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Review on Solvents for Extraction of Metals from Waste Electrical and Electronic Equipment (WEEE)

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Abstract: ***Waste Electrical and Electronic Equipment (WEEE) are electrical and electronic gadgets known to have reached their end-of-life. They are made of printed circuit boards (PCBs) containing valuable metals like copper, gold, iron, lead nickel, silver, tin and zinc which can leach into the environment when landfilled. Current extraction methods for the recovery and recycling of metals from WEEE uses various solvents which are not selective, releases toxic gases and recover metals in a mixed form which requires further purification steps to recover individual metals. This paper has reviewed the use of inorganic acids, organic acids and designer solvents which do not release toxic gases when used for extraction of metals from WEEE. The results reveal that ionic liquids ae promising solvents for extracting metals.***
Keywords: e-waste, WEEE, metals, leaching, ionic liquids, inorganic acids, solvents

I. INTRODUCTION

When wastes have the potential to be recycled and converted to useful materials they are considered as secondary raw materials with great value. Rich ores for the refining of metals are getting scarce gradually and other materials such as low-grade ores and other secondary sources such as tailings, solid and liquid wastes are now considered as economical sources of metal by metallurgical industries. Urban mining is a term widely used to describe the recovery of metals from anthropogenic wastes. In other words, it is a process of recovering elements or compounds from wastes. Some examples of such wastes are Waste Electrical and Electronic Equipment (WEEE), electroplating wastes and tannery waste. The metals present in these mixed waste streams include both hazardous, transition and precious group metals (mercury, lead, lithium, antimony, beryllium, cadmium, copper, silver, platinum, gold, nickel, zinc). When WEEE and other metal bearing wastes are sent to landfills they may contaminate groundwater due to leaching of metals; they may also pollute soil and air due to fire outbreak or release of hazardous components; they can also fill up landfill volume (Sum, 1991; Spalvins, 2008; Adediran & Abdulkarim, 2012; Damodaran *et al.*, 2013; He and Xu, 2014; Kumar *et al.*, 2014; Letsrecycle, 2020; Zhang & Xu, 2016).

Wastes containing valuable or hazardous metals may need to be sorted for reuse or recycling. In WEEE, the mixture of metals and other materials is heterogenous and this has led to a serious challenge in selective recovery of desired materials. The recovery is low as metals are lost in slag and gaseous effluents is high. However, researchers have also combined complexants and oxidants to study the dissolution of metals. It has been reported by Kumar *et al.*, 2014 that 100 % of zinc and copper were dissolved when a combination of 2 mol/L H_2SO_4 and 0.2 mol/L H_2O_2 were used to leach printed circuit board (PCB) at 85 ^{0}C for 8 hours. According to Dhawan *et al.*, 2009, HNO_3 is more effective than HCl and H_2SO_4 in leaching metals from PCB and these mineral acids are known to be really aggressive for metal recovery they are disadvantaged as they release toxic gases (NO_x, Cl_2 & SO_2). Metal recovery through this process is non-selective as the metals are extracted in a mix and a further purification step is required (Sum, 1991; Oh *et* al, 2003; Veit *et al.*, 2005; Dalrymple, 2007; Oishi *et al* 2007; Eswaraiah *et al.*, 2008; Wu *et al.*, 2008; Dhawan *et al.*, 2009; He and Xu, 2014; Kumar *et al.*, 2014; Jadhav & Hocheng, 2015; Wang *et al.* 2016; Zhang & Xu, 2016). Various types of organic acids are considered as environmentally friendly leaching agents and have been used for the extraction of Pb and PbO from scrap battery paste by Sonmez & Kumar, 2009. Citric acid and acetic acid were used to leach large PCB but poor metal slubilization was observed as only 9.89 % and 19.57 % of copper respectively was recovered. However, 100 % Li and 90 % Co have been recovered using 1.25 M citric acid and 1 % vol H_2O_2 at 90 ^{0}C for 30 min and a solid to liquid ratio of 20 g/L. The combination of IL extractants have yielded more results than organic solvents in metal ion extraction (Seal *et al.*, 2003; Chen *et al.*, 2004; Chen & Tsai, 2004; Du *et al.*, 2004; Pandija *et al.* 2007; Sonmez & Kumar, 2009; Li *et al.*, 2010; Jadhav & Hocheng, 2015; Wang *et al.* 2016).

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II. WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT (WEEE)

Waste Electrical and Electronic Equipment (WEEE) is defined as equipment that require the use of electricity for its function and they are also regarded as equipment which works with electrical networks. Examples are cell phones, computers, televisions, batteries, refrigerators which have reached their end-of-life. These gadgets are made up of wires, printed circuit boards (PCBs), cathode ray tubes (CRT) and liquid crystal display (LCD). Some of the valuable materials WEEE is made up of are metals, plastics, glass and other materials (Figure 2.1 and Table 2.1). These materials contain precious group metals like gold and silver, heavy metals like iron, copper, nickel, lead, cobalt, chromium, cadmium along with other hazardous materials like brominated flame retardant (BFR). Table 2.2 shows some useful and hazardous components present in WEEE. Every year, between 34 - 54 million metric tons of Waste Electrical and electronic equipment (WEEE) are generated globally and this figure is growing yearly (Habashi, 1999; EU, 2003; Huang, 2009; Terada, 2012; Ogunseitan, 2013; He and Xu, 2014; Zhang & Xu, 2016; Statista, 2021). The research by Kiddee *et al.*, 2013 showed that 500 million tons of computers were discarded in the United States while at the end of 2010 about 610 million tons of computers became outdated in Japan (Kiddee *et al*., 2013; Park *et al*., 2014; Hadi *et al*., 2015; Zhang & Xu, 2016). In Nigeria for instance, 60,000 – 71,000 tons of used equipment are imported yearly and the largest market for computers in Ikeja, Lagos and the Computer and Allied Product Dealers Association stated that about 75 % of the electronics shipped to the country are considered wastes from the source country; 19 % of these electronics do not function properly and are already near their end-of-life but they become useful to the Nigerian second-hand market as the level of poverty does not allow the people to afford new gadgets hence the reason for the large market of e-waste. The solid waste heap is a source for mixed metals (Adediran & Abdulkarim, 2012; Letsrecycle, 2020).

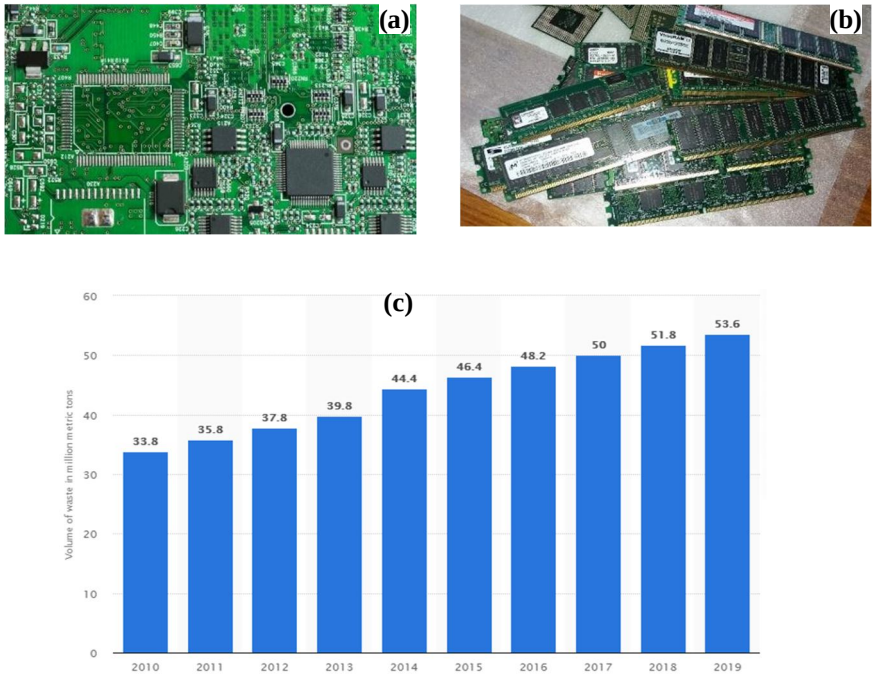

Figure 2.1 (a & b) PCB boards (c) Electronic waste generated worldwide (million metric tons)
Source: (Statista, 2021)

Table 2.1. Main components of WEEE

WEEE	Main components
Cell phone	LCDs, PCBs, wires, battery
Computer	LCDs, PCBs, wires, CRTs, speakers, battery
Television	LCDs, PCBs, wires, CRTs, speakers, demagnetized coil, deflection yoke
Refrigerator	Refrigerant, wires, tubes, liners

Adapted from: (He and Xu, 2014; Zhang & Xu, 2016)

Table 2.2. Useful and Hazardous Components in WEEE

Component	Useful components	Hazardous materials
PCBs	Resin, copper, glass, fibre	Brominated flame retardant, heavy metals
CRT	Glass	Pb (PbO)
LCD	Glass, In_2O_3	Liquid crystal, TAC, PVA
Wire	Plastic, copper, aluminium	Polychlorinated biphenyls

Adapted from: (He and Xu, 2014)

The United States Environmental Protection Agency (USEPA) stated that e-waste of 80 – 85 % by weight ends up in landfills and when they are leached the soil gets contaminated along with groundwater in adjacent regions. The study by Splavins *et al*., 2008 showed that when e-waste is mixed with municipal wastes the leaching of lead increased due to more aggressive acidic conditions. It has been reported by Vehlow *et al.*, 2000 that the incineration of e-waste with municipal waste will lead to the formation of brominated and chlorinated dioxins and furans which are extremely toxic chemicals. Therefore, the use of open indiscriminate dumping, burning (**Figure 2.2 a-b**), landfill and incineration for the management of WEEE are not environmentally friendly options and don't comply with the sustainability principles (Vehlow *et al*., 2000; Splavins *et al*., 2008; Adediran & Abdulkarim, 2012; Tuncuk *et al.*, 2012; Hadi *et al*., 2015; Wang and Xu, 2015).

Figure 2.2 (a) Discarded WEEE (b) Burning of e-waste
Source: (Haqshenas, 2018; Tribuneonlineng, 2018)

There is high value of precious metals in e-wastes and PCBs contains larger portions of precious metals since microelectronic components like capacitors and semiconductor chips are mounted on them. Most electric and electronic equipment contain PCBs which make up 3 % of all WEEE produced. Nearly 160 – 210 kg of copper and 80 – 1,500 g of gold can be contained in one metric ton of circuit boards and, when compared to mining in the United States, the amount of gold is 40 – 800 times and the amount copper is 30 – 40 times the amounts present in the ores which are currently being processed. PCBs are the most economically attractive portion of WEEE but as they are mixed with both hazardous and precious materials such as metals, organics, fibre glass, plastics in small volumes it poses difficulty in extraction, recovery and recycling of materials of interest. **Table 2.3** shows the composition of materials in a populated PCB. The separation techniques also limit the exploitation of the materials that can be recovered and the pre-treatment of PCBs is important in the recycling process (Grossman, 2007; Adediran & Abdulkarim, 2012; Tuncuk *et al.*, 2012; Canal *et al.*, 2013; He & Xu 2014; Hadi *et al.*, 2015; Wang & Xu, 2015; Akbari, 2019). When the value of resale for a metal can cover the cost of recovery it is given a high priority (Yordanov, 1998).

Table 2.3 Composition of Materials in Populated PCBs

Component	Mass (%)
Gold	0.03
Copper	16
Silver	0.05
Nickel	2
Iron	3
Palladium	0.01
Solder	4
Glass-reinforced plastic	> 70

Adapted from: (Hadi *et al.*, 2015)

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III. PRE-TREATMENT OF PCBS

In recycling WEEE, a pre-treatment step is carried out and this is a physical process of mechanically breaking and then crushing the PCBs. At first, the electronic components are dismantled and are further concentrated based on their physical properties. The physical properties mainly considered are metals and non-metals and this is achieved by using one of the following methods: magnetic separation, eddy current separation, screening, pneumatic separation and electrostatic separation. To completely separate magnetic fractions of the crushed PCBs it is best to use the magnetic separation. However, some non-ferrous metals might be included as a result of insufficient liberation. Eddy-current is more suitable for aluminium fractions and sieving crushed PCBs is necessary as this will help to prevent the influence of different particle sizes during separation. The hazardous components on PCBs are selectively disassembled as this would reduce the amount of toxic elements ending up in the mainstream of the recycling process. During the crushing of PCBs the local temperature of the PCBs increase and some researchers have argued that this process may result in agglomeration and localized pyrolysis of plastics. However, Yuan *et al.* 2007 researched on using low temperature for crushing PCBs but the method involved high energy cost (Zhang *et al.*, 2012; Havlik *et al.*, 2014; Ghosh *et al*., 2015; Silvas, 2015).

IV. HYDROMETALLURGY

Hydrometallurgy process uses a procedure known as leaching where a solution is used to solubilize the crushed metal waste. It also involves purification (solvent extraction or ion exchange) and metal recovery. Hydrometallurgy has one or more aqueous phase and it has been studied as an independent discipline from the alchemist's days. Over the years researches have been conducted to determine hydrometallurgical processes with less setup costs which may be suitable for small scale with high metal yields. Hydrometallurgy is cheap since it requires less capital and high metal recovery but it is disadvantaged by the high level of toxic pollutants such as NO_x, Cl_2 & SO_2. Hydrometallurgy is more suitable method of metal extraction as the primary ores needed for metal refining has become lower in grade (Conard, 1992; Salgado *et al*., 2003; Mooiman *et al*., 2005; Arens & Chernyak, 2008; Sepulveda, 2010; Jadhav & Hocheng, 2015; Jadhav *et al*., 2016). Hydrometallurgy involves the use of acid or base for leaching; it may be combined with electrowinning. Examples of these acidic and basic solvents used for hydrometallurgy are hydrochloric acid (HCl), nitric acid (HNO_3), sulfuric acid (H_2SO_4), thiosulphate ($S_2O_3^{2-}$), thiourea ($(NH_2)_2CS$), sodium cyanide (NaCN). They are known to have several effects on health and environment because the acids solubilize metals and the use of sulfates to remove metals from its solid phase produces harmful sulfate-rich by-product. A large-scale release of this by-product could affect drainage systems. The use of H_2SO_4, HCl and HNO_3 or *aqua-regia* have been investigated by several researchers as very effective leaching agent for heavy metals but the gases released through this process comprises Cl_2, SO_2 and NO_x which poses threat to the persons involved in the experiment and the environment. Some other hydrometallurgical problems include solid-liquid separation difficulty and the impact of impurities during purification, time it takes to recover high amount of metals as the process is done in lower temperatures (Li *et al.*, 2010, Park *et al*., 2013, Park *et al.*, 2014).

Some researchers have considered microwave-assisted leaching as a way of improving metal extraction yield and also reducing the process time. Connel & Moe 1966 were the earliest to research the use of microwave energy for heating minerals. Microwave technology is a type of electromagnetic energy which moves through high frequency waves. The microwave energy is a non-contact form of heating also known in the family of electro-heat techniques like infrared heating, radio frequency, direct resistance and induction. It is a very selective heating that is rapid with very efficient energy transfer. It initiates quickly and also terminates quickly. Microwave energy operates within a wavelength of 1 mm to 1 m and a frequency between 300 MHz to 300 GHz. The frequency used the most for the purpose of heating is 915 MHz to 2.45 GHz. In the dissolution stage, metals can be separated if one metal is insoluble in the solvent used. To remove components from the mixture selectively the leaching process usually follows the separation process (Connell & Moe, 1966; Fleming, 1992; Mooiman *et al*., 2005; Demim *et al*, 2013a; Demim *et al*, 2013b; Demim *et al*, 2014; Leyma *et al*, 2016; Yang *et al*., 2016).

A. Solvents for Leaching

Common solvents for recovery of metals as reported by other researchers are HNO_3, HCl, H_2SO_4 and *aqua-regia*. Other solvents which are reported in the literature for the extraction of different metals consist of ionic liquids (ILs), cyanide (CN), thiosulfates, thiourea, and Ethylenediaminetetraacetic acid (EDTA). The rate of leaching can be affected by adjusting factors like temperature, stirring intensity, granularity, solid to solution ratio, acid-adding method and acid concentration. A typical leaching setup is shown in Figure 2.3. Recycling cost would benefit from reducing the sizes of the PCB as this was reported in the research by Dalrymple, 2007. (Dalrymple, 2007; Oishi *et al* 2007; Dhawan *et al.*, 2009; Jadhav & Hocheng, 2015). Acid, base and salts may be combined in varying proportions to enhance the leaching efficiency of various types of leaching agents. Consequently, the addition of reducing

agents such as SO_2 & Fe^{2+} and oxidizing agents like HClO, H_2O_2, NaClO & Cl_2 can also be used to enhance leaching process. One of the most widely used oxidizing agents is H_2O_2 because of its good properties; it is relatively versatile, powerful and safe. It is known to be stronger than potassium permanganate, chlorine and chlorine dioxide (Oh *et al.*, 2003; Havlik *et al*, 2005; Oustadakis *et al*., 2010; Shawabkeh, 2010; Jadhav & Hocheng, 2015; Wu *et al*., 2015).

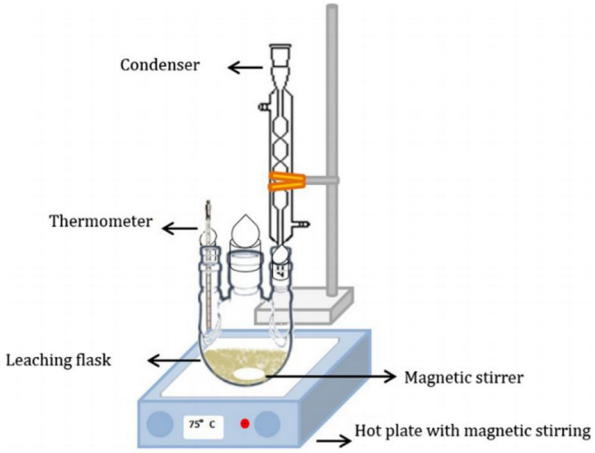


Figure 2.3 A Typical Leaching setup
Source: (Silvas *et al.*, 2015)

B. Traditional Solvents - Mineral Acids

Mineral acids are formed from inorganic compounds and when dissolved in water they form conjugate base and hydrogen ion. Dhawan *et al.*, 2009's report suggested that HNO_3 is more effective than HCl and H_2SO_4 in leaching metals from PCB. Oishi *et al* 2007 reported that a leach liquor of 45 – 50 g/L was obtained when ammonium sulphate and chloride solutions with oxidizing agent (copper ammine complexes) were used to leach PCB. Almost 100 % of zinc and copper were dissolved when a combination of 2 mol/L H_2SO_4 and 0.2 mol/L H_2O_2 were used to leach PCB at 85 ^{0}C for 8 hours. Although Habbache *et al*, 2009 reported nitrate, chloride and sulfate ions as really aggressive for metal recovery but these inorganic acids are disadvantaged as they release toxic gases (NO_x, Cl_2 & SO_2) and further purification steps are required. Metal recovery through this process is non-selective as the metals are extracted as mixed metal solutions and a further purification step is required to separate individual metals. When PCBs were shredded to less than 1mm, 95 % aluminium, iron and nickel were leached within 12 hours. Ground PCBs have also been researched by Veit *et al.*, 2005, Wu *et al.*, 2008. Other researchers have also combined complexants and oxidants to study the dissolution of copper (Oh *et* al, 2003; Du, 2004; Veit *et al.*, 2005; Dalrymple, 2007; Oishi *et al* 2007; Wu *et al.*, 2008; Dhawan *et al.*, 2009; Kumar *et al.*, 2014; Jadhav & Hocheng, 2015; Wang *et al.* 2016).

C. Traditional Solvents - Organic Acids

Organic acids are compounds composed mainly of carbon and hydrogen atoms. Examples of organic acids used for leaching are citric acid, malic, tartaric acid, and EDTA. Researchers have studied the dissolution behaviour of copper in citric acid using H_2O_2 as oxidizer. Also, glycine as complexing agent and H_2O_2 as oxidizing agent has been used for copper dissolution; copper dissolution was also studied using oxalic acid and H_2O_2 by Pandija *et al.* 2007. Organic acids are considered environmentally friendly and are attracting attention lately since they are biodegradable. The recovery of Pb and PbO from scrap battery paste has been studied by Sonmez & Kumar, 2009 using citric acid monohydrate; 4 M of citric acid monohydrate with H_2O_2 was sufficient to leach PbO_2. Citric acid is a natural acid, biodegradable and can dissolve in water with ease; it degrades in both aerobic and anaerobic conditions as it has also been used for the recovery of metals from sewage sludge. Jadhav *et al.*, 2016 research showed that citric acid and acetic acid were used to leach large PCB for 96 hours and 364 hours but poor metal slubilization was observed as only 9.89 % and 19.57 % of copper respectively was recovered. However, Li *et al.*, 2010 research recovered 100 % Li and 90 % Co using 1.25 M citric acid and 1 % vol H_2O_2 at 90 ^{0}C for 30 min and a solid to liquid ratio of 20 g/L (Seal *et al.*, 2003; Chen *et al.*, 2004; Chen & Tsai, 2004; Du *et al.*, 2004; Pandija *et al.* 2007; Sonmez & Kumar, 2009; Li *et al.*, 2010; Jadhav & Hocheng, 2015; Wang *et al.* 2016).

Biswas & Mulaba-Bafubiandi, 2016 leached oxidized ores using citric acid, oxalic and gluconic acid, 83.6 % Cu and 77.2 % Co were obtained with 0.15 M citric acid at 80 ^{0}C. Other organic acids that have been studied with H_2O_2 as reducing agent are oxalic acid by Sun & Qui, 2012 and malic acid. Ascorbic acid has been used as reducing agent along with citric acid and in the research sintered metal oxides (Cr-substituted hematites) were dissolved. Table 4.1 shows the best leaching conditions of different metals in organic acids (Manjanna *et al.*, 2001; Li *et al.*, 2012; Li *et al.*, 2013; Sun & Qui, 2012; Biswas & Mulaba-Bafubiandi, 2016).

Table 4.1 Best leaching conditions of metals in different organic acids

Leaching agent	Experimental Condition	% Extraction	Reference
1.25M Ascobic acid	70 ^{0}C, 20 min	98 % Li & 95 % Co	Li *et al.*, 2012
1M Oxalic Acid + 15 vol % H_2O_2	80 ^{0}C, 120 min	98 % Li & 68 % Co	Sun & Qju, 2012
0.1M Citric acid + 0.02M Ascobic acid	80 ^{0}C, 360 min	100 % Li & 80 % Co	Nayaka *et al.*, 2015
1.5M Succinic acid + 4 vol % H_2O_2	70 ^{0}C, 40 min	96 % Li & 100 % Co	Li *et al.*, 2015
1.25M Citric acid + 1 vol % H_2O_2	90 ^{0}C, 30 min	100 % Li & 90 % Co	Li *et al.*, 2013
0.1M Citric acid + 0.02M Ascobic acid	80 ^{0}C, 360 min	100 % Li & 80 % Co	Li *et al.*, 2013
1.5M Aspartic acid + 4 vol % H_2O_2	90 ^{0}C, 120 min	60 % Li & 60 % Co	Li *et al.*, 2013

Adapted from: (Li *et al.*, 2012; Sun and Qiu 2012; Li *et al.*, 2013; Li *et al.*, 2015; Nayaka *et al.*, 2015; Nayaka *et al.*, 2016)

D. Designer Solvents - Ionic Liquids (ILs)

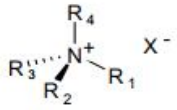
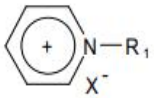
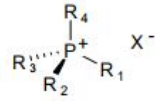
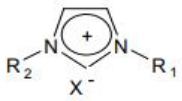
Ionic liquid (IL) is a molten salt made of cations and anions with melting points below 100 ^{0}C. ILs with below 25 ^{0}C is regarded as a room-temperature ionic liquid (RTIL). ILs have non-flammable property and a negligible low vapour pressure. They also have properties that can be tuned to suit specific purpose or design. ILs also have distribution coefficients that is enhanced. Ionic liquids have specific properties that make them unique and some of these properties are miscibility with water and organic solvents, high solubility which means they only need small reactor volumes; they have good extractability for metal ions and organic compounds, good thermal stability up to 200 ^{0}C, large spectra transparency and good solvating properties; they are easy to prepare and relatively cheap. Other properties of ILs include exhibition of Franklin acidity, Bronsted Lewis and super-acidity. ILs are very good solvents as they do not dissolve glass or polythene and are good for organic, inorganic and polymeric materials. A researcher like Kenneth R Seddon earlier predicted that IL has the potentials to revolutionize activities where liquids are used. It is a task-specific method which is faster than using traditional solvents and the process does not release toxic gases (Seddon, K.R., 1997; Suarez *et al,* 1998; Welton,1999; Visser *et al*, 2001a; Berthod *et al*, 2008; Domanska & Rekawek, 2009; Leyma et al, 2016).

The most common ionic liquids used for the separation of metal ions is 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF6], 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF6], or 1-hexyl-3-methylimidazolium hexafluorophosphate, [HMIM][PF6] or other ILs with hexafluorophosphate, PF−6 , or bis[(trifluoromethyl)sulfonyl]imide, NTf−2, anions. Ionic liquids have a character that is hydrophobic and this enables them to extract compounds that are also hydrophilic in biphase separation. However, in a system that is biphasic the extractant would remain in the hydrophobic phase to enable the removal of the metal ion from the aqueous phase. There is a challenge of determining new classes of solvents for traditional separation with the ability to partition the solvent phase quantitatively and can also complex target metal ions readily or even identifying suitable conditions for which specific metal ion species could be extracted selectively from aqueous streams which contains complexing ions that are inorganic (Seddon, K.R., 1997; Visser et al, 2001a; Domanska & Rekawek, 2009).

The combination of IL extractants have yielded improved results than molecular organic solvents in metal ion extraction. Due to the unique physical and chemical properties of ionic liquids they have been used as alternatives for solvents in various applications. ILs are also used particularly in clean technology in place of conventional solvents. The most common formulation of ILs are the imidazolium or pyridilium cations which bears a simple appendage of the alkyl cation group. The physical properties of these ILs have been achieved by altering length of the alkyl group in the ring. This allows modifying the melting points, viscosity and hydrophobicity (Gordon *et al*., 1998; Visser *et al*., 2001a; Visser *et al*., 2001b; Domanska & Rekawek, 2009).

Other aspects of ILs formulation include appendage of side chains like ions and heterocyclic aromatic molecules with complex functions and structures. However, some researches show that the use of ILs is faced with the challenge of recovering the extracted metal ions and solubilization losses. ILs can be prepared by combining bulky organic cations like 1-butyl-3-methylimidazolium or 1-butylpyridinium with a wide variety of anions with different types of anions. The variation in the anions and cations of ILs are used to control the properties of ILs. Altering the anion of ILs has been well investigated and the effect has been understood. An example is the preparation of salts based on aluminium (III) chloride which are basic, acidic and very water sensitive while those anions based like triflate and hexafluorophosphate are highly hydrophobic and neutral. However, chemical modification effect of cations in ILs has been less studied and not well understood. An increase in cation chain length is expected to alter the melting point as well as the hydrophobicity and viscosity of the liquids. Liquid crystalline phase on melting point could be formed as a further effect. 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF6] has found an increasing use as it is easy to produce and almost insoluble in water (Gordon *et al*., 1998; Visser *et al*., 2001a; Visser *et al*., 2001b; Domanska & Rekawek, 2009).
Table 4.2 and 4.3 shows the generic structure of common ILs and some selected properties. The choice of anion and the length of the alkyl chain in the cation determines the properties of alkylimidazolium ILs. The anion chosen determines the water miscibility of the IL which in turn affects the property of the liquid. Increasing the length of the cation chain from butyl to hexyl or butyl to octyl increases the viscosity and hydrophobicity of the ILs while the surface tension and density is decreased (Stepnowski, 2006).

Table 4.2 Common ionic liquids

Type of Ionic liquid & Structure	Type of Ionic liquid Structure
 Alkyammonium	 Alkylpyridinium
 Alkylphosphonium	 Alkylimidazolium

Where R_x: -CH_3 to -C_9H_{19}; X^-: $AlCl_4^-$, SbF_6^-, $CF_3SO_3^-$, PF_6^-, $(CF_3SO_2)_2N^-$
Source: (Stepnowski, 2006)

Table 4.3 Selected properties of 1-butyl- and 1-hexyl-3-methylimidazolium chlorides, tetrafluoroborates and hexafluorophosphates

Ionic Liquid	Water Solubility	Melting Point (^{0}C)	Viscosity (cP)	Temperature Limit (^{0}C)	Density g/ml)
[BMIM][PF_6]	NS	10	371	349	1.37
[BMIM][Cl]	S	41	716	254	1.08
[BMIM][BF_4]	S	-81	219	360	1.12
[HMIM][PF_6]	NS	-61	582	376	1.30
[HMIM][Cl]	S	-70	-	253	1.03
[HMIM][BF_4]	PS	-82	314	-	1.21

Where S: Soluble, NS: non-soluble, PS: Partly soluble
Source: (Stepnowski, 2006)

Imidazolium cations commonly used for the preparation of ILs can be made to possess functions that is task-specific. An example is metal legating group which could enhance the partitioning of target metal ions from water into the ILs phase. When imidazolium cations are used in less expensive ILs it also improves the partitioning of target metals. **Table 4.4** shows some physicochemical properties of selected ionic liquids (Gordon *et al*., 1998; Visser *et al*., 2001a; Visser *et al*., 2001b; Domanska & Rekawek, 2009).

Due to the unique properties like negative vapour pressure and flame resistance possessed by ionic liquids they have been highlighted as green solvents which are also alternative to conventional solvents. By combining the ion pairs of ionic liquids their physicochemical properties can be readily tunable. Also, the development of extractant compatibility with hydrophobic ILs have been developed by researchers. However, difficulty has been encountered in discovering a commercial extractant that would be soluble in ILs or in stripping metals ions from extracting ILs phase. Typical examples are the organophosphorus extractants like the di(2-ehtylhexyl) phosphoric acid (D2EHPA) and PC-88A (2-ethylhexylphosphonic acid mono-2-ethylhexyl ester) are used as extractant which separates and purifies rare earth metals since they exhibit high extraction and selectivity for rare earth metals but the solubility of these extractants in ionic liquids are still poor. However, N, N-dioctyldiglycol amic acid (DODGAA) is a phosphorus-free green extractant which was developed recently. This new extractant works well as a carrier for an IL-based membrane or as an extractant of rare earth metal in ILs. Researchers like Yang *et al*., 2012 previously confirmed that DODGAA should be suitable for extracting rare earth metals using imidazolium based IL (Freemantle, 1998; Renner, 2001; Binnemans, 2005; Sun *et al.*, 2012; Baba *et al.*, 2011; Naganawa, *et al*., 2007; Shimojo *et al*., 2007; Kubota, *et al.*, 2010; Kubota *et al*., 2011; Yang *et al*., 2012; Yang *et al*, 2013).

Alternative leaching agents which do not release toxic substances are gaining more attention. Ionic liquids (ILs) and organic solvents are some of the environment-friendly solvents useful for hydrometallurgy. There are a good number of literatures on the study of aprotic ILs but there are limited literatures on the ionicity of protic ILs. Rogers and Coworkers used 1-butyl-3-methylimidazolium hexafluorophosphate [C4mim][PF6] as extractant for Hg^{2+} and Cd^{2+} (Wei *et al.*, 2003; Li *et al.*, 2010, Park *et al*., 2013, Park *et al*., 2014).

Table 4.4 Physicochemical properties of selected ionic liquids

Class	Ionic liquid	Cation name	Melting point (^{0}C)	Density (25 ^{0}C)	Viscosity, cP (25 ^{0}C)	Solubility in water
Bis(trifluoromethylsulfonyl) amide	EMIM $NTfO_2$	1-Ethyl-3-methyl imidazolium	-17	1.52	18	N
	MM2PMIM $NtfO_2$	1,2- Dimethyl-3-propylimidazolium	15	1.46	41	N
Halogenate	EMIM Cl	1-Ethyl-3-methyl imidazolium	89	1.12	Solid	S
	BMIM Cl	1-Butyl-3-methyl imidazolium	65	1.10	Solid	S
	Na Cl	Sodium	801	2.16	-	S
	Na Br	Sodium	747	2.17	-	S
	Na I	Sodium	661	3.66	-	S
	Na F	Sodium	993	2.56	-	S
Dicyanamide	EMIM DCA	1-ethyl-3-methyl imidazolium	-21	1.06	21	-
	BMIM DCA	1-butyl-3-methyl immidazolium	-6	1.06	27	S
Tetrafluoroborate	EMIM BF_4	1-ethyl-3-methyl imidazolium	6	1.248	66	S
	BMIM BF_4	1-butyl-3-methyl imidazolium	-82	1.208	233	S
Hexafluorophosphate	BMIM PF_6	1-butyl-3-methyl imidazolium	10	1.373	400	18g/L
	HMIM PF_6	1-Hexyl-3-methyl imidazolium	-61	1.304	800	N
Perfluroalkylsulfate	EMIM TfO	1-ethyl-3-methyl imidazolium	-9	1.39	45	S
	EEIM TfO	1,3-diethyl imidazolium	23	1.33	53	-
Formate (methanoate)	EAF	Ethyl ammonium	-10	0.990	11.5	S
	BAF	Butyl ammonium	-10	0.973	22.2	S

Acetate (ethanoate)	EMIM Act	1-ethyl-3-methyl imidazolium	-20	1.03	91	S
	BMIM Act	1-butyl-3-methyl imidazolium	-20	1.06	525	S
Thiocyanate	BA SCN	Butylammonium	20.5	0.949	97	S
	DPA SCN	Dipropylammonium	5.5	0.964	86	S
Nitrate	EA NO_3	Ethylammonium	12.5	1.122	32	S
	PA NO_3	Propylammonium	4	1.157	67	S

Where S: soluble, N: non-soluble, Tfo: triflate anion or trifluoromethyl sulfate
Adapted from: (Welton,1999; Liu *et al,* 2005; Stepnowski, 2006; Berthod *et al,* 2008)

V. CONCLUSION

This paper summarized the extraction of metals from waste electrical and electronic equipment (WEEE) using traditional and designer solvents. About 54 million metric tons of WEEE are generated globally every year and the metals present in these WEEE are of high value and could be recycled instead of sending them to landfill. The initial recycling steps involve pre-treatment of WEEE such as breaking and crushing of the PCBs. Leaching is then carried out using suitable solvents. The hotplate and microwave methods could be used. The solvents most suitable to effectively extract metals are the inorganic acids but as they release toxic gases, they are not environmentally friendly. Leaching is improved with the addition of an oxidizing agent such as H_2O_2 which is safe. Organic acids are biodegradable and do not release toxic gases hence they are environmentally friendly. Leaching is also improved with the addition of an oxidizing agent such as H_2O_2 which is safe. Ionic liquids have good extraction ability for metal ions and they do not release toxic gases. Ionic liquids can be tuned to suit meet specific needs which makes it task specific. Combination of IL extractants have yielded improved results than organic acids. More research is needed the use of ionic liquids as they do not release toxic gases and they have shown promising features in extracting metals.

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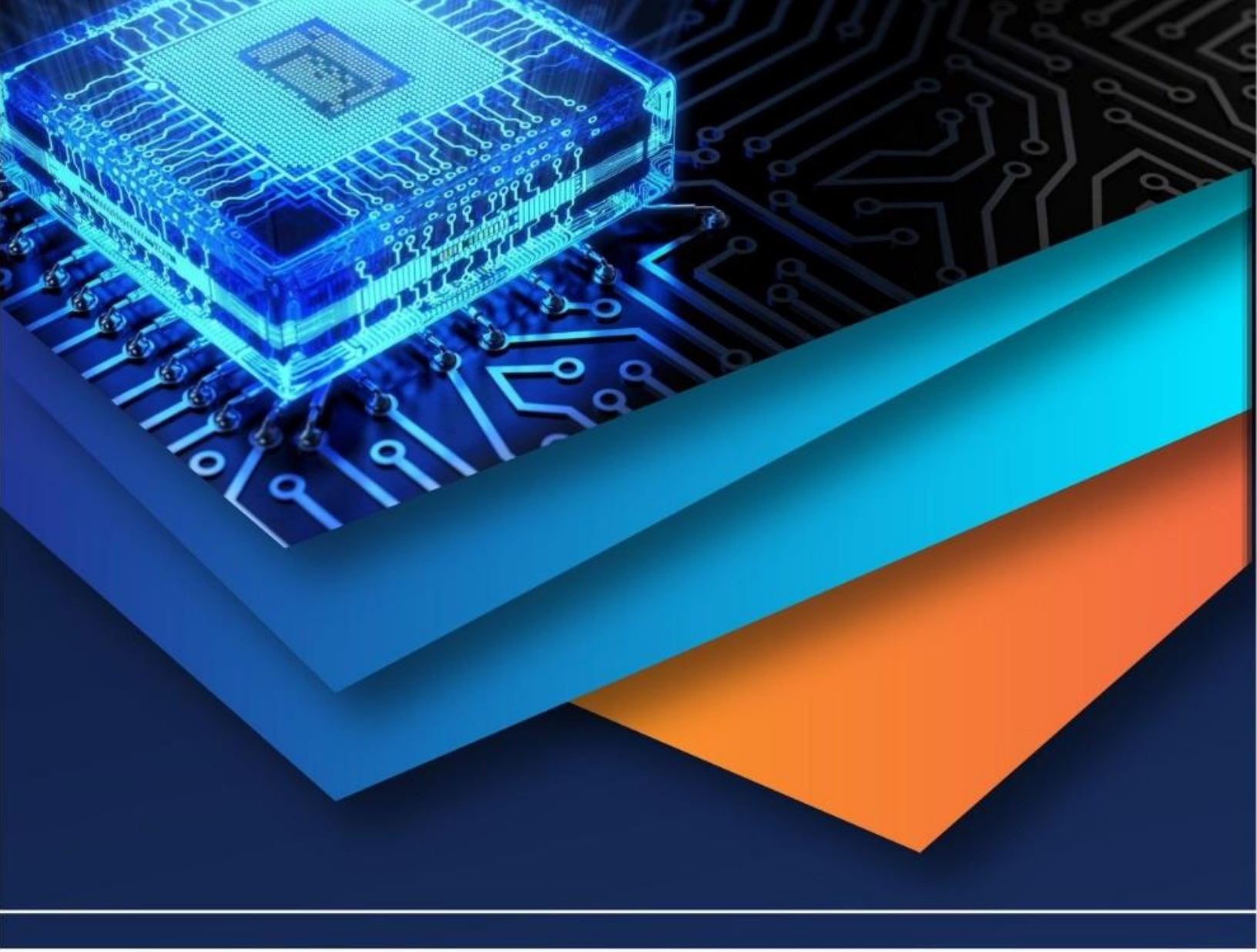

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