RV College of Engineering®

*Go, change the world*

RASHTREEYA SHIKSHAN SAMITHI TRUST

**R.V. COLLEGE OF ENGINEERING**

*(An Autonomous Institution affiliated to Visvesvaraya Technological University, Belagavi)*

# *Department of Chemistry*

# Unit-I: Sustainable chemistry and E-waste management

**Syllabus**

Biomaterials: Introduction, Bio-degradable and bio-compatible polymeric materials: synthesis and applications (Polymers and hydrogels in drug delivery).

Green Chemistry: Introduction, 12 principles with real life examples, Validation of greenness using software.

E-waste: Hazards and toxicity, segregation and recycling (Hydrometallurgy, pyrometallurgy and direct recycling). Extraction of valuable metals from E-waste.

Battery waste management and recycling, circular economy - case studies.

**Abstract**

This unit delves into the realms of biomaterials, green chemistry, e-waste management, and circular economy approaches, offering a multidisciplinary perspective on sustainable material utilization and waste reduction. The biomaterials section discusses bio-degradable and bio-compatible polymeric materials, emphasizing synthesis techniques and their diverse applications, particularly in drug delivery systems. In the realm of green chemistry, an overview of its principles is provided, accompanied by real-life examples demonstrating its application in environmentally benign chemical processes. Additionally, this section highlights the validation of greenness through software tools, promoting sustainable chemical design and production. Shifting focus to E-waste, the discussion centres on hazards, toxicity, and efficient segregation methods, with a keen emphasis on recycling approaches such as hydrometallurgy, pyrometallurgy, and direct recycling. Further exploration entails the extraction of valuable metals from e-waste, showcasing its potential in resource recovery.

**Blow-up Syllabus**

| Sl No | Topic to be taught | Duration |
|---|---|---|
| 1 | Biodegradable polymers: Introduction and their requirements, synthesis and properties of Poly lactic acid. | 1 hour |
| 2 | Applications of biodegradable polymers in the medical industry, Bio-compatible polymeric materials: Introduction, synthesis of Poly(3-hydroxybutyrate-co-3-hydroxyvalerate), degradation and its applications. | 1 hour |
| 3 | Introduction to Green chemistry, explanation of basic principles of green chemistry (1-6) | 1 hour |
| 4 | Explanation of remaining basic principles of green chemistry with examples (7-12). | 1 hour |
| 5 | E-waste: Introduction, common types, environment and health hazards of Pb, Hg, Cd, PAH | 1 hour |
| 6 | Benefits of E-waste recycling, general steps of E-waste recycling process with explanation. | 1 hour |
| 7 | Hydrometallurgical process extraction of copper from PCB's. | 1 hour |
| 8 | Battery recycling- advantages, disadvantages, recycling of Lead-Acid Batteries. | 1 hour |
| 9 | Self-learning: Circular economy - case studies. | Self-study |

## 1.1 Biodegradable polymers:

It is observed that plastic bucket kept in sunlight and rain for long time loses its lustre and strength. This deterioration in properties is due to a phenomenon called ‘polymer degradation’, which is characterised by an uncontrolled change in the molecular weight or constitution of the polymer. Conventionally, the degradation is a reduction in the molecular weight of the polymer.

In developing countries, environmental pollution by synthetic polymers has assumed dangerous proportions. Petroleum-derived plastics are not readily biodegradable and because of their resistance to microbial degradation, they accumulate in the environment. In addition, in recent times oil prices have increased markedly. These facts have helped to stimulate interest in biodegradable polymers. Biodegradable plastics and polymers were first introduced in 1980s. Polymers from renewable resources have attracted an increasing amount of attention over the last two decades, predominantly due to two major reasons: firstly environmental concerns, and secondly the realization that our petroleum resources are finite. There are many sources of biodegradable plastics, from synthetic to natural polymers. Natural polymers are available in large quantities from renewable sources, while synthetic polymers are produced from non-renewable petroleum resources. Biodegradation of polymeric biomaterials involves cleavage of hydrolytically or enzymatically sensitive bonds in the polymer leading to polymer erosion. A vast number of biodegradable polymers have been synthesized recently and some microorganisms and enzymes capable of degrading them have been identified.

“Thus, the biodegradable polymers are the polymers which will degrade by the action of naturally occurring microorganisms like bacteria, fungi or sunlight”.

**Requirements of Biodegradable polymers:**

1. Biodegradable polymers should have hydrolysable linkages like esters, amides or ether.
2. They should be hygroscopic in nature.
3. The product formed after degradation should act as compost.

**Classification of biodegradable polymers:**

The biodegradable polymers can be classified according to their chemical composition, origin and synthesis method, processing method, economic importance, application, etc.

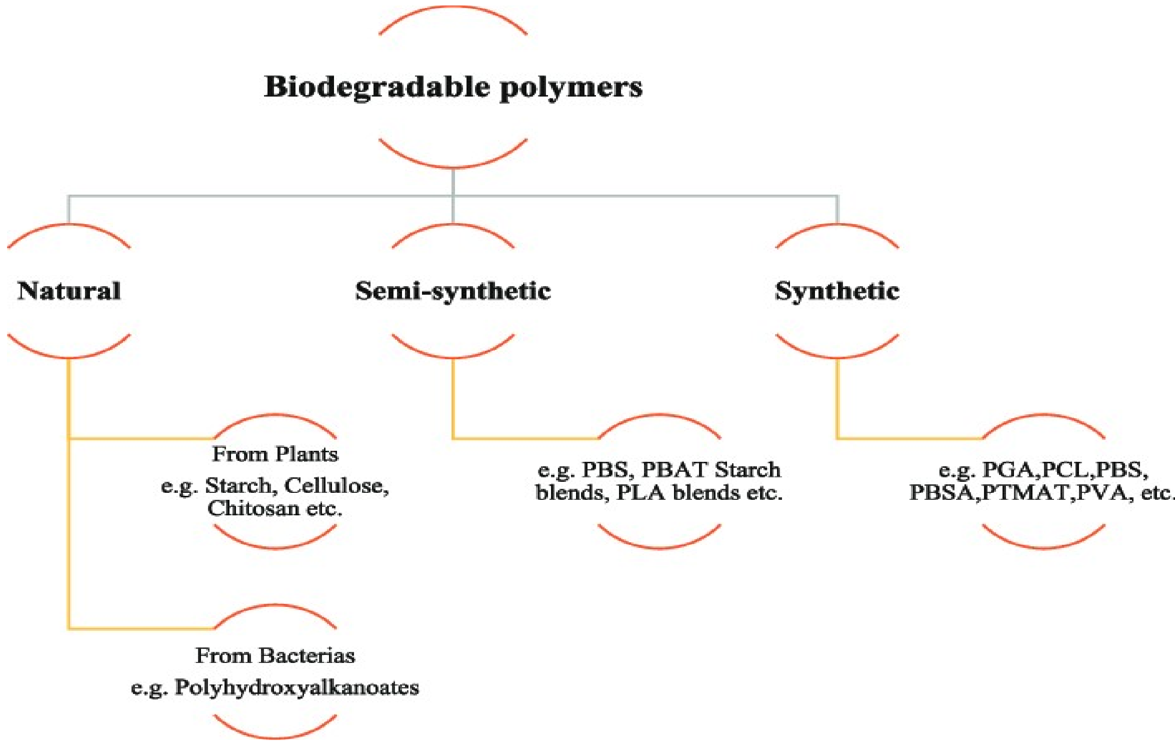



**Figure 1. 1.** Classification of Biodegradable polymers

## Poly lactic acid (PLA):

The basic building block of PLA is the lactic acid (LA). It is a simple chiral molecule which exists as two enantiomers, L- and D-lactic acid, optically active. It can be produced by fermentative or chemical synthesis. Today the most popular route is fermentation, in which sugars and starches are converted into lactic acid by bacterial fermentation using an optimized strain of Lactobacillus.

**Properties:**

(i) The PLA is a semi-crystalline polymer with glass transition temperature around 55 to 59 °C and melting point 174-184 °C.

(ii) It shows a good mechanical strength, high Young's modulus, thermal plasticity and has good processability.

(iii) It is unstable in wet conditions, which can undergo chain disruption in the human body and degrades into nontoxic by products, lactic acid, carbon dioxide and water which are subsequently eliminated through the Krebs cycle and in the urine.

## Synthesis of Poly Lactic Acid:

There are two important methods for PLA synthesis:

(i) Direct polycondensation of lactic acid and

(ii) Ring opening polymerization of lactic acid cyclic dimer, known as lactide.

Following reactions show the reaction mechanism for both of them.

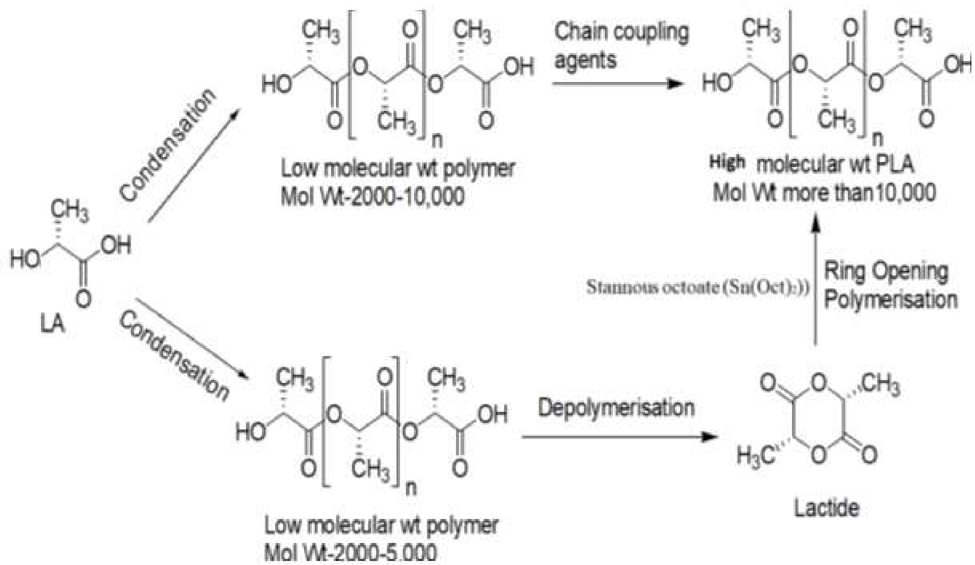



**Figure 1.1: Synthetic root for the synthesis of Poly lactic acid**

**In direct condensation,** solvent is used and higher reaction times are required. The resulting polymer is a material of low to intermediate molecular weight.

**Ring-opening polymerization (ROP)** of the lactide needs catalyst (Stannous octoate ($Sn(Oct)_2$)) but results in PLA with controlled molecular weight. Depending on monomer used and controlling reaction conditions, it is possible to control the ratio and sequence of Dand L-lactic acid units in the final polymer.

**Applications of biodegradable polymers in medical field**:

| Wound management | Orthopedic devices |
|---|---|
| • Sutures<br>• Staples<br>• Clips<br>• Adhesives<br>• Surgical meshes | • Pins<br>• Rods<br>• Screws<br>• Tacks<br>• Ligaments<br>• PLA are used in Fracture fixation and Ligament augmentation |

**Table 1.1:** Applications of biodegradable polymers

## 1.2 Bio-compatible polymeric materials:

Biocompatible polymers are both synthetic (man-made) and natural and aid in the close vicinity of a living system or work in intimacy with living cells. These are used to gauge, treat, boost, or substitute any tissue, organ or function of the body.

**Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) OR PHBV**

It is a thermoplastic linear aliphatic polyester. It is obtained by the copolymerization of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.

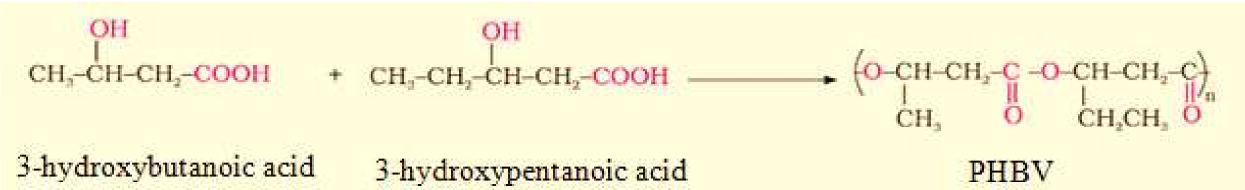



**Figure 1.2:** Synthetic root for PHBB

**Properties:** It is biodegradable, nontoxic, biocompatible plastic produced naturally by bacteria and a good alternative for many non-biodegradable synthetic polymers. PHBV undergoes bacterial degradation in the environment.

**Degradation**

When disposed, PHBV degrades into carbon dioxide and water. PHBV undergo bacterial degradation. PHBV, just like fats to human, is an energy source to microorganisms. Enzymes produced by them degrade it and are consumed.

**Applications**:

(1) It is used in controlled release of drugs, medical implants and repairs, specialty packaging, orthopedic devices and manufacturing bottles for consumer goods.

(2) It is also biodegradable which can be used as an alternative to non-biodegradable plastics

## 1.3 Hydrogels

Is a water-swollen, and cross-linked polymeric network produced by the simple reaction of one or more monomers.

**OR**

A polymeric material that exhibits the ability to swell and retain a significant fraction of water within its structure, but will not dissolve in water is known as **Hydrogel**.

**Important features of hydrogels:**

- The ability of hydrogels to absorb water arises from hydrophilic functional groups attached to the polymeric backbone, while their resistance to dissolution arises from cross-links between network chains.
- Hydrogels have similarities with human soft tissues in composition, structure, and properties.
- Due to their superior biocompatibility and low toxicity, hydrogels play a significant role in the biomedical fields
- Hydrogels are considered to be the most prospective alternative materials for soft tissue due to their exceptional mechanical properties.

Therefore, they are widely used in drug delivery, cell culture, tissue engineering, and other biomedical and biomimetic applications.

**Classification of Hydrogels**

Hydrogels can be divided in two categories by the forming molecule types, natural polymer and synthetic polymer.

**Natural hydrogels** include collagen, silk fibroin, hyaluronic acid, chitosan, alginate and hydrogels derived from decellularized tissues.

Their unique properties include: biocompatibility, biodegradability, low cytotoxicity, the possibility to tailor the hydrogel into an injectable gel and their similarity to physiological environment.

**Synthetic hydrogel includes** Polyhydroxyethyl methacrylate (PMMA), Polyvinyl alcohol (PVA), Polyethylene glycol (PEG), etc

**Application of Hydrogel in Drug delivery**

Due to their compatibility with living tissues and ability to preserve embedded proteins in their natural state, hydrogels are good vehicles for delivering drugs into the body.

Hydrogels as drug delivery agents are appealing for a number of reasons. They are mainly composed of water so they can shrink in their dry state to become small enough to swallow, and then can expand and swell in the stomach to avoid passing into the small intestine. They can also be loaded with medicine and release it in a controlled manner.

Such controlled drug delivery systems are used to deliver drugs at certain rates for predefined periods of time. These systems have been used to overcome the limitations of regular drug formulations.

Polymers are generally used as **drug delivery systems** (DDSs) because the drug release from these systems is predominantly controlled by the polymeric matrix. The drug release takes place from the polymeric DDSs with different mechanisms which are known as diffusion, swelling, erosion and stimulus-based methods that are presented schematically in Figure 1.3

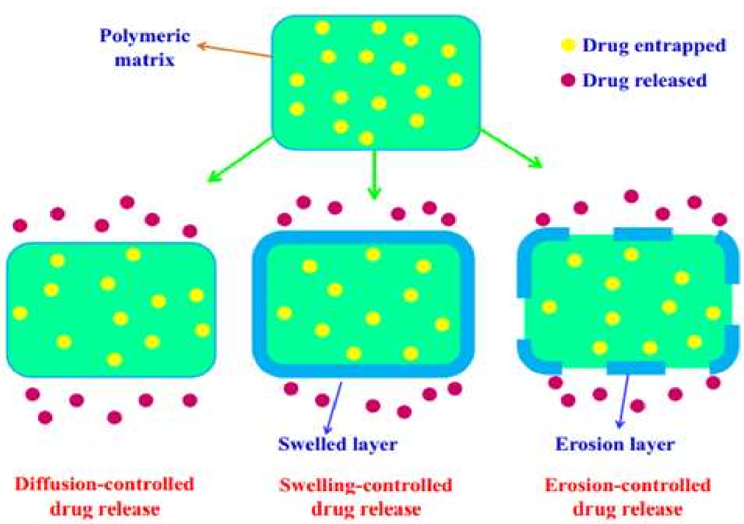



**Figure 1.3:** Mechanism of drug release from a polymeric matrix including diffusion, swelling, and erosion-controlled methods

**Chitosan:** It is a polysaccharide industrially obtained by N-deacetylation of chitin, the second most common natural polysaccharide in biomass after cellulose.
It is a linear copolymer composed of two sub-units, D-glucosamine and N-acetyl-D-glucosamine units 45 linked by a β (1⟶4) glycosidic bond (**Figure 1.4**).

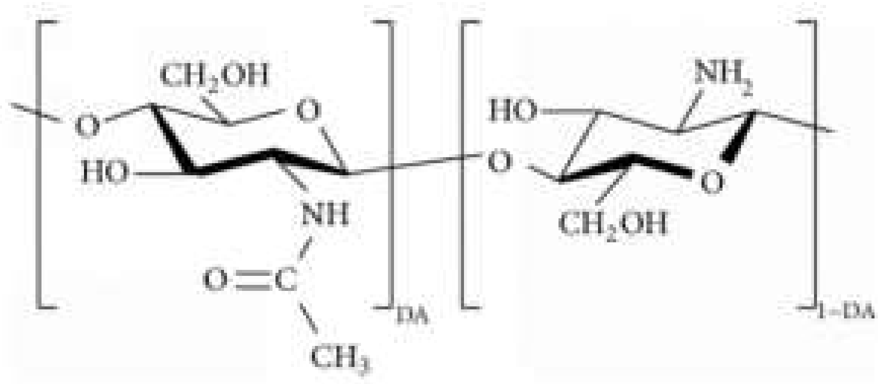


**Figure 1.4:** Chitosan chemical structure

## 1.4 Green Chemistry: Introduction-Basic principles.

Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances.
Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal. Green chemistry is also known as **sustainable chemistry**.
Green Chemistry helps us solve many future problems, including sustainable energy and food production, protecting our environment by proper management, providing safe drinking water, and promoting better human and environmental health. Everything around us, all commodities that we use day and night is the inventions of chemistry. We cannot exist without chemistry as what we breathe is itself a result of chemical reactions.

**Importance of Green Chemistry:**

- Prevents pollution at the molecular level.
- Applies innovative scientific solutions to real-world environmental problems.
- Results in source reduction because it prevents the generation of pollution.
- Reduces the negative impacts of chemical products and processes on human health and the environment.
- Lessens and sometimes eliminates hazard from existing products and processes.
- Designs chemical products and processes to reduce their intrinsic hazards.

**Chemical disasters:**

(i) 1956: Minamata disease was first discovered in Minamata city in Japan. It was caused by the release of methyl mercury in the industrial wastewater from a chemical factory.

(ii) 1961: Itai-itai disease was caused by cadmium poisoning due to mining in Toyama Prefecture in Japan.

(iii) 1976: The Seveso disaster was an industrial accident that occurred in a small chemical manufacturing plant near Milan in Italy. It resulted in the highest known exposure to 2, 3, 7, 8-tetrachlorodibenzo-p-dioxinin residential population.

(iv) 1984: The Bhopal disaster was an industrial catastrophy that took place at a pesticide plant owned and operated by Union Carbide (UCIL) in Bhopal India resulting in the exposure of over 500,000 people. It was caused by methyl Iso cyanate (MIC) gas.

(v) 1986: The Chernobyl disaster was a nuclear accident at the Chernobyl nuclear plant in Ukraine. It resulted in a severe release of radioactive materials. Most fatalities from the accident were caused by radiation poisoning.

(vi) 1989: Exxon Valdez, an oil tanker hit a reef and spilled an estimated minimum 10.8 million US gallons (40.9 million litres) of crude oil. This has been recorded as one of the largest spills in United States history and one of the largest ecological disasters.

**History of Green chemistry:**

1. In 1990 the Pollution Prevention Act was passed in the United States. This act helped create a modus operandi for dealing with pollution in an original and innovative way. This paved the way to the green chemistry concept.
2. **Paul Anastas and John Warner** coined the two letter word “**green chemistry**” and developed the twelve principles of green chemistry.
3. In 2005, Ryoji Noyori identified three key developments in green chemistry: use of supercritical carbon dioxide as green solvent, aqueous hydrogen peroxide for clean oxidations and the use of hydrogen in asymmetric synthesis.

**Green chemistry focuses on to**


**Nobel Prize in Green chemistry:**

1. The Nobel Prize Committee recognized the importance of green chemistry in 2005 by awarding Yves Chauvin, Robert H. Grubbs, and Richard R. Schrock the Nobel Prize for Chemistry for "the development of the metathesis method in organic synthesis”.
2. Frances Arnold won in 2018, it for the directed evolution of enzymes, a technique she has pioneered over the past 25 years and has used to pursue new avenues within green chemistry and to engineer reactions completely new to nature.

**Principles of Green chemistry**

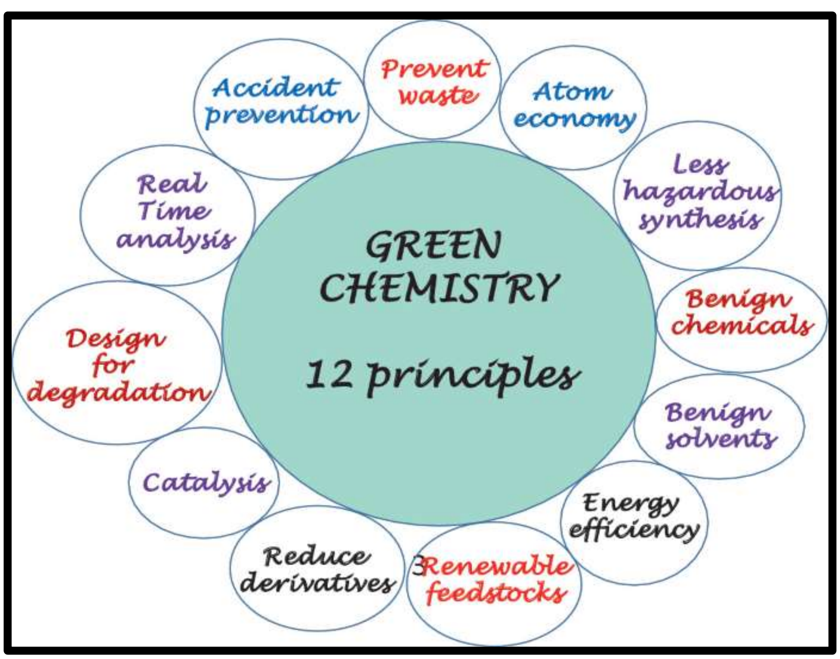



**Figure 1.5:** Green principles of Chemistry

**The twelve principles of green chemistry are:**

**(1) Prevention:** It is better to prevent waste than to treat or clean up waste after it has been created.

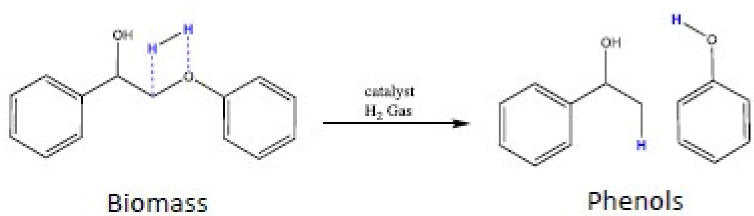
- Carry out a synthesis in such a way so that formation of waste (by-products) is minimum or absent.
- Cost involved in the treatment and disposal of waste adds to the overall production cost.
- The unreacted starting materials also form part of the waste.
- If discharged causes pollution and requires expenditure for cleaning-up

**Case study: Phenols**

Phenols are widely used in household products and as intermediates for industrial synthesis.

Conventional method of obtaining phenols from petroleum products/derivatives of phenols (benzene, toluene, xylenes). As this method is not sustainable it is dependent on depleting resources.

**Alternative method suggested**: Production of phenols from biomass waste using depolymerisation. This method uses abundant product (waste) as a starting material.




(2) **Atom economy: Synthetic methods should be designed to maximize incorporation of all materials used in the process into the final product.**

In 1990, Barry Trost introduced the concept of synthetic efficiency: Atom Economy. It refers to the concept of maximizing the use of raw materials so that the final product contains the maximum number of atoms from the reactants.

- The ideal reaction would incorporate all of the atoms of the reactants.
- The atomic economy is measured as the ratio of the molecular weight of the desired product over the molecular weights of all reactants used in the reaction.

Chemists globally consider that if the yield of a reaction is above 90%, the reaction is good.

$$\boxed{\%\ yield = \frac{Actual\ yield\ of\ the\ product}{Theoretical\ yield\ of\ the\ product} \text{ X } 100}$$

$$\%\ atom\ economy = \frac{Formula\ weight\ of\ atoms\ utilized}{Formula\ weight\ of\ the\ reactants\ used\ in\ reaction} \times 100$$

The following equation illustrated the atom economy of this reaction by showing all of the reactant atoms that are incorporated into the desired product in green,

$$\underset{1}{H_3C{-}CH_2{-}CH_2{-}CH_2{-}OH} + \underset{2}{Na{-}Br} + \underset{3}{H_2SO_4} \longrightarrow \underset{4}{H_3C{-}CH_2{-}CH_2{-}CH_2{-}Br} + \underset{5}{NaHSO_4} + \underset{6}{H_2O}$$

While those that are wasted are shown in brown. Likewise the atoms of the desired product are in green and the atoms composing the unwanted products are in brown. **Table 2** provides another view of the atom economy of this reaction. In columns 1 and 2 of this table, the formulas and formula weights (FW) of the reactants are listed. Shown in green (columns 3 and 4) are the atoms and weights of the atoms of the reactants that are incorporated into the desired product (4), and shown in brown (columns 5 and 6) are the atoms and weights of atoms of the reactants that end up in unwanted side products. Focusing on the last row of this table it can be seen that of all the atoms of the reactants (4C, 12H, 5O, 1Br, 1Na and 1S) only 4C, 9H, and 1Br are utilized in the desired product and the bulk (3H, 5O, 1Na, 1S) are wasted as components of unwanted products. This is an example of poor atom economy!

A logical extension of Trost's concept of atom economy is to calculate

| Reagents Formula | Reagents FW | Utilized Atoms | Weight of Utilized Atoms | Unutilized Atoms | Weight of Unutilized Atoms |
|---|---|---|---|---|---|
| 1 $C_4H_9OH$ | 74 | 4C,9H | 57 | HO | 17 |
| 2 NaBr | 103 | Br | 80 | Na | 23 |
| 3 $H_2SO_4$ | 98 | —— | 0 | 2H,4O,S | 98 |
| **Total** 4C,12H,5O,BrNaS | 275 | 4C,9H,Br | 137 | 3H,5O,Na,S | 138 |

**Table 1.2:** Calculation of Atom economy

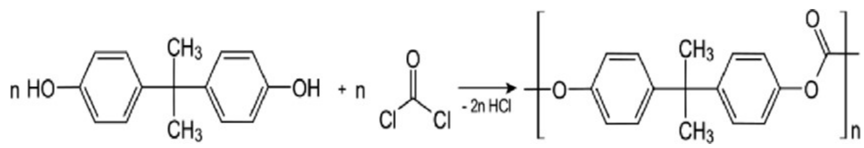
The percentage atom economy can be done by taking the ratio of the mass of the utilized atoms (137) to the total mass of the atoms of all the reactants (275) and multiplying by 100. As shown below this reaction has only 50% atom economy.

$$\% \textbf{ Atom Economy} = (\text{FW of atoms utilized/FW of all reactants}) \times 100$$

$$= (137/275) \times 100 = 50\%$$

(3) **Less hazardous chemical syntheses:** Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

**Case study: Synthesis of Polycarbonate: Phosgene process**

| | |
|---|---|
|  Monomers: Bisphenol-A and Phosgene | **Disadvantages:**<br>(i) Phosgene is highly toxic and corrosive<br>(ii) It requires large amount of $CH_2Cl_2$ (Phosgene)<br>(iii) Polycarbonate is contaminated with Cl impurities |

**Alternative method (Greenery approach)** for above synthesis of Polycarbonate suggested using Bisphenol-A & Diphenyl carbonate.

Its advantages are (i) eliminates the use of phosgene (ii) It produces higher-quality Polycarbonates.

**(4) Designing safer chemicals:** Chemical products should be designed to preserve efficacy of function while reducing toxicity.

Safer chemicals can be designed by

(a) Manipulation of chemical bonds, chemical functional groups:

- Reactive functional groups have a greater potential to be toxic. Removing these groups is likely to reduce toxicity.

(b) Elimination of the molecular initiating event that activates pathway

- While difficult to achieve, if the chemical is modified not to interact with the biological pathway, no biological effect is triggered and the toxicity can be avoided.

(c) Reducing or eliminating bioavailability.

- If a chemical does not absorb into a body, it cannot cause harm.

**Before synthesizing any chemicals we can make use of**

(i) Related literature report if already available.

(ii) **Toxicology study** -that involves the study of the adverse effects of chemical substances on living organisms.

(iii) **Software** related to above viz., Toxicity estimation software tool (TEST), OLED test guidelines for toxicity software testing, Tox Navigation, etc.

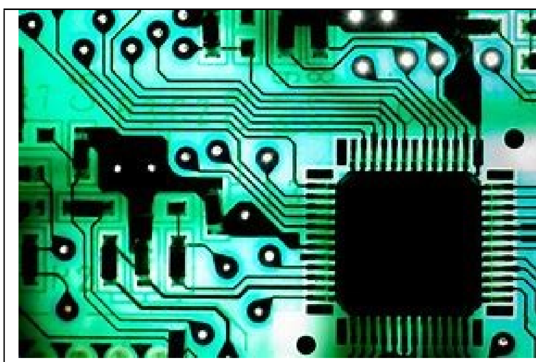
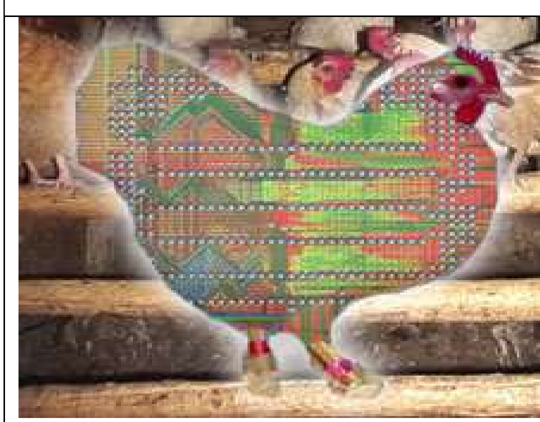
(5) **Safer solvents, and auxiliaries:** The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and, innocuous when used.

Solvents account for the vast majority of mass wasted in syntheses and processes. Moreover, many conventional solvents are toxic, flammable, and/or corrosive.

Solvents volatility and solubility have contributed to air, water and land pollution, have increased the risk of workers' exposure, and have led to serious accidents.

**Green solvents: Water, Acetone, Ethanol, 2-Propanol, 1-Propanol, Ethyl acetate, Isopropyl acetate**

**Case study: Chicken feathers used in computer chips**

<table>
<tr><td></td><td rowspan="2">To manufacture computer chips- many chemicals, large amount of water and energy are required. Washing chemicals requires lot of water. In 2003, Industrial estimate of chemicals and fossil fuels require to make computer chip was 630: 1<br><u>That means it takes 630 times the weight of the chip in source material just to make one chip.</u><br>Researchers in the University of Delaware's ACRES program -Affordable Composites from renewable sources have developed a computer processor made from chicken feathers.<br>Chicken feathers because they have shafts that are hollow but strong, and made mostly of air, a great conductor of electricity.</td></tr>
<tr><td></td></tr>
</table>

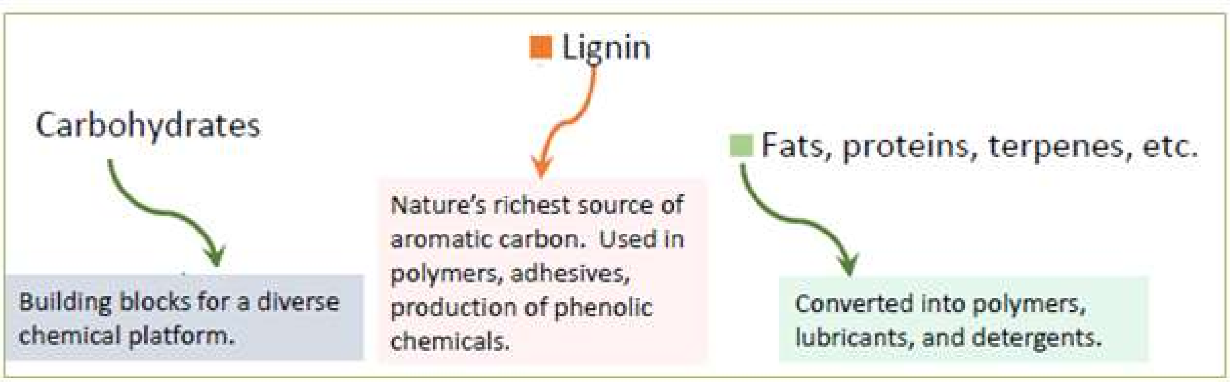
(6) **Design for energy efficiency:** Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

Most energy is used for heating, cooling, separations and pumping. Ideally, all reactions are performed at 'ambient' conditions room temperature and atmospheric pressure in order to minimize energy usage. Sonochemistry, microwave, and photo assisted chemistry are known to save energy, improve reaction time, and catalytic activity.

| Sonochemistry | Microwave | Photo assisted |
|---|---|---|
| Uses of high frequency (20-100 kHz) sound waves to promote chemical reaction.<br>Used in the production of methyl esters from triglycerides transesterification. | •Uses a high-frequency electric field to heat or cool the local environment with electrical charges.<br>•Avoids unnecessarily prolonged residence time at a given temperature. | Naturally occurring, such as using the sun as a catalyst. |

(7) **Use of renewable feedstock:** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

Biomass production in nature nearly around 180 billion metric tons/year. But only about 4% utilized by humans (food, ethanol, sweeteners).




**Case study: Producing polymers from renewable resources (PHAs) Polyhydroxyalkanoates** (PHAs) are a broadly useful family of natural, environmentally friendly, and high performing, bio based plastics.

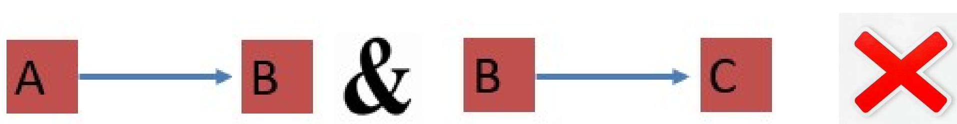
| | |
|---|---|
| The development of microorganisms that produce polyhydroxyalkanoates (PHAs) are from renewable feedstocks such as cornstarch and cellulose hydrolysate.<br>•The microorganisms have proven to be applicable to conventional commercial equipment and can even be recycled using this same equipment.<br>**•They can be used in biodegradable products, such as credit cards.**<br>•They are comparable with polyolefin which are made from petroleum feedstocks in terms of strength, melting point, and can be manufactured with the existing equipment. |  |

(8) **Reduce derivatives:** Unnecessary derivatization (use of blocking groups, protection/deprotection and temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

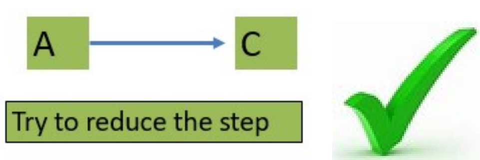
**What is derivatization?**

Increasing the number of steps which can be done by protection/deprotection, temporary modification of physical/chemical processes is known as derivatization.

**Conventional approach**




**Green approach**




- Time saved
- Additional reagent/s saved
- Cost of the process reduced

**Case study:** Synthesis of **Ibuprofen** developed by the Boots Company of England has 6 step process, with **atom economy 40%** and lot of waste (by-products).

**Greenery approach:** Contains only 3 steps for the synthesis of Ibuprofen with **atom economy 77 %** with less number by-products.

(9) **Catalysis:** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

Catalysts can facilitate complex reactions by:

• Lowering the activation energy of the reaction.

• Reducing temperature necessary to achieve a reaction.

• Controlling the site of the reaction (selectivity enhancement).

**Case study: Hydroquinone synthesis**

| | Conventional Approach | Green approach |
|---|---|---|
| Waste produced (per kg of product) | 10 Kg | < 1 Kg |
| Comments | Produced by oxidation of Aniline using $MnO_2$ | Hydroxylation of Phenol with aqueous $H_2O_2$ using Titanium silicate as a **catalyst** |

(10) **Design for degradation:** Chemical products should be designed so that at the end of their function they break down into harmless degradation products and do not persist in the environment.

Example: Insecticides and polymers are **non-biodegradable**.

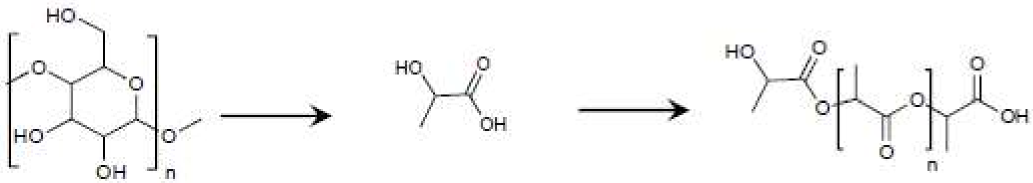
DDT-Bioaccumulate in many plant and animal species and. Incorporate into the **food chain.**

Some of the insecticides are also responsible for population decline of beneficial insects

**Greenery approach:**

- Insecticides must be biodegradable during degradation the products themselves should not possess any toxic effects or be harmful to human health.
- It is possible to have a molecule which may possess functional groups that facilitate it for biodegradation.

**Case study: Synthesis of Polylactic acid**



Starch → Lactic Acid → PolyLacticAcid PLA

The development of a bio based, compostable, and recyclable polylactic acid (PLA) polymer that uses 20–50 percent less fossil fuel resources than comparable petroleum-based polymers.

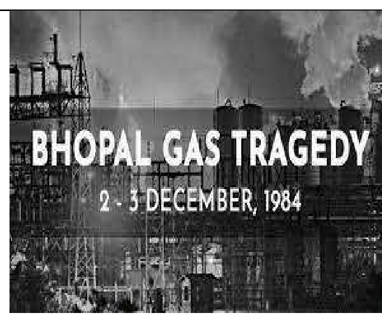
(11) **Real-time analysis for pollution prevention:** Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

**Knowing when your product is “done” can save a lot of waste, time, and energy!**

Analytical and modern methods helps in real time analysis for pollution prevention.

- Analytical methodologies should be so designed so that they require minimum usage chemical, like recycling of some unreacted chemicals, for the completion of the reaction.
- Placement of sensors to monitor the generation of hazardous products during chemical reaction is also advantageous.

(12) **Inherently safer chemistry for accident prevention:** Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

| | | |
|---|---|---|
|  |  | <br>**Explosion in Hindustan petroleum industry** |

**Case study; Tragedy in Bhopal, India 1984**

In arguably the worst industrial accident in history, 40 tons of methyl isocyanate were accidentally released when a holding tank overheated at a Union Carbide pesticide plant, located in the heart of the city of Bhopal. 15,000 people died and hundreds of thousands more were injured.

The hazards posed by toxicity, explosion, fire etc might be looked into and manufacturing plants should be so designed to eliminate the possibility of accidents.

**In the end we can say that Green chemistry is not a solution to all environmental problems but the most fundamental approach to preventing pollution**.

## 1.5 E-Waste

**E-Waste** is short for Electronic-Waste and the term is used to describe old, end-of-life or **discarded electronic appliances**.

**OR**

**E-waste** refers to any electronic devices that have reached the end of life.

It includes their components, consumables, parts and spares. Electronic products have become an integral part of the common man's life. The rapid growth in the electronic industry with technological advancements has resulted in significant changes in consumer patterns. This has accelerated the rate at which this equipment reach their end of 'useful' life leading to an increased rate of obsolescence in the electronics industry. This has resulted in an increase in e-waste generated, rendering it the fastest-growing segment of municipal waste.

**The most common types of E-waste are**

| **Small Equipment's** | **Large Equipment** | **Temperature Exchange Equipment** |
|---|---|---|
| • Vacuum cleaners<br>• Microwaves<br>• Ventilation equipment<br>• Toasters | • Washing machines<br>• Clothes dryers<br>• Dish-washing machines<br>• Electric stoves | • Refrigerators<br>• Freezers<br>• Air conditioners<br>• Heat pumps |

| | | |
|---|---|---|
| • Electric kettles, shavers<br>• Video cameras, Calculators<br>• Electrical and electronic toys<br>• Small medical devices | • Large printing machines<br>• Solar panels | |

**Health and environmental impact of E-waste**

The quantum of E-waste generated is increasing at a rate of 5–10% per year and is a growing concern globally because of its toxicity. RoHS (Restriction of Hazardous Substance) directive restricts the use of certain hazardous substances like Pb, Hg, Cd, Cr, and polybrominated biphenyls in electrical and electronic equipment. These pose a risk to health or environment when treated inappropriate RoHS requires minimizing or substitution of these toxic substances with safer materials. This will reduce the load on a recycling plant and the negative impact on the environment.

**Environment and health hazards**

**Lead**: Exerts toxic effects on various systems in the body such as the central (organic affective syndrome) and peripheral nervous systems (motor neuropathy), the hemopoietic system (anaemia), the genitourinary system (capable of causing damage to all parts of nephron) and the reproductive systems (male and female).

**Mercury**: causes damage to the genitourinary system (tubular dysfunction), the central and peripheral nervous systems as well as the foetus. When inorganic mercury spreads out in the water, it is transformed into methylated mercury, which bio-accumulates in living organisms and concentrates through the food chain, particularly by fish.

**Cadmium:** is a potentially long-term cumulative poison. Toxic cadmium compounds accumulate in the human body, especially in the kidneys. There is evidence of the role of cadmium and beryllium in carcinogenicity.

**Polycyclic aromatic hydrocarbons (PAH):** Affects lung, skin and bladder. Epidemiological studies in the past on occupational exposure to PAH provide sufficient evidence of the role of PAH in the induction of skin and lung cancers.

## Benefits of E-waste Recycling

The benefits of the E-waste recycling process are obvious. Almost everyone owns an electronic device in today's environment. Recycling electronic garbage has become a need to preserve energy, resources, and landfill space. Consider the following benefits to better comprehend the positive impact of E-waste recycling.

- **Conserve natural resources**

- **Protects the environment**
- **Create Jobs**
- **Reduces global warming and saves landfills**
- **Makes things more affordable**
- **Reduces business costs**
- **Supports non-renewable recycling**
- **Conserve both land and energy**

## E-waste recycling process flowchart with explanation

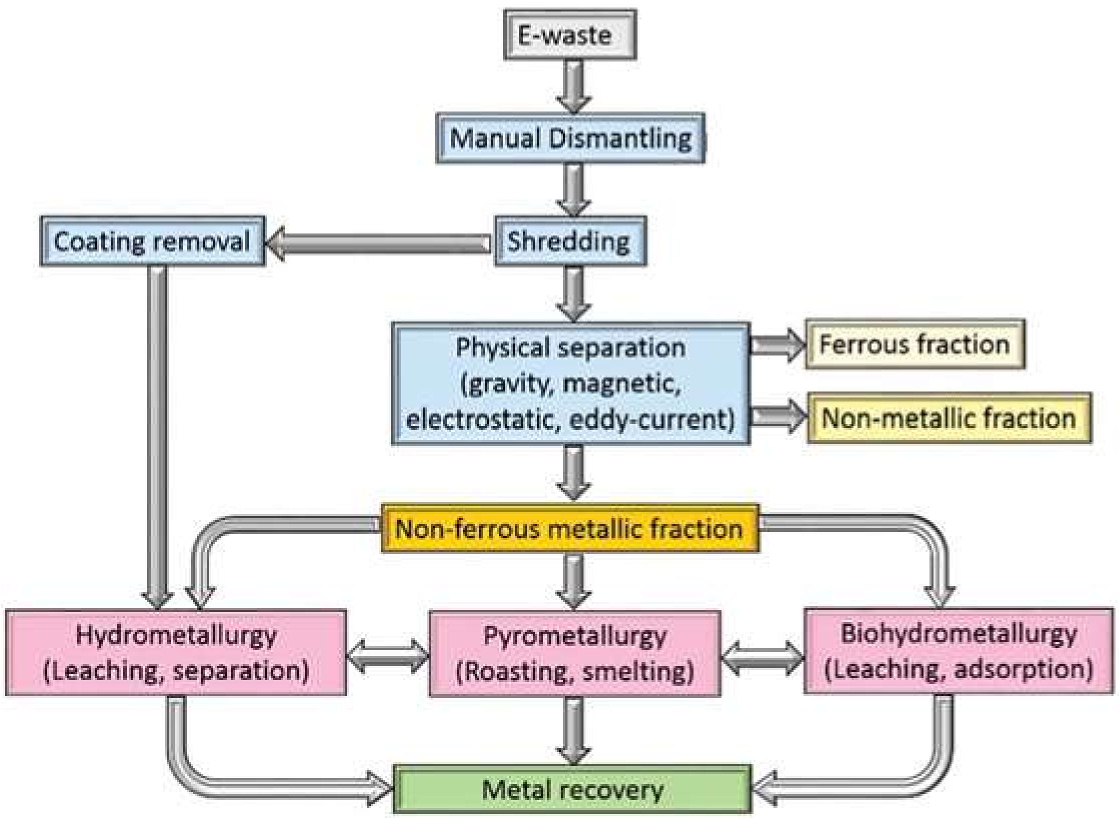



**Figure 1.6:** General steps for recycling of E-waste

**General steps:**

**(1) Collection:** Gathering E-waste from various sources, enterprises, organizations and individuals.

**(2) Storage:** While safe storage may not appear critical, it can prove very important.

For example, the glass screens of Cathode Ray Tubes (CRT), TVs and monitors are highly contaminated by lead. In the past, they were recycled into new computer monitors, but the growth of new technology and subsequent decline in demand for CRT products means much of this glass is now simply being stored indefinitely.

**(3) Manual Sorting, Dismantling and Shredding:** Disintegration of all the components and materials of the E-waste to analyse which can be reused and which can go as scrap. E-waste is then shredded into small pieces allowing for accurate sorting of materials, a key part of the process.

**(4) Mechanical Separation:** The mechanical separation of the different materials actually consists of several processes one after the other. The two key steps are magnetic separation and water separation.

**a) Magnetic separation**: The shredded E-waste is passed under a giant magnet, which is able to pull ferrous metals such as iron and steel from the mix of waste. In addition to this, an eddy current may also be used, separating the nonferrous metals. These materials can then be diverted to dedicated recycling plants for smelting. Other materials such as metal-embedded plastic and circuit boards are also separated at this stage.

b) **Water separation:** With a solid waste stream that now consists mainly of plastic and glass, water is used to separate the materials, further purifying for the separation of different plastics as well as hand-sorting obvious contaminants.

**(5) Recovery:** The materials, now separated, are prepared for sale and reuse. For some materials, such as plastic or steel, this means joining another recycling stream. Others may be processed onsite and sold directly alongside usable components separated in the early stages

**Extraction of valuable metals from E-waste**

E-waste is classified as hazardous material therefore should be managed properly. However, the presence of precious metals (PMs) in E-waste such as gold (Au), silver (Ag), platinum (Pt), Gallium (Ga), palladium (Pd), tantalum (Ta), tellurium (Te), germanium (Ge) and selenium (Se) makes it attractive for recycling.

Electronic products have become an integral part of the common man’s life. The rapid growth in the electronic industry with technological advancements has resulted in significant changes in consumer patterns. This has accelerated the rate at which these equipment reach their end of ‘useful’ life leading to an increased rate of obsolescence in the electronics industry. This has resulted in an increase in e-waste generated, rendering it the fastest-growing segment of municipal waste. The Basel Convention requires waste substances or objects to be disposed

The quantum of E-waste generated is increasing at a rate of 5–10% per year and is a growing concern globally because of its toxicity. RoHS (Restriction of Hazardous Substance) directive restricts the use of certain hazardous substances like Pb, Hg, Cd, Cr, and polybrominated biphenyls in electrical and electronic equipment. These pose a risk to health or environment when treated inappropriate ROHS requires minimizing or substitution of these toxic substances with safer materials. This will reduce the load on a recycling plant and the negative impact on the environment.

**Different techniques to Treat E-waste:-**

During pre-processing metal fraction separated from E-waste. Once this operation is carried out there are various routes for E-waste processing. The following section will explain in more detail about various routes.

1) Hydrometallurgical processes 2) Pyro metallurgical processes 3) Bio-metallurgical processes

**Pyrometallurgy**, as traditional method to recover precious and non-ferrous metals from E-waste, includes different treatments on high temperatures: incineration, melting etc.

Pyrometallurgy is a heat-based extraction and purification process. As with the water-based process, pyrometallurgy generally involves three steps:

Roasting: This refers to the heating of compounds in air and transforming sulphide ores into oxides, creating gas.

Smelting: Smelting is used in furnaces to reduce metals and usually involves the formation of carbon dioxide, for example, reducing iron ore in a blast furnace. In addition, tin, copper, and lead ores are smelted.

Refining: In refining processes, metals are sorted by exploiting their chemical and metallurgical properties. The separation of metals is achieved by smelting in furnaces at high temperatures. Refining covers a wide range of processes involving different kinds of furnaces and electrolytic processes.

Pyrometallurgical processes could not be considered as best available recycling techniques anymore because some of the PCB components, especially plastics and flame retardants, produce toxic and carcinogenic compounds.

**Hydrometallurgy** is the process used to extract metals from ore, which is achieved by recovering and dissolving the metals as salt in successive water-based steps, including leaching, purification, and recovery of the targeted metal by selective precipitation or electrowinning. This method plays an essential role in extracting strategic and rare metals.

Hydrometallurgy process is divided into three stages;

a) Leaching, b) Solution concentration and purification c) Metal recovery

**Leaching** is an important and first stage of Hydrometallurgical process.

It is the extraction process in which soluble substances are extracted from a solid by means of a solvent. After that the extract obtain from leaching is often subjected to concentration and purification before the metal recovery. The final step may involve precipitation or cementation process.

**Hydrometallurgical process extraction of copper from PCB's**

**Composition of PCB's:** Printed circuit board is an essential part of the all electrical and electronic equipment's. It is composed of polymers, ceramics and metals which all are come under Hazardous and non-hazardous categories. About 40% heavy metals present in it which are turned into hazardous residue if the discarded PCB's are not disposing properly.

PCBs are varies according to the manufacturer and the year of its manufacturing and technology **Table 1.3** shows the composition of PCB.

| Metals | Availability (wt%) |
|---|---|
| Copper | 30.57 |
| Aluminium | 11.69 |
| Zinc | 1.86 |
| Tin | 7.3 |
| Nickel | 1.58 |
| Iron | 15.21 |
| Lead | 6.71 |

**Table 1.3:** Composition of PCB

**Methodology**

The waste PCB of a discarded computer used in study. It is commonly used PCB that can be easily available at the E-waste disposal area or an electronic shops. For the recovery of metals, waste PCB was cut into small pieces and finally into powdered form.

(1) The grinded E-Waste powder contains plastic, ferrous and nonferrous metals.

(2) Density separation method is used to separate the Metallic and non-metallic parts.

(3) For separation of ferrous and nonferrous metals, Electromagnetic separator is used.

(4) For experimental purpose 8 gm of nonferrous metal was taken.

(5) The metal powder was dissolved into $H_2SO_4$ and stirred at 80 °C, temperature for about 4 hr.

(6) The solution was transferred and 40 ml of **Aquaregia** (30 ml HCl and 10 ml $HNO_3$) was added to the filtered solution. The resulting solution was stirred for 60 mins at a temperature 80 °C,

The following reactions took place:

$$HNO_{3\,(aq)} + 3\,HCl_{(aq)} \rightarrow NOCl_{(g)} + Cl_{2\,(g)} + 2\,H_2O$$

$$H_2SO_4 + HCl \rightarrow H_2O + Cl_2 + SO_2$$

$$Cu + Cl_2 \rightarrow CuCl_2$$

$$CuCl_2 + H_2SO_4 \rightarrow CuSO_4 + HCl$$

(7) Electrolysis: From the above solution, copper is extracted by electrolysis process.

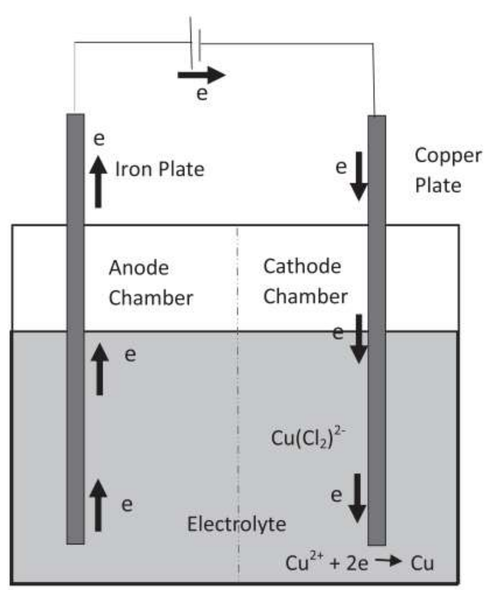


**Figure 1.7**: Electrolytic process

The sample was taken for electrolysis. To extract Cu from the solution, electrolysis process was carried out in a cubic reactor of size 12 cm X 8 cm X 7 cm as shown in **Figure 1.7.** Iron Anode and Copper cathode were used for electrolysis. The anode and cathode chambers were separated by an anti-acid filter cloth. The required potential was maintained to carry to electrolysis process. Finally copper metal is deposited.

**Advantages**

1. Economically viable for low-grade E-waste materials.
2. Feasible for small scale applications with high metal recoveries.

**Advantages of Battery recycling**

**Reduces landfills**: as the wasted batteries are taken to the recycling units, the amount dumped in the landfills are reduced considerably. This in turn reduces land, air and water pollution.

**Saving of resources**: battery recycling saves resources. In short, fewer resources are utilized in the creation of new batteries because most of the contents used as recycled. The existing resources are reused for the making if new product.

**Pollution is minimized**: this is one of the major attractions of recycling of batteries. Since it is abundantly found, it is very important to recycle as it is non-biodegradable. This reduces pollution to a great extent.

**Job opportunities**: a lot of job opportunities are created in the recycling industry. Right from collection of batteries from waste dumping areas and collection centres till the delivery of the final product to the market, a lot of opportunities are created.

**Environment becomes clean**: the cleanliness of the surrounding increases as very little waste is dumped. This has a positive impact on the environment. This in turn protects the biodiversity.

**Reduces global warming**: the dumping of waste and its burning causes emission of various toxin gases like sulphur, carbon, nitrogen and so on. This gets absorbed into the atmosphere which in turn triggers global warming and climate change.

**Disadvantages of battery recycling**

- The value of the recycled products is comparatively low as compared to newer products.
- Recycling is not a cost effective method as huge investment is required in setting up of industries.
- Recycling does not guarantee good quality products.
- The breakdown of batteries in the recycling process causes emission of toxins that are harmful and thus polluting the environment.

**Recycling of Lead-Acid Batteries**

The major source of raw material for lead recycling are starter batteries from motor vehicles. Modern car batteries consist of a PP (Polypropylene)-casing, plates (grids and paste), connectors/poles and bridges and PP-separators as insulators between the plates. Paste consists of Pb, $PbO_2$ and $PbSO_4$.

**Composition of a 12V-44Ah-210 A-starter battery in a hard rubber casing**

| | |
|---|---|
| lead containing components | 58,8% |
| hard rubber | 17,7% |
| sulphuric acid | 26,2% |
| separators (PVC) | 2,3% |
| | ---------- |
| | 100,0% |
| total weight | approximately 15 kg |

**Figure 1.8:** (a) Composition of Lead acid battery (b) Diagram of Lead –acid battery

The electro-chemical reactions which take place during charge and discharge of a lead acid battery are:

**Charging**:

$2PbSO_4 + 2H_2O \rightarrow PbO_2 + Pb + H_2SO_4$

**Discharging:**

$PbO_2 + Pb + H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$

## Metallurgical aspects of lead recycling from battery scrap

Lead acid batteries are recycled pyrometallurgically with initial physical separation and subsequent hydrometallurgical steps

1. Spent batteries are broken/crushed into small pieces.
2. After breaking, the material is passed to a sink/float operation. This hydrodynamic process separates the metal from separators and casing material.
3. The casing material is usually polypropylene (PP), although acrylonitrile butadiene styrene is becoming more widespread because of its higher strength. Separation is accomplished by virtue of the density difference between materials using a fluid of intermediate density between the solid phases. Since the density of PP is less than that of water, while the density of lead metal/compound is much higher, sink/float operation is extremely effective, achieving almost complete quantitative segregation.
4. Plastics are subsequently cleaned and sent for recycling into new battery cases or for other uses. Lead, grid straps and battery paste (a combination of the $PbO_2$, PbO and $PbSO_4$) are removed from the bottom of the sink/float operation and sent to storage for water removal prior to smelting.

A typical flowchart for secondary lead recycling is shown in **Figure 1.9**.

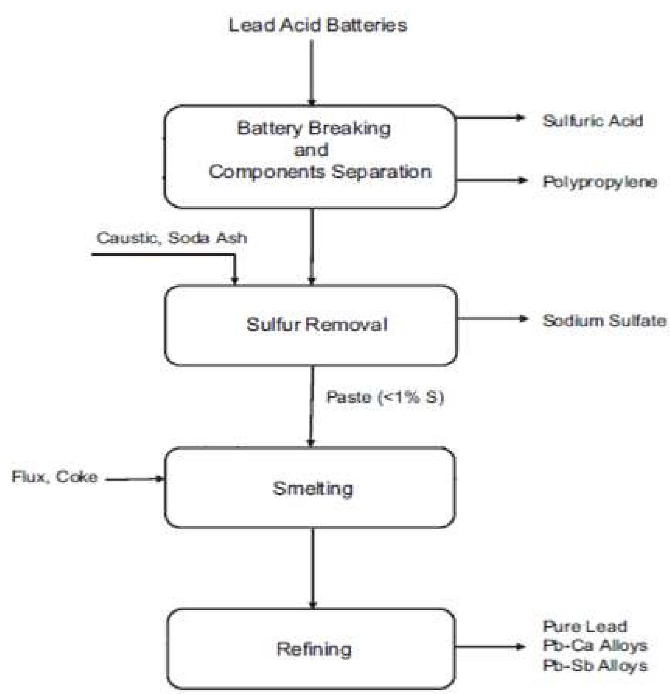



**Figure 1.9:** Flow chart for Recycling of Lead-Acid Batteries

**Lead recovery:** Either the components of an accumulators like lead, plastics, acids, etc. are at first separated and then processed individually.

The first type of chemical reaction converts $PbO_2$ into Pb through a reduction process:

$$PbO_2 + C \rightarrow Pb + CO_2$$

**Sulphur removal:** The second type converts $PbSO_4$ into PbS, again through a reduction process:

$$PbSO_4 + 2\,C \rightarrow PbS + 2\,CO_2$$

Finally PbS is converted into Pb through the following reaction

$$PbS + Fe \rightarrow Pb + FeS$$

Removal of Sulphuric acid can be done by neutralizing with soda ash or caustic soda

$$2\,NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2\,H_2O$$

**Pyrometallurgical extraction of cobalt form spent mobile phone**

This process is widely used for the commercial recovery of Co from spent mobile phones. The commonly used treatment of spent Lithium ion batteries (LIBs) is similar to the ore smelting.

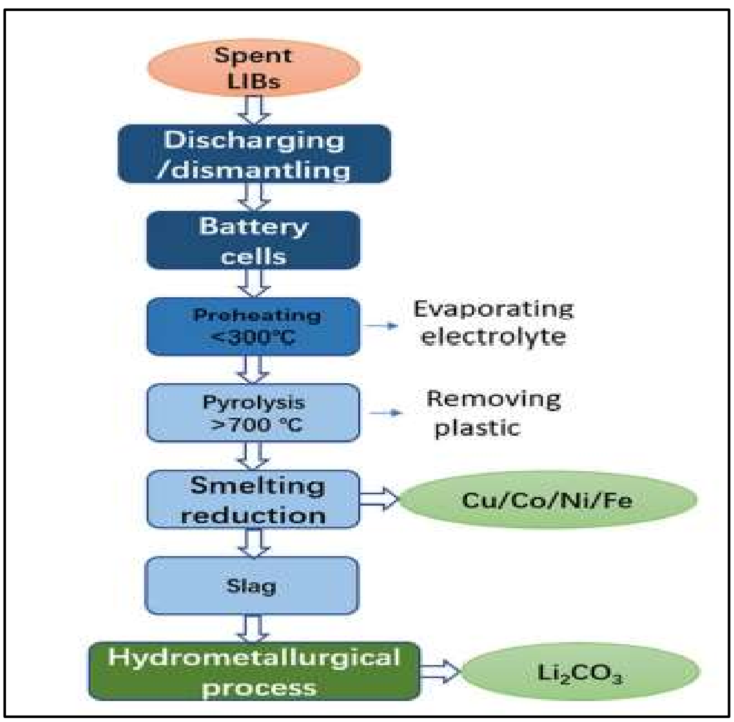



**Figure 1.10:** Flow chat for extraction of metal

1. Before the smelting process, the modular LIBs are first disassembled into separate cells and then fed into a heating furnace. These materials further are reduced by preheating, pyrolysis and smelting, successively.
2. In the preheating zone, the heating temperature should be lower than 300 °C to ensure complete evaporation of the electrolyte without explosion. And in the pyrolysis zone, the furnace temperature is controlled above 700 °C. The purpose of this is to remove the plastic from the battery.
3. In the smelting reduction zone, the material is smelted into alloys of Cu, Co, Ni, and Fe, with the aid of carbon reductant, along with Li, Al, Si, Ca, and some Fe slag.
   Since Co plays an irreplaceable role in commercial LIBs, and thermal metallurgy has a high efficiency in recovering Co rather than Li, the economy of this recovery method depends largely on the amount of Co contained in spent LIBs and the fluctuation of market value of cobalt.
4. In order to recover Li from the spent LIBs, the **selective pyrolysis** method of an arc furnace can be used to convert some electrode materials into Co alloys and Li concentrate. After that, the Li is extracted by hydrometallurgy, and then it is transshipped and stored through the form of $Li_2CO_3$. And other components can be extracted further.
   The specific steps are shown in the flow sheet (**Figure 1.10**). This method can be used not only to recycle electrode materials, but also to recycle Li and Fe, etc. in the electrolyte, which greatly improve the recovery efficiency.

### 1.6 A Circular Economy approach to E-Waste Management

The origin of the concept of circular economy (CE) dates back to 1989, when environmental Economists David W. Pears and R. Kerry Turner introduced the circular economic system.

A circular economy not only minimizes wastes by closing the products and/or material loops in the industrial ecosystem; but it also changes the economic logic by replacing ‘production’ with ‘sufficiency’ by the means of **reuse, refurbishment, remanufacturing and recycling**.

The Conventional Economic System was based on linear models where natural resources were exploited and converted into some products which were to become waste eventually. There was no flexibility in crafting and design of products so that they could be reused or recycled. On the other hand, the Circular Economy Approach works on an innovative economic model to tackle the global crises of pollution, loss of biodiversity, climate change and e-waste management.

A circular economy approach favours closed loop systems where resources are employed carefully to create innovative products which can be used for longer periods of time by reusing, sharing, refurbishing and recycling. Longer periods and smart design also imply greater productivity. Therefore, the circular economy approach is going to be the backbone of sustainable economies of the future.

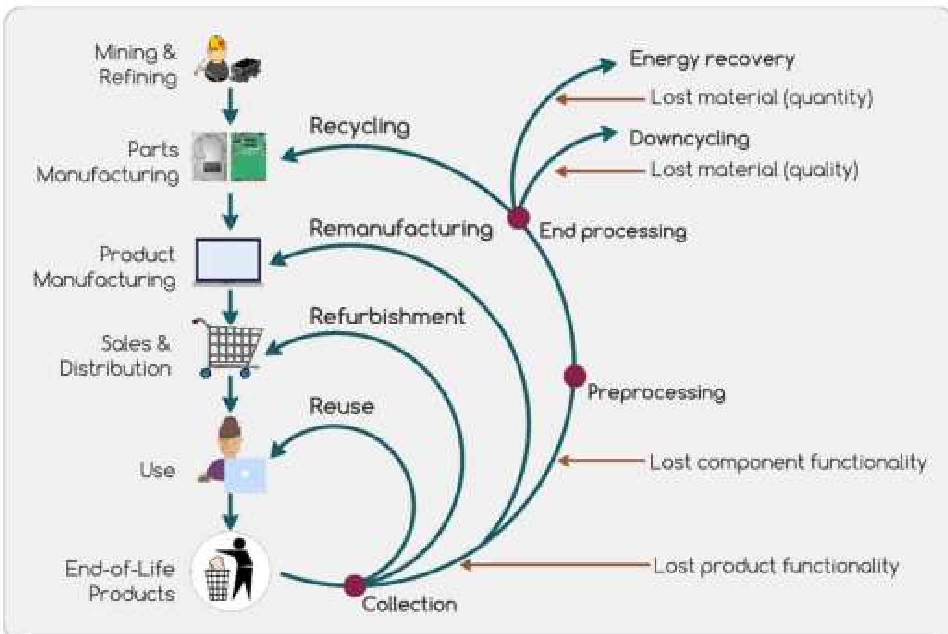



**Figure 1.11:** Illustration of the circular economy concept