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Introduction to Sustainability and Green Chemistry

"We need a new system of values, a system of the organic unity between humankind and nature and the ethic of global responsibility."
Mikhail Gorbachev

1.1 Introduction

The growing necessity in the past few decades has initiated a mechanical thinking. Rapid industrialization has the impetus to increase the consumption of natural resources and consequently to degrade the environment by disposing off industrial effluents into the soil–water–air continuum in a cavalier manner. These activities result in change in weather patterns, global warming, foodborne contamination, and increasing rate of health risk, which have led to significant concern of researchers toward the concept of sustainable development (SD). A call for sustainability is required for preserving nonrenewable natural resources and improving industrial economy.

The World Commission on Environment and Development (WCED) launched the concept of SD to illustrate new schemes orientated to economic, social, and ecological benefits. A major step toward SD was initiated in 1987 by a commission under the Chair of Gro Harlem Brundtland (WCED 1987), convened by the United Nations in 1983. The report was commissioned to address issues such as the accelerating rate of deterioration of the environment and natural resources and its consequences on economic and social development. In the Brundtland report, SD was defined as "The development that meets the needs of present generation without compromising the ability of future generations to meet their own needs." This widely popular definition of SD posed several challenges to researchers and industrialists to equilibrate the ecological, economic, and technical development. Eventually, in order to respond to this challenge, the concept of Green Chemistry was nurtured.

Green chemistry is defined as "The process of manufacturing of chemical product in which raw materials are environment friendly, without use of any hazardous or toxic chemicals, energy efficient, inherently safer processes and involves minimum production of waste."

Sustainable Metal Extraction from Waste Streams, First Edition.
Garima Chauhan, Perminder Jit Kaur, K.K. Pant, and K.D.P. Nigam.

Although the terms “Green chemistry” and “Sustainability” are similar constructs that are used interchangeably in general, it is believed that the goal of sustainability is achieved using Green chemistry approaches. An overview of sustainability-related constructs is provided in this chapter to encourage readers, paying particular attention to the use of these terms in their studies. Dimensions of sustainability and new frameworks to define SD are also outlined. Green chemistry terminology and value stream mapping (VSM) are discussed in brief to make readers aware of the basic concepts of the green processes. A section at the end introduces the readers to the core theme of the book, which is centered around the recovery of metals from waste in a sustainable manner using green chemistry approaches.

1.2 Defining “Sustainability”

Sustainability can be defined as “The expectations of improving the social and environmental performance of the present generation without comprising the ability of future generations to meet their social and environmental needs” (Hart and Milsten 2003). Sustainability was cited in various ways in the literature based on the source; however, the core concept always refers to the society and the environment. Aras and Crowther (2009) referred to it as a fundamental and complex construct that mandates the balance of several factors on the planet to continually exist. This construct is also delineated as a belief of the preservation of natural resources.

Sustainability also considers the financial advantages in the present along with the assurance of benefits for the future generations. Elkington (2005) suggested “economics” as an integral factor along with social and environmental factors to attain sustainability and coined the term “triple bottom line (TBL).” This term was cited as the practical framework of sustainability by Rogers and Hudson (2011). The economic line of TBL framework concerns the capability of economy to survive and evolve into the future in order to support future generations. Industrial practices that are beneficial and fair to the human capital and to the community are included in the social line (Elkington 2005). Environmental line refers to the efficient use of energy resources and reducing the environmental pollution. A complex balance among the economy, environment, and society is the construct that leads to SD. These aspects of SD are essential to be considered by individuals and industries.

However, the lack of a rigid framework and poor interpretation of the term “sustainability” confronted inconsistency in its usage. Some sustainability studies are centered on one line only whereas some authors tried to include two or more lines in their studies. Yan et al. (2009) employed the term “sustainability” to refer to the environmental line, whereas the social line was emphasized by Bibri (2008). Some of the literature studies included the importance of the economic line into the term “sustainability” (Collins et al. 2007). Although very few studies managed to use this term to refer to all three bottom lines together (Marcus and Fremeth 2009), efforts are being made across the world to emphasize SD at national and international levels. Several organizations/industries are trying to incorporate these three lines of sustainability in their policies and cultures. For example, the International Organization for Standardization (ISO) provides Ecolabels to market products under various categories as follows:

Type 1 (ISO 14024: Environment labels and declaration): This type of products are in accordance with environmental criteria released by a third party organization. For instance, European Ecolabels are awarded on the basis of life cycle assessment (LCA) of a product under the supervision of the Ecolabel Committee. These labels are considered as a clear sign of environmental excellence. The products labeled under the European Ecolabel can become a product of choice for the consumers who are concerned for sustainability.

Type II (ISO 14021: Self-declared environmental claims): These labels are self-declared by companies or producers, based on environmental performances of their products, for example, the recyclability at end of the product life.

Type III (ISO 14025: Environment labels and declaration): These labels require a quantified declaration of the life cycle of the product, which can be verified by a third party organization. This helps to provide transparent information to the consumer for comparison purposes.

These labels consider the source of raw material, processing involved in the preparation of the final product, use, and end of life of the product. Moreover, these international environment sustainability labels are also based on the following aspects of a product:

i. Amount of energy and natural resources consumed during the production process
ii. Emission of toxic substances to the environment
iii. Impact of process on habitat and natural resources such as water, air, and soil
iv. Waste management practices followed by the organization.

Therefore, here it has become necessary to understand the dimensions of sustainability in order to maximize profits as well as to handle all the social and environmental responsibilities.

1.3 Dimensions of Sustainability

Three fundamental factors, i.e. People, Planet, and Profit (the three Ps) associated with the TBL construct, can be accounted as the dimensions of sustainability and outlined here as the traditional sustainable governance. Sustainability of any process thus banks upon the economic, social, and environmental pillars as shown in Figure 1.1. If any of these pillars is weak then the process cannot be considered a sustainable practice. The interlocking circles indicate that these three dimensions should be integrated in such a way as to be able to maintain balance between all the factors. It is observed that even most of the distinguished organizations focus on only one dimension at a time. The United Nations Environment Programme (UNEP), the Environmental Protection Agencies (EPAs) of

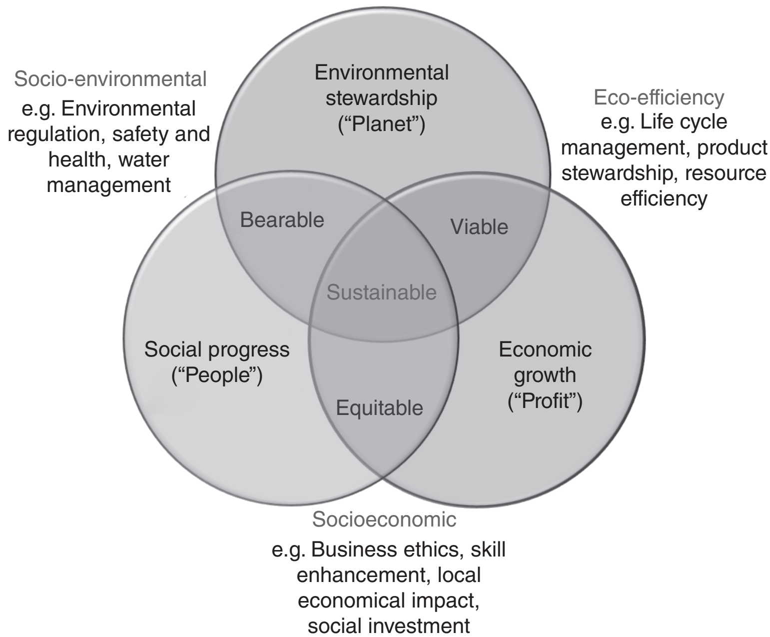


Figure 1.1 Dimensions of sustainability (three Ps).

many nations, and environmental nongovernmental organizations (NGOs) focus only on the environmental pillar. On the other hand, the primary focus area of the World Trade Organization (WTO) and the Organization for Economic Cooperation and Development (OECD) is centered on economic growth. It is difficult to include all the three pillars in one process; still efforts should be made in this direction for the continuance of natural resources indefinitely in future.

Economic pillar (the "profit" factor) of sustainability is referred to as the condition of necessary economic benefits projected indefinitely into the future. Economically sustainable industry should focus on the maximization of profit per unit of product, maintenance of a strong competitive position in the industry, and high level of operational efficiency along with being consistently profitable. Carroll (1991) presented a corporate socio-economic model that suggests that "initiating a strategy on socio-economic responsibility is the foundation on which other three dimensions are based on." Any new concept for sustainability should consider the costs of implementing sustainability and identify potential benefits to ensure long-term financial benefits. Thus, economic feasibility and process productivity are the most desired characteristics to define sustainable practices.

Social dimension of sustainability (the "people" factor) refers to a shared sense of social purpose to foster social integration and cohesion. An organization with social responsibility must ensure that it contributes the resources to the community and improves quality of life. Social responsibilities are also connected to the environmental pillar in order to provide a healthy ecosystem to the society. In this regard, safety, health care, environmental regulations, access to potable water, crisis management, and many other environmental practices become a part of the social pillar to achieve sustainability.

The contribution of the environment (the "planet" factor) to the economy and society is perceived to be through the operation of a wide range of environmental functions. De Groot (1992), defines "environmental functions" as "the capacity of natural processes and resources to provide services in order to satisfy human needs." Also, a natural process is based on complex interactions between living organisms, i.e. biotic components and chemical and physical components of ecosystems through the universal driving forces of matter and energy.

In support of the aforementioned definition, preservation of natural resources is one of the major responsibilities of the scientific community, which is further extended to the three Rs (Reduce, Recycle, Reuse) scheme to achieve sustainability. Several research efforts are being made in order to develop novel environment-friendly technologies, minimize waste generation, use open- and closed-loop recycling processes, use alternative energy sources, effectively utilize renewable/nonrenewable resources, and foster harmony between supply chains and nature.

1.4 New Conceptual Frameworks to Define Sustainability

1.4.1 Five Dimension Framework

The aforementioned WCED definition (WCED 1987) is widely accepted to delineate the term "sustainability"; however, some authors contended the anthropocentrism of the WCED definition. Anthropocentrism indicates that the gratification of human needs inherently contravenes with environmental constraints and, therefore, society and environment are represented as separate "pillars" to define the dimensions of sustainability.

Seghezzo (2009) considered this limitation of the WCED sustainability definition and proposed a new conceptual framework that includes five dimensions of sustainability. Territorial (place), temporal (permanence), and personal (persons) aspects of development were covered in this new definition of sustainability as shown in Figure 1.2. Place contains the three dimensions of space, Permanence is the fourth dimension of time, and the Persons category represents a fifth, human dimension. The importance of economy is also considered to be overestimated in the WCED definition, which has also been addressed in the Seghezzo framework. Spatial and temporal boundaries must also be taken into account to assess sustainability, which has been ignored in the WCED definition of sustainability. The importance of time in the complexities associated with problem solving is also acknowledged.

1.4.2 Four Force Model

A conceptual framework, the "Four Force Model," assists in the transformation of unsustainable development (USD) to SD. It is a structured approach to identify

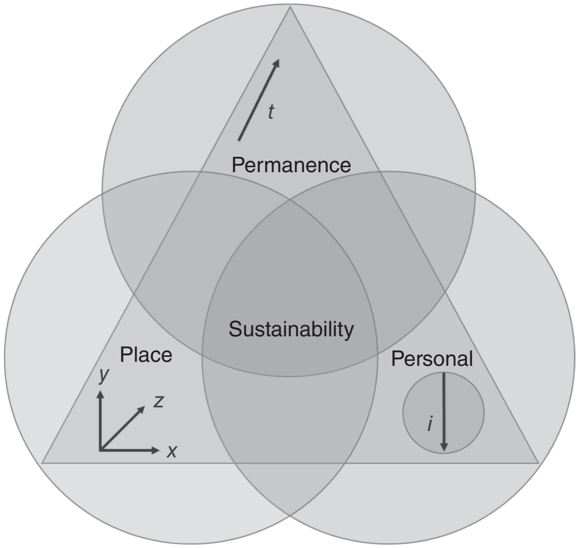


Figure 1.2 The new five-dimensional sustainability triangle. Source: Seghezzo (2009). Reproduced with permission of Taylor & Francis.

the need, cause, and process to accomplish SD. Five issues, i.e. current USD, environmental degradation, future SD, greening force, and greening process, have been emphasized in this model (Gandhi et al. 2006). The model suggests that the move of an enterprise lower end solution to a higher end solution leads to a green process. By enhancing the resource utilization, recycling, and extraction of maximum valuable components from waste streams, an organization can easily meet the target of minimum waste and green process. With increasing international cooperation and technology transfer, it is possible to minimize waste without causing any harm to the environment.

Figure 1.3 illustrates the link between current growth with USD and the most requisite SD in future. The back-casting approach utilizes a particular future scenario to be considered initially. Backward direction was defined by fulfilling the needed outcomes in order to link the future with the present. The four force model defines the four indicators of environment as the driving force, state, reactive response, and proactive response (Banerjee 2002). The model shows the present state as environment degradation. The future state is targeted as SD using either proactive or reactive responses. It is also known as a process of determining the steps to be taken or events to be realized for the needed future.

In the present context, environmental degradation is the major outcome of the current USD. Industrial growth occurs by extracting and utilizing natural resources and therefore nature shrinks with the expansion in industrial activities and economics. Certain factors such as rapid industrialization, increase in per capita income, subsequent changes in resource consumption pattern, exponential increase in population, and continuous depletion of nonrenewable resources are responsible for the increasing rate of environmental degradation. The greening process may be either reactive or proactive responses to the four driving forces. These four driving forces include three external forces (regulatory, community, and consumer force) and one internal force (financial advantage). These

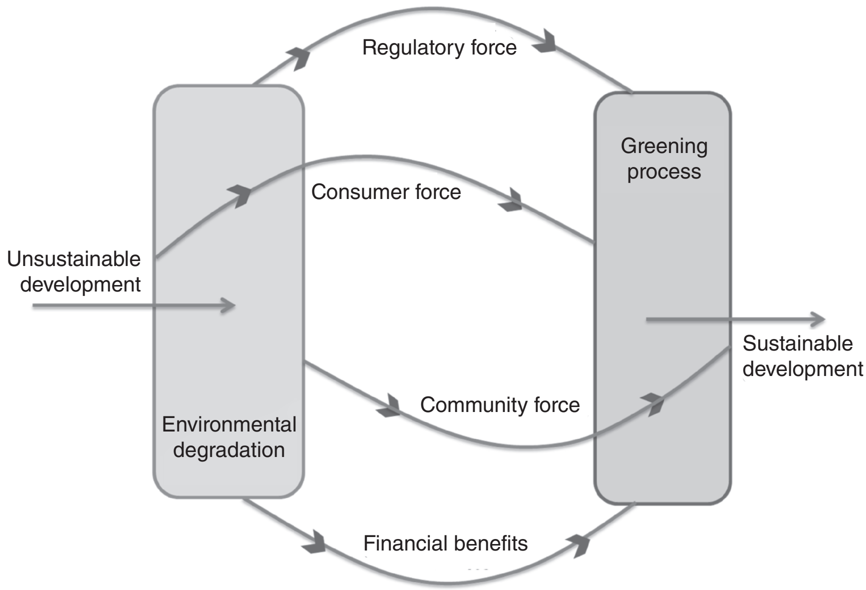


Figure 1.3 Four force model. Source: Gandhi et al. (2006). Reproduced with permission of Emerald Group Publishing Limited.

forces exert extreme pressure on the industries to adopt green processes, which may lead from USD to novel sustainable technologies and products.

1.4.3 Corporate Sustainable Management

Corporate sustainable management is a very new concept that is adopted by several industries to involve their own framework to manage sustainability issues. Companies are constantly making efforts to differentiate their products on the basis of sustainability practices. Some companies have developed the "carbon neutral" programs, whereas other industries are working to minimize hazardous gas emissions and waste generation from the source. Corporate sustainability index is also an emerging idea to measure sustainability performance. The index provides vital and timely information to customers and shareholders on the environmental health and sustainability of companies. Industries are coerced to pay sincere attention to minimize environmental impacts such as waste generation, greenhouse gas emissions, deforestation, and other environmental hazards due to industrial activities.

1.5 Green Value Stream Mapping (GVSM)

The sequence of activities to develop novel green products and services plays an important role in attaining sustainability. Therefore, a process mapping method named as the "value stream mapping (VSM)" is compiled to understand the sequence of activities, to identify and eliminate the non-value-added activities, and to streamline the process. Constrained environmental rules have extended the conventional VSM to include both eco-friendly green elements in its mapping technique. Green value stream mapping (GVSM) is an extension to achieve the same goal by ruling out the non-value-added materials, reducing costs, identifying ways to minimize waste generation, and ascertaining opportunities to improve performance. It focuses on excess usage of energy, water, and raw material; release of pollutants, and hazardous and solid waste discharge into the ecosystem; use of hazardous substances in the production process, etc.

1.6 "Greening the Waste"

"Greening the waste" concept refers to an approach in which industry shifts from less preferred methods of waste treatment including treatment with toxic chemicals and incineration toward the "three R: Reduce, Reuse, and Recycle" principle of sustainability. Further, researchers are aware of the fourth dimension of sustainability, Recovery. By integration of the construct of "recovery" in solid waste management, we can move in the desired upstream direction in solid waste management hierarchy.

This calls for the integrated solid waste management (ISWM) approach, based on appropriate waste treatment and recovery technology, to bridge the gap between community and waste management authorities. Considerations regarding the environmental impacts, social impact, and financial constraints have to factored in while designing the relevant ISWM strategy (Figure 1.4).

In order to apply the concept of "Greening the waste," the "three 3 R" principles of sustainability should be applied: reuse the resource wherever possible to abstain from the waste of virgin resources. Recycle the waste by converting waste into suitable products and recover the energy from waste using pertinent techniques. Use of resource optimization techniques assists in minimizing resource wastage. Proper collection and segregation of waste at source ensures efficient waste treatment. Further, resources should be reserved and be used prudently to avert their overconsumption. Landfilling of the waste should be avoided as leachates from it are hazardous to nearby environment. Resource optimization techniques need to be applied to improve the consumption of resources.

The greening of the waste sector should be facilitated by significant breakthroughs in technologies required for collection, reprocessing, and recycling of waste, extracting energy from organic waste, and efficient gas capture from landfills. Recovering energy and other useful products from waste is being enabled by considerable technological breakthroughs. Many countries have moved from incineration to energy generation as a part of waste treatment. Mechanical and biological treatment (MBT) and biomethanation are also being recognized as suitable for processing organic wet waste in developing countries. However, incomplete segregation of dry and wet organic waste has been a major barrier to the widespread successful adoption of these technologies in these countries. Techniques such as vermi-composting and rapid composting have led to conversion of organic waste into useful agricultural manure at a pace faster

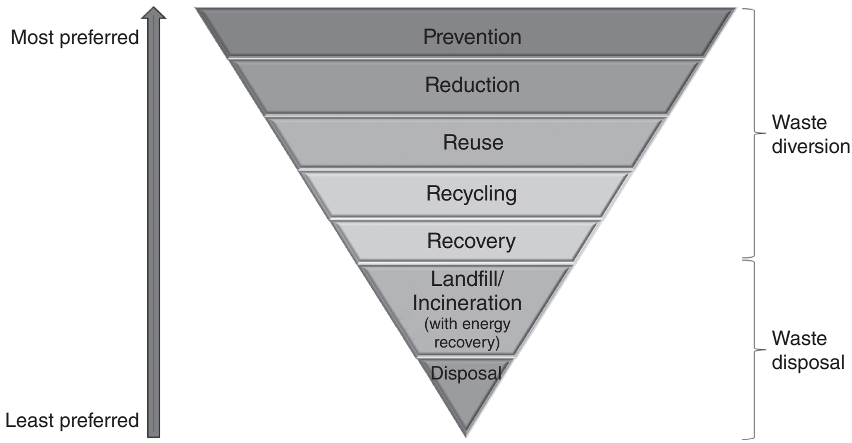


Figure 1.4 Waste management hierarchy.

than natural decomposition. Advanced technologies are employed to convert waste into value-added products. For instance, waste with high calorific value is used to generate refuse derived fuel (RDF).

In spite of the efforts made by researchers in the field of valorization of waste, no specific targets for greening the waste sectors have been established by international conventions. Appreciable efforts have been made by northern Europe, the Republic of Korea, and Singapore, by subjecting over 50% of waste materials to the material recovery process (Gaillochet and Chalmin 2009). Many Asian countries, such as Japan, have initiated efforts to evaluate the yearly developments in recycling rates by setting material flow indicators under three categories, i.e. "input," "cycle," and "output." Based on indicators such as resource productivity (increased from 210 000 yen/tonne in 1990 to 390 000 yen/tonne in 2010), recycle use rate (increased from 8% in 1990 to 14% in 2010), and final disposal amount (decreased from 110 million tonnes in 1990 to 28 million tonnes in 2010), recycling of material is encouraged (Ministry of Environment, Government of Japan 2008). Similarly, the concept of circular economy (CE) has been included in the 11th five-yearly plans of China. Efforts on the practice of three Rs policy – Reduce, Reuse, and Recycle are made in European countries to foster sustainable materials management. Earlier in 2011, cities of the United Kingdom, especially London, drafted a policy to manage waste by setting up 70% commercial/industrial waste's recycling/composting by 2020 and 95% reuse and recycling of waste by 2020 (Mayor of London 2010). However, The Netherland's waste management policy (also known as the "Lansink's Ladder") is based on the concept of the wise use of existing resources, along with the reduction of waste generation and recovery of resources and energy from waste (Zimring and Rathje 2012). The country uses stony waste that meets the criteria of Dutch Building Materials Decree for construction applications (Liu et al. 2015). The United States too, through the EPA, has laws to deal with release of waste that are toxic for public health, welfare, and environment. Quantitative risk assessment policy is followed in the country to evaluate the effect of waste on public health and environment.

Thus, global awareness about increasing waste generation and potential of resource recovery from waste has given rise to the term "Greening the waste." The various aspects of valorization of product are economic benefits (energy generation, new business avenues, creation of jobs, secondary sources of metals), environmental protection (resource conservation, reduction in greenhouse gases (GHG)), and social benefits such as compost production supporting organic agriculture, contributions to equity, and poverty eradication. Better management of waste improves public health and the condition of water bodies. This consequently leads to reduced health costs, which is an important stream of benefits of "Greening the Waste."

1.7 Green Chemistry Terminology

In green chemistry, environment factor (E-factor) is an important term to illustrate the process efficiency. Figure 1.5 illustrates a general process flow diagram demonstrating input of raw material, which in turn results in product and waste generation.

To define the environmental efficiency, E-factor is defined as the mass ratio of waste produced (excluding water) to the desired product. E-factor is related to the yield of the process as defined in Eq. (1.1):

$$\text{E-factor} = \frac{\text{mass of waste}}{\text{mass of desired product}} \quad (1.1)$$

It is recommended that a process should be designed to minimize the E-factor. There are various factors that affect the value of the E-factor, including the following:

i. Yield of the desired product
ii. Reagents used
iii. Number of steps and reaction sequences
iv. Extraction and purification solvents.

The average E-factor varies for the oil refining (<0.1) to bulk chemical (1–5), to fine chemical (5–50), to pharmaceutical industries (25–>100).

In addition, there is another term known as "atom efficiency." It is defined as the ratio of molecular weight of the desired product to the sum of molecular weights of all substances produced in a stoichiometric equation.

$$\text{Atom efficiency} = \frac{\text{molecular weight of desired product}}{\text{sum of molecular weight of all products}} \times 100\% \quad (1.2)$$

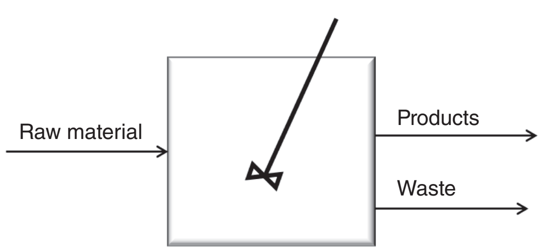


Figure 1.5 General chemical process showing input and output.

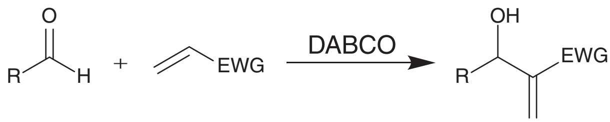


Figure 1.6 Example of an atom-efficient reaction.

Atom efficiency is a tool to show the efficiency of a process to utilize all atoms involved. It is useful to compare different pathways to obtain the desired product, without considering the yield.

Baylis–Hillman reaction, shown in Figure 1.6, is a 100% atom-efficient process. In this reaction, an activated alkene derivative reacts with an aldehyde, catalyzed by a tertiary amine (for example, DABCO = 1,4-diazabicyclo[2,2,2]octane). No co-products are known to be formed. All atoms are efficiently converted into the desired product, resulting in complete efficiency of the process.

Effective mass yield is also used to define the "greenness" of a reaction. This term can be explained as

$$\text{Effective mass yield} = \frac{\text{mass of desired products}}{\text{mass of non-benign reagents}} \times 100\% \tag{1.3}$$

1.8 Green Ways of Metal Extraction: Core of the Book

It is clear from the previous discussion that sustainable management is of utmost importance for the accomplished growth of any industry. Environment is one of the pillars of the sustainability triangle that is generally ignored by various industries in order to add financial benefits. However, these days, the constrained environmental regulations are forcing industries to pay sincere attention toward waste minimization and resource optimization. Waste minimization is a process of increasing resource utilization and extracting maximum from the waste before final disposal. With the new technological innovations, the concept of waste minimization can be directly referred to as Green Technology Development, which includes energy generation, resource extraction, pollution prevention, and recycling of resources and disposal with energy recovery.

The core of this book is based on the belief that transdisciplinary research can be considered as the executable direction to achieve the sustainable governance of natural resources and solid waste management. The dominant waste streams, i.e. electronic waste (waste electrical and electronic equipment [WEEE]), agro-residue waste, and industrial waste originated from petrochemical/fertilizer/textile industries, have been covered in detail in the Chapters 3–7 to illustrate various conventional, emerging, and future technologies for the recovery of metals from these waste streams.

The growing proportion of heavy metals in soil and water is a threat to human health. Some of the negative impacts of heavy metals on plants include decrease of seed germination and lipid content by cadmium, decreased enzyme activity and plant growth by chromium, the inhibition of photosynthesis by copper and mercury, the reduction of seed germination by nickel, and the reduction of chlorophyll production and plant growth by lead. The impacts on animals include reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. In addition, metals are also an ineluctable contributor in the industrial development. Globally, scarcity of heavy metal resources is an important matter of concern, keeping in view the increasing rate of industrialization Therefore, recovery of metals from waste (industrial/agricultural/electronic) is of significant importance from the environmental as well as industrial perspectives. Numerous approaches have been widely reported in the literature for recovery of metals from contaminated sites. Adsorption has been considered a good alternative for efficient extraction of metals from industrial waste water. Membrane separation, electrotreatment, photocatalytic processes, and absorption by aquatic plants have also been employed to remove metals and other pollutants from water. Various techniques such as vitrification, excavation, removal of contaminated soil layer, phytoremediation, and soil washing using surfactants, acids, alkalis, and chelating agents have been investigated for soil remediation. Various hydrometallurgical (leaching, solvent extraction, and biological methods) and pyrometallurgical processes such as calcination followed by leaching or roasting at high temperatures have been employed for extraction of heavy metals from spent catalysts, soil, and other industrial wastes. All these processes have shown potential in removing metals from industrial wastes; however, use of hazardous chemicals, secondary pollution possibility by these chemicals, less acceptance of biological processes in the environment, and high process cost restrict their use on a large scale.

This excogitation is now assisting researchers to move toward greener approaches such as chelation technology, ionic liquids (ILs), and other green extractants. A new term “Green Adsorption” has also been introduced recently for metal extraction from waste water, which includes low-cost ecofriendly materials originated from agricultural sources and by-products (fruits, vegetables, food), agricultural residues, and wastes. Several authors employed natural bentonite and zeolites, rice/peanut husk and fly ash, banana and orange peel, and anaerobic granular sludges for metal extraction. Some authors also employed modified biopolymer adsorbents derived from chitin, chitosan, and starch for metal removal from contaminated sites. Chelation technology, evolved over the century for being used in metal intoxication, has also emerged as a green chemical engineering approach for metal extraction from contaminated sites (soil, waste water, spent catalyst) in recent years. It is believed that technical applicability, operational simplicity, and economic feasibility are the key factors in selecting the most suitable technology for metal extraction.

In the following chapters of this book, the technical applicability of various new greener approaches for metal removal from solid waste and contaminated sites will be identified. Recent developments related to these new technologies in order to accomplish the concept of “Greening the Waste” will also be discussed.

Questions

1 How do you define the terminology "Sustainability" and "Green chemistry"?

2 Explain the dimensions of sustainability on the basis of TBL?

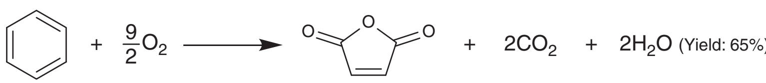
3 Does the five dimensional framework define additional information to "Sustainability"? If yes, please explain how.

4 Explain how the four force model illustrates connecting dots between current USD and the future SD.

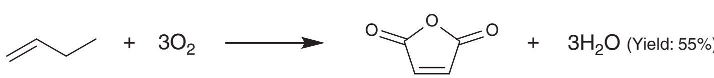
5 Discuss the concept of "Greening the Waste."

6 Following two different routes illustrate the formation of maleic anhydride:

a. *Oxidation of benzene:*



b. *Oxidation of but-1-ene:*



i. Assuming that each reaction is performed in the gas phase only and that no additional chemicals are required, calculate (i) the atom economy and (ii) the effective mass yield of both reactions. You should assume that O_2, CO_2, and H_2O are not toxic.

ii. Which route would you recommend to industry? Outline the factors that might influence your decision.

7 Calculate the E-factor for the following reaction:

$$\underset{(4.5\ g)}{K_2PtCl_4} + \underset{(\sim 2\ g)}{C_2H_4} + \underset{(8.21\ g)}{HCl\ (in\ water)} \xrightarrow{SnCl_2\ (40\ mg)}$$

$$\underset{(3.86\ g)}{K[PtCl_3(C_2H_4)] \cdot H_2O} + KCl + \underset{(unreacted)}{C_2H_4}$$