CHAPTER 1

Introduction

1. Introduction

1.1 E-waste: Origin and its impact

In the present era of rapid development in technology, the growth of sophisticated instruments is lucidly visible. The plethora of commonly used electronic equipment and gadgets make the human life easier by manifolds. Rapid advancement in technology on even the smallest equipment has led to the decrease in the life of the electrical and electronic equipment (EEE). With the upgradation in features of EEE like-computers, laptops, mobile/ cellular phones, printers, modems, liquid crystal display, etc.; the old gadgets are being discarded at faster rates generating enormous pile of electronic waste (e-waste).

On one front, the demand for better electronic equipment and gadget shows no sign of abating, whereas on the other side, e-waste generation has drastically increased. The world production of e- waste was 62.0 MT in the year 2022 (figure-1.1) with annual growth of 3–5% (Baldé et al., 2024). Being caught up by the growth of consumers' base and increased supply of greater variety of such WEEEs, the pile up of the e-waste becomes the spotlight for the researchers across the globe to handle it properly.

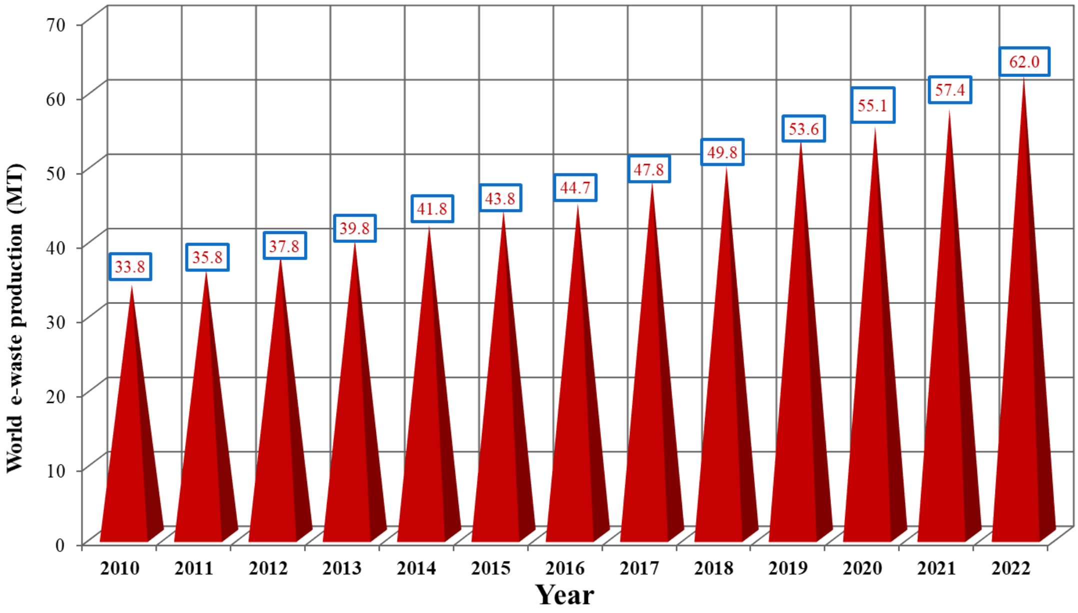

Figure 1.1-Global e-waste generation (Baldé et al., 2024; Jha et al., 2020)

According to WEEE directive (directive 2002/96/EC), any equipment which depends on electrical currents or electromagnetic field to work is listed under the category of electrical and electronic equipment. WEEE directive, Annex1A categorize following equipment under the list of electrical and electronic equipment (UNEP, 2007): 1. Large household appliances 2. Small household appliances 3. IT and telecommunications equipment 4. Consumer equipment 5. Lighting equipment 6. Electrical and electronic tools (with the exception of large-scale stationary industrial tools) 7. Toys, leisure and sports equipment 8. Medical devices (with the exception of all implanted and infected products) 9. Monitoring and control instruments 10. Automatic dispensers.

Reuse, remanufacturing, and recycling, along with burning & dumping are the foremost possibilities for the handling of e-waste at present. The hierarchy of e-waste treatment has been shown in figure-1.2. The incineration & landfilling are not environmental friendly treatment because of the hazardous material content of the e-waste. Moreover, the incineration produces dioxin and other gases due to the existence of flame retardants (FRs), chlorofluorocarbons (CFCs), and copper content (acts as catalyst for dioxin formation) in constituents of e-waste (Rao et al., 2020; Rautela et al., 2021).

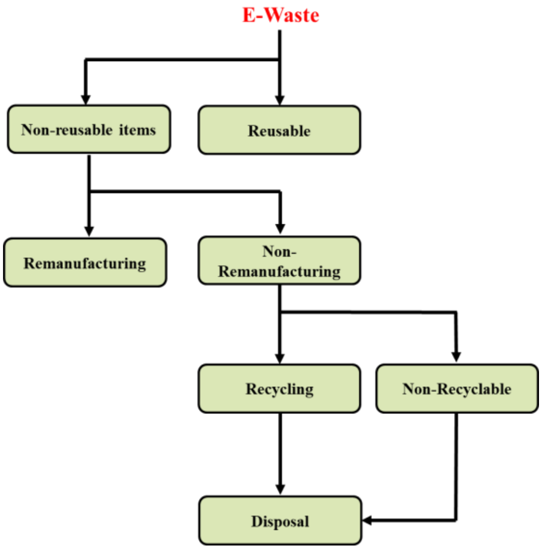

Figure 1.2- Hierarchy of e-waste management and its handling (Cui and Zhang, 2008)

1.2 Printed circuit boards

Printed circuit boards (PCBs) are essential constituents of all EEE (Xue et al., 2015). The etched copper sheets are laminated onto a non-conductive glass-fiber reinforced epoxy resin substrate and then utilized as the base plate to connect various electronic components in a regulated manner via conductive tracks; these sheets are a chief source of metallic values (Ghosh et al., 2015; Verma et al., 2016). PCBs can be one-sided, double-sided, or multi-layer structures characterized by the number of copper layers applied with the substrate (Işildar et al., 2017). Though, the PCBs are associated to all EEE, a major part of the PCBs come from the computers, laptops and mobile phone consumers only. The e-waste generated all over the world has around 3% fraction accounted as waste printed circuit boards (WPCBs) (Ghosh et al., 2015; Luda, 2011; Zong Gao et al., 2002). Taking the rapid growth of the electronic equipment into account, it is fairly justified that nearly 8.7% annual growth in WPCBs generation is observed (Ghosh et al., 2015; Ning et al., 2017). WPCBs contain metals (40%), base metals (copper, iron, tin, and zinc), precious metals (platinum, gold, silver), and hazardous metals (cadmium, lead, and mercury) along with 30% polymers (polystyrene (PS), and epoxies with halogenated flame retardants (HFRs)), 30% ceramics (SiO_2, Al_2O_3, etc.) as shown in figure-1.3.

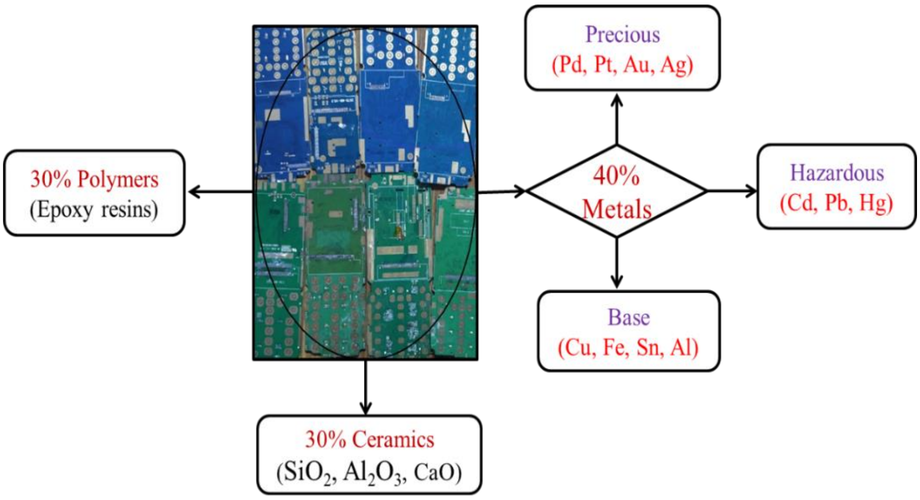

Figure 1.3- Material classification of WPCBs (Ghosh et al., 2015; Ning et al., 2017; Silvas et al., 2015; Szalatkiewicz Jakub, 2014)

1.3 Recycling of WPCBs; Secondary resources of metals

The WPCBs require recycling because these are affluent in base metals, precious and heavy metals. It has also been found that the overall amount of metals present in the WPCBs is quite large when compared to the conventional ores of from which these metals are extracted (Cui and Zhang, 2008; Kubota et al., 2018a). Table-1.1 shows the various metal content in WPCBs as reported in previous works. Taking the example of copper, it is clearly understood that around 10-30% of weight of WPCBs is metallic copper and it can be recycled to utilize it in various applications. Comparing it to the amount of copper in the chalcopyrite ore (~1% copper), WPCBs simply become a very lucrative raw material for extracting copper (Cayumil et al., 2014; Silvas et al., 2015). The proper recycling of the WPCBs is absolutely necessary because the smelting and leaching of the heavy and toxic metals such as lead, cadmium and mercury into the various resources can drastically disturb the ecosystem, harm the surrounding flora, fauna and the environment (Cayumil et al., 2018). This can have adverse effects on the complete hierarchy of the life cycle. Hence it becomes essential to recover the important metallic values present in the WPCBs and its proper handling.

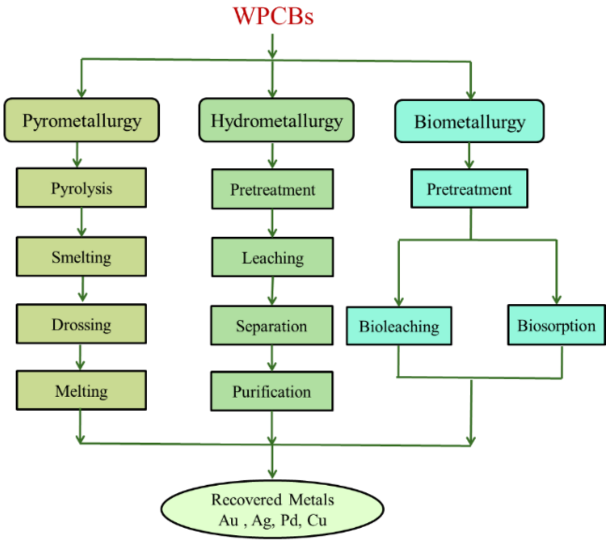

Figure 1.4- Routes of recycling of WPCBs Cui and Zhang, (2008); Iannicelli-Zubiani et al., (2017); Jadhav and Hocheng, (2015); Ning et al., (2017); Xiu and Zhang, (2012)

Table 1.1- Weight composition of some metallic elements of WPCBs from literatures

Weight (%)											
Pd	**Pt**	**Au**	**Ag**	**Cu**	**Sn**	**Fe**	**Ni**	**Zn**	**Pb**	**Al**	**Refs.**
0.01		0.023	0.06	9.7	2.15	9.2	0.69		2.24	5.8	Jinglei Yu et al.,(2009)
		0.004	0.30	32.5	0.9	1.4	0.3	0.6		3.7	Silvas et al., (2015)
0.03	0.0003	0.057	0.33	23.47	1.54	1.22	2.35	1.51	0.99	1.33	Ogunniyi and Vermaak, (2009)
		0.024	0.069	30.57	7.36	15.21	1.58	1.86	6.70	11.69	Birloaga et al., (2013)
		0.013	0.070	19.19	0.69	1.13	0.17	0.84	0.39	4.01	Behnamfard et al., (2013)
0.01		0.025	0.100	16.0	3.0	5.0	1.0	1.0	2.0	5.0	Park and Fray, (2009)

Concurring the urgency and necessity of recycling the WPCBs, many methods have been tried and studied for the purpose as shown in figure-1.4. Pyrometallurgy, hydrometallurgy and biometallurgy routes are mainly employed for the recycling of WPCBs. Fusion by melting of metallic phase of WPCBs is one of the most common methods chosen for metal extraction. The pyrometallurgical approaches to liberate and extract metals from WPCBs include incineration, plasma arc melting, blast furnace melting and drossing (Cui and Zhang, 2008). High temperature reactions and melting taking place during these operations assist the metal recovery. The main disadvantage associated with the pyrometallurgical operations is the generation of the harmful gases during the melting process (Rao et al., 2020; Sethurajan et al., 2019). This is due to the presence of the polymers, plastics, organic resins and ceramic components attached to it. The presence of lead and tin in the WPCBs leads to the generation of harmful oxides causing health disorders.

With the health hazard associated with the pyrometallurgical operations, hydrometallurgical routes are preferred to extract the metallic values from WPCBs. Just as any other hydrometallurgical operation, the process of extraction involves the leaching of metallic values in acidic or alkaline media, followed by purification process such as cementation, ion exchange, solvent extraction or membrane processes (Croft et al., 2018; Djokić, 1996; Kavitha and Palanivelu, 2012; Lozano et al., 2011; Park and Fray, 2009; Yin and Deng, 2015). . Although these methods are less hazardous as compared to their pyrometallurgical counterparts, the amount of aqueous media required for efficient extraction of metallic values is quite large. For instance, when employing solvent extraction, the process couples' extraction and stripping steps which need large volume of solution which increases the cost of process. Therefore, it is quite a trade-off between the pyrometallurgical and hydrometallurgical operations and both these routes have their inherent advantages and disadvantages.

1.4 Hydrometallurgical route for metal recovery from WPCBs

As mentioned in the previous section, few advantages of the hydrometallurgical routes over other routes are its relatively low capital cost, higher recovery of metals with relatively little energy consumption, reduced environmental impact, no dust generation and low levels of toxic gases out (Birloaga and Vegliò, 2016; Iannicelli-Zubiani et al., 2017; Jadhav and Hocheng, 2015).. Due to these advantages, hydrometallurgy is widely accepted and successful technique to recover the metals from their ores, concentrates and waste materials. Hydrometallurgical route is very successful for the extraction of the valuable metals (particularly gold and silver) from WPCBs (Eng et al., 2016). To obtain the end product this route involved various steps; leaching, purification, and recovery of metals extraction as described in figure-1.5. The pre-processing of WPCBs is one of the crucial steps before employing the hydrometallurgy route. Several researchers worked on the different kind of raw feed such as delaminated, powdered and large size WPCBs for leaching.

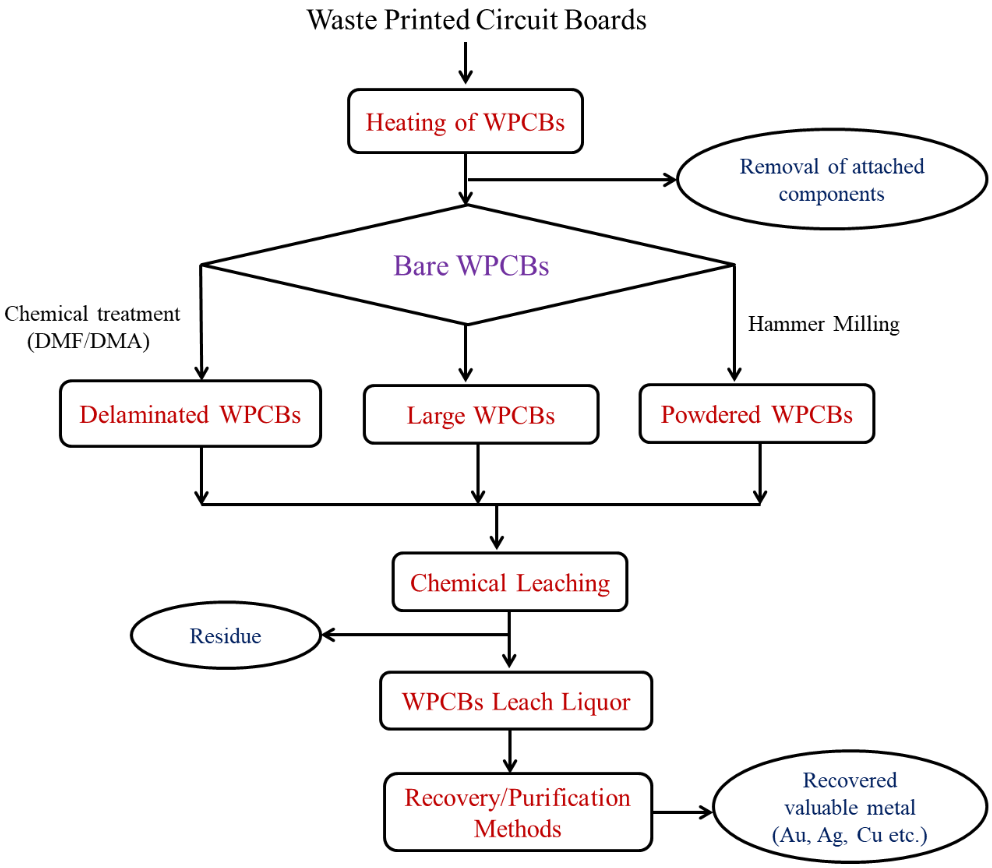

Figure 1.5- Process flow of hydrometallurgical treatment of WPCBs (Hsu et al., 2019; Rao et al., 2021b; Sethurajan et al., 2019)

1.4.1 Pre-treatment of WPCBs

With the understanding of WPCBs, the pre-treatment processes, and their applications are discussed in this section. The complex structure and heterogeneity in the composition of WPCBs is a critical factor that designs the pre-treatment processes (Li et al., 2004). Similar to conventional mineral engineering operations, the choice of pre-treatment method primarily depends on the extraction routes. For instance, delamination of metallic layers is applicable before the hydrometallurgical route, and pyrolysis is required before pyro- metallurgy. WPCBs are processed to remove the attached components. The bare WPCBs may be sent for further downsizing before the pre-treatment step. Suitable pre-treatment routes such as thermal, mechanical, or chemical treatments are followed after downsizing. The process classification is shown in figure-1.6.

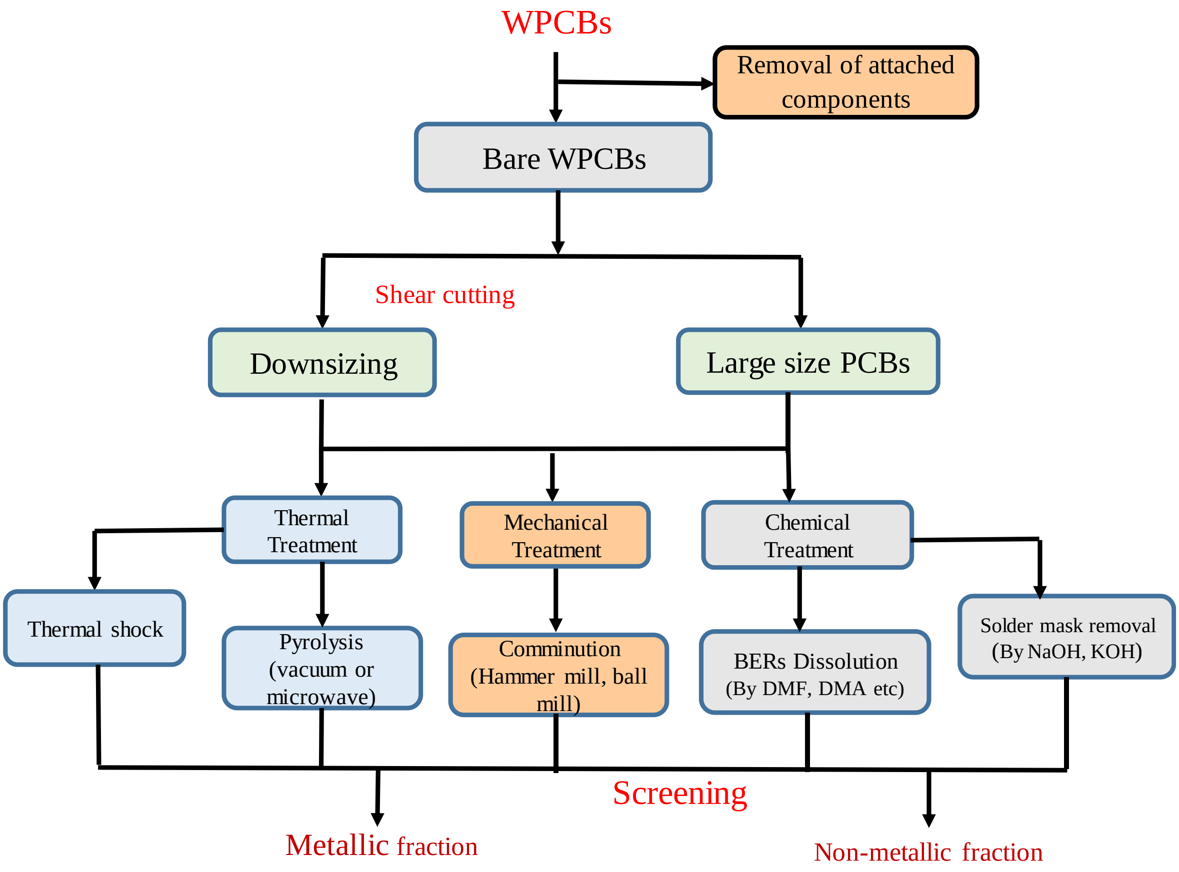

Figure 1.6-Classification of various pre-treatment processes of WPCBs (Cui and Zhang, 2008; Jha et al., 2023; Rao et al., 2020)

The most important factor that decides the efficacy of any pre- treatment process is the availability of a sorted stream of raw feed. When sorting of raw materials is performed before pre-treatment, the categorisation of the waste stream is better, and the recovery of metals is higher. The flow of the process with the sorted stream involves the selection of proper pre-treatment operation(s). The finished product of pre-treatment process will be used as the raw material for metal recovery by either pyrometallurgy, hydrometallurgy or electrometallurgy. A combination of these processes is also possible to achieve higher recovery. Post recovery, the development of valuable products is equally important, which can involve separate chemical/physical operations. To properly execute hydrometallurgical recycling, an efficient pre-treatment process is also required, that does not lead to loss of volatile material and ensures higher efficiency.

1.4.1.1 Thermal treatment

The thermal treatment uses the effect of heat energy to liberate the metallic and non-metallic fractions of WPCBs. The two chief types of thermal pre-treatment are thermal shock treatment and pyrolysis (figure-1.6). The critical difference between these processes lies in the end effect of heat and the property exploited. The working temperature (200–300 °C) is relatively lower. The components (epoxy resin, glass fibre, and metallic layer) of the WPCBs are separated due to the mismatch in the thermal expansion coefficients of individual components. The cohesive forces responsible for the strength of the epoxy resin are reduced drastically under thermal effect. Application of mechanical pre- treatment post-thermal treatment can achieve better recycling of WPCBs.

Chen et al., (2011) worked on the thermal shock method using residual steam as the heat source. It was demonstrated that steam generated at 227 °C effectively weakens the WPCBs layer; the process effectively reduces impact, tensile and flexural strengths. Similarly, Taylor et al., (2012) have found that the cracking of WPCBs layers starts at 200 °C, and the complete delamination occurs at 250 °C. WPCBs of size 100–150 cm^2 were treated at 250 ° C to get 100% liberation. Characterisation of thermally treated and untreated PCBs showed that liberation could be achieved due to a mismatch of thermal expansion among the polymeric resins and the glass reinforcement or metallic elements of WPCBs.

Liu et al., (2019) worked on thermal shock treatment parameters such as peak temperature, holding time, and thermal shock cycle times. The optimum temperature of 300 °C and 30 min of soaking time were fixed to maintain the thermal shock level and study the mechanical properties (mainly peel strength) of delaminated layers. It was concluded that the bonding strength between metallic and non-metallic could be reduced, and the separation of these two layers could be achieved 100% by manual separation after thermal shock treatment. Similarly, heating before crushing was done for liberation of metal by Yan et al.,(2020) to enhance the resultant copper content. Heat pre-treatment technology before crushing (HPBC-Around 200°C) changed the breakage mode from longitudinal fracture to horizontal fracture, thus changed the morphology of the crushed products and improved the liberation of metal from non-metal components. As noted in the other studies, the dissimilar thermal conductivities of metallic and non-metallic fractions weaken bonds between the components and improve the liberation during the crushing.

Pyrolysis is done to delaminate the WPCBs by applying higher temperatures (300-800°C) under the nitrogen atmosphere in fixed-bed reactors. The weight loss of WPCBs and energy consumption are critical parameters in choosing the pyrolysis temperature. The decomposition of organic material causes structural damage to WPCBs, and it can be confirmed by studying the weight loss at different temperatures during the pyrolysis process (Y. Chen et al., 2021). Because after a particular temperature (pyrolysis temperature), there would not be any weight loss in WPCBs. Therefore, further temperature increases may only consume energy without contributing to pyrolysis. Vacuum pyrolysis and microwave-induced pyrolysis are different forms of pyrolysis used for the treatment of WPCBs (Huang et al., 2020; Long et al., 2010). Wang et al., (2020) worked on determining the optimised pyrolysis temperature to recover copper and tin by combining pyrolysis and physical separation processes. Rapid decomposition of organic matter was reported between 290–600 °C. The weight loss of WPCBs was found to be 35.44% at 700 °C; no weight loss changes were observed beyond this temperature. Hence, the pyrolysis temperature was set to be 700 °C. The metallic and non-metallic residues were collected separately and sent for further processing. The metallic fractions were processed through different comminution, sizing, and concentration processes (gravity and magnetic separators) to recover or separate the base metals like copper and tin.

Chen et al., (2021) combined crushing with pyrolysis to recover valuable metals from the WPCBs. The recovery efficiency for Cu and Sn was found to be 92.38 and 99.80 wt.%, respectively, by crushing the WPCBs in size of 4 cm, and pyrolysis was done at 330 °C. The by-product of this process was phenol, which could be purified to use as fuel and other potential applications. Similarly, Long et al., (2010) worked on the vacuum pyrolysis and mechanical processing of WPCBs to recover various metals. The WPCBs were pyrolysed under the vacuum in a fixed bed reactor. 74.7 wt.% residues containing copper, carbon, and glass fibre along with oil and gases were obtained by this process. The oil and gases can be reused as fuel. The vertical jig-jag separator was used for the separation of copper and non-metallic reactors from the crushed WPCBs. Huang et al., (2020) compared conventional pyrolysis with microwave pyrolysis and found that the pyrolysis under microwave shows a higher weight loss of WPCBs with the same parameters. The higher weight loss signifies more organic materials of WPCBs are decomposed, which implies higher metallic recovery in leaching.

With microwave pyrolysis, 96% and 80% of copper and gold were recovered. Compared to smelting, the lower working temperature decomposes organic materials into flammable gases and liquid tar. Therefore, one expected benefit of pyrolysis is getting the by-products of oil, tar, and gas (rich in hydroxyl-benzene and other brominated aromatics) (Li et al., 2010). These by-products may be used as fuel for further applications. However, the main limitations of this process are the generation of toxic gases such as dioxins and furans formation of organo-brominated compounds (Ortuño et al., 2014). The specific processes, optimised parameters, and outcomes of various literature related to thermal pre-treatment have been shown in table-1.2.

Table 1.2-Numerous outcomes of thermal pre-treatment of WPCBs reported in various literature

Process	Optimized Parameters	Outcomes	References
Thermal shock + crushing	T-226.8 °C	• Thermal cracking of WPCBs with steam at 226.8 °C leads to a decrease in the mechanical properties of WPCBs, which helps in the separation of metallic and nonmetallic layers.	Chen et al., (2011)
Thermal shock + crushing	T-250 °C, Time:10 min.	• 100 % liberation was achieved. • Enhanced copper recovery was observed.	Taylor et al., (2012)
Thermal shock + crushing	T-226.8 °C. Time: 3 min	• Thermal cracking of WPCBs has been done by steam at different temperatures 181.8 °C, 226.8 °C, and 276.8 °C. • Thermal Cracking of WPCBs was found effective enough to increase the crushing efficiency. • Enhanced separation of metallic and nonmetallic fractions has been achieved.	Liu et al., (2019)
Heat pre-treatment before crushing (HPBC)	T-200 °C	• HPBC changed the mode of fracture from longitudinal to horizontal. • Heat pre-treatment reduces the bonding between metallic and nonmetallic components, which enhances the crushing effect on WPCBs. • 85.66 % Copper recovery rate was achieved.	Yan et al., (2020)
Vacuum Pyrolysis +Mechanical processing	T-550°C Time: 120 min.	• Vacuum pyrolysis results in 74.7 wt.% residues, 15.0 wt.% oils, and 10.3 wt.% gases on average. • Gravity separation was used for the efficient recovery of copper from nonmetallic fractions. • 99.86% copper recovery was found.	Long et al., (2010)

Burning/Pyrolysis	T-900 °C Time: 15 min.	• 35% of plastic removal efficiency was achieved at these optimum conditions. • The pyrolysis of WPCBs enhanced the copper recovery.	Havlik et al., (2010)
Vacuum Pyrolysis +Physical beneficiation	T-300 °C Time: 60 min.	• Effective separation of metallic and nonmetallic fractions was observed after vacuum pyrolysis. • 97.8% of the metallic fraction was concentrated by scrubbing/washing without using any additional additives.	Kumari et al., (2016)
Microwave pyrolysis+ leaching	T-320 °C	• Conventional and microwave pyrolysis were compared for the recovery of copper, and it was found that microwave pyrolysis yields enhanced Cu recovery (96%) from WPCBs. • 80% of Gold recovery was also achieved	Huang et al., (2020)
Pyrolysis +Physical separation	T-700 °C, under nitrogen atmosphere	• 35.44% of weight loss was observed at 700 °C. • Crushing, gravity, and magnetic separation were used for the separation of copper, iron, tin, and other base metals. • Maximum recovery (95%) of Cu was achieved.	Wang et al., (2020)
Pyrolysis +Ultra sonication	T-400 °C Time: 20 min.	• 60 wt.% of solid residue (mixed metallic and nonmetallic fractions) along with 35 wt.% combustible gases (H_2, CH_4, CO, and CO_2) were acquired. • The metallic fractions were separated by using an ultrasonic process.	Jadhao et al., (2020)
Microwave-assisted pyrolysis	T-350 °C, 450 °C, 550 °C and 650 °C. Heating time: 15 min & 30 min	• 93.3% of pyrolysis conversion took place at 650 °C. • 91.15% of phenols were present in oil at 350 °C.	Zhang et al., (2021)

While most of the researchers coupled thermal pre- treatment with a suitable recovery process, it is necessary to appreciate the importance of appropriate facilities to conduct these pre-treatment operations on a scale-up pilot setup and achieve high recovery of marketable materials. For an initial assessment, it is noteworthy to determine the capital investment essential for establishing a thermal pre-treatment, followed by a recovery process. The separation of non-metallic values from the WPCB stream post pre-treatment is also an important step to further increase the metallic concentration, adding to the overall cost of the initial investment. With these insights, it is vital to analyse other pre-treatment avenues as well.

1.4.1.2 Mechanical and physical treatment

The mechanical treatment of WPCBs involves energy- intensive comminution, screening, and concentration of metallic values. One of the objectives of the mechanical treatment of WPCBs is to reduce the particle size to provide raw feed for the further processing of metallic and non-metallic fractions. Screening and classifications are the next steps in the mechanical processing of WPCBs, which ensure the enrichment of metallic content by separating and isolating the non-metallic particles (Zhang and Forssberg, 1997).These processes play an essential role in the recovery of metallic fractions such as copper, nickel, and other valuable metals. Moreover, it was observed that up to 80% recovery of metallic fraction is possible from PCBs (Veit et al., 2002).

Crushing is essential for metal liberation, improving the efficiency of consequent leaching processes. Some of the necessary equipment in crushing involves a band saw, hammer mill, stamp mill, roll crusher, guillotine, shear crusher, universal crusher, etc., for reducing the coarse particles into fine particles (Dutta et al., 2018; Ruan and Xu, 2016). A few secondary stages based on the physical properties, such as screening, specific gravity separation, magnetic separation, eddy current separation, and electrostatic separation, also play a vital role in pre-treatment (Menad, 2016; Yoo et al., 2009). Figure-1.7 illustrates the various physical and mechanical techniques employed on WPCBs for efficient metal recovery. Veit et al., (2002) worked on crushing WPCBs and applied density differences to enrich the copper content. The WPCBs were cut into 1 mm size by cutting a mill to feed into secondary milling. Further, vibrating screens were used for separating different sized particles of milled powder. Tetrabromoethane (TBE) was used for the separation by density. It was observed that 30% of metal was separated just by size separation, while the density difference separation achieved 65% separation. A newer technique for extracting copper from WPCBs using mesophilic and moderate thermophile cultures in a rotating-drum reactor was developed by Rodrigues et al., (2015). As a pre-treatment step, hammer milling of WPCBs was done to get particles of different size ranges before employing bioleaching. First, they used a metal guillotine for WPCBs fragmentation (2 cm size) followed by hammer milling and dry sieving. A particle size of −208 µm + 147 µm was selected for further bioleaching. Another sample was crushed by using jaw crushers as a pre-weakening of WPCBs for further efficient recovery of copper. Swollen and non-swollen WPCBs were used as feed for shear crushing by Han et al., (2019). WPCBs were cut by scissors into 3×3 cm^2 and reacted with DMA solution at 100 °C water for 2 h. Swollen WPCBs were removed from the water after 2 h of span for further processing. A shear crusher was used to crunch swollen and non- swollen PCBs at the rpm of 1500 for 5 min with a dis- charge section of 0.5 mm sieve. They observed increased crushing efficiency in the case of swollen WPCBs, and the recovery of copper was also increased by 7.35% com- pared to the untreated samples. It has also been observed that crusher loss and energy consumption were less in treated sample crushing. Similarly, Zhou et al., (2016) investigated low-temperature crushing of WPCBs. A double roll crusher was used to crush the WPCBs into a 2 cm particle, and then it was placed in a cryogenic system. The temperature was maintained by injecting nitrogen along with ethanol. Cryogenic crushing was done by using a shredder after the temperature reached −20 °C. An air table was used for separating metallic and non-metallic fractions from the crushed particle. It was reported that at −20 °C, the strength of WPCBs decreased and brittleness increased, promoting crushing operation. Yan et al., (2020) used a shear force-based universal crusher for WPCBs crushing. The WPCBs were preheated to check their effect on the breakage and liberation. Heating before crushing was found suitable for altering the fracture mode (longitudinal fracture to horizontal fracture) of WPCBs. This study reported an 85.66% copper recovery rate at optimised conditions.

Various methods for pre-treatments of WPCBs were studied and compared for higher efficiency, cost-effectiveness, and viability to use at an industrial scale by Moyo et al., (2020). PCBs were cut into 2×1.5 cm^2 and fed into a hammer mill for further size reduction. About 39 wt.% loss took place during the milling of WPCBs. Unfortunately, they could not find this process as suitable as chemical pre-treatments.

Table-1.3 illustrates the outcomes associated with the mechanical and physical processing of WPCBs. In most studies, mechanical treatments were done to recover copper only. Moreover, these processes are energy intensive, increasing the overall cost of the process. In a few of the studies, it was found that mechanical treatment alone is not sufficient for higher recovery of metals. Hence, one has to perform additional chemical or thermal treatment, which increases the cost of the processes. Considering mechanical and physical pre-treatment processes, the recovery of the metallic fraction depends on the type of pre-treatment operation performed on the WPCBs. Dismantling, followed by shredding and sieving leads to the generation of various degrees of fines. A holistic organisation for utilisation of fines will be required if mechanical pre-treatment is followed.

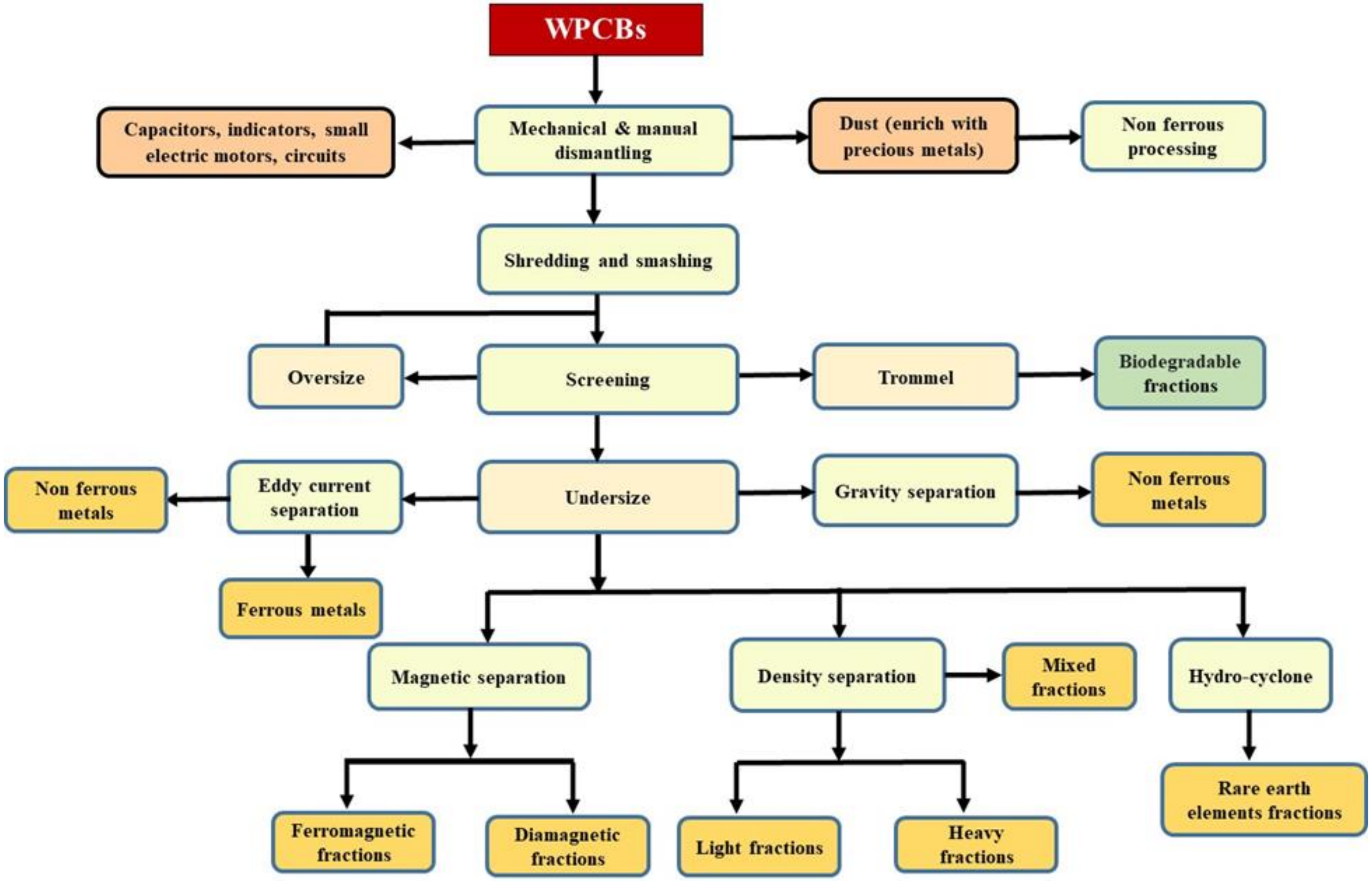

Figure 1.7- Process flow chart of various mechanical and physical treatments employed in WPCBs recycling (Y. Chen et al., 2021; Dutta et al., 2018; Nie et al., 2021)

Table 1.3-Mechanical and physical pre-treatment of WPCBs reported by various researchers

Process	Additional steps for the separation of metallic and nonmetallic fractions	Outcomes/Remarks	References
Comminution	A vibration screen was used for the size separation. Organic liquids such as tetra bromoethane (TBE) were used for the separation by density difference.	• 30 % of metallic fractions recovery by size separation. • The difference in density separation obtained 65% metallic fractions of total weight. • Focused on mainly Copper recovery	Veit et al., (2002)
Stamp Milling	The concentration of base metals was done by gravity& magnetic separation	• 95 % of metallic fractions were separated by a jig-jag classifier. • 83% nickel and iron were recovered as metallic fractions and 92% copper in nonmetallic fractions in magnetic separation.	Yoo et al., (2009)
Hammer milling & Jaw crushing	Dry sieving was used for getting different particle size fractions.	• Improved metal recovery yield during bioleaching • Jaw crushing was used as a pre-weakening step before the hammer milling of WPCBs.	Rodrigues et al., (2015)
Crushing	Cryogenic grinding was used for further reduction in the size of WPCBs coarse particles.	• The reduction in strength and increase in brittleness of the WPCBs layer was observed at -20 °C, and this increases the crushing efficiency. • The power consumption in crushing can be reduced by cooling WPCBs, and it also increases the liberation of metallic fractions.	Zhou et al., (2016)
Crushing	Dimethyl acetamide (DMA) was used as an organic swelling reagent.	• The chemically treated WPCBs required a relatively low load to crush.	Han et al., (2019)

		• A combination of chemically treated and crushing PCBs may reduce energy consumption, crusher loss and increase crushing efficiency. Therefore, the overall cost of the process may also get reduced	
Crushing	Heat pre-treatment was done before crushing	• Pre-heating of WPCBs decreases the bonding between nonmetallic and metallic components. Hence, it increases the crushing efficiency. • 85.66% of copper was recovered.	Yan et al., (2020)
Hammer milling	A band saw was used for cutting WPCBs.	• 39% loss of the sample was observed after hammer milling. • A few of the pieces were still completely locked in the copper foil layers. • Around 10% of copper was lost in hammer milling. The more significant mass loss while milling may be due to the absence of any filter.	Moyo et al., (2020)
Impact hammer milling	A band saw was used for cutting WPCBs. Air and water fluidization was employed for the separation of metallic and nonmetallic fractions.	• Physical separation processes were used for the hydrometallurgical recovery of gold and copper. • The air and water fluidization process was found effective for the separation of toxic nonmetallic fractions from the hammer-milled WPCBs powder.	Barnwal and Dhawan, (2020)
Hammer Milling	An abrasive wheel cutter was used for cutting WPCBs. Leach liquor was prepared for copper purification.	• 94% of WPCBs were crushed at a 3kg/h feed rate within 7 minutes. • 43 wt. % of copper was found along with nonmetallic fractions in quantitative analysis.	Verma et al., (2018)

1.4.1.3 Chemical treatment

Earlier in this section, thermal and physical pre-treatment processes were discussed. WPCBs contain various layers, including solder mask coatings, which protect the metallic layer (Kang et al., 2021). Also, the solder mask or the chemical coatings on the WPCBs don't allow the leaching reagent to penetrate through it to recover valuable metals (Jadhav and Hocheng, 2015). Therefore, different chemicals having sufficient potential to remove the solder mask or dis- solve the brominated epoxy resins (BERs) are used in chemical treatment methods. In most of the studies, strong alkalis such as sodium hydroxide and potassium hydroxide were applied for the removal of the solder mask from the metallic layer of WPCBs (Adhapure et al., 2014; Ippolito et al., 2021; Moyo et al., 2020; Yildirir et al., 2015)..

In one of the studies on the bioleaching of metals from WPCBs, it was observed that the bioleaching was restricted by the solder mask layer on the metallic part because the solder mask does not permit the bacteria to enter through it; the bacteria fail to reach the metal. Therefore, removing these chemical coatings (solder mask) is necessary before the bioleaching. Adhapure et al., (2014) used 10M Sodium hydroxide to remove the solder mask just before exposing the bacteria on the metallic layers. Similarly, Jadhav and Hocheng, (2015) worked on large size (4×4 cm^2) WPCBs to recover valuable metals through the hydrometallurgy route. They identified that the leachate was unable to penetrate through the solder mask. Thus, WPCBs were dipped in 10M NaOH and left overnight. The WPCBs were washed to remove the adhered NaOH, and the pH value of irrigated water confirmed the complete removal of NaOH. It ensured the removal of the solder mask. Various solvents such as NaOH, KOH, acetic acid, ethanol, acetone, and diethyl ether for the removal of the chemical coating were evaluated by the group of Yildirir et al., (2015). A simple depolymerisation process at different temperatures with different solvents, including water was evaluated for removing chemical coatings for WPCBs. It was found that the minimum and maximum resin dissolution took place with acetone and NaOH, respectively. Acetone and ethanol were inappropriate for completing depolymerisation of WPCBs up to 300 °C. Further raising the temperature didn’t show any further dissolution of resins. Moreover, higher temperatures caused ethanol to decompose in hydrogen and methane-rich gases. Finally, NaOH was suggested as the most effective reagent for the removal of solder masks from WPCBs. Moyo et al., (2020) worked on various pre-treatment techniques of WPCBs to check their feasibility for industrial scale. They found that the pulverised WPCBs effectively remove the surface coating and get the delaminated metallic layer. However, this process is not advisable to carry on a large scale due to associated health hazards. In addition, a combined method of band saw cutting of WPCBs and soaking with NaOH for the removal of the solder mask was found to be suitable and recommended pre-treatment for further processing. Recently, a novel work on epoxy coating removal from WPCBs was done by Ravi et al., (2021).They used an autoclave (121 °C with 1.07 bar) with different concentrations of NaOH (0.25 M to 4 M) and reported 100% epoxy removal from WPCBs metallic layer without any additional soaking time as earlier practice. NaOH consumption is relatively lower, and regeneration of NaOH is also possible in this method. However, working under autoclave conditions may add some cost to the process and make it costly. In one of the other chemical methods, the dissolution of halogenated epoxy resin substrate (HERS) from WPCBs is also very effective for separating metallic fractions (figure-1.8) This process is mostly used in the hydrometallurgical recovery of metals.

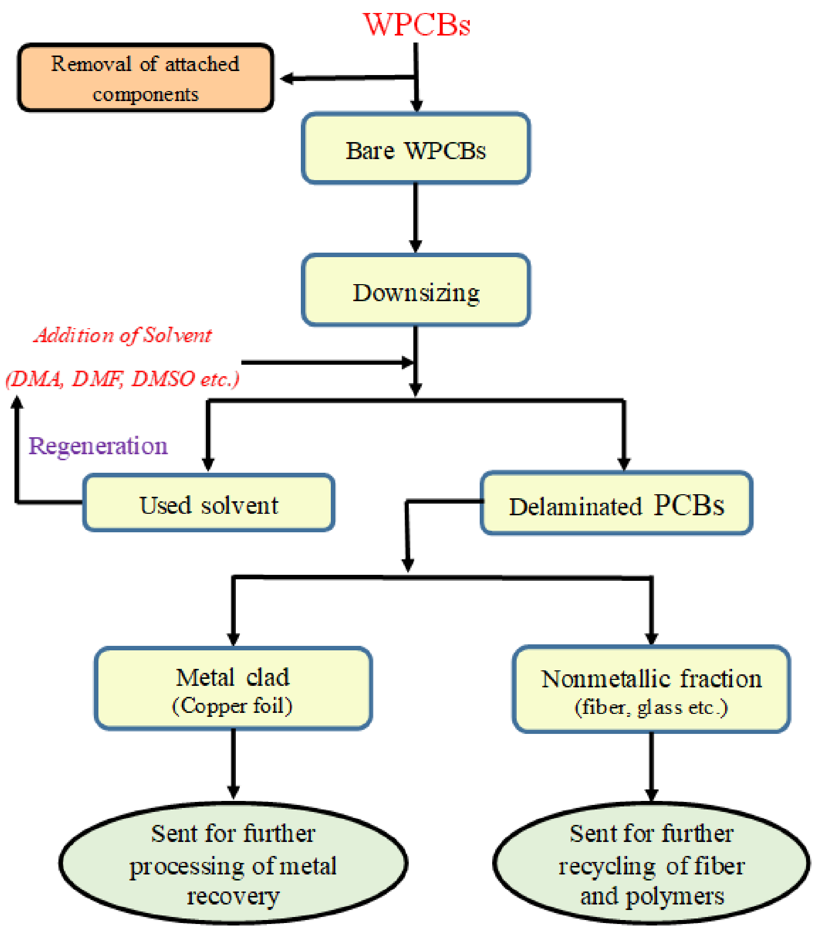

Figure 1.8- Process flow of delamination of WPCBs by the dissolution of BERs (Verma et al., 2016; Wath et al., 2015)

Numerous organic solvents such as N-methyl-2-pyrrolidone (NMP) and dimethyl sulfoxide (DMSO), dimethylacetamide (DMA), dimethylformamide (DMF) were used for the effective delamination of WPCBs (Verma et al., 2017a, 2016; Wath et al., 2015). Zhu et al., (2013) developed a novel, clean and non-polluting method to separate metallic layers from the WPCBs .They used DMSO as a solvent to dissolve the brominated epoxy resins (BERs) from WPCBs. 4×4 mm^2 size WPCBs were delaminated within 1h on optimum condition (Solid/liquid (S:L)-1:7, temp-145°C). Moreover, the DMSO may be regenerated by using rotary evaporation.

Wath et al., (2015) worked on separating metallic fractions from WPCBs by dissolving the BERs using NMP and DMSO. NMP was found better for the dissolution of BERs and completely separating the metallic and non-metallic fractions. It was also found that both solvents dissolved the BERs without reacting with the metals. Moreover, the regeneration of these solvents makes this process cost-effective and commercially viable at a larger scale.

The BERs dissolution potential of DMF and DMA were studied in the work of Verma et al., (2016) and Verma et al., (2017b). The different parameters were studied for the optimisation of delamination, and they found that the delamination of WPCBs is directly dependent on the temperature and the solid–liquid (WPCBs: DMA/DMF) ratio at the same time, it varies inversely with the size of WPCBs. It was also observed that the increase in the WPCBs size hinders the BERs dissolution. The process flow sheet indicating BERs dissolution for the delamination of WPCBs has been shown figure-1.8. It was revealed that BERs dissolution took place due to the breakage of internal van der Waal's bonds of BER at elevated temperatures, and this bond breakage is responsible for the hydrogen bond formation between BERs and DMA/DMF. Therefore, the BERs are transferred in the solvent (DMF/DMA), and delamination of multi-layers of WPCBs takes place.

The comparative study of both DMF and DMA reported by Verma et al., (2017a) shows that the DMA is more effective in dissolving the resin than DMF for the different sizes of WPCBs at optimised parameters. As per the chemistry of dissolution, the slow delamination rate by DMF may be due to slow hydrogen bond formation in the case of DMF. Moreover, it has been revealed that the regeneration of DMA and cyclic usages of DMA may reduce the process cost. Supercritical water oxidation (SCWO) treatment is one of the attractive methods in WPCBs recycling. Water is non-polar in the case of supercritical conditions because of weakened hydrogen bonding (Ding et al., 1998; Huang et al., 2000). Hence, organic compounds, oxygen, and water form a single phase, which permits oxidation to proceed quickly. In supercritical water, most poisonous organic species can rapidly oxidise to carbon dioxide and water in a short residence period (Martino and Savage, 1997; Xiu et al., 2015).

Chien et al., (2000) reported the feasibility of WPCBs oxidation with NaOH in supercritical water. They found that the oxidation of WPCBs was improved in the presence of NaOH and 63.2% of bromine from the BERs was observed in the liquid phase. In contrast, solid residue contained the oxides of copper (Cu_2O, CuO) and copper hydroxide ($Cu(OH)_2$). Xiu and Zhang, (2009) used SCWO for WPCBs pre-treatment for decomposing organic components before applying an electro kinetic process. The polymers in WPCBs were decomposed into water and carbon di oxide at optimum conditions (713 K, 30 MPa) within 60 min. Copper and lead were found in solid residue as their oxides form (CuO, Cu_2O and β-PbO_2). However, they observed the incomplete oxidation of copper in the present process.

Xing and Zhang, (2013) used a batch-type reactor to perform sub- and supercritical water (sub/SCW) to recover metals. BERs were decomposed rapidly and efficiently in the sub/SCW process. 97.8% of de-bromination was achieved at 400 °C within 120 min. It was observed that most of the Br gets changed in HBr, and Br free oil was obtained as a by-product. Glass fibre and metallic fractions (mostly Cu foil) were sent for further processing. A total of 98.11% recovery rate was obtained after employing the current process. In one of the pre-treatment processes, Xiu et al., (2013) explored two approaches, namely supercritical water oxidation (SCWO) and supercritical water depolymerisation (SCWD) under SCW for decomposing the organic materials of WPCBs. They found that SCWO is relatively efficient in concentrating copper and lead from WPCBs. Moreover, the decomposition efficiency in SCWD was lower at the same conditions used for SCWO. It was concluded that SCWO had a noteworthy improvement in the recovery of copper and lead but needed to be found suitable for the recovery of tin and chromium. The outcomes of various chemical pre-treatment routes have been illustrated in Table-1.4

Table 1.4-Assessment of several chemical pre-treatments used to separate metallic and non-metallic fractions of WPCBs.

Method used	Raw Materials (Chemical/solvent)	Optimized Process Parameters (S/L, Temp (°C) Time (min))	Outcomes	References
Solder mask removal	NaOH,	NA	• The chemical coatings were removed by sodium hydroxide for unrestricted leaching of metals from WPCBs. • Solder mask removal was found efficient for the large-size WPCBs treatment.	(Adhapure et al., 2014; Jadhav and Hocheng, 2015)
	NaOH & KOH	NA, 300-400, 1440	• The presence of NaOH and KOH improved the resin removal efficiency. • 94% resin removal was achieved with NaOH along with water at 400°C	Yildirir et al., (2015)
	NaOH WPCBs size (5 cm×5 cm and 2 cm×1.5 cm)	NA, 25-30, 1440	• Different sizes of WPCBs were treated with NaOH to remove the solder mask. • NaoH removed the solder mask and exposed the copper clads. • WPCBs of 2 cm×1.5 cm size shows more effective result in exposing copper clads, and it was found as the potential process for further recycling of WPCBs.	Moyo et al., (2020)
	NaOH WPCBs size: 3 cm × 3 cm	NA, 121, 60	• NaOH treatment with autoclave conditions was employed for the solder mask removal. • The epoxy coating was removed within 1h of treatment. • The autoclave conditions eliminated soaking time for WPCBs treatment, and 100% epoxy removal was achieved at optimized parameters.	Ravi et al., (2021)

	NaOH	NA, 25-30, 480	• Sonication was used after soaking of WPCBs in 5N NaOH. • Sonication has been proven as an efficient technique in terms of no toxic gas generation and reduced time (5 min) for epoxy removal.	Loganath and Meenambal, (2018)
Dissolution of BERs	Dimethyl sulfoxide WPCBs Size: 4 mm x 4 mm	1:7; 145, 60	• DMSO was found to be a suitable solvent for the dissolution of BERs from WPCBs. • Secondary environmental pollutants (bromine volatilize) were not generated in the current process. • Slightly increase in temperature decreases the delamination time.	Zhu et al., (2013)
	Dimethyl sulfoxide	1:2; 170, 30		Zhu et al., (2013a)
	N-methyl-2-pyrrolidone (NMP) WPCBs Size: 4 mm x4 mm	1:5, 100, 90	• A comparative study of BERs dissolution from WPCBs has been done by using two solvents; NMP and DMSO. • NMP was found superior in terms of BERs dissolution for the separation of metallic and nonmetallic fractions. • Regeneration of both solvents could be achieved efficiently.	Wath et al., (2015)
	dimethyl sulfoxide (DMSO) WPCBs Size: 6 mm x6 mm	1:2, 90, 90		
	Dimethylformamide WPCBs Size: 10 mm x10 mm, 20 mm x20 mm, 30 mm x30 mm.	1:3.3; 135, 240	• WPCBs with different sizes were evaluated, and DMF was found appropriate for dissolution of BERs under optimized conditions. • 20 mm x 20 mm were delaminated within 180 min under optimized parameters. However, 10 mm x10 mm and 30 mm x30 mm required 240 min to get separated into copper foil.	Verma et al., (2016)

	Dimethylformamide WPCBs Size: 10 mm x10 mm	1:3.3; 160, 180	• It has been proven that the increase in WPCBs size retards the rate of BERs dissolution. • An increase in temperature may increase the rate of dissolution. Hence, it reduces the total dissolution time. • Regeneration and cyclic use of DMA may reduce the overall cost of the delamination steps.	Verma et al., (2017)
	Dimethylacetamide WPCBs Size: 10 mm x10 mm 40 mm x40 mm 90 mm x90 mm 160 mm x160 mm	1:3.3; 160, 140–420	• The current study showed that WPCBs of 10 mm^2, 40 mm^2, 90 mm^2 and 160 mm^2 area may be excellently delaminated within 150, 180, 300, and 420 min of reaction time, respectively, with DMA. • Larger-size WPCBs may also be delaminated by using the DMA without prior treatment. • The current study of delamination was found as environmentally friendly and cost-effective for setting up the e-waste recycling plant.	Verma et al., (2017b)
Supercritical fluid treatment	NaOH in Supercritical water	NA, 320-520, 5-10	• Oxidation of WPCBs in supercritical water in the presence of NaOH was found suitable for the dissolution of resins. • Copper was found in oxides/hydroxide form in solid residue, while 63.2% of Br was retained in liquid.	Chien et al., (2000)
	30 wt.% H_2O_2 with water	NA, 370-440, 15-120	• Two processes, supercritical water oxidation (SCWO) and supercritical water depolymerization (SCWD) were employed for the resin dissolution from WPCBs. • 99.8% Cu and 80% Pb were recovered at working temp 420°C.	Xiu et al., (2013)

			• SCWD process was employed to recover Sn, Zn, Cr, Cd, and Mn at 440°C. • The process doesn't show the recovery of any precious metals.	
	30 wt.% H_2O_2 with water	NA, 440, 60	• The process was found suitable for the recovery of Cu and Pb. • Copper and lead were oxidized into CuO, Cu_2O and β-PbO_2. • The electrokinetic process was used as a post-treatment step for the recovery of Cu and Pb from the solid residue produced by the SCWO process.	Xiu and Zhang, (2009)
	Sub and supercritical water WPCBs size:100 mm x 15 mm	1:4, 200-400, 30-240	• 97.8% of de-bromination took place at the optimized parameters (400 °C, 1:4 g/ml, and 120 min). • Most of the bromine was changed into HBr, and bromine-free oil was recovered as a by-product of this process. • The current process recovered 98.11% Cu.	Xing and Zhang, (2013)
	30 wt.% H_2O_2 with water	NA, 370–450, 15–150	• The current study demonstrates the recovery of precious metals by using SCWO pre-treatment process. • The optimum parameters used in the SCWO process are 420 °C and 60 min for Au and Pd and 410 °C and 30 min for Ag. • Hydrochloric acid leaching was used as post-treatment for the recovery of copper and the isolation of precious metals from the solid residue generated by the SCWO process.	Xiu et al., (2015)

All pre-treatment processes have their limitations. For instance, thermal treatment could produce poisonous gases, mechanical treatment requires a lot of energy, and some chemical treatment techniques require more time, all of which increase the cost of processes. Justifying a specific method for achieving a higher metal recovery will require process optimisation and cost analysis. Overall, the chemical pre-treatment processes are promising and efficient for recovering valuable metals from the WPCBs and detoxifying and removing BERs/ BFRs. Most chemical pre-treatment processes are economically and environmentally feasible and consume less energy. However, researchers should focus on the reduction of reaction time in chemical treatment and also focus should be on liquid waste minimisation.

1.4.2 Leaching

The most commonly used leaching reagents are sulphuric acid, nitric acid and aqua regia for copper leaching from WPCBs (Jha et al., 2011; Kumar et al., 2014). However, to recover precious metals like gold and silver, cyanide, halide and thiosulphate leaching is carried out (Ficeriová et al., 2011; Petter et al., 2015). Kumar et al., (2014) worked on the acid leaching behaviour of metals from WPCBs; they used H_2SO_4 and HNO_3 as leaching agents for 2–4 mm size WPCBs containing copper, tin, lead, and aluminium. They found that HNO_3 leaching was more effective than sulphuric acid with H_2O_2 as an oxidiser for copper leaching at optimum conditions (800 rev min^{-1} stirring speed, and 90 °C for 5 h). The extensive work on the leaching of base and precious metals together from WPCBs has been done by Ficeriová et al., (2011). They used crushed WPCBs as raw material for the leaching of metals. H_2SO_4 with H_2O_2 was used for the leaching of base metals such as zinc, iron, aluminium, nickel etc. with optimum conditions shown in Table 1.5. To recover gold and silver, ammonium thiosulphate leaching was done, whereas aqua regia was used for the leaching of palladium. A summary of different leaching reagents used for leaching base and precious metal has been shown in Table 1.5. Xiu et al., (2015) used SCWO pre-treatment, followed by hydrochloric acid leaching to generate two solutions such as one containing precious metals along with tin and another solution containing base and hazardous metals. Iodine–iodide leaching was performed next, for the complete removal of tin. The resultant solution contained gold, silver and palladium.

Table 1.5-Chemical leaching techniques used for metal recovery from WPCBs

Raw Material	Leaching Reagent	Leaching Parameters (Stirring Speed, Temperature & Time)	Metal leached	Ref.
Shredded WPCBs & metal chips	H_2SO_4 in the presence of H_2O_2	800 rpm, 90 °C, 5 h.	96% copper	(Kumar et al., 2014)
WPCBs	H_2SO_4 containing 15% H_2O_2	NIL, 150 °C, 1.5 h	97.01% copper	(Jha et al., 2011)
Shredded WPCBs	HNO_3	500 rpm, 30 °C, 2h	99.9% copper	(Rao et al., 2021a)
WPCBs	$H_2SO_4 + H_2O_2$	500 rpm, 80 °C, 8h	76 % zinc, 85 % copper, 82 % iron, 77% aluminum, 70 % nickel	(Ficeriová et al., 2011)
Crushed WPCBs	NaCl	500 rpm, 25 °C, 2h	88 % lead 83% tin	(Ficeriová et al., 2011)
WPCBs	$CS(HN_2)_2 + H_2SO_4$	500 rpm, 45 °C, 2 h	32% silver	(Gurung et al., 2013)
WPCBs	$CS(HN_2)_2 + Fe^{3+} + H_2SO_4$	500 rpm, 50 °C, 2 h	68% gold	(Gurung et al., 2013)

Scrap Integrated circuit	$CS(HN_2)_2$+ $Fe_2(SO_4)_3 + H_2SO_4$	150 rpm, 20 °C, 24 h	100% gold 100% silver	(Lee et al., 2011)
Crushed WPCBs	$(NH_4)_2S_2O_3$+ $CuSO_4.5H_2O + NH_3$	500 rpm, 40 °C, 48 h	98 % gold 93 % silver	(Ficeriová et al., 2011)
Crushed WPCBs	HCl + HNO3	500 rpm, 25 °C, 2h	90% palladium	(Ficeriová et al., 2011)
WPCBs	$CS(NH_2)_2$+ $Fe_2(SO_4)_3 + H_2SO_4$	200 rpm, 25 °C, 1 h	90% gold 75% silver	(Birloaga and Vegliò, 2016)
WPCBs mounted with electronic components	1-butyl-3-methyl-imidazolium hydrogen sulfate	250rpm, 70 °C, 2h	100% Copper	(Huang et al., 2014)
WPCBs	1-carboxymethyl-3-methylimidazolium bisulfate ([CM-MIM]HSO4)	--, 80 °C, 2h	98.30% Copper	(Zhang et al., 2018)

Various ionic liquids (ILs) such as 1-butyl-3-methyl-imidazolium hydrogen sulfate, N-sulfobutylpyr- idinium hydrosulfate, 1-sulfobuty-3-methylimidazolium hydrosulfate etc. have also been used specifically to recover both valuable and hazardous metals from WPCBs (Chen et al., 2015; Oke and Potgieter, 2024; Zhang et al., 2018). Huang et al., (2014) explored the leaching of copper and other essential metals from WPCBs using a Brønsted acidic ionic liquid, 1-butyl-3-methyl-imidazolium hydrogen sulfate, [BMIM][HSO4]. The copper leaching rate exceeded 99%, approaching 100%, when 1 g of WPCB powder was processed under optimal conditions: particle size of 0.1–0.25 mm, 25 mL of 80% (v/v) ionic liquid, 10 mL of 30% hydrogen peroxide, a solid/liquid ratio of 1/25, at 70 °C for 2 hours. A study by Chen et al., (2015) research team investigated the leaching characteristics of copper and lead in DPCBs using various acidic ionic liquids as leaching agents. After optimization, they achieved an impressive copper leaching rate of nearly 100.0%, while lead had a significantly lower leaching rate of less than 30.0%. Under specific optimal conditions, which included a 30.0% concentration of hydrogen peroxide, a solid-to-ionic liquid ratio of 1:20, a temperature of 80.0 °C, and a duration of 2.0 hours, similar results were observed.

Several groups worked on the organic acids such as oxalic acids, citric acids etc. for leaching of base metals from the WPCBs (Jadhav et al., 2016; Krishnamoorthy et al., 2021; Nagarajan and Panchatcharam, 2023). Jadhav et al., (2016) explored a combination of citric acid (0.5 M) and 1.76 M hydrogen peroxide (H_2O_2) for leaching of base metals from WPCBs. Recently, Nagarajan and Panchatcharam, (2023) and team had also worked with organic acids such as citric and acetic acids for designing cost effective route of metal leaching from WPCBs. A 3 × 3 cm^2 piece of WPCB was fully leached in 24 hours at 30 °C using different concentrations of citric acid, acetic acid, and hydrogen peroxide. One major drawback of organic acid leaching is that its kinetics are slower compared to inorganic acids. Additionally, organic acids require oxidants, such as H_2O_2, which makes the overall process more expensive.

1.4.3 Conventional techniques of metal recovery

One of the simplest, most profitable, and widely accepted processes for the recovery of metal from leachate is cementation. Metals with high reduction potential are used to cement those with lower reduction potential, leading to cementing of the metals. Usually, the ions present in the aqueous solution are reduced over the surface of the reductant to render the cathodic cementation of the target metal. Fe (0.41 V), Zn (−0.76 V), and Al (−1.66 V) are the most preferred cementing agents because of their standard reduction potential (Li et al., 2018). A typical electrochemical reaction that takes place during the cementation process is shown in eq-1.1. where M^{n+} and M^0 are the ionic and metallic forms of noble metals and N^0 and N^{m+} signify the same entities for reductive metals.

$$mM^{n+} + nN^0 = mN^{m+} + nM^0 \qquad (1.1)$$

where, M^{n+} and M^0 are the ionic and metallic forms of noble metals and N^0 and N^{m+} signify the same entities for reductive metals.

Since the 1890s, Merrill-Crowe Process is the commercially accepted procedure for the recovery of Au and Ag from cyanide leach solution employing Zn as the cementing agent. In the process, pregnant leach solution is passed through the shavings of Zn to precipitate out the target metal, taking the advantage of high affinity of Zn for cyanide ions as well as low reduction potential of Zn (Fleming, 1992). The major reactions that take place during the cementation of Au are shown in the following equation (1.2):

$$2\mathrm{Au}\ (\mathrm{CN})2^- +\ \mathrm{Zn} \rightarrow 2\mathrm{Au} + \mathrm{Zn}\ (\mathrm{CN})4^{2-} \qquad (1.2)$$

However, impurities such as lead, arsenic, nickel, antimony and sulphur present in the leach liquor are detrimental for the cementation of gold. Besides that, too low concentration of cyanide into the solution might lead to the formation of passive layer of $Zn(OH)_2$ over the surface of Zn, that hinders the further reaction (Cui and Zhang, 2008).

Deveci et al., (2016) have examined the consequences of different metals on the cementation of Ag. More than 90% of Ag has been recovered using metallic Zn and Cu, whereas cementation of Ag by Al was limited to only 40.4% even after 2000-fold excess of dosage. The lower recovery efficiency onto Al might be attributed to the effect of passivation of aluminium surface by formation of oxide.

Kamberovi, (2018) have employed a two step phase separation for cementing Ag from WPCBs leachate solution. A total of 96.8% of Ag has been successfully recovered using this novel approach.

Birloaga and Vegliò, (2016) have applied counter and cross current leaching followed by cementation for the extrcation of gold, silver and copper from WPCBs solution. In counter-current leaching, the WPCBs and the leaching reagent flow in the opposite direction This method is designed to maximize efficiency by maintaining a concentration gradient along the leaching process. However, the WPCBs and leaching reagent flow in same direction in the case of cross counter leaching. Cross counter leaching may result in lower efficiency due to reduced concentration gradients over time. High recovery grade (99.76%) of copper with good purity (87-89%) is reported by introducing zinc with an excess of 50% by the stoichiometric ratio. Also, the recovery of Au and Ag has been >80% and ~50% respectively from acid thiourea leach solution.

Sodha et al., (2019) have developed an eco-friendly, bearable, and closed-loop system for the cementation of Cu from bio-leachate of WPCBs. The recovery of Cu has been reported to be 99% with a purity of 93% with the use of iron scrap. The study indicated diffusion of cementing chemical species as the chief rate controlling factor for cementation of Cu.

Quinet et al., (2005) have examined the cementation of Pd using aluminium and copper as cementing agent from chloride leach solution. Using Cu, the recovery yeild was reported to be poor, whereas Al provides yield of ~ 98% of Pd depositon. The two major disadvantages of cementation process encountered in the recovery of metals are the passivation of cementing metal due to formation of oxide or hydroxide layer over the surface inhibiting further electrochemical reaction and excess consumption of sacrificial metal (Li et al., 2018).

Several researchers have worked on the precipitation of various metals such as gold, copper from leach liquor using some precipitants such as triphenyl phosphine oxide (TPPO), tertiary diamide and quaternary ammonium salt etc (Nag et al., 2023; Nogueira et al., 2023; Vance et al., 2024). Nag et al., (2023) studied the selective precipitation of gold from hydrochloric acid using TPPO and also investigated the precipitation of copper using 2,3-pyrazinedicarboxylic acid (2,3-PDCA). By combining these two methods, they successfully recovered 99.5% of the gold and 98.5% of the copper found in the connector pins of end-of-life computer processing units. Nogueira et al., (2023) focused on using quaternary ammonium salts, such as tetrabutylammonium nitrate, to precipitate gold from e-waste solutions, achieving a recovery rate of 70%. The yield of precipitation was influenced by the Au-to-ionic liquid ratio, acid concentration, and the structures of the resulting precipitates.

Ion-exchange process employs a cation-exchange polymer resin to recover a given metal from a leach liquor containing multiple metal ions (Gomes et al., 2001). Similar to the carbon in column (CIC) adsorption, ion exchange does not require high temperature for elution of target metal. An interesting observation is reported in the ion exchange process involving 3D printed meshes and columns of nylon-12 with leach liquor of aqua regia. These meshes and columns have amide-group scavengers are intrinsically and ~78% $[AuCl_4]^-$ has been observed. 99% gold recovery was achieved by Several wash stages using dilute nitric acid (Lahtinen et al., 2017).

Kim et al., (2011) worked on the selective separation of gold from e-waste. They proposed an innovative method, which includes chlorine gas as an oxidant in an HCl leach stream. In that, the copper was separated first, followed by gold recovery (99.99 % purity) by ion-exchange.

In one of the recent works on ion exchange processes, Neto and Soares, (2021) worked on the chlorination process for gold recovery from WPCBs. In first step, copper and other base metal were recovered and then ion exchange method was employed. DOW™ XZ-91419.00 and Purogold™ A194 resins were used for the gold recovery. DOW™ XZ-91419.00 resin was capable to extract gold with 94% pure gold with small contaminations of lead and tin. However, 92% of pure gold was recovered by using Purogold™ A194. silver, lead and palladium was as a major contamination in this case. (Neto and Soares, 2021)

The chief advantages of ion exchange process include less equipment and operation cost coupled with very low energy requirement. The resin beds are utilized for multiple cycles for the many years with nominal maintenance. The chemicals required for regeneration of organic resins are cheap and easily available. The major drawbacks of the process are soaking of organic matter, organic fouling from the resin, bacterial impurity and chlorine desecration.

Solvent extraction is an alternative and a measurable procedure for the selective recovery of a certain metal from a feed containing various metal in feed (Izatt et al., 2014; Wilson et al., 2014). A significant feature of this process is the growth of very selective extractant that can separate single metal from an aqueous phase (containing multi metal ions) into another extractant (organic) phase, so maximizing chemical sustainability and reducing the number of extraction stages. This is imperative for the recycling of WPCBs, where the concentrations of gold and silver are very less compared to the concentrations of base metals. Selectivity is attained through coordination and molecular chemistry principles by designing carriers that can distinguish among the various metal ions on the basis of dimensions, charge and shape (Carson et al., 2015; Turkington et al., 2012; Wilson et al., 2014).

Common carriers for copper are the hydroxyl-oximes including aldehydes and ket-oxime (Eng et al., 2016) and widely used extractants are existing under the brand names of LIX and ACORGA (Deep et al., 2010). In addition to the oximes, organophosphorus acids and carboxylic acids are also used to extract other base metals by monitoring the pH of the aqueous solution (Chauhan and Patel, 2014). Similarly, for the solvent extraction of gold from halide leach liquor, viable reagents such as isobutyl methyl ketone (MIBK), diethylene glycol butyl ether or (2-EH) 2-ethylhexanol (DBC) can be used, though these reagents show selectivity, safety and mass balance issues (Doidge et al., 2016). Recently, the primary organic amide along with secondary and tertiary variants have been reported to provide excellently high selectivity and extraction of gold from mixed metal solution of a mobile-phone leachate (Narita et al., 2006; Rao et al., 2021b). Enemona and Felix, (2023) investigated a solvent extraction route using bis(2,2,4-trimethylpentyl) phosphinic acid (Cyanex 272) for recovering copper and iron from computer WPCBs. Under optimal conditions temperature of 25±2 °C, a 1:2 phase ratio, and a leaching time of 30 minutes, they achieved recoveries of 96.80% for copper and 97.1% for iron, with pH levels of 4.6 and 3.4, respectively.

With recent advances in the conventional methods of recycling of WPCBs, better efficiencies have been reported. However, a complete recovery is still not achieved in terms of purity level of metal recovered, cost of the production etc. The focus of research has expanded to the complementary processes, serving in complete recovery of metallic values from WPCBs.

1.5 Polymer inclusion membrane process for metal recovery

Separation and recovery systems employing the liquid membranes have been introduced about 40 years ago (Almeida et al., 2017). Supported liquid membranes (SLMs) have been extensively accepted for the removal of metal species among the various types of liquid membranes (Bulk liquid membranes, Emulsion liquid membranes) (Fontàs et al., 2005; Nghiem et al., 2006), however, the shorter life of the membranes under industrial operations limits its further employment in diverse applications. The loss of the membrane takes place due to the operations on the aqueous phases on both ends (Lozano et al., 2011).

PIMs were synthesized and classified as solvent polymer membrane (SPM) (Goldman et al., 1963; Sugiura, 1981). The primary application of these membranes were as a sensing component in an optical chemical sensor (Optode) and Ion-selective electrodes (ISEs) (Bakker et al., 1997; Suah et al., 2015, 2014; Suah and Ahmad, 2017). Upon further examination of the stability and versatility of these PIMs in comparison to the other liquid membranes, the notion of utilizing it as separation media came forth. PIMs were first applied in the field of waste water handling for the selective elimination of metal species from waste water (Goldman et al., 1963). In the present day, one of the main applications of PIMs is to remove and extract metal species from various streams of waste (Kubota et al., 2018a; Ogunniyi and Vermaak, 2009). These membranes are eco-friendly and are easily used for separations of heavy and toxics metals from aqueous solutions (Cristina Veronica I. Gherasim et al., 2011). Also, PIMs are simple to design, have great selectivity and their application is quite lucrative (Sellami et al., 2019). The extraction and stripping of the metal ions is relatively uncomplicated (Kubota et al., 2018a; Wang et al., 2017). The PIMs basically involves complexation and de-complexation reactions to transfer the metal from feed phase to strip phase (see section-1.6).

PIMs can be prepared at laboratory scale by dissolving all these components; polymer, plasticizer and extracting agent in an appropriate solvent like Chloroform and Tetra hydrofuran. These solvents are subsequently evaporated slowly and the leftover residue is the desired membrane. Figure-1.9 shows Schematic representation of PIMs preparation. It is essential to inspect the consequence of various components on the separation and transportation of the target metal ions to select the correct set of compatible components of the membrane to make sure its superior extraction factor.

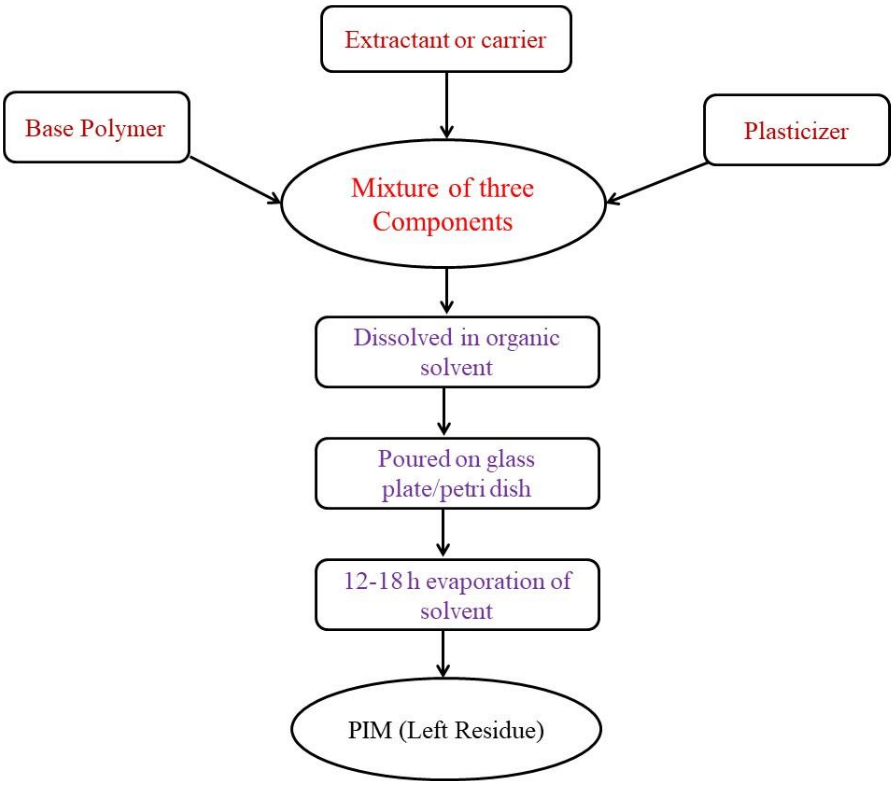

Figure 1.9- Schematic representation of synthesis of polymer inclusion membrane (Jha et al., 2020; Kavitha and Palanivelu, 2012a; Zaheri and Ghassabzadeh, 2017)

1.5.1 Base Polymer

The base polymer of the PIMs provides the mechanical strength to the membrane (Nghiem et al., 2006). In the preparation of PIMs, a thermoplastic polymer is used that has its polymer chains attached mutually by fragile physical bonds. The complication of the long polymer chains and the intermolecular fragile forces is responsible for providing the mechanical strength of the polymer (Cristina Veronica I Gherasim et al., 2011; Pośpiech and Walkowiak, 2007). The PVC, CTA and PVDF-HFP are the commonly used polymer for PIMs synthesis (Cristina Veronica I Gherasim et al., 2011; Yildiz et al., 2014). These polymers impart sufficient strength and have higher compatibility with the extracting agent, compared to other polymers. PVC based PIMs are exceptionally stable in both basic and acidic solutions and show an outstanding mechanical strength with greater elasticity (Cristina Veronica I Gherasim et al., 2011; Witt et al., 2018). Also, PIMs based on PVC polymers are more resistant to chemical attacks than PIMs based on CTA. The mechanical strength is admirable for CTA-based PIMs because of the inherent crystalline structure (Cristina Veronica I Gherasim et al., 2011). Kebiche et al.,(2010) developed PIMs with different types of polymer matrix and carrier, Tri octyl methyl ammonium chloride known with its commercial trade name Aliquat336. CTA and PVC (three different molecular masses) as base polymer were used for this transportation purposes. The consequence of various polymer matrixes on the transport of Chromium ions was explored in this experiment. It has been found that the transport efficiency of the membrane was not much influenced by the nature of the base polymer and membranes based on PVC with the lowest molecular mass showed the best extraction efficiencies during the transport and extraction of Chromium ions from acidic sulphate liquor in the existence of Cadmium, Zinc, Cobalt and Nickel ions. Yaftian et al., (2018) conducted the experiment for the selective separation of vanadium(V) from its sulfate solutions by implementing PIMs in the presence of Cu(II), Mn(II), Fe(III), Mo(VI), Co(II), Al(III) and Ni(II). They used neutral and solvating extractant namely Tri hexyl (tetradecyl)phosphonium chloride (well-known by its trade name Cyphos® IL 101) and two different base polymers (PVDF-HFP and PVC) for the preparation of membrane. They made a comparison between two different polymeric based for the recovery of V (V) and found that PIMs with the base-polymer PVDF-HFP showed better result than PIMs based on PVC by the means of extraction efficiency and amount extracted. Sellami et al., (2019) developed a membrane with the use of base polymer Cellulose triacetate (CTA) and Poly (butylene adipate-co-terephthalate) (PBAT) for the selective recovery of Cr(IV). They use Aliquat336 as carrier for this purpose. Almost all chromium with a recovery factor of 91.5% was transported selectively to the stripping phase from the solution containing other heavy metal ions such as cobalt, cadmium, and lead. In a recent work of Wang et al., (2019), a PIM was developed with the use of base polymer PVDF with plasticizer 2-NPOE. This membrane was used for the recovery of gold ions from alkaline solutions. For the evaluation of membrane stability, this membrane was reused for 10 cycles. Therefore, the recovery factor of gold was found 82%, which was remain same till 9th cycle. At the 10th cycle the recovery of gold was decreased by 3.5-4%. They proved that the stability of the present PIMs with [A336][SCN] as the carrier and PVDF as the polymer matrix was superior to that of the PIMs system and a majority of the SLM systems previously reported. Recently, several studies have been done in the field of PIMs devoted to modify the base polymer and its functional behaviour by using various new structures. Various polymers such as Cellulose Acetate Butyrate (CAB), Cellulose Tri Benzoate (CTB) and Cellulose Acetate Phthalate (CAP) have been explored with different carriers and plasticizers (Almeida et al., 2012; Shahira et al., 2018).

1.5.2 Extracting agent

The major function of the extracting agent in PIMs is to act as an Ion-Exchanger (complexion agent). It also provides selectivity of the membrane in extracting the target metal ions. It has been proven by the investigations that metal ions transport cannot occur without the extracting agents. Also, the extracting agents are accountable for binding with the ions of interest from the aqueous solution and also helps during its transportation across the membrane (Almeida et al., 2012; Shahira et al., 2018).There are many types of extracting agents used in the metal ion extraction studies: basic, acidic and chelating, neutral and solvating and macro-cyclic and macromolecular; Basic extracting agent is majorly amine based compounds with higher molecular mass such as quaternary ammonium compounds (Aliquat336/capriquat) and tertiary amines (trimethylamine, EDTA). Aliquat336, a commercial solvent extraction reagent has been used widely as the extracting agent in metal ion extraction using PIMs because of its plasticizing properties. Apart from serving as extracting agent, Aliquat336 acts as a plasticizer and there is no requirement of additional plasticizer in presence of Aliquat336 in PIMs (Shahira et al., 2018; Yildiz et al., 2014). Polat et al., (2016) synthesized PIMs using base polymer

(PVC) and the extractants Tri-iso octyl amine (TIOA) to recover Cadmium ions from simulated Ni-Cd battery leaching solution in H_2SO_4 and potassium iodide (KI). It has been found that the increased concentration of TIOA increases mass flux of Cadmium ions, however an extra increase of TIOA hinders the permeability of the target ions because the formation of additional layer between the feed and PIM which leads to the diminution in the mass flux of Cd(II). Similarly, the acidic and chelating extractants are applied in PIMs for the metal ions extraction. In this type of extractants the metal ion is exchanged with the hydrogen ion in extractants. There are several compounds that fall under the category of acidic and chelating extractants such as carboxylic acids, thiophosphorus acid esters, phosphinic acids, sulfonic acid compounds (Nghiem et al., 2006; Shahira et al., 2018). Kolev et al.,(2009) reported PIMs based on base polymer PVC and use of D2EHPA as extracting agent for the selective and quantitative extraction of Zinc ions with the existence of various metal species, such as Cu(II), Co(II), Cd(II), Fe(II) and Ni(II) from acidic chloride solutions. In the present experiment, D2EHPA, an acidic and chelating carrier was used which itself has plasticizing properties so no additional plasticizer is requisite for the preparation of PIMs. The membrane composition was containing 45% D2EHPA and 55% PVC. John et al., (2012) developed PIMs with different commercial extracting agents such as Aliquat 336, TBP, D2EHPA and Cyanex 272 with base polymer PVC to test the ability for the elimination and extraction of uranium ions from its sulfate solutions (acidic). They found that the membrane with composition of D2EHPA and PVC (with 40:60) was to be better in its capability to recover uranium ions in contrast with the other PIMs studied. Neutral and solvating extracting agents are phosphorous based extraction reagents having high selectivity towards the actinides and lanthanides. These extracting agents are used to recover heavy metals. Commercially available neutral or solvating carriers are phosphonium ionic liquid (IL), TBP, TOPO, and di-butylbutylphosphonate(DBBP) (Nghiem et al., 2006; Shahira et al., 2018). Bayou et al., (2010) have produced a CTA-base PIM containing TOPO and NPOE carrier for the extraction of uranium and molybdenum. It has been reported that the efficiency of transport of uranium and molybdenum is higher in PIM when compared to the SLM with the same carrier. The transport efficiency also increases by a factor of five for PIM with TOPO extracting agent vis-à-vis SLM. Macrocyclic and Macromolecular type carrier has outstanding selectivity by means of extraction and also form stable complexes with the different types of molecules (cations, anions and neutral). Crown ethers, Calix crowns, calixarenes and cyclodextrins are the few examples of Macrocyclic and Macromolecular extractant (Shahira et al., 2018). Benosmane et al., (2009) used derivatives of calixresorcinarene in PIMs and performed experiments for transportation of Zn, Pb and Cd ions from their aqueous liquor. Kozlowski and Kozlowska, (2009) have developed PIMs using bis-PNP-lariat ethers as extracting agent, NPPE as a plasticizer with the base polymer CTA. They used it for competitive transport of Zn(II), Pb(II) and Cd(II). It has been shown that extraction of Zn(II), Pb(II) and Cd(II) took place more proficiently than ordinary PNP-lariat ethers. Different types of extracting agents employed for the preparation of PIMs and subsequent recovery of target ions are shown in table 1.6.

Table 1.6-Classification of extractants employed for recovery of the target ions.

Extractant	Example	Target ions	Ref.
Basic	Aliquat 336	Co(II) Cr(IV)	Yildiz et al., (2014) Agaya et al.,(2017)
	TOA	Cr(VI) Cu(II), Co(II), Ni(II)	Kozlowski et al.,(2002)
	TIOA	Cu(II), Co(II) , Ni(II)	Pośpiech and Walkowiak, (2007)
Acidic and Chelating	D2EHPA	Cr(IV) Zn(II)	Kolev et al., (2009) Croft et al., (2018)
	Cyanex 272	In((III)	Gyves et al., (2008)
	LIX 841	Cu(II)	Kumar et al., (2011)
Neutral and solvating extractant	TBP	Cd(II), Pb(II)	Arous et al., (2017)
	Cyphos® IL 101	Zn(II), Fe(II), Fe(III) Fe(II), Fe(III)	Baczyńska et al.,(2016) Baczynska et al.,(2015)
	Cyphos®IL 104	Zn(II), Fe(II), Fe(III) Fe(II), Fe(III)	Baczyńska et al.,(2016) Baczynska et al.,(2015)
Macrocyclic and Macromolecular	Calix[4]-crown-6	Zn(II), Cd(II), Pb(II)	Ulewicz et al., (2007)
	1-Alkylimidazole	Cu(II)	Radzyminska-lenarcik and Ulewicz, (2012)
	Proton ionizable lariat ether	Zn(II), Cd(II), Pb(II)	Małgorzata Ulewicz, (2006)

1.5.3 Plasticizers

Plasticizers are used to improve the flexibility of the membrane, retention of the metal species and subsequent transportation of these species across the membrane. Plasticizers are organic compounds which are the combination of extremely solvating polar groups and hydrophobic alkyl backbone (Cristina Veronica I Gherasim et al., 2011). The main function of hydrophobic alkyl backbone is to establish the compatibility of the plasticizer with the PIMs while the interaction of the base polymer takes place by the solvating polar groups and hence "counterbalance" them with its own polar groups. Therefore, the most important factor is to maintain equilibrium between the polar and non-polar part of the molecules of plasticizer for improved plasticizing properties. The plasticizers enter inside the chains of the polymer and increase the distance between them and this reduces the intermolecular forces (Nghiem et al., 2006). The necessary properties often required for the good plasticizer is it must have high dielectric constant, good affinity with the base polymer and also plasticizer must be low volatile, less viscous (Shahira et al., 2018; Witt et al., 2018). The immovability of metal ion complexes produced in the membrane part is determined by the dielectric constant and viscosity of the chemicals. If the high dielectric constant media are used, then the ion separation takes place efficiently. It balances the efficiencies of involvement and separation of the metal species from supply to receiving phase (Fontàs et al., 2005). The most commonly used plasticizers are Dibutylsebacate (DBS), Bis(1-butylpentyl) adipate (BBPA), NPOE and NPPE. Yildiz et al., (2014) used PIMs for the recovery of copper, nickel, cadmium and Cobalt ions from solutions. They prepared PIMs using Plasticizers; NPOE, NPPE and also investigated the consequence of membrane thickness on the recovery factors for cobalt and cadmium. They concluded that if thickness increased, the extraction would decrease. PIMs frequently contains an supplementary plasticizer but there is possibility to prepare it without additional plasticizers but a loss of their extracting and transporting properties is experienced in such cases (Almeida et al., 2012; Cristina Veronica I Gherasim et al., 2011). It is notable that numerous extracting agents like quaternary ammonium salts (Aliquat336) and phosphoric acid esters can also function as plasticizer. Consequently, in this type of cases, no supplementary plasticizers may be essential (Nghiem et al., 2006; Shahira et al., 2018). Gherasim et al., (2011) prepared PIMs without use of plasticizers the membrane was containing only the polymer PVC and the extractant D2EHPA. PIMs characterization showed that D2EHPA itself behaves as a plasticizer of the PVC network and it was also concluded that the absence of plasticizers from PIM reduces the price compared to the plasticized ones. The combination of various base polymers, extracting agent and plasticizers from previous work has been summarized in table-1.7. The successful application of PIMs for removal and transport of metal ions from waste water showed a potential to researchers for the utility of PIMs for WPCBs.

Table 1.7-PIMs applied for the separation and recovery of target ions reported by various researchers.

Polymer	Carrier	Plasticizer	Target ions	Ref
CTA	Cyphos® IL-101	NPOE	Fe(II), Fe(III)	Figueira et al., (2000)
CTA	Cyphos® IL-104	ONPOE	Cu(II), Cd(II)	Mack et al., (2007)
CTA	Cyphos® IL-104	ONPOE	Cd(II)	Pospiech, (2015a)
CTA	D2EHPA	DOP	Cu(II)	Kavitha and Palanivelu, (2012)
CTA	Aliquat336	NPPE	Co(II)	Yildiz et al., (2014)
CTA	Cyphos® IL-104	ONPOE	Cu(II), Cd(II)	Pospiech, (2015b)
CTA	TOA	NPPE	Cu(II), Co(II), Ni(II)	Pośpiech and Walkowiak, (2007)
CTA	D2EHAG	DOP	Co(II)	Baba et al., (2016)

PVC	D2EHPA	-	In(III)	Meng et al., (2017)
PVC	Aliquat336	-	Cr(IV)	Agaya et al., (2017)
PVC	Aliquat336	-	Au(III)	Argiropoulos et al., (1998)
PVC	D2EHPA	-	U(VI)	St John et al., (2012)
PVD-FHP	LIX841	NPOE	Cu(II)	Wang et al., (2017)
PVD-FHP	Cyphos® IL-101	NPOE	V(V)	Yaftian et al.,(2018)
PVC	D2EHAG	2-NPOE	Au(III)	Kubota et al., (2018)

1.6 Potential of PIMs in recycling of WPCBs

The recovery of metals from WPCBs has been the subject of attention due to its reuse in the WEEE industries. From a financial and environmental point of view, recycling of WPCBs becomes very essential. Solvent extraction, ion exchange, cementation processes are considered efficient to recover the metals from WPCBs. However, the application of membranes by hydrometallurgical route for the removal of metals has concerned significant interest for green technology and monetary reasons. Growth in the recovery of metals from the liquor leads to the replacement of conventional solvent extraction techniques, SLMs and other separation techniques with PIMs because of the extensive stability with negligible carrier loss and easy design and operation of PIMs (Pośpiech and Walkowiak, 2007).

Figure-1.10 shows Schematic representation of transport mechanism of metal ions through PIMs in two compartment cells in which the combine extraction and back extraction processes take place. Leached liquor of WPCBs is used as the feed phase and H_2SO_4 as strip phase as an example for better understanding of the transport mechanism by the schematic diagram. The metal ions exchange via the membrane phase take place during the transport process across PIMs and the removal of metal ions is not restricted by the conditions of equilibrium.

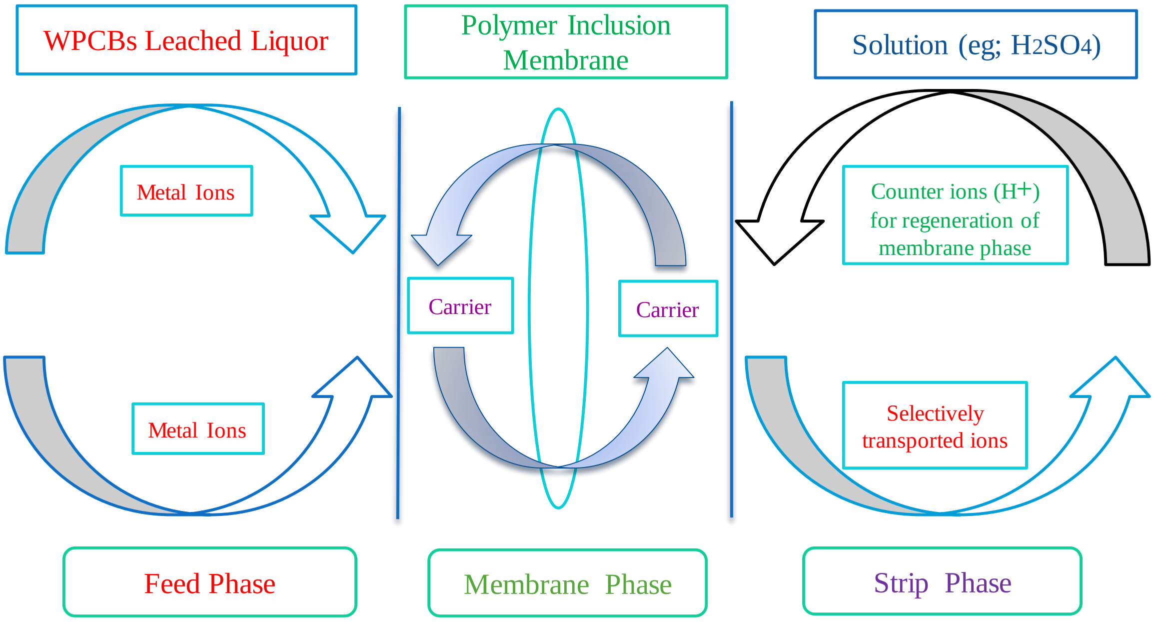

Figure 1.10- Schematic representation of transport mechanism of metal ions from leached liquor of WPCBs using PIMs

Kavitha and Palanivelu, (2012) performed the experiments to inspect the capacity of polymer inclusion membranes in the WPCBs treatment. For the synthesis of the membrane they used base polymer CTA, alkyl phosphoric acid carrier (D2EHPA) and DOP as a plasticizer. It has been observed that no transport of ions from feed to the strip phase occur without a carrier which specifies that the carrier concentration had a considerable effect on the metal ion transport across the PIMs. The transportation and recovery of copper from the feed aqueous solutions is achieved successfully by the use of carrier with different concentration. They concluded that the transfer of copper ions increases as the D2EHPA concentration increases and it is also possible to use the PIMs many times for the transportation experiment. In their experiment, more than 99% copper ions were recovered (in the presence of heavy metals such as cadmium, lead, nickel) after 7-8 h membrane transport process with different conditions of feed, strip and membrane phase.

Argiropoulos et al., (1998) developed PIMs with PVC as base polymer and Aliquat 336 as a carrier for the extraction of gold from WPCBs digested in aqua regia. The process has limitations such as diluting the aqua regia to a lower concentration and stripping of Au(III) from PIMs. The use of SLMs, Kelex100, Cyanex921, Thiacalixarenes, and ω-thiocaprolactum has revealed that gold can be selectively recovered from HCl solution in the occurrence of other metal ions. The stripping of the gold from the membrane is the key challenge associated with this process. They proved that an alternative technology PIMs eliminate the use of toxic, volatile and flammable diluents, which is used in the conventional solvent extraction processes and also PIMS magnificently disables back extraction issues related with the use of other PIM-based systems.

Guo et al., (2011) used a bifunctional ionic liquid with various concentrations of cyphos® IL 104 in PVC based PIMs which can extract both cations and anions simultaneously but, in this technique, the stability of the membrane is the main limitation. To overcome the above disadvantage, Bonggotgetsakul et al., (2016) developed a highly stable PVDF and PVDF-HFP based PIMs with cyphos® IL 104 for the extraction of gold from aqua regia. Cyphos$^{®}$ IL with approximate 35% provides flexible, homogeneous, and transparent PIM along with shape retaining property. At its higher concentration, phase separation of PIM takes place due to incompatibility. Addition of plasticizers such as 1-dodeconol, NPOE to the PIM has proven to help and improve the compatibility and the overall percentage of recovery of metallic ions (Guo et al., 2011). Finally, Bonggotgetsakul et al., (2016) optimized PVDF-HFP with 30 % cyphos® IL 104 as the best PIMs for the removal of gold along with 100 % back extraction capability with PVDF possesses excellent chemical and thermal resistance and good mechanical strength along with successful compatibility with thiourea or thiosemicarbazide that further enhances the strength for better recovery of gold from the solutions (Amosova et al., 2004).

Li et al., (2015) developed a membrane which is PVDF grafted with thiosemicarbazide in different weight ratios to extract gold ions from aqueous liquor. The used membrane can be easily reactivated by thiourea acidified with HCl and used separately for three times without any loss of membrane properties. The sensitivity of the membranes was also studied by filtrating tap water to capture the trace amount of gold. This is more selective for silver over gold, so silver recovery could do first followed by gold.

Kubota et al., (2018) investigated the appropriateness PIMs (PVC-based) with the extracting agent D2EHAG and plasticizer 2NOPE to separate the gold ions from leach liquor of redundant mobile phones. They concluded that the PIMs showed the enhanced selectivity and extraction factor for gold ions in comparison to the equivalent solvent extraction system. Approximately, 96 % gold ions were selectively transported and recovered from feed phase to strip phase in 48h in the presence of several metal ions such as platinum, palladium, zinc, lead.

Overall, this technique has a very high potential to overcome the drawbacks of existing techniques and thus further exploration will prove as a critical milestone in the field of e-waste recycling by a relatively energy efficient way and low environmental concerns. Table-1.8 shows the utilization and outcomes of the various PIMs process for metal recovery from e-waste solution.

Table 1.8-The literature survey on PIMs process for the recovery of metal species from e-waste

Materials used for		PIM Thickness (µm)	Outcomes	Ref
Feed Solution (Raw material & leachant)	PIMs (Polymer, carrier plasticizer & solvent)			
Computer WPCBs H_2SO_4	CTA D2EHPA DOP dichloromethane	40	• 99% copper ions were recovered in the presence of heavy metals (Pb, Cd, Cr) • The constancy of membrane was steady up to 10 cycles. One cycle run was carried for 12 h.	Kavitha and Palanivelu, (2012)
Discarded Mobile phones Aqua regia	PVC D2EHAG 2NPOE THF	68± 5	• Recognized that gold concentrations in useless mobile are much better than in naturally occurring gold ores. • 96% of the gold ions were extracted	Kubota et al., (2018)
WPCBs Aqua regia	PVC Aliquat336 - THF	Not Specified	• Extraction of gold in the existence of high concentrations of Cu ions. • PIM has significant stability. • The failure of reagent to the aqueous phase is lucidly little in strong acid solutions.	Argiropoulos et al., (1998)
Discarded computer (Motherboards) Aqua regia	PVDF-HFP Cyphos® IL 104 - THF	50± 5	• PVDF-HFP is appropriate polymer for the synthesis of PIMs using the ionic liquid extractants. • Selective extraction of gold ions in presence of higher concentration of Cu ions. • Significant stability of PIM in highly acidic solutions • A minor drop in recovery factor at the 5th cycle	Bonggotgetsakul et al., (2016)

Electronic waste digest	PVC, CTA, PVDF-HFP Cyphos®1L104 THF/DCM	20.1 ± 4.0	• Demonstrated the first cross-linked PIM for the gold recovery • More than 94% of gold was recovered from electronic waste solutions. • The performance of cross-linked PIMs was found better in comparison to non-cross-linked PIMs	(Hoque et al., 2021)

1.7 Aim and scope of the present work

The current research involves the application of Polymer Inclusion Membranes (PIMs) to enhance a specific hydrometallurgical process used in electronic waste (e-waste) recycling. This approach aims to recover low-concentration or trace metals that are typically overlooked. While existing methods effectively recover metals like copper, gold, and silver, other metals such as nickel can introduce contamination to these recovered metals. The current study serves as a complementary method to efficiently recover low-concentration metals such as nickel and gold, ensuring the comprehensive recovery of metals with high purity.

Delamination using organic solvents is an effective chemical method for separating metallic and non-metallic fractions from WPCBs in hydrometallurgy. However, this process typically requires an average of 12-13 hours at temperatures ranging from 100 to 150°C with individual organic solvents, rendering it relatively costly and not environmentally friendly. Consequently, it currently lacks industrial feasibility for WPCB recycling. These limitations highlight the need for developing newer, environmentally and economically friendly approaches to enable industrial-scale recycling of WPCBs.

The present study initially aims to separate metallic fractions from WPCBs using a greener method. Specifically, direct ultra-sonication of hammer-milled WPCBs is employed to extract metal-rich powder. Importantly, this pretreatment route avoids the use of any organic or toxic solvents. Subsequently, a hydrometallurgical process involving nitric acid leaching in the first stage and sodium bromide under acidic conditions in the second stage was applied to recover metal ions from the metallic powder. Our objective was to optimize leaching conditions to enable a two-stage metal separation process, prioritizing the separation of base metals followed by precious metals. To achieve this, Response Surface Methodology (RSM), a statistical modeling technique used to optimize leaching parameters is employed. Additionally, Polymer inclusion membranes (PIMs) for recovering metal ions such as gold and nickel from the leach liquor is explored. To assess their viability, two novel types of PIMs specifically tailored for metal purification from WPCBs leach liquor are synthesized and characterized, while also addressing the associated challenges in membrane fabrication. For the recovery of nickel from the raffinate of the solvent extraction stage, polyvinyl chloride (PVC)/5-nonylsalicylaldoxime (ACORGAM5640) based PIMs have been utilized. The thorough investigation of the effects of carrier concentration on nickel recovery, pH on nickel recovery from the feed phase, and the concentration of stripping agents has been done. Similarly, for the recovery of gold from the second stage leach liquor, cellulose triacetate/TBAN-based PIMs is employed. The effect of carrier concentration, effect of stripping agents and transport studies have been performed to check the feasibility of this route.