) [199] by refluxing in a round bottom flask for one hour at 100ºC. The solution was allowed to cool and the volume was made up to 100 mL with deionized water. After that, the solution was passed through glass fiber filters (PALL-GF-A/E-I) to guarantee particle free suspensions and stored at 4ºC for further analysis. The concentrations of dissolved metal ions were determined by atomic absorption spectrometer (PerkinElmer AAnalyst 400 Spectrometer) at the following wavelengths (nm): Ag (328.1), Au (242.8), Co (240.7), Cu (324.8), Cr (357.9), Fe (248.3), Ni (232.0), Se (196.0), and Zn (213.9). Finely ground e-waste sample was sterilized by autoclaving at 121°C for 15 min prior to bioleaching studies.

Two-step bioleaching studies

For bioleaching studies, bacterial strains (*P. fluorescens* (MTCC-103) and *C. violaceum* (MTCC-2656) were procured from Institute of Microbial Technology, Chandigarh, India. *P. aeruginosa* used for these studies, was previously isolated in our laboratory [200]. A two-step bioleaching process is believed to be appropriate to increase metal leaching efficiency of microorganisms from e-waste [201]. For more efficient metal mobilization, direct growth of microorganisms in the presence of e-waste is not advisable due to its toxic effects [104]. Microorganisms were grown in the absence of e-waste to produce biomass followed by addition of different concentrations of e-waste for metal mobilization for an additional time period of seven days. Experiments on two-step bioleaching of metals from e-waste powder were conducted in 250 mL baffled Erlenmeyer flasks containing 100 mL LB medium having 0.5 g glycine at pH 7.2. The flasks were autoclaved at 121°C and 15 psi pressure for 15 min. For two-step bioleaching studies with single cyanogenic bacterial strains, the experimental flasks were inoculated with biomass of 5.0 mL inoculum pellet (single culture) (O.D. = 1.0, 660 nm) aseptically and incubated at 30°C temperature and 150 rpm. Likewise in case of mixed cultures (*P. fluorescens* + *P. aeruginosa*; *P. aeruginosa* + *C. violaceum*; *and P. fluorescens* + *C. violaceum*), biomass of 2.5 mL of inoculum pellet (O.D. =1.0, 660 nm) from each bacterial strain was added to the experimental flasks. After two days of incubation, 1.0 g of sterilized e-waste (1% w/v) was added to each flask under aseptic conditions. Un-inoculated control was run in parallel. Subsequently, the experimental flasks were incubated at 30ºC temperature and 150 rpm for another seven days' time period. The same two-step bioleaching experiments were performed with higher concentration of e-waste (5% w/v and 10% w/v) with *C. violaceum, P. aeruginosa* and *P. fluorescens.*

Sampling and analysis of bioleachable samples

All flasks were weighed before sampling and any decrease in volume due to evaporation during incubation was compensated by adding corresponding volume of sterilized distilled water. During the course of the bioleaching experiments, 5.0 mL of sample was taken out from each flask periodically for analyzing the pH, total protein content and total metal ions content. The pH was measured by digital pH meter (Eutech pH 510). The samples were filtered through Whatman No. 1 filter paper to remove solid particles and centrifuged at 10,000 rpm for 10 min to remove bacterial cells. The cell pellets were preserved for determining the total protein content while the supernatants were analyzed for metal ions concentration of Au, Cu, Zn, Fe, and Ag using atomic absorption spectrometer (PerkinElmer AAnalyst 400). Before analysis on atomic absorption spectrometer, the supernatants were filtered through glass fiber filter (PALL-GF-A/E-I) to guarantee particle free suspensions. The total protein content was determined by micro-biuret method [202] after dissolving the cell pellet in 4.0M NaOH solution using bovine serum albumin as standard.

Statistical analysis

All experimental data were statistically interpreted with one-way and two-way analysis of variance (ANOVA). All statistical tests were performed at probability level $p < 0.05$ using statistical package MSTAT/Minitab (Minitab Inc. USA, Version 13, 2004 for Windows®)

4.1.1.2 Results and discussions

Metal composition of e-waste by chemical analysis

Chemical analysis of ground powder of printed circuit boards was carried out to determine the concentrations of various metals present in it. The major metals were observed to be Cu (12.06%), and Fe (2.08%). Precious metals like Au (0.08%) and Ag (0.06%) were also present but in low concentration (Table 4.2). Heterogeneity was observed when comparison was made among the concentrations of different metal ions obtained in these studies and those reported by other researchers [104, 203]. This difference may be attributed, to some extent, to the analytical methods used, but on the basis of large differences in the concentrations of some metals, (e.g. Zn, Ni, and Fe) it seems to be mainly dependent upon the origin of the material.

Table 4.2: Metal analysis of e-waste

Metals	% w/w
Cu	12.06±0.60
Fe	2.086±0.03
Se	0.945±0.014
Zn	0.115±0.004
Au	0.084±0.005
Ag	0.068±0.008
Cr	0.058±0.005
Ni	0.038±0.004
Co	0.0127±0.017

Metal bioleaching studies

In the same set of bioleaching experimental conditions, rate of bioleaching of Au, Cu, Zn and Fe appeared to be dependent upon their respective concentration in the e-waste, and metals having high concentrations being leached out at higher rates. Better rates were observed when mixed culture of cyanogenic bacteria was used in bioleaching process (Table 4.3).

Maximum percent bioleachabilities of metals, after 7 days of bioleaching under same set of experimental conditions with single and mixed cultures are shown in Figure 4.1.

Among single bacterial cultures, *C. violaceum* exhibited maximum bioleachability of all metals i.e. Cu (79.3% w/w), Au (69.3% w/w), Zn (46.12% w/w), Fe (9.86% w/w) and Ag (7.08% w/w) followed by *P. aeruginosa*. Among mixed cultures, the mixture of *P. aeruginosa* and *C. violaceum* exhibited maximum bioleachability 83.46%, 73.17%, 49.11%, 13.98% and 8.42% w/w of total Cu, Au, Zn, Fe and Ag, respectively. It was also observed that significantly high concentration of Cu (77.12% w/w) and Au (63.14% w/w) were leached out by the mixed cultures of *P. fluorescens* and *C. violaceum.* Cu exhibited maximum leachability followed by Au, Zn, Fe and Ag. Precious metal Au leached out around 73.17% w/w by mixed cultures of *P. aeruginosa* and *C. violaceum* and 69.3% w/w by *C. violaceum* alone which were most noteworthy results. It was observed that mixed cultures of *P. aeruginosa* and *C. violaceum* exhibited more leaching capability for all metals than other combination of mixed cultures as well as single cultures. This might be due to higher tolerance to metal toxicity, formulation of stable metal complexes in presence of e-waste releasing additional secondary metabolites for metal leaching and enhanced growth compared to other biological treatments [107, 204]. Although *C. violaceum* and *P. fluorecens* have been reported for their metal leaching capabilities [108, 109, 205], the use of *P. aeruginosa* in bioleaching of e-waste was carried out for the first time in the present study. *P. aeruginosa* contributed significantly to the leaching results of Au, Cu, and Zn mobilization with 52%, 52% and 39% w/w respectively at 1% w/v of e-waste concentration.

Table 4.3: Rates of bioleaching of metals from electronic waste with different types of bacteria under same set up of experimental conditions. The data presented in this table presents mean of those obtained from triplicate experiments at significant level ($p < 0.05$) based on one-way ANOVA analysis.

Bacterial culture	Maximum rate of metal leaching (mg/L/day)			
	Au	Cu	Zn	Fe
P. fluorescens	0.25	19.34	0.05	0.48
P. aeruginosa	0.54	74.65	0.05	0.26
C. violaceum	0.72	110.79	0.06	0.27
P. aeruginosa +*P. fluorescens*	0.52	88.94	0.08	0.60
P. aeruginosa + *C. violaceum*	0.72	114.45	0.06	0.37
P. fluorescens + *C. violaceum*	0.65	103.96	0.05	0.42

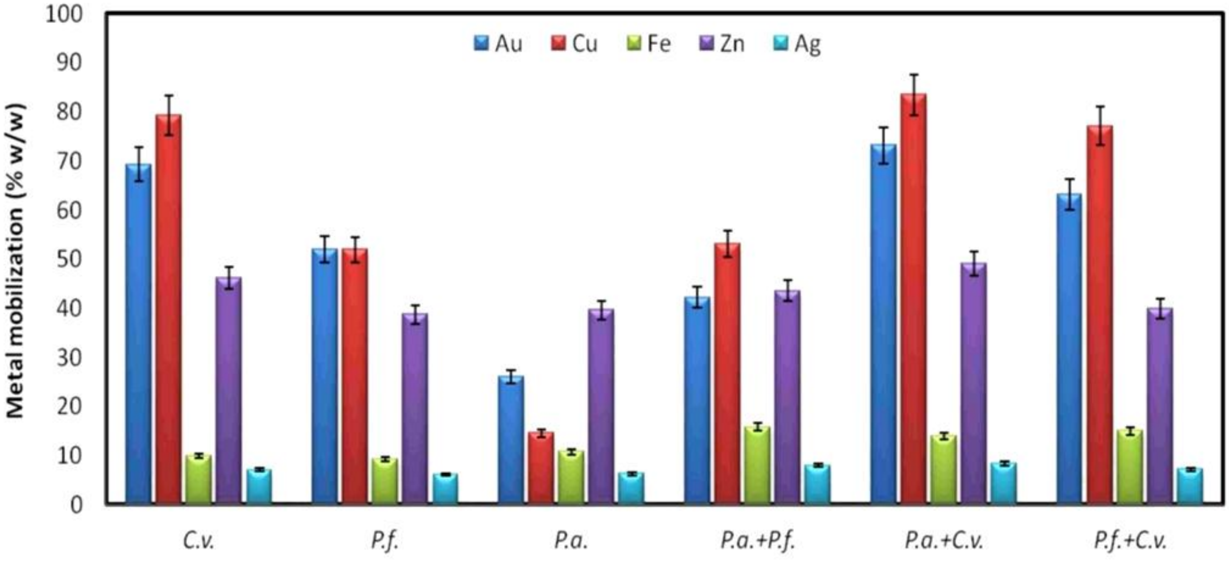


Figure 4.1: Percent metal solubilisation after bioleaching of e-waste with *C. violaceum, P. fluorescens, P. aeruginosa* and mixed cultures. The data presented in this figure presents mean value of metals obtained from triplicate experiments at significance level ($p < 0.05$) based on one-way ANOVA analysis

Figure 4.2 and 4.3 displays the trends of metal mobilization (%) and concentration (mg/L) of Au, Cu, Zn, Fe, and Ag with respect to single bacterial strains and mixed culture of these strains respectively during two-step bioleaching experiments. From these results it was observed that, especially when *P. fluorescens* alone or a mixed culture of *P. fluorescens and P. aeruginosa* was used for two-step bioleaching, the concentration of Au, Cu, Zn, Fe and Ag decreased with prolonged incubation time. This might be due to sorption processes onto biomass or biodegradation because metal cyanides serve as carbon or nitrogen source [107, 206]. The leaching of Ag initiated after 3rd day of incubation and was observed to be least bioleachable metal at concentration of around 9% w/w with both single and mixed cultures as compared to other four metals (Au, Cu, Zn and Fe) after 7 days of incubation. Slow mobilization of Ag was observed when individual strains were grown in the presence of e-waste. After three days of incubation about 3.5% w/w of Ag was mobilized by *P. aeruginosa* whereas after four days of incubation *C. violaceum* and *P. fluorescens* mobilized Ag about 4.8% and 4.3% w/w, respectively. But in case of all mixed cultures, Ag was mobilized after two days of incubation which was about 2.7% w/w. After this the Ag concentration increased only slightly until the end of the incubation period in both single and mixed cultures.

Mobilization of Ag by cyanogenic microorganisms proved to be promising. However, the process has to be optimized by reducing inhibitory effects, e.g. by trapping the dicyanoargentate formed or by applying a sequential two-step process where biological cyanide formation is separated from metal mobilization.

Differences were observed in the bioleaching pattern of three single bacterial strains applied in presence of 1% w/v, 5% w/v and 10% w/v e-waste concentration (Figure 4.4). *C. violaceum* was able to mobilize more metal concentrations as compared to other bacterial strains. Indeed, *C. violaceum* exhibited higher growth, a higher metal resistance and hence better metal leaching performance followed by *P. aeruginosa* which exhibited higher metal resistance and more growth than *P. fluorescence.* As the concentration of e-waste increased from 1% w/v to 10% w/v, the metal mobilization by these microorganisms also decreased. *C. violaceum* and *P. aeruginosa* mobilized Au 20.28% and 19.26% respectively at 10% w/v e-waste concentration. Perhaps this is due to the toxic effect of e-waste and decreased metal tolerance of microorganisms [104]. There was no significant difference between single bacterial strains and between interactions for Fe mobilization at $p < 0.05$ based on 2-way ANOVA analysis while bioleaching of Fe with different concentration of e-waste with single bacterial strains.

The maximum leachability (0.8%) was exhibited by Cu in case of un-inoculated control which was run parallel with two-step bioleaching experiments. Under same set of experimental conditions for other metal ions, the percent leachabilities were “considerably” not as good as above mentioned metal leaching value. It was seen that, the media used for microorganisms was insignificant for the leaching of metals from e-waste. The bioleaching data from above studies is specifically applicable to above mentioned concentration of metal (chemical leaching) presented in e-waste procured from E-Parisaraa Company (after processing).

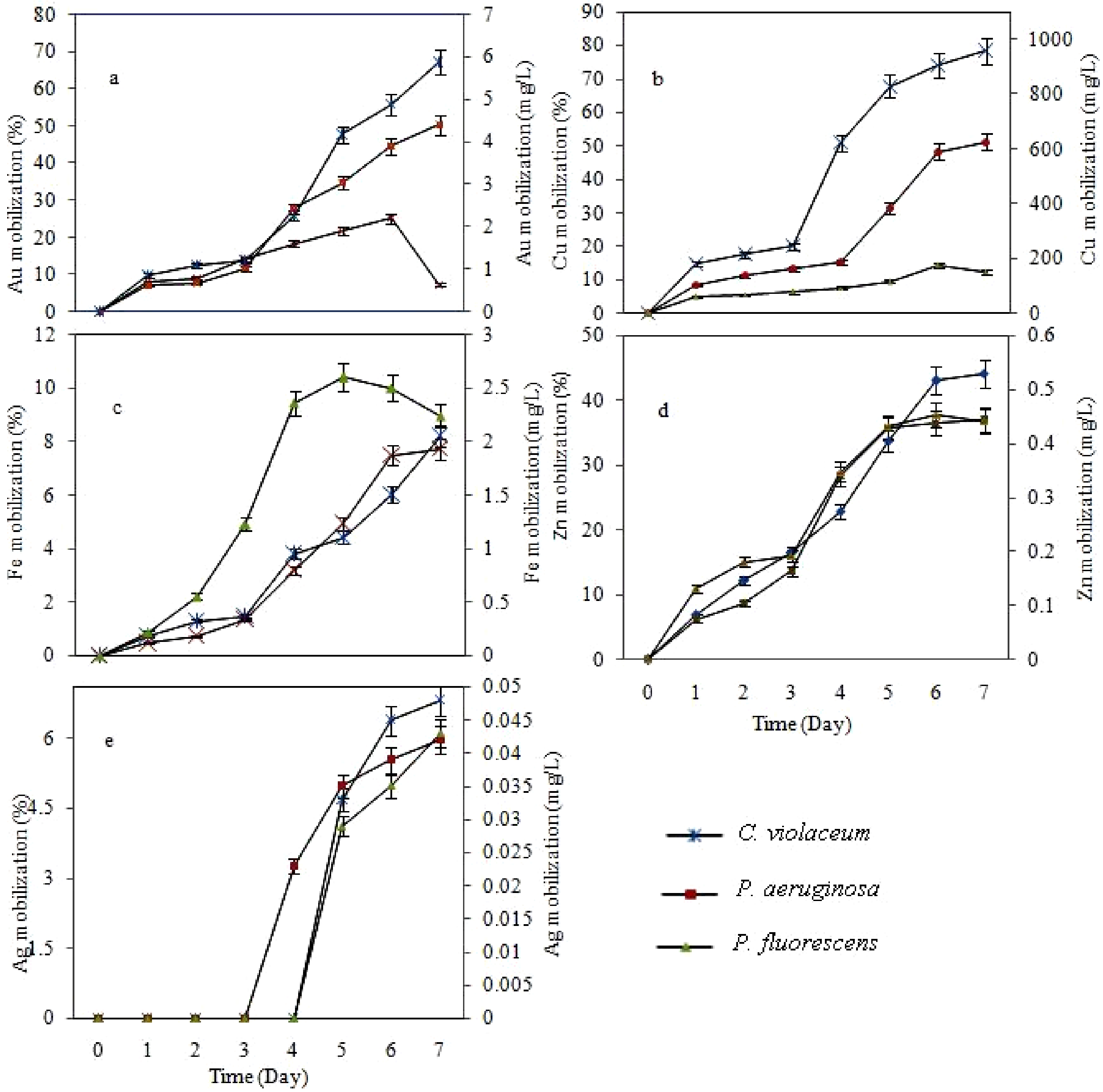


Figure 4.2: Trends of metal mobilization (%) and concentrations (mg/L) during bioleaching of e- waste by *C. violaceum*, *P. fluorescens*, and *P. aeruginosa*: (a) Au, (b) Cu, (c) Fe, (d) Zn and (e) Ag. The data presented in this figure presents mean of those obtained from triplicate experiments at significant level ($p < 0.05$) based on two-way ANOVA analysis

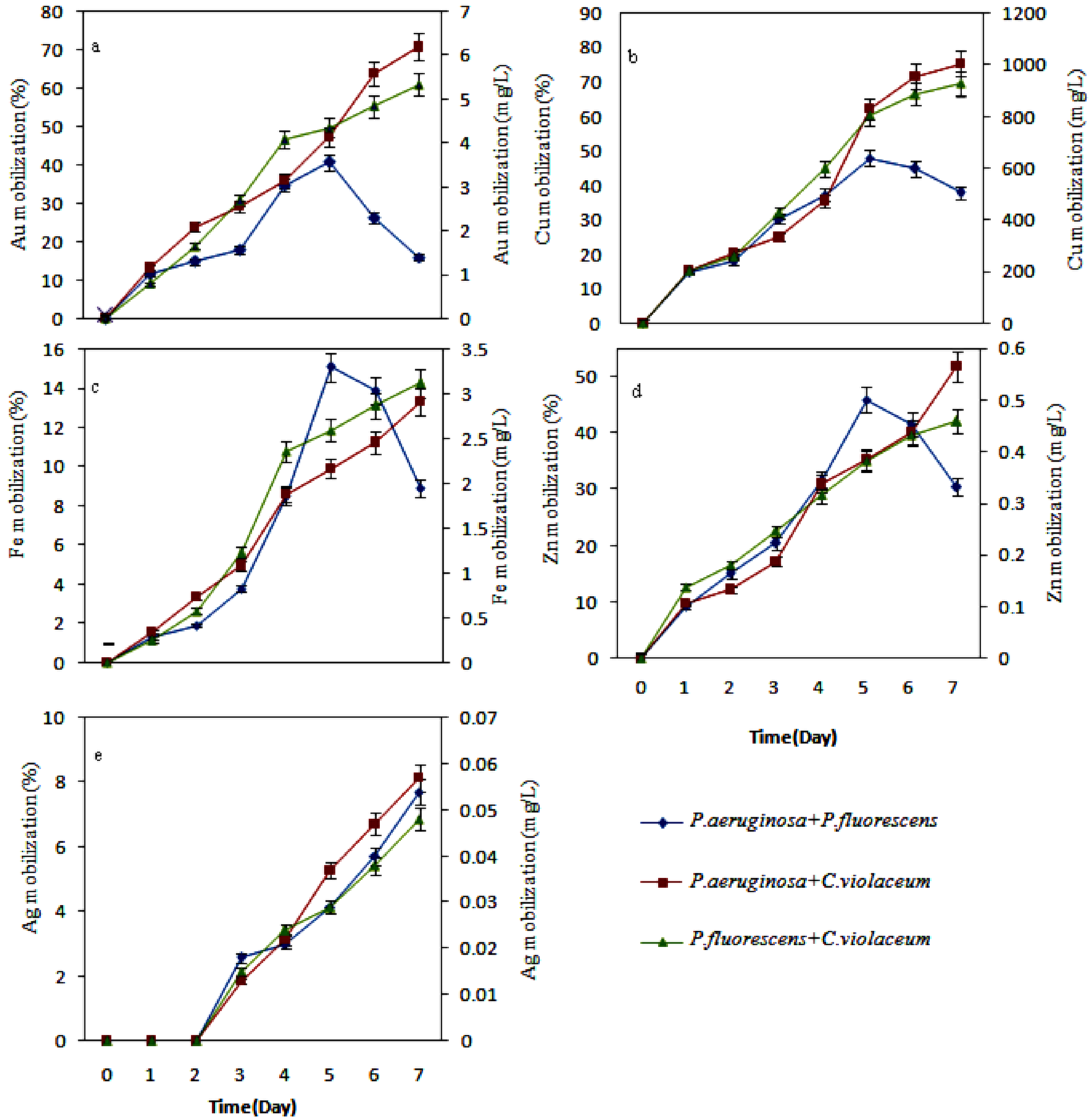


Figure 4.3: Trends of metal mobilization (%) and concentrations (mg/L) during bioleaching of e- waste by different mixed cultures (*P. aeruginosa* + *P. fluorescens*; *P. aeruginosa* + *C. violaceum*; and *P. fluorescens* + *C. violaceum*): (a) Au, (b) Cu, (c) Fe, (d) Zn and (e) Ag. The data presented in this figure presents mean of those obtained from triplicate experiments at significant level ($p < 0.05$) based on two-way ANOVA analysis

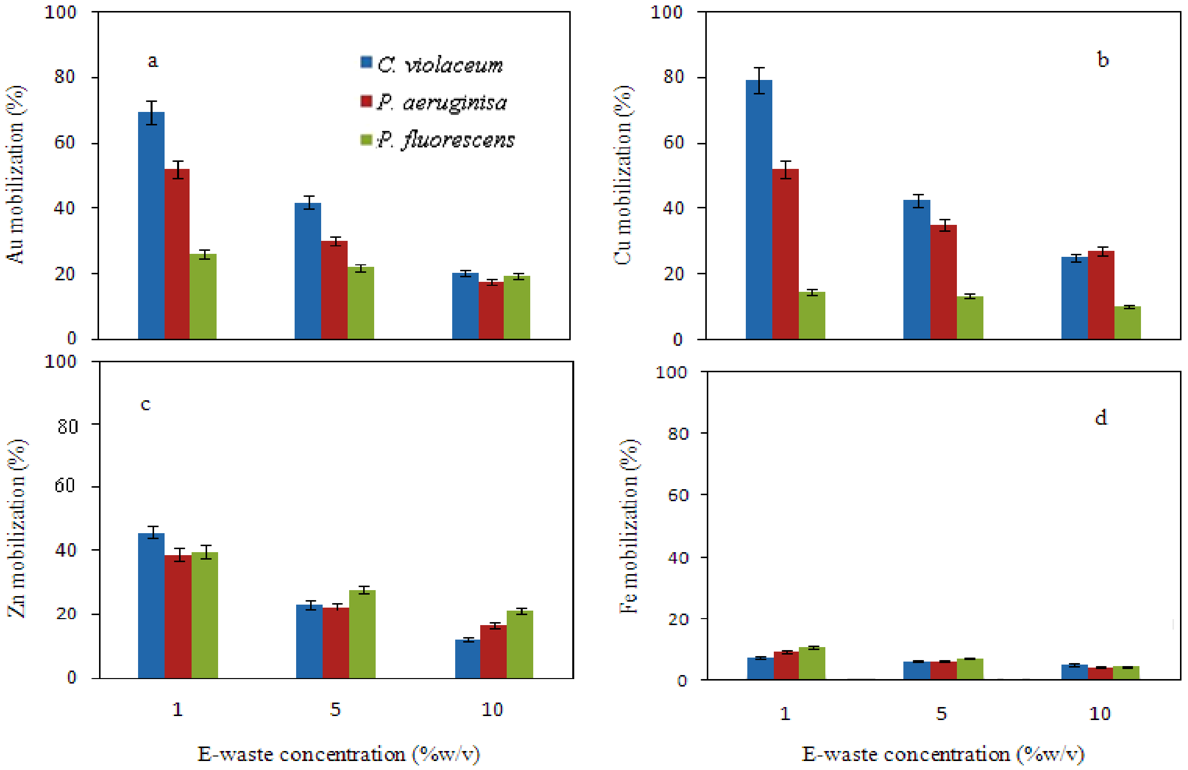


Figure 4.4: Leaching of metals from electronic waste by *C. violaceum, P. fluorescens* and *P. aeruginosa* during bioleaching experiment with different concentrations of electronic waste: (a) Au, (b) Cu, (c) Zn and (d) Fe. The data presented in this figure presents mean of those obtained from triplicate experiments at significant level ($p < 0.05$) based on two-way ANOVA analysis

pH *change during bioleaching of metals from e-waste*

In the present study, pH profile of two-step bioleaching medium having 1% w/v concentration of e-waste was studied with single cyanogenic bacterial strains as well as with mixed cultures. Figure 4.5 (a) indicates the trends in changes of pH of the medium during bioleaching of e-waste with single cyanogenic bacterial strains and Figure 4.5 (b) shows the change in pH during bioleaching with mixed cultures. Using *P. fluorescens* with e-waste for two-step bioleaching, the pH was increased linearly from 7.2 to 9.2 during the incubation period of 7 days. In case of mixed cultures of *P. aeurginosa* and *P. fluorescens,* the pH was increased from 7.2 to 7.96 after two days of incubation and then increased gradually up to 9.3 till 7th day of incubation whereas in the case of *P. fluorescens* culture pH was observed to be 7.48. Increase in pH was only observed when the e-waste was subjected to two-step bioleaching studies. In similar studies [205, 207], cyanide was found to be the cause of increase of pH. At physiological pH 7.0, cyanide is present mainly as HCN due to its pK_a value of 9.3 and is, therefore, volatile. In the presence of salts this value decreases to approximately 8.3 and the volatility is reduced [108]. Hence, the pH increased by the formation of HCN and formulates complexes with metals. Use of cyanogenic bacteria for the mobilization of metals from solid under alkaline conditions can be of industrial interest since metal chemistry (e.g. solubility, mobility, sorption, precipitation, formation of secondary minerals) especially in the presence of cyanide aids in recovery of metals more easily (by sorption onto activated carbon) compared to acidic conditions [112, 207].

Determination of microbial growth during two-step bioleaching

Microbial growth was determined as total cellular protein as mentioned in methods section. It may be mentioned that these results provide a rough estimate of the growth and do not give exact measurement of the biomass in the flask, as the readings were only for plankotonic cells, while cells attached to the particular matter were not accounted for [189]. The growth (determined as total cellular protein) of *C. violaceum, P. fluorescens,* and *P. aeruginosa* is shown in Figure 4.5 (c) and the trend of increase in growth of mixed cultures (*P. aeurginosa* + *P. fluorescens, P. aeurginosa* + *C.violaceum*and *P. fluorescens* + *C.violaceum*) in Figure 4.5 (d) during the two-step bioleaching with 1% w/v e-waste concentration at 30ºC temperature and 150 rpm. The results indicate the increase in growth with respect to metal bioleaching for all bacterial strains as well as mixed cultures in presence of e-waste. The metal bioleaching capability was associated with bacterial growth as they release secondary metabolites which mobilize metals from e-waste [112]. In case of *P. fluorescens* the growth was suddenly increased on second day and decreased gradually towords the seventh day. This may be due to shortage of carbon source or toxic effect of secondary metabolites [107, 204]. The same was also observed in case of mixed cultures of *P. fluorescens* and *P. aeruginosa*. Furthermore, the growth plot for mixed cultures should not be regarded as a true growth curve due to presence of two different types of bacteria [189]. Growth curve in case of mixed cultures showed the higher rate of biomass production than the individual bacterial strains in presence of e-waste.

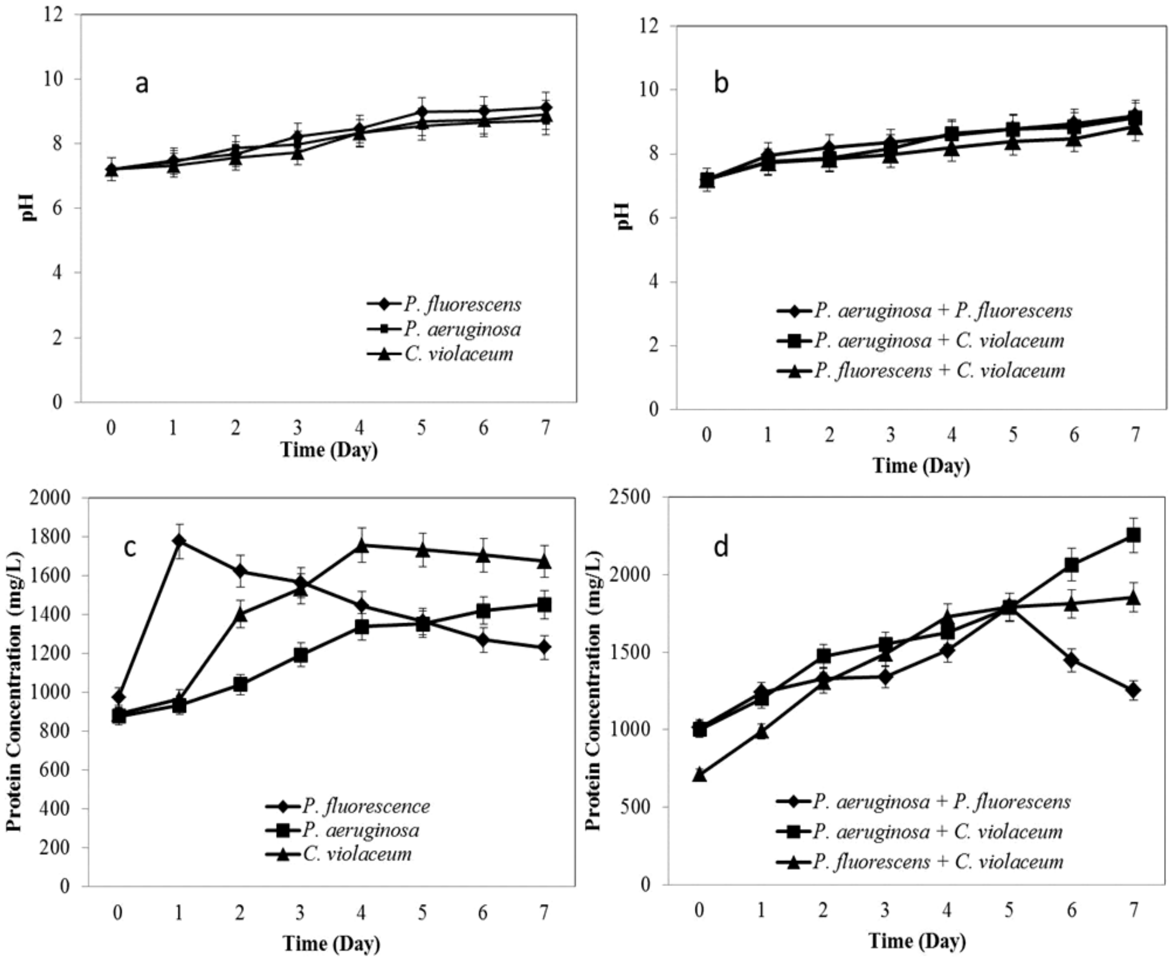


Figure 4.5: pH change and growth curve (total cellular protein) during bioleaching with e-waste: (a) Trends of pH change by single bacterial strains, (b) trends of pH change by mixed cultures, (c) growth curve of single bacterial strains, and (d) growth curve of mixed cultures. The data presented in this figure presents mean of those obtained from triplicate experiments at significance level ($p < 0.05$) based on two-way ANOVA analysis

4.1.1.3 Conclusions

Results from this study revealed that in alkaline condition using cyanogenic bacterial strains such as *Chromobacterium violaceum, Pseudomonas fluorescens,* and *Pseudomonas aeruginosa*, and their mixed culture had capability to leach out metals (Gold, Cupper, Iron, Zinc and Silver) from e-waste. Higher metal bioleaching capabilities were achieved by using combinations of mixed cultures of cyanogenic bacterial strains. *Pseudomonas aeruginosa* was used for the bioleaching study of e-waste for the first time and in combination with *Chromobacterium violaceum* exhibited higher metal leaching capabilities than other combinations. Precious metal like gold was mobilized by cyanogenic bacteria which can be developed as industrial application of bioleaching in alkaline conditions (biocyanidation). Heterogeneity in mobilization of metals by bioleaching from e-waste was observed. These results may vary with different growth conditions applied, concentration of e-waste used and depending on microorganism used. Extensive optimization studies are required to study the parameters influencing the bioleaching of metals from e-waste. Issue of heterogeneity of the e-waste should be addressed at first hand to make the process of bioleaching cost-effective and successful at industrial scale.

4.1.2 Bioleaching studies by thermophilic bacteria

4.1.2.1 Materials and Methods

Isolation and growth assessment

Microorganisms were isolated from water samples which were collected from Panamic hot springs of Siachen base, Nubra Valley, Leh Ladakh, India (altitude10585.00, latitude 34.46.749 and longitude 077.32.580) (Figure 4.6). Water sample (0.1 mL) was spread over nutrient agar medium plates in triplicates and incubated at temperature ranging from 50°C to 70°C. At 60°C temperature, five prominent bacterial colonies were found. Then the dominant bacterial colonies were selected and sub cultured periodically. All five cultures were named as: SJ1, SJ2, SJ3, SJ4, and SJ5.

Figure 4.6: Panamic hot spring, Nubra valley, Siachen, Leh Ladakh, India

pH *optimization for growth of thermophiles*

For optimal growth of thermophiles, pH range was set from 5.0 to 10.0 as initial pH of hot spring water was 6.97. For this purpose minimal media was used with different pH range buffer (Citrate buffer, pH 5.0; Phosphate buffer, pH 6.0, 7.0 & 8.0; Glycine-NaOH buffer, pH 9.0 & 10.0).

Preparation of Minimal Media

To prepare 1L of media, 200 mL of 5X M9 salt solutions [64.00g Na_2HPO_4-$7H_2O$, 15.00g KH_2PO_4, 2.5g NaCl, and 5.0g NH_4Cl per litre of de-ionized water] was added to 800 mL of distilled water. After autoclaving, cooled to room temperature and then 2.0 mL of 1.0M $MgSO_4$, 0.1 mL of $CaCl_2$ solution and 20.0 mL of 20% glucose was added and swirl to mix evenly. The pH of minimal media was 7.4. For preparing pH 5.0 of minimal media, citrate buffer was used. Phosphate buffer was used for preparing pH 6.0, 7.0, and 8.0, whereas glycine-NaOH buffer was used for maintaining pH of 9.0 and 10.0.

Composition of citrate buffer (pH 5.0)

Stock solutions: (A) 0.1M solution of citric acid (21.01g in 1L); (B) 0.1M solution of sodium citrate (29.41g of sodium citrate in 1L). 20.5 mL of solution A was added to 29.5 mL of B and diluted to total 100 mL.

Composition of phosphate buffer (pH 6.0, 7.0 8.0)

Stock solutions: (A) 0.2M solution of monobasic sodium phosphate (27.8g in 1L); (B) 0.2M solution of dibasic sodium phosphate (53.6g of $Na_2HPO_4.7H_2O$ or 71.7g of $Na_2HPO_4.12H_2O$ in 1L).

pH 6.0: 87.7 mL of solution A + 12.3 mL of solution B

pH 7.0: 39.0 mL of Solution A + 61.0 mL of solution B

pH 8.0: 5.3 mL of Solution A + 94.7 mL of solution B

Composition of Glycine-NaOH buffer (pH 9.0, 10.0)

Stock solutions: (A) 0.2M solution of glycine (15.01g in 1L); (B) 0.2M solution of NaOH (8.0g in 1L).

pH 9.0: 50.0 mL of solution A + 8.8 mL of solution B

pH 10.0: 50.0 mL of Solution A + 32.0 mL of solution B

The above mixture of solutions was diluted to total volume of 200mL using distilled water.

The thermophilic bacterial strain SJ1 (0.5 mL) with optical density (0.56) was inoculated with 100 mL of minimal media having desired pH with specified buffer in 250 mL of Erlenmeyer flask. Then the medium was incubated at 60ºC in a rotary shaker at 140 rpm for a period of seven days. Periodically pH and optical density were measured as a function of growth of bacteria.

Temperature optimization for growth of thermophiles

After optimization of pH for optimal growth of bacteria, temperature was optimized with 5ºC variation of temperature within a range of 60-70ºC i.e. 60ºC, 65ºC and 70ºC. The thermophile bacterial strain (0.5 mL) with optical density (0.56) was inoculated with 100 mL of minimal media having pH 7.4 in 250 mL of Erlenmeyer flask. Then the medium was incubated at specific temperature in a rotary shaker at 140 rpm for a period of seven days. Periodically pH and optical density was measured as a function of growth of bacteria.

Bioleaching of e-waste using thermophilic bacteria

For bioleaching experiment, minimal media having pH 7.4 was taken as leaching medium at 60ºC. The thermophilic bacterial strain (0.5 mL) with optical density (0.59) was used for bioleaching studies with 1% w/v e-waste. Control flask was contained only minimal media with same concentration of e-waste.

All flasks were weighed before sampling and any decrease in volume due to evaporation during incubation was compensated by adding corresponding volume of sterilized distilled water. During the course of the bioleaching experiments, 5.0 mL of sample was taken out from each flask periodically for analyzing the pH, optical density and total metal ions content. The pH was measured by digital pH meter (Eutech pH 510). After centrifugation at 1000 rpm for 5 minutes the supernatants were analyzed for metal ions concentration of Al, Cu, Zn, Fe, Ni and Cr using atomic absorption spectrometer (PerkinElmer AAnalyst 400 Spectrometer). Before analysis on atomic absorption spectrometer, the supernatants were filtered through glass fiber filter (PALL-GF-A/E-I) to guarantee particle free suspensions.

Bacterial genomic DNA extraction

The extraction of total bacterial genomic DNA was performed according to the procedures described by Hesham et al. (2006) [209]. In brief, cells from 50 mL cultures were harvested by centrifugation, and the pellets were re-suspended by adding 400 µL lysis buffer

(1% SDS, 100 mM NaCl, 10 mM Tris with pH at 8.0, and 1 mM EDTA with pH at 8.0) and 600 µL of phenol–chloroform (v/v = 25:24). The cells were then homogenized by vortexing and incubated at 60ºC for 10 min. After centrifugation, the supernatant was extracted once with 1 volume of phenol– chloroform–isoamyl alcohol (v/v/v = 25:24:1, pH = 8.0) and once with 1 volume of chloroform–isoamyl alcohol (v/v = 24:1, pH = 8.0), and the extracts were mixed. Nucleic acids were precipitated by adding 0.1 volume of sodium acetate (pH = 5.2) and 0.6 volume of isopropanol to the supernatant. The mixture was incubated in ice for 30 min and centrifuged (15,000 g for 20 min at 4ºC) to recover the precipitated nucleic acids. The pellets were washed with 70 % ice-cold ethanol and centrifuged (15,000 g for 20 min at 4ºC). The pellets were dissolved in 60 µL TE buffer (10 mM Tris/HCl, 1 mM EDTA, pH 8.0). The genomic DNA was resolved using 0.8% agarose gel electrophoresis and visualized using Gel documentation system (Molecular Imager® Gel Doc™ XR-170-8171).

Amplification of the 16S RNA gene

Identification of the bacterial isolate was performed by amplification of 16S rRNA gene with bacterial universal primers 27F (5-AGAGTTTGATCCTGGCTCAG-3) and 1492R (5-CGGCTACCTTGTTACGACTT-3) (Lane 1991) generating a PCR product corresponding to nucleotide positions 27–1492 of the *Escherichia coli* 16S rDNA sequence. PCR reaction was carried out in a final volume of 50 µL which contained 50 ng template DNA (genomic DNA extracted as described above), 0. 25 U Taq DNA polymerase, 2.0 mM dNTPs, 1X Taq DNA polymerase buffer (Mg^{2+} plus) and 20 µM primer. PCR was performed according to the following program: 5 min denaturation at 95ºC, followed by 30 cycles of 30 sec denaturation at 94ºC; 45 sec annealing at 54ºC; 30 sec extension at 72ºC; and a final extension step of 7 min at 72ºC. 5 µL of the amplified mixture was then analyzed using 1% 1X TBE agarose gel electrophoresis. The gel was stained with ethidium bromide, visualized under UV light and photographed using using Gel documentation system (Molecular Imager® Gel Doc™ XR-170-8171).

16S rRNA gene sequences and phylogenetic analysis

To verify the presence of appropriately sized amplicons, the PCR product was subjected to electrophoresis in 1% agarose gel according to the standard methods. Product of the correct size was purified and sequenced in both directions using an ABI 3730 automated sequencer. The whole 16S rRNA sequencing of our PCR products were carried out at Xcelris

Genomics, Xcelris Labs Ltd., Ahmadabad, India. The bacterial 16S rDNA sequences obtained were then aligned with known 16S rDNA sequences in GenBank database using the basic local alignment search tool (BLAST) at the National Center for Biotechnology Information (http://www.ncbi.nlm.nih.gov/BLAST/), and percent homology scores were generated to identify bacteria. A phylogenetic tree was constructed by means of MEGA version 4.0 using a neighbor-joining algorithm, and the Jukes-Cantor distance estimation method with bootstrap analyses for 1,000 replicates was performed.

Nucleotide sequence accession number

The 16S ribosomal DNA sequence of strain SJ1 and SJ4 has been deposited in the GenBank nucleotide sequence databases under Accession Nos. JX465654 and JX465655, respectively.

4.1.2.2 Results and discussions

Initial morphological characterization revealed that, bacteria were gram positive and rod shaped. Figure 4.7 shows the morphology of bacteria. The dominant bacterium SJ1 was optimized for pH and temperature before bioleaching studies and it was observed that at pH 7.4, SJ1 exhibited maximum growth in respect of O.D. at 60ºC (Figure 4.8) with normal minimal media. No growth was observed at temperature 65ºC and 70ºC with the pH range 5.0-10.0. During the course of both one-step and two-step bioleaching studies, SJ1 strain did not exhibit any metal leaching as well as growth with minimal media at pH 7.4 and temperature 60ºC.

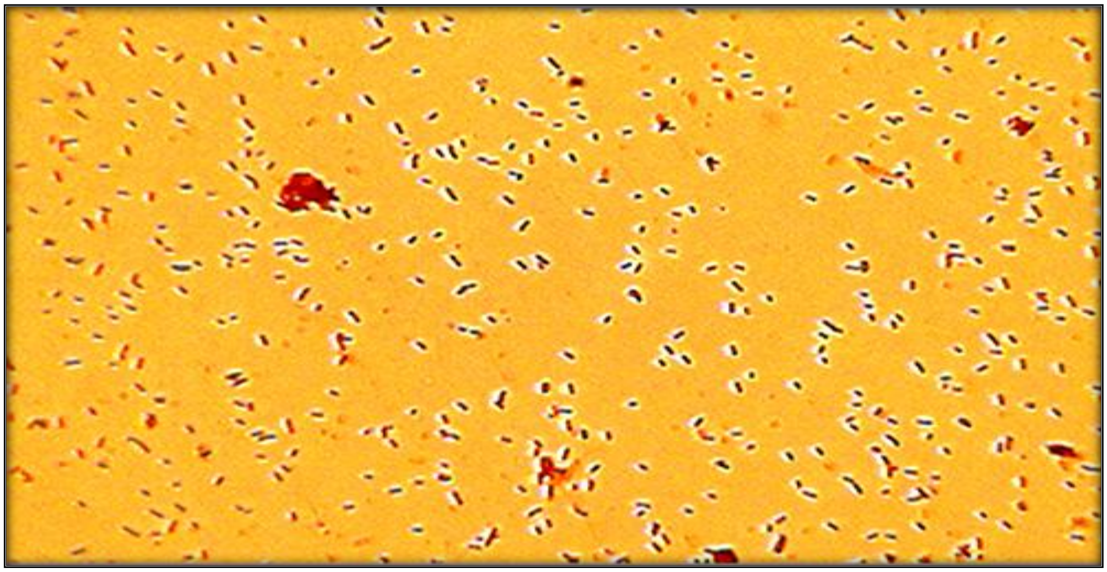


Figure 4.7: Isolated bacteria as seen under image analyzer (magnification 100X)

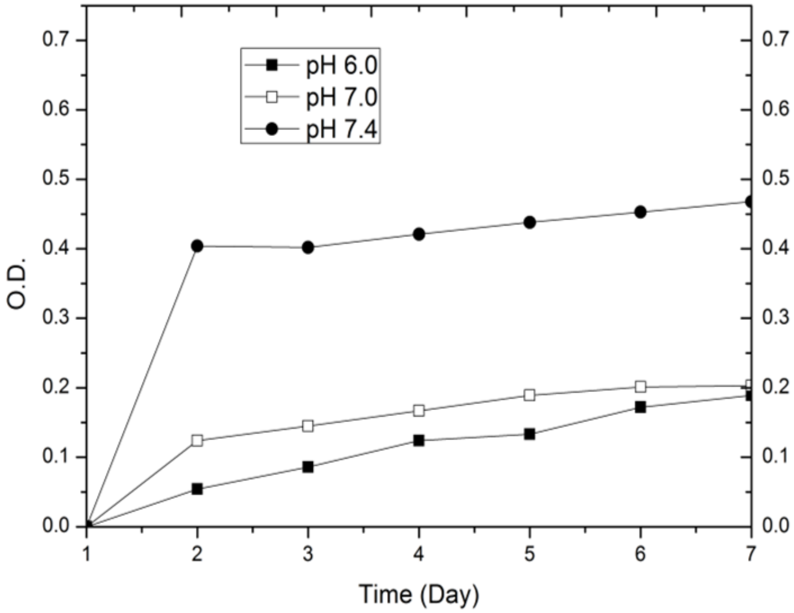


Figure 4.8: Growth curve of SJ1 under different pH conditions at 60ºC temperature

Molecular identification and phylogenetic analysis using 16S rRNA gene sequence comparison

Results show that the 16S rRNA sequence of two isolated strains SJ1 and SJ5 were highly homologous to *Geobacillus pallidus (Aeribacillus pallidus),* with 96% and 84% sequence similarity respectively. Another three strains SJ2, SJ3 and SJ4 were highly homologous to *Aneurinibacillus thermoaerophilus*, with 97%, 98% and 98% sequence similarity respectively. SJ1 and SJ4 assembled sequences were submitted to GenBank database because these two strains showed maximum homologous similarity as compared to SJ2, SJ3 and SJ5. To confirm the position of the strain SJ1 and SJ4 in phylogeny, a number of sequences representative some *Bacillus* sp. were selected from GenBank database for the construction of a phylogenetic tree. As shown in Figure 4.9 and 4.10, the phylogenetic trees indicated that strain SJ1 and *Geobacillus pallidus* shared one clade cluster whereas SJ4 and *Aneurinibacillus thermoaerophilus* shared clad cluster. Therefore, the strains SJ1 and SJ4 were identified as *Geobacillus pallidus* and *Aneurinibacillu sthermoaerophilu*, respectively.

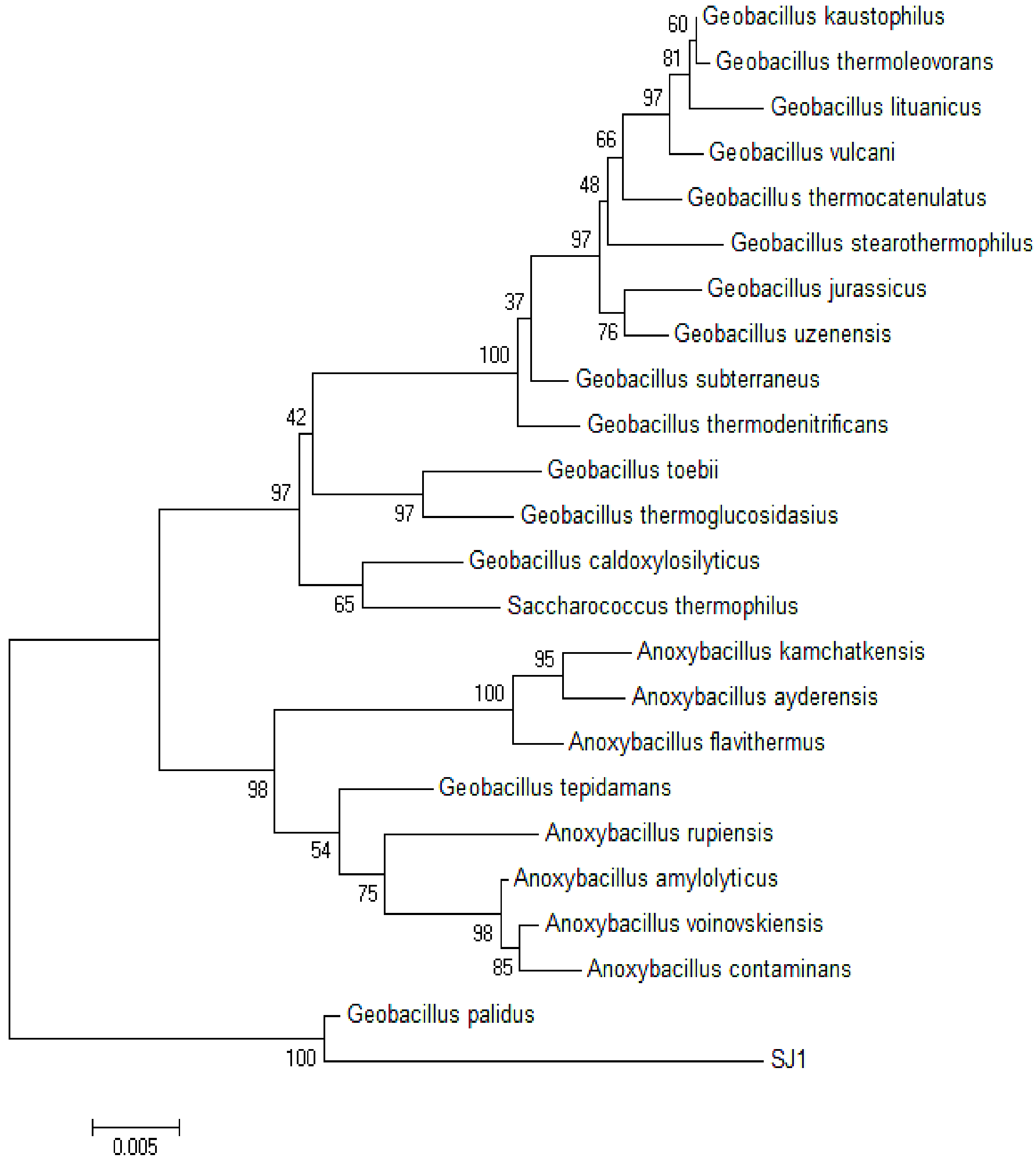


Figure 4.9: Phylogenetic relationship between the SJ1 and other 16S rDNA sequences of published strains. In the phylogenetic tree, SJ1 and *Geobacillus pallidus* were clustered together as one clade

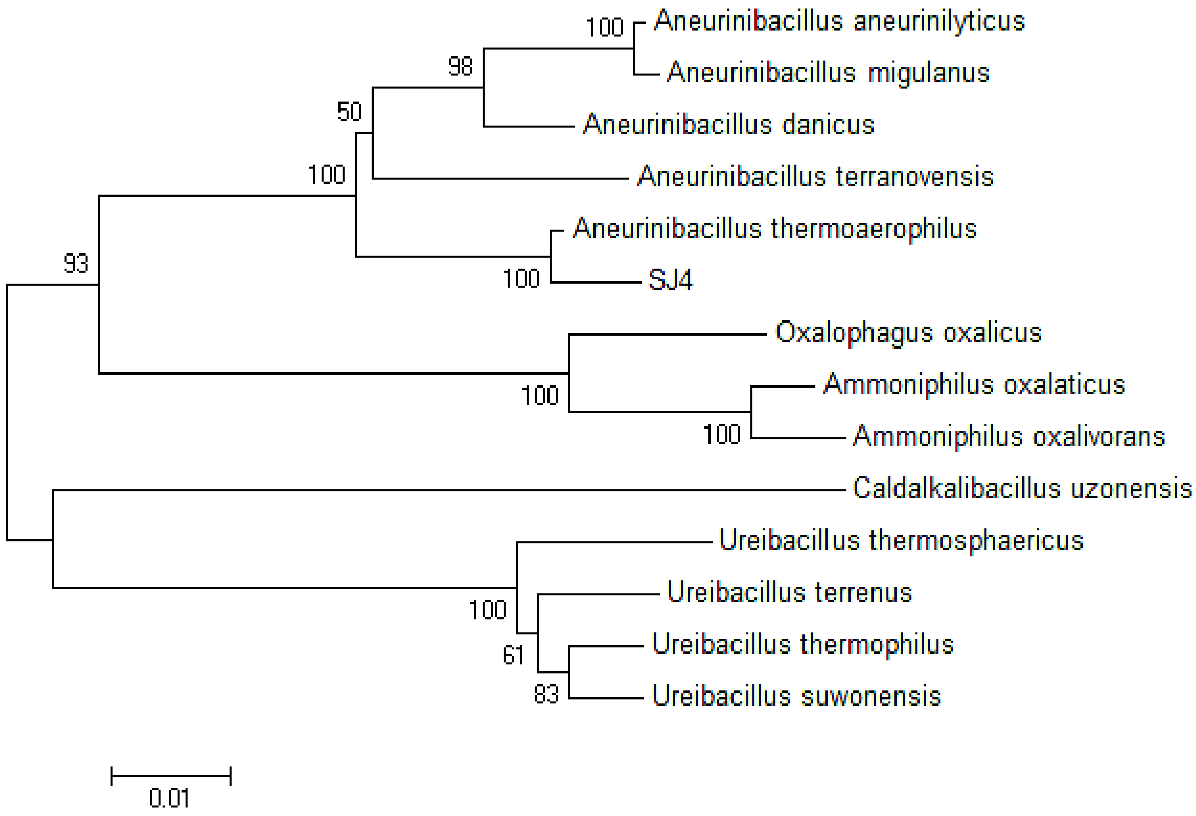


Figure 4.10: Phylogenetic relationship between the SJ4 and other 16S rDNA sequences of published strains. In the phylogenetic tree, SJ4 and *Aneurinibacillus thermoaerophilus*were clustered together as one clade

4.1.2.3 Conclusions

Two bacterial species, *Geobacillus pallidus* (SJ1 & SJ5) and *Aneurinibacillus thermoaerophilus* (SJ2, SJ3 & SJ4) were identified. These species are reported to be thermophilic and grow optimally at pH 7.4 and 60ºC temperature under aerobic condition without any metal leaching. In literature also, we did not find metal solubilization with *Geobacillus pallidus* and *Aneurinibacillus thermoaerophilus.* These two bacteria have not been reported as metal solubilizing microorganisms [55, 56].

4.1.3 Bioleaching studies with acidophilic bacteria

4.1.3.1 Materials and methods

Procurement and metals content analysis in e-waste

The waste motherboards of personal computers were obtained from a local electronics shop in Jamshedpur, Jharkhand, India and ground at Minerals Processing (MNP) Division, National Metallurgical Laboratory, Jamshedpur, India. Figure 4.11 shows the flowchart of process used for grinding of waste motherboards. The generated particles were sieved with different mesh sizes i.e. <14; 14-28; 28-48 and 48-65 and applied for bioleaching analysis. The powdered motherboard waste sample was digested by chemical method and metal content was analyzed by atomic absorption spectrometer (PerkinElmer AAnalyst 400 Spectrometer) [24].

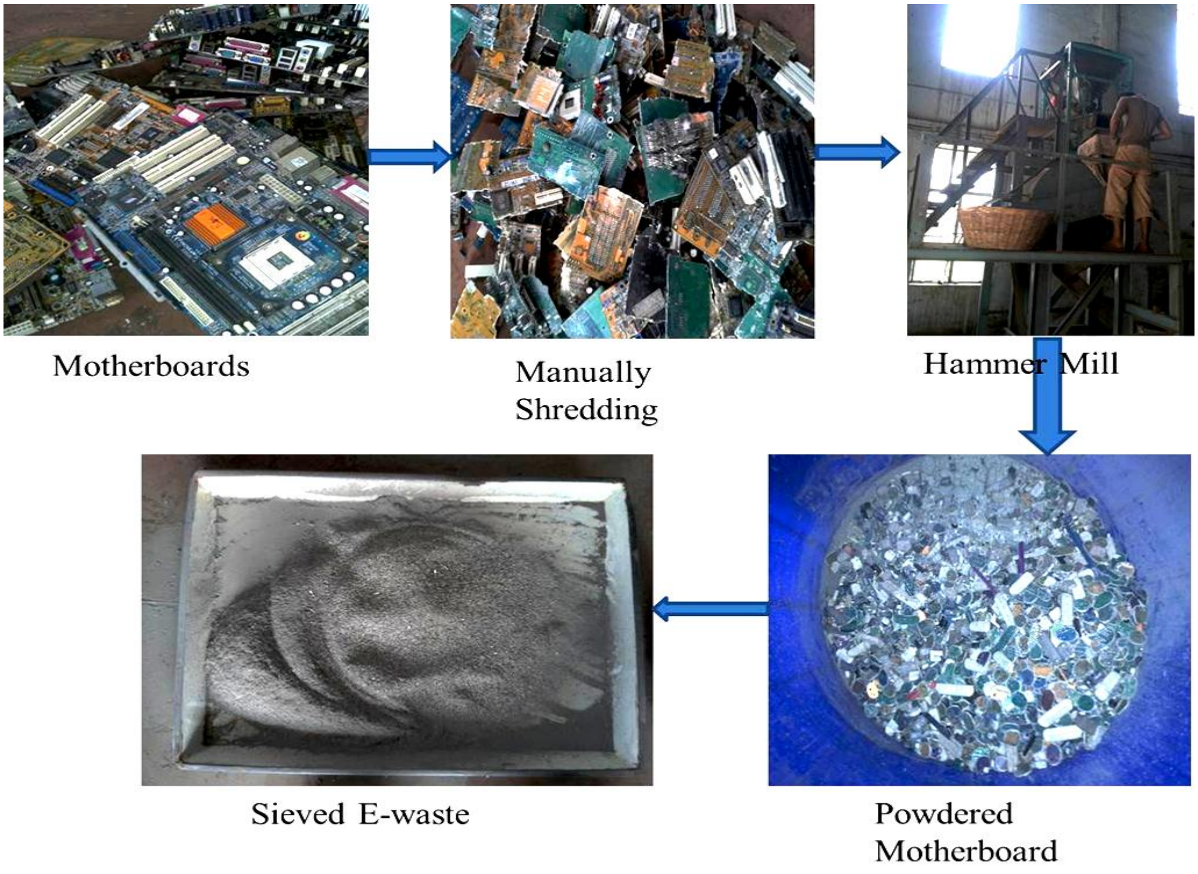


Figure 4.11: Flowchart of PC motherboards processing for bioleaching study

Procurement of acidophilic bacteria

A mixed culture of acidophilic bacteria (MCAB) was collected from acid mine drainage of heap leaching of low grade ores (Bio-resource Engineering Division, Institute of Mineral and Material Technology, CSIR Lab, Bhubaneswar, Odisha). MCAB was enriched with the Silverman and Lundgren $9K^+$ medium [210] of initial pH 1.96. The flasks were incubated in a shaking incubator at 35ºC and 140 rpm for 7 days when reddish brown precipitate was observed in solutions. The average microbial concentration was enumerated $2x10^7$cells/mL by using hemocytometer counting method.

Bioleaching experiments

Two-step bioleaching experiments were conducted in 250 mL Erlenmeyer flasks containing 100 mL $9K^+$ medium and 10 mL as prepared MCAB. The pH was adjusted with 10N sulfuric acid. After two days of MCAB growth, e-waste (ground motherboards) was added to test flasks for bioleaching studies. In order to investigate the influence of particle size, dosage of metal concentrate and inoculation quantity on bioleaching process, a series of flasks were arranged with a)various particle size (<14 mesh, 14-28 mesh, 28-48 mesh and 48-65 mesh), b) e-waste concentrate powder (1, 2 and 4 % w/v) and c) Inoculation quantities (10%, 20% and 30%). Cell free controls were maintained under the same conditions. All flasks were incubated in a shaking incubator at 35ºC and 140 rpm. Each experiment was carried out in duplicates. The leaching solutions were periodically analyzed for pH and metal ions (Cu, Zn and Al) concentration. Any decrease in weight due to evaporation and sampling was compensated with de-ionized water.

4.1.3.2 Results and discussions

Metal content in PC motherboards

The metal content in ground motherboards are presented in Table 4.4. As the size of particles decreased all metals concentration except Ag, Cu, and Co increased. Ag, Cu and Co exhibited same concentration with all sized of e-waste (ground motherboards).

Influence of particle size on bioleaching of metals from e-waste (PC motherboards)

Two-step bioleaching of ground motherboards (1% w/v) was experimented with different particle size. It was observed that the MCAB was able to mobilize Cu, Zn and Al. Smaller particles exhibited maximum leaching efficiency than others (Figure 4.12). Microbial leaching of Cu is mainly accomplished indirectly through oxidation by ferric ions.

The higher Cu leaching efficiency was achieved with smaller sized e-waste, because the contact between ferric ions and Cu was closer. Maximum leaching efficiency of Cu, Zn and Al was obtained at 0.3-0.212 mm particle size i.e. 93%, 87% and 84.7%, respectively. Thus 0.3-0.212 mm metal concentrate of e-waste (PC motherboards) was used in further experiments. It is considered that the enhancement of bioleaching efficiency can mainly be attributed to the effect of the particle size on the surface area of the mineral. By decreasing the particle size, the surface area per unit mass of the mineral is increased. However, the reduction of particle size below the critical level could increase the extent of the particle-particle collision and impose severs attrition on the cells [212]. That is one reason why different particle size metal concentrate showed different bioleaching efficiencies. More importantly, different leaching efficiencies of different particle sizes may contribute to the toxicity of metal ions. It was reported by Sampson that Cu was found to cause the largest inhibition followed by nickel and cobalt [211].

Table 4.4: Metal content in different sized e-waste

Metal (g/kg)	<14 Mesh	14-28 Mesh	28-48 Mesh	48-65 Mesh
	Fraction			
	<1.18mm	1.18-0.6mm	0.6-0.3mm	0.3-0.212mm
Ag	0.701±0.21	0.678±0.14	0.711±0.1	0.703±0.16
Al	3.77±0.34	5.76±0.23	7.35±0.26	8.25±0.40
Au	0.0024±0.00	0.0025±0.00	0.0045±0.001	0.0075±0.003
Cu	11.86±0.76	11.93±0.26	11.96±0.82	11.97±0.45
Co	0.03±0.01	0.03±0.005	0.028±0.006	0.033±0.004
Cr	0.037±0.007	0.012±0.002	0.013±0.005	0.022±0.003
Fe	13.82±0.89	15.08±1.46	16.01±1.23	18.06±2.01
Ni	0.782±0.30	0.81±0.41	0.87±0.28	1.06±0.18
Se	0.525±0.13	0.505±0.20	0.473±0.18	0.773±0.24
Zn	1.83±0.53	1.85±0.23	1.87±0.12	3.23±0.34

Influence of e-waste dosage on bioleaching

The initial pH of two-step bioleaching medium was 1.96. After addition of different amounts of ground motherboards, the initial pH increased to 2.47 (1% w/v), 2.89 (2% w/v) and 3.41 (4% w/v). After two days incubation period the pH of medium changed to 2.01 (1%

w/v), 2.22 (2% w/v) and 2.71 (4% w/v) and then remain constant throughout the leaching period. Due to the alkalinity properties of e-waste, the addition of elevated amounts of e-waste led to an increase of initial pH. Metal leaching efficiencies at different dosages of ground motherboards (0.3-0.212 mm) with bacterial consortium are presented in Figure 4.13. Maximum leaching for Cu, Zn and Al was observed at e-waste concentration of 1% w/v. The leaching efficiency was lowest at 4% w/v dosage. After 7 days, Cu leaching efficiencies were 93%, 88.65%, and 81.45% at 1% w/v, 2% w/v and 4% w/v metal concentrate dosages, respectively. The data directly demonstrated that the extractions of metals decreased with the increase of metal concentrate dosage. It was believed that high ground motherboards dosage resulted in lower metal extraction mainly due to limitation in air distribution and oxygen mass transfer [104, 213], thus inhibited both the efficiency and degree of the oxidation of Fe^{+2} by bacterial consortium. The toxicity of metal ions might be another important factor when powder dosage was beyond the limitation of the bacteria in solution.

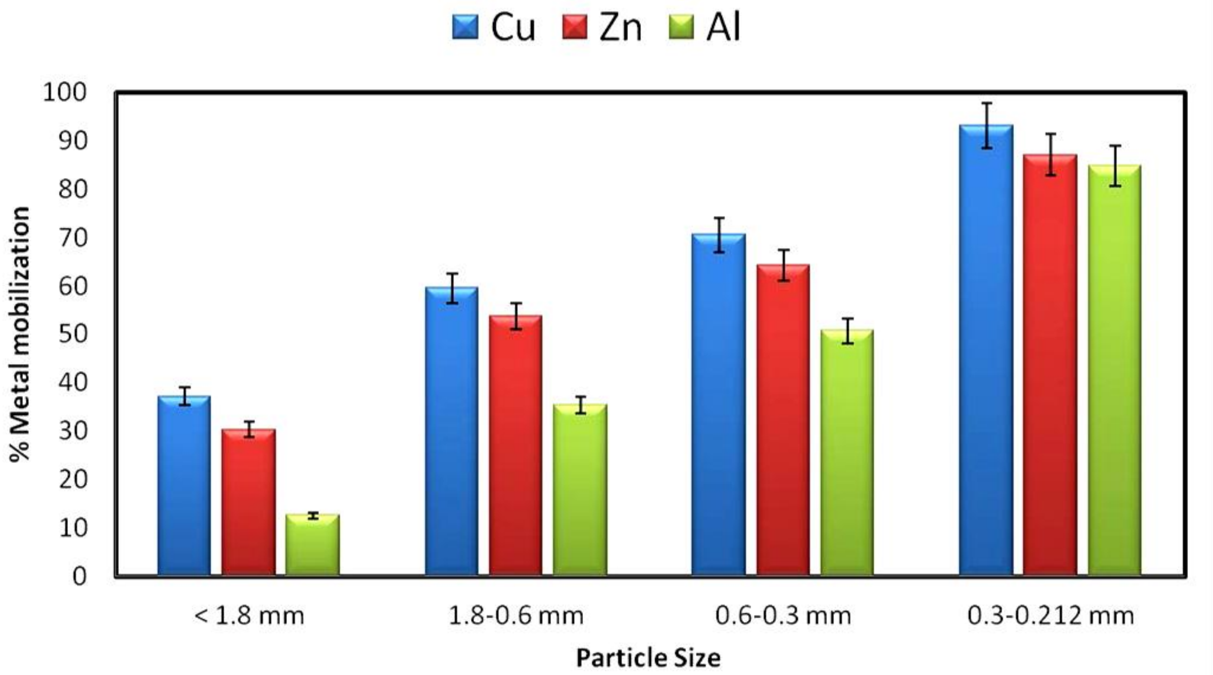


Figure 4.12: Percent metal mobilization after bioleaching of E- waste with MCAB at various particle size of e-waste. The data presented in this figure presents mean value of metals obtained from duplicate experiments at significance level ($p < 0.05$) based on one-way ANOVA analysis

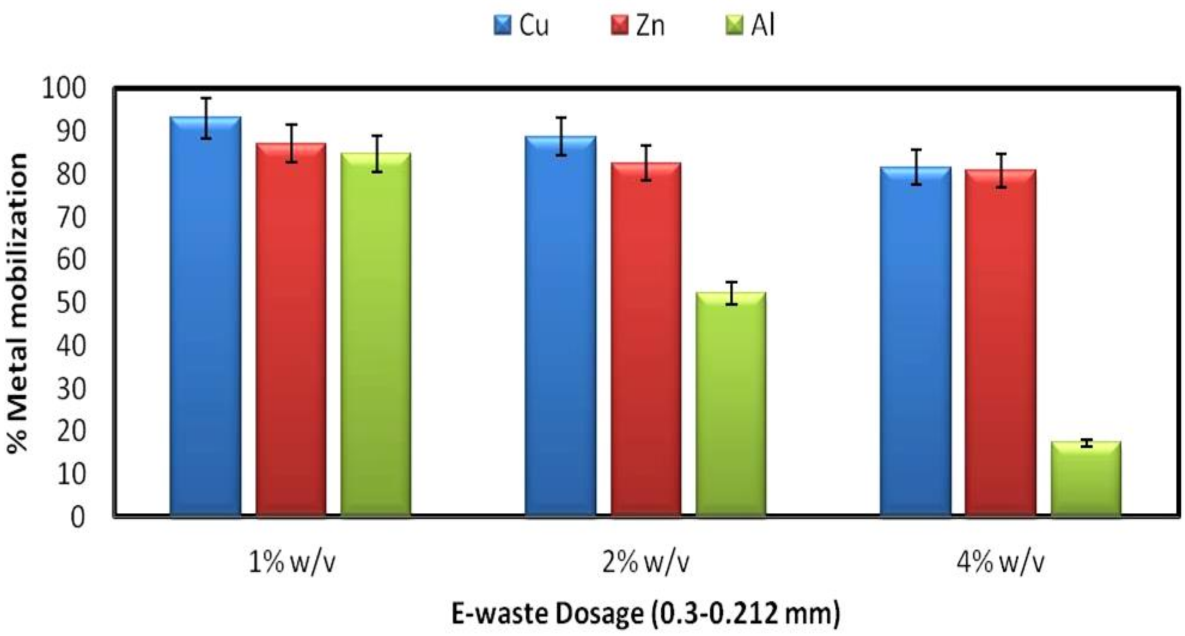


Figure 4.13: Percent metal mobilization after bioleaching of E- waste with MCAB at various dosage of e-waste (0.3-0.212 mm). The data presented in this figure presents mean value of metals obtained from duplicate experiments at significance level ($p < 0.05$) based on one-way ANOVA analysis

Influence of inoculation quantity on bioleaching

It was observed that maximum leaching of metals exhibited at 1% w/v e-waste of 0.3-0.212 mm particle size with 10% inoculation size ($2x10^7$cells/mL). So, 1% w/v e-waste 0.3-0.212 mm particle size was used with different inoculation quantity to observe the influence of inoculation quantity on bioleaching of metals. Figure 4.14 showed the influence of inoculation quantity on leaching of Cu, Zn and Al from metal concentrate of waste motherboards. While the flasks were inoculated with 10%, 20%, and 30% MCAB, 93%, 94.46%, and 97.38% Cu was mobilized into the solution after 7 days, respectively. It could be observed that the greater the MCAB inoculation quantity the faster Cu, Zn and Al was leached (Figure 4.14). It implied that the large amounts of bacteria accelerated metal leaching. It probably resulted from more Fe^{3+} ions formation by greater addition of MCAB. However, without MCAB inoculation, ferrous ion could only be oxidized to ferric ion by oxygen from air, but this process was very slow and took long time. Without MCAB in the medium (0% inoculation quantity), the Cu leaching efficiency was observed to be just 30.14% after 7 days (data not shown).

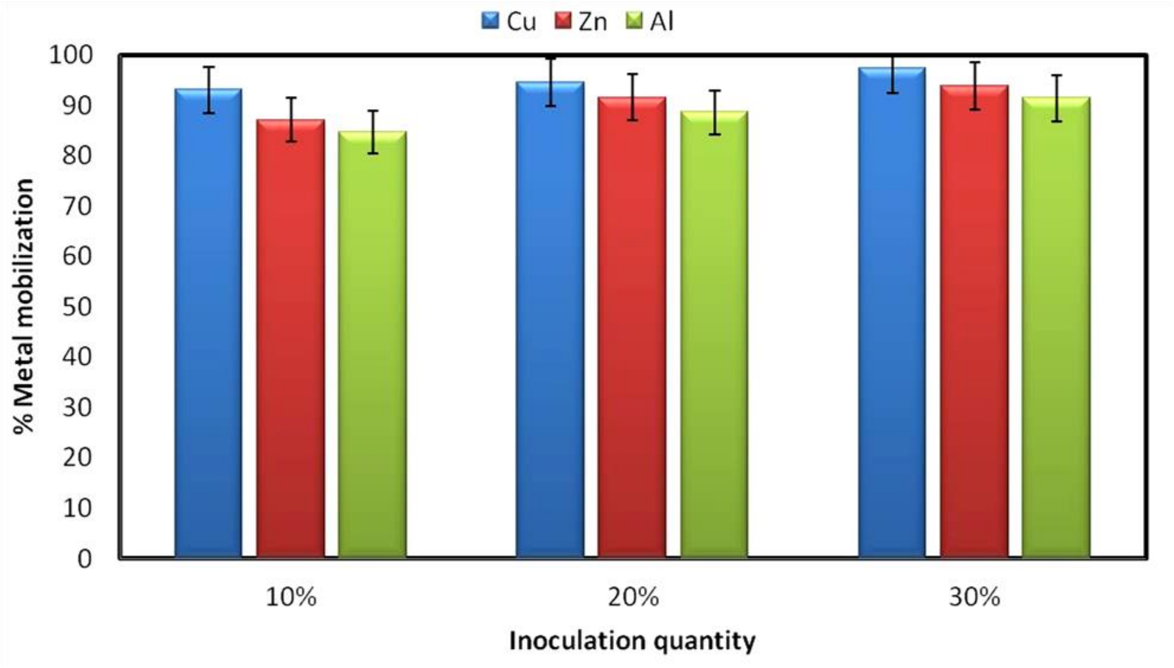


Figure 4.14: Percent metal mobilization after bioleaching of E- waste (0.3-0.212 mm) at various inoculation quantity of MCAB. The data presented in this figure presents mean value of metals obtained from duplicate experiments at significance level ($p < 0.05$) based on one-way ANOVA analysis

4.1.3.3 Conclusions

The results from this work demonstrate that mixed culture of acidophilic bacteria (MCAB) was able to grow in the presence of e-waste and the metals such as Cu, Zn, and Al can be recovered from personal computer motherboards by the application of mixed culture of acidophilic bacteria (MCAB). Various percentages of metals can be leached depending on the sieve fractions of experimental samples, ground motherboards concentration within 7 days of leaching time. Copper as the main metal of ground motherboards, almost complete solubilization was achieved. For other minor metals such as Zn and Al present in ground motherboards, considerably high percentages of metal solubilization were also achieved. These MCAB cultures have the solubilizing capabilities for Cu, Zn and Al by the following order: Cu > Zn > Al. The results might have the potential for industrial applications regarding the treatment of metal-containing solids such as ground motherboards of e-waste since acidophilic bacteria are widely used bacteria in nature and from 4 to 7 days of bioleaching time when most of metals are solubilized into leaching solution is acceptable in industrial applications.

4.1.4 Bioleaching studies by fungus (*Aspergillus niger*)

4.1.4.1 Materials and methods

Procurement and characterization of e-waste (PC motherboards)

Particle sieved under 0.3-0.212 mm was applied for bioleaching analysis. The powdered motherboard waste sample was digested by chemical method and metal content was analyzed by atomic absorption spectrometer (PerkinElmer AAnalyst 400) [26]. The same sample was also subjected to energy dispersive X-ray fluorescence (EDXRF) (PANalytical 3D XRF) (Advanced Instrumentation Research Facility, Jawaharlal Nehru University, New Delhi). Sample was taken in grams and 0.1 gram of cellulose powder was added to it. It was finely ground in mortar and pestle to reduce the scattering. Pellets were made using the pressure machine by adding adequate boric acid for proper binding. 8 ton pressure was given for 20 seconds while preparing the pellets. Semi-quantitative analysis was carried out using the PANalytical 3D XRF and elemental analysis using the PANalytical epsilon 5.0 software. Al_20_3.Zr, Ge, Ti, Al of uniform thickness 6 and densities like 3.96, 6.49, 5.35, 4.52, and 2.7 respectively were used as secondary targets. XRF spectroscopy is widely used for the qualitative and quantitative elemental analysis environmental, geological, biological, industrial and other types of samples. Compared to some competitive techniques such as Atomic Absorption Spectroscopy (AAS), Inductive Coupled Plasma Spectroscopy (ICPS) and Neutron Activation Analysis (NAA), XRF has advantages of generally being non-destructive, multi-elemental, fast and cost effective. It also provides a fairly uniform detection limit across a large portion of the periodic table and is applicable to a wide range of concentrations, from a 100 % to few parts per million. A main disadvantage is that analyses are generally restricted to elements heavier than fluorine.

Adaptation of Aspegillus niger

Adaptation of the fungus was carried out through a series of repeated sub-culturing of the fungi after exposure to different concentrations of e-waste. The multi-metals solution was produced using different proportion of ground motherboard i.e., 1% w/v, 5%w/v and 10% w/v. A process of serial acclimatization of *A. niger* was performed in potato dextrose broth medium with and without supplementation of e-waste for tests and controls, respectively. The agar plates were inoculated at the center with 6-day-old conidia of *A. niger* harvested from potato dextrose agar surface using a sterile platinum loop, and incubated at 28-30°C. Growth was monitored over time by measuring the spread of the culture from the point of inoculation. This was continued until the growth of the strain was identical to that of the control (i.e. the culture in the absence of the metal ions). In this way, adaptation was successfully carried out by progressively increasing the concentration of the desired metal ion.

Different methods of bioleaching

In order to obtain sufficient numbers of spores, the culture was incubated at 30 °C for 5 days. The mature conidia were then washed off from the surface of the potato dextrose agar (PDA) medium using de-ionized water. The number of spores was counted using a Neubauer counting chamber and adjusted using de-ionized water to approximately 10^7 spores/mL. 2 mL of spore suspension was added to 250 mL Erlenmeyer flasks containing 100 mL of sucrose medium with the e-waste at various pulp densities (1, 2, 3, 4 and 5 %w/v). All experiments were carried out in an orbital shaking incubator at 30±1°C and 120 rpm. Three Different methods of bioleaching were carried out: (a) The fungus was incubated together with the medium and e-waste (one-step bioleaching), (b) The fungus was first cultured in sucrose medium without e-waste for 4 days, after a sudden reduction in pH (beginning of organic acid production), sterilized e-waste was added (two-step bioleaching), and (c) The fungus was first cultured in sucrose medium for 14 days. Then the suspensions was filtered through Whatman 41 and 0.2µm (PALL) filter paper, respectively, to obtain the cell-free spent medium, and the filtrate that contained bio- produced metabolites was used for the leaching of e-waste. Control experiments were conducted using fresh sucrose medium.

Analytical methods

At regular time intervals, the fungal culture from each flask was filtered and the filtrate was analyzed for the concentration of various metal ions and fungal excretions of organic acids using atomic absorption spectrophotometer (AAS) and high performance liquid chromatography (HPLC), respectively. Additionally, the pH of the leached liquor was also measured using a digital pH meter (Eutech pH 510). Analysis of biomass accumulation and associated metals was performed as described by Sathiya and Ting, 2005 [214]. The Scanning Electron Microscope was used to observe the morphology of the e-waste. Fourier transform infrared spectroscopy (PE-1600 FTIR, PerkinElmer) was used for determination of presence of organic acids in the leaching solution.

Determination of organic acids produced by A. niger

Samples were analyzed for organic acids after centrifugation at 3500 rpm for 10 min. Then the samples were filtered using a 0.45 µm micro filter. Detection and quantification of organic acids was done on Waters 600E High Performance Liquid Chromatography (HPLC) equipped with PDA detector (Waters PDA detector 2996), Waters 717 plus auto sampler, Waters 600 controller, Waters delta 600 pump, Waters inline degasser AF, and Lichrosphere RP-18 column 250 mm × 4.6 mm and 5 µm particle size (Waters). The mobile phase was 50 mM, di-hydrogen orthophosphoric acid (Merck, Germany) adjusted to pH 2.80 with orthophosporic acid (Sigma, USA) in the isocratic elution of flow rate 0.70 mL/min at 20ºC temperature. After equilibrate all the conditions the samples (10 µL) were injected for 15 min. Elutes were detected at λ 214.0 nm and identified by retention time and co-chromatography by spiking the sample with the authentic organic acids. The organic acids were quantified by reference to the peak areas obtained for the authentic standards for 0.1% of gluconic acid, oxalic acid, malic acid, succinic acid, citric acid, and tartaric acid (Sigma-Aldrich, USA). Each replicate was analyzed in a single run on HPLC for all samples. The values were presented as the mean of three replicates. The HPLC analysis was carried out at Defense Institute of High Altitude Research (DIHAR), Defense Research & Development Organization (DRDO), Leh-Ladakh, India.

4.1.4.2 Results and discussions

Characterization of e-waste (ground motherboards)

Table 4.5 shows the elemental composition of waste motherboards after subjected to AAS and XRF. From both of the techniques, it was observed that, major elements (>1.0 g/kg) in e-waste included Al, Cu, Fe, and Zn. On the other hand, heavy metals such as Pb, Hg, Co, Cr, Se, Ba and Sb were found in trace amount (<1.0 g/kg).

Bioleaching of e-waste with un-adapted A. niger

Pure culture (without e-waste) experiments were carried out as control under identical conditions of bioleaching. Figure 4.15 shows the changes in biomass and pH of control during 30 days of incubation. Along with the biomass production, the pH was decreased to 2.74 at the end of incubation. pH decreased to 4.07 after 5 days incubation and remained constant at about 2.74. Biomass attained a constant dry weight of about 22 g/L during the stationary phase with a little variation of 2-3%.

In one-step bioleaching, the initial pH (≈ 6.09) of the sucrose media with different ground motherboards concentration i.e. 1% w/v, 2% w/v, 3% w/v, 4% w/v and 5% w/v rapidly decreased to about pH 4.21, 4.31, 4.66, 4.73, and 4.89, respectively after 5 days of incubation (Figure 4.16a). It clearly indicated that, e-waste having alkaline properties affected pH change. In case of two-step bioleaching the initial pH was about 4.26, and with the addition of e-waste, it gradually decreased to about 2.45 after incubation for 30 days (Figure 4.16b). The decrease in pH during fungal growth was due to the production of organic acids (citric, oxalic and gluconic) [104, 111, 193].In the one-step bioleaching, the fungus grew well at 1% w/v i.e. 21.29 g/L. With the increase in the concentration of e-waste the growth of fungus decreased indicating a negative relationship between waste concentration and biomass production (Figure 4.16c). During the two step bioleaching, the initial average biomass was 13.37 g/L and growth trend was observed similar to one step bioleaching (Figure 4.16d). In case of 5% w/v e-waste, the biomass was approximately same as initial biomass throughout the leaching period. Comparison of biomass with pH showed negative correlation. It is also evident from the study that long lag period occurred during the one-step process, whereas the culture in the two-step process attained and early stationary phase. In both of these processes, however, the biomass concentration was found to be about 20–25 g/L at the end of incubation period.

Table 4.5: Metal content in waste motherboards (e-waste)

Elements (g/kg)	AAS	XRF
Ag	0.703	0.076
Al	8.25	21.35
As	ND	ND
Ba	NT	1.785
Be	NT	ND
Br	NT	ND
C	NT	ND
Ca	NT	37.20
Co	0.033	ND
Cu	11.97	6.56
Cr	0.022	ND
Fe	18.06	25.50
Hg	ND	0.014
Ni	1.06	0.144
Pb	2.341	2.21
Sb	NT	0.154
Se	0.773	NT
Zn	3.23	0.451

NT: not tested, ND: not detected

In control experiments, the leaching yield of Al, and Fe was found to be zero under all pulp densities, except for Cu and Zn (Figure 4.17). Cu exhibited 14.23% leach ability with 1% w/v e-waste, whereas Zn exhibited around 10.42% with 5% of w/v e-waste concentration. The optimum pulp density for the e-waste leaching occurred at 1% (w/v) in one-step as well as for two-step leaching process. In general, an increase in the pulp density led to a decrease in the leaching yield. At 1% pulp density, *A. niger* leached virtually all Al, Zn, Cu and Fe while the extraction yield of Al, Zn, Cu and Fe was about 86%, 74%, 80%, and 50%, respectively, in two-step bioleaching. At 5% pulp density, the bioleaching efficiency for Al, Zn, Cu and Fe decreased significantly to 50–60%, 20-25%, 25-30% and 30-35%, respectively in both one step and two step bioleaching. In contrast, Al, Zn and Cu were still leached at a very high yield (70–80%). The bioleaching of Zn remained at 60–70% in the presence of 1% (w/v) e-waste pulp density and was independent of the e-waste pulp density up to 4% (w/v). These findings in general corroborate the results of work previously reported on bioleaching of e-waste [21].

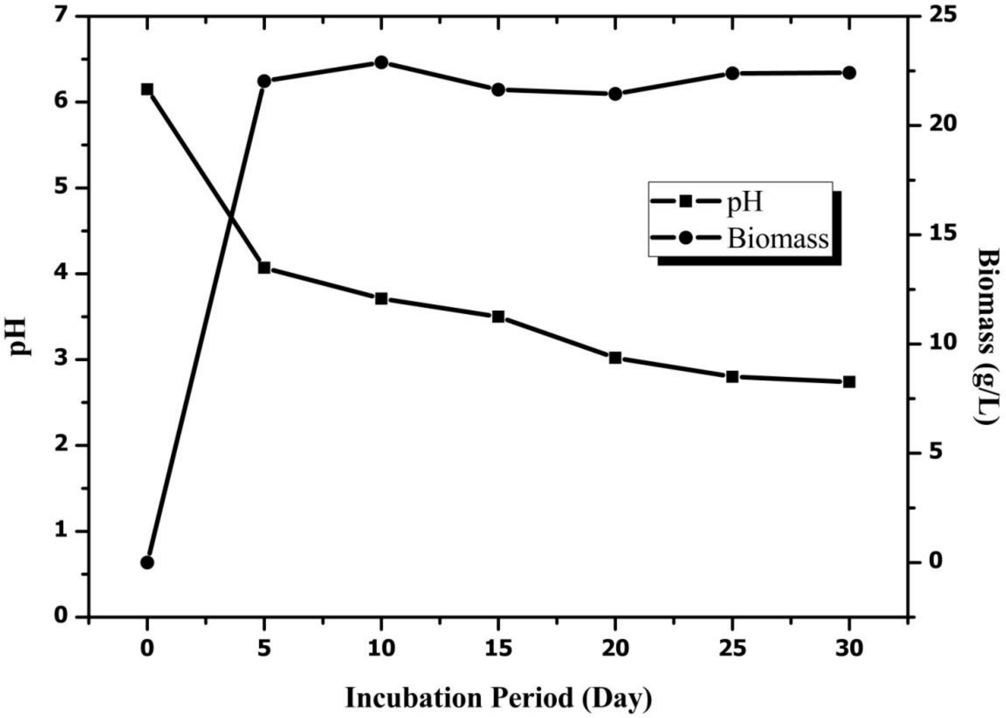


Figure 4.15: Change in biomass and pH during the growth of *A. niger* without e-waste

Bioleaching of e-waste with adapted Aspergillus niger.

Like bioleaching with un-adapted *A. niger*, the similar trend of pH and biomass was observed in case of adapted culture. In one-step bioleaching, the initial pH (≈ 6.24) of the sucrose media with different e-waste concentration i.e. 1% w/v, 2% w/v, 3% w/v, 4% w/v and 5% w/v rapidly decreased to about pH 2.67, 2.71, 2.76, 2.59, and 2.82, respectively after 30 days of incubation (Figure 4.18a). In case of two-step bioleaching, it gradually decreased to about 2.23 after incubation of 30 days (Figure 4.18b). In the one-step bioleaching, the fungal biomass at 1% w/v of e-waste concentration was 21.99 g/L (Figure 4.18c), whereas it was 22.96 g/L in case of two-step bioleaching (Figure 4.18d). From this study, it was observed that e-waste concentration and fungal growth shows a negative correlation. But comparatively, a higher biomass and lower pH was observed in case of e-waste adapted *A. niger* bioleaching than un-adapted *A. niger* bioleaching with increasing concentration of e-waste. This might be due to an increase in the metal tolerance capacity of *A. niger* after getting adapted to e-waste.

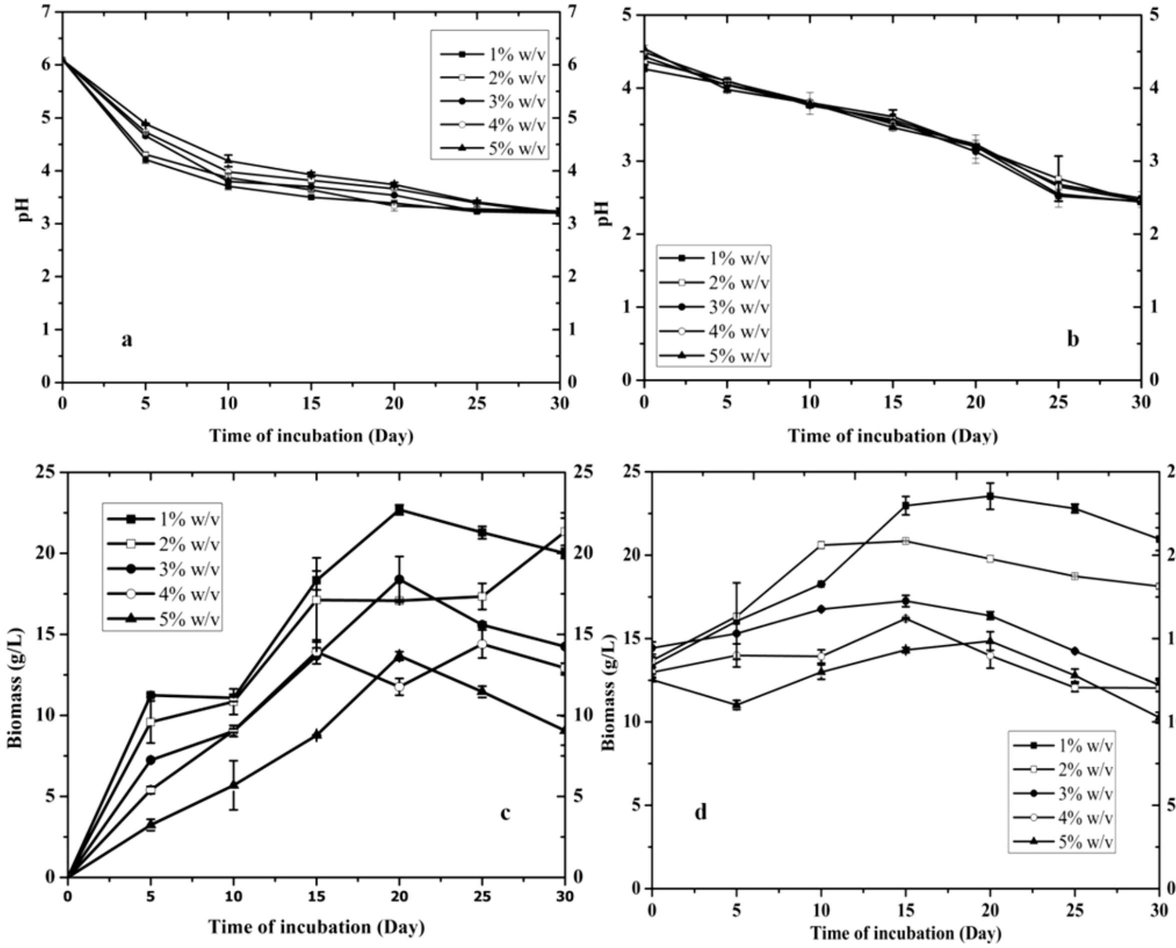


Figure 4.16: Change in pH and biomass profile at various concentrations of e-waste during bioleaching with un-adapted *A. niger* (a) change in pH during one-step bioleaching; (b) change in pH during two-step bioleaching; (c) change in biomass during one-step

bioleaching; and (d) change in biomass during two-step bioleaching. The data presented in this figure presents mean of those obtained from duplicate experiments at significant level ($p < 0.05$) based on one-way ANOVA analysis.

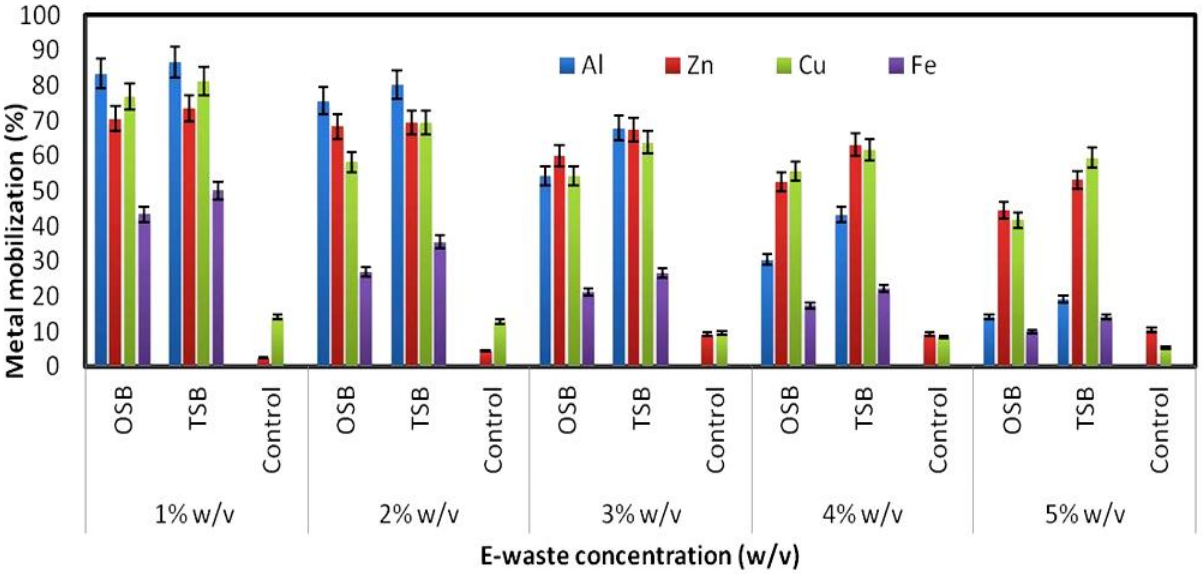


Figure 4.17: Leaching of metals from e-waste by un-adapted *A. niger* after 30 days of incubation with different concentrations of waste. The data presented in this figure presents mean of those obtained from duplicate experiments at significant level ($p < 0.05$) based on one-way ANOVA analysis. (OSB: One-step bioleaching; TSB: Two-step bioleaching)

The metal leaching with adapted *A. niger* was higher as compared to un-adapted culture in both of the bioleaching processes. Figure 4.19 presents the metal leaching from e-waste with adapted *A. niger* at different concentrations of e-waste in both of the bioleaching processes. The optimum pulp density at 1% (w/v) for the e-waste leaching occurred in both one-step and two-step bioleaching. At 1% pulp density, adapted *A. niger* leached all Al (85.34%), Zn (82.78%), Cu (81.67%) and Fe (60.56%) while the extraction yield of Al, Zn, Cu and Fe was about 89%, 88%, 91%, and 67%, respectively in two-step bioleaching after 30 days incubation period. At 5% pulp density, the bioleaching efficiency for Al, Zn, Cu and Fe decreased significantly to 40-60%, 15-20%, 20-25% and 40-50%, respectively in both one step and two step bioleaching. In contrast, Al, Zn and Cu were still leached at a very high yield (85-90%). These findings in general corroborate the results of work previously reported on bioleaching of e-waste [104].

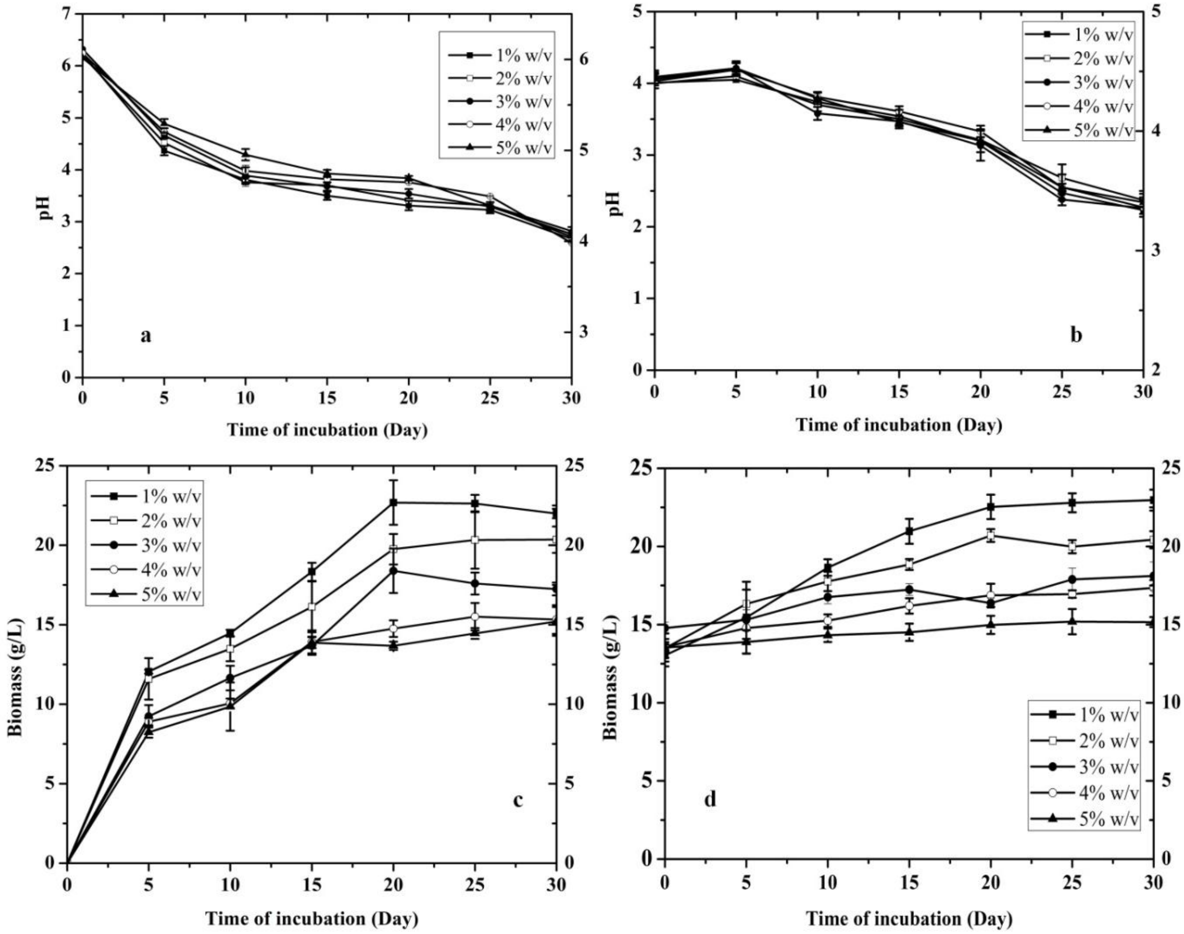


Figure 4.18: Change in pH and biomass profile at various concentrations of e-waste during bioleaching with adapted *A. niger* (a) change in pH during one-step bioleaching; (b) change in pH during two-step bioleaching; (c) change in biomass during one-step bioleaching; and (d) change in biomass during two-step bioleaching. The data presented in this figure presents mean of those obtained from duplicate experiments at significant level ($p < 0.05$) based on one-way ANOVA analysis.

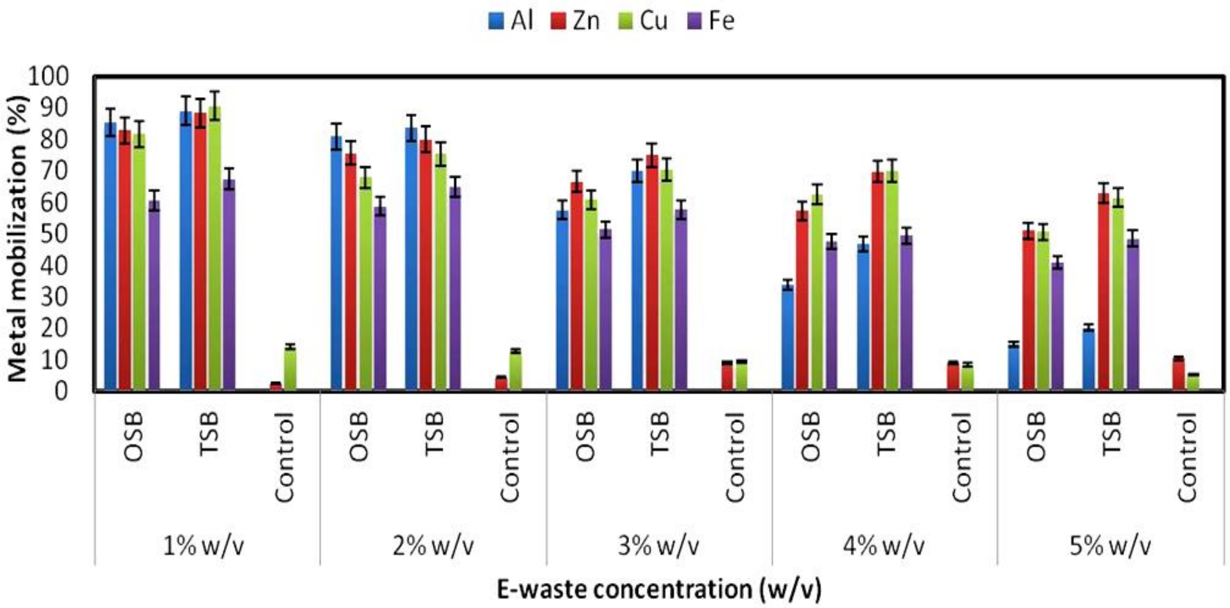


Figure 4.19: Leaching of metals from e-waste by adapted *A. niger* after 30 days of incubation with different concentrations of waste. The data presented in this figure presents mean of those obtained from duplicate experiments at significant level ($p < 0.05$) based on one-way ANOVA analysis. (OSB: One-step bioleaching; TSB: Two-step bioleaching)

Bioleaching of e-waste with spent medium of Aspergillus niger

Figure 4.20 shows the change in the pH of spent medium during leaching at various e-waste pulp densities. Upon addition of e-waste, pH of the spent medium increased. Increase in the e-waste pulp density (1% to 5% w/v) significantly increased the initial pH of the spent medium. The pH remained constant for 7 days of incubation.

The leaching yield of spent medium for ground motherboards (1% w/v pulp density) was lower than the bioleaching for all metals except for Cu (Figure 4.21). The spent medium leached 78% Al, 80% Zn, 87% Cu and 22% Fe at 1% w/v e-waste pulp density. In the case of spent medium leaching, the decrease in leaching yield with increase in pulp density is likely to be due to the constant metabolite concentration in all pulp densities. These results indicated that spent medium bioleaching is better over other processes (One-step and two-step bioleaching) as there is no need of direct contact with the microorganisms.

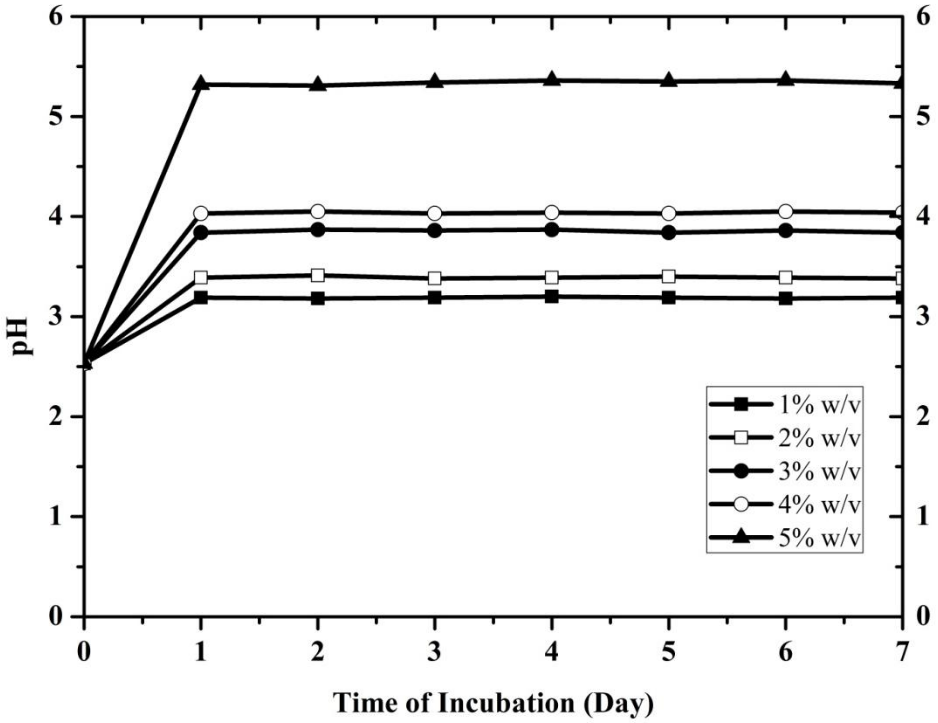


Figure 4.20: Change in pH at various concentrations of e-waste during spent bioleaching with *A. niger*

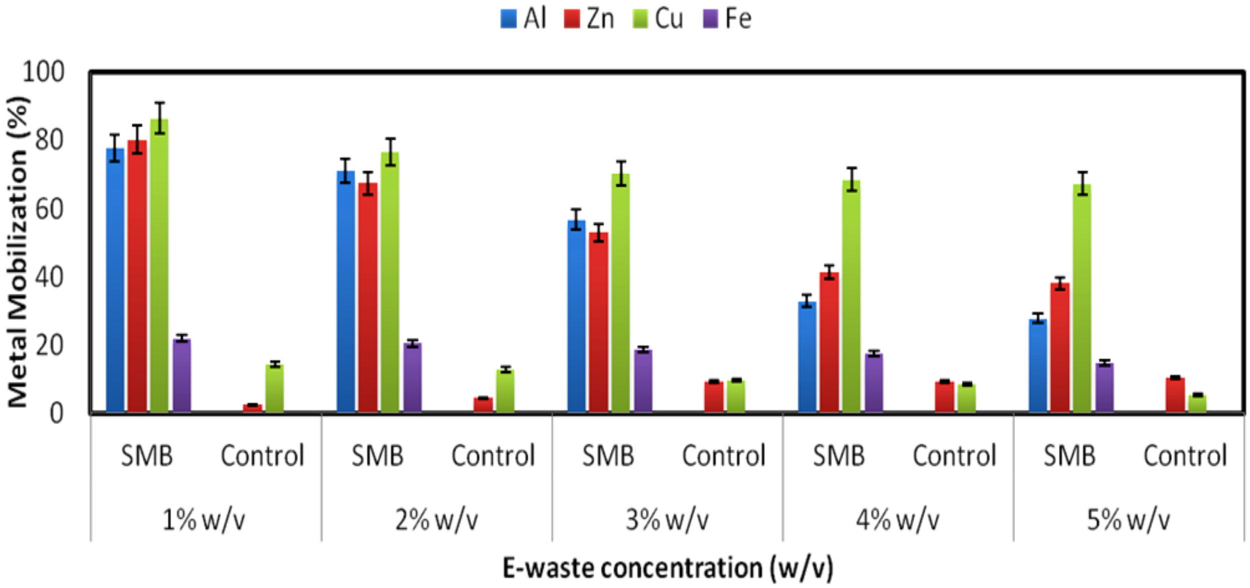


Figure 4.21: Leaching of metals from e-waste by spent medium bioleaching after 7 days of incubation at various e-waste pulp densities. The data presented in this figure presents mean of those obtained from duplicate experiments at significant level ($p < 0.05$) based on one-way ANOVA analysis. (SMB: spent medium bioleaching)

Post bioleaching characterization of e-waste and leachate

SEM (Scanning electron microscope) analysis

The fresh e-waste and bioleached e-waste were subjected to scanning electron microscope (Institute of Life Sciences, Bhubaneswar, Odisha) to observe the surface morphology after bioleaching study. SEM showed that the e-waste surface prior to leaching was rough (Figure 4.22a). In contrast, the e-waste surface became smooth after bioleaching with *A. niger* (Figure 4.22b). There were several holes on the e-waste surface (Figure 4.22b) when cells were added, whereas no such holes were observed without cells (Figure 4.22b), possibly due to the effect of bioleaching. The bioleached e-waste surface was probably covered with mycelia of *A. niger*. The attached fine particles and deposits on fresh e-waste surface were gone due to the effect of bioleaching.

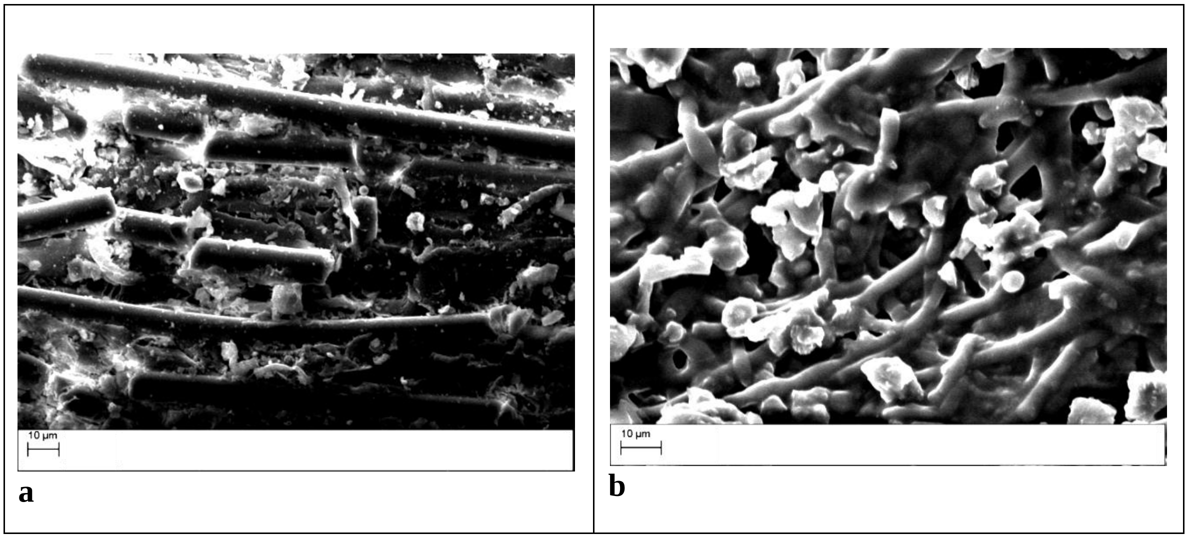


Figure 4.22: SEM photomicrograph of e-waste: (a) Fresh e-waste, (b) Bioleached e-waste

FTIR spectroscopic studies

Fourier transform infrared spectra of the biogenically produced organic acid leach liquors of the one-step, two step and spent medium bioleaching are shown in Figure 4.23. It is interesting to note that spectra for TSB, SMB, and OSB showed similar transmittance bands at 1390, 1610, 1273 and 3400 cm-1 is related to -COO-, -C=O, -C-C-, and RCO-OH respectively. This confirmed the presence of organic acids and a probable reason of decrease in pH during bioleaching studies as reported by other authors [104, 111, 189]

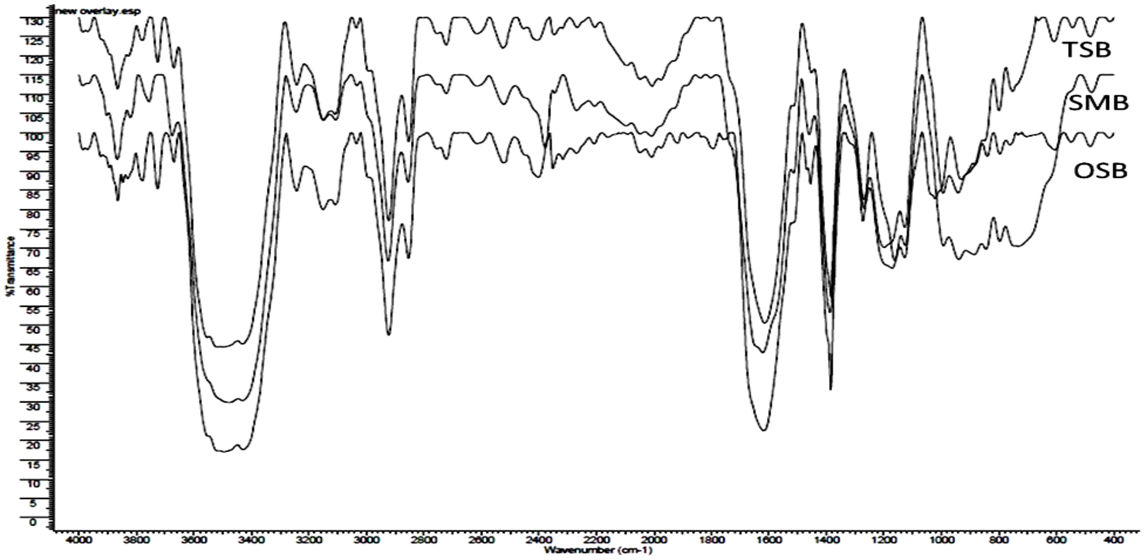


Figure 4.23: FTIR spectra of biogenically produced organic acid leach liquors. (OSB: One-step bioleaching; TSB: Two-step bioleaching; SMB: Spent medium bioleaching)

HPLC analysis of organic acids produced during bioleaching studies

Fungal bioleaching is based on four mechanisms: acidolysis, complexolysis, redoxolysis and bioaccumulation [111, 215]. As the first three processes are mediated through the secondary metabolites produced by the fungus, it is important to determine these metabolites in order to better understand the bioleaching mechanisms. The organic acids secreted by the fungus *A. niger* were analyzed in the absence and presence of the e-waste, and are listed in Table 4.6. In the absence of e-waste, *A. niger* secreted 0.432, 0.16 and 0.12 % w/v of citric acid, oxalic acid and gluconic acid were produced after 14 days of incubation, respectively. It was observed that, increase in the concentration of organic acids occurred with increase in e-waste pulp density in both one step and two step bioleaching. The concentration of oxalic acid secretion was found to be very low compared to citric and gluconic acid and remained relatively independent of the concentration of e-waste.

Table 4.6: Concentration of organic acids produced in the presence and absence of e-waste

Organic acids (% w/v)	OSB (w/v)					TSB (w/v)					SMB
	1%	2%	3%	4%	5%	1%	2%	3%	4%	5%	
Citric acid	0.21	0.26	0.29	0.32	0.37	0.27	0.28	0.33	0.37	0.42	0.432
Oxalic acid	0.11	0.14	0.13	0.16	0.18	0.14	0.19	0.21	0.24	0.29	0.16
Gluconic acid	0.23	0.27	0.29	0.31	0.35	0.27	0.29	0.34	0.56	0.57	0.12

4.1.4.3 Conclusions

Bioleaching of e-waste is strongly influenced by the pulp density. The inhibition of fungal growth at higher pulp densities is due to the higher concentration of toxic metals in the e-waste as well as an increase in the initial pH of the e-waste suspension. The results showed that the optimum pulp density for e-waste bioleaching occurred at 1% in one-step, two-step and spent medium leaching, with metal leaching yield decreasing with increase in pulp densities. The main lixiviant in bioleaching was shown to be gluconic acid. This metabolite was produced dominantly in the presence of e-waste (in the one-step and two-step bioleaching). In addition, the higher pH of the e-waste suspension also causes *A. niger* to accumulate gluconic acid by inhibiting citric acid secretion. In the case of spent medium leaching, the decrease in the leaching yield with increase in the pulp density is likely to be due to the increase in alkalinity in the corresponding suspension containing the spent medium and e-waste. The major leaching agent in the spent medium is citric acid. It has been demonstrated that *A. niger* may be used in the bioleaching of metals from e-waste, under a one-step process, two-step process, and spent medium leaching. The two-step process is preferable as it enables a faster removal of heavy metals. Although bioleaching generally requires a longer period of operation compared to chemical leaching, it achieves higher removal efficiency for some heavy metals. These results suggest that bioleaching by *A. niger* may be an alternative or adjunct to conventional physicochemical treatment of e-waste for the removal hazardous heavy metals.

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CONCLUSIONS

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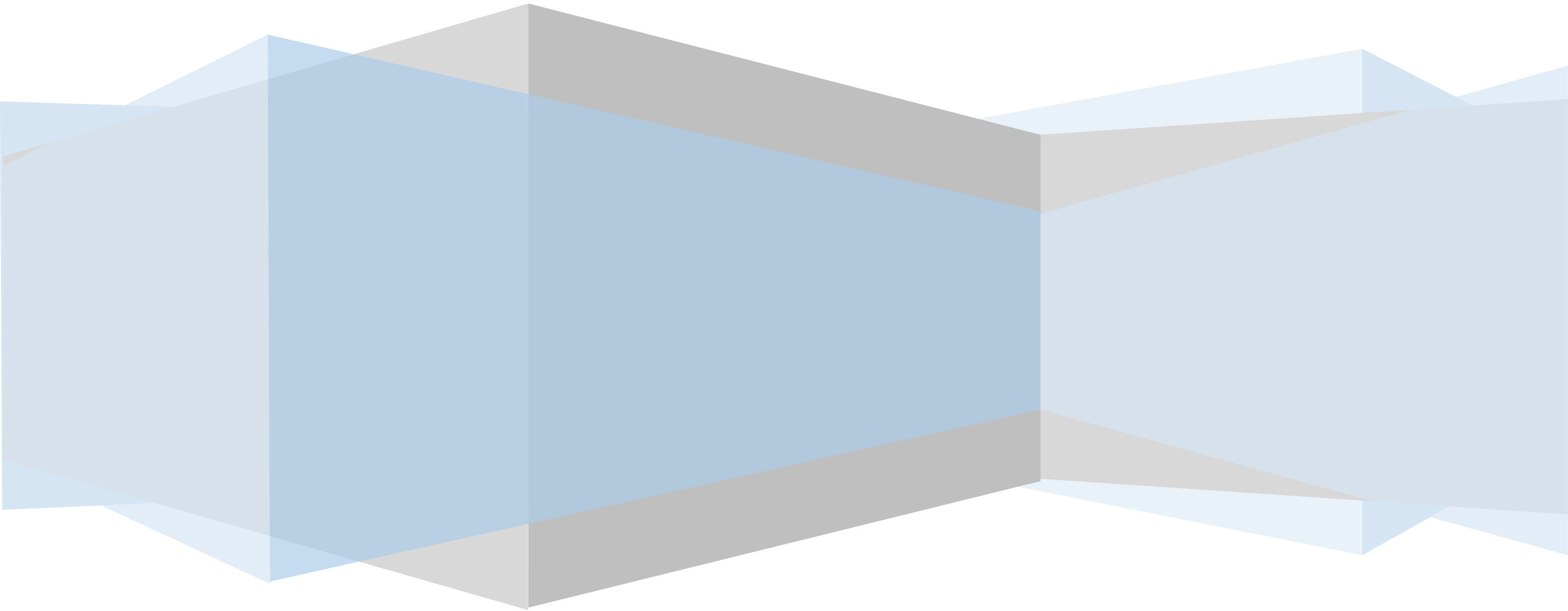

- E-waste is a great challenge from both environment and technology point of view as its rate of growth is much higher than the rate of disposed, reuse and recycles. Socioeconomic, infrastructural, and legal reasons are the barriers of e-waste management in India. The majority of the e-waste recycling and recovery options practiced in India are rude and hazardous, causing severe environmental and occupational hazards. There is an urgent need to focus more on treatment systems involving recycling and recovery options for better e-waste treatment and management. E-waste may be measured as a ‘secondary ore’ or ‘artificial ore’ for the concentrations of precious metals richer than natural ores, which makes their recycling important from both economic and environmental perspectives. For the environmentally safe treatment and recycling of e-waste, the high initial investment is required for setting facility fitted with technologically advanced equipment and processes. There is a need of further research and consideration on policy as well as at technical level to answer on how to successfully manage the e-waste problems with the current e-waste system in India.
- The study in Mandoli industrial area has provided a snapshot of work place, environmental pollution (soil, water and plant contamination) of the industrial units and dump sites associated with the e-waste recycling units. Generally, Cu, Al, Fe, and Pb were high in soils from recycling area as compared to village soils. On the contrary, Hg and As was detected from recycling units in surface soils. It was observed that the plants (common grass) from discarded area of e-waste recycling units contain higher amount of heavy metals as compared to the grass samples of the adjoining village. Whereas, As, Cr, Hg and Se were not observed in the plant samples. Heavy metal concentration in water sample from industrial area is higher than the village waster sample. The resulted data was also compared with Indian Water Standard (IWS)-2012 and it was observed that heavy metal concentrations are less than the desired limit of IWS except copper and iron. The high heavy metal concentrations in the studied area resulted from the crude methods of recycling which, may add to the higher levels of these elements to the environment.
- In TCLP study Pb, the most concerned heavy metal in e-waste can be leached easily using standard EPA3011 method, but in our study it was not detected in the leachate during the one year simulation study. This outcome suggests that Pb may readily leach out from e-waste buried in MSW landfills, but is strongly retained by the solid waste around the e-waste

through the mechanisms of adsorption and chemical complexation. This does not necessarily mean that Pb can be permanently immobilized in the solid waste. With the change of conditions and the transport of moisture, Pb may migrate and eventually reach the bottom of the landfill polluting groundwater. Efforts to divert e-waste from landfills are necessary for the protection of the environment in a long run. Besides this, concentration of other metals (Al, Fe, Cu, Zn, Ni & Cr) examined was found to be below the regulatory level of TCLP standard values.

- In an alkaline condition using cyanogenic bacterial strains such as *C. violaceum*, *P. fluorescens* and *P. aeruginosa* and their mixed culture had capability to leach out metals (Au, Cu, Fe, Zn, and Ag) from e-waste. Higher metal bioleaching capabilities were achieved by using combinations of mixed cultures of cyanogenic bacterial strains. *Pseudomonas aeruginosa* was used for the bioleaching study of e-waste for the first time and in combination with *C. violaceum* exhibited higher metal leaching capabilities than other combinations. Precious metal such as Au was mobilized by cyanogenic bacteria which can be developed as an industrial application of bioleaching in alkaline conditions (biocyanidation). The mixed culture acidophilic bacteria (MCAB) and fungus (*A. niger*) exhibited a good performance in bioleaching metals from personal computer motherboards. The extraction of metals was generally higher at lower pulp densities; the highest extraction efficiency was achieved with 1% (w/v) e-waste. The more favourable results were obtained in the bioleaching process which, suggests that the mechanism is not simply a direct chemical attack on the e-waste but that the bacteria and fungus participates in the leaching process. Two-step bioleaching process is recommended for better recovery of metals from e-waste. From the prospective of environmental pollution and recovery of metals, biological leaching was more promising than chemical leaching. There is need of extensive research for large scale recovery of metals from e-waste as heterogeneity was observed in the mobilization of metals by bioleaching from e-waste.

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REFERENCES

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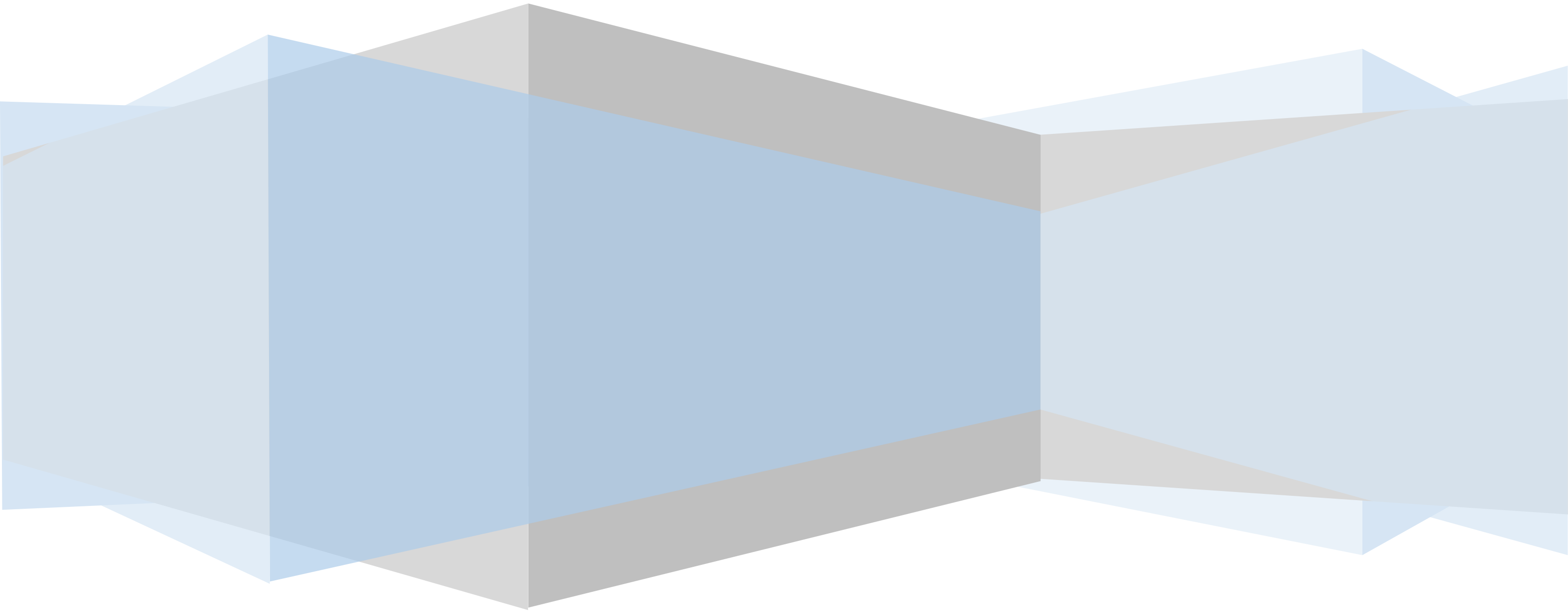

[1] Hischier R., Wager P. and Gauglhofer J. (2005). Does WEEE recycling make sense from an environmental perspective? The environmental impacts of the Swiss take-back and recycling systems for waste electrical and electronic equipment (WEEE). Environmental Impact Assessment Review, 25(5) 525–539.

[2] Robinson B. H. (2009). E-waste: An assessment of global production and environmental impacts. Science of the Total Environment, 408(2): 183–191.

[3] Røpke I. (2001). New technology in everyday life-social processes and environmental impact. Ecological Economics, 38(3): 403–422.

[4] Wagner T. P. (2009). Shared responsibility for managing electronic waste: A case study of Maine, USA. Waste Management, 29(12): 3014–3021.

[5] CPCB. (2008). <www.cpcb.nic.in/.../27.06.08%20guidelines%20for%20E-Waste.pdf>. [Access date: 12 Oct. 2012].

[6] OECD. (2001). Extended producer responsibility; a guidance manual for governments. Organization of Economic Co-operation and Development (OECD). Paris.

[7] EU. (2002). European Union Waste Electronic Electrical Waste (WEEE) Directive. Brussels.

[8] Sushant B., Wath P., Dutt S. and Chakrabarti T. (2001). E-waste scenario in India, its management and implications. Environ Monit Assess, 172: 249–262.

[9] Robinson B. H. (2009). E-waste: an assessment of global production and environmental impacts. Science of the Total Environment, 408(2): 183–191.

[10] DEFRA. (2004). Department for Environment, Food and Rural Affairs (DEFRA) Report. <www. defra.gov.uk>. [Access date: 12 Oct. 2012].

[11] Science Daily. (2012). <www.sciencedaily.com/releases/2012/07/120706164159.htm>. [Access date: 12 Oct. 2012].

[12] UNEP. (2006). Nairobi Conference on Basel Convention to Address the Growing Challenge of Electronic Wastes. <http://www.unep.org/documents.multilingual/default.asp?DocumentID=485&ArticleID=5431&I=en> [Access date: 12 Oct. 2012].

[13] Ravi V., Shanker R. and Tiwari M. K. (2005). Analyzing alternatives in reverse logistics for end-of-life computers: ANP and balanced scorecard approach. Computer and Industrial Engineering, 48: 327–356.

[14] Hageluken C. (2006). Improving metal returns and eco-efficiency in electronic recycling – a holistic approach to interface optimization between pre-processing and integrated metal smelting and refining. In: Proc. 2006 IEEE International Symposium on Electronics and the Environment, May 8–11, 2006, San Francisco, CA, 218–223.

[15] UNEP DEWA/GRID-Europe. (2005). E-waste, the hidden side of IT equipment's manufacturing and use. Chapter 5 – Early Warning on Emerging Environmental Threats. <http://www.grid.unep.ch/product/publication/download/ew_ewaste.en.pdf>. [Access date: 12 Oct. 2012].

[16] Schmidt C. W. (2006). Unfair trade: e-waste in Africa. Environ. Health Perspect, 114: 232-235.

[17] Herat S. and Agamuthu P. (2012). E-waste: a problem or an opportunity? Review of issues, challenges and solutions in Asian countries. Waste Management & Research, DOI: 10.1177/0734242X12453378

[18] Liu X., Tanaka M. and Matsui Y. (2006). Electrical and electronic waste management in China: progress and the barrier to overcome. Waste Management & Research, 24: 92–101.

[19] European Union Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment. Official Journal of the European Union 46 pp 19–23. 2003a

[20] European Union Directive 2002/96/EC of the European Parliament and the Council of 27 January 2003 on waste electrical and electronic equipment (WEEE). Official Journal of the European Union 46 pp 24–39. 2003b

[21] Empa. (2004). Federal Laboratories for Materials Testing and Research (Empa), E-waste pilot study Delhi: Knowledge partnerships with developing and transition countries. St. Gallen: Empa <http://www.ewaste.ch/>. [Access date: 12 Oct. 2012].

[22] Sinha-Khetriwal D., Kraeuchi P. and Schwaninger M. A. (2005). Comparison of electronic waste recycling in Switzerland and in India. Environmental Impact Assessment Review, 25: 492–504.

[23] Bandyopadhyay A. (2008). Indian Initiatives on E-Waste Management-A Critical Review. Environmental Engineering Science, 1507-1526. DOI:10.1089/ees.2007.0342.

[24] Jain A. (2006a). E-waste Management in India (Current Status & Needs): Creation of Optimum Knowledge Bank for Efficient e-Waste Management in India. Workshop on efficient e-waste management, May 8–9, Venue Hotel Intercontinental Eros, Nehru Place, New Delhi, India.

[25] MOEF. (2008). Guidelines for Environmentally Sound Management of E-waste. <www.envfor.nic.in/divisions/hsmd/guidelines-e-waste.pdf >. [Access date: 12 Oct. 2012].

[26] Chatterjee S. (2007). National Scenario of Electronics Waste in India. Department of Information Technology New Delhi, India.

[27] Urban hazard: Mumbai choking on e-waste. <http://www.timesofindia.indiatimes.com/NEWS/India/Urban_hazard_Mumbai_choking_on_e-waste/RssArticle/articleshow/1671262>. [Access date: 12 Oct. 2012].

[28] Pandve H. T. (2007). E-waste management in India: An emerging environmental and health issue. Indian J Occup Environ Med, 11(3): 116. DOI: 10.4103/0019-5278.38461

[29] MPCB. (2007). Report on Assessment of Electronic Wastes in Mumbai-Pune Area (MPCB report- March, 2007).

[30] Shankar J. (2006). Bangalore chokes under tons of e-waste. http://sify.com/news/fullstory.php? id=13601252. [Access date: 12 Oct. 2012].

[31] Johri R. (2008). E-waste management, implications, regulations and management in India and current global best practices. New Delhi: Teri.

[32] MoEF. (2003). Hazardous Wastes (Management and Handling) Amendments Rules, 2003. Ministry of Environment and Forests, Government of India, New Delhi. <http://www. envfor.nic.in/legis/hsm/so593e.pdf>. [Access date: 12 Oct. 2012].

[33] GTZ German Technical Co-operation. (2004). Draft report on e-waste recycling in Delhi Region as part of “Knowledge Partnerships with Developing and Transition Countries in e-waste Recycling” prepared by EMPA, sponsored by GTZ, and assisted by CPCB, DPCC, and MAIT. New Delhi, India. Study conducted by IRG, Toxics Link.

[34] Widmer R. (2006). Indo-Swiss-German e-Waste Initiative: Development of the Initiative Objectives and Activities Clean e-Waste Channel Organizational Set-up. Workshop on efficient e-waste management, May 8–9, 2006. Venue Hotel Intercontinental Eros, Nehru Place, New Delhi, India.

[35] MOEF. (2011). E-wastes (Management and Handling) Rules. <envfor.nic.in/downloads/rules-and-regulations/1035e_eng.pdf>. [Access date: 12 Oct. 2012].

[36] EC. (2000). Draft proposal for a European parliament and council directive on waste electrical and electronic equipment, European Commission (EC) Report, Brussels, Belgium.

[37] Cui. J. and Forssberg E. (2003). Mechanical recycling of waste electric and electronic equipment: a review. J. Hazard. Mater, 99(3): 243–263.

[38] EPCEU (2003). Directive 2002/96/EC of the European Parliament and of the Council of 27 January 2003 on waste electrical and electronic equipment (WEEE), Off. J. Eur. Union L pp 24–38.

[39] SVTC (2007). Just say no to E-waste: Background document on hazards and waste from computers. <http://svtc.igc.org/cleancc/pubs/sayno.htm. 2007>. [Access date: 12 Oct. 2012].

[40] Niu X. and Li Y. (2007). Treatment of waste printed wire boards in electronic waste for safe disposal. J. Hazard. Mater, 145(3): 410–416.

[41] Williams J. and Shu L. H. (2001). Analysis of remanufacturer waste streams for electronic products IEEE International Symposium on Electronics and the Environment, 279–284.

[42] ISRI, (2006). Scrap recycling: where tomorrow begins, Institute of scrap recycling industries Inc. (ISRI) Report. Washington DC, USA, 2003. <http://www.isri.org/isri-downloads/scrap2.pdf> [Access date: 12 Oct. 2012].

[43] Cui J. and Forssberg E. (2007). Characterization of shredded television scrap and implications for materials recovery. Waste Manage, 27(3): 415–424.

[44] Veit H. M., Bernardes A. M., Ferreira J. Z., Tenorio J. A. S. and Malfatti C. F. (2006). Recovery of copper from printed circuit boards scraps by mechanical processing and electrometallurgy. J. Hazard. Mater, 137(3): 1704-1709.

[45] Mohabuth N., Hall P. and Miles N. (2007). Investigating the use of vertical vibration to recover metal from electrical and electronic waste. Miner. Eng, 20(9): 926–932.

[46] Li J., Lu H., Guo J., Zhenming Xu Z. and Zhou Y. (2007). Recycle technology for recovering resources and products from waste printed circuit boards. Environ. Sci. Technol, 41(6): 1995–2000.

[47] Kang H. Y. and Schoenung J. M. (2006). Economic analysis of electronic waste recycling: modeling the cost and revenue of a materials recovery facility in California. Environ. Sci. Technol, 40(5): 1672–1680.

[48] Li J., Lu H., Xu Z. and Zhou Y. (2008). A model for computing the trajectories of the conducting particles from waste printed circuit boards in corona electrostatic separators. J. Hazard. Mater, 151(1): 52–57.

[49] MJC. (2004). Screening Level Human Health and Ecological Risk Assessment for Generic E-waste Processing Facility. MJC & Associates for Environment Canada.

[50] Morf L. S., Tremp J., Gloor R., Huber Y., Stengele M., and Zennegg M. (2005). Brominated flame retardants in waste electric and electronic equipment: substance flows in a recycling plant. Environmental Science and Technology, 39: 8691–8699.

[51] Takigami H., Hirai Y., Matsuzawa Y. and Sakai S. (2006). Brominated flame retardants and brominated dioxins in the working environment and environmental emission-a case study at an electronics recycling plant. Organohalogen Compounds, 68: 2190–2193.

[52] Caballero B. M. and Chomon M. J. (2008). Pyrolysis of electrical and electronic wastes. Journal of Analytical and Applied Pyrolysis, 82: 179-183.

[53] Hall W. F. and Williams P. T. (2007). Processing waste printed circuit boards for material recovery. Circuit World, 33(4): 43-50.

[54] Hoffmann, J.E. Recovering precious metals from electronic scrap, Jom-J. Miner. Met. Mater. Soc. 44(7) pp 43–48. 1992

[55] Sum E. Y. L. (1991). The Recovery of Metals from Electronic Scrap. J. Miner. Met. Mater. Soc., 43(4): 53–61.

[56] Lee J. C., Song H. T. and Yoo J. M. (2007). Present status of the recycling of waste electrical and electronic equipment in Korea. Resour. Conserv. Recycl., 50(4): 380–397.

[57] Yu J., Williams E., and Ju M. (2009). Review and prospects of recycling methods for waste printed circuit boards. Proceedings of IEEE International Symposium on Sustainable Systems and Technology (ISSST '09), Phoenix, AZ, 18-20 May, pp. 1-5.

[58] Hageluken C. (2007). Recycling of e-scrap in a global environment: opportunities and challenges, in: K.V. Rajeshwari, S. Basu, R. Johri (Eds.), Tackling e-Waste Towards Efficient Management Techniques, TERI Press, New Delhi, pp. 87–104.

[59] Tsydenova O. and Bengtsson M. (2011). Chemical hazards associated with treatment of waste electrical and electronic equipment. Waste Manage, 31: 45-58.

[60] Wai C. M. and Wang J. S. (2005). Dissolution and recovery of precious metals in supercritical carbon dioxide, Abstracts of Papers of the American Chemical Society, 229, U930-U931, Mar 13, 2005.

[61] Gloe K., Muhl P. and Knothe M. (1990). Recovery of precious metals from electronic scrap, in particular from waste products of the thick-layer technique. Hydrometallurgy, 25(1): 99-110.

[62] Baba H. (1987). An efficient recovery of gold and other noble-metals from electronic and other scraps. Conserv. Recycl., 10(4): 247–252.

[63] Quinet P., Proost J. and Van Lierde A. (2005). Recovery of precious metals from electronic scrap by hydrometallurgical processing routes. Miner. Metall. Process., 22(1): 17–22.

[64] Macaskie L. E., Creamer N. J., Essa A. M. and Brown N. L. (2007). A new approach for the recovery of precious metals from solution and from leachates derived from electronic scrap. Biotechnol. Bioeng., 96(4): 631–639.

[65] Vinals J. E., Juan A. and Roca et al. (2004). The metalozon [registered trademark] process for the recovery and recycling of precious metals, REWAS’04 – Global Symposium on Recycling, Waste Treatment and Clean Technology, 1859–1869.

[66] Ogata T. and Nakano Y. (2005). Mechanisms of gold recovery from aqueous solutions using a novel tannin gel adsorbent synthesized from natural condensed tannin. Water Res., 39(18): 4281–4286.

[67] Paretsky V. M., Antipov N. I. and Tarasov A. V. (2005) Hydrometallurgical method for treating special alloys, jewelry, electronic and electrotechnical scrap, TMS Annual Meeting, pp 713–721.

[68] Andrews D., Raychaudhuri A. and Frias C. (2000). Environmentally sound technologies for recycling secondary lead. J. Power Sources (Switzerland), 124–129.

[69] Sadegh Safarzadeh M., Bafghi M. S., Moradkhani D. and Ojaghi I. (2007). A review on hydrometallurgical extraction and recovery of cadmium from various resources. Miner. Eng. 20(3): 211–220.

[70] Ritcey G. M. (2006). Solvent extraction in hydrometallurgy: present and future. Tsinghua Sci. Technol. 11(2): 137–152.

[71] Yang B. (1994). Ion exchange in organic extractant system, Lizi Jiaohuan Yu Xifu/Ion Exchange and Adsorption, 10(2): 168–179.

[72] Shamsuddin M. (1986). Metal recovery from scrap and waste. J. Metals, 38(2): 24–31.

[73] Tavlarides L. L., Bae J. H. and Lee C. K. (1985). Solvent extraction, membranes, and ion exchange in hydrometallurgical dilute metals separation. Sep. Sci. Technol. 22(2–3): 581-617.

[74] Scott M. K. (2002). Leaching and electrochemical recovery of copper, lead and tin from scrap printed circuit boards. Journal of Chemical Technology and Biotechnology, 77: 449–457.

[75] Yu J., Williams E. and Ju M. (2009). Review and prospects of recycling methods for waste printed circuit boards. In Proc. ISSST; 1-5.

[76] Bosecker K. (1997). Bioleaching: metal solubilization by microorganisms. FEMS Microbiol. Rev, 20: 591-604.

[77] Krebs W., Brombacher C. P., Bosshard P., Bachofen R. and Brandl H. (1997). Microbial recovery of metals from solids. FEMS Microbil. Rev 20: 605-617.

[78] Agate A. D. (1996). Recent advances in microbial mining. World Journal of Microbiology and Biotechnology, 12: 487–495.

[79] Lee J. C., Song H. T and Yoo J. M. (2007). Present status of the recycling of waste electrical and electronic equipment in Korea. Resources, Conservation and Recycling, 50: 380–397.

[80] Ehrlich H. L. (1988). Bioleaching of manganese ores. In: Biogeochemistry of Ancient and Modern Environments (Trudinger, P.A., Walter, M.R. and Raloh, B.J. Eds.), Australian Academy of Science, Canberra. pp 609-614.

[81] Bosecker K. (1988). Bioleaching of non-sulfide minerals with heterotrophic microorganisms. 8th International Biotechnology symposium, Paris1988, Proceedings (Durand, G., Bobichin, L. and Florent, J., Eds.), Societe Francaise de Microbiologie, 2 pp 1106-1118.

[82] Brierley J. A., (1990). Acidophilic thermophilic archaebacteria: potential application for metals recovery. FEMS Microbiology, 75 (2–3): 287–292.

[83] Duarte J. C., Estrada P. C., Pereira P. C. and Beaumont H. P. (1993). Thermophilic vs. mesophilic bioleaching process performance. FEMS Microbiology Reviews, 11: 97-102.

[84] Kelly R. M. and Deming J. W. (1988). Extremely thermophilic archaebacteria: Biological and engineering considerations. Biotechnology Progress, 4(2): 47–62.

[85] Norris P. R. (1997). Thermophiles and Bioleaching, in Biomining: Theory, Microbes and Industrial Processes, (ed.), D.E. Rawlings. Springer-Verlag and Landes Bioscience. pp. 247–258.

[86] Clark D. A. and Norris P. R. (1996). Oxidation of mineral sulphides by thermophilic micro-organisms. Minerals Engineering, 9(11): 1119–1125.

[87] Konishi Y., Yoshida S. and Asai S. (1995). Bioleaching of pyrite by acidophilic thermophile *Acidianus brierleyi*. Biotechnology and Bioengineering, 48: 592–600.

[88] Berthelin J. (1983). In: Microbial Geochemistry. W.E. Krumbein (ed.), Blackwell, Oxford, pp 223.

[89] Furrer G. and Stumm W. A (1986). Coordination chemical approach to the kinetics of weathering. I. Dissolution of δ-Al2O3 and BeO. Geochim. Cosmochim. Acta 50 pp 1847-1860.

[90] Bosker K. (1997). Bioleaching: metal solubilisation by microorganisms. FEMS Microbiology Reviews, 20: 591-604.

[91] Brandl H. (2001). Microbial leaching of metals. In: Rehm, H.-J. (ed). Biotechnology, vol. 10. Wiley-VCH, Weinheim, Germany, pp 191-224.

[92] Haddadin H., Dagot C. and Fick M. (1995). Models of bacterial leaching. Enzyme and Microbial Technology, 17: 290-305.

[93] Ojumu T. V., Petersen J., Searby G. E. and Hansford G. S. (2006). A review of rate equations proposed for microbial ferrous-iron oxidation with a view to application to heap bioleaching. Hydrometallurgy, 83: 21-28.

[94] Rawlings D. E., Dew D. and du Plessis C. (2003). Biomineralization of metal-containing ores and concentrates. Trends in Biotechnology, 21: 38-44.

[95] Watling H. R. (2006). The bioleaching of sulphide minerals with emphasis on copper sulphides-a review. Hydrometallurgy, 84: 81-108.

[96] Rawlings D. E. (2005). Characteristics and adaptability of iron- and sulphur-oxidizing microorganisms used for the recovery of metals from minerals and their concentrates. Microbial Cell Factories, 4 pp 1-15.

[97] Rawlings D. E., Johnson D. B. (2007). The microbiology of biomining: development and optimization of mineral-oxidizing microbial consortia. Microbiology, 153: 315-324.

[98] Ahonen L., Tuovinen O. H. (1995). Bacterial leaching of complex sulphide ore samples in bench-scale column reactors. Hydrometallurgy, 37: 1-21.

[99] Somasundaran P., Ren Y. Z. and Rao M. Y. (1998). Applications of biological processes in mineral processing. Colloids Surfaces a-Physicochem. Eng. Asp. 133(1–2): 13–23.

[100] Ehrlich H. L. (1997). Microbes and metals. Appl. Microbiol. Biotechnol, 48(6): 687–692.

[101] Muraleedharan T. R., Iyengar L. and Venkobachar C. (1991). Biosorption-an attractive alternative for metal removal and recovery. Curr. Sci. 61(6): 379–385.

[102] Bosshard P. P., Bachofen R. and Brandl H. (1996). Metal leaching of fly ash from municipal waste incineration by *Aspergillus niger*, Environmental Science Technology, 30: 3066–3070.

[103] Brombacher C., Bachofen R. and Brandl H. (1998). Development of a laboratory scale leaching plant for metal extraction from fly ash by Thiobacillus strains. Appl. Environ. Microbiol, 64:1237–1241.

[104] Choi M., Cho K., Kim D. and Kim D. (2004). Microbial recovery of copper from printed circuit boards of waste computer by *Acidithiobacillus ferroxidans*. J. Environ. Sci. Health, Part A, Environ. Sci. Eng. Toxic Hazard. Substances control, A39 (11-12): 2973-2982.

[105] Wang J. W., Bai J. F., Xu J. Q. and Liang B. (2009). Bioleaching of metals from printed wire boards by *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* and their mixture. J. Hazard. Mater, 172: 1100–1105.

[106] Ten W. K. and Ting Y. P. (2003). Bioleaching of electronic scrap material by *Aspergillus niger*, 15th International Biohydrometallurgy Symposium (IBS 2003) September 14-19, Athens, Hellas "Biohydrometallurgy: a sustainable technology in evolution"

[107] Brandl H., Faramarzi M. A. and Stagars M. A. (2003). Novel type of microbial metal mobilization: cyanogenic bacteria and fungi solubilize metals as cyanide complexes. Proceedings of the International Biohydrometallurgy Symposium, IBS2003, 13–18 September, Athens, Greece, National Technical University of Athens.

[108] Faramarzi M. A., Stagars M., Pensini E., Krebs W. and Brandl H. (2004). Metal solubilization from metal-containing solid materials by cyanogenic *Chromobacterium violaceum*. J. Biotechnol, 113: 321-326.

[109] Ting Y. P., Tan C. C. and Pham V. A. (2008). Cyanide-generating bacteria for gold recovery from electronic scrap material. Journal of Biotechnology 136: S647–S677.

[110] Blumer C. and Hass D. (2000). Mechanism, regulation, and ecological role of bacterial cyanide biosynthesis. Arch Microbiol, 173: 170-177.

[111] Knowles C. J. and Bunch A. W. (1986). Microbial cyanide metabolism. Adv Microb Physiol, 27: 73–111.

[112] Brandl H., Lehmann S., Faramarzi M. A. and Martinelli D. (2008). Biomobilization of silver, gold, and platinum from solid waste materials by HCN-forming microorganisms. Hydrometallurgy, 94(1–4): 14–17.

[113] Zhu N., Xiang Y., Zhang T., Wu P., Dang Z., Li P. and Wu J. (2011). Bioleaching of metal concentrates of waste printed circuit boards by mixed culture of acidophilic bacteria. Journal of Hazardous Materials, DOI:10.1019/j.jhazmat.2011.05.062.

[114] Isaac R. A. and Kerber J. D. (1971). Atomic Absorption and Flame Photometry: Techniques and Uses in Soil, Plant and Water Analysis in *Instrumental Methods for Analysis of Soils and Plant Tissue*, (L. M. Walsh *ed.*) Soil Science Society of America, Madison WI.

[115] Adrian W. J. (1973). A Comparison of a Wet Pressure Digestion Method with Other Commonly Used Wet and Dry-Ashing Methods", Analyst, 98: 213.

[116] Fishman M. J. and Downs S. C. (1966). Methods for Analysis of Selected Metals in Water by Atomic Absorption," Geological Survey Water-Supply Paper 1540-C, U. S. Government Printing office, Washington, D. C.

[117] Shaw P. J. A. (2003). Multivariate statistics for the environmental sciences. New York: Arnold Publishers Oxford University Press Inc.

[118] Wold S., Esbensen K. and Geladi P. (1987). Principal Component analysis. Chemometrics and Intelligent Laboratory System, 2: 37–52.

[119] Vandeginste B. G. M., Massart D. L., Buydens L. M. C., DeJong S., Lewi P. J., and Verbeke J. S. (2003). Handbook of chemometrics and qualimetrics: Part B. Amsterdam: Elsevier.

[120] Daud M., Wasim M., Khalid N., Zaidi J. H. and Iqbal J. (2009). Assessment of elemental pollution in soil of Islamabad city using instrumental neutron activation analysis and atomic absorption spectrometry techniques. Radiochimica Acta, 97:p 117–119.

[121] Sharma S. (1996). Applied multivariate techniques. New York: Wiley.

[122] Cui J. and Zhang L. (2008). Metallurgical recovery of metals from electronic waste: A review. Journal of Hazardous Materials, 158: 228-256.

[123] CPCB. (2007). Draft Guidelines for Environmentally Sound Management of e-waste. Central Pollution Control Board (CPCB), Ministry of Environment and Forests (MoEF), Government of India. New Delhi, India. <http://www.cpcb.nic.in/Electronic%20Waste/E-Waste-draft-3.html>. [Access date: 12 Oct. 2012].

[124] Wu B.Y., Chan Y. C., Middendorf A., Gu X. and Zhong H. W. (2008). Assessment of toxicity potential of metallic elements in discarded electronics: A case study of mobile phones in China. Journal of Environmental Science, 20: 1403–1408.

[125] Brigden K., Labunska I., Santillo D. and Allsopp M. (2005). Recycling of Electronic Wastes in China and India: Workplace and Environmental Contamination. The Netherlands: Greenpeace International.

[126] Hino T., Agawa R., Moriya Y., Nishida M., Tsugita Y. and Araki T. (2009). Techniques to separate metal from waste printed circuit boards from discarded personal computers. Journal of Material Cycles and Waste Management, 11: 42–54.

[127] Sourty E., Sullivana L. and Bijker M. D. (2003). Chromium oxide coatings applied to magnetic tape heads for improved wear resistance. Tribology International, 36: 389–396.

[128] Basel Convention Technical Guideline on Environmentally Sound Management of Mercury Waste. Technique from Basel convention. 2007

[129] Basel. (2007). <http://www.basel.int/techmatters/mercury/guide lines/240707.pdf>. [Access date: 12 Oct. 2012].

[130] Muller G. (1969). Index of geoaccumulation in sediments of the Rhine River. Geojournal, 2: 108– 18.

[131] Taylor S. R. and McLennan S. M. (1995). The geochemical evolution of the continental crust. Rev Geophys, 33: 241– 65.

[132] Bowen H. J. M. (1979). Environmental chemistry of the elements. London: Academic.

[133] Muller G. (1981). Die Schwermetallbelastung der Sedimenten des Neckars und Seiner Nebenflusse. Chemiker-Zeitung 6: 157– 164.

[134] Pacyna J. M. and Winchester J. W. (1990). Contamination of the global environment as observed in the Arctic. Palaeogeogr Palaeoclimatol Palaeoecol, 82: 149– 57.

[135] Quevauviller P., Lavigne R. and Cortez L. (1989). Impact of industrial and mine drainage wastes on the heavy metal distribution in the drainage basin and estuary of the Sado River (Portugal). Environ Pollut, 59: 267– 86.

[136] Reimann C., de Caritat P. (2003). Intrinsic flaws of element enrichment factors (EFs) in environmental geochemistry. Environ Sci Technol, 34: 5084– 5091.

[137] Schiff K. C. and Weisberg S. B. (1999). Iron as a reference element for determining trace metal enrichment in Southern California coastal shelf sediments. Mar Environ Res, 48: 161– 76.

[138] Sutherland R. A. (2000). Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. Environ Geol, 39: 611–27.

[139] Buat-Menard P. and Chesselet R. (1979). Variable influence of the atmospheric flux on the trace metal chemistry of oceanic suspended matter. Earth Planet Sci Lett, 42: 398–411.

[140] Daud M., Wasim M., Khalid N., Zaidi J. H. and Iqbal J. (2009). Assessment of elemental pollution in soil of Islamabad city using instrumental neutron activation analysis and atomic absorption spectrometry techniques. Radio chimica Acta, 97: 117–119.

[141] Hakanson L. (1980). An ecological risk index for aquatic pollution control. A sedimentological approach. Water Res, 14: 975–1001.

[142] Mason B. and Moore C. B. (1982). Principles of geochemistry (4th ed.). New York: Wiley.

[143] Faiz Y., Tufail M., Javed M. T., Chaudhry M. M. and Siddique N. (2009). Road dust pollution of Cd, Cu, Ni, Pb and Zn along Islamabad expressway, Pakistan. Microchemical Journal, 92: 186–192.

[144] Sajid I., Mohammad W., Muhammad T., Mohammad A. and Muhammad M. (2012). Elemental contamination in urban parks of Rawalpindi/ Islamabad-a source identification and pollution level assessment study, Environ Monit Assess, 184: 5497–5510.

[145] Martin S. P., Rolf W., Amit J., Hans-Peter B., Ruth S. and Susanne K. (2005). Key drivers of the e-waste recycling system: Assessing and modelling e-waste processing in the informal sector in Delhi. Environmental Impact Assessment Review, 25: 472–491.

[146] Agarwal A., Singhmar A., Kulshrestha M. and Mitta A. K. (2005). Municipal waste recycling and associated markets in Delhi, India. Resources. Conservation and Recycling, 73-90.

[147] Lisk D. J. (1998). Environmental implications of incineration of municipal solid waste and ash disposal. Science of the Total Environment, 74: 39–66.

[148] Lemieux P. M., Lutes C. C., Abbott J. A. and Aldous K. M. (2000). Emissions of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans from the open burning of household waste in barrels. Environmental Science & Technology, 34: 377–384.

[149] Wong M. H., Wu S.C., Deng W. J., Yu X. Z. and Luo Q. et al. (2007c). Export of toxic chemicals: A review of the case of uncontrolled electronic-waste recycling. Environmental Pollution, 149: 131-140.

[150] Ha N. N., Agusa T., Ramu K., Phuc Cam Tu N., Murata S., Keshav A., Bulbule Peethmbaram P. Takahashi, Shin Annamalai S. Tanabe, S. (2009). Contamination by trace elements at e-waste recycling sites in Bangalore, India. Chemosphere, 76: 9-15.

[151] Li J., Duan H. and Shi P. (2011). Heavy metal contamination of surface soil in electronic waste dismantling area: site investigation and source-apportionment analysis. Waste Manag Res, 29(7): 727–738.

[152] US EPA (2012). Regional Screening Levels (Formerly PRGs) Screening Levels for Chemical Contaminants, <http://www.epa.gov/region9/superfund/prg/ >. [Access date: 12 Oct. 2012].

[153] Nordic Council of Ministers (NCM), (1995). Waste from Electrical and Electronic Products: A Survey of the Contents of Materials and Hazardous Substances in Electric and Electronic Products, TemaNord Copenhagen, Denmark.

[154] U.S. Environmental Protection Agency. (1989). Characterization of Products Containing Lead and Cadmium in Municipal Solid Waste in the United States, 1970 to 2000; EPA/530-SW-89-015B; Office of Solid Waste: Washington, DC.

[155] Waldron H. (1980). Metals in the Environment; Academic Press: New York.

[156] Gosselin R., Smith R. and Hodge H. (1984). Clinical Toxicology of Commercial Products, 5th ed.; Williams and Wilkins: Baltimore, MD.

[157] Sittig M. (1985). Handbook of Toxic and Hazardous Chemicals and Carcinogens, 2nd ed.; Noyes Data Corporation: Park Ridge, NJ.

[158] U.S. Environmental Protection Agency, (1992). Method 1311: Toxicity Characteristic Leaching Procedure, SW-846 Test Methods for Evaluating Solid Wastes, 1992,

<http://www.epa.gov/epawaste/hazard/testmethods/sw846/online/index.htm>. [Access date: 12 Oct.2012].

[159] Jang Y. and Townsend T. (2003). Leaching of lead from computer printed wire boards and cathode ray tubes by municipal solid waste landfill leachates, Environ. Sci. Technol., 37: 4778–4784.

[160] Hopper K., Iskander M., Sivia G., Hussein F., Hus J., Deguzman M., Odion Z., Ilejay Z., Sy F. Petreas M. and Petreas B. X. (1998). Toxicity characteristic leaching procedure fails to extract oxoanion-forming elements that are extracted by municipal solid waste leachates, Environ. Sci. Technol., 32(23): 3825–3830.

[161] Halim C., Scott J., Nattwardaya H., Amal R., Beydoun D. and Low G. (2004). Comparison between acetic acid and landfill leachates for the leaching of Pb(II), Cd(II), As(V), and Cr(VI) from cementitious wastes. Environ. Sci. Technol., 38(14): 3977–3983.

[162] Ghosh A., Mukiibi M. and Ela W. (2004). TCLP underestimates leaching of arsenic from solid residuals under landfill conditions. Environ. Sci. Technol., 38(17): 4677–4682.

[163] Nelson D. W. and Sommers L. E. (1982). Total carbon, organic carbon and organic matter. In: page, A. L., Miller R. H. and Keeney D. R. (eds.) Methods of Soil Analysis, Part 2. American Society of Agronomy, Madison. Pp 539-579.

[164] US Environmental Protection Agency (USEPA). (1992). SW-846 Test Methods for Evaluating Solid Wastes, Method 3010A. Office of Solid Waste and Emergency Response, Washington, DC.

[165] US Environmental Protection Agency (USEPA). (2003). SW-846 Test Methods for Evaluating Solid Wastes, Method 3050B. Office of Solid Waste and Emergency Response, Washington, DC.

[166] U.S. Environmental Protection Agency, (1999). Identification and Listing of Hazardous Waste, The Code of Federal Regulations, Office of Federal Register, National Archives and Records Administration, Washington, DC.

[167] Electronics Industry Environmental Road Map (1996); Microelectronics and Computer Technology Corporation (MCC) Document no. MCC-ECESM-001-96; MCC: Austin, TX.

[168] Waste from Electrical and Electronic Products: A Survey of the Contents of Materials and Hazardous Substances in Electric and Electronic Products; TemaNord: Copenhagen, Denmark, 1995.

[169] Municipal Solid Waste in the United States: 2001 Facts and Figures; EPA530-R-03-011; Office of Solid Waste and Emergency Response (5305W): Washington, DC, 2003.

[170] Townsend T. G., Musson S., Dubey B. and Pearson B. (2008). Leachability of printed wire boards containing leaded and lead-free solder. J. Envinr. Manage, 88: 926–931.

[171] Ghosh A., Mukiibi M. and Ela A. (2004). TCLP underestimates leaching of arsenic from solid residuals under landfill conditions. Environ. Sci. Technol, 38: 4677–4682.

[172] Hooper K., Iskander M., Sivia G., Hussein F., Hsu J., Deguzman M., Odion Z., Ilezay Z., Petreas F. and Simmons B. (1998). Toxicity characteristic leaching procedure fails to extract oxyanion-forming elements that are extracted by municipal solid waste leachates. Environ. Sci. Technol, 32: 3825–3830.

[173] Vann K., Musson S. and Townsend T. (2006). Evaluation of a modified TCLP methodology for RCRA toxicity characterization of computer CPUs. Journal of Hazardous Materials, B129: 101–109.

[174] Fisher M., Mark F. E., Kingsbury T., Vehlow J. and Yamawaki T. (2005). Energy Recovery in the Sustainable Recycling of Plastics from End-of-Life Electrical and Electronic Products, Proc., 2005 IEEE International Symposium on Electronics & the Environment (2005 ISEE/SUMMIT), 16-19 May, New Orleans, LA USA.

[175] Bertram M., Graedel T. E., Rechberger H. and Spatari S. (2002). The contemporary European copper cycle: waste management subsystem. Ecol Econ, 42: 43–57.

[176] Zhang C. (2008). Metallurgical Recovery of Metals from Electronic Waste: A Review, Journal of Hazardous Materials, 158(2-3): pp 228-256.

[177] Veit H. M., Diehl T. R., AP S. et al. (2005). Utilization of magnetic and electrostatic separation in the recycling of printed circuit boards' scrap. Waste Management, 25: 67–74.

[178] Robinson B. H. (2009). E-waste: an assessment of gloabal production and environmental impacts. Science of the Total Environment, 408(2): 183–191.

[179] Hoffman J. E. (1992). Recovering Precious Metals from Electronic Scrap. JOM, 43-48.

[180] Noakes M. J. (1999). Using mineral processing technologies for the treatment of hazardous substances. REWAS V.1. TMS, 27–36.

[181] Veit H. M., Diehl T. R., Salami, A. P., Rodrigues J. S. and Bernardes A. M. (2007). Waste multilayer ceramic capacitors. Hydrometallurgy, 86: 89-95.

[182] Li J., Lu H. and Guo J. (2008). Recycle technology for recovering resources and products from waste printed circuit boards. Environmental Science & Technology, 41: 1995-2000.

[183] Krebs W., Brombacher C., Bosshard P. P., Bachofen R. and Brandl H. (1997). Microbial recovery of metals from solids. FEMS Microbiology Reviews, 20: 605-617.

[184] Menad N., Björkman B. and Allain E. G. (1998). Combustion of plastics contained in electric and electronic scrap. Resources, Conservation and Recycling, 24: 65-85.

[185] Ehrlich H. L. (1997). Microbes and metals, Appl. Microbiol. Biotechnol. 48(6): 687–692.

[186] Schinner F. and Burgstaller W. (1989). Extraction of zinc from industrial waste by *Penicillium* sp. Appl Environ Microbio, 55: 1153-60.

[187] Agate A. D. Recent advances in microbial mining, World Journal of Microbiology and Biotechnology, 12: 487-495.

[188] Olson G. J., Brierley J. A. and. Brierley C. L. (2003). Bioleaching review part B: progress in bioleaching: applications of microbial processes by the mineral industries. Applied Microbiology and Biochemistry Journal, 251: 691-699.

[189] Ilyas S., Anwar M. A., Niazi S. B. and Ghauri M. A. (2007). Bioleaching of metals from electronic scrap by moderately thermophilic acidophilic bacteria. Hydrometallurgy, 88: 180-188.

[190] Ilyas S., Ruan C., Bhatti H. N., Ghauri M. A. and Anwar M. A. (2010). Column bioleaching of metals from electronic scrap. Hydrometallurgy, 101:135–140.

[191] Zheng G., Zhou L. and Wang S. (2009). An acid-tolerant heterotrophic microorganism role in improving tannery sludge bioleaching conducted in successive multi batch reaction systems. Environmental Science and Technology, 43: 4152-4156.

[192] Cheng H. N. and Hu Y. H. (2007). Bioleaching of anilite using pure and mixed culture of *Acidithiobacillus ferroxidans* and *Acidithioballus caldus*. Mineral Engineering, 20: 1187-1190.

[193] Castro I. M., Fietto J. L. R., Vieira R. X. M., Tropia J. M., Campos L. M., M. Paniago E. B. and Brandao R. L. (2000). Bioleaching of zinc and nickel from silicates using *Aspergillus niger* cultures. Hydrometallurgy, 57: 39–49.

[194] Mulligan C. N., Kamali M. and Gibbs B. F. (2004). Bioleaching of heavy metals from a low-grade mining ore using *Aspergillus niger*. Journal of Hazardous Materials, 110: 77–84.

[195] Aung K. M. M. and Ting Y. P. (2005). Bioleaching of spent fluid catalytic cracking catalyst using *Aspergillus niger*. Journal of Biotechnology, 116: 159–170.

[196] Wu H. Y. and Ting Y. P. (2006). Metal extraction from municipal solid waste (MSW) incinerator fly ash-chemical leaching and fungal bioleaching. Enzyme and Microbial Technology, 38: 839–84.

[197] Jain N. and Sharma D. K. (2004). Biohydrometallurgy for non-sulfidic minerals-a review. Geomicrobiology Journal, 21: 135–144.

[198] Gupta V., Laul P. and Syal S. (2008). E-waste – A waste or a fortune? Current Science. 94(5): 554–555.

[199] Sheng P. and Etsell T. H. (2007). Recovery of gold from computer circuit board scrap using aqua regia. Waste Management and Resources, 25(4): 380–383.

[200] Awasthi P., Sood I. and Syal S. (2008). Isolating diesel-degrading bacteria from air. Current Science, 94: 178–180.

[201] Mishra D. and Rhee Y. H. (2010). Current research trends of microbiological leaching for metal recovery from industrial wastes, In: Méndez- Vilas A (ed.), Current Research, Technology and Education topics in Applied Microbiology and Microbial Biotechnology, Badajoz, Spain: Formatex Research Center, pp 1289–1296.

[202] Itzhaki R. F. and Gill D. M. (1964). A micro-biuret method for estimating proteins. Analytical Biochemistry, 9: 401–410.

[203] Veit H. M., Pereira, C. C. and Bernardes A. M. (2002). Using mechanical processing in recycling printed wiring boards. The Journal of the Minerals, Metals & Materials Society (TMS), 54: 45–47.

[204] Patil Y. B. and Paknikar K. M. (1999). Removal and recovery of metal cyanides using a combination of biosorption and biodegradation processes. Biotechnology Letters, 21: 913-919.

[205] Campbell S. C., Olson G. J. et al. (2001). Biogenic production of cyanide and its application to gold recovery. Journal of Industrial Microbiology & Biotechnology, 26: 134–139.

[206] Baxter J. and Cummings S. P. (2006). The impact of bioaugmentation on metal cyanide degradation and soil bacteria community structure. Biodegradation, 17: 207–217.

[207] Mascher F., Schnider-Keel U. D. et al. (2003). Persistence and cell culturability of biocontrol strain *Pseudomonas fluorescens* CHA0 under plough pan conditions in soil and influence of anaerobic regulator gene *anr.* Environmental Microbiology, 5: 103–115.

[208] Ibragimova R. I., Mil'chenko A. I. and Vorob'ev-Desyatovskii N. V. (2007). Criteria for choice of a brand of activated carbon for hydrometallurgical recovery of gold from ore pulps in carbon-in leaching and carbon-in-pulp processes. Russian Journal of Applied Chemistry, 80: 891-903.

[209] El-Latif Hesham Abd. Mohamed N. H., Mady A., Ismail A. A., Shoreit M. (2012). 16S rRNA gene sequences analysis of *Ficus elastica* rubber latex degrading thermophilic Bacillus strain ASU7 isolated from Egypt, Biodegradation, 23:. 717–724.

[210] Silverman M. P. and Lundgren D. G. (1959). Studies on the chemoautotrophic iron bacterium *Ferrobacillus ferrooxidans*. An improved medium and a harvesting procedure for securing high cell yields. Journal of. Bacteriology, 77: 642–647.

[211] Sampson M. I. and Phillips C. V. (2000). Influence of base metals on the oxidising ability of acidophilic bacteria during the oxidation of ferrous sulphate and mineral sulfide concentrates using mesophiles and moderate thermophiles. Mineral Engineering, 14: 317–340.

[212] Nemati M., Lowenadler J. and Harrison S. T. (2000). Particle size effects in bioleaching of pyrite by acidophilic thermophile *Sulfolobus metallicus* (BC). Appl Microbiol Biotechnol, 53 (2): 173-9.

[213] Marhual N., Pradhan P. N., Kar R. N., Sukla L. B. and Mishra B. K. (2008). Differential bioleaching of copper by mesophilic and moderately thermophilic acidophilic consortium enriched from same copper mine water sample. Bioresourse Technology, 99: 8331–8336.

[214] Santhiya D., and Ting Y. P. (2005). Bioleaching of spent refinery processing catalyst using *Aspergillus niger* with high-yield oxalic acid. Journal of Biotechnology, 116: 171–184.

[215] Schinner F. and Burgstaller W. (1989). Extraction of zinc from industrial waste by *Penicillium sp.* Appl Environ Microbio, 55: 1153-1160.

[216] IWS. Drinking Water Quality Standards (IS: 10500); 2012. <http://www.bis.org.in/> [Access date: 19 Oct. 2012].

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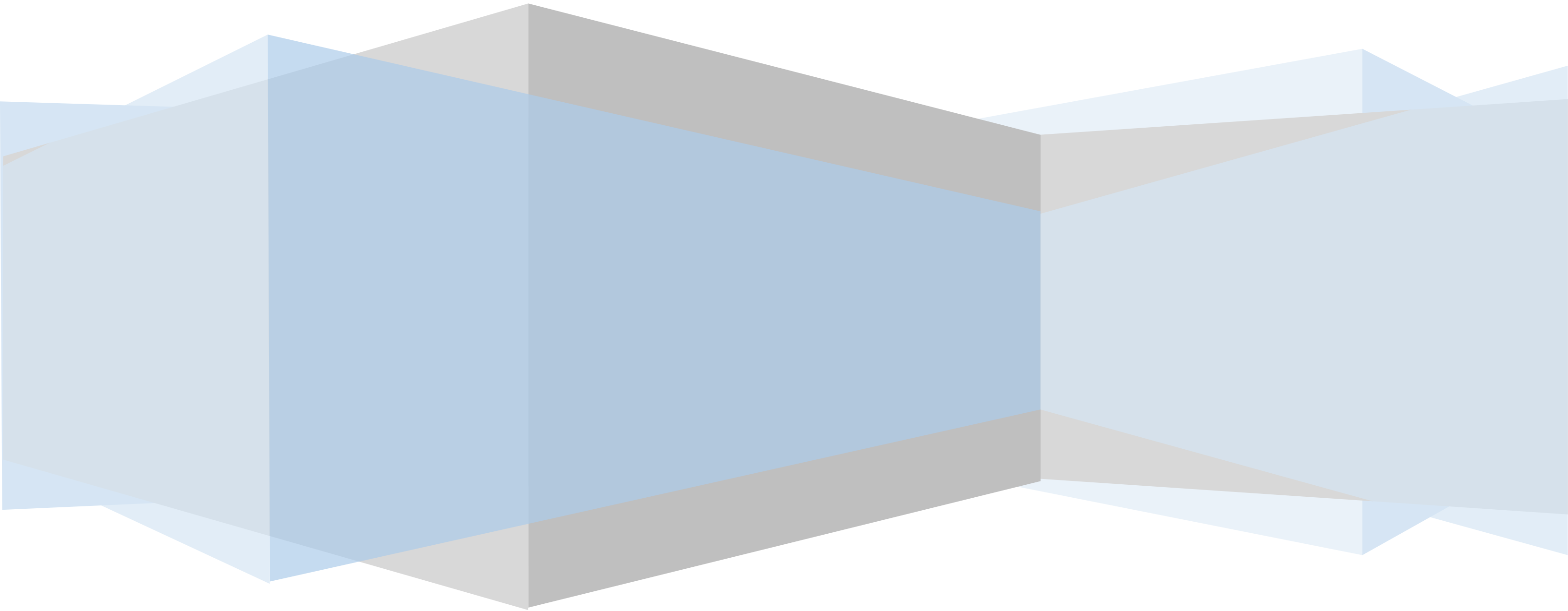
LIST OF AUTHOR’S PUBLICATIONS

JATINDRA KUMAR PRADHAN



A. Peer Reviewed Journals

1. **Pradhan J. K.** and **Kumar S**. (2009). E-Waste Management: A Case Study of Bangalore, India. Research Journal of Environmental and Earth Sciences, 1: 111-115. (**DOAJ**, Print ISSN: 2041-0484, Online ISSN: 2041-0492).
2. **Pradhan J. K.** and **Kumar S**. (2012). Metals Bioleaching from Electronic Waste by *Chromobacterium violaceum* and *Pseudomonad sp.* Waste Management and Research, 30 (11): 1151-1159. DOI: 10.1177/0734242X12437565 (**PubMed**, PMID: 22452961).

A. International Conference/Seminar Presentations

1. **Pradhan J. K.** and **Kumar S**. (2009). A case study on E-waste management in India. Poster presentation, **International Conference** on Biotechnological Solutions for Environmental Sustainability, School of Bio Sciences and technology, VIT University: pp-105, October 21-23, 2009. **[Oral presentation by Pradhan J. K.]**

2. **Kumar S.**, Kumari M., **Pradhan J. K.,** Neema A. and Kalia T. (2011). Biological Treatment of Solid Waste: An Overview. Invited seminar talk at Department of Chemical and Biological Engineering, South Dakota School of Mines and Technology, Rapid City, South Dakota, USA. October 11, 2011. [**Invited talk by Kumar S.]**

A. NCBI Gene Submission

Pradhan J. K. and **Kumar S**. 16S rRNA gene sequence analysis of thermopilic strains isolated from Panamic hot spring, Nubra Valley, Leh-Ladakh, India

- JX465654, JX465655

B. Manuscript Communicated

1. **Pradhan J. K.** and **Kumar S**. (2013). Heavy metal contamination of surface soils, plants, and groundwater at e-waste recycling site in Mandoli industrial area, Delhi, India. Science of the Total Environment.

E. Manuscript under Preparation

1. **Pradhan J. K.** and **Kumar S**. (2013). Bioleaching of personal computer motherboards by fungus (*Aspergillus niger*). Bioresource Technology.
2. **Pradhan J. K.** and **Kumar S**. (2013). Mobilization of metal concentrate of motherboards by mixed culture of acidophilic bacteria. Biodegradation.