Review Article

Journal of Advanced Research in Biotechnology Open Access

E-Waste: Metal Pollution Threat or Metal Resource?

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Received: 05 February, 2016; Accepted: 03 March, 2016; Published: 13 March, 2016

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Abstract

The decreasing costs and increasing availability of electronic equipments like mobiles, televisions, computers and their accessories with advanced technology and the fast rate at which the outdated units are changed, has given rise to a new stream of waste known as Electronic waste (E-waste). 'E-waste' is one of the rapidly growing problems of the present world. The article provides a concise overview of the current scenario of global and national E-waste generation, environmental and health hazards, existing legal networks as well as organizations working on this issue and current technologies for E-waste treatment namely pyrometallurgy, hydrometallurgy and bio hydrometallurgy. It further confers why researchers have shown more interest in bio hydrometallurgical techniques for recovery of metals from E-waste as compared to the conventional methods. If a sustainable technique of metal extraction from E-waste is developed, it would help to conserve the depleting high grade metallic ores, provide the extracted metals to industries and conserve the biotic and abiotic components of the ecosystem from the hazards of E-waste. Moreover, the purity of base and precious metals in E-wastes is about ten times higher than the ores hence, if potential E-waste recycling methods are developed and implemented, it would change the problem of pollution into a profitable metal resource.

Keywords: Autotrophs; Bio hydrometallurgy; Bioleaching; Biosorption; Cyanogenic microbes; Electronic waste; Global problem; Printed circuit board

Introduction

Stone Age cultures began around 10,000 BC, giving way to Copper Age in 3500 BC and Bronze Age in 2500 BC. Cultures continued to grow in complexity and technical advancement through the Iron Age (1200 BC), eventually giving rise to present day "Electronic Age". It is also known as the 'Digital Age" [1]. The increased necessities of mankind in Modern Era have led to a myriad of inventions from a simple calculator to a highly improvised super computer [2]. It has reduced the reliance on human labour, simplified the day-to-day activities and has made the life more comfortable. It has helped in shaping the future of the people, business and nation. In the early 1970, the occurrence of first battery powered calculator marked the beginning of new era in technology. Calculators were not the end of the technological evolutionary process [1]. The tremendous consumer demand drove manufacturers to improve the integrated circuit process with greater performance, better production yields and lower prices which gave rise to personal computers, mobile-phones, laptops and several other electronic equipments [3]. The whole world remains connected through various sophisticated electronic devices like a palmtop, mobile-phone or laptop which has also made the world's populace severely addicted to the technology [4]. But the murky side of this technological roar is the accumulation of the electronic wastes (e-waste).

Electronic Waste: Classification, Composition and Hazards

E-waste classification

Although, electronics have immensely helped in the nation's development, education, trade and commerce, it has also given mankind a reason to worry [5]. The active use of electronic equipments has led to a remarkable increase in their production and at the same time it has given rise to the problem of discarding them [6]. The massive generation of EEE due to the escalating consumer demands has created a new channel of waste, known as e-waste. Each and every electronic equipment has a predetermined life-span after which they become obsolete. These obsolete electronic equipments are now known as Waste Electrical and Electronic Equipments (WEEE) or more commonly Electronic waste (e-waste) [7,8].

EMPA (Eidgenossische Materialprufungs-und Forschungs Anstalt) Swiss federal laboratories have classified WEEE into two categories viz. Electrical waste and Electronic waste collectively forming Waste Electrical and Electronic Equipments [9]. Approximately 50% of the WEEE consists of electrical wastes, which include household appliances like refrigerators, washing machines, dryers, air-conditioners, vacuum cleaners, coffee machines, toasters, irons, etc. The remaining 50% of WEEE consists of electronic wastes, which includes monitors, televisions and other electronic appliances like computers, telephones, faxes, printers, Video Compaq Disk (VCD) players, radios, other electronic tools like medical instruments, drilling and sewing machines, etc. The EEE are classified into three categories viz. white, brown and grey goods on the basis of their types and utility [10]. The typically large electrical goods and heavy consumer equipments which are mostly painted with white enamel are called white goods. It includes refrigerator, stoves, washing machines, etc. The relatively light consumer equipments as well as the IT and telecommunication equipments such as television, computers, mobile-phones, radio-sets, printers, etc. are called brown goods. Whereas; branded goods sold outside the authorized territory by unauthorized dealers at a price lower than the manufacturing territory are called grey goods [11]. They are presented in market as the resale of new products through channels unintended by the original manufacturers, which mostly includes automatic dispensers for money, cold drinks, sewing machines, video-games, etc. Categories of waste electrical and electronic equipments along with their classification as per the WEEE Directive are listed in Table 1 [12].

Chemical and physical composition of E-waste

On the basis of chemical composition, the WEEE consists of various metals, metalloids, precious metals, halogenated compounds and radioactive elements. Metals and metalloids include Aluminium, Arsenic, Antimony, Barium, Beryllium, Cadmium, Chromium, Copper, Europium, Lead, Lithium, Iron, Manganese, Mercury, Nickel, Selenium, Silica, Tin, Yttrium, Zinc, etc. Precious metals include Gold, Indium, Silver, Palladium, Platinum, etc. Halogenated compounds like Polychlorinated Biphenyls (PCB), Tetrabromobisphenol (TBBA), Polybrominated Biphenyls (PBB), Polybrominated Diphenyl Ethers (PBDE), Chlorofluorocarbon (CFC), Polyvinylchloride (PVC) are present. Radioactive metal like Americium is found in the electronic scrap. The percent composition of the above mentioned types can be represented as 60% metallic content, 30% sophisticated blends of plastics and 10% of dangerous pollutants [13,14].

On the basis of physical composition, the harmful substances found in large quantities include Cathode Ray Tubes (CRT), Printed Circuit Boards (PCB), epoxy resins, Polyvinyl Chlorides (PVC), thermosetting plastics, fibreglass, lead glass, concrete, ceramics, rubber and plywood [15,16]. The composition of e-waste is very diverse and differs in products belonging to different categories. It contains more than 1000 different substances, which are hazardous upon disposal. Many materials and wastes are currently traded internationally, but e-waste has drawn particular attention from government officials,

NGOs, researchers, and practitioners at both the domestic and international levels [6].

E-Waste hazards and its effect on human health

Fast technological progress, industrial growth in the developed and developing countries and product obsolescence have led to the rise in all types of WEEE. The human health and environmental impacts have become rising concerns due to rapidly growing e-waste and the complex and hazardous mixture of materials and metals contained in them. The amount of E-waste was estimated to be around 6 million tonnes in the European Union (EU) and the growth rate of E-waste is expected to rise by 3-5% per year [17]. Presently, the e-waste is one of the fastest growing waste streams in the world [18]. The e-wastes from developed countries enter into developing countries, easily, in the name of free trade or donation. They are transported largely through waterways or roadways, further complicating the problems associated with waste management. With the presence of deadly chemicals and toxic substances present in the electronic devices, disposal of e-waste is becoming an environmental and health nightmare [19,20]. It is reported that only 15-20% of the total 50 million tonnes of global e-wastes are recycled properly. If not, they are exported to the developing or under-developed countries where there are no standard methods of WEEE treatment [18]. Thus it is an alarming threat, especially for the workers who are employed to separate the e-waste components for obtaining valuable metals [21]. Some of the e-waste toxins and their effects on human health are depicted in Table 2 [22,23]. The ill-effects are mainly due to improper dismantling and treatment methods adapted generally and the workers involved for the treatment of e-waste in particular. These workers are mostly unaware of hazardous health effects due to toxic substances in e-wastes and moreover, they are not provided with the protective attires, gloves, glasses and the masks [24,25]. The disassembling and separation of certain parts of e-wastes with the bare hands can cause skin and respiratory disorders [26] whereas; using an open flame to separate and

No	Categories	Electrical and electronic equipments	Groups		
l.	Large household equipments	Refrigerator, washing machines, microwaves, electric radiators, stoves, large medical utility equipments, etc.	White goods		
	Small household equipments	Vacuum cleaners, iron, toasters, clocks and watches, etc.	Brown goods		
	Information Technology and telecommunication equipments	Printers, type-writers, telephones, calculators, facsimile, computers, mobile-phones, etc.	Brown goods		
	Consumer equipments	Radio, television, video-cameras, musical instruments, recorders, etc.	Brown goods		
	Lightning equipments	Fluorescent lamps, high intensity discharge lamps, sodium lamps, etc.	Brown goods		
	Medical devices	Radiotherapy equipment, laboratory equipments for in-vitro diagnosis, dialysis machine, pulmonary ventilators, etc.	White or Brown goods		
	Monitoring and control instruments	Smoke detector, thermostats, weighing and measuring appliances, etc.	Brown goods		
	Automatic dispensers	Automatic dispensers for hot drinks and cold drinks, automatic dispenser for money	Grey Goods		
	Electrical and electronic tools	Drills, sewing machines, tools for riveting, nailing or screwing, etc.	Grey Goods		
0.	Toys, leisure and sports equipments	Video-games, electric trains or car racing toy set, etc.	Grey Goods		

No.	Sources	Constituents	Hazards and health effects	
1.	Solder in printed circuit boards, glass panels and gaskets in computer monitors	Lead	Damage to kidney, central nervous system, circulatory systems and adverse effect on brain development of children	
2.	Chip resistors and semi-conductors	Cadmium	Toxic irreversible effects on human health, damage to kidney, liver and nervous system	
3.	Relays, Switches and printed circuit boards	Mercury	Chronic damage to the brain, respiratory and skin disorders	
4.	Galvanized steel plates and decorator or hardener for steel housing	Chromium	Causes bronchitis and other respiratory disorders	
5.	Cabling and computer housing	Plastics and PVC	Burning produces dioxin that causes reproductive and developmental problems	
6.	Electronic scrap and circuit boards	Brominated flame retardants	Disorder of Endocrine system	
7.	Front panels of CRT's	Barium, phosphorus and heavy metals	Causes muscular problems, damage to heart, liver and spleen	
8.	Copper wires and PCB	Copper	Stomach cramps, nausea, liver damage or Wilsons's disease	
9.	Lithium ion batteries	Lithium	Lithium can pass into breast milk and may harm a nursing baby, inhalation causes lung edema	
10.	Nickel-cadmium rechargeable batteries	Nickel	Dermatitis, Asthma	
11.	Motherboard	Beryllium	Lung cancer, inhalation causes chronic beryllium disease or Beryllicosis	

No.	States	E-waste (metric tonnes/year)	Cities	E-waste (metric tonnes/year)
1.	Maharashtra	20,271	Mumbai	11,017
2	Tamil Nadu	13,486	Delhi	9729
3.	Andhra Pradesh	12,780	Bangalore	4648
4.	West Bengal	10,059	Chennai	4132
5.	Uttar Pradesh	10,381	Kolkata	4025
6.	Delhi	9,729	Ahmedabad	3287
7.	Karnataka	9,119	Hyderabad	2833
8.	Gujarat	8,994	Pune	2584
9.	Madhya Pradesh	7,800	Surat	1836
10.	Punjab	6,958	Nagpur	1769

dismantle the e-waste component can lead to the exposure of volatilized contaminants and may lead to the chronic respiratory disorders to the workers who are working in the place and the nearby vicinity [27]. It was observed that majority of the e-waste contaminants are spread through air which is the main pathway for their entry into the humans through inhalation, ingestion or skin absorption [28].

Environmental hazards due to E-wastes

Every year, large quantities of WEEE are discarded by several countries, most of which either end up in landfill or incineration or unauthorized recycling yards [20] which cause severe air, water and soil pollution. Solid waste management, which is already a huge task, is becoming more complicated by the incursion of e-waste, particularly computer waste. The CRT and personal computer constitute the first and second largest component of the e-waste stream, respectively [29]. The heavy metals, halogenated compounds and radioactive element present

in e-waste affect the environment during their inappropriate recycling processes. While burning the e-waste in the open environment, polycyclic aromatic compounds and dioxins are produced which are hundred times more toxic than domestic waste burning [30]. It was reported by Bertram et al. [31] that, approximately 5000 tonnes of Cu released into the environment, globally, was due to the e-wastes disposal.

If the combustion retardants like PBDEs from e-wastes are released into the environment, they are bio accumulated in living organisms due to their lipophilic nature [32] whereas; release of CFCs from the e-waste dumping site would eventually destroy the ozone layer [33]. The Toxicity Characteristic Leaching Procedure (TCLP) reported that the leachate generated from the e-wastes dumping sites has proved to be fatal for aquatic organisms and has made the water resources non-potable. The non-governmental organization such as Greenpeace reported the secret flow of tonnes of e-waste to the countries like China, India, Pakistan, Vietnam, Philippines, Malayasia, Nigeria, Ghana, etc. where strict environmental set of laws do not exist [34].

Statistics of E-Waste Generation

Global scenario

The US Environmental Protection Agency (EPA) estimated that the world generates 20-50 million tonnes (MT) of E-wastes each year [35] and it is expected to rise to 65-72 MT by the year 2017 [36,37]. The United Nation's Solving the E-waste Problem (UN StEP) Initiative forecasted that by the year 2017, the mass of the e-waste generated will be equal to eleven times of The Great Pyramid of Giza and 200 times of The Empire State Building of New York [38]. At present, majority of e-wastes are generated in Europe, the United States and Australasia. Whereas, in the next ten years, China, Eastern Europe and Latin America will become major e-waste producers in the world [39]. In the year 2005, the U.S. was leading the way with 3.0 MT of e-waste per year followed by China with 2.3 MT and India not far behind 0.3 MT per year [40]. The present report by Un StEP Initiative states that in the year 2012, the highest amount of e-waste was generated by European Union (EU) followed by, U.S., China, India, Japan, Russia, Brazil and Mexico. Whereas, a year later in 2013, China generated 11.1 MT of e-wastes which was higher than the U.S. with 10.0 MT [38].

In the year 2014, the U.S. and China produced the highest amount of e-waste weighing 10.0-11.0 MT in the world followed by Japan, Germany and India [41]. The top three Asian Nations with the highest e-waste generation were China, Japan and India which produced 16.0 MT corresponding to 3.7 kg per inhabitant. The lowest amount of e-waste generating continent was Africa with 1.9 MT of total e-waste in the year 2015 [41].

The inspection of 18 European sea-ports in 2005 revealed that 47% of e-waste intended to export, was illegal [42]. In UK alone, at least 23,000 tonnes of undeclared 'Grey market' electronic waste was illegally shipped to the Far East, India, Africa and China [18]. In the 1990s, governments in the European Union, Japan and some places of the United States had set up an e-waste recycling systems but they could not manage the increasing e-wastes they had generated. So they began exporting the problem to the developing countries where laws to protect workers and the environment are inadequate or not compulsory and moreover, these countries were unaware with the hazardous nature of e-waste [43]. Additionally, it was also cheaper to recycle e-waste in developing countries, for e.g.; the cost of recycling of computer monitors in the China is ten times cheaper than the U.S [44]. In the United States, it was estimated that 50-80% of the e-waste collected every year for recycling is being exported in this way [40]. This practice was legal because the US had not ratified the Basel Convention [45]. At the other end of the world, the average annual e-waste production in Greece for the period 2003-2006 came up to approximately 1,70,000 tonnes, representing 3.8% of the total amount of domestic solid waste [14]. The demand for electronic waste in the Asian countries began to grow when it was found that scrap yards could extract valuable metals such as copper, iron, aluminium, silicon, nickel, silver and gold during the recycling processes [46,47]. The e-waste dumping grounds in Asia are China, India and Pakistan. China is facing a dual problem of E-waste treatment both from domestic generation and illegal trans boundary movement [48]. The amounts of E-waste in China are increasing at the rate of 5-10% annually. A small town Guiyu situated in Hong Kong city of China is the largest e-waste collector in the world [48]. It was affirmed that the e-waste collected at Guiyu mainly came from the US, Canada, Japan and South Korea [41]. Guiyu is followed by Accra in Ghana and Lagos port in Nigeria (Africa) in the import of e-wastes [18]. A study on e-wastes dumping showed that an average of 5 million secondhand computers weighing 60,000 tonnes entered the country through Lagos port, out of which nearly 30,000 tonnes were nonfunctional or irreparable [21]. The Basel Action Network (BAN) estimated that about 45% of the imports in Africa were from the European Union, 45% from the U.S. and the remaining 10% from Japan, Korea, Finland, Germany, Norway, Netherlands, Italy and Singapore [29]. Other e-waste dumping places include Karachi and Islamabad in Pakistan and Delhi in India [1].

Indian scenario

In the last twenty years, the information and communication sector in India has revolutionized life of one and all, creating a huge effect on electronic industries and leading to a phenomenal rise in every nation [20]. In India, e-waste scenario has undergone a drastic change. After China imposed a ban on the import of e-waste in 2002, India has emerged as one of the largest dumping grounds for the developed countries of the world [49-51]. In India, it has been observed that the electronic items are stored unattended because of lack of knowledge about their management. Such e-wastes lie in houses, offices, warehouses etc. Many a times, these wastes are mixed with household wastes, which are finally disposed of in landfills or incinerated to reduce the bulk [52]. Moreover, there are no strict environmental laws or specific guidelines for e-waste disposal in India [45]. The obsolescence rate of e-wastes in India has been estimated to be 1,46,180 tonnes for the year 2005, which reached 8,00,000 tonnes in the year 2012 [15,51] and is expected to reach to more than 12,00,000 tonnes by the year 2020 [53-55]. During the year 2005, about 80% of the e-waste generated in the United States was exported to China, India and Pakistan [20] out of which, only 3% of total e-waste generated was recycled properly in India while the remaining e-waste was handled by the workers with bare hands, under unhygienic conditions without masks in order to earn their livelihood [56]. Ever since then, over 1 million poor people in India are involved in the manual recycling operations. Most of the people working in this recycling sector are the urban poor with very low literacy levels and hence very little awareness regarding the hazards of e-waste toxins [1]. Several laws were framed but these laws failed to stop this informal recycling. Sixtyfive cities in India generate more than 60% of the total e-waste generated in the country [57]. The top ten states generating 70% of the total e-waste in India are Maharashtra, Tamil Nadu, Andhra Pradesh, Uttar Pradesh, West Bengal, Delhi, Karnataka, Gujarat, Madhya Pradesh and Punjab [3] and among the top ten cities generating e-waste, Mumbai ranks first followed by Delhi, Bengaluru, Chennai, Kolkata, Ahmedabad, Hyderabad, Pune, Surat and Nagpur [15,57]. The data of e-waste generated in metric tonnes by the top ten states and cities in India are depicted in Table 3. The state of art recyclers have been set up in India for recovery of metals from e-waste [1]. Central Pollution Control Board (CPCB) has participated in registering 23 formal recycling unit in India for e-waste [57] whereas; the informal recycling units include Mandoli industrial area, Kantinagar, Ibrahimpur, Brijgang and Shastri park area of East Delhi as well as workshops in Gaziabad and Zafarabad in Delhi which are well-known e-waste dismantling areas of India [58]. These areas are considered as the danger zone due to the grave health faced by the workers. In addition to Delhi, another rising concern area is the e-waste dismantling unit in Mumbai [59]. According to the study conducted by the NGO Toxics Link, some remote areas of Mumbai faces critical health and environmental risk posed by a huge 19,000 tonnes of e-waste produced here apart from a good amount of same being imported illegally [47].

India has become the fifth biggest producer of the e-waste in the world which generated 1.7 million tonnes of e-waste in 2014 [41]. It also stated that in the year 2014, the total e-waste generated in India contained approximately 16,500, 1900, 300 and 100-200 tonnes of iron, copper, gold and mixture of silver, aluminium and palladium which was equivalent to 52 billion USD (United States Dollar). However, none of the existing environmental laws has taken strict action on the inappropriate e-waste recycling or its hazardous nature [54]. In India, there are only two authorized functional e-waste dismantling facilities; one in Chennai and second in Bangalore. These facilities are M/s. Trishiraya Recycling Facilities, Chennai and M/s E-Parisara, Bangalore [60]. A report by United Nations predicted that by the year 2020, e-waste from old computers would jump by 400% in China whereas; as high as 500% in India as compared to 2007 e-waste records [41]. Additionally, amount of e-waste from discarded mobile phones would be about seven times higher in China and 18 times higher in India by the year 2020 as compared to the 2007 records [36,61]. The escalating e-waste and its hazardous content would definitely constitute a toxic mine in India and the world however, if managed with extreme care and appropriate technology can convert e-wastes to valuable urban mine as it has a large potential reservoir of recyclable materials [62].

A survey by CPCB accounted Ahmedabad and Surat amongst the highest e-waste generators in Gujarat (CPCB, 2011). A case by Toxic Link reported, import of 30 metric tonnes of e-waste in Ahmedabad in a single month [63,64]. Due to the ever increasing information and communication technology sector, Gujarat generates quite a large amount of e-waste annually [15,57]. But unfortunately only 5% of the total e-waste generated in the state reaches the recycling sites [56,65]. The rest is sold to the informal and local markets where the workers dismantle the computers, mobiles, television in an unsystematic manner to extract out the valuable and precious metals unknowingly, damaging their own health and posing a threat to the environment [20]. Looking to the up-front problem faced by many regions across the state and nation, Gujarat Pollution Control Board (GPCB) has authorized seven private e-waste management projects in the state. The e-waste recyclers are M/s. E-Process House in Valsad, M/s. E-coli Waste Management Pvt. Ltd. in Sabarkantha, M/s. ECS Environment Ltd. in Ahmedabad, M/s. Pruthvi E-recycler Pvt. Ltd. and M/s. Green care E-recycle Company in Rajkot, M/s. Earth e-waste management Pvt. Ltd. in Surat and M/s. Gujarat refilling centre in Vadodara. These recycling units have received no-objection certificate for treatment of e-waste and their registration is valid till the year 2019 [15]. These projects absolutely follow the norms laid by Central Pollution Control Board of India and Ministry of Environment and Forests (MOEF). To implement the project, government has approved Special Purpose Vehicles (SPV) in the name of Gujarat e-Nirmal Ltd. and these vehicles help the recycling units to collect e-waste from door-to-door in closed vans. A report from Sulaimani, [66] states that, the collected e-waste by the recycling plants is then separated into functional and non-functional parts [66]. The functional parts are renovated and sold. Non-functional parts are dismantled and shredded into small sizes. These shredded parts are then differentiated on the basis of recyclable and reusable components like metals, non-metals, glass, plastic, etc. The hazardous components are carefully separated from the recyclable material during e-waste processing and then disposed off according to the guidelines laid by CPCB. The Guidelines for Environmentally Sound Management of E-waste published by CPCB provide the approach and methodology for environmentally sound management of e-waste. The set-up of e-recycling units in Gujarat has created a wave in bringing about an improvement in e-waste management, operational treatment plans, and protective protocols for workers and awareness amongst the public [56].

Organizations/Networks Working On E-Wastes Issues and Hazards

International networks

- The Consumer Electronics Association (CEA) (GreenerGadgets.org)
- The Basel Action Network (BAN.org)
- Silicon Valley Toxics Coalition (SVTC.org)
- The World Reuse, Repair and Recycling Association (wr3a.org)
- Texas Campaign for the Environment (texasenvironment. org)
- U.S. Environmental Protection Agency (US EPA)
- Greenpeace association (greenpeace.org)
- European Union (EU) directives such as WEEE (Waste Electrical and Electronic Equipment) and ROHS (Restrictions of Hazardous Substances)
- Solving the E-waste problem Initiative (Step-Initiative) (www.step-initiative.org)

National networks

- The E-waste Guide, India (www.ewaste.in)
- Solid Waste Association of India (NSWAI) (www.nswai. com)

• Toxics Link (www.toxicslink.org)

Other networks are WEEE Forum, Umicore (www.umicore. com), Clean India, Indian Environmental Society, India Habitat Centre, Microbial Biotechnology Area of Tata Energy Research Institute. These networks prevent all forms of toxic trade, monitor and control e-waste management systems, settle e-waste recycling and disposal standards, thereby strengthening cooperation and harmonization of global e-waste related activities [10,63,67]. Switzerland was the first country in the world where an official e-waste management system was established and operated [7]. The legislation regarding e-waste management was introduced for the first time in 1998 through ORDEA Law (Ordinance on the Return, The Taking Back and the Disposal of Electrical and Electronic Appliances) [68]. Two different e-waste recycling systems were established in the country viz. SWICO Recycling Guarantee (The Swiss Association for Information, Communication and Organizational Technology) which manages the brown goods and S.EN.S (Stiftung Entsorgung Schweiz) system which manages the white goods [7,14].

Printed circuit board as an essential part of electrical and electronic equipments

E-waste differs physically and chemically from the domestic and industrial wastes. It contains both, valuable and dangerous components which require special attention and recycling practices to avoid adverse environmental impact [69]. The concentration of selected metals in earth-crust, ores and solid waste compared to the metal content of e-scrap and e-waste PCB is listed in Table 4. Whereas; the detailed metal content data of mobile phone, computer, television, LongXiang (LX) and tube-light PCB is presented in Table 5 [70]. All the PCBs showed presence of 10 to 12 metals. Copper content range from 6.4 to as high as 36.0% lead 1.2 to 15.5% and silver is 0.02 to 0.05%. The data presented in these tables indicates that e-waste is a rich source of base and precious metals as compared to other metal resources [71-73] which can be exploited to compensate the diminishing high grade ores and can also meet up the increasing demands of heavy metals in the industries [51,74]. According to the report by Li et al. [75] and Erust et al. [2], PCB is the basic component of almost all EEE present right from simple calculators and transistors to largest super computers. Thus the rise in e-waste generation, PCB accumulation has also increased creating a danger zone due to the presence of high metallic content and hazardous materials in the PCB.

According to solid waste management professionals, the PCB waste generation, their trans-boundary movement and disposal are the new issues of concern which is equivalent to the existing global environmental problems like acid rain, ozone depletion and global warming [29]. The PCBs are the platform upon which microelectronic components such as semiconductor chips and capacitors are mounted. The PCB is a base which provides the electrical interconnections between components [76]. The compositions of PCB are metals, polymers and ceramics however; it varies depending on the type of the electronic devices [77,55]. The PCBs show metal content of around 28%, plastics 19%, bromine 4%, glass and ceramics 49%. Precious metals like gold, platinum and silver are also present and they constitute around 0.3-0.4%. In PCB, the average metal contents detected are Cu 12.6%, Zn 5.6%, Pb 3.1%, Ni 2.4%, Al 1.4%, Fe 1.2%, Ag 0.003% and Au 0.0014% [25]. Besides these, inorganic elements like isocyanates and phosgenes from polyurethanes, acrylic and phenolic resins, epoxides and phenols from microchips are also found in the PCB [40]. Due to its complex composition, PCB recycling requires a multidisciplinary approach to separate valuable metals, fibres and plastic fractions and thereby reduce the environmental pollution [5, 26].

The e-waste recycling generally starts from the disassembling stage in which reusable and toxic parts are separated. Thereafter, the PCBs are treated using physical recycling process [78]. The physical recycling process involves a preliminary step where, size reduction of the PCB e-waste is performed, followed by a step in which metallic and non-metallic fractions are separated and collected for further treatments [79]. Physical process for separating the metallic and non-metallic fraction of e-waste includes shape separation, magnetic separation, electric conductivity-based separation, density-based separation and corona electrostatic separation [73,80]. At the end of the physical process, non-metals are finally separated from the metallic fractions. The obtained metallic fractions can be treated by pyrometallurgical, hydrometallurgical or by biotechnological methods.

Tuble 1. doneemi ucion	on of selected metals in E-scrap and PCB compared to earth-crust, ore, fly ash and slag. Li, et al. [25], Krebs, et al. [71]. Metal concentration (%)							
Metals	Various metal resources							
	Fly ash	Slag	Earth crust	Ore	E-scrap	E-waste PCB		
Cu	0.09	0.16	0.007	0.2	8.0 - 26	12.6		
Ni	0.014	0.014	0.008	1.5	0.5 - 2.0	2.4		
Pb	0.8	0.06	0.0016	4.0	1.0 - 3.15	3.1		
Zn	2.7	0.19	0.008	4.0	2.6	5.6		
Sn	0.6	0.05	0.004	1.0	2.3	3.5		
Precious metals (Ag, Au, Pd)	ND	ND	ND	BDL	0.01-0.33	0.002-0.003		

*ND: Not Detected, BDL: Below Detectable Limit, PCB: Printed Circuit Board

Table 5: Metal content of	of various e-wastes PCB studie	d (Shah et al. (2014))[/0].				
Metals	Solubilized metals in various e-waste PCB (mg.g ⁻¹)						
	Mobile-phone	Computer	Television	Long Xiang (LX) PCB	Tube-light		
Cu	360.00	300.00	118.25	64.25	167.75		
Zn	7.96	37.00	19.27	1.23	22.70		
Ni	8.55	3.84	13.00	0.62	1.48		
Al	6.66	45.93	56.27	14.28	53.22		
Pb	12.07	136.5	154.80	133.70	80.50		
Fe	10.50	60.12	64.00	9.46	69.75		
As	4.34	7.82	5.33	5.52	1.65		
Cr	0.59	1.61	1.10	0.93	1.21		
Au	0.10	0.14	ND	ND	ND		
Ag	0.28	0.23	0.50	0.22	0.22		
Pd	0.64	0.27	0.37	0.27	0.68		
Cd, Co, K, Na, Se	BDL	BDL	BDL	BDL	BDL		

^{*}ND: Not Detected; BDL: Below Detectable Limit

Current Technologies for the Recycling of E-Waste and PCB

State-of-the-art e-waste recycling technology

Due to the hazardous nature of the land filling, incineration and open-burning technique for e-waste treatment [81-84], new recycling technologies with reduced environmental pollution and dealing with the metal recovery from e-waste came into existence. These technologies working on a large scale and treating tonnes of e-waste are known as the state-of-the-art technologies. The technology for e-waste recycling comprises of three steps. The first step is known as the detoxification step in which the critical components like lead glass from CRT and chlorofluorocarbon (CFC) gases from refrigerator, light bulbs and batteries are removed in order to prevent contamination of these toxic substances during the downstream processing [85]. In the second step known as shredding or mechanical processing, the recyclable materials like metals, plastics and glass are separated by crushing, grinding, magnetic and eddy current separation and air separation. Whereas, the hazardous materials and emissions like PBDE, BFR, flue gas, furans and dioxins are filtered and treated to minimize the environmental impact [86]. The third step of the state-of-art recycling is the refining step. In this step, the separated recyclable fractions of metals, plastics and glass, obtained from the second step are refined and conditioned to be sold as secondary raw materials. The residues of the refining process are disposed of at the final disposal site as per the norms set up by CPCB [3].

Drawbacks of State-of-the-art E-waste recycling technologies

- The residual particulate matter in the form of ash is prone to spread in the vicinity and can be dangerous when inhaled.
- Vaporization of the toxic dimethylene mercury can cause

respiratory disorders.

Susceptible to uncontrolled fires which can release toxic fumes.

Pyrometallurgical and hydrometallurgical technologies

The pyrometallurgy consists of the treatment of e-wastes at a very high temperature of around $600-800^\circ\text{C}$ in the pre-combustion step and 900-1200°C in the post combustion step [73] to bring about physical and chemical transformations and recover the metals. In this process, the crushed scraps are burned in a smelter or a furnace to remove plastics in one fraction and the refractory matter in another. Thereafter, these refractory matter form a slag phase with the metal oxides [73,87] from which the metals are recovered. A typical Umicore Isa Smelt process involves two steps for metal extraction. The first step is the recovery of precious metals, known as Precious Metal Operations (PMO) is done by Isa Smelt furnace [73,88]. It includes incineration, smelting in a plasma-arc or blast furnace, drossing, sintering, melting and reactions in a gas phase at a high temperature [89]. Plastic and other organic substances are also removed from the feed in this step. The smelter separates the precious metals from the base metals at the end of the first step. The second step involves the recovery of base metals which is known as Base metal operation (BMO) where the metals are mostly concentrated in a lead slag. It is further treated with lead refining to separate different base metals [90,91]. Consequently, pure metals are recovered in a special metal refinery. Pyrometallurgical treatment has now become a traditional method for recovery of precious metals from e-wastes in the past twenty years [91].

Comparing with the pyrometallurgical processing, hydrometallurgical method is more reliable and easily controlled [5,92]. It involves the use of aqueous solutions containing a lixiviant (acid, cyanide, halide) which is brought in contact with a material containing a valuable metal. After the extraction of metals, they are recovered by using precipitation, chemical

reduction, cementation and solvent extraction or ion exchange processes [51]. Various researches have been carried out and few hydrometallurgical methods have been patented [93]. It is a vast field and involves variable methods for recovery of precious and base metals. Few studies have been carried out with acid leaching [93,94], cyanide leaching [95], halide leaching [96,97], thiourea leaching [98] and thiosulphate leaching [99]. These methods mostly have their starting point with sulphuric acid leaching in which the base metals are recovered followed by the chloride, cyanide and halide leaching sequentially to recover silver, gold and palladium, respectively [100]. A patent by Zhou et al. [94], described a technique for recovery of metals from e-waste. The scrap is first heated at 400-500°C for 8-12 h to remove the plastic. In the second step, the crude metal residue is treated with HCl or H₂SO₄ at 90°C to dissolve base metals like Cu, Zn, Ni, Al, etc. and the third step involves the use of dilute HNO₂ with a solid liquid ratio of 1:2 at 60°C to dissolve Ag. Finally, the last step involves the recovery of gold and palladium by using HCl and $NaClO_3$. Various other techniques and recycling methods have been developed which involves series of reactions for metal extraction but it is not the main aim, hence the detail of each are not included.

Drawbacks of pyrometallurgical and hydrometallurgical techniques

- The pyrometallurgical technique generates atmospheric pollution through the release of toxic gases like dioxins and furans and they are very expensive due to high energy consumption in the mechanical process for separation of metals in one fraction and polymers and ceramics in another fraction [101,102].
- Moreover, precious metal recovery is not so efficient by pyrometallurgical methods [73,103].
- Hydrometallurgical processes generate high volume of acidic water due to the use of concentrated acids which create a problem for discarding it [70]. Moreover, it requires different chemical lixiviants for separation of base and precious metals which increases the number of steps for metal recovery.
- Both the processes are highly dependent on investment and regarded as uneconomical ways to extract metals from e-waste [3,55].

Bio hydrometallurgical technology

It was observed that pyrometallurgy was the predominant method during the year 1970s and mid-1980s for metal recovery, which was taken over by the hydrometallurgy during mid-1980s and 2005, and presently it has been overtaken by the bio hydrometallurgy. In the last decade, recovery of metals by bio hydrometallurgy is one of the most promising and revolutionary biotechnology [55,104,105]. However, pyrometallurgy and hydrometallurgy are still being applied for metal extraction from e-wastes and the threat to the environmental pollution due to these methods persists. Bio hydrometallurgical technique exploits microbiological processes for recovery of base and precious metal ions. It is soon-to-be a major technology break-

through for the materials and mineral industry. Moreover, great interest is shown by the international and national companies for adopting the bio hydrometallurgical techniques due to its eco-friendly nature. It mainly includes two individual processes namely 'Bioleaching' and 'Bio sorption'. Over the past 40 years many researchers have investigated the application of biotechnology in mining industries [106]. Bioleaching has been applied commercially for extracting copper, zinc, nickel, cobalt and precious metals from low-grade ores and tailings for many years and now even extended to recover metals from concentrates and fly ash [72]. In bioleaching processes, solubilization of metals is based on the interactions between metals and microorganisms. This technique allows metal recycling by processes similar to that in the natural biogeochemical cycles and is therefore eco-friendly and competent technique [3,107].

Sand and colleagues [108,109] worked on mechanisms for bacterial leaching of metal sulphide ores via thiosulphate and polysulphate pathways and also described bioleaching mechanism involving Fe³⁺ ions. From the reports by Sand et al. [109] and Ehrlich, [110]. It was inferred that the direct leaching mechanism involved the enzymatic oxidation of the sulphur moiety present in the heavy metal sulphides. Whereas; in indirect mechanism, there is a non-enzymatic metal sulphide oxidation by Fe3+ iron in combination with an enzymatic re-oxidation of the resulting Fe²⁺ iron. Studies carried out by Rawlings, [111] and Rohwerder et al. [112] justifies indirect mechanism as the relevant and better approach as compared to direct mechanism. The indirect mechanism can be divided into two sub-types viz. the "contact" and "non-contact" mechanisms. In the contact mechanism, the microbial cells attach to the surface of sulphide mineral due to the presence of the exopolymeric layer whereas, in non-contact mechanism, plank tonic cells oxidize the Fe2+ iron in the medium and regenerate the Fe^{3+} iron resulting from the Fe2+ iron due to bioleaching, which react chemically with metal sulphides afterwards. Studies carried out with ores using various sulphur and iron-oxidizing microbes as well as heterotrophic fungi showed 50-90% of various metal extractions under different experimental conditions [113]. The bioleaching experiments carried out by Tipre and Dave, [114] for metal extraction from polymetallic concentrate showed 80.0-88.0% of Cu and Zn extraction in a shake flask and 5 L laboratory stirred tank reactor under optimized conditions. The iron and sulphur oxidizers were employed in the latter study and it exhibited direct mechanism whereas; indirect process carried out by Patel et al. [115] showed 80.0-81.0% of Cu and Zn extraction from polymetallic concentrate in comparatively shorter time period. Though these processes have been successfully applied for the leaching of metals from ores and concentrates, data pertaining to their application for the extraction of metals from e-wastes are still scanty. The ability of microorganisms to leach and mobilize metals from e-wastes comprises of three principles viz. redox reactions, formation of organic acids, inorganic acids and metal leaching agents.

Bioleaching of metals by chemolithoautotrophs

Chiefly acidophilic group of bacteria plays an important role in bioleaching of base and precious metals [113]. Formation of

sulphuric acid by Acidithiobacillus thiooxidans and Fe3+ iron by Leptospirillium spp. help in dissolving the metallic fraction from e-wastes [116,117]. Metal extraction from e-wastes was carried out using various acidophiles like Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans, Leptospirillium ferriphilum, Sulfolobus thermosulfidooxidans, etc. which resulted in efficient metal extraction [2]. Studies by Brandl et al. [71], showed more than 90% of the Cu, Zn, Ni, Al solubilization by Acidithiobacillus thiooxidans at scrap concentration of 5-10 g/L. Choi et al. [118] reported that the iron oxidation rates of A. ferrooxidans did not change much with the addition of c-PCB to the medium. An interesting finding was that the concentration of leached copper in the solution increased with the addition of 1 g/L of citric acid as chelating agent. The latter studies showed 37-40% of Cu leaching without adding citric acid and 81-83% of Cu leaching with the addition of citric acid. Precious metals like Au and Ag were extracted using Acidithiobacillus sp, Leptospirillium sp. and Acidiphiliumsp. [119]. But, better results for Au leaching were obtained using cyanogenic bacterial strains [113]. It was also observed that the mixed cultures of A. thiooxidans and A. ferrooxidans were more efficient than each taken separately for the extraction of metals like Cu, Ni, Zn and Pb from PCB scrap [120]. To improve copper recovery from PCB, a multiple point PCB addition was adopted in which the PCB was added in instalments to prevent the toxic effects of e-waste on the viable cells [121]. Brandl et al. [71] and Yang et al. [122], proposed the effect of single step and two-step bioleaching process and the latter was found to be more effective for substantial metal extraction from e-waste. In two-step process, the bacterially generated lixiviant plays the main role in metal extraction and the microbe-metal interaction is not much significant. Moreover, these processes employ the independent lixiviant generation and helps in optimizing each parameter thereby maximizing the productivity [123]. Comparisons of metals extractions from computer and mobile PCB by chemical and biological means showed more

than 90% copper, zinc and nickel extractions [55,103]. Table 6 [124-131] enlists some of the chemolithoautotrophs employed in extraction of metals from e-wastes.

Bioleaching of metals by cyanogenic microbes

Cyanide is formed by a variety of cyanogenic bacteria viz. Chromo bacterium violaceum, Pseudomonas aeruginosa, Pseudomonas fluorescens, Bacillus megateriumand fungi viz. Maramiusoreades, Clitocybe sp., Polysporussp. etc. many of them belonging to soil micro flora [132]. The microbially produced cyanide helps in bioleaching of metals like Cu, Zn, Fe, Ni, Pt, Au and Ag. It is believed that cyanide formation has a benefit for the organism by inhibiting the growth of competing microorganisms growing with the cyanogenic microbes in the soil. Glycine is the precursor for cyanide synthesis which is formed by oxidative decarboxylation reaction [133,134]. Cyanide occurs in solution in two forms viz., the cyanide anion (CN⁻) and hydrogen cyanide (HCN). At pH 7, cyanide is mostly present as HCN, according to its pKa of 9.3. Both the forms have their roles in extraction of metals at pH 7-10 [134,135]. The formation HCN by an organism was first described in mesophilic bacterium Chromo bacterium violaceum by Sneath in 1953 and in the basidiomycete Marasmius in 1871 by Losecke [135,136]. In the presence of CN⁻ or HCN, many metals and metalloids such as Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Cd, Pd, Ag, Pt, Au, Hg, Po, and U form well-defined metalcyanide complexes, which show a very good water solubility and exhibit high chemical stability [137,138]. The cyanogenic microbes are capable to form water soluble metal cyanides with different efficiencies [139]. Gold was microbially solubilized as dicyanoaurate [Au(CN), and nickel was solubilized as tetracyanonickelate [Ni(CN)₄²⁻] [138]. Pham and Ting [140] extracted Au from e-waste by Chromo bacterium violaceum and Pseudomonas fluorescens after the biooxidation of e-waste by A. ferrooxidans which specifically removes Cu leaving Au residues behind. The HCN forming *Pseudomonas aeruginosa* was

Table 6: List of microorganisms used for extraction of metals from E-waste.						
No.	Microorganisms used in the study	Metals extracted	% metal recovery	References		
1.	Acidiphilium acidophilum	Ni, Zn	40 - 86	Hudec, et al. [124]		
2.	Acidithiobacillus ferrooxidans, Leptospirillium ferrooxidans, Acidithiobacillus thiooxidans	Cu, Ni, Zn	89 – 98	Groudev, et al. [125]; Liang, et al. [120]; Choi, et al. [118]; Bas, et al. [126]		
3.	Aspergillus Niger, Penicillium simplicissimum	Cu, Sn, Al, Ni, Pb, Zn	65 – 95	Brandl, et al. [72]		
4.	Aspergillus Niger, Acidithiobacillus thiooxidans	Cu	82	Saidan and Valix, [127]		
5.	Desulfovibrio desulphuricans	Au, Pb	68, 95	Creamer, et al. [128]		
6.	Chromobacterium violaceum, Pseudomonas fluorescens, Bacillus megaterium	Ni, Au	43.5, 14.9, respectively	Faramarzi, et al. [138]		
7.	Chromobacterium violaceum and Pseudomonas aeruginosa mixed culture	Cu, Zn, Fe, Au, Ag	8 - 83	Pradhan and Kumar, [141]		
8.	Pseudomonas plecoglossicida, Pseudomonas fluorescens, Chromobacerium violaceum	Au, Ag, Pt	5 - 68.5	Brandl, et al. [129]		
9.	Sulfobacillus thermosulfidooxidans, Thermoplasma acidiphilum	Cu, Ni, Zn, Pb, Sn, Al, Fe, Ag	74 – 89	Ilyas, et al. [130], Ilyas, et al. [131]		
10.	Leptospirillum ferriphilum dominated consortium	Cu, Zn, Ni	86-99.8%	Shah, et al. [70] Shah, et al. [55]		

applied in the bioleaching process for the first time by Pradhan and Kumar, [141] for mobilization of metals from electronic waste. The studies showed that mixture of *C. violaceum* and *P. aeruginosa* exhibited higher metal mobilization as compared to *C. violaceum* alone. The mixture of *C. violaceum* and *P. aeruginosa* exhibited more than 83, 73, 49, 13 and 8% of total Cu, Au, Zn, Fe, and Ag solubilization, respectively as compared to 79, 69, 46, 9 and 7% of Cu, Au, Zn, Fe and Ag solubilization, respectively with *C. violaceum* alone at a scrap concentration of 10 g/L. The cyanogenic microbes play a main role in precious metal recovery which is a shortcoming when iron-oxidizers are used [142].

Bioleaching of metals by organic acid producing fungi

Heterotrophic fungi like Aspergillus Niger, Penicilliumsimplicissimum, Penicilliumbilaiae, Saccharomyces cerevisiae, Yarrowialipolytica, etc. have been reported to grow in presence of electronic scrap. These fungi produce organic acids like citric acid, tartaric acid and oxalic acid which act as complexing agents and help in extraction of metals like Cu, Cd, Sn, Al, Ni, Pb, Zn etc. The studies carried out by Brandl et al. [71] showed feasibility for using A. niger and P.simplicissimum to leach metals from e-wastes. The findings showed that the one-step leaching experiments with fungi adversely affected its growth and resulted in only 25-55% metal solubilization. On the other hand, when the fungal biomass was separated from medium after maximum production of organic acid (two-step), it resulted in 65% of Cu and Sn extraction and 95% of Al, Ni, Pb and Zn extraction. The two-step leaching process was demonstrated using a gluconic acid producing fungi A. Niger. Ren etal. [143] found that A. Niger can be utilized to extract Cd and Al from metal containing wastes. Bosshard et al. [144] and Brombacher et al. [145] demonstrated the application of fungal bioleaching for metal extraction from fly ash. The reports of fungal bioleaching with e-wastes are very limited due to the heterogeneity of the e-wastes and its toxicity on developing fungal mycelium. Table 6 enlists involvement of different microbes for the recovery of various metals present in e-waste.

The metals extracted by bioleaching are further recovered by bio sorption methods. It involves the use of biomass of bacteria, fungi, algae, microbial proteins and chitosan (deacetylated derivative of chitin) etc. as adsorbents. Studies carried out by Dave et al. [146], showed Eichhornia sp. biomass played an important role in copper sorption from metal containing waste. As high as 85% of copper was removed from waste in 24 h contact time at pH 5. Parameswari et al. [147] reported around 86-95% sorption of heavy metals like Cr (VI) and Ni by Azotobacter chroococcum, Bacillus sp. and P. fluorescens within 72 h at 35°C temperature. Ilhan et al. [148] investigated effects of pH, temperature and initial concentration of metal ions on the bio sorption capacity by Staphylococcus saprophyticus. The optimum pH values for chromium, lead and copper was found to be 2.0, 4.5 and 3.5, respectively and the maximum adsorption for Cr3+, Pb2+ and Cu2+ was observed at initial concentrations of 193.66 mg/L, 100 mg/L and 105 mg/L, respectively which resulted in 46, 100 and 43% bio sorption of Cr, Pb and Cu. This infers that pH, initial metal concentration and bio sorbent capacity have a great influence on bio sorption studies.

Savitha et al. [149] demonstrated manganese bio sorption from e-waste by *Helminthosporium solani, Aspergillus Niger, Fusarium oxysporum* and *Cladosporiumcladosporoides*, amongst which *H. solani* showed the best results. The maximum adsorption was found to be 97% at pH 7. Various other bio sorbents used for metal sorption are *Streptomyces erythraeus, Spirulina plantensis, Desulfovibriodesulfuricans, Bacillus subtilis, Neurosporacrassa, Rhizopusarrhizus, Chlorella vulgaris* which belong to either bacteria, fungi or algae whereas, animal bio sorbents include hen eggshell membrane, ovalbumin, lysozyme, bovine serum albumin, etc. [113].

Compared with other existing methods, biohydrometallurgy offers a number of advantages including low operating costs, eco-friendly nature, minimization of the volume of chemicals and biological sludge to be handled and high efficiency in detoxifying effluents. Moreover, this technology is well accepted by industry as it goes along with the current need of maintaining nature's harmony. It has become a widely accepted option for the cleanup of contaminated sites and aquifers [113]. However, few more developments in this field are required for its application in metal extraction from e-wastes on large scale and thus solving the problem in an environmentally friendly manner.

Conclusions

In the recent decades, the world has witnessed a technological development fuelled by continuous demand for latest gadgets and devices. In no case, this revolution will decline, thus making electronic waste; a major global issue. Management of E-waste is thus a daunting task and need to be tackled efficiently. Recycling of E-waste for the extraction of base and precious metals are of real concern not only due to the presence of high concentration of these metals but also its hazardous nature. Pyrometallurgy and hydrometallurgy have their own limitations in recycling of metals from E-waste. Bio hydrometallurgical recovery of metals from E-waste appears to be an attractive treatment technique, which can result in more than 90% of metal extraction. This would lead to an acceptable solution of some of the metallic pollutants and would provide value-added metal recovery thereby helping to compensate the gap between the demand and supply of metals. Looking to the brighter side of the current issue, E-waste can be a resource of base and precious metals if appropriate recycling technologies are applied. However, there is a need to scale-up the process to advance commercial application of bio hydrometallurgy for remediation and profitable recovery

Acknowledgements

The authors are thankful to Gujarat State Biotechnology Mission (GSBTM), Financial Assistance Program (FAP-10), Gujarat, India, for the project Grant (No. GSBTM/MD/PROJECTS/FAP/451/2010-11) and research scholarship to Monal B. Shah.

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