Bioprocessing of Metals from Packaging Wastes

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Abstract Packaging refers to the covering used to protect the product inside. Metals—such as iron, copper, and their alloys, i.e., brass and bronze, have been used for the packaging and storage of goods since ancient times. Unique properties of metals, particularly the ease of fabrication, strength, thermal and electrical conductivities, and ability to hold diverse materials securely in different states, make them an essential packaging material either as such or as composites with materials such as polymers, fibers, plastics, and ceramics. Boxes, cans, cylinders, and foils made from iron, aluminum, tin, copper, etc., are the most common and everyday examples of metal-based packaging; however, specialized packaging requirements, e.g., for electronic parts, composites based on different metals are preferred. After its end use, discarded packaging becomes a major contributor to waste generation. Completely metal-based packages can be recycled; however, this becomes expensive for composites. In such cases, landfilling is the most common disposal method, which may cause adverse impacts on human health through the contamination of groundwater and soil. This calls for effective and better alternate metal waste-management options that can help metal recycling and recovery. In this chapter, we present a brief introduction of metal-based packaging, their various methods of disposal, and recovery and recycling options with particular focus on biotechnological approaches. With the help of different examples and recent developments in the recovery and reuse of waste metals, potential sustainable and cost-effective solutions in managing metallic or metal-based packaging waste are discussed.

Keywords Metals · Composites · Recycling · Packaging waste

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1 Introduction

Packaging is an essential part of our daily lives and is associated with all consumer products, transportation of goods, and services. Moreover, packaging reflects cultures, traditions, and lifestyles. In industrial goods, packaging is a technical and crucial component because it is not merely a covering but a protection, and many times it may have functional roles. Metals have always been an essential packaging material due to their strength, their ability to easily contain solids as well as liquids, fine finishing and crafting options, and durability. However, current packaging materials have become extremely diverse and specialized for packaging purposes. Modern packaging materials also contain metals as their key components specifically to impart properties of electrical and thermal conductivities, malleability, ductility, and mechanical strengths such as coordination polymers, plastic-like metallized polyethylene terephthalate, and metal-matrix composites (MMCs).

After removal of a product from its packaging, the packaging is usually rendered useless and ends up as a waste. For instance, packing materials from households constitute nearly 30 % of total municipal solid wastes (MSW). However, packing materials generated at domestic levels are largely recyclable; in fact, 48.5 % of it is recycled in United States. The recycling rates of metal-based packaging waste, e.g., steel, aluminum, glass, plastic, paper, and paperboard, were approximately 69.0, 35.8, 33.4, 13.5, and 71.3 %, respectively (US-EPA 2010). Because the production of goods, their transportation, and their consumption are increasing, there has been a surge in discarded packaging, the proper disposal, recycling, and reuse of which poses a huge challenge. In this scenario, recovering metals from such discarded materials becomes crucial because they are limited resources, and they contaminate the environment.

In this chapter, we provide an overview of different types of metal-based packaging, the evolution of such packaging, and the emergence of new materials that contain metals in different proportions as their constituents. Then the chapter discusses the issue of waste generation due to these packaging materials, the implications for the environment, and the practices adopted for managing such waste. The focal point is to present the prevalent and potential reuse and recycling techniques for metal-based packing waste. The chapter concludes with an outlook for the sustainable management of metal-based packaging materials in light of the ongoing progress in this direction.

2 Types of Metal-Based Packaging Materials

Metals have been in use since ancient times, and they were also some of the first materials used for the storage and transportation of goods in the form of boxes and containers. Precious metals, such as silver, were being used by royal families, whereas brass, aluminum, iron, and tin offered much cheaper alternatives for common use and also helped with the long-term storage and long-distance transportation of materials. In time, cheaper metals, stronger and lighter alloys, thinner foils and gauges, and versatile metal composites with polymers and other materials have evolved, which serve different packaging requirements. In addition to being used in their original form, metals also impart color, strength, and conducting properties, which make them an essential constituent of many other packing materials such as glass, polymers, plastics, papers, paperboards, etc. The most common metals used are chromium (Cr), lead (Pb), arsenic (As), cadmium (Cd), aluminum (Al), etc. Most of these metals become toxic to plants, animals, and humans when present in high concentrations in the environment.

2.1 Metals and Alloys

Metallurgy was invented in ancient times, and metals have become an important packaging material since then because they offer a multitude of design options, strength, and versatility for reuse. Even in modern times, metals as such are an unrivalled premium packaging option. One of the most common type metal-based packaging items is to use it directly in the form of barrels, cans, and boxes. Even though metal containers contain all kinds of items, including liquids, it was not a convenient option until an easy method of opening them was invented. The can opener was invented in 1875 and made metal packaging a suitable option even for households. Thereafter, more improvements were made leading to pop-top and tear-tab can lids near 1950, and currently tear tapes and screw tops have been invented for small packaging (Hook and Heimlich 2011). Besides their use in their pure form, metals are increasingly been used in combination with other materials such as glass, wood, plastic, and polymers. They form different parts such as lids, frames, screws, springs, and decorations. Such types of packaging are particularly useful in the food industry and even for small-scale domestic storage. Metals are impermeable to air and water and hence greatly reduce the chances of contamination. This property therefore provides longer shelf life, tamper evidence, total protection against external damage, and safe containment of reactive items such as food, paints, medicines, etc. Working with metal containers is easy and efficient because there are minimal losses at all stages of filling, sealing, packing, distribution, and sale. Therefore, metals are the popular choice in the form of drink cans, food cans, aerosol containers, tubes, open trays, caps, foil containers, etc. In addition, they are fully recyclable. Some commonly used metals and alloys are detailed below.

2.1.1 Aluminum

Al is a silvery white, nontoxic metal that is commonly used for making cans, foils, and laminated paper or plastic sheets. It is one of the safest packaging options when it comes to contact storage of food items. At $pH < 4.5$, Al uptake from uncoated food contact materials made of pure Al is affected by the acidity of the food product and the solubility of the salt formed (Cutter 2002). Hence, pure Al is not a preferable packing option for such items. Foodstuff having higher salt concentrations inside the packaging material may also increase the migration of metals (Elinder and Sjogren 1986). Al is normally coated for packaging applications. Moreover, in a range of applications in many industries, Al containers are used for different processes of transformation of food such as refrigeration, freezing, cooking, preservation, modified atmosphere sterilization, and pasteurization (Holdsworth and Simpson 2007). To improve its properties, Al is often made into alloys which are resistant toward corrosion. Al alloys may contain magnesium (Mg), silicon (Si), iron (Fe), manganese (Mn), copper (Cu), and zinc (Zn) (CEN 2004). Its compounds, particularly aluminum oxide, are used as coatings creating a barrier against air, temperature variation, moisture, and chemical attack.

2.1.2 Steel

Steel, an alloy of Fe and carbon with some other elements depending on the type and quality to be achieved, is one of the most popular packaging options when it comes to strength, ease of fabrication, reusability, and heavy-duty use. Steel is used for the fabrication of strong frames for the packaging and transportation of industrial goods and equipment. Thus, it is also popular for food-contact packaging applications because different grades of steel can offer hygienic and convenient options. Food-containing grades of steel are essentially electrolytic tinplate (ETP) and electrolytic chromium/chromium oxide coated steel (ECCS) (CEN 2001). The Cr coating prevents atmospheric oxidation and sulphur staining and improves lacquer adhesion. ECCS also has an additional organic coating and is normally used for drawn cans, can ends, and lug closures where welding is not required. The Cr coating provides excellent protection against corrosion due to sulfide staining by certain foods. Many times the sulphur present in the food products reacts with electrolytic tinplate as well as with ECCS causing the deposition of black SnS and white FeS, respectively.

2.1.3 Tin and Tinplate

Tin (Sn) is typically used in its pure form or is applied as an additional thin layer on steel used for packaging. Tinplate, on the other hand, is produced from low-carbon steel by coating it with thin layers of Sn. Coating is performed by dipping the steel sheets in molten Sn (hot-dipped tinplate) or by the electro-deposition of Sn on the steel sheet (electrolytic tinplate). Although Sn provides corrosion resistance to steel, tinplate containers are often lacquered to create an inert barrier between the metal and the product, especially if it is used for packing food items. The commonly used lacquers in the process are epoxy phenolic and oleo-resinous groups and vinyl resins. Thus, acting as an excellent barrier against gases, water vapor, light, and odors, tinplate can be heat-treated and sealed hermetically, thus making it effective for packaging sterile products. It is also an excellent substrate for litho-printing and is an outstanding graphical decoration. Its relatively low weight and high mechanical strength make it easy to ship and store. At end use, tinplate can be easily and economically recycled multiple times without loss of quality.

2.1.4 Tin-Free Steel

Tin-free steel often requires a coating of organic material to provide complete corrosion resistance, and it is marginally less expensive than tinplate. Even though the chrome/chrome oxide makes Sn-free steel unsuitable for welding, it offers excellent adhesion of coatings such as paints, lacquers, and inks (Fellows and Axtell 2002).

2.2 Glass

For generations, glass material has been widely used for packaging of reactive substances such as chemicals. Moreover, glass is more a traditional and attractive packaging material when it comes to traditional preparations including drinks and processed food. Glass can be made in different colors and molded into a variety of shapes. Manufacturing and processing of glass involves different metals. Glass is manufactured from sand, soda ash, limestone, and cullet as well as their mixtures. To impart colors in glass, oxides of Fe, chromium (Cr), cobalt (Co), nickel (Ni), and selenium (Se) are used, respectively, for yellow/green, green, blue, violet/brown, and red colours. Lead glazes are widely used on pottery because they are inexpensive and easy to use (Colomban 2005).

2.3 Paper and Paperboards

Paper and paperboard are one of the most common packing materials worldwide (Table 1). Although they are made from wood, plants, and recycled paper and paperboard waste, they contain several metals such as Pb, Cr, Cu, and Ni in very low concentrations as contaminants. Packaging industries mostly use corrugated paperboard for making paper packaging. According to the European Parliament and Council Directive 94/62/EC norm (w.e.f. 2001), the amount of Pb and Cd in packaging materials should not exceed 100 ppm to prevent migration from packaging to food by weight over 5 years (Rozaslin et al. 2010). Metal migration from food packaging and food containers to food and beverages could be due to pH and salt concentrations of the food products and the coating of packaging. Lithopone used in the filled paper coating uses zinc sulfide and barium sulfate. Cd or Zn

Table 1 List of packaging materials from paper and paperboards

Paperboards	Paper
1. Corrugated container 2. Folding cartons 3. Sanitary food containers (milk and beverages, cartons and trays, lipid tight) 4. Fibre and composite packaging (cans, drums) 5. Rigid boxes 6. Moulded pulp products	1. Flexible packing 2. Converted wraps 3. All papers 4. Paper foil 5. Wrappers 6. Specialty bags 7. Label and tags 8. Heavy-duty bags 9. Tapes 10. Wadding

pigments are sometimes used for the improvement of the fluorescence properties of papers, whereas zinc oxide is used to enhance the cohesive strength of paper coatings. During recycling of paper mill sludge, concentrations of metals such as Zn, Pb, Cd, Ni, and Cu increases. Rozaslin et al. (2010) studied heavy metals in raw recycled paper mill sludge and found Cu, Zn, Ni, and Pb concentrations $\leq$88, 251, 26, and 177 mg/kg, respectively.

2.4 Textile

Growing demand for reusable packages and containers is opening new opportunities for textile products in this market. Packaging comprises numerous flexible packaging materials made of textiles are used for packing a variety of commodities for industrial, agricultural, consumer, and other use. Metals, being an essential constituent of most dyes, are used in textiles in low concentrations. For example, C.I. Mordant Black 11, the most common black dye, is Cr based and is used in the coloration of textiles (Rybicki et al. 2004). On-demand customization and supply of sacks and bags made of traditional jute, cotton, or other natural fibers are gradually increasing and are now termed “Packtech”. They can range from heavy weight, densely woven fabrics—such as bags, sacks, flexible intermediate bulk carriers, and wrappings—to light weight, non woven material such as durable papers, tea bags, and wrappings. Other common examples of textile packaging include laundry bags and other bulk-packaging products; sacks for storage; twine and string to tie packages; non-paper tea bags and coffee filters; soaker pads (food); net and woven fiber strapping; lightweight mailbags; and soft luggage.

2.5 Laminates and Metallized Films

Laminates involve the binding of aluminum foil to paper or plastic film, whereas metallized films are plastics containing a thin layer of aluminum for the improvement of barrier properties against moisture, oil, air, and odor (Fellows and Axtell

2002). Lamination is mainly used for high-value foods such as dried soups, herbs, and spices. Although the components of laminates and metallized films are technically recyclable, the difficult processes before recycling include sorting and separating the material, which precludes economically feasible recycling.

2.6 Metals Composites

Composites are one of the most recent classes of materials that possess greater strength, are lighter in weight, low in maintenance, and high in durability. Their use is increasing in engineering applications. Composites can be in the form of particulates, fiber-reinforced, or structural. Based on the general composition, composites can be classified into polymer-matrix, metal-matrix, and ceramic-matrix composites. MMCs are important packaging materials being used in the electronics, automobile, and aviation industries. However, their cost-effectiveness remains an area in need of research and development.

Among different types of MMC, "cermet" or "cemented carbides" consisting of ceramic particles in a metal matrix is an important and widely used class of materials. In these composites, tungsten carbide or other similar particles are bound together by high temperature and thus can withstand high temperatures. These can provide protection from high-temperature destruction. Currently, Al and Cu reinforced with high thermal-conductivity carbon fibres and SiC particle-reinforced Al are the most preferred packaging MMC options. Boron fiber-reinforced Al (B/AI) heat sinks are in a few production systems, and particle-reinforced (BeO)/AI has recently been commercialized.

2.7 Antistatic Packaging

Antistatic packaging is used to protect the materials from electrostatic charges. It is usually used for the packaging and transportation of sensitive electronic components such as populated printed circuit boards. Antistatic packaging usually comprises plastic polyethylene terephthalate, which is generally metallized, which gives them a characteristic silvery black color (Yam 2009). With the increase in manufacturing and transportation of electronic products and pieces, the use of antistatic packing materials is also increasing, and their after-use management will pose a large challenge in the future.

The metallization of plastic polyethylene terephthalate makes it slightly conductive; hence, the product kept inside such a close packet forms a "Faraday cage," thus preventing it from static charges that otherwise accumulate on other materials being rubbed when bags are handled. The other variants of antistatic packing materials that include different polymers are made of low-charging material that does not allow a build-up of charges, but it cannot protect the packaged item from electrical fields as effectively as the metallized variants do. Table 2

Table 2 Metal-matrix composites for different levels of electronics packaging (based on Zweben 1992)

S. no.	Level	Application	Requirement	Components used for MMC packaging
1	Package	Heat sink/cold pates	Heat dissipation (high thermal conductivity) Low thermal stresses Hermeticity Electromagnetic shielding	Carriers Eectronic packages Microwave packages Photonics packages Laser diode packages
2	Printed circuit boards Package support plate		Heat dissipation Low thermal stresses Vibration (high stiffness, damping) Lightweight	Printed circuit boards Printed circuit board heat sinks Package-mounting plates
3	Subsystem (box)		Heat dissipation, insulation vibration and shock (high stiffness, strength) Electromagnetic shielding Light eight	Electronic enclosures (chassis, black boxes) Covers
4	Support structure		Vibration and shock Lightweight	Support structures

provides the desirable characteristics for the packaging of electronic items and application of MMCs. Disposal of electrostatic packaging materials is commonly through land filling. However, a few variants have entered the market that degrade in approximately 9 months.

3 Post-use Management of Metal-Based Packaging Materials

After use, the packaging material either turns into waste or is reused and recycled depending on its after-use conditions, its properties, and the cost-effectiveness and practical feasibility of recovery and recycling. The most convenient and common method of disposing waste is landfilling or incineration. This technique, however, contaminates the environment by way of leaching to groundwater, surface-water runoff, air emission of toxic contaminants, and deteriorating soil quality. However, when it comes to metals, a major fraction of these are recyclable. Where metals are present in small quantities, such as in textiles and paper, recovery techniques are being developed. In composites, where metals are intricately associated with non biodegradable polymers, methods are being developed to promote their reuse and biodegradation. Most of these are in primary phases of research and development, but they offer potential solutions for the future. In subsequent sections of this chapter, we briefly discuss the implications of metal contamination in the environment resulting from waste disposal as well as developments in the recycling, reuse, and recovery of metal-based packaging.

4 Human Health Effects of Toxic Metals

Metals are worldwide-distributed pollutants and are notable for their tendency to bioaccumulate and biomagnify with their increase in the tropic level. Some metals, such as Cu, Mg, Zn, Fe, etc., are essential for human and plant life and play a significant role in the functioning of enzymatic systems. However, metals exceeding their threshold limit for human consumption or exposure may cause improper functioning of human physiology and metabolism. Other metals, such as Pb, Cd, Hg, As, Cr, etc., have no useful role in human physiology, and moreover they may cause harmful effects on human health. Table 3 shows the effects of various metals on human health.

Table 3 Harmful effects of selected metals on human health

Metals	Adverse effects on human health	References
Iron	Neoplasia, cardiomyopathy, atherosclerosis, and chronic diseases	Gackowski et al. (2002), Kruszewski (2004)
Copper	Weakness, lethargy, anorexia, dysfunction of kidney, liver, and brain; vascular collapse; cirrhosis, obstructive hepatobiliary disease; extrahepatic biliary atresia; neonatal hepatitis, choledochal cysts; and a-1-antitrypsin deficiency	Semple et al. (1960), Winge and Mehra (1990), Beshgetoor and Hambidge (1998)
Zinc	Decreased immunity, lethargy, focal neural deficit, respiratory disorder, nausea/vomiting, epigastric pain, diarrhea, prostate cancer, altered lymphocyte function, Cu deficiency	Mocchegiani et al. (2001), Plum et al. (2010)
Manganese	Psychiatric symptoms such as hyperirritability, violent-acts hallucinations, decrease of libido and incoordination, crippling of extrapyramidal system, neurological disorder, paralytic disease, and pancreatitis	Cotzias et al. (1968)
Magnesium	Muscular weakness, difficulty in breathing, electrocardiogram changes	Workman et al. (2013)
Cobalt	Cardiomyopathy, hypothyroidism, neurological damage, impaired senses, polycythemia, neuropathy, seizures, headaches, liver damage, blindness, cancer	Sauni et al. (2010), Catalani et al. (2012)

(continued)

Table 3 (continued)

Metals	Adverse effects on human health	References
Molybdenum	Increased blood uric acid, gout, pneumoconiosis, liver cirrhosis	Hanaa et al. (2000)
Chromium	Dermatitis, allergy, asthma, eczema, ulcer, gastroenteritis, perforation of the nasal septum, bronchial carcinomas, hepatocellular deficiency, renal oligoanuric deficiency	Baruthio (1992)
Lead	Learning disabilities, behavioral problems, mental retardation, seizures, coma, death at higher doses	Harvey (2002)
Cadmium	Hypertension, arthritis, diabetes, anemia, arteriosclerosis, impaired bone healing, cancer, cardiovascular disease, cirrhosis, reduced fertility, hyperlipidemia, hypoglycemia, headaches, osteoporosis, schizophrenia, strokes	Benoff et al. (2000)
Arsenic	Anorexia, edema, fluid loss, goiter, herpes, interferes with the uptake of folic acid, inhibition of sulfhydryl enzyme systems, jaundice, kidney and liver damage, pallor, peripheral neuritis, stupor, vasodilation, vertigo, vitiligo	Col et al. (1999)
Mercury	Miniamata disease, adrenal gland dysfunction, alopecia, anorexia, ataxia, bipolar disorder, birth defects, dizziness, fatigue, hearing loss, hyperactivity, immune system dysfunction, kidney damage, numbness and tingling, excessive salivation, schizophrenia, thyroid dysfunction, timidity, tremors, peripheral vision loss, blindness	Grandjean et al. (2010), Trasande et al. (2005)
Aluminum	Amyotrophic lateral sclerosis, anemia, colic, fatigue, dental caries, dementia, dialactia, hypoparathyroidism, malfunctioning of the kidney and liver, neuromuscular disorders, osteomalacia, Parkinson's disease, Alzheimar's disease	Yokel (2000), Reddy (2014)
Nickel	Vertigo, cyanosis, tachycardia, palpitations, lassitude, kidney dysfunction, lethargy, ataxia, hypothermia, asthma, bronchitis, rhinitis and pneumoconiosis, and enetic, developmental, immunological, neural, and reproductive defects	Das et al. (2008)

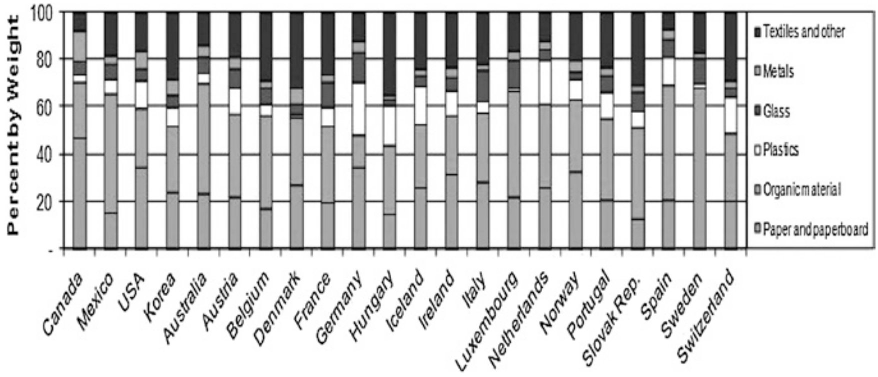

Fig. 1 Municipal solid-waste composition in different countries (adapted from http://faculty.mercer.edu/)

5 Share of Metal-Based Packaging Materials to Waste Composition

There is lack of information on how much metal-containing packaging waste is generated in different parts of the world and from different sectors; however, there are few studies in certain parts of the world focusing mainly on municipal waste. As is clear from Fig. 1, metals are the smallest constituent of waste generated in most countries. Paneque et al. (2008) observed that between 1997 and 2005, packaging waste-generation increased significantly and was directly correlated with an increase in GDP. During this period, metal packaging waste increased by 37.47 %.

6 Management of Metal-Based Packaging Waste

To manage the increasing quantity and complexity of waste generation from different sectors, smart, economic, and environmentally friendly management systems are required. Currently the most common mode of waste management is landfilling incineration. Landfill sites are large areas meant for waste disposal. It is also a cost-effective way of waste management. Contrary to this, resource recovery and incineration both requires extensive investments for infrastructure. Modern landfills are well-engineered facilities with several measures—such as appropriate location, design, operational procedure, and monitoring at regular time intervals—to ensure compliance with federal regulations. Municipal solid-waste landfills receive household waste, packaging waste, non hazardous sludge, industrial solid waste, and construction and demolition debris. In most countries, landfills must comply with certain criteria including the following:

- Establishment of the landfill site in suitable geological areas away from faults, wetlands, flood plains, or other restricted areas;
- Bottom and sides of the landfill must be compacted, e.g., with clay soil, to prevent leaching;
- Treatment and disposal of leachates from landfill;
- Covering of landfill site to reduce odor; control litter, insects, and rodents; and protect public health;
- Regular qualitative analysis of groundwater to monitor leachates (if released);
- Covering of landfill along with long-term management of the landfill site; and
- Control and clean landfill contaminants released and maintain groundwater quality.

Several reports have suggested that metals entering the landfills is large enough to call them “future urban mines” (UNEP-International Resource Panel 2011). For Cu only, the global landfill stockpile is estimated to be 225 million metric tons. Incineration is another common technique of waste disposal. It offers the advantage of volume reduction of wastes and the destruction of much of the organic materials that could contribute to the production of toxic leachates and air emissions during landfilling.

Incineration is a significant technique of volume reduction and concentrates the metals present in waste to be disposed. However, it increases the mobility of the metals present, thus making them more bioavailable to be much more readily absorbed by living organisms, (Denison and Ruston 1990). Generally, incinerated waste is then dumped into landfills.

Although landfills stocks could be potentially reusable, their recovery may not be economically feasible. Several metallurgical techniques have been applied to recover metals from landfills and wastes (Jones et al. 2013). Mostly they consist of pyrometallurgical, hydrometallurgical, and biometallurgical techniques.

(a) Pyrometallurgical processing: Pyrometallurgy is a stepwise process including incineration, smelting, drossing, sintering, melting, and reactions in a gas phase at high temperatures (Gramatyka et al. 2007). The waste material is immersed in a molten metal bath at 1250 °C and churned by 39 % oxygenated air. During processing, plastics and other flammable materials degrade resulting in oxidative conversion of impurities, such as Fe, Pd, and Zn, into oxides fixed in an Si-slag. Thereafter, the metals are recovered from the slag. Cu film containing other precious metals is refined by electrolysis with nearly 99.1 % recovery of Cu along with precious metals such as gold, silver, platinum, palladium, selenium, tellurium, and Ni. However, the integrated smelters used for pyrometallurgy cannot recover Al and Fe because of their negative implications on the properties of the slag. Similarly, ceramics and glasses increase the amount of the slag from blast furnace and reduce the recovery of precious metals. Thus, pyrometallurgy favors the partial recovery of metals from wastes.

(b) Hydrometallurgical processing: During the past few years, hydrometallurgical techniques have been favoured over the pyrometallurgical processing due to its more predictable, easy, controlled processing. The hydrometallurgical processing consists of a series of acidic and alkaline treatments of solid materials. The initial steps involve the extraction of soluble constituents from solid waste using solvents in the forms of cyanide, halide, thiourea, and thiosulfate. Metal recovery from leachates is performed by cementation (Orhan 2005), solvent extraction (Navarro et al. 2007), adsorption onto activated carbon (Alorro et al. 2009), and ion exchange (Vasilyev et al. 2015). Furthermore, the metal-recovery process consists of low-temperature carbonization and roasting of the wastes, leaching with nitric acid solution to remove Ag and other metals, and the use of aqua regia for the extraction of gold.
(c) Biometallurgical processing: This may also be used as an alternative to the above-mentioned processes, although it is still in the very initial stages of application. Biometallurgy is a biotechnological process that utilizes the interaction between microorganisms and metals or metal-bearing substances. For example, solubilizing heterotrophic microorganisms, including bacteria and fungi, which secrete citric, oxalic, and gluconic acids (Henderson and Duff 1963; Avakyan and Robotnova 1971; Valix et al. 2001), can dissociate metallic ores or metals from solid wastes.

Although the extraction of metals from landfill sites may be feasible, recycling is the most preferable and environment friendly option; wherever recycling is not possible, it is recommended that their concentrations in the environment could be maintained below the recommended levels, a challenge or which biorecovery, bioleaching, and biodegradation offer a potential solution. Following sections discuss these waste management techniques.

7 Recycling and Reuse

Pure metallic or alloy wastes are among the most economically recycled wastes, and doing so has been in practice all over the world for a very long time. Graedel et al. (2011) analyzed the information available on metal recycling and found that the most commonly used metals have recycling rates of >50 %. Sorting, cleaning, melting, and casting are the four basic steps in metal recycling. However, the recycling process become complicated and eventually cost-intensive as the complexity of material to be recycled, e.g., composites, increases.

The major challenge in the recycling of the composites is the economic feasibility of the recycling processes and the recovery of various materials. This owes to the complex nature of the composites, differences in the composition of composites used for different products, and the unique physical properties of composites. For example, metals can be reclaimed from different alloys by subjecting wastes to high temperatures, which melt and separate into different components. This technique, however, does not work on thermoset composites.

Although technological advancements have made composite recycling more practical, lowering the price of the process and creating a suitable market for these recycled and reclaimed components remain challenging. However, a few companies have emerged that are making profits with the chopped and milled carbon fibres recovered from the aerospace industry.

Recycling technologies have also been developed for other types of composite materials such as thermoplastic matrix- and metal matrix-based composites. The common methods of recycling and metal recovery techniques from these materials include remelting–casting for MMC and direct remelting for dirty scrap. Remelting-casting of MMC is relatively costlier than the same technique being followed for alloys or reinforcements. For foundary scrap, direct remelting is performed under the inert atmosphere of dry Ar. To reuse MMC and dirty scrap, a combination of remelting, fluxing, and degassing cleaning are performed. Very dirty scrap, on the other hand, is used only for recovering metals following the techniques of remelting and refining to separate reinforcement from Al alloys. During various processes, ferrous metals are removed through magnetic separation. The techniques vary according to the MMC properties and compositions.

7.1 Recycling of Metal-Matrix Composites (MMC)

MMC materials have relatively much higher economic values than its constituent base metals or alloys. This makes the recycling of the MMCs economically infeasible, but their direct reuse is preferred. When the MMC packages become dirty or old after a single or several uses, their qualities can be restored to a degree by fluxing and cleaning by degassing. However reuse cannot go on indefinitely, and hence better recycling solutions become an important area of research and development.

Recovering metals from MMCs makes use of mechanical and chemical methods. In the mechanical method, the matrix metal is squeezed or filtered out of the composite after melting. The chemical method employs the use of a molten flux to absorb and wet reinforcement particles to facilitate easy separation from the molten metal. Electrorefining is carried out in ionic liquid composed of 1-butyl-3-methylimidazolium chloride and anhydrous $AlCl_3$. For some Al-based MMCs, Al metal or alloys are recovered through remelting. In the case where recycling of the whole material is not practical, the matrix metal is recovered by melting.

Another recycling approach is to use alternating layers of metal foils and fibre/matrix resin stacked and then consolidated under pressure, which leads to the formation of fibre–metal laminates usable in certain industries, most notably the automobile and aviation industries. The first such laminates, called ARALL (aramid-reinforced Al laminate), was produced by Vogelsang et al. (1981) and consisted of Al sheets and aramid fibre/epoxy prepreg. These laminates are now known as GLAss Reinforced (GLARE) FML (Vlot 2001). For example, GLARE FML as already been used in an Airbus model.

When it comes to recycling FMLs, their low production cost makes them a poor candidate for recycling. Although research is directed toward its recycling and reuse, due to the low market value of epoxy resin and glass fibre, only Al recovery is the main focus in the recycling of GLARE FML (Tempelman 1999). For this, GLARE is delaminated by cryogenic liberation to separate the Al foils from the epoxy resin and glass fibres. The next step is to subject the mixture of liberated Al and unseparated GLARE FML to an eddy current separator. The cost of low-temperature cryogenic liberation is high compared with the market value of the recovered Al scrap. For this, delamination occurs at high temperature of approximately 220 to 500 °C in an open furnace, which destroys the epoxy resin. Delamination in a fluidised bed reactor is another possibility. After thermal delamination, relatively clean glass fibres and Al plates are generated. For effective separation of the matrix metal/alloy from the reinforcement fibres and filaments, a mixture of NaCl and KCl—along with some fluorides such as Na_2SiF_6 and NaF—are used in molten form as a flux (Nishida 2001). Melting is conducted inside furnaces of different shapes and based on different techniques. The most common types are induction furnaces, reverberatory melters, hearth furnaces, and rotary barrel furnaces. The recycling and recovery of usable portions of metal and nonmetal components of carbon fiber are also being attempted. Boeing Company presents a great example: It recovers and recycles the scraps of its retired planes.

For thermosetting composites, reclamation is a three-step process comprised of the first thermal pretreatment followed by two wet chemical processes. Tertiary recycling reclaims fibres, thermoplastics, and thermosetting polymers. The thermosetting polymers are recovered into usable hydrocarbon fractions, which serve as building materials for new polymers, fuels, and chemicals. Various methods are employed to reduce size (crushing, chopping, drying, etc.), perform off-gas treatment and distillation, and recover metals, fibers, and carbon chars.

The most promising way of utilizing thermoset composites is to use them as filler materials in combination with conventional fillers, such as asphalt, after grinding them into granules. On the other hand, reclaimed short fibres are used to reinforce sheet molding compound and bulk molding compounds.

To promote the recycling and reuse of composites, most of the European Union (EU) member countries forbade landfill disposal of composites in 2004. In the United Kingdom, the planning of recyclability of components after their end use must be considered at the time of designing the product.

8 Toward Biodegradable Packaging Options of Metal Composites

One such composite is to use cellulose as the matrix. Besides being the most abundant and widespread biopolymer on the earth, cellulose also holds specific properties that make it a suitable candidate for the development of environmentally friendly, biocompatible, and functional composites. The molecular structure of cellulose and its tendency to form intramolecular and intermolecular bonding give it suitable properties to be used into composites. To make cellulose-based MMCs, varieties of metal nanoparticles can be used as dispersed phases in cellulosic bio-nanocomposites (Dankovich and Gray 2011; Wu and Fang 2003; Ma and Fang 2006). The synthesis of colloidal metal nanoparticles has received great attention, and significant advancement in their synthesis has been made during the last decade. Their large specific surface area and unique optical, electronic, magnetic, and antimicrobial properties have introduced them as a potential option in composite materials. Silver is one of the most common metals used in these biocomposites.

With proven efficacy as antimicrobial materials, silver nanoparticles have led researchers to formulate silver nanoparticles-cellulose matrix composites (Pinto et al. 2009), which can be used for antibacterial medical- and food-packaging materials.

9 Bioleaching

Bioleaching is the process to help solubilizing the metals from solid phase using biological processes such as the use of acid-producing microorganisms, fungi (*Astraeus odoratus*; Kumla et al. 2014), and sulfur-oxidizing bacteria (*Acidithiobacillus thiooxidans* and *Thiobacillus oxidans*; Dhakar et al. 2015). It is a cost-effective way of recovering metals from a much diffused state such as when they are present in compost or waste mixes, landfill, and soil (Pathak et al. 2009). Similarly, iron-oxidizing bacteria such as *T. ferooxidans* and *Leptospirillum ferooxidans* are used to oxidize ferrous compounds (Johnson and Mc Ginness 1991). Bioleaching techniques can be used in both direct and indirect ways. Direct mechanisms are employed generally to leach metal sulfide. Metals in wastes often get transformed into respective sulfides under reducing conditions of the waste layer. Tateda et al. (1998) reported that 0.7 % metals such as Cd, Cu, Pb, and Zn can be easily recovered by >50 % under the action of sulfur-oxidizing bacterium *Thiobacillus thiooxidans*. Bioleaching processes also depend on the physicochemical properties of the material, which affect metal solubility and microbial activities such as pH. Krebs et al. (2001) found that eight semicontinuous inoculations of the waste ash with *T. thiooxidans* resulted in high leach ability, e.g., >80 % for Cd, Cu, and Zn; 60 % for A; and 30 % for Fe and Ni.

10 Biosorption

Biosorption refers to the passive (i.e., not metabolically mediated) uptake of metal or nonmetal species by living or dead biomass (Fig. 2). This process plays a significant role in the removal and recovery of metals from wastes. Compared with other techniques, such as precipitation and synthetic ion exchange resins,

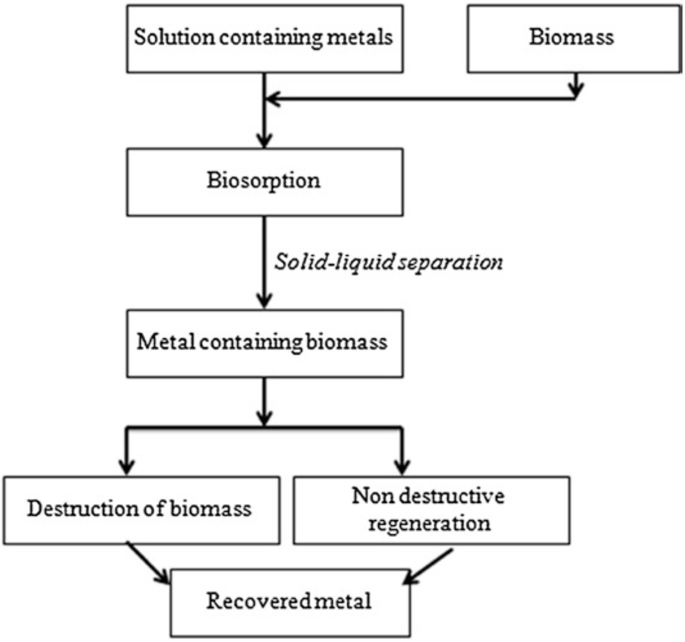

Fig. 2 Biosorption of metals from wastes using biosorbent material (based on Araujo et al. 2013)

biosorption is advantageous as a cost-effective and more efficient option (Volesky and Naja 2005). It encompasses a physicochemical mechanistic approach where metal species are removed from an aqueous medium by microbial biomass and certain products (Fomina and Gadd 2014).

A variety of microbial organisms and other biomass options have been reported to have good biosorption potential in removing metals such as Pb and Cr from wastes (Orhan and Buyukgungor 1993; Bahadir et al. 2007). For example, several species of algae (red and brown algae) possess high metal-binding capacity (Schiewer and Volesky 2000) whereby their cell walls bind to metals. The presence of carboxyl and sulphate groups in algal cell wall acts as active sites for metal binding. Alginate and fucoidan in brown algae are known for their metal-binding properties (Davis et al. 2003). The biosorption properties greatly depend on the environment, and pH plays a main role. Both carboxyl and sulphate groups become protonated at low pH and therefore become less available for binding metals. In addition to pH value, ionic strength also plays an important role in the process. Wastes are generally characterized by greater concentrations of sodium, thereby increasing the ionic strength and hence reducing biosorption (Greene et al. 1987; Ramelow et al. 1992) of weakly bound metals (Zn, Ni). However, strongly bound metals are unaffected by greater Na concentrations. Among diverse algal species, *Petalonia* sp. and *Sargassum* sp. appear to be the most promising biosorbing agents due to the presence of higher metal-binding sites (Schiewer and Wong 2000).

11 Metal Degradation

Metals corrode naturally through an electrochemical process, but this process can be enhanced by certain biological activities (Breslin 1993; Gu et al. 1998a, b; Ford and Mitchell 1990). As shown in Fig. 3, the microbial habitat on the surface of a metal forms a differential aeration zone under aerobic condition, which results in an electrochemical gradient at the interface of the microbial biofilm and the surface of the metal. The area exposed to oxygen serves as a cathode, whereas the area beneath the biofilm serves as anode. Electrons are transported from the anode to the cathode due to the electrochemical gradient resulting in metal dissolution, crevice corrosion, and pitting (Gu et al. 2000; Videla 1996; Ford and Mitchell 1990). Furthermore, the decline in the oxygen level results in the establishment of an anaerobic zone, thus supporting the growth of anaerobic microbes. These anaerobic microbial communities cause corrosion of underlying metals by cathode depolarization. Under anaerobic conditions, methanogenic microorganisms also participate in metal corrosion (Daniels et al. 1987). This biological process can be used for degrading metals present in the environment. A wide range of aerobic and anaerobic microorganisms cause biodegradation of metal alloys by the process of corrosion. Amongst aerobic microorganisms, sulphate-reducing (SRB), thermophilic, Fe-oxidizing, exopolymer, and acid-producing bacteria are the most common metal degraders. The mechanism involved is either metal transformation or complex formation, including the functional groups of exopolymers, with the release of metal species in the solution (Chen et al. 2006; Gu et al. 2000; Dexter 1993; Ford and Mitchell 1990).

In presence of the Fe-oxidizing bacteria (*Sphaerotilus* sp., *Leptothrix* sp., *Gallionella* sp., and *Siderocapsa* sp.) under oxygenic conditions and neutral pH, Fe^{2+} is oxidized to Fe^{3} thereby increasing the rate of Fe degradation. Fe_3O_4 thus formed is deposited enzymatically by *Gallionella ferruginea* and nonenzymatically by *Leptothrix* sp., *Siderocapsa* sp., and *Siderococcus* sp. (Ehrlich 1996). Similarly, Mn deposition takes place by the action of bacteria such as *Aeromonas* sp., *Caulobacter* sp., *Caulococcus* sp., *Citrobacter* sp., *Clonothrix* sp.,

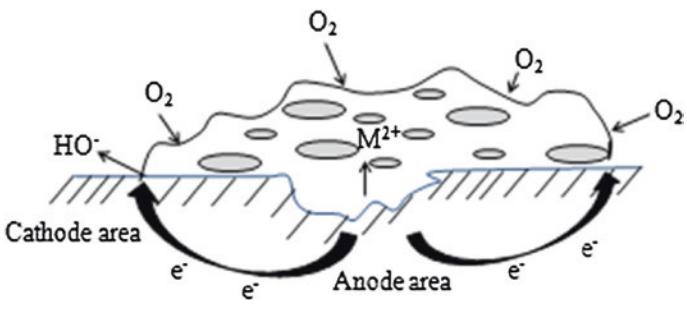

Fig. 3 Release of metal (M^{2+}) ions from anode area due to corrosion by microbial biofilm

Flavobacterium sp., *Pseudomona* sp., *Streptomyces* sp., and *Vibrio* sp. (Dickinson et al. 1996; Olesen et al. 1998).

Nonferrous metals are acted on by sulphate-reducing bacteria, which immobilize and precipitate them (Sakaguchi et al. 1993). This technique is particularly helpful in the conversion of toxic to nontoxic forms of metals. For example, the more toxic form Cr^{6+} is oxidized to the less toxic metal Cr^{3+} under the action of a range of microbes including *Aeromonas dechromatica*, *Agrobacterium radiobacter*, *Arthobacter* sp., *Bacillus subtilis*, *B. cereus*, *Desulfovibrio vulgaris*, *Eschericia coli*, *Enterobacter cloacae*, and *Flavobacterium devorans* (Ehrlich 1996).

12 Phytoremediation of Heavy Metals from Landfill Sites

Vegetation cover at landfill sites is effective in controlling erosion and the removal of contaminants and in the treatment of leachates (Maurice 1998). Phytoremediation is a plant-based technology that uses plants for the removal of pollutants such as metals, pesticides, solvents, explosives, crude oil and its derivatives, and various other contaminants from environmental media (air, soil and water) (Mc Cutcheon and Schnoor 2003). It is cost-effective facilitating easy monitoring of plant performance and potentially a least harmful method of metal removal that preserves the environment in its natural state. Phytoextraction, phytostabilisation, phytotransformation, phytostimulation, phytovolatilization, and rhizofiltration are other phytoremediation techniques. A generalized picture of the concept is given in Fig. 4.

12.1 Phytoextraction

Phytoextraction is the process of the removal of contaminants from contaminated soil, sediments, or water and their storage in harvestable plant biomass. Water hyacinth (*Eichhornia crassipes*) grown in tap water supplemented with 0.35, 0.70, and 1.05 mg l^{-1} of Cu or 0.27, 0.54, and 0.81 mg l^{-1} of Cd for 25 days effectively extracted approximately >90 % of Cu and Cd (Swain et al. 2014).

12.2 Phytostabilisation

This reduces the mobility of metals, thereby stabilizing them in the substrate or roots. For instance, poplar tree plantation is an effective tool in immobilizing water-soluble contaminants and arresting heavy metals at a contaminated site (Schnoor 2000).

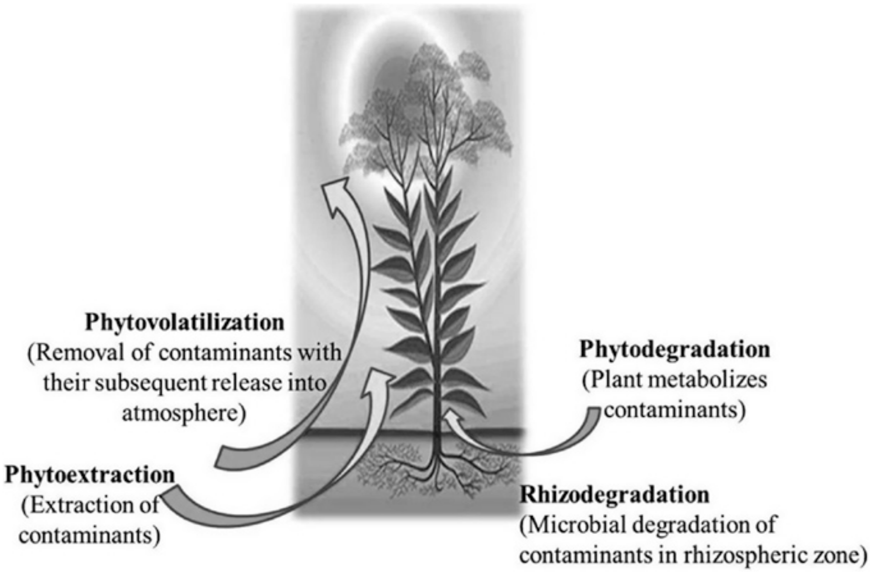

Fig. 4 Phytoremediation techniques for the removal of heavy metals from contaminated sites

12.3 Phytostimulation

An enhancement of soil microbial activities for the degradation of contaminants, typically in association with a rhizospheric zone, is termed "phytostimulation". Bacterial associations in the rhizospheric zone, which usually are also considered as plant growth-promoting bacteria, decrease metal toxicity to plants. Common bacterial species identified as phytostimulants are *Bacillus* sp., *Pseudomonas* sp., *Azotobacter* sp., *Rhizobium* sp., *Klebsiella* sp., and *Paenibacillus polymyxa* (Joseph et al. 2007; Phi et al. 2010).

Phosphate-solubilizing bacteria—such as *Rhodococcus* sp., *Arthrobacter* sp., *Serratia* sp., *Chryseobacterium* sp., *Gordonia* sp., *Phyllobacterium* sp., *Delftia* sp., *Xanthomonas* sp., *Azotobacter* sp., *Klebsiella* sp., *Vibrio proteolyticus*, *Enterobacter* sp., and *Pantoea* sp.—have also been found to be very effective in reducing metal toxicities in plants (Wani et al. 2005; Chen et al. 2006; Kumar et al. 2001; Chung et al. 2005; Vazquez et al. 2000).

12.4 Phytovolatilization

The process of uptake and release of the contaminant or a modified form of the contaminant into the atmosphere by transpiration is known as "phytovolatilization". It is not a very significant removal process for most metals; only for selected metals, such as Hg and Se, has it been reported as effective. For the uptake of Se by plants and its bioconversion into nontoxic gas, dimethyl selenide has been reported as effective (Terry et al. 1995).

12.5 Rhizofiltration

Rhizofiltration is the process where roots or whole plants absorb metals from polluted effluents and are later harvested to diminish metals in the effluents. Hence, it is primarily used to remediate extracted groundwater, surface water, and wastewater with low levels of metals (Ensley 2000).

12.6 Remediation and Biodegradation Potential of Earthworm Species

Leachates from landfill sites are the prime source of toxic and persistent metals. Remobilization of these toxic metals may harm both humans and our ecosystem. There are some bioprocessing methods to manage solid wastes. Vermicomposting of wastes has been recognized as a preferential option to stabilize various kinds of wastes (Negi and Suthar 2013). Gut microflora of earthworm degrades waste materials to finer substrates by mineralizing the organically bound nutrients into bioavailable form with the release of mineral nutrients through excreta. In addition, earthworm remediates heavy metals in processed products by accumulating metals in their intestine as metal-bound protein metallothionein (Sahariah et al. 2015). After the death of earthworm, metal-bound protein molecules exposed to the soil environment are retained in humic substances in immobilized forms (Nannoni et al. 2011). Saharia et al. (2015) reported a significant reduction in heavy-metal content after vermicomposting of MSW with cow-dung amendment.

13 Conclusion

Metals have been a preferred choice for packaging and storage since ancient times. Metals such as Fe, Al, Sn, and Cu were used as boxes, cans, and cylinders for containing and facilitating the transport of goods. In modern times, other metals, such as Pb, Cd, and Cr, in pure form or as alloys have been used, and are also mixed with other materials such as polymers, fibres, and plastics to produce next-generation packaging materials such as composites and laminates. These different metal-based materials enable the protection, transportation, and storage of variety of goods ranging from food material (e.g., cans, secure caps, food processing, and microbially protected containers) to sensitive electronic components (e.g., electrostatic packaging materials). However, with our increasing usage of packaging material, the generation of associated waste is also increasing. Common disposal techniques of packaging-related wastes are dumping them into landfills and incineration. Because metals can contaminate the environment and lead to serious human health hazards, metal-elated wastes are recycled, reused, and recovered. Due to their long life and retention of original material properties even after use, pure metals and alloys are easily recycled by remelting, purification, and casting. Composites and laminates are not economically beneficial to recycle, but methods have been developed to recover metals and other useful components based on different physical, chemical, and biological separation techniques at different stages of waste management. Among the different approaches, biotechnological methods offer technically as well as economically potential ways to recover metals from packaging wastes, landfills, and sites contaminated by metals. Among these, the development of biodegradable composites and biosorption appears to be a promising techniques that can improve the sustainable use of metal-based packaging by different sectors.

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