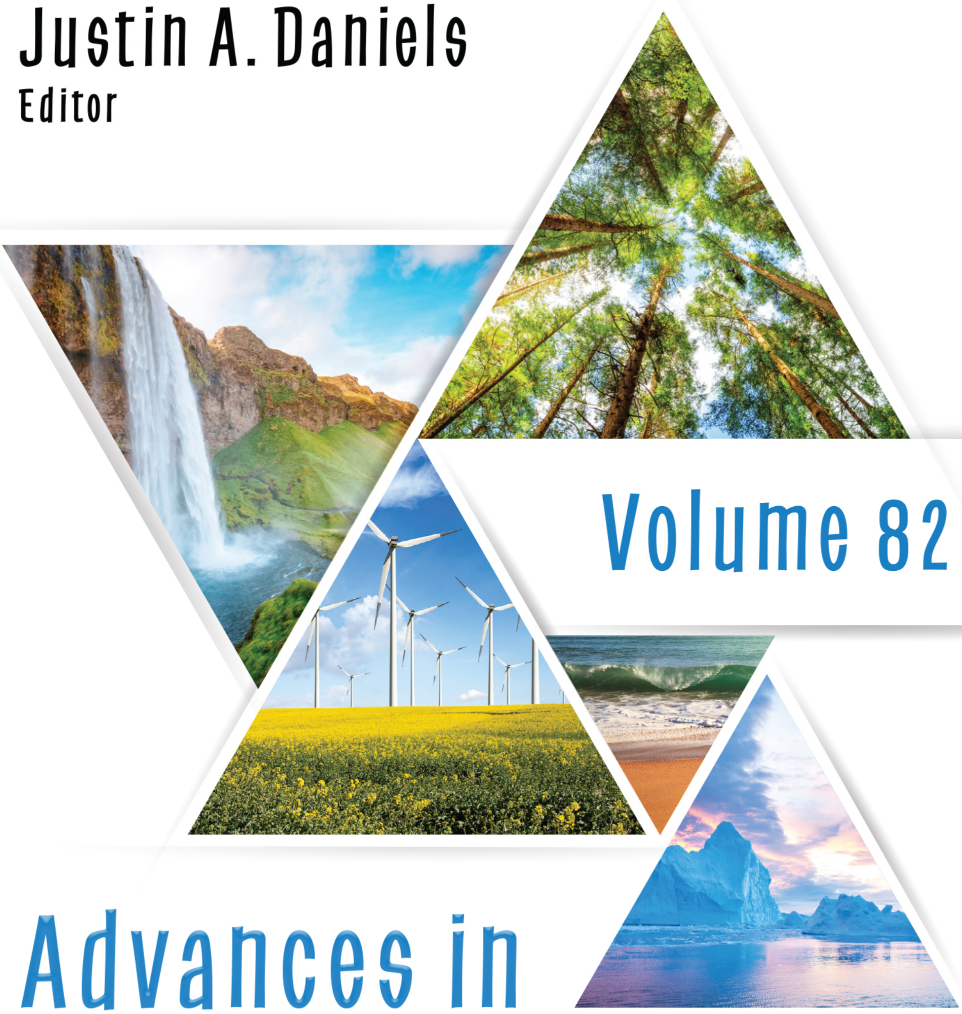
Justin A. Daniels
Editor



Volume 82

Advances in Environmental Research

ADVANCES IN ENVIRONMENTAL RESEARCH

VOLUME 82

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ADVANCES IN ENVIRONMENTAL RESEARCH

VOLUME 82

JUSTIN A. DANIELS
EDITOR

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PREFACE

This edited volume presents various advancements in the field of environmental research. Chapter one scrutinizes the inherent value of mangrove forests from the perspectives of ethnoscience, ethnobotany, phytotechnology, and ecological aspects. Chapter two highlights the latest research about abscisic acid biosynthesis, abscisic acid signaling pathways, and their implications in plant development and response to environmental stresses. Chapter three assesses the policies on methane emissions of several countries, including the U.S., China, and Russia. Chapter four describes various methods of extracting precious metals from electronic waste in detail. Chapter five summarizes the research achievements of recent years in connection with the use of electrochemical technology for removal of volatile organic compounds. Finally, Chapter six reviews microalgae-based processes and their relationship to carbon footprints.

Chapter 1 - The transformation from ethno-botany uses of mangrove forests (food, medicine, and utilities) to scientific studies of mangroves, like application of Phyto-technology is looking for prospective evolution. This chapter scrutinises the inherent value of mangrove forests from another perspective, especially ethnoscience, ethnobotany, phytotechnology, and ecological aspects. Apart from rendering ecological value, like coastal safeguard, mangrove forests facilitate administration of timber as well as non-timber yields, food, aesthetic and recreational approval. Furthermore, this research work highlights the perspectives of local publics to espouse and acclimate to their surroundings as a natural means in day-to-day life, which will signify the community, ethos, and belief along with environmental circumstance. For years, conventional knowledge of mangroves has been dissected. Mangroves comprise a unique ecosystem that acts as a boundary between land and the sea; hence, mangroves have immense potential as environmental monitors by indicating the levels of certain heavy elements polluting the mangrove environment. Critical properties for environmental indicators include plants located in the community, enough abundance, and sufficient dominance to affect the habitat adequately. This natural occurrence can also be utilised to evaluate the past or to forecast prospective status of the environment. Information about ecological factors can be beneficial tools to ascertain the quality of water and soil, kinds of toxins, the existence of specific metal or mineral as well as universal climate changes. A difficulty in formulating and implementing ecological metrics is identifying the most potent agents that help monitor the required ecosystem. Presently, the authors' use plants to evaluate environmental situations and state in order to have warning signals or act as yardsticks for determining climate trends and variations in ecological aspects. The concurrent use of such indicators with landscape ecology is presently complex yet promising. Landscape ecological aspects emphasise mutual interactions between anthropogenic activity and spatial use. Considering this factor, tight integration with ecology is expected to improve landscape functioning, approaches and create an enhanced systematic understanding of the correlations between plants, humans, patterns, and metrics or indicators. Such applications have two-sided use because anthropogenic impact on the environmental might be changed due to landscape state monitoring or evaluation to determine structural characteristics, constituents, and functions of natural or artificial environments comprising community populations, landscape trends, disturbance phenomena, and other aspects.

Chapter 2 - Abiotic stress is considered as severe environmental stress that reduces the growth and yield of every crop everywhere. Many hormones were involved in plant defense against all forms of stresses.

Abscisic acid (ABA), judged as the major phytohormone, was closely linked to plant defense toward many stresses such as thermal stress, heavy metal stress, low temperature, drought, high salinity and radiation stress. At the molecular level, ABA changes the expression level of many ABA-responsive genes to ensure the control of several developmental operations including seed germination/dormancy, fruit ripening and senescence as well as closure of stomata. In addition, ABA coordinates with other phytohormones to maintain plant survival under unfavorable conditions. This chapter highlights the last outcomes about ABA biosynthesis, ABA signaling pathways and its implication in plant development and response to environmental stresses.

Chapter 3 - Methane is a greenhouse gas (GHG), 21 times more powerful than carbon dioxide (CO_2) in its effect on climate change. Additionally, coalbed methane is a new energy mineral and an unconventional natural gas resource. The coal mining industry contributes 8% of total global anthropogenic methane released from open-cut and underground mines. U.S. and other countries cooperated under the Climate and Clean Air Coalition to Reduce Short-Lived Climate Pollutants and the Global Methane Initiative (GMI) to reduce GHG emissions. Thus, the International Council of Mining and Metals (ICMM) focused on CH_4 recovery and utilization in coal mines. Coal mine methane (CMM) utilization and recovery reduces GHG emissions and improves energy, mine safety and job creation. This chapter assesses the policies on methane (CH_4) emissions of the U.S., China, Russia, Turkey, Asia, European Union, South Africa and Australia. Some countries have succeeded, others have worked hard to implement policies.

Chapter 4 - Electronic wastes are electric and electronic equipment and devices which have ceased to be useful and are being discarded. The accumulation of e-waste has become a global issue and has raised concern among the public as well as governmental bodies due to the hazardous contents within the e-wastes. In this chapter the sources and current situation of the global scenario of the electronic wastes are discussed in detail along with e-waste management strategies. The global status of e-waste pollution is one of the major concerns as deposition of electronic wastes has been growing exponentially over the years. The current progress of electronic waste management worldwide should be investigated with much focus to understand the remediation rate of the hazardous components present within the electronic wastes. The methods of extracting the precious metals from the electronic wastes include pyrometallurgical, hydrometallurgical and biometallurgical processes. This article deals with an elaborate description of the three processes with their advantages and disadvantages. Bioleaching techniques are introduced in recent research to obtain precious metal ions. The mechanisms of the bioleaching process are focused in detail with its comparison to the traditional techniques involved in management of electronic wastes.

Chapter 5 - Volatile organic compounds (VOCs) is a kind of pollutants mainly produced by human production and living. At present, there are many ways to remove VOCs in industry, such as electrochemical method, adsorption, absorption, heat treatment, biological treatment, photocatalysis and so on. Among these methods, electrochemical technology, as a new VOCs treatment technology, has been considered as a god choice for VOCs removal. The electron is used to realize the oxidation and reduction of substances in electrochemical technology, which can easily control electron potential and current density. This method has been applied to VOCs removal by many researchers. Different types of VOCs could be removed due to the difference of electrode materials and catalysts, and the efficiency of removal is also different. This chapter is based on research achievements of recent years, and the authors' reorganized the concrete application of electrochemical technology, discussed the influence of electrochemical battery electrolyte, electrodes, the reaction product and current density on the removal of VOCs. The relevant literature data is collected for comparative study. The electrochemical technology is also compared with other treatment methods. This is of strategic significance for the effective and extensive application of electrochemical technology in industrial VOCs removal.

Chapter 6 - In the last 7 decades, microalgae-based processes have been the scene of an incessant duel to try to curb excessive consumption of a wide range of feedstocks and natural resources, working on technologies for the recovery of solid, liquid, and gaseous waste, in order to avoid the global collapse of ecosystems. However, the authors' cannot combat environmental problems with emitting devices. It is necessary to use tools that leave no doubt about their applicability and competence. Thus, immersed in the environmental uncertainties generated by biotechnological processes, scientists have deepened their research to bring to the surface the real environmental impacts and their relations with the social and economic triad, providing the true global status of sustainability. Therefore, focused on solving the hottest point of the investigation, that is, the reduction of carbon dioxide emissions, the carbon footprint mechanism has become the key tool of today. In light of this, this chapter will address a brief review of the main microalgae-based processes and their relationship to carbon footprints. In addition, the chapter will provide a compilation of information regarding the main methodologies currently used to quantify the carbon footprints of biological systems, as well as direct the reader to use them appropriately. Finally, the last part of the chapter emphasizes and guides researchers in the area to get to know some general views about the global carbon market and the perspectives to be elucidated and developed on carbon credits involving microalgae-based processes.

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Chapter 1

TRANSFORMATION OF MANGROVE FOREST INTRINSIC VALUES FROM TRADITIONAL TO CONTEMPORARY

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ABSTRACT

The transformation from ethno-botany uses of mangrove forests (food, medicine, and utilities) to scientific studies of mangroves, like application of Phyto-technology is looking for prospective evolution. This chapter scrutinises the inherent value of mangrove forests from another perspective, especially ethnoscience, ethnobotany, phytotechnology, and ecological aspects. Apart from rendering ecological value, like coastal safeguard, mangrove forests facilitate administration of timber as well as non-timber yields, food, aesthetic and recreational approval. Furthermore, this research work highlights the perspectives of local publics to espouse and acclimate to their surroundings as a natural means in day-to-day life, which will signify the community, ethos, and belief along with environmental circumstance. For years, conventional knowledge of mangroves has been dissected. Mangroves comprise a unique ecosystem that acts as a boundary between land and the sea; hence, mangroves have immense potential as environmental monitors by indicating the levels of certain heavy elements polluting the mangrove environment. Critical properties for environmental indicators include plants located in the community, enough abundance, and sufficient dominance to affect the habitat adequately. This natural occurrence can also be utilised to evaluate the past or to forecast prospective status of the environment. Information about ecological factors can be beneficial tools to ascertain the quality of water and soil, kinds of toxins, the existence of specific metal or mineral as well as universal climate changes. A difficulty in formulating and implementing ecological metrics is identifying the most potent agents that help monitor the required ecosystem. Presently, we use plants to evaluate environmental situations and state in order to have warning signals or act as yardsticks for determining climate trends and variations in ecological aspects. The concurrent use of such indicators with landscape ecology is presently complex yet promising. Landscape ecological aspects emphasise mutual interactions between anthropogenic activity and spatial use. Considering this factor, tight integration with ecology is expected to improve landscape functioning, approaches and create an enhanced systematic understanding of the correlations between plants, humans, patterns, and metrics or indicators. Such applications have two-sided use because anthropogenic impact on the environmental might be changed due to landscape state monitoring or evaluation to determine structural characteristics, constituents, and functions of natural or artificial environments comprising community populations, landscape trends, disturbance phenomena, and other aspects.

Keywords: mangrove, ethnobotany, landscape ecology, ecological indicators, phytotechnology

INTRODUCTION

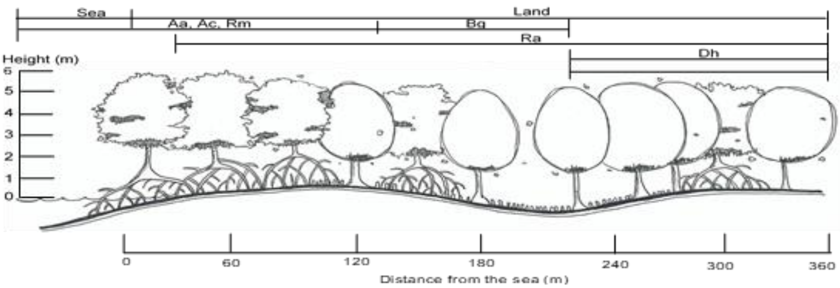
Mangrove plantations are wooded wetlands which are particularly adjusted to the intertidal region, covering less than 14 million ha of the Amazon rainforests. The most extensive mangroves have been seen in the estuaries of major rivers flowing over shallow continental margins in India and Bangladesh, the Mekong Delta in Vietnam, and the Fly River in Papua New Guinea (Biswas et al., 2018). Coastlines of over 118 nations are covered in subtropical, tropical, and temperate regions (Bunting et al., 2018). Forests, conversely, frequently overlay with growing human populace concentrations.

A mangrove is occasionally termed as "intertidal forest," "mangal vegetation," "halophytic vegetation," and "tidal forest" when talking about a mangrove forest (Biswas et al, 2018). Such forests are vital as they stop erosion, offer habitation to fishery species, safeguard coastal populations from severe weather events, and stockpile huge volumes of blue carbon, all while facilitating moderation of universal climate change (Bryan-Brown et al., 2020). Mangroves have economic, ecological, and protective effects. They provide flora and fauna habitat, pole, fuel and timber wood. Moreover, mangroves are used for the fibre industry, different non-timber substances like wax, tannin, and honey, and also support numerous terrestrial and aquatic species. Mangroves offer fish breeding grounds and habitat for molluscs, crustaceans, and many other aquatic and terrestrial species. Additionally, mangroves resist wave erosion, facilitate sediment retention/ land accretion, entry of organic detritus in coastal areas, thereby enhancing water productivity. Other functions include resisting natural problems like cyclones, tides, and tsunamis and working as carbon sinks. Mangroves are understood as the highest-density global carbon ecosystems, where carbon is sequestered into the soil. Nevertheless, human activity caused sea-level rise, and decreasing forest area endangers mangroves (Biswas et al., 2018).

Mangroves have numerous functions and provide diverse value; at the same time, their cultural aspect should also be considered. Tourism and leisure are aspects attracting little attention. Notwithstanding these aspects, they are extensively visited for leisure (Spalding and Parrett, 2019). Boating and hiking and two of the many leisure activities possible around mangroves. These activities facilitate fishing and wildlife observation. Mangroves might not be the sole aspect influencing travel motivation; however, they act as tourist attractions affecting travel plans, and their popularity seems to be increasing. Mangroves are uniquely structured with specific vegetation characteristics; moreover, these species have extraordinary physiological and morphological changes to adapt to the harsh environmental conditions. Additionally, research concerning recreation and tourism is increasing, specifically for nature-based tourism (Spalding and Parrett, 2019).

Mangroves are the only woody special thriving at the land-sea boundary. They have been typically used for timber, food, medicine, and fuel. Mangroves occupy about 181000 km^2 along the subtropical and tropical coastlines (Alongi, 2002). Coastal regions have distinct environments like mangroves that have a vital role in regulating ecological value and human establishment. The estuarine ecosystem comprises mangroves extensively affected by abiotic aspects like sedimentation, freshwater runoff, and quick temperature change due to sun, wind, and tides (Nagelkern et al., 2008). Estuarine systems act as nurseries for trophic resources (freshwater nutrient capture and tidal mixing), turbidity, and systematic diversity (Baran and Hambrey, 1998). Like wetlands, mangroves are essentially cost-effective natural wastewater treatment systems having a considerable capacity for maintaining and processing nutrients and heavy metals. The complex biogeochemically active nature of mangroves provides for a transitional association between land, water, low water flow, and substance exchange (nutrients and carbon) when inundated by tidal waters (Adame and Livelock, 2011).

Mangrove species are prevalent near river banks, coastlines, and estuaries having ample brackish water or bodies with enough saline and fresh water content (Gandaseca et al., 2011). Mangroves have immense value and functions (Karami et al., 2009), like ecological stability and socioeconomic impact. These are essential for flourishing biodiversity, healthy coastlines, and communities residing nearby. These species are store river and marine-based contaminants (Rambok et al., 2010). In particular, mangrove forests act as a ‘sink’ to trap pollutants, including inorganic and organic contaminants, which reacted with anaerobic activity in the bottom of sediment. The adsorptions of metals usually interact with the presence of oxides and hydroxides of manganese and iron, humic acid, clay structure and sulphide (Perin et al., 1997). Meanwhile, the nutrients depend on flood frequency, fresh water availability, redox potential, and pH and chemical element availability (Lacerda et al., 1988). There are several mangrove forest zones highlighted by Noor et al., (2006). They elaborated that there are different species of mangrove in every layer and there is zonation of the mangrove ecosystem according to mangrove species.



Legend:		
Aa-*Avicennia alba*	Bp- *B. parviflora*	Rm- *R. mucronata*
Ac-*Aegiceras corniculatum*	Ct- *Ceriops tagal*	Sb- *Sarcolobus banksii*
Bc- *Bruguiera cylindrical*	Dh- *Derris heterophylla*	Xg- *X. granatum*
Bg- B. gymnorrhiza	*Ra- R. apiculata*	

Figure 1. Mangove zonation.

Noor et al., (2006) mentioned that mangroves have four zones which are open, middle, brackish water and land mangrove zone. They elaborated that there are different species of mangrove in every layer and the zonation of the mangrove ecosystem according to mangrove species (Figure 1).

1) Open zone. This zone comprises the beachfront located in the estuarine region. *Avicennia alba* and *Sonneratia alba* are prevalent along the coasts. *S. alba* is typically abundant in areas having abundant sand, while *Avicennia marina* and *Rhizophora mucronata* flourish when soil salinity is high.
2) Middle zone. It is next to the open zone. *Rhizophora* sp., *R. mucronata*, *Bruguiera cylindrical*, *B. gymnorrhiza*, *B. eriopetale*, *Excoecaria agallocha*, *Xylocarous granatum*, and *X. moluccensis* are abundant.
3) Brackish water zone. This zone is situated near brackish water banks and is found till fresh water zones. Common species comprise *Nypa fruticans* and *Sonneratia* sp. Estuarine systems have *Sonneratia caseolaris* abundance. *Nypa fruticans* are typically associated with *Cerbera* sp., *Gluta renghas*, *Xylorcarpus granatum*, and *Stenochlaena palustris.*
4) Land mangrove. These are situated between freshwater and brackish regions. Abundant species comprise *Intsia bijuga*, *Ficus microcarpus*, *Lumnitzera racemosa*, *Nypa fruticans*, *Xylocarpus moluccensis*, and *Pandanus* sp. This area comprises several mangrove species, unlike other zones.

In another significant zonation, mangroves can be split into four species: red, black, white, and buttonwood mangroves.

1) Red mangrove. The red mangrove (*Rhizophora mangle*) can be easily differentiated from other species through its tangled, reddish prop roots and it is seen to grow along the edge of the shoreline with the harshest conditions. These prop roots stem from the trunk wherein the roots would protrude downwards from the branches.

Growing ≥3 feet (1 m) above the soil surface, prop roots enhance the tree’s stability and also enable oxygen supply towards underground roots. Under good conditions, the mangrove tree can grow more than 80 feet (25 m) in terms of height. The mangrove’s smooth-edged, elliptical leaves possess shiny, dark-green upper sides as well as pale green undersides, which tend to occur opposite from each other alongside the branches. A grey bark covers the trunks and limbs, over a dark red wood, as derived by its common name. During spring and early summers, a cluster of white to pale yellow flowers blooms. Due to reproductive adaptations, seedlings can germinate even when they are still attached to the parent tree. Seeds can sprout into pencil-shaped propagules that can measure 6 inches (15 cm). As the seed can germinate while still attached to the parent tree, it provides a higher chance of survival for this mangrove. When a seedling drops into the water, it could either take on roots alongside the parent tree or get washed away by the currents and tides to another habitat that is deemed suitable.

2) Black mangrove. *Avicennia germinans*, also known as the black mangrove, can be characterised by its long horizontal roots as well as root-like projections called as pneumatophores. It grows at slightly higher elevations compared with the red mangrove in which the roots are exposed to air due to tidal change. The pencil-shaped pneumatophores stem from the underground horizontal roots coming out from the soil near the tree's trunk, supplying oxygen to both the underground and underwater root systems. The height of black mangrove can reach almost 65 feet (20 m) while the leaves occur opposing to each other alongside the branches, with shiny upper sides and undersides enclosed with hairs densely. This mangrove’s bark is characterised by being scaly and dark. In spring and early summer, black mangroves would blossom, yielding white flowers. Due to reproductive adaptations, seedlings can germinate even when they are still attached to the parent tree. Seeds would sprout into lima bean-shaped propagules that are 1

inch (2-3 cm). Since seen germination can happen while still being attached to the parent tree, this increases the survival chances even in adverse environment.

3) White mangrove. Occupying higher land when compared with black and red mangroves, no visible aerial roots are associated with the white mangrove (*Languncularia racemosa*), unlike the red mangrove that has prop roots and the black mangrove that incudes pneumatophores. However, it often develops peg roots when present in oxygen-depleted sediments or the region is flooded for extended time periods. This small tree or shrub can rapidly grow up to 50 feet (15 m) in height. The leaves are light yellow-green in colour and are broad and flat possessing two glands near the leaf base wherein the stem originates. Salts are excreted by these glands, which are taken via the underground root system. The flowers bloom from spring to early summer, which are greenish-white flowers in spikes.
4) Buttonwood. Generally seen in the upland transitional zone, the buttonwood (*Conocarpus erectus*) is usually linked with mangrove communities. The name originates from its dense flower heads that appear button-like and grow in branched clusters, producing cone-like fruit. This plant produces seed cases instead of reproducing through propagules. While all the three mangrove species mentioned earlier possessed leaves that occur as opposite of each other, the leaves of buttonwood are generally alternate. The leaves are characterised by its leathery appearance along with smooth edges and pointed tips. At the base of each leaf, two salt-excreting glands are present. Flowers are greenish in colour with appearance of cone-like heads.

Based on the review, the mangrove ecosystem is regarded to involve a harsh environment that can be impacted by various factors that could impact the natural cycle:

1) Abiotic factors (salinity, freshwater runoff, salt content of the soil, soil types, sedimentation and temperature fluctuation);
2) Climate changes (sea level rise, precipitation, storm and wind, CO_2 concentration); and
3) Pollutants (heavy metals and nutrients).

These factors could have a role in changes in mangrove species' phonological patterns (lifecycle), composition and zonation as rating tools in order to balance the mangrove. Also, a crucial role is played by mangrove ecosystems as a transitional area between marine ecosystems and freshwater, and as a key 'sink' to trap pollutants either from marine habitats or inland freshwater. However, some of the studies have dealt with the function pertaining to the mangrove ecosystem as an ecological indicator to identify heavy metal pollutants as well as excess nutrients in sediment or water.

A wealth of natural treasures is associated with the mangrove forests. Its roots, leaves, stems, flowers, bark, and fruits can be employed for numerous therapeutic purposes. With regards to medical efficacy, each of these plant parts could be employed for the treatment of different infectious and non-infectious diseases, like ear infection, smallpox, urinary claudin in women, neutralise poison, herpes, wound healing, diarrhoea and haematuria, while others would contribute to health as a pain reliever, pregnancy prevention, appetite enhancer, body slimming as well as antioxidant source (Arbiastutie and Diba, 2021). Based on pharmacological recommendations, active compounds in these plant components include carotenoids, glycosides, steroids, saponins, polyphenols, alkaloids, tannins and flavonoids. Medicinal plants can be categorised as active substances possessing therapeutic elements with regards to the specific portions of the plants that can yield different kinds of phytochemical components (Anand et al., 2020). Such phytochemicals can be present in a broad range of concentrations and possess various pharmacological effects, such as antimicrobial, antidiabetic, antiviral, antioxidant, anticancer, neuroprotective, antihypertensive and other pharmacological effects (Arbiastutie and Diba, 2021).

It has been found that mangroves possess the ability to take up or bio-accumulate contaminants such as heavy metals, which are also recognised as its regulating potentials or characteristics (Aljahdali and Alhassan, 2020). Other variables such as physico-chemicals have also increased considerably due to toxic heavy metal dispersion, persistence and abundance in the aquatic ecosystem, which has also become a global issue. The evaluation of heavy metals in order to detect ecological risk could also offer info pertaining to the level of metal bioavailability as well as their effect on the natural aquatic ecosystems by determining biotic response in plants (Bakshi et al., 2018, Aljahdali and Alhassan, 2020). Physicochemical factor is an element that has been studied to determine environmental influences. Phytoremediation is employed for the treatment of soil contaminated with toxic compounds (Chagnon and Jacques, 2017). Phytoremediation, which can be defined as a technique that involves using plants to volatilise, stabilise or remove inorganic or organic pollutants, can be one of the low-cost techniques to enhance soil conditions.

Due to this, further research is required to understand the unique characteristics pertaining to mangrove forests and all other natural treasures present there. A plethora of natural treasures are associated with the mangrove forests, which are yet to be fully explored with regards to ecological, ethnobotanical, chemical and phytotechnological significance. Additional research studies are being carried out to learn more about mangrove ecosystems and their valuable intrinsic contents.

Ethnobotany and Mangrove Forest Ecosystem

Ethnobotany is a branch of study that is focussed on evaluating the mutual relationship that exists between traditional people and plants, along with a specific focus on the use of plants to meet different human needs. Traditional knowledge pertaining to different parts of the world shows that cultural and ecological availability and also historical significance have an impact on the traditional medicinal plant selection (Phumthum and Balslev, 2019). In ethnobotany, the interaction between the plant kingdom and human societies is studied, and especially focus on how indigenous people would manage, perceive and use plants in their respective environments. Since the dawn of civilisation, plants have always been a key part of human society, offering food, fuel, dye colours, edibles, ethno-medicine, packaging material, ethno-veterinary medicine, utensils and utility, as well as pesticides and herbicides to safeguard crops.

Factors like floral heterogeneity, plant secrecy, altitudinal variations, current and historical enclaves' distribution, group's population size, extent of contact with unknowns, proximity of local groups to each other, interaction between local groups, and ecological background in which the group inhabits are among the aspects that affect ethnobotanical use (Coe, 2008; Laleye et al., 2015). In addition, there have been several ethnobotanical studies based on the ethnobotanical information pattern, which is connected to social aspects, such as age, medicine, and conventional knowledge, with respect to which the life-cycle gets built up. That is, the knowledge of the people may differ depending on the extent to which social parameters exist. Ethnobotanical investigation is crucial for economic progress and development, preservation, healthcare and medicinal purposes; therefore, a potential resource of drugs may be exhausted because of the rapid damage to biodiversity (Laleye et al., 2015).

Mangrove reserves and products have conventional medicinal, economic, and other values even though their industrial values are not widely known; thus, a mangrove ecosystem and products can be found. Bandaranayake (1998) reported that utilisation of mangroves encompasses conventional farming, conventional products, foodstuff from mangroves, mangrove poison, medicinal uses and a variety of other uses. Different mangroves products, such as pesticides and insecticides, have been utilised in traditional treatments. Hundreds of millions of countryside people were reliant on the financial and cultural resources of non-timbered jungle products for religious and cultural purposes. Rama ethnobotany is the chief purpose of species of plant used in medicines (190 species) which is followed by feed (80 species) as well as other uses, like crafts and construction, drinks and fuel (99 species) of one of 3 Amerindian group of

East Nicaragua represented (Coe, 2008). The largest regions of the Rama are the damp tropical forest, mangrove forest and swamp forest. It exhibited how people relate plant species to one another in their daily lives. Fuel wood, charcoal, boat building and housing mangroves are a primary resource of wood. Mangroves are utilised for medicinal and pharmaceutical purposes, furniture products and tanning (Dahdouh-Guebas et al., 2000). Ethnobotany usually refers to every facet of the direct connection between humans and plants. Ethnobotany of the mangroves provides a novel approach to the subject, which includes significant uses like wood, fuel wood, shores, indigenous medicines and food, including food material used by the community in times of crisis (Sathe et al., 2012).

As per Atheull et al., (2009), the local community depends on the mangroves which has several uses of *Avicennia germinans*, *Rhizophora racemosa*, *Conocarpus erectus* and *Laguncularia racemosa* timbers for fuel wood, smoking fish, fences, and furniture. Lastly, *Nypa fruticans* leaves were utilised as thatching material for roofs and walls of the houses. In the Pacific of Colombia region, Rhizophora spp. is the main fuel wood source, whereas Mora oleifera which is a mangrove associate offers 100% of wood for stilt-house compared to other mangroves like *Pelliciera rhizophorae*, *Avicennia germinans* and *Laguncularia racemose* (Palacios and Cantera 2017). Moreover, mangroves are more and more used for wood items such as posts, poles, charcoal, fuel wood, and timber. The wood is unaffected by rot and insects, making it enormously valuable. The *Xylocarpus mekongensis* and *Xylocarpus granatum* wood is suitable and long-lasting for making furniture (Chowdhury et al., 2014). Fuel wood is composed of firewood and can be transformed into wood. It is in the form of dead branches and logs washed by tides and gathered by the women on shore, meaning that this usage does not involve a preferred species. Charcoal is produced for commercial purposes. *Bruguiera gymnorrhiza*, *Ceriops tagal*, and *Rhizophora mucronata* are primary resources for house building and fuel wood, whereas *Xylocarpus granatum* and *Sonneratia alba* were reported to be used for medicine production and boat building (Dahdouh-Guebas et al., 2000). Bandaranayake (1998) mentioned that that there are several traditional uses of mangrove species to make products such as furniture, wood, rafters, dugout canoes, frames, doors, boats, charcoal, fuelwood, pile-ups, wood chips and petroleum coke. A stem from *Bruguiera* sp., *Ceriops tagal* and *Rhizophora* sp. can be used to make frames. Timber from *Ceiba madagascariensis*, *Hazomalania voyroini*, *Entada pervillei* and *Gluta tourtou* can be used for designing a door. Timber from *Xylocarpus moluccensis* and *Instia bijuga* can be used for making furniture. Timber from *Xylorcarpus* spp., *Excoecaria agallocha*, *Ceriops* sp., *Barringtonia* spp. and *Rhizophora* spp. are used for boat building. Timber from *Rhizophora* spp., *Ceriops* sp. and *Bruguiera* sp. can be utilised as charcoal and fuelwood, and thus the *Rhizophora* spp. timber can also be used as fuel for boiler locomotives as well as making woodchip.

Dyes, including tanning mixtures, are produced using the bark of the stems of *Rhizophora mucronata*, and used for applying to the interiors of boats and canoes and valued for their protective quality (Dahdouh-Guebas et al., 2000). The mangroves application as insecticides is mentioned to come chiefly from logs of green *Avicennia marina* which produce a lot of smoke when burnt, warding off mosquitoes and other such nocturnal biting insects (Dahdouh-Guebas et al., 2000). The roots of *Derris heterophylla* are used as fish venom and as larvicide while the bark of *Ceriops decandra* is used for dyeing the fishing net. *Clerodendron inerme*'s leaves' sap is used for cleaning dishes (Pullaiah et al., 2016). As verified by Bandaranayake (1998), a conventional product of mangrove species also includes an 'attap', extracted from *Nypa fruticans*' leaves, ropes or fibre from the *Hibiscus tiliaceus* pepper vine, baskets and mats from the *Cyperus articulates* leaves, natural carving and pencil from the *Xylocarpus* spp.'s roots, fishing floats, heels for shoes and corks from wood and pneumatophores of *Annona* spp., *S. caseolaris* and *Sonneratia alba*, puppets, masks and figurines from the *Cerbera manghas* timber, dye for decorating mats and batik manufacture from *Ceriops tagal*'s barks, condiments and perfumes from pneumatophores of *Bruguiera gymnorrhiza* and *B. sexangula*, extract for skin cosmetics from *Sonneratia caseolaris* and extract for hair treatment from *Xylocarpus* spp., *Acanthus ebracteatus* and *A. ilicifolius.*

Agricultural communities use wild food plants due to their high contribution to cultural and culinary diversity as well as food safety and nutrition. Many studies have mentioned regarding mangrove species use in culinary and food. The fruits of *Nypa fruticans* can be used to make alcohol by fermenting their pulp while the fruits of *Sonneratia apetala* are used as a flavour in cookery (Chowdhury et al., 2014). The fruit obtained from *S. caseolaris* and *Sonneratia griffithii* is edible and used for enhancing taste of cooked food (Pullaiah et al., 2016). The leaves obtained from *A. africana*, *Salicornia brachiate* and *Aegialitis rotundifolia* are used to extract salt, the heartwood of *A. officinalis* and *Avicennia alba* is used as tonic, pollens from *Aegialitis rotundifolian*, *Pongamia pinnata*, *Cynometra ramifolia*, *Ceriops* sp. and *Avicennia marina* can be used to obtain honey, *Terminallia catapa*'s fruit kernel and Inocarpus fagifer's seed can be eaten raw, *Avicennia* sp.'s fruits as a fruit dip, fruits obtained from Bruguiera gymnorrhiza, *B. eriopetala*, and *Kandelia candel* are used for pastry and cakes, *Acrostichum aureum*'s fiddleheads are used as a vegetable, *Osbornia octodonta*'s flowers are used as flavouring agent and leaves of *R. mucronata, R. lamarckii, R. apiculata, Ceriops decandra* and *B. cylindrica* are used for making tea (Bandaranayake 1998).

Native human health approaches understand conventional medicine as a significant field, specifically for developing nations having limited access to allopathy professionals and medicines (Nabatanzi et al., 2020). About 70-80% of the global population employs forest-derived plant-based medicines for. Traditional doctors typically pass on the treatment approaches to the descendants, thereby transferring knowledge over generations. Over the last few centuries, such physicians have grown familiar with plant species, habitat, and regions that must be looked at to address different ailments (Ali Ahmed et al., 2014). Herbal healers employ plant-based treatment for improving reproductive health and controlling the disease. Considering present-day treatment expenses, such methods are significant for poor communities. Conventional medicine comprises the use of plants, exercise, spiritual techniques, manual approaches, belief, and accumulated knowledge for disease prevention, diagnosis, and treatment.

Moreover, the use of this exotic treatment approach has declined because (Coe 2008);

i. access scarcity to significant population centres having an abundance of exotic treatment;
ii. exotic therapy material is typically sold in regional stores;
iii. cash scarcity for buying medicine or remedies, and
iv. great diversity of native medicinal species.

Traditional medicine comprises mineral, herbal, and animal-based substances; nevertheless, herbal medicine is used extensively for medicinal purposes and is a vital cultural aspect connected to rural heritage, considering its relative significance is more diminutive than western medicine. Medications typically comprise mangrove bark crushed and assimilated; it is then boiled with other organic extracts or substances (Dahdouh-Guebas et al., 2000).

Avicennia officinalis is a medically significant mangrove species employed by conventional medicine for managing various disorders like asthma, rheumatism, dyspepsia, tumours, and paralysis (Das et al., 2018). Nevertheless, it is highly inappropriate to consider herbal products absolutely safe except for laboratory scenarios. These substances might have side effects that could cause significant health issues or even be fatal. Conventional therapy safety and efficacy for biological systems must be assessed through a comprehensive analysis, in vitro assessments, and clinical evaluation (Nabatanzi et al., 2020). There was a high degree of resemblance between the plants employed for medical material from the same floristic area than plants used for an ethnic group (Phumthum and Balslev, 2019). Rhizophora leaf chewing precedes social ceremonies because this herb offsets the effects of drinking. Also, the essence of *Avicennia germinans* bark is employed for controlling diarrhoea, enhance wound healing, and control haemorrhoids (Palacios and Cantera, 2017). Chowdhury et al., (2014) suggested that approximately thirty mangrove varieties are usable for the medicinal purpose; these include *Acanthus illicifolius* (for healing tiger bites, while the roots are helpful for paralysis and asthma treatment), *Acanthus volubilis* (gastric ulcer treatment), *Acrostichum aureum* (boils and carbuncles can be eased using rhizome paste), *Avicennia marina* (facilitates abortion), *Avicennia officinalis* (seeds are used for treating boils), *Bruguiera gymnorrhiza* and *Bruguiera sexangula* (barks help address diarrhoea), *Casytha filiformis* (the fruit that helps prevent the transmission of sexually transmitted diseases), *Ceriops tagal* (the bark helps peptic-ulcer like problems). Moreover, root bark material is understood to repel demons from possessed individuals; *Rhizophora mucronata* roots are considered to bring lost power back to the family (Dahdouh-Guebas et al., 2000).

Pullaiah et al., (2016) asserted that about thirty-five mangrove varieties are used for traditional medicine in Indian regions comprising the West Peninsular Coast and the Western Ghats. The authors noted that *Xylocarpus granatum* (bark extract is used for dysentery treatment), *Suaeda nudiflora* (leaf paste is used for wound healing), *Sonneratia alba* (fruits are helpful for reducing swellings and haemorrhage), *Scyphiphora hyrophyllaceae* (shoot extracts help with liver and enteric disease), *Salicornia brachiata* (treatment of itch using plant ash), *Rhizophora mucronata* (bark extract helps address diarrhoea, vomiting, and nausea), *Rhizophora lamarkii* (leaves help with hepatitis treatment), *R. apiculata* (bark extract helps address nausea, diarrhoea, vomiting, haemorrhage, and amoebiasis; besides it has antiseptic characteristics), *Lumnitzera racemose* (used for fertility issues, snake bites, asthma, and diabetes), *Kandelia candel* (bark helps treat diabetes), *Hibiscus tiliaceus* (leaf extract has laxative properties), *H. fomes* (grounded seeds help control dysentery), *Excoecaria agallocha* (latex has medicinal characteristics that alleviate toothache, *Dolichandrone spathaceae* (antiseptic characteristics; also used for enteric spasm treatment) and *Ceriops decandra* (hepatitis treatment). Leaves of *Blumea lacera* are shown to alleviate most colds. Warm leaf paste has diuretic characteristics, while black pepper and leaf paste is used for treating dog bites (Ali Ahmed et al., 2014). *Blumea lacera* is used for fuel, while leaf juice has astringent, anthelmintic, diuretic, and febrifuge properties and is used in the Rajshahi area in Bangladesh (Rahman, 2013).

Threats in Mangrove Ecosystem

Mangrove or brackish environments are disturbed directly by natural adversities and transitions concerning inland freshwater handling. A reduction in coastal mangroves will threaten human safety and affect the shoreline characteristics by flooding, erosion, storm currents, and tsunamis. Environmental dynamics comprise transformative phenomena caused by natural and anthropogenic activity depending on environmental resources and coastal regions. Mangroves are affected by changing change due to sea level changes, events causing high water levels, storms, temperature, precipitation, CO_2 concentration in the atmosphere, and human adaptations because of changing climate. Atmospheric composition change and increase in sea level are the most significant threats. Increasing sea levels and higher incidence of extreme weather events concerning water might influence the mangrove health and areas in ways similar to storms. Storms cause a higher incidence of fast wind velocity, and the development of low-pressure increases because of climate change. Higher storm frequency might affect mangroves adversely (Church et al., 2001). Water quality and quantity are affected because of climatic factors, including changes to evolving land-use patterns, water consumption, and habitat invasion.

Mangrove species are affected by a 0.7ºC increase in temperature; consequently, phonological aspects like fruiting and flowering, composition, mangrove productivity, and expansion to higher latitudes restricted by temperature are affected. Furthermore, the temperature is a critical aspect that immensely impacts mangroves' forest types and geographical distribution, thereby decreasing seedling areas (Krauss et al., 2008; Gilman, 2008). Brackish waters with high silt content are favourable for mangroves; therefore, river estuaries in the proximity of the Malaysian Peninsular coast are essential measures of coastline health (Wang, 2009).

Heavy metal contamination is another aspect that adversely impacts aquatic ecosystems. Heavy metals accumulate due to gradual leaching from rock and soil, agriculture, and industrial discharge. Heavy metal contamination comprises a risky concentration of lead (Pb), mercury (Hg), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), and zinc (Zn)

(Liang et al., 2004). The effects of overabundant nutrients in riverine and palustrine systems, coastal regions, and estuaries are considered critical global issues. Heavy metal contamination might lead to mutagenic and cytotoxic effects on living beings (Olgun and Sanchez-Galvan, 2010). Consequently, the complete aquatic environment suffers because of structural and functional degradation. Extensive research concerning freshwater environment indicates stressors like oil presence, soil acidification, pesticide contamination, and copper pollution causing a higher incidence of algal bloom, nitrogen fixation and less carbon assimilation because phytoplankton is affected due to copper exposure (Xu et al., 1999).

Sediment excess deposited by rivers (agricultural activity, industrial use, and land clearing), untreated sewage pollution, and sand mining affect coral reefs adversely. In the context of mangroves, excessive timber harvesting and aquaculture stresses cause continuing conditions caused by high levels of acid sulphides produced anaerobically and originating from highly organic mangrove soils (Wilinson et al., 2006).

Types of Contaminants in Mangrove Ecosystem

Wetland environments are of great intrinsic importance since they efficiently degrade and eliminate nutrients, contaminants, and heavy metals comprising underwater and floating plants, ventilation regulation, and changes in microbial characteristic due to rhizomes or roots (Groudeva et al., 2001). Nevertheless, massive mangrove regions create extensive pollutant sinks for nutrient removal, eliminating organic pollution and heavy metals from oceanic and inland freshwater ecosystems. Redox reactions, clay concentration, and tidal flooding are other significant aspects. Moreover, mangroves can naturally process and develop resistance against heavy metals. These aspects vary with species (Jia et al., 2010).

Point and diffused (organic substances) are two different pollution sources; their level in water cannot be understood directly. It must be measured using total phosphorus, BOD, COD, NH_3-N, pesticides, Cd, Pb, Cr, Cu, and Zn levels. Effluents from industrial activity, oil, and solid residue might damage mangrove roots, affecting osmoregulation and respiration. Heavy metals cause maximum harm due to their presence and persistence. The United Nations Environment Programme (UNEP) indicates that sedimentation and erosion, temperature difference, nutrient acidity, and inorganic pollution (metallic and non-metallic contaminants), and organic pollution (excess organic matter and pesticides) alter water pollutants (Smits, 2005):

1) Temperature: Biological functioning is extensively influenced by water temperature, which has a critical declining or stimulating effect on aquatic beings. Higher water temperature can store lesser oxygen, thereby slowing metabolic activities.
2) Erosion and sedimentation: Sediment increase might reduce primary efficiency (photosynthetic production) and habitat cycle of fauna and flora because of erosion, leading to sediment and organic substances being introduced into aquatic ecosystems.
3) Nutrients: Nutrient concentration in aquatic systems is a significant determinant of water quality. Nutrient build-up comprises phosphorus and nitrogen due to agricultural runoff; moreover, the industrial discharge might lead to nutrient overabundance, excessive growth of vascular species (algal bloom), reduction in dissolved oxygen (DO) levels, and increased stress on aquatic beings. Nutrient abundance might lead to higher acidity in freshwater environments, thereby impacting biodiversity adversely.
4) Acidification: The aquatic environment is immensely affected by pH, which affects the biological aspects of the environment. For example, high industrial activity and rain acidification represent aquatic environment acidification. Excess acidification might impact young organisms and affect soil containing many oxides of nitrogen and sulphur.
5) Salinity: Freshwater organisms are not as tolerant to high salinity as mangroves. Pollutants like agricultural residue increase water

salt content, whose chemical characteristics do not match those of water salt. This condition might change riparian and growing vegetation and influence the properties of natural wetlands by causing a decline in marine population.

6) Organic contaminant: Persistent organic pollutants (POPs) are another term for organic pollutants that are typically present as contaminating substances in groundwater through soil leaching, landscape and agricultural runoff, and groundwater contamination. POPs are typically manufactured using synthetic and xenobiotic microorganisms that are introduced into ecosystems using military equipment (chemical), industry (petrochemical), agriculture (pesticide), wood processing, and other ways that lead to volatilization, capture, and breakdown. Hence, phytoremediation is used for processing trichloroethylene (TCE) (groundwater contaminants), hydrocarbons present in petroleum, herbicides, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs). PCBs are typically produced as by-products from industrial activity; these substances are introduced to the environment when used or disposed of. Organic pollutants comprise numerous chemicals origination from various industries like pharmaceutical, herbicides, cleaning agents, flame retardants, and others, including combustion products. Substances like nitrogen and phosphorus comprise a significant portion of these effluents. Mangrove forests can sequester phosphorus from wastewater at a faster rate than nitrogen.

7) Inorganic contaminant: Inorganic contaminants are typically in the form of chemical elements present in the biosphere or caused by human activity. Metals are chemical elements having excellent electrical conductivity, and their electrical resistance rises with absolute temperature. On the other hand, heavy metals, also called transition metals, have atomic number over 20 and density of around 50g cm^{-3}. These elements are very toxic to animals and vegetation despite extremely low levels. These elements are produced due to natural or human-caused activity; about 10%

originate from biogenic causes or forest fire, while about 80% are introduced due to volcanic activity, which is eroded due to atmospheric phenomena. Human activities contributing to such contamination include effluent discharge, garbage disposal, agricultural and urban runoff, sewage, residential waste, mining, boating, and industrial pollutants introduced into the environment but not broken down (Table 1).

Additionally, metals (metalloids), also referred to as Trace Metals (TMs), are regarded as "contaminants" if they are present but not required or have a level that causes harm to humans and the environment. Metals considered mild contaminants include cobalt (Co), aluminium (Al), manganese (Mn), caesium (Cs), strontium (Sr), molybdenum (Mo), and uranium (U). Such metals are introduced due to pollution sources like industrial waste, leaded petrol, metal leaching and introduction into the ecosystems through acid rain. Heavy metals comprise most inorganic pollutants caused due to emissions, municipal compost, industrial activity, and pesticide use (Singh et al., 2011).

For example, heavy elements might be phytoremediated through sequestration in plants or stabilization. Plant macronutrients like phosphate and nitrate are part of the process; moreover, plant trace metals like Cr, Fe, Cu, Mo, Mn, and Zn along with unrequired metals like Cd, F, Co, Se, Pb, Hg, V and W and radioisotopes like ^{137}Cs, ^{238}U, and ^{90}Sr (Smits, 2005). Heavy metal cycling is a crucial question that has been researched extensively in the mangrove environment context because they are toxic, possess bio-accumulation ability, and persist for extended periods (Lacerda et al., 1988; Tam and Wong, 2000). Pollutants present in water and soil loaded with metals are critical issues specifically for human health and the environment. Hence, potent technology must be identified to process these metals, either nonradioactive such as phytoremediator, Cd, Cu, Hg, Pb and Zn or radioactive such as Sr, Cs and U (Raskin et al., 1997).

Table 1. Effect of heavy metals in plant growth

Heavy metals	Effect on plant
Chromium (Cr)	Oxidising elements lead to extensive cell membrane damage bind as complex compounds of nucleic acids, proteins, and organic substances
Lead (Pb)	Disrupts metabolic phenomena hindering plant development; photosynthesis in plants is affected by Pb contamination
Iron (Fe)	Undergoes oxidation to produce Fe^{3+} ions in the aquatic root, thereby reducing toxic substances from permeating into the plant root
Copper (Cu)	Strongly reduces photosystem activity, inhibits biomass development, disrupts the antioxidant mechanism, thereby stressing plants
Cadmium (Cd)	Slows physiological phenomena (photosynthesis, respiration, and exchange of gases)
Nickel (Ni)	Changes physiological characteristics, causing systemic toxicity like chlorosis and cell death in plants
Zinc (Zn)	Inhibits chlorosis and development, leaves get purplish-red in response to phosphorus inadequacy

Yadav, 2010; Dewez et al., 2005; Hou et al., 2007.

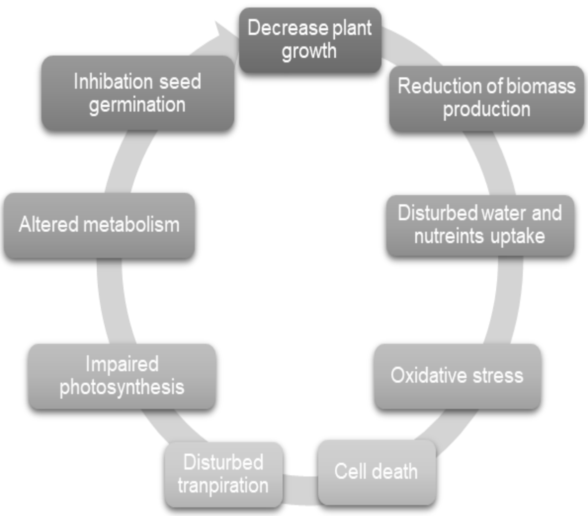


Figure 2. Common effects of metal toxicity on plants.

Additionally, prevalent metals originating from industrial waste entering the estuarine environment include Pb, Cu, and Zn (Morrisey et al., 2003). Organic pollutants may be oxidised into CO_2 by microorganisms; however, inorganic pollutants comprise transformations to their chemical characteristics and bioavailability. Inorganic material is resistant to chemical and microbial breakdown, thereby persisting for extended periods (Bolan et al., 2003) and causing metal toxicity, as depicted in Figure 2.

Landscape Ecological Approach

Contemporary ecology encompasses the landscape aspects in a new branch that deals with the association between humans and the landscape, both natural and artificial. It emphasises the spatial associations between landscape aspects or environment, energy flow, minerals and nutrients, and species for the elements and ecological characteristics (Pickett and Cadenso, 1995). Numerous studies have indicated a substantial correlation between water and quantity and run-off and landscape aspects (Jones et al., 2001). Reduction of vegetation is an indicator of possible problems concerning water quality (Hunsaker and Levine, 1995; Smith et al., 1997).

Additional research indicates watershed-specific land might cause relatively high variability in estuary water and stream quality (Behrendt et al., 1999; de Whit and Behrendt, 1999). Empirical research suggests a strong causal correlation between watershed properties and sediment and nutrient presence (Yates and Sheridan, 1983). Transition in landscape characteristics specific to the riparian area might cause a significant change in water quality on a broader scale and watershed environments (Peterjohn and Correll, 1984). The significance of near-site, landscape aspects might differ based on biophysical scenarios (Clarke et al., 1991). Wetlands have a vital role in regulating nutrient quantities on surface waters (Weller et al., 1996). Wetlands possess three macro aspects: hydro soil, hydroperiod, and vegetation that use natural biochemical processes to eliminate divalent metals (Gillespie et al., 2000).

Researchers and environmental managers are worried about the extensive transformation in land-use trends and landscape aspects and their combined effects on ecological and hydrological activity that regulates wetlands, streams, and estuary properties (Hunsaker and Levine, 1995; O'Neill et al., 1997). There is a specific concern about the influence levels of landscape characteristics at watershed scales on phosphorus, nitrogen, and sediment loading on surface water (Hunsaker and Levine, 1995). Water loaded with a high concentration of sediment and nutrients leads to extensive ecological concerns and human health risks. Agricultural activity with upwards of 3% slope leads to higher soil erosion likelihood, thereby facilitating nutrient and sediment increase on surface waters. A high quantity of resistant surfaces and roads on watersheds might cause high nutrient loadings additional sediment flowing to streams (Arnold and Gibbons, 1996). Moreover, atmospheric-based deposition might cause nitrogen to accumulate in surface waters. Despite several attempts to observe and create nutrient and sediment model to understand loading levels on streams and estuaries (Yates and Sheridan, 1983; Weller et al., 1996), there is no holistic technique that assesses potential loading values specific to streams using landscape characteristics and trends on regional levels. Additionally, we must identify water bodies having maximum risks due to extensive sediment and nutrient loads. Accordingly, mitigation might be undertaken to reduce the impact. Sustainable landscape ecology planning and management remain scarce; it must be explicitly enhanced for developing nations. The emphasis should be on modelling spaces accounting for biophysical, cultural, and socioeconomic phenomena to maintain healthy ecosystems (Pearson and McAlpine, 2010).

Ecological Indicator Application

Ecological metrics are objective properties concerning the structure, function, and composition of ecological environments comprising landscape trends, community population, ecosystem aspects, landscape disturbance phenomena and additional landscapes that reflect environmental characteristics and allow the implementation of corrective action. Metrics can be applied in different scenarios because anthropogenic and societal factors affect the environment similarly (Niemeijer, 2002).

Ecological markers are used to observe environmental alterations, access state of environment which need a clear goal of study, temporal and spatial scale, variable of statistics evaluation, accurate and precise, specific stressors of correlation and social indicators. The species of indicators reflect the abiotic and biotic elements in the environment, assess environmental changes and discern the diversity of other species. Moreover, multitude of species communities suggests specific conditions. Some policy-relevant markers have been underlined to detect alterations in natural environment (Dale and Beyeler, 2001):

1) Assessment of both existing and emerging problems;
2) Analysis of the anthropogenic stressors leading to destruction;
3) Formation of trends for identifying environmental policy and program performance;
4) Ease of communication with the public; and
5) Soil quality indicators should relate with management procedures, and conform to ecosystem process and prevailing components. Indicators of soil quality can determine the region productivity and soil function on the basis of certain characteristics of soil such as physical and chemical properties that can have several kinds of soil quality with different indicators that are different for different goals or uses of the ecosystem, namely:
   - Nitrogen availability;
   - Litter decomposition;
   - Soil micro arthropod population; and
   - Carbon availability.

Ecological indicators are generally used to evaluate the health of ecosystems (Shin et al., 2018). It provides knowledge regarding habitats and the impact of human affairs on ecosystems to different audiences, including administrative policymakers and the general public. Ecosystems are complex, and ecological indicators can help in demonstrating to the public or laymen the application in environmental regulative decisions. As per (Marques et al., 2019), human activities have reduced the efficiency of some marine habitats globally as they suffer from anthropogenic stressors on a local and global scale such as pollution, climate change, urbanisation and deforestation. In aquatic ecosystem, the stability of the life depends upon the value of chemical and physical factors such as pH, temperature, total hardness (TH), dissolved solids (TDS), chloride (Cl^-), magnesium (Mg^{2+}), calcium (Ca^{2+}), carbonates (CO_3^{2-}), bicarbonates (HCO_3^-), dissolved oxygen (DO), sulphates and organic matter, and biological properties in order to determine the ecological health which in turn can be used to assess the level of pollution (Srinivas et al., 2018). The ecological indicators' role can be considered as one of the major aspects to respond to the alterations in the specific environment, ecosystem or surroundings to measure or assess the ecological health. There is a research by (Shin et al., 2018) that stated that the principle used for ecological indicators is to evaluate and measure particularity of the presence of 2 kinds of environmental change which are by "random," such as interannual climate change, or by "directional," which means climate change.

Healthy ecosystem depends on several indicators and precise judgment of certain conditions and health here implies the absence of indications of ecosystem breakdown. A healthy ecosystem is vital for humans and the natural world as well to receive the provisions they need, and it has immense economic and social value. The notion of ecosystem health is examined, as well as what comprises health and what is the meaning of being healthy. To evaluate ecosystem health, several metrics must be used to determine ecosystem conditions (Lu et al., 2015). In the South Brazil marine ecosystem, basic ecological indicators were used for landings and market data to assess environmental stresses over time, so as to contribute to ocean and fisheries assessments of delicate ecosystems (Pincinato and Gasalla, 2019). In addition, to promote an ecosystem strategy for fisheries, indicators have been used in the marine habitat to determine the ecosystem impacts of fishing (Shin et al., 2018). In some other applications, the ecosystem health was measured by relating the distribution of chemical and physical characteristics such as polycyclic aromatic hydrocarbons (PAHs) and total petroleum hydrocarbons (TPHs) to identify potential sources of such hydrocarbons and assess their effect on the health of marine ecosystems. The outcome of the measurement is intended to help administrators make better decisions regarding this crucial water resource

(El-Kady et al., 2018). As per Othman et al. (2016), a range of chemicals is scattered by industrial, agricultural, pesticides, petroleum and residential usage; meanwhile, mangrove forests function as a sink for pollution from sea or inland freshwater. The ecosystem health can be assessed by analysing the concentration of chemical and physical properties in the plants and water in mangrove forests through phytoremediation process. For instance, organ mercurial and bacteria mercuric reductive are formed by plants and can transform the toxic ion into metallic substance from the leaf surfaces.

The state of the mangrove, resilience, and distribution of the ecosystems are affected by several independent or interacting factors. Mangrove ecosystems can fully grow only in extremely humid areas because of precipitation gradients and the climate forms a primary disturbance cycle because of their sensitivity to cold and regular harm or recovery cycles following freeze occurrences. Moreover, mangroves are subject to human disturbances like impact on water or soil qualities, or even to species along the area's densely inhabited coastlines. There are several indicators to detect change in the habitat like phytoplankton biomass seen a result of substitute for environmental condition. Heavy metals are main contaminants in the physical environment owing to their negative effects on the environment. As a result of high anthropogenic prolonged pollution, increased amounts of heavy metal have been observed in mangrove sediments throughout the world (Shin et al., 2018). The mangrove ecosystem is used as an exceptional pollution sink, with contaminants from different anthropogenic and industrial activities being poured into it.

Mangrove has great potential for landscape ecological indicator organisms to show unique heavy metal pollutants; since it is an exclusive ecosystem and transitional zone between terrestrial and sea. Environmental alterations force the mangrove plant varieties to form a phytochemical because of their plant resistance and endurance to toxicity levels in a rough environment. They are vital for the preservation of marine animals, habitats, resources, and livelihoods of the people who reside along the coastline. Using wild species like crab, shrimp, fish, and molluscs as specimens, mangrove plants can rejuvenate environmental conditions for the habitation of marine organisms, like mangrove resistance indicators of mangrove density and cover value. Besides, the variety of mangrove crabs as a biological indicator for estimating the existing ecological conditions of mangrove biotas is one of the process in environmental evaluation. The mangrove ecosystems of the coves and islands are compatible with respect to biological and ecological connections. Consequently, crab diversity functions as a useful biological indicator for explaining the ecological properties of a particular mangrove forest region. According to another observation by (Chaudhuri et al., 2021), there are many heavy metallic elements such as Pb, Cu and Zn which were measured in root, stem and leaf mangrove species in 3 seasons around Indian Sundarbans region during 2015. It was observed that the concentrations of all these three metals were discovered to be greatest during the monsoon, which was followed by premonsoon and postmonsoon. Irrespective of the vegetative locations and parts, the greatest concentration of metallic element was that of Zn, which was followed by Cu and Pb.

Mangroves are a significant forest habitat that prevails along the tropical and subtropical shorelines throughout the world. A strong marine environment relies on the mangrove forests being healthy. Mangroves last in very salty soils and waters since they are well adapted to their environment, capable of eliminating or rejecting. Mangrove ecosystems are natural resources that may generate a wide variety of services and products for coastal people and society at large. The ecological advantage of mangroves has been extensively studied and recognised in most tropical nations. Nonetheless, their extent, state, and correlations to other ecosystems are inadequately understood, hindering efforts to preserve and manage them, leading to unsustainable utilisation of these profitable coastal resources. Thus, every nation must examine the condition of mangrove biological variety, realise its commercial potential, and identify domains of application, all of which are vital in planning balanced mangrove management.

Phytoremediation Application

Phyto-remediation is a combination of the Greek word "Phyto" meaning plant and "remedium" which is the Latin suffix that means restore or to cure. It is a fairly new technology which uses green plant habitats to clean soil and water contaminated by hazardous organic and inorganic compounds. The integration of this Phyto-remediation method may be able to clean polluted water or soil rapidly. Phyto-remediation application is called bioremediation that makes use of plants to separate, extract, decompose or disable toxic pollutants from waters, soils or sediments which include metalloids, salt, nutrients, heavy metals and radioactive substances including organic (PCBs and PAHs) and inorganic pollutants (metals) (Farraji et al., 2020). The probable plants include trees, shrubs and herbs which are able to amass heavy metals and organics high above the amounts found in nature (Brown, 1995). Ex situ or in situ treatment of polluted soil and sediment is an efficient and cost-effective technique to clean up certain harmful waste at site either for gaseous, liquid and solid substrates (Schnoor et al., 1995).

At present, Phyto-remediation is still a growing technology that strives to exploit metabolic abilities and growth patterns of higher plants. From terrain architecture viewpoints, Phyto-remediation can be useful in developing sustainable green space, providing a natural barricade for visual screening, lessening noise, and requiring less intensive human interaction. Sustainable strategy and practice are needed to be stressed and elements are required to be assessed for the clean-up project which benefit from various approaches of green remediation (Pedron and Petruzzelli, 2011). The condition of metal-contaminated soil depends on the overall metal concentrations present in soils that can estimate the level of soil contamination and metal concentration or their harmfulness which affect bioavailability of plants (Lukkari et al., 2004; Sue and Wong, 2003).

Table 2. Phyto-remediation process and mechanism involved

Process	**Description**	**Mechanism**
Phyto-degradation/ Phyto-transformation	Plant ability to absorb and degrade pollutants in the transpiration stream using intrinsic enzymatic processes and photosynthesis-aided oxidation/reduction	Degradation in plant (Organic)
Phyto-volatilization	Plant ability to absorb, move, and release volitive pollutants by transpiration	Volatilization by leaves (Inorganic/Organic)
Phyto-stabilization	Plant roots absorb and collect soil pollutants and eliminate them	Complexation (Inorganic)
Rhizofiltration	Terrestrial/aquatic plants facilitate phytoremediation by increased metal update from contaminants; these metals are then precipitated. Phyto-remediation by using to uptake and precipitate metals from contaminated source	Rhizophere accumulation (Inorganic/Organic)
Phyto-sequestration	Plants' ability to remove specific contaminants from rhizosphere by exuding phytochemicals; the root performs this by transporting proteins and cellular phenomena	Plant root (Inorganic/Organic)
Rhizo-degradation	Pollutant bio-degradation in soil due to microbial processes in the rhizosphere	Fungi and bacteria (Inorganic/Organic)
Phyto-hydraulics	Plants' ability to absorb and transpire water from the plant or absorb water from the atmosphere	Evapotranspiration (Inorganic/Organic)
Phyto-extraction/ Phyto-accumulation	Plants' ability to absorb contaminants using transpiration process	Hyper-accumulation (Inorganic)

Ghosh and Singh, 2005; Dhir et al., 2009; Paz-Alberto and Sigua, 2014.

Furthermore, heavy metals are significant environmental problems owing to their toxicity, permanence and bioaccumulation based on chemical and physical properties of mangrove deposit. They have an ability to expel into marine ecosystem substances that consist of anaerobic and which are rich in organic and sulphide matter and the ensuing sulphide oxidation between tides allows metal mobility and bioavailability (Burcheet and MacFarlane, 2000).

Table 3. Advantages and disadvantages of Phyto-remediation application

Advantages	**Disadvantages**
Less maintenance, passive, in situ	Development pattern of planted species
Can be used in remote areas having less facility	Shallow root depth is determined by plant species; hence, water or soil contamination remediation is affected
Reduced secondary waste production and water/air emitted	Restricted by land availability
Sites having several contaminants or a mix can be remediated	Higher likelihood of ailments and infestation
Regulates surface runoff and soil erosion	High level of contaminant bioaccumulation in vegetation
It can be used concurrently with different Phyto-technologies	Phytoextracted by-products might be very toxic, thereby requiring careful waste handling
Completion of habitat restoration or creation that facilitates land reclamation	Restricted capacity for bulk movement of pollutants to the treatment area
Publicly favoured; has better noise and aesthetic properties	Restricted public knowledge
Green and economical technology	Plants must be maintained; hence pollutant elimination might be over extended periods
Absorption of GHG and carbon	Slower than other active remediation techniques
Less maintenance, passive, in situ	The development pattern of planted species
Can be used in remote areas having less facility	Plant species determine shallow root depth; hence, water or soil contamination remediation is affected
Can process inorganic and organic effluents	Climatic conditions might affect phytoremediation by exotic plans and affect biodiversity
A natural approach that can be used sustainably	-
Comprises mainstream processing methods (wetland, constructions, landfills, and ecological revival)	-
May be used for extensive areas	-

Ghosh and Singh, 2005; Paz-Alberto and Sigua, 2014.

The process of Phyto-remediation is dependent upon plant physiological process induced by solar energy, rhizospheric process as well as available pioneer. It involves the build-up of chemicals in plants to eliminate or decompose inorganic and organic pollutants by decomposition of microbes, volatilisation and absorption and bioavailability of inhibition in environment (Paz-Alberto et al., 2014). There are nine mechanisms that have been stressed as Phyto-remediation techniques, as shown in Table 2. Moreover, advantages and disadvantages of the process of Phyto-remediation have been detailed in Table 3. Phyto-remediation process can be used as a green technology strategy and tool that may be beneficial based on 4 perspectives:

1) Economy - Cost efficacy;
2) Ecology - Improvement of aesthetic value and eco-friendly nature;
3) Long-term use; and
4) Green approach - Able to remediate multiple pollutants (water, soil, and air).

Although Phyto-remediation process has few disadvantages, the significance of using this green technology in the ecosystems is yet to be explored properly. Furthermore, the mechanisms involved in the process of Phyto-remediation need to be comprehended about how the structure of plants can release, eliminate, stabilise and volatilise the pollutants through soil, air and water.

Phytoremediation as Green Solution for Mangrove Pollution

A key role is played by the mangrove forest with regards to socioeconomical and ecological contexts, which need to be highly accounted in the conservation agenda (Islam et al., 2005). However, clearing of the mangrove areas in most of the countries for anthropogenic activities has been done, majorly because of land conversion pertaining to aquaculture, agriculture and urban development (Dahdouh-Guebas et al., 2002; Senarath and Visvanathan 2001). On a global scale, it has been seen that degradation of a third of mangrove forests has already been done. The same issue was also faced by Malaysia, in which it lost 278 km^2 from the year 2000 to 2014 (Azad et al., 2009). These days, most researchers are concentrating on the impacts cast by intensive shrimp aquaculture on pollution pertaining to coastal environment as the water requirement here is greater versus other forms of aquaculture besides its reliance on huge input quantity pertaining to fertilisers, synthetic feeds and various chemical additives (Lacerda et al., 2011). The destruction with regards to the mangrove ecosystem due to poor shrimp aquaculture management has resulted in various issues like possibility to degrade the existing natural habitats as well as populations, exposure of coastlines towards storm and tidal surges, resulting in water pollution as well as soil acidification (Azad et al., 2009).

The poor management pertaining to aquaculture effluents has negatively impacted the quality of mangrove land - for example, water pollution caused by the release of inorganic contaminants, like phosphorus, nitrogen and heavy metals. Although, to resolve this issue, various alternatives have been put forward, they are still regarded to be ineffective with regards to cost, energy and maintenance. For waste treatment, although numerous approaches like centrifugal systems, settling systems and mechanical filters have been put forward, these are still regarded to be ineffective as they yield large amounts of sludge deposits, require frequent maintenance and consume more energy (Akinbile and Yusoff, 2012). Thus, in order to confirm the effectiveness pertaining to aquaculture practices, different alternatives need to be put forward to reduce the negative impact of aquaculture effluent (Shimoda et al., 2005). Few of the developed tropical countries were found to employ a popular alternative approach to deal with this issue, i.e., by growing algae species in the effluent (Rao et al., 2011).

Thus, the landscape ecological approach needs to be practiced as a substitute in order to remediate contaminated soil as well as water for the aquaculture industry. A brief study on this technology's effectiveness could result in maintaining a sustainable aquaculture industry with regards to economic, ecological and social advantages. Thus, phytoremediation, which involves employing plants as well as related microorganisms-based technologies, is being accepted widely to assess the issues and offer sustainable solutions (Farraji et al., 2020; Rai 2008). Phytoremediation is also regarded as an efficient approach as it offers eco-friendly solutions to restore and rehabilitate polluted areas, improve food safety, and contribute to decrease in global warming via carbon sequestration.

Good phytoremediators can tolerate the pollutant, possess extensive and branched root systems, can degrade or concentrate high-level contaminants present in the biomass, grow at quicker rates, can absorb large amounts of water from the soil, have high levels of biomass, be easy to harvest, can be distributed widely, and be easy to cultivate (Ali et al., 2013; Barceló and Poschenrieder 2003). Different types of pollutants have been successfully remediated by using technologies like volatilisation, degradation, sequestration, stabilisation, rhizofiltration, extraction and accumulation (Ali et al., 2013; Barceló and Poschenrieder, 2003).

Generally, phytotechnology have several advantages which are (Aisien et al., 2012):

i. system is solar-powered, autoregulating, and requires less maintenance,
ii. controls aspects like surface runoff, soil erosion, fugitive dust release, and infiltration,
iii. can be used for remediating areas having a mix of pollutants,
iv. Create or revive habitat, thereby facilitating reclaiming land when complete,
v. Better public perception enhances noise and aesthetic properties,
vi. GHG and carbon sequestration, and
vii. Economical and green approach.

Thus, in environmental management, a key role is played by the plants in maintaining environmental quality by safeguarding biological diversity, restoring ecological balance as well as others.

Halophytes as Phytoremediation Agent

In *Avicennia marina* or grey mangroves, the root tissue contains accumulation of three types of heavy metals with high copper (Cu) and lead (Pb) versus sediment and high zinc (Zn) in leaves. *A. marina* roots could be regarded as bio-indicator species pertaining to the environment for Pb and Cu, while leaves for Zn (MacFarlane and Burchett, 2002; MacFarlane et al., 2003). However, a similarity of heavy metals concentration exists in roots as well as adjacent sediments that possess root bio-concentration factors (BCF ≤ 1) (MacFarlane et al., 2003). In the plants' structure, Pb concentration was found to be greater, whereas Zn and Cd were found to exist in the normal range (Nirmal Kumar et al., 2011). In the sediment of *A. marina*, the concentration of nickel (Ni) and Zn were found to be higher versus cadmium (Cd), Pb and Cu (Parvaresh et al., 2011). For bioaccumulation of heavy metals, *A. marina* is regarded to be a highly efficient plant, particularly for Cr and Cu that were found to be highly bio-accumulated in leaves versus sediment (Usman et al., 2013). A comparison study between the mangrove nearest to pollution areas of *A. marina* and natural mangrove forests identified that Ni and Fe (p values ≤ 0.01) were in a greater concentration in leaves and pneumatophores, while Mn, Pb, Cu, and Zn were present in greater concentration in natural mangrove forests (Nath et al., 2013). The metal pollution pertaining to *A. marina* suggests that a much higher concentration of Cd, Pb and Ni is present in roots when compared with the sediment (Nowrouzi et al., 2012). Higher heavy metal concentration was found in plant shoots versus water and soil samples of *A. marina*, particularly Cu versus Cd level. Therefore, this species can be regarded as an optimum candidate for phytostabilisation pertaining to industrially polluted coastal areas (Almahasheer et al., 2014). A separate study of *A. officinalis* of sediment, leaves, root and bark identified that the sediment would accumulate a greater number of heavy metals (Zn, Cu, Pb and Cr) versus leaves and bark, while roots possessing

BCF <1 as vital species decrease heavy metals transport towards adjacent estuarine as well as marine ecosystems (Chakraborty et al., 2013).

Accumulation of various concentrations of heavy metals like Cu, Zn, Pb, Mn, Ni, Cr and Cd was seen in different parts of *Rhizophora stylosa* in which Cd was found to be the highest while the others were negligible. Higher accumulative number concentration pertaining to Cu and Pb in *R. apiculata* was seen in root tissues versus bark and leaf tissues (Kamaruzzaman et al., 2009). Bark (Cd and Pb) and leaves (Ni and Cr) were found to possess the highest concentration. Meanwhile, for *R. mucronate,* it was seen that the roots (Mn and Fe) and the trend of phytostabilisation capacity would vary in metals (Pahalawattaarachchi et al., 2009).

The growth pertaining to *Sonneratia apetala* species was found to enhance with wastewater pollution levels like Total Phosphorus (TP), Total Nitrogen (TN), Cu, Zn, Pb and Cd. Meanwhile, in the leaves, chlorophyll content accumulation was found to reduce (Zhang et al., 2011). The total concentration pertaining to Cr, Cd and Zn was found be lower than the general critical soil concentration and Pb and Cu were seen to be in high concentrations in *S. caseolaris* leaves and roots. For the mangrove ecosystem, this species can also be regarded as an optimum phytoremediator species (Nazli and Hashim 2010).

A comparative study pertaining to various mangrove vegetations has showed that Pb in *A. marina* is better when it comes to accumulating pollutants versus *R. stylosa*. Certain factors like heavy metal concentration, plant species, and exposure could also impact the process (Chen et al., 2003). The concentration of *A. marina* has also been referred as salt-excretion mangrove, while for *R. stylosa*, it is also regarded as salt-exclusion mangrove. Metals like Zn, Pb, Cu, Mn, Fe and Cd get mostly accumulated in root tissues, versus in foliage (leaves) like in *Avicenna sp., Kandelia sp*. and *Rhizophora sp*. (Peters et al., 1997). Also, a variation with regards to the concentrations was also seen for Zn and Cu and this is found to be present in high concentration in *A. officinalis;* in *Barringtonia racemose*, high levels of Fe, Mn and Co were seen versus other species such as *Acanthus ilicifolius, Sonneratia caseolaris* and *Bruguiera* *gymnorrhiza* (Thomas and Fernandez 1997). The results pertaining to *S. apetala* and *A. marina* showed that the roots of *A. marina* could also accumulate and survive even in conditions such as heavy metals concentration. A high concentration of Zn versus Pb could also get impacted by plant part, species and localities (Shete et al., 2007). Among these three mangrove species, *R. stylosa, A. marina* and *S. alba*, the total uptake pertaining to Pb from sediment was found to be significant ($p \leq 0.001$), with *S. alba* displaying the highest followed by *A. marina* and *R. stylosa* (Paz-Alberto et al., 2014).

Various studies imply that mangroves tend to accumulate and translocate few metals with leaf BCFs >1. High accumulation pertaining to heavy metals was seen in leaves with 1.5-2.4 for *A. marina* (Sadiq and Zaidi 1994), 1.2 for *Kandelia candel* (Chen et al., 2003) and 1.7 for *Aegiceras corniculatum*. Cu and Zn tend to get more concentrated in young leaves versus old leaves in *A. marina*; however, no significant difference was seen amongst metals with regards to old and young leaves for *Excoecaria agallocha, Hibiscus tiliaceus, Ceriops tagal* and *Bruguiera gymnorhiza* (Saenger and McConchie 2004). For Ni and Cu, high BCFs were seen versus other metals and a positive relationship existed between root (pneumatophores) and sediment for *A. marina* (Nath et al., 2014). A treatment evaluation pertaining to *A. marina* germination with Co, Mn, Pb and Zn showed significant value ($p \leq 0.001$) in all treatments (polluted seawater, root, shoot and soil) and were calculated for values pertaining to Biological Transfer Coefficient (BTC), Biological Accumulation Coefficient (BAC) and Bio-concentration Factor (BCF). As per the results, *A. marina* was found to be a phytoremediator with regards to select heavy metals (Nazim et al., 2014).

A positive linear relationship exists between peroxidase activity as well as leaf tissue with regards to Pb concentration decrease in photosynthetic pigment of leaf tissue which include great amounts of Zn and Cu. Thus, these can be applied as bio-indicators pertaining to Cu and Zn in *Avicennia marina* (MacFarlane and Burchett 2001). A correlation is involved with peroxides' activity in varying physiological processes' potential to act as a sensitive indicator pertaining to compromised metabolic activities like photosynthesis, respiration, transpiration, gas exchange and CO_2-fixation (Singh et al., 2016). For *Laguncularia racemose*, the pigment, growth and gas exchange were assessed with Cr with various concentrations of 0.00, 0.05 and 0.50 mg L^{-1}. Post 30 days, the intermediate dose was found to impact the photochemical efficiency. Highest concentration of Cr was found in roots versus leaves and stems that were not impacted by the tested dose (Rocha et al., 2009).

The availability of metal changes based on the site's physicochemical characteristics, including pH, cation exchange capacity, metal concentration, nutrient availability, redox status and sediments' salinity, as well as abiotic components like light, frequency of inundation and temperature could also impact the uptake of metal by plants (Greger et al., 2005). In estuarine, the sediment metals' initial bioavailability is mostly low because sediment could have characteristics such as being anoxic, low pH, waterlogged, and high organic content, thus the participation of metals could be done as insoluble sulphides (MacFarlane et al., 2003). As per many studies, mangroves are regarded as poor accumulators of trace metals, which occur at higher levels in root levels and sediment compared with mangrove leaves that generally include low concentration rates (MacFarlane et al., 2003; Sadiq and Zaidi 1994). However, indicator species are deemed vital as they can specify and reflect the level of existing pollutants, including heavy metals that are present within the biological system, while mangroves and their sediments are key due to their ecological value (Al Anouti 2014). In *Rhizophora sp.*, decomposition pertaining to organic enrichment of sediment from salt flats was found to induce trace metals' transfer to sulphide and organic forms from the oxide form (Marchand et al., 2012). Numerous studies have focussed on heavy metals contamination pertaining to mangrove sediments as well as organisms; however, as mentioned by Nazli and Hashim (2010), there is not much information on heavy metals uptake by mangrove plant species and other parameters:

1) Zonation: Few numbers based on previous studies have highlighted the relationship of heavy metals concentration

pertaining to various species in each zone. There is no specific group of plants species that can be said to accumulate particular heavy metals as well as its function as Phyto-indicator. A lack in the number of studies has been reported with regards to the group of true mangrove species present in opened zone (i.e., *Rhizophora sp., Avicennia sp.* and *Sonneratia sp.*

2) Heavy metal: Identification of various types of heavy metals (Cr, Zn, Cu, Pb, Mn, Ni and Cd) has been done and some studies have mentioned regarding Fe concentration in relation to the mangrove ecosystem. However, high concentrations of Pb, Cu and Zn are seen to typically found in estuary area. Therefore, it is key to identify certain mangrove species as well as their capability to eliminate or/ and uptake heavy metals.
3) Bio-indicator: Accumulation of heavy metals greatly varies and also relies on the kind of plant species. Compared with the water, studies focussing on sediment as well as plant tissues (bark, leave and root) have been reported frequently. The heavy mental concentration in water can be impacted by factors like water tidal and season.
4) Physico-chemical properties: Metal uptake by plants could also get impacted by cation exchange capacity, redox status, pH, nutrient availability, metal concentration and salinity of sediments, and also abiotic components like light, frequency of inundation and temperature.
5) Location: The capability pertaining to heavy metals accumulation by mangrove plants species could also get impacted by the locality. This is because of the fact that few of the mangrove's areas tend to remain natural while others could be located near to non-point sources (aquaculture, industrial production and tourism) and thus the rate of removing waste in the aquatic ecosystem could vary.

CONCLUSION

In this chapter, a comprehensive approach has been provided to further explain mangrove species as a Phyto-indicator with regards to mangrove ecosystem and it has established that both abiotic and biotic factors and also the source of contaminants can impact the distribution pertaining to mangrove species, except mangrove zonation. Threats pertaining to mangrove ecosystem as well as the intrinsic values of this forest have also been described as in how such factors could impact the seedling development, mangrove growth and distribution. This research has also shown that a Phyto-technology application as well as mechanism could also remediate heavy metals contaminants via water, atmosphere and soil. Thus, it is also crucial to study the kinds of accumulated heavy metals for each zone like open zone via the group of true mangroves (*Avicennia* sp., *Rhizophora* sp. and *Sonneratia* sp.). Due to the location in coastline areas, for healthy mangrove ecosystem, open zone is regarded to be the first strata to become bio-indicator as well as rating tools. The mangrove plants' capacity to take up heavy metals varies; it is crucial for this research study to identify suitable species as Phyto-indicator and also Phyto-remediator with regards to mangrove conservation. Certain heavy metals form a part of plants nutrient, and because of the overload amount, it could lead to plants' growth. Thus, plants require to volatise or remediate those amounts via air, sediment and water. Yet, it is crucial to study the Phyto-remediation process to gain an understanding the mechanism of how the plants release or sustain heavy metals concentration and also study the relationship that exists amongst the different types of species, sediments, plants tissues and localities and also the effect towards landscape ecology.

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Chapter 2

ROLE OF ABSCISIC ACID IN PLANT DEVELOPMENT AND SIGNALING: AN OVERVIEW

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ABSTRACT

Abiotic stress is considered as severe environmental stress that reduces the growth and yield of every crop everywhere. Many hormones were involved in plant defense against all forms of stresses. Abscisic acid (ABA), judged as the major phytohormone, was closely linked to plant defense toward many stresses such as thermal stress, heavy metal stress, low temperature, drought, high salinity and radiation stress. At the molecular level, ABA changes the expression level of many ABA-responsive genes to ensure the control of several developmental operations including seed germination/dormancy, fruit ripening and senescence as well as closure of stomata. In addition, ABA coordinates with other phytohormones to maintain plant survival under unfavorable conditions. This chapter highlights the last outcomes about ABA biosynthesis, ABA signaling pathways and its implication in plant development and response to environmental stresses.

Keywords: ABA, ABA receptors, phytohormones, seed development, signaling pathways, stomatal closure, stress tolerance

INTRODUCTION

Plant growth and development as well as other physiological processes are always stimulated by chemical messengers synthesized by plants known as phytohormones. These compounds are involved in diverse physiological and biochemical processes and act at tiny concentrations. Moreover, phytohormones control plant response to different biotic and abiotic stresses to ensure plant adaptation to environmental conditions. Some phytohormones such as Jasmonic Acid (JA); Salicylic Acid (SA); Brassinosteroids (BR); Auxin and their precursors and synthesized analogs control those responses, yet, the master hormone that coordinates plant response to abiotic stress is the Abscissic Acid (ABA) or "stress hormone" (Zhang, 2014). Many reports described the biological effect of ABA on plants especially in angiosperms (Hubbard et al., 2010). ABA biosynthesis occurs in photosynthetic organisms from carotenoid precursors (Seo et al., 2002). It is also synthetized by an alternative, direct pathway in fungi (Takino et al., 2019), but the role of this hormone in fungi remains unclear as it is not essential for growth and may enhance pathogenicity (Spence et al., 2015). In 1963, ABA was discovered in cotton fruits. Its concentration was elevated in abscising fruits (Ohkuma et al., 1963). Later, ABA was discovered in water-stressed leaves (Wright and Hiron, 1969) and to regulate atmospheric gas control between plants and the environment (Ruth and Mansfield, 1970), especially in drought stress to minimize water loss. Based on these findings, a great number of researches showed the importance of this phytohormone in root elongation and shoot and leaf abscission (Vishwakarma et al., 2017; Zhao et al., 2016); stomatal development (Jalakas et al., 2018; Chater et al., 2014); desiccation tolerance (Yoshida et al., 2010); growth and development control (Sharp et al., 2000). Furthermore, ABA controls different growing processes in plants and in the response to abiotic stresses including drought (Yao et al., 2018), cold (Kashiwakura et al., 2016), salinity (Jeong et al., 2018), and heavy metals (Chmielowska-Bak et al., 2014; Mittler and Blumwald, 2015; Chen et al., 2017; Hauser et al., 2017; Chen et al., 2019; Zhang et al., 2019; Zhao et al., 2020). Further, ABA controls many functions at cellular level like enzyme production (enzymes necessary for cell protection from dehydration (Li et al., 2014), thermal stress and regulating other processes like transfer of water (Parent et al., 2009), tissue hydraulic conductivity (Parent et al., 2009) and iron metabolism (Vishwakarma, et al., 2017). Notwithstanding, ABA signaling in angiosperms, especially in *Arabidopsis thaliana*, is well investigated (de Geiger et al., 2011; Hausser et al., 2011). ABA is thought to play a crucial role in Roots/Shoots communication under water and salt stress conditions and interaction with some other plant derived signals, but it also interacts with other plant signals concerned with organ-to-organ communication. The biosynthesis, catabolism, transport, signal perception and transduction, downstream response, and modulation of ABA have been extensively investigated in angiosperms, in particular in *Arabidopsis thaliana* (Hauser et al., 2011; Cai et al., 2017; Hauser et al., 2017; Chen et al., 2020).

The current literature on the ABA biosynthesis, action and its role in plant tolerance in some abiotic stress as well as the crosstalk between ABA and other phytohormones are studied and discussed.

ABA Biosynthesis in Plants

ABA biosynthesis occurs *(de novo)* during dehydration process while its degradation takes place in rehydration that follows drying (Roychoudhury et al., 2013). ABA biosynthesis carried out in plant roots and terminal buds at the top of plant. Endogen ABA level is stimulated in plant system due to various ecological stress signals such as mineral deprivation (Xiong and Zhu, 2003), iron metabolism, cold stress and water movement through the plant (Assmann, 2003; Parent et al., 2009). The revealed stresses stimulate several genes that encode for enzymes which forms ABA from β-carotene (Roychoudhury and Basu, 2012). Generally, ABA is implicated in controlling stomata movement which is considered as the most important role of this hormone at organ level (Assmann, 2003; Christmann et al., 2007). This role is crucial for ensuring tissue hydraulic conductivity and root/shoot growth (Parent et al., 2009). In addition, it is thought that ABA acts as a master regulator of communication between roots and shoot during stress related to water and salt as well as organ-to-organ communication. Moreover, Abscisic acid is also implicated in multiple cellular processes such as development of seed, vegetative growth, inhibition of seed germination, development and germination of seeds (Xiong and Zhu, 2003), controlling the production of enzymes required for cell protection from dehydration (Li et al., 2014), Researchers have shown that ABA, a small-scale molecule, is a terpenoids (isoprenoids). This hormone is stable under high temperatures and is able to be dissolved in boiling water without undergoing degradation (Zhang, 2014). Moreover, ABA is stable under a wide pH range, but it could be transformed into g-lactone in strictly acidic environment such as formic acid–hydrochloric acid (Mallaby and Ryback, 1972).

ABA Anabolism

Several enzymes are implicated in ABA biosynthesis which utilizes β-carotene to synthesize ABA (Nambara and Marion-Poll 2005; Tuteja, 2007). The majority of the genes involved in ABA *de novo*-biosynthetic pathways have been identified (Table 1) and holed in plastids and cytosol. Initiated/stimulated by abiotic stress, ABA biosynthesis starting from the plastidic precursor isopentenyl diphosphate (IPP), generated from glyceraldehyde 3-phosphate and pyruvate which produces phytoene and lycopene and other intermediate (Dong et al., 2015; Nambara and Marion-Poll, 2005) to finally produce the oxygenated carotenoid known as Zeaxanthin. *AtABA1* (encodes for Zeaxanthin epoxidase) catalyzes the epoxidation of zeaxanthin via antheraxanthin to produce all-trans-violaxanthin, a step catalyzed by zeaxanthin-epoxidase (ZEP) (Nambara and Marion-Poll, 2005). *ZEP* gene has been identified in various plant species. It is present in every plant part but is highly associated with basal expression in leaves (Xiong et al., 2002). The study shows that, *ZEP* gene controls ABA biosynthesis level in different plant portions; in different developmental stages and in different plant species (Xiong et al., 2002a). *AtABA4* is involved in the conversion of violaxanthin to neoxanthin (North et al., 2007). The cleavage process from cis-isomers of violaxanthin and neoxanthin to xanthoxin (a C15 compound) is carried out by nine-cis-epoxy-carotenoid dioxygenase (NCED) enzymes. This step is the rate limiting process during *de novo* ABA biosynthesis in plants. In *Arabidopsis thaliana*, nine *NCED* genes were identified but only five (*AtNCED 2.3.5.6* and *9*) are well studied. All detected enzymes are localized in the chloroplast and exhibit different binding activities of the thylakoid membrane; *AtNCED2/3* and *6* are located in both stroma and thylakoid membrane bound compartments. *AtNCED5* is exclusively bound to thylakoids, while *AtNCED9* is found soluble in stroma. *AtNCED2* and *5* are the main transcripts in flowers (Tan et al., 2003). In *Arabidopsis thaliana*, *NCED3* gene is a dominant contributor to ABA biosynthesis under water deficit, whereas other *NCEDs* and the other enzymes implicated in the ABA synthesis pathway play a relatively limited role (Tan et al., 2003; Endo et al., 2008; Seo et al., 2000). Recently, it has been demonstrated that *NCED3* gene was strongly induced by sulfate (Malcheska et al., 2017). This component is a potential chemical signal of drought which increases ABA level and promotes stomatal closure (Malcheska et al., 2017). The expression of *NCED3* in leaves is regulated by *CLE25* (Clavata3/ESR-Related 25), a root-derived peptide, rapidly induced in plants suffering from drought stresses. *CLE25* is transported from root to leaves and interacts with *BAM1* (Barely Any Meristem 1) and *BAM3*, receptor-like protein kinases (RLKs). This interaction induces

NCED3 expression and thus, an increase in ABA level in cells (Takahashi et al., 2018). The *cle25* and *bam1/3* mutants were more sensitive to drought stress compared with wild type plants and showed low ABA level. *BAM1/3* function in leaves rather than roots under drought stress (Takahashi et al., 2018). Moreover, *NCED3* genes are also induced fast when leaf turgor decreases (Sussmilch et al., 2017); whereas *NCED3* and *NCED5* are rapidly induced in cold and high salt environments (Perea-Resa et al., 2016). All the steps of the de novo biosynthetic pathway except the last two steps occur in plastids. Xanthoxin is transported to the cytosol via an unknown mechanism to achieve the last two steps. The conversion of xanthoxin to abscisic aldehyde is catalyzed by an alcohol dehydrogenase known as *AtABA2* which belongs to the SDR family (Short-Chain Dehydrogenase/Reductase and Related Enzymes) (Cheng et al., 2002; Gonzalez-Guzman et al., 2002). Loss of function of *AtABA2* in *Arabidopsis* suggests that *AtABA2* is encoded by a single gene in *Arabidopsis* genome (Chen et al., 2002). The final step, the oxidation of abscisic aldehyde to ABA, is catalyzed by abscisic aldehyde oxidase AAO3 (Seo et al., 2004). ABA biosynthesis steps in *Arabidopsis* are summarized in Figure 1.

A second ABA synthesis pathway is to produce ABA by the hydrolysis of the stored ABA glucosyl esters (ABA-GE). The production of ABA-GE is controlled by ABA glucosyl-transferases (ABA-GTs) via a direct glycosylation of the carboxyl group (Liu et al., 2015). In *Arabidopsis*, this pathway is a one-step procedure controlled by β-glucosidases (*AtBG1* and *AtBG2*), localized in endoplasmic reticulum and vacuole, respectively (Xu et al., 2012). *AtBG1* and *AtBG2* produce active ABA form by hydrolyzing ABA-GE. As consequence, the intracellular ABA contents in cells increases rapidly (Xu et al., 2012). In strawberry fruit, two β-glucosidases FaBG3 and FaBG1 (Li et al., 2013; Zhang et al., 2014) were identified. These proteins regulated the endogenous ABA levels. Moreover, down-regulation of these genes decreases ABA endogen levels and inhibits fruit ripening (Li et al., 2013; Zhang et al., 2014). It has been shown that ABA synthesized under the control of the two enzymes presents various physiological responses as the *atbg1* loss of- function mutant exhibits a severe ABA-deficient phenotype whereas the *atbg2* mutant shows a mild phenotype.

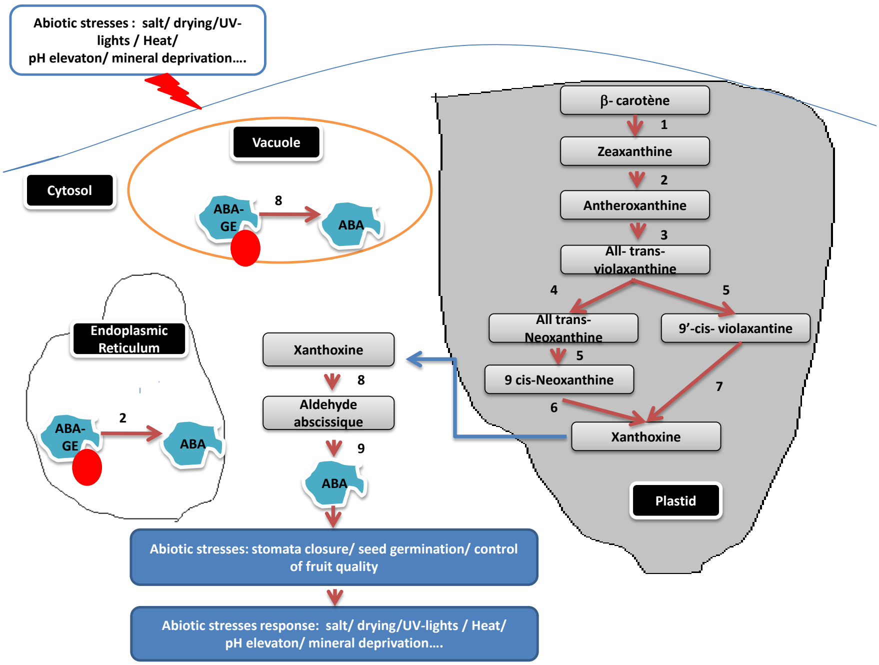

Figure 1. A simplified schematic presentation of the ABA biosynthesis pathway in *Arabidopsis* cells and implicated genes. ABA biosynthesis occurs in plastids then the last 2 reactions occur in the cytosol. Enzymes involved in ABA biosynthesis are represented in order with numbers: 1: β-carotene hydroxylase, 2: zeaxanthine epoxydase AtABA1, 3: Zeaxanthinepoxidase ZEP, 4: AtABA4, 5: isomerase, 6 and 7: 9-cis-epoxycarotenoid dioxygenases: NCEDs, 8: xanthoxine dehydrogenase AtABA2 (SDR family), 9: abscissic aldehyde oxidase AAO3.

Although the hydroxylation pathway has been extensively explored, the conjugation pathway is less clear. Recently, it has been reported that an increase in ABA level was observed due to a mutation in *UGT71C5* and down-expression of *UGT71C5* genes. Moreover, overexpression of *UGT71C5* gene resulted also in reduced level of ABA (Liu et al., 2015). At the same time, ABA transport across the plasma membrane via ATP-binding cassette (ABC) is also an important pathway to control cellular ABA homeostasis (Xu et al., 2013).

Table 1. ABA synthetic and catabolic enzymes in Arabidopsis

Enzyme	Reaction	Localization	Gene expression	Reference
Zeaxanthin epoxidase (At ZEP)	synthesize the violaxanthin	Chloroplast	Induced by stress conditions	Xiong et al. (2002)
AtNCEDs	Cleavage of the substrates violaxanthin and neoxanthin to xanthoxin		Induced by stress conditions	Tan et al. (2003)
AtABA2	Oxidation of xanthoxin	Cytosol	Induced by sugar	Gonzalez-Guzman et al. (2002)
AtABA3	Sulfurylation of dioxo form of Moco to mono-oxo form		Induced by stress conditions	Xiong et al. (2001)
AtABA4	Conversion of violaxanthin to neoxanthin	Chloroplast	Induced by stress conditions	North et al. (2007)
AtAAO3	Oxidation of abscisic aldehyde		Induced by stress conditions	Seo et al. (2000, 2004) Seo and Koshiba (2011)
AtBG1	Hydrolysis of ABA-GE to ABA	Endoplasmic reticulum	Induced by stress conditions	Lee et al. (2006)
AtBG2	Hydrolysis of ABA-GE to ABA	Vacuole	Induced by stress conditions	Xu et al. (2012)
AtCYP707A (1,2,3 and 4)	ABA C-80 position hydroxylation	?	Induced by high-humidity	Saito et al. (2004)
ABA UDP-glucosyltransferases (UGTs),	Produces ABA-GE.	cytosol	?	Liu et al. (2015) Dong et al. (2015)

ABA Catabolism

ABA degradation is far simpler comparing with its biosynthesis. The catabolism of ABA is ensured through two different pathways. It could be hydroxylated by 8'-hydroxylase (*CYP707A*) gene family (in *Arabidopsis*, *AtCYP707A1, 2, 3* and *4* are identified; Saito et al., 2004). Hydroxylation occurs at three different methyl groups (C-70, C-80 and C-90), Hydroxylated ABA is isomerized to phaseic acid (PA), then catalyzed to dihydrophaseic acid (DPA). PA and DPA are the major ABA catabolites that show weak and no bioactivity, respectively (Eggels et al., 2018). ABA degradation could also occur via conjugation of ABA by uridine diphosphate glucosyl-transferase (UGT) to form ABA-GE, a physiologically inactive form stored in the vacuole (Zeevaart, 1983), which contributes to the decrease in endogen ABA levels (Nambara and Marion-Poll, 2005; Xu et al., 2012; 2013).

ABA homeostasis maintained through a balance between the production, catabolism and transport, rather than simply by the biosynthesis. In fact, it has been shown in peanuts that genes involved in ABA synthesis (such as *AhAAO2*, *AhBG12*, *AhBG24*, *AhZEP*, *AhNCED1* and *AhABA3*), transport (*AhABCG22.1* and *AhABCG22.2*) and catabolism (*AhCYP707A3* and *AhUGT71K1*) were up-regulated after drought stress exposure with a more pronounced induction of biosynthetic gene (*AhNCED1*) compared to the catabolic genes (*AhCYP707A3* and *AhUGT71K1*) which could justify the pronounced accumulation of ABA (Long et al., 2019).

Recently, *HAT1* and *HAT3* belonging to class II HD-ZIP transcription factors were identified as new regulators of ABA homeostasis. In fact, overexpressing of *HAT1* causes an ABA-insensitive phenotype as a result plants become less tolerant to dehydration. Moreover, *Hat1Hat3* double mutants are more tolerant to drought stress compared to wild type plants. Chromatin immunoprecipitation showed that *HAT1* binds to the *NCED3* promoter region and represses its expression. This suggests that *HAT1* and *HAT3* TFs negatively control ABA homeostasis by inhibiting the biosynthetic pathway (Tan et al., 2018). Besides, other TFs such as

WRKY57 (WRKY DNA-binding protein 57), *BDG1* (9-cis epoxycarotenoid dioxygenase defective 1) and *ANAC2* (*Arabidopsis* NAC domain containing protein 2) are implicated in *NCED3* expression modulation in *Arabidopsis* which allows an improved plant tolerance to drying a heat stresses (Frey et al., 2012; Xu et al., 2012; Jensen et al., 2013) proving main role of *NCEDs* gene family in plant maturation under multiple stress conditions.

ABA Transporters

ABA accumulated in xylem (Jiang and Hartung, 2008) and in root tissues in drying conditions is accompanied with a decrease in leaf stomatal conductance (Taiz and Zeiger, 2006). ABA transport is an essential element in determining the intracellular concentrations of the phytohormone at the site of action, and thus, it is a fundamental process in physiological responses (Seo and Koshiba, 2011). ABA could be produced in most tissues such as leaves and roots with a higher expression of ABA production- related genes in vascular parenchyma cells. Therefore, ABA is transported from xylem (production site) to the guard cells to control stomatal closing during drying conditions. ABA formed in vegetative tissues is transported through the vascular system to the seeds. ABA transported from roots to the apoplastic space of leaf, known as long distance transport as ABA (pKa = 4.7), is able to penetrate lipid bilayers and infiltrates into the leaf cytoplasm by simple diffusion (Wilkinson and Davies, 2002; Seo and Koshiba, 2011). It is interesting to mention that in stressed conditions, pH increases in cells which causes an unfavorable condition for ABA to penetrate by simple diffusion to cells and it is transported from the apoplast to the cytoplasm by specific ABA transporter. Indeed, three specific ABA transporters have been identified in *Arabidopsis* (Kang et al., 2010; Kanno et al., 2012; Kuromori et al., 2010). *AtABCG25* contains an ATP dependent ABA-efflux activity. This plasma membrane transporter is highly expressed in vascular tissues of roots and shoots but not in guard cells. Thus, *AtABCG25* acts as an exporter that transports ABA into the apoplastic area around the guard cells. The *atabcg25* mutants showed hypersensitive phenotypes in different developmental stages (Kuromori et al., 2010). *AtABCG40/AtPDR12* transporter is located at the plasma membrane of guard cells and plays the role of an ABA importer. This transporter is responsible for ABA uptake (Kang et al., 2010). These findings showed that there is a synergy between ABCG25 and ABCG40 to modulate the ABA content in guard cells which play an essential role in ABA homoeostasis. The third receptor is the low-affinity nitrate transporter; *AtNRT1.2* implicated in seed germination and post-germination growth, and enhanced sensitivity to dehydration stress (Kanno et al., 2012). The inactive ABA-GE form is also implicated in long distance transport (Wilkinson and Davies, 2002), but its ability to diffuse across cellular membranes is limited (Jiang and Hartung, 2008).

ROLE OF ABA IN PLANT GROWTH AND MATURATION

Seed Germination and Dormancy

ABA regulates key events during seed formation, such as the deposition of storage reserves, prevention of precocious germination, acquisition of desiccation tolerance, and induction of dormancy. Its regulatory role is achieved in part by cross-talk with other hormones and their associated signaling networks, via mechanisms that are largely unknown (Kermode, 2005). Embryonic ABA plays a central role in induction and maintenance of seed dormancy and also inhibits the transition from embryonic to germination growth. Therefore, the ABA metabolism must be highly regulated at both temporal and spatial levels during the phase of desiccation tolerance (Rodriguez-Gacio et al., 2009). It has been reported that ABA biosynthesis, signaling, and degradation genes play important functions in induction, stabilization, and release of dormancy. The mutation or over-expression of key ABA-related genes results in germination-associated phenotypes (Ma et al., 2009; Park et al., 2009). ABA is *de novo* synthesized in embryo during embryo development, as well as accumulates during seed maturation, facilitates late seed maturation processes, synthesis of storage proteins to prevent seed abortion, induces primary dormancy and allows successful germination as well as a successive seedling enterprise (Kermode, 2005). Consequently, *de novo* synthesis of active ABA plays a more important role in seed development and later germination.

ABA functions via a complex signaling network and initiates the cell response through activating downstream signaling genes to induce the response according to physiological effects (Shinozaki and Yamaguchi-Shinozaki, 2007). In seed development and maturation, the role of ABA has been recognized by analyzing the mutants that were insensitive to ABA. The ABA insensitive mutants fail to promote ABA response due to the defects in the ABA signaling pathway, which steadily affects seed maturation and several other important traits of the dormant seed (Finkelstein et al., 2008). The identification of PYR/PYL/RCAR family (*Pyrabactin Resistance 1/PYR1-like/Regulatory Components of ABA Receptors*) proteins verified that ABA receptor PYLs are essential ABA signaling components and predominantly function in seed (Miao et al., 2018). In *Arabidopsis*, fourteen members of the PYR/PYL/RCAR protein family were documented that have vital roles in seed, such as *pyr1/prl1/prl2/prl4* quadruple and *pyl* duodecuple mutants show reduced seed dormancy and insensitivity to ABA (Ma et al., 2009; Zhao et al., 2018). In the presence of ABA, PYR/PYL/RCAR protein binds with both the ABA and the PP2C proteins to stop the phosphatase activity of the Serine/threonine protein phosphatase 2Cs (PP2Cs), which releases and enables the SNF1-related protein kinase 2 (SnRK2) function. It is showed that all members of PYLs protein family from *Arabidopsis* can interact with PP2C family members and function in ABA mediating response (Zhao et al., 2013). Totally, three *SnRK2s* (*SnRK2.2*, *SnRK2.3*, and *SnRK2.6*) were found as positive regulators of the ABA signaling network and involved in various seed developmental processes such as the de-greening process, accumulation of seed storage products, seed maturation, desiccation-tolerant, and germination in *Arabidopsis* (Finkelstein et al., 2008).

Stomatal Closure

Drought stress causes an increase in the level of the plant hormone abscisic acid (ABA), which initiates a signaling cascade to close stomata and reduce water loss. Recent studies have revealed that guard cells control cytosolic ABA concentration through the concerted actions of biosynthesis, catabolism as well as transport across membranes (Munemasa et al., 2015). In response to drought, plants synthesize ABA that induces stomatal closure, thereby reducing transpirational water loss. It has been shown that ABA is *de-novo* synthesized from C_{40} carotenoids and has also been proposed to be rapidly released from its inactive conjugate, ABA glucose ester (ABA-GE) (Finkelstein, 2013). Through complex signaling mechanisms ABA generates efflux of anions and potassium via guard cell plasma membrane ion channels, resulting in decrease of turgor pressure in guard cells and stomatal closure. Recent *in vitro* and *in vivo* studies have revealed the molecular mechanisms of how ABA signaling is initiated and transduced into the turgor regulation response in guard cells. The sensing of ABA or other compounds and the final response of stomatal closure follows a common signaling pathway involving receptors, protein kinases, secondary messengers, ion channels, ion efflux, and turgor loss in guard cells. Amongst kinases, OPEN STOMATA 1 (*OST1*) is a primary activating factor NADPH oxidase as it raises the Reactive Oxygen species (ROS) levels of guard cells. During ABA-induced stomatal closure, an increase in OST1 kinase was followed by the activation of Respiratory Burst Oxidase Homologs (RBOHD and RBOHF), and increases in ROS/NO/Ca^{2+} levels. In turn, Ca^{2+} dependent CDPKs activated slow anion channel 1 (*SLAC1*), S-type anion channel 3 (*SLAH3*) and K^+ out channels to promote ion efflux from guard cells and forced stomata to close (Figure 2) (Bharath et al., 2021). Moreover, its action through ROS/NO/Ca^{2+}, *OST1* could directly modulate ion channels to cause stomatal closure. In a recent study, the events involving *OST1/SnRK2s* were studied in real-time using Fluorescence Resonance Energy Transfer (FRET) sensors (Zhang et al., 2020). These experiments provided a visual evidence of the interaction of *OST1* with signaling components of ABA and elevated CO_2. It is obvious that *OST1* is an important point of convergence of signals from abiotic and biotic factors.

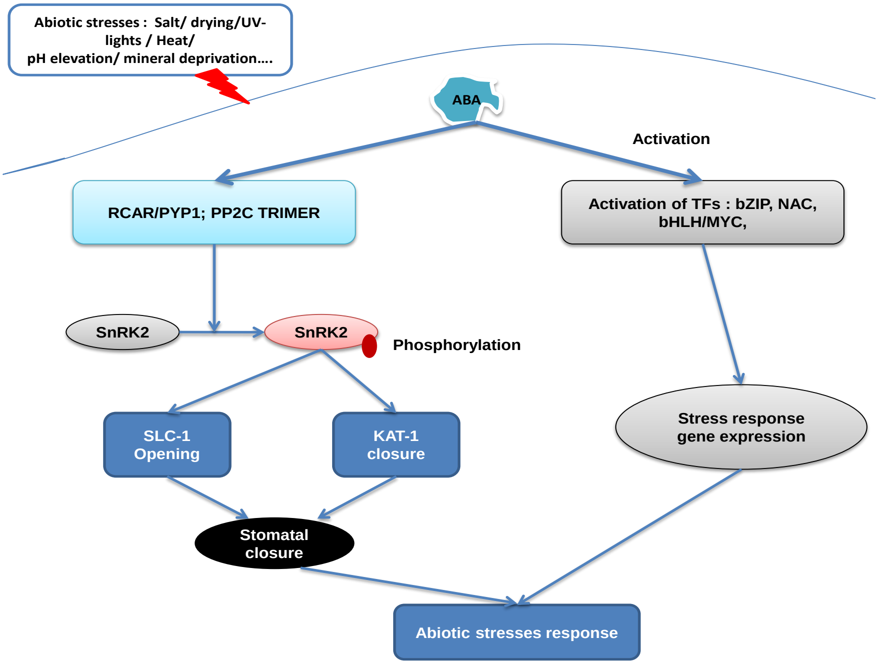

Figure 2. ABA mediated abiotic stress signaling in plants. After stress perception, endogen ABA stimulates many Transcription factors such as bHLH, and NAC type which stimulates the expression of genes implicated in stress response. In another hand, ABA modulates the activity of PP2C proteins which leads to the activation of SnRK2 type protein kinases by phosphorylation. Activated SnRK2 proteins stimulates SLC1 opening and KAT-1 closure ensuring stomatal closure and thus an adequate response to abiotic stresses.

Fruit Ripening

Fruit ripening process is a complex network of endogenous and exogenous signals (Gray, 2004). These signals produce in fruits several physiological and morphological changes such as fruit softening (Rosli et al., 2004; Figueroa et al., 2008, 2010; Ramos et al., 2018; Morales-Quintana and Ramos 2019; Moya-Leon et al. 2019) which was explained as a cell wall breakdown (Ramos et al. 2018; Morales-Quintana and Ramos 2019; Moya-Leon et al. 2019).

ABA is also implicated, along with Ethylen (ET), in controlling fruit ripening processes (Jessica et al., 2020; Jia et al., 2016; Zhang et al., 2019a). ABA controls fruit ripening / senescence in both ethylene-dependent and non-ethylene-dependent ways. In fact, it was reported that endogen ABA level peaks earlier than ET in many plants such as banana (Lohani et al., 2004), tomato (Zhang et al., 2009) and mango (Zaharah et al., 2013). Moreover, application of ABA on tomato fruits promotes ET biosynthesis by activating the expression of ethylene oxidase *ACO1* and ethylene reductase *ACS2* genes (Zhang et al., 2009). In tomato, this application also accelerates fruit ripening by enhancing accumulations of total phenolic and flavonoid contents after stimulation of phenylalanine ammonia-lyase (PAL), peroxidase (POD), polyphenol oxidase (PPO), catalase (CAT), and ascorbate peroxidase (APX) activities during tomato ripening (Tao et al., 2020). Furthermore, inhibition of *SlUGT75C1* gene expression, a key regulator of ABA synthesis, stimulates ABA biosynthesis production in fruits as well as the production of ET which accelerates fruit ripening (Sun et al., 2012).

In the other hand, several works have suggested that ABA hormone is implicated in ripening process especially in non-climacteric fruit, particularly strawberries fruits, a model of non-climacteric fruit ripening (Kim et al., 2019; Gu et al., 2019; Jia et al., 2020). Exogenous ABA application stimulates strawberry fruit ripening (Kadomura-Ishikawa et al., 2015; Gu et al., 2019), but the application of nordihydroguaiaretic acid (NDGA), an ABA biosynthesis inhibitor, retarded strawberry fruit ripening (Li et al., 2015). Moreover, in strawberries fruits, ABA and ABA-GE contents increased in both in receptacle tissue and in achenes during ripening (Gu et al., 2019; Figueroa et al., 2020). It has been proved that, ABA-GE contents increases dramatically during the late developmental stage (Figueroa et al., 2020). Moreover, the transcript level of β-glucosidases displaying activities towards ABA-GE increases during strawberry fruit ripening (Figueroa et al., 2020). Finally, recent work described the modifications in the primary cell wall in strawberries under

ABA treatment. Cell wall modifications are correlated with xyloglucan-cellulose loss as well as pectin solubilization under the control of ABA (Castro et al., 2021). In watermelon, the examination of ABA level showed that this hormone has the highest concentration in seed 14 days after flowering (DAF) but started the decrease until 35 DAF. The pulp increased also in ABA levels until 21 DAF considered as the stage of cell expansion, but decreased to 35 DAF (Kojima et al., 2020). These findings show that ABA promotes watermelon fruits growth (Dou et al., 2017; Kojima et al., 2020) and stimulates the pulp red coloring (Kojima et al., 2020).

ABA controls the growth and development, quality formation, coloration and softening, ripening and senescence processes in non-climacteric fruit and vegetable such as grapes, citrus, watermelon, strawberry, and cucumber, and plays a central role in the ripening of these fruits (Zaharah et al., 2013; Figueroa et al., 2020). It is relevant to note that ABA could have a negative effect on fruit ripening. In fact, Soto et al. (2013) proved that ABA application down regulates the expression of some genes that controls ET production and cell wall softening in peach fruit, which retards fruit ripening.

In Citrus Fruit, application of 1-naphthaleneacetic acid (known as NAA) and ABA hormones accelerated the change of fruit colors from green to orange compared with treatment with gibberellic acid (GA) and/or Prohydrojasmon (PDJ) in the fruit ripening stage. Moreover, those treatments rapidly decreased chlorophylls and lutein contents but the carotenoid contents (β-cryptoxanthin, all-trans-violaxanthin, and 9-cis-violaxanthin) increased significantly (Ma et al., 2021). Furthermore, the expression of genes implicated in controlling chlorophyll and carotenoid was up-regulated in ABA and NAA treatments comparing with control plants.

ABA and Abiotic Stress Signaling

ABA acts as a master regulator of plant tolerance to such stresses (Sah et al., 2016). The mechanisms by which plants respond to stress include both ABA-dependent and ABA-independent processes. Various transcription factors such as DREB2A/2B, AREB1, RD22BP1 and MYC/MYB are known to regulate the ABA-responsive gene expression through interacting with their corresponding cis-acting elements such as DRE/CRT, ABRE and MYCRS/MYBRS, respectively (Figure 2). Understanding these mechanisms is important to improve stress tolerance in crops plants (Tuteja, 2007).

ABA and Osmotic Stress

Drought and high salinity generate osmotic stress in plant cells. Endogenous ABA levels are elevated in response to osmotic stress, which in turn coordinates the plant's response to reduced water availability. The role of ABA in drought and salt stress is twofold: water balance and cellular dehydration tolerance. Water balance is achieved through guard cell regulation and the latter role by induction of genes that encode dehydration tolerance proteins in nearly all cells. ABA accumulation is induced by osmotic stress and this is as a result of the activation of ABA biosynthesis as well as the inhibition of ABA degradation (Zhu, 2002). Thus, ABA-mediated adaptive stress responses of plants to environmental stimuli occur via ABA-responsive gene expression and regulation of stomatal pore size. ABA-responsive gene expression involves various transcription factors, ABA receptors, secondary messengers, protein kinase/phosphatase cascades, and chromatin remodeling factors (Fujita et al., 2011). Both drought stress and salinity stress up-regulate osmotic stress responsive genes that are ABA-inducible. Most of the high-salinity-induced genes are also induced by drought, suggesting that there is an overlap between salt and drought stress tolerance mechanisms (Roychoudhury et al., 2013). A large number of transcription factors are induced by multiple stress conditions. AREB1/ABF2, AREB2/ABF4, ABF3, and MYB41 are some of the main transcription factors that are induced by both salt and drought in vegetative tissues (Fujita et al., 2011). Studies suggest that osmotic stress imposed by high salt or drought is transmitted through at least two pathways; one is ABA-dependent and the other ABA-independent. Cold exerts its effects on gene expression largely through an ABA-independent pathway (Shinozaki and Yamaguchi-Shinozaki, 2000). ABA induced expression often relies on the presence of cis-acting element called ABRE element (ABA-responsive element) (Shinozaki and Yamaguchi-Shinozaki, 2000; Uno et al., 2000). Genetic analysis indicates that there is no clear line of demarcation between ABA-dependent and ABA-independent pathways and the components involved may often cross talk or even converge in the signaling pathway. Calcium, which serves as a second messenger for various stresses, represents a strong candidate, which can mediate such cross talks. Several studies have demonstrated that ABA, drought, cold and high salt result in rapid increase in calcium levels in plant cells (Xiong et al., 2002; Mahajan and Tuteja, 2005; Chinnusamy et al., 2004). The transcript accumulation of *RD29A* gene is reported to be regulated in both ABA-dependent and ABA-independent manner (Yamaguchi-Shinozaki and Shinozaki, 1993). Proline accumulation in plants can be mediated by both ABA-dependent and ABA-independent signaling pathways (Mahajan and Tuteja, 2005). The role of calcium in ABA-dependent induction of P5CS gene during salinity stress has been reported by Kinight et al. (1997). It is known that the expression of *RD29A*, *RD22*, *COR15A*, *COR47* and *P5CS* genes was reduced in the *los5* mutant (Xiong et al., 2001). The signaling mechanism behind the activation of these genes are not well known, but the transcriptional activation of few stresses induced genes represented by *RD29A* is known to some extent (Xiong et al., 2002). It is also suggested that phospholipase D (PLD) along with ABA and calcium act as a negative regulator of proline biosynthesis in *Arabidopsis* (Thiery et al., 2004).

ABA and Heavy Metal Stress

Heavy metals (such as cadmium, aluminum, copper, lead, arsenic…) are considered as the main environmental pollutants of our environments. This abiotic stress restrains universal crop productivity and food security, and their accumulation in water and soil are increasing widely (Bowell et al., 2014; Zhu et al., 2014; Zhao et al., 2015). In plants, toxic metals concentrate in consumable parts of plants and also affect growth and senescence. It has been proved that Heavy metals enhance ABA biosynthesis in plants and alleviate heavy metal stress in plants (Fediuc et al., 2005).

Cadmium Stress

The divalent heavy metal cation, cadmium (Cd), is one of the extreme toxic heavy metals which come generally from many sources such as fertilization in fields with sewage sludge and phosphate which contaminates generally water, air and soil. Cadmium is not essential for plant development and can cause an oxidative stress when present in cells (Gratão et al., 2015). This cation easily penetrates to plants and causes a growth reduction and some other negative effects like photosynthesis perturbation (Siedlecka and Baszynski, 1993), minimization of chlorophyll level (Larsson et al., 1998) and the inhibition of stomata movements (Zhang, 2014). Augmentation in endogenous ABA in plants was correlated with Cd application in many plants such as oilseed rape (*Brassica napus*), *Malus hupehensis*, rice (*Oryza sativa*), *Sedum alfredii*, potato (*Solanum tuberosum*) and lettuce (*Lactuca sativa*). Those plants showed an up-regulation of genes for ABA biosynthesis (Shi et al., 2019a; Zhang et al., 2019b; Lu et al., 2020a; Tang et al., 2020). In fact, *OsNCED3/4* and *OsNCED5* genes were upregulated in rice after Cd treatment (Tan et al., 2017). Moreover, this rapid ABA production was more significant in Cd tolerant cultivars than the Cd sensitive plants (Hsu and Kao, 2003). In *Arabidopsis*, ABA deficient mutants (*aba-1, aba-3, aba-4, nced3*) having an altered ABA biosynthesis and ABA-insensitive mutants (*abi2-1, abi3-1*), that present an alteration in ABA signalization, accumulates more cadmium and present an enhanced Cd sensitivity (Zhang et al., 2019b). The same result was observed in *bglu10* and *bglu18 Arabidopsis* mutants that represent reduced root cytoplasmic ABA levels (Wang et al., 2018). Many results have shown a specie dependent response to Cd/ABA accumulation. In fact, the increase of endogenous level of ABA biosynthesis can reduce Cd uptake in rice seedlings (Hsu and Kao, 2008) but not in Indian mustard, *A. helleri* and *Solanum photeinocarpum* (Wang et al., 2016). This could be explained by the fact that ABA/Cd interaction involves histological and biochemical alterations or to a different Cd uptake pathway in these species. Iron Regulated Transporter 1 (IRT1) acts as a transporter for Cd uptake from the rhizosphere (Lux et al., 2011). In *Arabidopsis*, *IRT1* expression is firmly regulated by FIT TF (FER-like Deficiency Induced Transcription Factor) and by the Ib subgroup of the *bHLH* (basic helix-loop-helix) transcriptional factors such as *bHLH38*, *bHLH39*, *bHLH100*, and *bHLH101* in *Arabidopsis* (Wang et al., 2013). Interestingly, Cd uptake decreased in *Arabidopsis* plants after application of low concentrations of ABA (0.1~1.0 mM) or after inoculation with ABA-generating bacteria strains. This decreased is justified by the inhibition of *IRT1* transcription which leads also to the alleviation of Cd induced growth inhibition (Fan et al., 2014; Zhang et al., 2019c; Pan et al., 2020). Moreover, other genes were also upregulated after Cd stress such as *ZIP1* (Zinc Regulated Transporter/IRT-like Protein 1) and *ZIP4* (Xu et al., 2018; Pan et al., 2019; Lu et al., 2020b). Besides, *abi-5 Arabidopsis* mutant and *snrk2.2/2.3* double mutants showed an abolished reduction of Cd accumulation after exogenous application of ABA or inoculation by ABA-generating bacteria. The transcription level of *IRT1* was minimized in *snrk2.2/2.3* mutant but enhanced *PP2Cs* mutant *abi1/hab1/abi2* triple mutant lines (ABA insensitive lines). These results prove that *ABI5*, *SnRK2s*, and *PP2Cs* genes are involved in Cd absorption mediated by *IRT1* (Fan et al., 2014; Xu et al., 2018; Pan et al., 2019; Zhang et al., 2019; Lu et al., 2020a). However, *SnRK2.2/2.3* directly phosphorylate *ABI5* and could be inactivated by dephosphorylation of *ABI1/ HAB1/ABI2* (Skubacz et al., 2016). A direct physical interaction between *ABI5* and *MYB49* (a Cd-induced TF) inhibits *ABI5* interaction with *bHLH38* and *bHLH101* leading to *IRT1* expression (Zhang et al., 2019c).

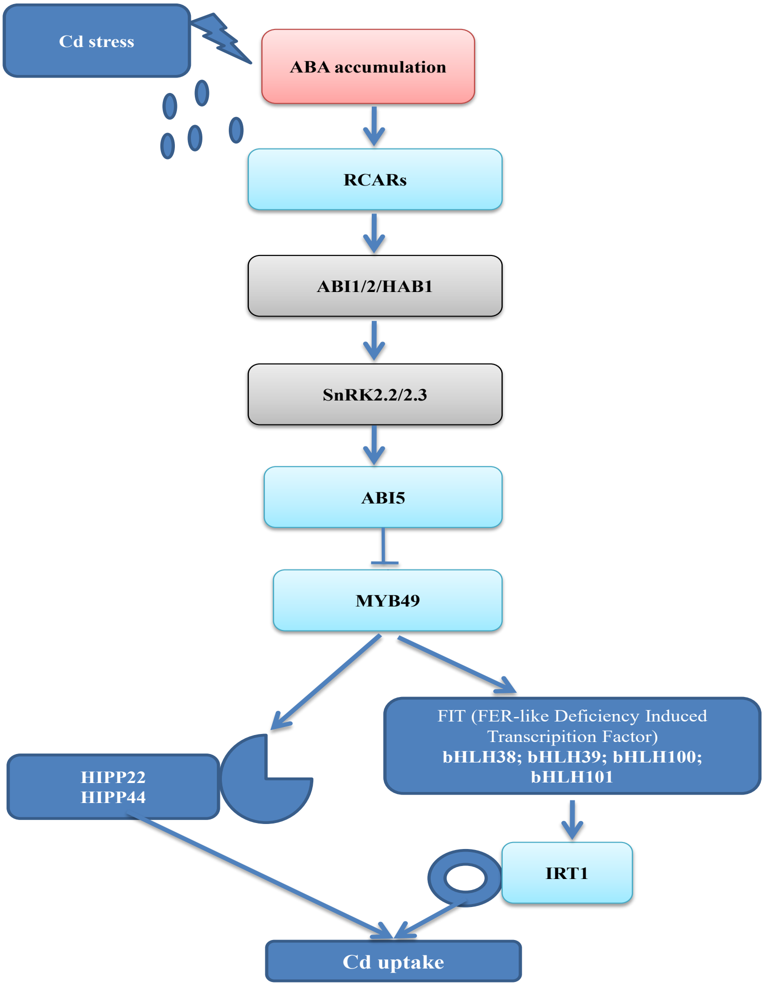

Figure 3. ABA inhibition of Cd^{2+} uptake in *Arabidopsis* plants. MYB49 TF activates IRT1 and HIPP proteins after ABA increase in cells but those proteins are inhibited by ABI5. IRT1, Iron Regulated Transporter 1; HIPP, Heavy metal-associated Isoprenylated Plant Proteins; ABI5, ABA-Insensitive 5.

Thus, *ABI5* is considered as a negative regulator of *IRT1* and Cd uptake. In addition, *MYB49* TF directly stimulates the expression of two members of Heavy metal-associated Isoprenylated Plant Proteins family (HIPPs) HIPP22 and HIPP44 positively implicated in controlling Cd accumulation (Zhang et al., 2019c). This is to reveal that there is a positive correlation between endogenous ABA content and Cd tolerance (Figure 3).

Arsenic, Plomb and Cupper Stresses

It has been reported by many authors that ABA alleviates the metallic stress caused by Arsenic (As) stress (Deng et al., 2020). As stress activates Phosphate Transporters (PHTs, PTs) implicated in arsenate (AsV) uptake (Shin et al., 2004) and Nodulin 26-like Intrinsic membrane Proteins (NIPs) important for arsenite (AsIII) uptake. In *Arabidopsis*, As(V) uptake is negatively regulated by *WRKY6* TFs which represses the expression of *PHT1;1* gene and removes PHT1;1 proteins from the plasma membrane (Castrillo et al., 2013). *WRKY46* expression is induced by ABA (Song et al., 2016). Thus, *WRKY6* knockout caused ABA insensitivity and its overexpression generates ABA-hypersensitive phenotypes in seed germination stage (Huang et al., 2016). Those data demonstrate that *WRKY6* acts as a positive regulator in ABA signaling during As(V) uptake. In As(III) stress, *NIP1;1*, *NIP3;1*, *NIP3;2*, and *NIP7;1* genes control As(III) uptake and accumulation (Deng et al., 2020) but the role of ABA in regulating those genes is still unknown.

The molecular response to Plomb (Pb) stress in plants is still obvious, but it has been demonstrated that the plasma membrane-localized G-type ABC members *AtABCG36* (known as PDR8, implicated in Cd and Pb transport), *AtABCG40* (called also PDR12, implicated in Pb transport) act as positive regulators of Pb stress as they limit Pb accumulation in *Arabidopsis* (Fu et al., 2019; Wang et al., 2019). In Gray poplar, Pb stress stimulates *PcABCG40* gene expression after ABA exposure (Shi et al., 2019b), while in *Arabidopsis* Pb-Sensitive 1 (AtPSE1) protein activates *AtABCG40* and confers Pb tolerance (Fan et al., 2016). Moreover, *AtWRKY13* physically binds to *ABCG36* promoter and positively regulate Pb stress response (Sheng et al., 2019). In addition, an increase in endogenous ABA content was detected in many plants grown under Pb stress such as chickpea (*Cicer arietinum*); pea (*Pisum sativum*) and Gray Poplar (Populus × canescens) (Parys et al., 1998; Atici et al., 2005; Shi et al., 2019b). Thus, more studies are important for explaining ABA involvement in Pb uptake in plants.

Copper (Cu) is crucial for plant development in low quantity but it becomes toxic at elevated concentrations (Berenguer et al., 2008). Cu^{2+} cations generate oxidative stress and stimulate ABA biosynthesis (Choudhary et al., 2010). Moreover, silicon (Si) application alleviates Cd/Cu stress in rice (*Oryza sativa*) (Kim et al., 2014).

These findings present a positive role of ABA in improving the accumulation and the toxicity of Cd/Pb/As and Cu in plants. ABA inhibits heavy metals uptake and alters their root to shoot translocation.

UV-B Stress

As sessile organisms, plants are constantly exposed to sunlight and thus to UV rays (Tossi et al., 2009). UV-b lights are able to enhance reactive oxygen species (ROS) generation in cells which have many negative effects such as biomolecules and cell morphology destruction, membrane permeabilization and inhibition of plant maturation (Banerjee and Roychoudhury, 2016; Tripathi et al., 2016; 2017). It has been demonstrated that ABA enhances stomata closure in plant response to drought and to UV-B stresses (Sangtarash et al., 2009), by inhibiting ET production (Zhang, 2014). In fact, UV-b lights stimulate ET production in cells which enhances plant response to drought stress (Li et al., 2014). In tomato plants, application of low UV-B radiation on the above part of plants causes a remarquable metabolism change. In fact, UV-B causes a decrease in ET and IAA biosynthesis but an increase in SA biosynthesis (Mannucci et al., 2020). In Soybean plants, application of UV-C radiation causes an attenuation of chlorophyll content and inhibition of PSII activity. It was obvious that H_2O_2, malondialdehyde (MDA) contents and O_2^- were markedly increased as well as the activities of antioxidant enzymes (SOD, POD and Cat). It should be noted that ABA application enhanced SOD, CAT and POD activities and ameliorates the flavonoids and chlorophyll contents. It also enhances PSII performance and biomass accumulation.

Moreover, H_2O_2, MDA and O_2^-, contents were decreased demonstrating that ABA alleviates UV-C stress applied on soybean plants by minimizing ROS generation (Yang et al., 2020). In maize leaves, ABA application alleviates UV-B irradiation stress as *vp14* mutants (mutation in *NECD* genes thus plants are unable to synthetize ABA) (Tan et al., 1997). The same result was found in grapevines (Berli et al., 2011). Moreover, UV-B exposure enhances plant response to *hyaloperonospora parasitica* pathogen in *Arabidopsis* (Kunz et al., 2008).

The Crosstalk between ABA and the Other Phytohormones

ABA and JA Crosstalk

ABA and JA have an antagonistic role in controlling plant maturation (Ghorbel et al., 2021), but MYC2 is able to modify ABA-JA crosstalk to make those phytohormones acting synergistically to regulate plant response to environmental stress (Ghorbel et al., 2021). In *Arabidopsis*, JA signaling pathway controls metabolic reprogramming via an ABA receptor protein known as PYLs (Per et al., 2018). After its production, ABA inhibits PP2C proteins by interacting with some PYL/RCAR/ABA receptors to initiate the signaling cascade. When endogen ABA increases in cells, PYL6/RCAR9 complex is linked with *MYC2* TF (Aleman et al., 2016). In addition, PYL6 could interact with JAZ6/8 to enhance the transcriptional activity of *MYC2*. This later activates *VSP2* gene expression, and suppresses *PTL1* and *PTL2* genes expression which leads to the inhibition of root development (Pauwels et al., 2010). Stomatal closure is activated by a small GTPase protein called NOG1-2 in both abiotic and biotic stress conditions (Lee et al., 2017; Lee et al., 2018). The genes down regulated in *nog1-2* and *jaz* mutants are induced in to the presence of increased intracellular concentrations of ABA or drought. This indicates that *JAZ9* and *NOG1-2* are implicated as ABA-responsive genes

(Lee et al., 2018). In another hand, NOG1-2 proteins stimulate ROS accumulation in cells which regulate ABA-mediated stomatal closure. Thus, NOG1-2 proteins mediate ABA / JA crosstalk to control stomatal closure (Lee et al., 2018). In the same way, JAZ proteins degradation is crucial for positive ABA/JA crosstalk via RING E3 ligase KEG. KEG is promoted for self-ubiquitination and subsequent degradation by ABA and it inhibits the COI1-mediated degradation of JAZ12, only under low endogen ABA conditions (Pauwels et al., 2015). It has been recently shown that *ORA47*, an ERF TF gene is up-regulated by JA treatment (Zander et al., 2020). *ORA47* directly binds to JA and ABA biosynthesis genes promoters and increases endogen JA concentration (and ABA also) under wounding conditions (Hickman et al., 2017; Zander et al., 2020).

ABA and GA Crosstalk

In stressed conditions, high ABA levels and low GA levels are detected in cells but normal conditions favorite the reverse situation. Seed dormancy is regulated by an increasing endogen ABA level from embryogenesis to embryo maturation (Karssen et al., 1983) by inhibiting water uptake which causes cell-wall loosening, a key step to start germination (Gimeno-Gilles et al., 2009). This effect was described in many plants such as soybean (Shu et al., 2017). In fact, NaCl negatively regulates GA biosynthesis but positively regulates ABA biogenesis thus it decreases GA/ABA ratio and delays seed germination. Using different soybean cultivars showing different genetic backgrounds, Shu et al. (2017) suggests that an ABA biogenesis inhibitor known as Fluridone (FLUN) could be a novel plant growth regulator that enhances soybean seed germination under salt stress conditions. Besides, transcription levels of ABA and GA biogenesis genes were altered after salt stress application leading to a decrease in GA_1, GA_3, and GA_4 levels but an increase in endogen ABA content. Moreover, ABA induces Late Embryogenesis Abundant (*LEA*) genes and ABSCISIC ACID INSENSITIVE 5 (*ABI5*) transcription factor activation (Finkelstein and Lynch, 2000). ABA indirectly activates *ABRE* elements by activating ABI5 and ABI3 (Park et al., 2011). Moreover, a clear interaction between ABA and GA are noticed to control dormancy and germination. Several studies showed also the regulation of GA and ABA hormones in light- and temperature-mediated seed germination and dormancy. The light-labile transcription factor, *PIL5* controls GA and ABA signaling to inhibit seed germination. In fact, *PIL5* TF controls GA biosynthesis and signaling genes. Moreover, PIL5 inhibits GA biosynthesis genes (*GA3ox1* and *GA3ox2*) expression and activates a GA catabolic gene (*GA2ox2*) indirectly (Gabriele et al., 2010). Besides, it binds to the promoter region of the GA signaling inhibits *GAI* and *RGA* transcription genes (Oh et al., 2007). The expression DELAY OF GERMINATION 1 (*DOG1*) gene acting on downstream of PIL5 induces GA biosynthesis repression and activates *ABI3* and *ABI5* expression (Skubacz and Daszkowska-Golec, 2017). Besides, NUCLEAR FACTOR-Y C (*NF-YC3, NF-YC4,* and *NF-YC9*) physically interact with the DELLA protein RGL2 and interact with ABI5 (Liu et al., 2016) to control seed germination by regulating GA- and ABA-responsive genes in *Arabidopsis*, and regulating germination. In addition, NF-YC9 was shown to interact with ABI5 to regulate ABA signaling (Bi et al., 2017). Furthermore, XERICO protein has a crucial role in modulating ABA endogen level to mediate plant stress response (Zeng et al., 2015). DELLA proteins are regulated by ubiquitin-proteasome system (with involvement of F-box E3 ubiquitin ligase, Skip and Cullin) and by SUMOylation (small ubiquitin-related modifier). In fact, it has been shown that the E3 SUMO ligase in *Arabidopsis* (*AtSIZ1*) negatively control ABA signaling by SUMOylation of ABI5 during seed germination (Liu and Hou, 2018), but AtSIZ1 positively modulate GA signaling by SUMOylating SLY1 proteins (Kim et al., 2015; Liu and Hou, 2018). Thus, SIZ1 could be considered as a potential regulator of GA and ABA signaling by modulating ABI5 and SLY1.

Several TFs have been reported to act as potential regulators between ABA and GA metabolism and signaling. Further, GA represses the expression level of ABA biosynthesis gene, *NCED6*, and increases expression of the GA-deactivating gene, *GA2ox7*, in an ABI4-dependent manner (Shu et al., 2016). In rice, *OsAP2-39*; an *APETALA 2* (AP2)-domain containing transcription factors (ATFs) induces ABA level by directly activating ABA biosynthesis gene *OsNCED1*, whereas it reduces GA level by directly activating GA-inactivating gene *OsEUI* (Elongated Uppermost Internode) (Shu et al., 2018). Further, enhanced ABA level due to activation of *OsNCED1* induces the *OsEU1* expression, which ultimately decreases GA accumulation (Shu et al., 2018). Another study showed that *CHOTTO1*, a double-AP2 domain-containing TF regulates seed germination in *Arabidopsis* through ABA-mediated repression of GA biosynthesis (Yano et al., 2009).

ABA and BR Crosstalk

ABA and BR act oppositely during various developmental stages (seed germination, root elongation...) (Jager et al., 2008). During different developmental stages, such as seed germination, hypocotyl and root elongation, ABA and BR were reported to function antagonistically (Seo et al., 2009; Xue et al., 2009). BR negatively controls ABA-induced stomatal closure at high endogen levels. Some mutants such as *sax1*, *det2*, and *bri1-9*, support the founding that ABA sensitivity is inversely related to endogen BR level or signaling capacity as those BR deficient mutants presented an enhanced ABA-induced stomatal closure (Xue et al., 2009). Recently, it was shown that the most active BR form known as brassinolide (BL), down regulates ABA biosynthesis gene but induces stomatal closure. However, this closure was enhanced by ABA phytohormone (Ha et al., 2018) but stomatal closure induced by ABA was more pronounced comparing with BL. Moreover, BR control of stomatal closure requires Open Stomata 1 (OST1) activity. Thus, ABA and BRs finely control stomatal movement in plants.

Conclusion and Future Prospects

ABA has a wide range of functions from plant development to biotic and abiotic stress signaling and tolerance. The primary functions of ABA in salt, drought, and heavy metal tolerance act via inhibiting seed germination, altering root architecture, and inducing stress-responsive genes as well as gene products that act as osmoprotectants. ABA presents different metabolic pathways located in various sub-cellular compartments. In addition, the existence of multiple ABA transporters suggests a complex regulatory mechanism to regulate ABA homeostasis during different plant development stages as well as during plant defense against aggressive environmental conditions. The mechanisms of action of ABA are conserved in plants from earlier plants. Those responses are almost the same when plants are subjected to different environmental constraints. Moreover, interaction of ABA with other phytohormones synergically or antagonistically paves the way to have different ABA signaling pathways to control ABA-mediated signaling in more sensitive and flexible ways to respond to various developmental and environmental responses.

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Chapter 3

METHANE EMISSION POLICIES OF COUNTRIES

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Dedicated to my dad, Dilaver Zeki Daloglu and thanks to the *Journal of Engineering and Applied Sciences*

ABSTRACT

Methane is a greenhouse gas (GHG), 21 times more powerful than carbon dioxide (CO_2) in its effect on climate change. Additionally, coalbed methane is a new energy mineral and an unconventional natural gas resource. The coal mining industry contributes 8% of total global anthropogenic methane released from open-cut and underground mines. U.S. and other countries cooperated under the Climate and Clean Air Coalition to Reduce Short-Lived Climate Pollutants and the Global Methane Initiative (GMI) to reduce GHG emissions. Thus, the

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International Council of Mining and Metals (ICMM) focused on CH_4 recovery and utilization in coal mines. Coal mine methane (CMM) utilization and recovery reduces GHG emissions and improves energy, mine safety and job creation. This chapter assesses the policies on methane (CH_4) emissions of the U.S., China, Russia, Turkey, Asia, European Union, South Africa and Australia. Some countries have succeeded, others have worked hard to implement policies.

Keywords: methane emissions, policy, greenhouse gas, Kyoto Protocol, energy, climate change

ABBREVIATIONS

AMM	Abandoned Mine Methane
ANN	Artificial Neural Networks
APEEP	Air Pollution Emissions Experiments and Policy
ASEAN	Association of Southeast Asian Nations
CAIR	Clean Air Interstate Rule
CBM	Coalbed Methane
CCAMP	Climate Change Adaptation and Mitigation Plan
CCEP	Conventional Centralized Energy Generation
CCS	Carbon Capture and Storage
CCUS	Carbon Capture, Utilization and Storage
CDM	Clean Development Mechanism
CMM	Coal Mine Methane
CMOP	Coalbed Methane Outreach Program
CPP	Clean Power Plan
CSAPR	Cross-State Air Pollutant Rule
CSG	Coal Seam Gas
CSIRO	Commonwealth Scientific and Industrial Research Organization
DES	Distributed Energy Systems
DOE	Department of Energy
ECP	Eastern Canadian Premiere
EISA	Energy Independence and Security Act

EMEA	Europe, Middle-East and Africa
ET	Emissions Trading
EU	European Union
EU ETS	EU Emissions Trading System
FERC	Federal Energy Regulatory Commission
GHG	Greenhouse Gas
GMI	Global Methane Initiative
GTS	Green Transport Strategy
ICMM	International Council of Mining and Metals
IEA	International Energy Agency
INDC	Intended Nationally Determined Contribution
IPA	Index of Policy Activity
IPAP	Industrial Policy Action Plan
IPCC	International Panel on Climate Change
IRP	Interpreted Resource Plan
JI	Joint Implementation
LCA	Life Cycle Assessment
LDAR	Leak Detection and Repair
LMP	Landfill Methane Outreach Program
MENR	Ministry of Energy and Natural Resource
MSI	Methane Supply Index
NATO	North Atlantic Treaty Organization
NEC	National Emission Reduction Commitments
NEG	New England Governors
NESHAP	National Emissions Standards for Hazardous Air Pollutants
NRCan	Natural Resources Canada
NWMS	National Waste Management Strategy
OECD	Organization for Economic Cooperation and Develop-ment
RES	Renewable Energy Sources
RGGI	Regional Greenhouse Gas Initiative
SA LEDS	South Africa's Low Emission Development Strategy
SCC	Social Cost of Carbon
TKI	Turkish Coal Enterprises
TKK	Turkish Hard Coal Enterprises

UNFCCC	United Nations Framework Convention on Climate Change
US	United States
USD	United States Dollars
USDA	U.S. Department of Agriculture
USDOE	U.S. Department of Energy
USEPA	U.S. Environmental Protect Agency
WEO	World Energy Outlook
VAT	Value-Added Tax

Units and Symbols

CH_4	Methane
CO_2	Carbon dioxide
D_i	Disturbances
HFC_S	Hydrofluorocarbons
$H_2O_{(g)}$	Water Vapor
I_a	Injurious Affection
Km	kilometer
kWh	Kilowatt hour
L_o	Land Occupied
m	Metric
$MMTCO_2E$	Million Metric Tons of CO_2 Equivalent
MW	Megawatt
Nm^3	Normal Cubic Meter
N_2O	Nitrous Oxide
PFC_S	Perfluorocarbons
Ppm	Parts Per Million
R&D	Research and Development
SFC_S	Sulfur Hexafluoride
S_v	Severance
Tcf	Trillion Cubic Feet
$TgCH_4yr^{-1}$	Teragram CH_4/ Year
Twh	Terawatt Hour

INTRODUCTION

Atmospheric methane originates from biogenic and non-biogenic sources. In addition, it is divided into anthropogenic and natural sources. The anthropogenic sources are biogenic including wetlands, rice agriculture, livestock, landfills, forests, oceans, termites, and municipal solid waste. Its emissions account for more than 70% of the total global emissions. Non biogenic sources include fossil fuel mining and burning, biomass burning, waste treatment and geologic sources [1]. The protected methane emissions of countries by 2020 are shown in Figure 1.

The main reason for the increase in CH_4 emissions is the rapid population growth in China, South and East Asia, Latin America and Africa. The sources of methane emissions are divided to sectors, such as wetlands, agriculture, energy, waste and biomass burning. The wetlands sector emits the highest amount of methane (CH_4), followed by the energy and agriculture sectors, as of the end of 2020 in Figure 2 [3].

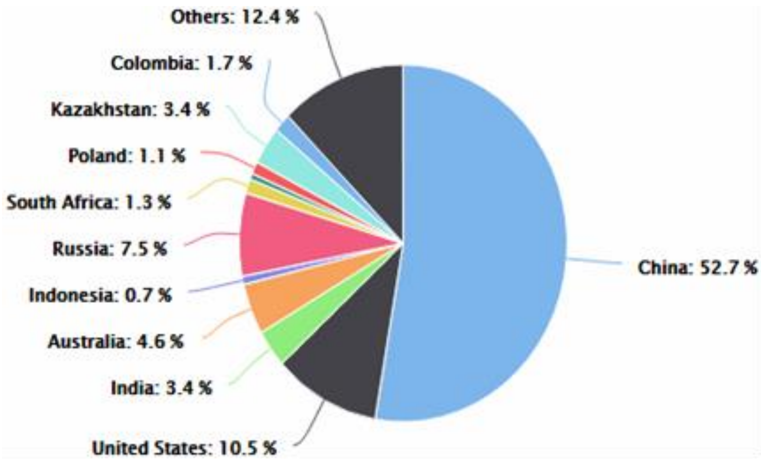

Figure 1. Protected methane emissions of countries by 2020 [2].

To increase population and living standards, CH_4 emissions are used as an energy resource of the world economy [4]. CH_4 emissions from the energy sector results from natural gas, oil systems, coal mining, biomass combustion and stationary and mobile combustion. The highest levels in

CH_4 emissions from natural gas and oil systems come from Russia (617.74 $MMTCO_2E$), U.S. (224.90 $MMTCO_2E$), India (30.10 $MMTCO_2E$), China (27.01 $MMTCO_2E$), Ukraine (21.84 $MMTCO_2E$) and Mexico (17.22 MMTCO2E) [5].

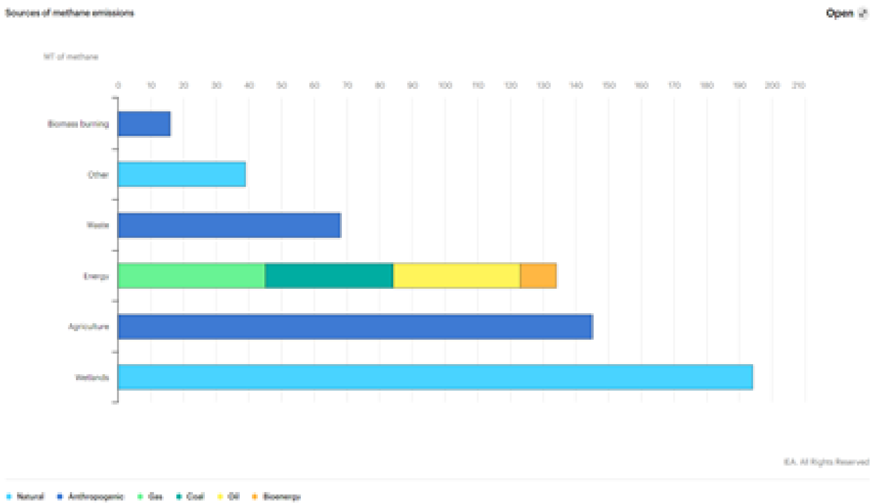

Figure 2. The sources of CH_4 emissions sectors in 2020 [3].

Coal provides 26% of global energy demand at the present time [6]. Global CH_4 emissions from active coal mines are predicted to reach nearly 671.4 $MMTCO_2E$ by 2020 [2]. China is the leader of the world with 660.42 $MMTCO_2E$ in 2020. Other global coal mine methane (CMM) producers are the U.S. (59.31 $MMTCO_2E$), Russia (59.04 $MMTCO_2E$), Australia (23.96 $MMTCO_2E$), Kazakhstan (17.56 $MMTCO_2E$) and India (22.40 $MMTCO_2E$) [5].

The coal mining industry is predicted to reach 11% of global CH_4 emissions [7]. USEPA (2017) reported that CH_4 emissions from coal mines was 67.3 million tons of CO_2 equivalents in 2015 [8]. 88% of them from coal mining topped by China, U.S., India, Ukraine and Australia [9]. Table 1 shows the total coal reserves (metric tons) and recovered coalbed methane (CBM) (cubic meters) of countries [10].

Table 1. Total coal reserves and recovered CBM of countries [10]

Countries	Total coal reserves (metric tons)	Recovered CBM (cubic meters)
Australia	76,2 billion	448 million
Canada	6,6 billion	-
China	317 billion	3,5 billion
The Czech Republic	4,5 billion	100 million
France	15 million	320 billion
Germany	6,7 billion	3 trillion
India	56,5 billion	4,6 trillion
Indonesia	4,3≈6,8 billion	12,8 trillion
Kazakhstan	31 billion	1,2≈1,7 trillion
Mexico	1,2 billion	-
Poland	7,5 billion	3 billion
Russia	157 billion	49 trillion
South Africa	236 million	140 billion≈1,1 trillion
Turkey	4,2 billion	-
Ukraine	34 billion	12 trillion
The United Kingdom	155 million	11-19 billion
U.S.	252 billion	2,7 trillion

CMM recovery is a clean technology to reduce mining costs and create a more economical and a safer, valuable energy resource. Gas drainage is a common method to reduce fugitive emissions by converting the methane (CH_4) to carbon dioxide (CO_2). It decreases CH_4 emissions from coal mines and mitigates air pollution because it is a clean-burning fuel [11].

Energy storage technologies work to reduce CH_4 emissions from the fossil fuels. New energy storage technologies have very large borders and improve on the following factors:

1. Jointed goals and policies,
2. Solution institutional and societal factors,
3. Specific policy initiatives to simplify energy storage,
4. Initiatives to simplify commercial or grid-scale employment.

They include the reconfiguration and transformation of energy systems. The energy storage strategies are developed in Canada (Ontorio, Alberta, Quebec, Manitoba and British Colombia), the U.S. (Federal level, New York, California, Hawaii, Massachusetts), and the EU (Germany, Denmark, UK). The specific issues are:

1. Eliminate the technical barriers of storage resources to market participation,
2. The foundation of new categories of market participants,
3. Contemporaneous storage resources participation in the simplification of multiple markets [12].

Countries have controlled storage by reducing CH_4 emissions in the atmosphere for global warming with CMM utilization and recovery techniques. Thus, they have taken measures using political decisions.

METHANE EMISSION POLICIES OF COUNTRIES

Methane is the main component of natural gas and is a clean energy. It is the second greenhouse gas (GHG) involved in global warming and is 25 times greater than CO_2 for global warming potential. The CH_4 emissions are 200 times lower than CO_2 emissions in the atmosphere.

The GHG affects the groundwater quality and global climate change. The major GHG contains water vapor ($H_2O_{(g)}$) (36-70%), carbon dioxide (CO_2) (9-26%), methane (CH_4) (4-9%) and nitrous oxide (N_2O) (3-7%) [4]. The International Panel on Climate Change (IPCC) explained that GHG increases global temperature by 2.4^0C. It reported that in order to reduce GHG emissions to net zero before 2030 we need to limit the global warming increase to 1.5^0 C. It suggests a 45% and 100% reduction in GHG emissions by 2030 and 2050, respectively [13]. Thus, the concentration of GHG in the atmosphere needs to be stabilized at around 450 ppm. According to Energy Technology Perspective, low or zero-carbon technologies will cost up to USD 200 per ton of CO_2 stabilized at 450 ppm by 2050. If it fails to reach this target, costs will rise to USD 500 per ton. GHG emissions will jump by 57% between 2005 and 2030 according to the World Energy Outlook (WEO). China is the biggest contributor, overtaking the U.S., Russia and India [14]. The U.S. (14%) and China (28%) are the largest economies of the world's total GHG emissions.

The United Nations Framework Convention on Climate Change (UNFCCC) is an international treaty and the Kyoto Protocol is an international agreement under UNFCCC to reduce GHG emissions. The United Nations Framework Convention on Climate Change (UNFCCC) was signed in Rio de Janerio in 1992. In 1997, 43 countries signed the Kyoto Protocol to reduce GHG emissions. Six GHG were identified for global warming and greenhouse effect. They are CO_2, CH_4, N_2O and three synthetic gases (hydrofluorocarbons-HFC_s, sulfur hexafluoride-SFC_S, perfluorocarbons-PFC_S) [15]. The first commitment period of the Kyoto Protocol was completed in 2008-2012, and the second period in 2013-2020 [16]. In the first period, EU countries and the U.S. reduced GHG emissions 8% and 7%, respectively. In the second period, EU countries reduced 20% on GHG emissions [17]. The U.S. declined to ratify the treaty and Canada withdrew from the treaty after the ratification the Kyoto Protocol in 2005. The social cost of carbon (SCC) is the most important reason for the U.S.'s withdrawal from the Kyoto Protocol and later the Paris Agreement. The Paris Agreement is the basis for regional and national climate goals. Then, it was signed by 170 countries.

The Kyoto Protocol identifiers limit environmental pollutants and the emission for developed countries. The Kyoto mechanisms were: Emissions Trading (ET), Joint Implementation (JI), and Clean Development Mechanism (CDM) [18]. Clean Development Mechanism (CDM) allows emission reduction projects in countries. The two goals of CDM projects are: meeting GHG emissions reduction targets cost-effectively and the promotion of sustainable development in countries. To ensure them, the UNFCCC secretariat managed the CDM with stakeholders in the CDM project. The CDM project includes project design, validation, registration, monitoring, verification, certification and issuance [19]. Methane emissions policies of countries are explained below.

U.S.

The global energy sector is mainly dependent on fossil resources. In the U.S., fossil fuels are the dominant energy source. U.S. has sixteen CMM areas and five main coal producing regions [20; 21]. They are:

1. The Appalachian Basin, located in Ohio, Pennsylvania, West Virginia, Tennessee and Eastern Kentucky,
2. The Warrior Basin, located in Alabama,
3. The IIIionis Basin, located in IIIilonis, Indiana and Western Kentucky,
4. The Southwestern Region, located in Colorado, Utah and New Mexico,
5. The Western Interior Region, including the Arkoma Basin of Oklahama and Arkansas [21].

According to a Kirchgessner et al. (2002) study, utilization systems are more of a success in the Warrior and Appalachian Regions than in other regions [22]. Utilization of gas recovered from the CH_4 control system in the IIIinois Basin doesn't have a positive economic effect, but the Western Region has a positive economic effect.

In the late 2000s, natural gas prices declined and coal and oil use rose in other countries. They took the place of renewable energy sources (RES) to mitigate CH_4 emissions. The U.S. federal initiatives had a goal to develop renewable energy technologies according to the energy policy Act of 2005 (E. P. Act 2005), the Energy Independence and Security Act of 2007 (Congress 2007), the American Recovery and Reinvestment Act of 2009 (R. Act 2011), and the Clean Air Act under Section 111 (d) (the Clean Power Plan). The policies include: renewable portfolio standards, renewable energy certificates, feed-in-tariffs, net metering, federal production tax credits, accelerated tax depreciation and low-interest loans [23].

Pischke et al. (2019) measured the long-term development (1998-2015) of federal and state renewable energy policies by the 'Index of Policy Activity (IPA)' in the Pan-American Region: U.S., Argentina, Brazil, Mexico and Canada [24]. IPA is a function of policy intensity or density. IPA has six indicators: objective, scope, integration, budget, monitoring and implementation. The objective includes specific targets to contribute to the policy's performance. The scope measures energy types and sectors by the policy. The integration measures the extent the policy and the budget reveal the public expenditure. The monitoring measures a plan for the policy. Finally, the implementation includes actors, rules, procedures and sanctions. The U.S., Argentina, Brazil, Mexico and Canada have the biggest populations and have similar federal political systems. [24].

The U.S. and Canada have the highest renewable energy policy density at both the national and sub-national levels. Canada's 10 provinces are responsible for 18 policies, whereas the U.S., with 50 states, produced 44 policies. Federal agencies (such as, the U.S. Department of Agriculture (USDA) and the U.S. Department of Energy (DOE)) have helped reduce CH_4 emissions. Canada has the most intense budget and the second-highest policy intensity. Natural Resources Canada (NRCan) and Trudeau's Liberal government divided uo to $126 million in funding for renewable energy policy in 2016. The Canadian province of Ontario is a leader in clean energy and Canada's federal government supports renewable energy policy and climate change. Argentina and Brazil have the least intense policy. Argentina is the second-highest budget behind Canada. The 2009 Renewable Generation Program aims to maximize renewable energy sources (RES). The new president of Brazil, Jair Bolsonaro didn't define the next renewable energy policies because of COVID-19. Mexico became a member the UNFCCC and Kyoto Protocol in 2000. It has the lowest policy intensity because of their weak budget [24].

Mexico's coal reserves are located in Coahuila State, Sonora (north-west) and Oaxaca (southern). Coal supplies 6.9% of Mexico's total energy. CH_4 emissions from coal mines are 208 million m^3. According to Mexico's 2015 Biennial Update Report, total GHG emissions rose to 49.3% between 1990 and 2012. Mexico's Project would produce 7.95 MW of power from captured CMM emissions in 2015. It is still in the planning stage. There are 192 CDM projects as of August, 2019. Mexico will reduce GHG emissions and coal by 22% and by 51% by 2030, respectively [25].

Some policies were applied by administrators to regulate CH_4 emissions in the U.S. In Figure 3, U.S.'s Presidents are shown and their policies are explained.

a) Bill Clinton (1993-2001) b) George W. Bush (2001-2009) c) Barack Obama (2009-2017) d) Donald Trump (2017-2021)

Figure 3. U.S.'s Presidents [26, 27, 28, 29].

President Bill Clinton signed the Kyoto Protocol during his last months in office. In 2001, President George W. Bush didn't ratify the Kyoto Protocol and proposed policy alternatives to the goals in the Kyoto Protocol [31]. He announced a climate change strategy in 2002, but it was ineffective and opposite to climate policy [24]. In 2003, 140 cities of U.S. established GHG emission mitigation targets. The U.S. coordinated agreements in New England (the New England Governors/Eastern Canadian Premiere's Agreement or NEG/ECP), the Northeast (the Regional Greenhouse Gas Initiative are RGGI), the West Cost (the West Cost Climate Initiative) and the Northern Midwest (the Powering the Plains Initiative). During the time of President Bush, climate policy and energy policy conflicted with each other. Thus, the U.S. took some measures to prevent this conflict. They are:

1. Reduce mitigation costs,
2. Promoting an open and democratic policy,
3. Promoting interregional cooperation,
4. Promoting equity across regions, generations and socio-economic groups.

According to these measures, Pennsylvania has been a leader in energy production and climate policy [31]. President Bush signed the Energy Independence and Security Act (EISA) in 2007 [24].

Under the Obama Administration, U.S. Federal agencies supported a decrease in U.S. GHG emissions. The Obama management intended to reduce CH_4 emissions for the “Climate Action Plan” in 2014. United States Environmental Protect Agency (USEPA) suggested to reduce oil and gas sector CH_4 emissions by 45% by 2025. This plan occurs in four sections: The Methane Challenge Program, the Coalbed Methane Outreach Program (CMOP), the AgSTAR program, and the Landfill Methane Outreach Program (LMOP). The Methane Challenge program supports companies in reducing CH_4 emissions. The CMOP planned to reduce emissions from coal mine’s CH_4 to the atmosphere. The AgSTAR program helps the “biogas opportunities roadmap” with the combined U.S. Department of Agriculture, USEPA and U.S. Department of Energy. USEPA proposed in 2015 to reduce landfill CH_4 emissions by 440,000 Tyr^{-1} by 2025 [32].

There is a decline in energy usage of 38% over the 1980-2013 period. The U.S. Federal Government applied three types of energy efficiency policies: 1) financial and nonfinancial incentives, such as grants for industries to upgrade equipment, 2) technical assistance programs, such as energy audits and 3) research and development (R&D) programs. First, incentives reduce the cost of energy-saving technologies and development of new industries. Second, technical assistance programs help to reduce energy consumption through improved efficiencies. Finally, research and development (R&D) programs play an important role for the sustainable structural change of the U.S. economy. Actually, the energy sector and green industries had a central position during the Obama Administration [30].

The U.S. tried to reduce CH_4 emissions in three main ways: fuel economy regulations, decreasing GHG emissions and increasing the share of renewable energy. President Obama and the USEPA announced the Clean Power Plan (CPP) in the Paris Agreement in 2015 to reduce national GHG emissions. The plan aims to reduce carbon pollution from the power sector 32% by the year 2030. The Clean Air Interstate Rule (CAIR), Cross-State Air Pollutant Rule (CSAPR), and National Emissions standards for Hazardous Air Pollutants (NESHAP) are regulations and legislation on GHG level controls [33]. These policies were repealed by the Trump Administration because of the social cost of carbon [34].

The social cost uses the benefit-cost analysis of laws across the government. The social cost of emissions is a measure of the economic damage and is called an externality. The externality is both positive and negative. A negative externality or cost occurs when fossil fuel energy produces a loss caused by air emission of the energy generation. The social cost of carbon emissions (equivalent GHG emissions as CO_2) is $42 per metric ton. The social cost of the emission tax is formulated on Distributed Energy Systems (DES) and Conventional Centralized Energy Generation (CCEP) using the Air Pollution Emissions Experiments and Policy (APEEP) model. A 67% cost reduction for the DES system happened due to current U.S. renewable policy incentives [23].

President Trump declared the U.S. withdrawal from the Paris Climate Agreement in 2015. The Trump Administration's environmental policy contrasted with the Obama Administration. After his election, Trump launched the "Energy Indepen-dence" policy. Thereby, it aimed to eliminate the Clean Power Plan of the Obama Administration to support clean energy production. Then, the USEPA changed the rules on GHG emissions in the Trump Administration [30]. The Trump Administration challenged energy storage issues raised by the Federal Energy Regulatory Commission (FERC) in November, 2016. California and Hawaii's jurisdictions lead to policy development and regulations around energy storage [12]. The U.S. Department of Agriculture (USDA) and U.S. Department of Energy (DOE) established multi-million-dollar funding for a biomass research program under the Energy Policy Act of 2005. Some states/provinces (California, Maryland, New York, Canada's New Brunswick, Nova Scotia and Ontario) have multiple policy targets. The Trump Administration had goals of increasing the coal industry, placing tariffs on solar energy panels and declining to promote renewable energy [24].

The White House recently announced that the U.S. will reduce CH_4 emissions by 28% by 2025 while China will increasethe consumption of non-fossil fuels, as main energy, by 20% in 2030 [32]. The President of the United States of America, Joseph R. Biden Jr., accepted the Paris Agreement and every clause on behalf of the U.S. on January 20th, 2021 [35]. The U.S. Energy Information Administration plans to produce 100% of new energy from RES by 2030 and finishing 100% conversion by 2050 [24].

China

Coal accounts for 70% of the main energy sources in China. It is unique that coal in underground mines supply 95% of the nation's coal [1]. The number of underground coal mines in China is 10 times more than in the U.S. [36]. CH_4 from coal mines in China release 6 times more than in the U.S. Energy-related CH_4 emissions in the U.S. were greater than in China before 1994, but then, by 2007, China's CH_4 emissions were 2.4 times larger than the U.S.'s. CH_4 emission components of China and the U.S. in 1990, 2007 and 2018 are shown in Table 2 [37; 3]. In recent years, the largest emission source in China, by 67.4% is coal mining.

Table 2. CH_4 emission components of China and U.S. [37: 3]

	China			**U.S.**		
	1990	2007	2018	1990	2007	2018
Coal mining (%)	77,3	85,8	67,4	32,4	29,8	16,5
Fuel consumption (%)	20	11,2	3,9	4,7	4,5	5,5
Oil system leakage (%)	1,9	1,2	2,1	13,0	14,8	41,4
Natural gas system leakage (%)	0,8	1,8	7,8	49,9	51,0	36,6

China has the third largest CBM resource next to Russia and Canada. There are 9 main CBM basins: Odors, Qinshui, Junggar, Diandongqianxi, Erlian, Tuha, Tarim, Hailaer and Tianshan [38]. There are four recoverable CMM: Northern (56.3%), North Western (28.1%), Southern (14.3%) and North Eastern (1.3%). 10 billion Nm^3 CMM is released every year during coal exploitation. Various systems are developed to minimize pollution caused by CMM and to support utilization. They are: power generation systems, combined-heat and power systems, thermal energy provision systems and fuel-gas provision systems etc… CMM utilization will access to 20≈40 billion m^3 in 2030. It provides energy and an economic future [39].

China is a leader in the recovery and use of CMM. China has the world's most CMM recovery projects and 25% of gas is used for electricity production. China set up 'Measures for Operation and Management of CDM Projects' in 2005. In 2012, 59 CDM projects implemented in the CMM sector and 169 projects were initiated in China [19]. 16 national projects have prepared to improve science and technology in China's National Medium and Long-term Science and Technology Development Program (2006-2020) [38]. The National CDM Board evaluates and monitors CDM projects. CDM projects related to mining focuse on:

1. Methane capturing and utilization (coalbed methane, enhanced coalbed methane, coal mine and ventilation air methane, non-hydrocarbon mining methane).
2. İmprove energy efficiency and mineral extraction.
3. Reduce fossil fuel use and increase use of renewable energy.

These projects have as follows:

1. Environmental benefits: air, land, water and conservation,
2. Social benefits: health, safety, employment and learning,
3. Economic benefits: growth, energy and balance of payments,
4. Other benefits: sustainability tax, technology transfer, corporate social responsibility.

30 Chinese CDM projects have air, safety, learning, energy, employment and technology transfer [19]. China has 84 projects for the optimization of degasification systems to reduce CH_4 emissions from coal mines [40]. Project developers have local partners and need to guarantee business opportunities for Chinese stakeholders [19]. Table 3 shows stakeholders in China CMM industry by 2020 [40].

Table 3. Stakeholders in China's CMM industry [40]

Stakeholder Category	Stakeholder	Role
Mining Companies	• Shenhua Group • China National Coal Group • Datong Coal Mine Group • Jizhong Energy Group • Shanxi Coking Coal Group • Shandong Energy Group • Shaanxi Coal and Chemical industry Group	Project hosts
Developers	• China National Petroleum Corporation • China United Coalbed Methane Corporation Ltd. • CBM Exploitation and Development Company of the Petro China Company Ltd. • Far East Energy • Lanyan CBM Company of the Jincheng Anthracite Coal Mining Group • Sindicatum Carbon Capital, SCC Americas	Project opportunity identification and planning
Engineering, Consultancy and Related Services	• China Coalbed Methane Clearinghouse • Guizhou International Cooperation Center for Environmental Protection	Technical assistance
Universities and Research Establishment	• China coal Research Institute • China University of Mining and Technology • China University of Petroleum, Beijing • China National Administration of Coal Geology • China Coal Information Institute	Research and technical assistance
Regulatory Agencies and Government Groups	• National Development and Reform Commission • National Energy Administration • Ministry of Ecological Environment • China National Coal Association • State Administration of Coal Mine Safety	Drafting of legislation, implementation of laws, government oversight

The rapid-growing urbanization was causing an energy problem. Thus, alternative energy sources were called for [32]. Coal supplies 60.4% of total China's energy consumption. China had 50% of the world's CMM emissions in 2019 [40]. China asks to develop CMM resources with a depth from 300 to 1500-meter supply to clean energy. But, there are some barriers. Barriers to CMM recovery and utilization in China are as follows.

1. Lack of information and expertise and degasification technologies.
2. Lack of methane use and market and capital investment from the private sector.
3. Lack of internal-combustion-engine (IC) generators [14].

Three major factors in China's economy are the CBM price, production rate and operating costs. Some parameters used for economic evaluation of CBM production are shown in Table 4 [41]. The CH_4 control cost occurred in four groups: direct production cost, indirect production cost, business tariff and annex, and period cost [42].

Table 4. Some parameters used for economic evaluation of CBM production [41]

Parameters	**Values**	**Units**
Investments		
Drilling and completion	1.38[a]	Million/well
Surface facilities	360	Million/block
Operating costs	0.32	Yuan/m^3
Wellhead price (VAT included)	1	Yuan/m^3
Government subsidy	0.2	Yuan/m^3
Producing life	30	- Year
Gas commodization rate	95%	-
Income tax	25%	-
Discount rate	12%	-

China's CBM industry is divided to three stages. Underground drainage and venting of coal gas, surface drilling and exploration of CBM, and the formation and develop of China's CBM industry. 42% of CBM price, production rate and operating costs affect the economic viability of CBM resource.

Additionally, value-added tax (VAT) reimbursement policy, financial subsidy policy and corporate income tax exemption policy are all meant to develop the economic viability of CBM resource [38]. Zhanting et al., (2011) expressed the following means to develop CBM [43]. They are:

1. Government should do scientific CBM development planning strategy to make CBM industry.
2. Government incentives, laws, regulations and markets should support the CBM industry.
3. Technology innovation should supply the CBM industry.
4. Infrastructure should improve the sales and market of CBM.

In recent years, the growth rate of CBM has been down because natural gas demand has grown. Thus, five main subjects are investigated to develop CBM industry: speed up the scale of medium-low rank CBM resources, increasing production and recovery factor of developed areas, strengthen the comprehensive of deep CBM and coal measure gas, develop the intelligent technology and the innovative management system. Since the "11th Five-Year Plan", China explored and developed the medium and high rank and medium and low rank CBMs. At the end of the "12th Five Year plan", China developed 7 technics of medium and low rank CBM. They are: medium-low cost seismic exploration technology, comprehensive CBM geological evaluation technology, high efficiency coal seam stimulation technology, quantitative drainage and production equipment, low cost automatic monitoring equipment, low pressure pipeline construction, skin-mounted equipment and technology. Since the "13th five Year Plan", China carried out the National Major Science and Technology Project and "Demonstration Project for Integrated Development of Deep CBM and of the Ordos Basin" [44]. In the 13th Five Year Plan, China has increased CBM reserves, extraction and utilization [40].

The Chinese government aims to rise CH_4 as a main energy source and to reduce GHG emissions to climate change per the Kyoto Protocol. Elzen et al. (2016) reviewed the policies analyzed in Table 5 [45].

Table 5. Summary of the current policies analyzed of China [45]

Sector	Policy/measure	Target
Energy supply	Increased renewable energy supply	Increase the share of renewable energy in electricity generation up to about 44% by 2030.
Transport	Fuel efficient	Achieve efficiency standarts in the EU with a five-year delay
Buildings	Building efficiency	New buildings are placed with highly efficient standart of 50 $kWh/m^2/a$
HFC_s	Phase-down of HFC_s	30% reduction in HFC consumption and production by 2025 and 60% by 2031
Forestry	Continued afforestation efforts after 2020	Yearly afforestation from 2020 to 2030

Under policy measures in the forestry, transport, buildings and power sectors, CH_4 emissions will keep increasing up to 2030 [45]. China CMM policies are summarized as following:

1. Coal is a major energy resource. The government made many policies and regulations to development, planning, safety, sustainability, royalty tax reforms, CMM recovery and utilization.
2. The government supported collaborations of coal mine enterprises with other enterprises, and different sectors in different countries.
3. China uses more technologies than human power to raise production.
4. China reduces the use of coal reserves while keeping the production level unchanged. For example: reusing coal mine water, gangue, ash and sludge, improving labor management and capacity building, cutting operation of ventilation air methane.

5. Monitoring and measuring of CMM and setting to the concentration of ventilation air methane.
6. The government encourages mines to improve CMM drainage and power generation units.
7. Import tax, value-added tax and import duties will be exempted for CMM equipment, development operations, etc. [14].

Turkey

Turkey mostly produces hard coal (1 billion metric tons) and lignite (3.2 billion metric tons). Lignite deposits are found in Afsin-Elbistan, Soma, Çay, Mugla and Bursa. Lignite is mined by Turkish Coal Enterprises (TKI) [10]. Coal is produced in Turkish Hard Coal Enterprises (TTK) with five collieries: Kozlu, Karadon, Armutçuk, Uzulmez and Amasra. Palmer et al. (2004) investigated the properties of Turkish coals and Black Sea coals have a higher fixed-carbon rate than other regions in the world [46]. Turkey imports 16 million tons of hard coal each year, mostly from the U.S., Russia, Australia and South Africa [47].

Turkey is a member in the Organization for Economic Cooperation and Development (OECD), Europe and NATO as a leading Muslim nation. Turkey signed the UNFCCC as the 189th member on May 24, 2004. It didn't sign the Kyoto Protocol until 2009. As a candidate country to the EU, Turkey signed the Kyoto Protocol on February 17th, 2009. The EU asked members to reduce environmental pollutants 30% by 2020 [18]. Turkey has the 20th largest GHG emissions in the world and it hasn't ratified the Paris Climate Accord [48]. Turkey didn't make a commitment to reduce GHG emissions by 2020. It declares to reduce emissions by 2030 in the Intended Nationally Determined Contribution (INDC) [49]. The Republic of Turkey Ministry of Energy and Natural Resource (MENR) aimed to meet the Kyoto Protocol's conditions by the year 2023 [17].

According to Kyoto Protocol requirements, 19.85 million m^3 CH_4 emissions should decrease the ventilation air methane mitigation, utilization options [50]. Sözen et al. (2007) modeled to preventing GHG and CH_4 emissions using the artificial neural networks (ANN) method in Turkey and summarized in Figure 4 [51].

Turkey has lower emissions compared to EU countries [52]. The Turkish policies to mitigate CH_4 emissions disclose the following:

1. To raise the use of renewable energy,
2. To decline energy loses,
3. To develop better fuel quality,
4. Using the technology to prevent GHG [18].

According to OECD/IEA, Turkey represents the “medium to long-term growth” in energy demand in the world after China [53]. But, Turkey’s energy consumption is much lower than OECD countries [47]. Coal supplies 28% of Turkey’s total energy consumption. 55% of total Turkish energy sector CH_4 is provided by coal mining [48].

In 2023, the Republic of Turkey Ministry of Energy and Natural Resource’s (MENR) goal was to reduce CH_4 emissions, minimization of the use of power plants that use fossil fuels that impact the environment, climate change and ecosystem under the UNFCCC and Kyoto Protocol. Turkey’s energy demand will increase 7.5% per year and will reach 538 TWh [17]. In the Vision 2023, coal will play a very important role and supply 25% energy capacity in Turkey (Table 6) [54]. If the coal reserves are supported for energy, Turkey won’t be dependent on foreign countries.

There are 436 coal mining companies with 38,000 people employed Table 7 summarizes the stakeholders in Turkey’s CMM industry.

Turkey is applying an “open door policy” to attract foreign investments. In 2013, 27% of electric and 29% energy from RES was obtained from hard coal and lignite power plants. Thus, new coal-fired power plants can be constructed and their investment costs are $750 million per MW.

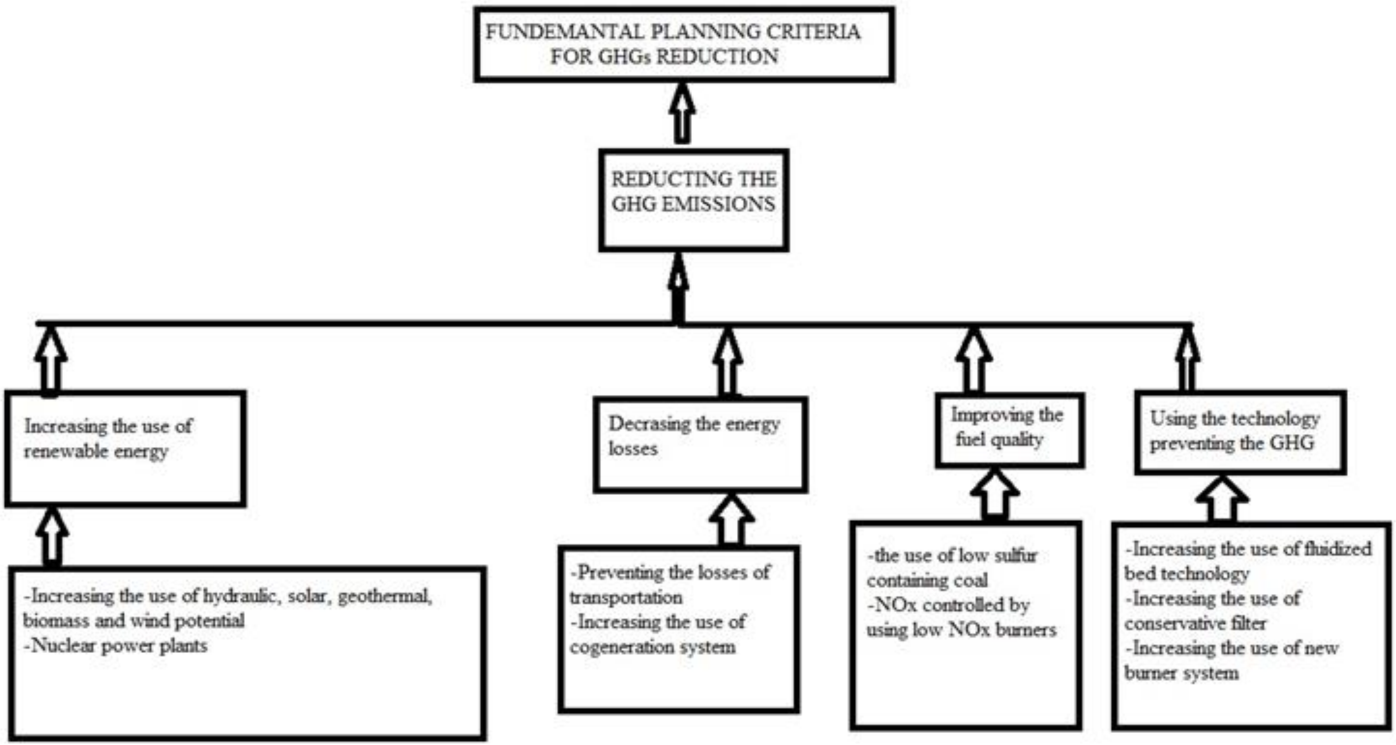

Figure 4. The flowchart for GHG and CH_4 emission reduction [51].

Table 6. Turkey's Vision 2023 targets for the energy sector [54]

Items	Goals
Renewable energy sources	
Share of renewable sources in energy production	30%
Hydroelectric generation capacity	Maximum or 36000 MW
Wind power installed capacity	20000 MW
Solar power installed capacity	3000 MW
Geothermal power installed capacity	600 MW
Biomass	2000 MW
Fossil fuels	
Coal	30000 MW
Infrastructure	
Length of transmission lines	60717 km
Reaching a power distribution unit capacity	158460 MVA
Use of smart grids	Established
Natural gas storage capacity	5 billion m^3
Energy stock exchange	Established
Nuclear power plants	2 operational (3rd under construction)
Installed power capacity	120000 MW

Table 7. Stakeholders in Turkey's CMM Industry [48]

Stakeholder Category	Stakeholder	Role
Mining Companies	• Turkish Hard Coal Enterprise • Turkish Coal Enterprise • HEMA Energy	Project host
Government Agencies	• Ministry of Energy and Natural Resources • Organization of Agean Lignite • Representation of Turkish Coal Enterprises	Legal and regulatory oversight of CMM/CBM

Turkey will supply 30% electric from RES by 2030. Turkey aims to increase its energy efficiency by 20% by 2023. The Energy Efficiency Strategy 2012-2023 includes:

1. To reduce energy losses.
2. To decrease energy demand and carbon emissions, to support RES.
3. To provide market transformation.
4. To increase efficiency in production, transmission and distribution.

5. To reduce fossil fuel consumption.
6. To use energy effectively in the public sector.
7. To develop financial mechanisms, technology and awareness activities [53].

Turkey has potential methane hydrate reservoirs under the Black Sea. It's unique in the world because it has coal reserves under the Black Sea. Thus, the Black Sea is a unique energy source to and contains 96 million tons CH_4 [47]. The Western Black Sea Gas Hydrate Exploration and Research Project (2014-2018) was completed in Turkey [54]. A CBM feasibility project was completed in the Zonguldak Region by the Turkish Petroleum Organization in 2019. Turkey could generate US $37 billion from CMM/CBM emissions' utilization in the Zonguldak basin [48]. Increased consumption of coal, lignite and biomass will decrease Turkey's foreign trade deficit based on imported energy sources.

Turkey had been limited to the natural gas supplied from Russia (57%), Iran (20%) and Azerbaijan (10%). But, President Recep Tayyip Erdogan announced that the natural gas reserves of 405 billion m^3 exist in the Black Sea in 2020 [55]. Additionally, the foundation of the first nuclear power plant was laid together by President R. Tayyip Erdogan and Russian Federation President Vladimir Putin in Akkuyu (Mersin) on 10, March, 2021 (Figure 5) [56]. It is a big attack on CH_4 emission policies.

Figure 5. Foundation of Akkuyu Nuclear Power Plant [57].

European Union (EU)

Methane releases in four main countries in Europe: Italy, Turkey, Greece and Iceland. Geothermal areas have the largest emissions but volcanoes aren't a main CH_4 source [58]. The European Union (EU) plays a role in the reduction CH_4 emission at a global level. 41% of global CH_4 emissions come from natural sources, the remaining 59% are anthropogenic. The main sources of CH_4 emissions in the EU are the agricultural sectors (53%), landfills (26%) and energy sectors (coal mining and gas production and distribution) (19%). 54% of CH_4 emissions in the energy sector are fugitive emissions of which 34% are from the coal sector and 11% are from other sectors [59]. The EU summarized its CH_4 emission mitigation strategy in 1998 as shown in Table 8 [60].

The EU's climate target plan indicates the most cost-effective CH_4 emission savings are in the energy sector [59]. The EU regulated CH_4 emissions and multiplate solid waste. The UK signed on to the Kyoto Protocol and Climate Policy Act to reduce CH_4 emissions. Therefore, coal mining has attracted widespread attention. Under the Kyoto Protocol, the EU agreed to an 8% reduction of GHG emissions between 2008 and 2012 [32].

Table 8. Summary of actions suggested in the European Commission [60]

Source	Suggested Action	Level for Action
Enteric fermentation	R&D	EU and National
Recover methane from animal waste	Demonstration	All
	Obligation	EU
Reduce landfilled organic waste	Promotion of measures	All
Landfill gas recovery	Legislation	EU
Energy production from landfill gas	Incentives	EU and National
Mining emissions	Encourage use of best available technologies	EU and National
Gas pipeline leakage	Set standard	EU
	Increase control frequncy	National

Every country has a different energy policy to reduce CH_4 emissions by their government policy. The 2015 COP21 Agreement in Paris was enacted because the Earth's temperature was projected to rise 2^0C in the 21th century [32]. 195 members of UNFCCC agreed with COP21 in November 2016. The EU is a leader supporting renewable energy in Europe, the Middle-East and Africa (EMEA). It aimed to have a 20% increase in energy generated from RES, a 20% cut of CH_4 emissions and 20% rise in energy efficiency under the 2020 Climate and Energy Package. In the 2030 agenda for sustainable development, the EU will generate 27% of energy from RES. But, the EU was unwilling to supply the financial wherewithal to cover the poorer members of the union [61].

The EU leads international collaboration to improve the monitoring and mitigation of global CH_4 emissions with the Copernicus program. The EU's Copernicus program is able to monitor global atmosphere CH_4. The commission considers the Zero Pollution Action Plan in 2021 and the EU Clean Air Outlook in 2022. It will review the National Emission Reduction Commitments (NEC) Directive by 2025. EU's policies are as following:

1. The Commission will support measurement and reporting of CH_4 emissions by companies through all sectors.
2. The Commission will establish an independent international CH_4 emissions observatory in cooperation with international partners.
3. The Commission will monitor the satellite-based detection of CH_4 emissions in the Earth with Copernicus program.
4. The Commission will review the EU climate and environmental legislation.
5. The Commission will accelerate the development of the market from sustainable sources.
6. The Commission will encourage the sealing of abandoned or unused coal mines to eliminate CH_4 emissions. The forthcoming Commission will suggest to reform the Research fund for Coal and Steel.
7. The Commission will promote the mitigation technologies and targeted research for different factors in the Horizon Europe Strategic Plan 2021-2024.

8. The EU will pursue cooperation with the U.S., Canada and Mexico for technical assistance.
9. The Commission will examine the methane supply index (MSI) for buyer countries.
10. The EU will support initiatives, such as International Public-private Global Methane Initiative, the World Bank's Gas Flaring Reduction Initiative, the World Bank's Initiative on Zero Routine Flaring by 2030, and the International Energy Agency.
11. Methane leakages from coal mines are very significant. Thus, the EU will establish leak-detection and repair (LDAR) with Copernicus [59].

Asia

Asia is one of the largest sources of CH_4 emissions. Total CH_4 emissions were estimated to be 69.7 $TgCH_4yr^{-1}$. Among the emission sectors, fossil fuel made the largest contribution (24.9%), followed by agricultural (22.7%), waste and landfill (15.5%) and livestock (14.9%) [62].

Due to the rapid revolution in economic growth in Asia, China has the largest energy demand, followed by India, Malaysia, Singapore, Vietnam, South Korean and Japan. In the Asia-Europe Energy Policy in 2017, low carbon technologies, government roles and incentives, energy policy and climate mitigation strategies are regularly discussed between Asia and Europe Foundation [61].

Indonesia has the second largest sources of CBM after China with 453 trillion cubic feet (Tcf) of reserves. The Indonesia government promised to reduce emissions by 26% in 2020 at the G-20 Forum in Pittsburgh (U.S.) in 2009. It cooperates with China about this subject. It adopted a National Energy Plan to increase the usage of renewable energy, energy mix, energy security and energy access. The National Energy Council aims to reduce fossil fuel consumption by 2025. The energy mix in 2025 shows coal 37%, oil 22.2%, gas 17.8%, renewable energy 19.2% and nuclear 4% [63].

Malaysia is a developing country and a member of the Association of Southeast Asian Nations (ASEAN). It ratified the 1972 Montreal and Kyoto Protocols to reduce CH_4 emissions [64].

Kazakhstan is a member of the Global Methane Initiatives (GMI) and a net coal exporter [65]. Additionally, it is a member tf the UNFCCC, the Kyoto Protocol and the Paris Agreement. It has four coal basins: Karaganda, Ekibastuz, Zavialov and Samarskiy. 84% of CBM reserves are located in the Karaganda basin. It is supporting privatization, especially in the energy production sector, opening the door for foreign investment. Coal supplies 53% of Kazakhstan's total energy consumption. It exports 90% of its coal to Russia [66].

India has the third largest coal reserves (131.6 billion tons) and 70 Tcf CBM. There are three CBM areas: Ranigunj (West Bengal), Jharia (Jharkhand) and Shgrauli (Madhya Pradesh) [39]. The coal production is dominated by surface mining and increases annually. But, the underground production is stagnant (12%). Coal is the main source of energy in the future and energy usage is growing with the population [67]. 56% of India's power production is provided by coal and India has third largest GHGs in the World [68]. India is a signatory of the Kyoto Protocol and committed to reduce CH_4 emission by 20-25% by 2020 [69]. Some factors hindering the growth of CBM in India:

1. Institutional problems related to resource ownership and payment to the nationalized companies.
2. A fixed price mechanism hasn't been finalized by the committee of CBM.
3. Lack of technology and experienced personnel.
4. Extremely cost conscious market.
5. Weather challenges in the CBM fields.
6. Lack of water supply and sand.
7. India's Oil and Gas Commission has conventional operations and complicated ownership [20].

Russian Federation

Russia has the second-largest coal reserves (160.364 million tons) and coal accounts for 13.2% of country's total energy consumption. Coal reserves are located in Siberia (80%) and the Far East Region (10%). Lignite is found mainly in Siberia and in Western Russia. CMM is mainly located in three coal basins: Kuznetsk (Kuzbass), Pechora and Donetsk. 70% of total CH_4 emissions from Russia's coal mining are emitted from Kuzbass. Russia is the third-largest coal exporter in the world, especially to Asia because of its rapid growth (Figure 6).

Figure 6. Share of Russia's coal exports by 2016 [70].

Russia, the fourth-largest contributor of GHG ratified the Paris Agreement on Climate Change [70]. Russian policy has interest in reducing CH_4 emissions. Oil and gas emissions dominate Russia's CH_4 emission balance. Russia supports the mitigation of CH_4 emissions at a lower cost [71]. There has been a proposal by USEPA and Gazprom for CH_4 emission reduction [72]. Table 9 shows the key stakeholders in Russia's CMM industry [70]. The CH_4 utilized by mines is 40 million cubic meters per year [10].

Table 9. Key stakeholders in Russia's CMM industry [70]

Stakeholder Category	**Stakeholder**	**Role**
Mining companies	• Severstal-Resource • Evraz Holding • Ural Mining and Metallurgical Company • Sibirsky Delovoy soyuz • Sibuglemet • Belon • Mechel • Siberian coal energy company • IMH-coal • MDM	Project hosts
Equipment manufacturers	• Kyshtym machine Works • Druzhkov machine Works • Artemovsk machine Works • Yurga machine Works • VENTPROM	Power generation equipment supplier
Universities/research establishments	• Federal Research center of coal and coal chemistry of SB RAS • Minig Institute of the Ural Branch of the russian Academy of sciences • National Universty of science and Technology "MISIS"/Mining Institute • Uglemetan service • Promgas • VostNII • Skochinsky Institute of mining (SIM)	Technical assistance
Stakeholder Category	Stakeholder	Role
Natural gas transmission& distribution companies	• Gazprom	Distribution and pipeline sales
Government groups	• Federal Ministry of Natural Resources • Russian Federation Ministry of energy • Russian Federal Mining and Industrial Inspectorate (Ros Tech Nadzor) • Regional administrations	Licensing Project approval Safety standarts for mines Regional environmental and safety rules requirements

Russia had 6 operational CMM utilization projects for power generation in 2015. Natural gas infrastructure and markets exist in CMM/CBM production areas. State laws keep the large gas supply at a low sales price and it is difficult for CMM projects to achieve financial viability. According to the Russian Energy Strategy for 2030, coal exports have increased 25% since 2013, however the economy's confidence in energy exports have decreased [70].

South Africa

South Africa ratified the UNFCCC and Kyoto Protocol in 1997 and 2002, respectively. Then, it adopted the Paris Agreement in December 2015. To reduce CH_4 emissions, it made policies, plans and strategies. They are the Interpreted Resource Plan (IRP), Energy Efficient Strategy, the Industrial Policy Action Plan (IPAP), the Green Transport Strategy (GTS), the Climate Change Adaptation and Mitigation Plan (CCAMP) and National Waste Management Strategy (NWMS). South Africa's Low-Emission Development Strategy (SA LEDS) 2050, takes measures in climate change and socio-economic perspectives [73].

Coal is a dominant energy resource and supplies 87% of the energy needs [73]. Medupi and Kusile coal have a significant role in energy generated with CCS, CCUS (carbon capture, utilization and storage) and HELE Technologies. HELE coal technologies include underground coal gasification, integrated gasification combined cycle, carbon capture utilization and storage, and ultra-supercritical technologies. They are significantly ahead in the future for high efficiency, low emission and cleaner coal technologies. The Organization for Economic Cooperation and Development (OECD) provides financing for them [74]. For the period post 2030, coal will account for less than 30% of the energy by 2040 and less than 20% by 2050 by decommissioning their coal plants [74].

Australia

Australia is dependent on coal and natural gas for energy production. Coal Seam Gas (CSG) contributes as a lower emissions source of energy. CSG facilities were established in Queensland and New South Wales. CSG exploration and extraction processes have impacts, such as changes in water quality, agricultural land degradation, farmers' stress and depression, and neighborhood tensions. CSG projects induce severe social and environmental impacts. In 2016-2017, 126 million cubic meters CSG were produced in New South Wales. There are two main CSG energy policies:

1. To establish compensation mechanisms for the long term impacts of CSG production by suitable policy and legislation.
2. To make further adjustments in policy and regulations.

CSG Project compensation includes land occupied (L_o) (by well heads, hardstands, roads, buried pipes), severance (S_v) (disruption of remaining land due to partial taking of the land), injurious affection (I_a) (disruption to the remaining landholders and stock due to operations and maintenance) and disturbances (D_i) (legal and professional fees, landholder's time, damages to land surfaces, crops, trees/grasses, buildings and residences). Their methods are the formulaic method, carrying capacity loss method and the rule of thumb method. The main offers for CSG Project compensation support a balanced community and industry discourse and reduces the tensions between landholders and energy firms. [75].

The Australian government's targets are reducing emissions by 28% and producing 40% energy by 2030 according to the Paris Agreement [61]. It rejected coal power plants to achieve a fossil fuel free economy by 2050. It has embraced low-carbon technologies, such as CCS (carbon capture and storage), biofuels and nuclear power plants. Emissions were reduced by 90% using CCS. The Commonwealth Scientific and Industrial Research Organization (CSIRO) sees a 30% energy savings by 2030. But, emissions will increase between 40 and 73 million $MtCO_2eq$ by 2050 [13].

The Effect of COVID-19 Pandemic

The majority of the world’s population and national economies are attached to fossil fuel usage. 80% of the main energy is fossil-based. The EU commission has a goal to better the economy by energy systems integration, climate plans and the clean energy transition as part of the COVID-19 process. Thus, it has suggested reducing by 55% GHG emissions by 2030.

Some member states have had positive developments, however some states (Austria, Denmark, Hungary, Estonia) reduced their fossil fuel subsidies during the COVID-19 pandemic. France, Greece, Poland, Belgium, Ireland, and Finland spent the most on fossil fuels subsidies. Subsidies occurred in the energy sector (EUR92 billion), industry (EUR20 billion), households (EUR17 billion), transport (EUR13 billion) and agriculture (EUR5 billion) in 2018, respectively. Fossil fuel subsidies were EUR50 billion and increased by 6% by 2018. Coal subsidies decreased by 9% and gas subsidies rose in the energy sector. Member states haven’t planned for fossil fuel subsidies due to COVID. The solar, wind and biomass renewable technologies accounted for 30%, 22% and 16% of the total energy sector subsidies, respectively [76].

Emissions from industry (2%) and power (15%) sectors declined with the EU emissions trading system (EU ETS) between 2013 and 2020. Renewable energy consumption increased 23.1% and investments were increased by market decisions. The renewable energy benefits were: reducing emissions and pollution, boosting energy independence and creating jobs. Energy poverty fell in Bulgaria, Poland, Latvia, Romania and Portugal. However, Greece was opposite case. The clean energy technologies have declined since 2012. Research and innovation (R&I) investments have also decreased. In 2020, wholesale prices have fallen and renewable penetration rose due to COVID. The EU supports energy storage technologies for the energy transition [77].

During the COVID-19 process, some countries had difficulties capturing and using CMM. CH_4 emissions and mine production decreased in 2020. CMM projects were declined and financing was difficult due to

COVID-19. China was the largest coal producer (3.75 billion tons) in the world in 2019. But, CH_4 emissions decreased in 2020 with the start of COVID-19. China's government policies have supported coal mining companies to recover and use CH_4 from active and abandoned coal mines. India's coal offtake and production fell during the lockdown in April 2020. U.S.'s coal production decreased by 29% in 2020 and 7% in 2021 as a result of COVID-19. CMM projects will be driven by Appalachian coal mines in the future. Abandoned mine methane (AMM) projects are less affected by COVID-19, but there are some delays. Poland's coal demand decreased because of COVID-19. A CH_4 drainage strategy is used for the mitigation of GHG emissions [78]. 70 participants agreed to the 29th meeting of the GMI coal mines subcommittee on 23 July, 2020. The European Commission made decisions regarding the use of CMM during COVID-19:

1. Monitoring, reporting and verifying CH_4 emissions from the coal sector.
2. Monitoring CH_4 emissions from surface mines and mine closures [78].

CONCLUSION

The CH_4 emission policy is related to energy policy. The Global Methane Initiative (GMI) was founded in 2004. It includes 43 countries. Every country must prepare a plan for CH_4 inventory, generation, abatement and reductions. The future technology choices for recovered gas are important to markets. The International Energy Agency (IEA) determined a lack of capital, ignorance of opportunities by decision-makers and some technical issues [32]. For the future, the type of energy systems will affect the ecosystem, climate change and environment. Thus, a successful energy strategy should be done for future. They are:

1. Developing energy efficiency and conservation by reducing energy and resource intensity.
2. Reducing the gap between energy demand and supply.
3. Supporting innovation and competition through research and development.
4. Reducing vulnerability to energy price fluctuations.
5. Obtaining the optimal energy mix.
6. Differentiating sources of energy supply.
7. Funding energy infrastructure development [47].

CBM resource is an important way to meet the energy demand, improve the energy mix and protect the natural environment. Many economical, geological and policy conditions affect the use and recovery of CH_4 at coal mines. They are energy prices, composition of gas flow, mine gassiness, regulatory processes, investment and institutions [65]. Methane policies and incentives include:

1. Institutional frameworks.
2. Defined gas property/ lease rights and licensing.
3. Access to power/gas markets.
4. Price of natural gas and electricity.
5. Tax incentives.
6. Mine safety requirements, sufficient technical regulations and their implementation.
7. Feed-in tariffs and obligations.
8. Environmental tax regulation and emission trading [65].

Financial policies are feed-in tariffs, tax incentives, power purchase requirements. The governments should provide education to project developers [32]. Incentives should encourage the recovery of CBM. In recent years, life cycle assessment (LCA) has been used to evaluate environmental performance and support decision-making in the mining industry. Regular monitoring of CH_4 emissions from coal mining activities should be done [8].

In this study, many methods were mentioned to reduce CH_4 emissions. They are: renewable energy sources, energy storage technologies, nuclear power plants, natural gas usage, clean development mechanism (CDM) projects, coal seam gas (CSM) energy projects, monitor and mitigation technologies, CCS, CCUS and HELE technologies. In recent years, methane hydrate has become a popular method to reduce CH_4 emissions and provide clean energy for the coming years.

Methane hydrate is a hydrocarbon energy and natural gas for the future. It is safe and economical [79]. Its exploration has many factors in major countries: economic growth potential, energy safety, infrastructure, national and international political situations and encourage a country to risk innovations, etc. The U.S. moved to promote gas hydrate program in 2000s. The U.S. Department of Energy is building plants for the next decade. EU and Turkey have resource projects around the Black Sea and North Sea [80].

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Chapter 4

Overview on Electronic Waste: Sources, Current Scenario and the Management Techniques

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Abstract

Electronic wastes are electric and electronic equipment and devices which have ceased to be useful and are being discarded. The accumulation of e-waste has become a global issue and has raised concern among the public as well as governmental bodies due to the hazardous contents within the e-wastes. In this chapter the sources and current situation of the global scenario of the electronic wastes are discussed in detail along with e-waste management strategies. The global status of e-waste pollution is one of the major concerns as deposition of electronic wastes has been growing exponentially over the years. The current progress of electronic waste management worldwide should be investigated with much focus to understand the remediation rate of the hazardous components present within the electronic wastes. The methods of extracting the precious metals from the electronic wastes include pyrometallurgical, hydrometallurgical and biometallurgical processes. This article deals with an elaborate description of the three processes with their advantages and disadvantages. Bioleaching techniques are introduced in recent research to obtain precious metal ions. The mechanisms of the bioleaching process are focused in detail with its comparison to the traditional techniques involved in management of electronic wastes.

Keywords: bioleaching, electronic wastes (E-wastes), management, metals, pollution

1. INTRODUCTION

Electronic wastes (e-waste) are the discarded electrical and electronic devices that have reached their end of life. These devices which are unfit for use are collectively specified as electrical and electronic wastes (Jang, 2010). In recent years there is an increasing number of outdated electronic products accumulating in dump yards. The exponential increase is due to the production of new electronic devices with comparatively shorter lifespans than the previous devices being replaced, with less option for repair or resale. This indicates that every time one device is upgraded, certain electronic accessories or devices are non-usable resulting in obsolescence and thus generating waste (Gabrys, 2011). E-waste waste has an impact on the ecological balance of nature in two major ways: Firstly, this results in a need for increased production which has a significant increase in mining for procurement of materials. Secondly, there is an increased quantity of e-waste collecting rapidly in the dump yard, which if not managed properly toxins will eventually seep into the soil over a period of time.

E-waste is a combination of metals comprising of precious metals, heavy metals, glass components, plastics and more and divided in three categories:

- Large appliances used in household activities which includes freezers, microwaves, refrigerators
- Information technology related digital devices such as, laptops, personal computers and monitors
- Consumer electronic accessories including televisions, digital versatile discs players, cellular phones, microwaves, watches and sports related equipment (Chatterjee and Abraham, 2017).

Along with the above-mentioned categories, printed circuit boards, batteries, cathode ray tubes and lead capacitors are some of the predominantly generated electronic wastes. The major components of electronic wastes include radioactive materials, capacitors, fluorescent lamps, ceramics, magnetrons, incandescent lamps, compressors, heating equipments, cathode ray tubes, liquid crystal displays, thermostats, batteries, rubbers, plastics and predominantly metals. Depending on the complications of handling the different components of e-wastes, they are classified in six categories, which are, (i) iron and steel, (ii) non-ferrous metals, (iii) glasses, (iv) plastics, (v) electronic materials and (vi) other miscellaneous category includes woods, ceramics and rubbers (MoEF, 2008). Medical equipment, such as, radiotherapy, cardiology and dialysis apparatus and several laboratory accessories are also considered as electronic wastes once dumped after application. Thus, according to the European Union Council along with the Directive of Parliament, all electronic wastes are minutely divided into ten distinct groups, including, large and small household devices, IT gadgets, consumer accessories, lamps, electrical tools, toys, medical apparatus, monitoring devices and dispensers (Label et al., 2005).

The electronic wastes vary are of different types. Appliances, such as, refrigerators and washing machines comprise mainly iron along with limited portions of electronic components whereas computers and their accessories involve more percentage of electronic components (Ficeriová et al., 2008). Printed circuit boards are a major kind of electrical and electronic wastes consisting of 40% metallic compounds along with plastics, ceramics and glasses. Among the metals, iron compounds constitute 45% of the printed circuit board. Apart from iron, non-ferric compounds such as copper and aluminium are predominantly found (Chauhan and Upadhyay, 2015). Existence of several emendable heavy metals including copper, aluminium, lead, nickel, zinc in electronic wastes are reported (Menad et al., 2013).

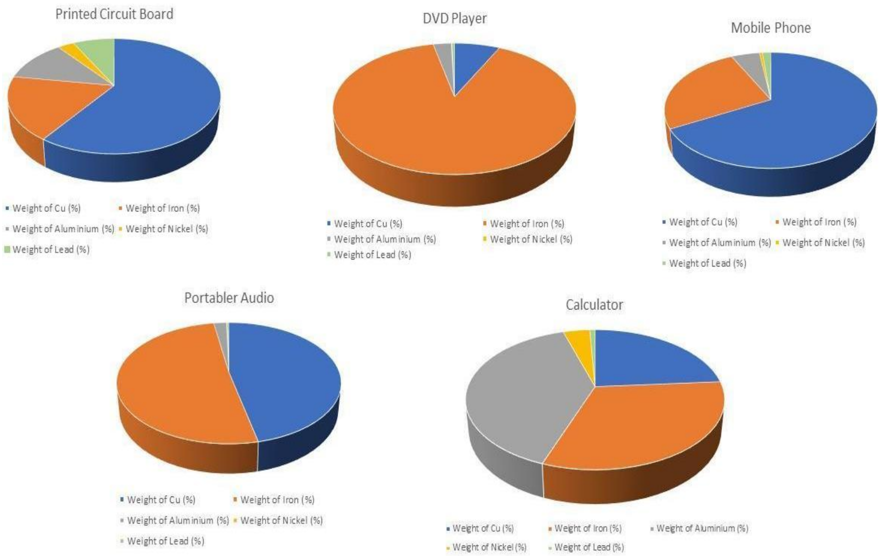

Figure 1. Percentage of weight (%) in predominantly found electronic wastes.

2. Sources and Negative Impacts of Electronic Wastes

Random deposition and haphazard disposal techniques of electronic wastes causes severe soil, air and water pollution. Pollution caused by electronic waste results in 40% of lead contamination in the landfills along with presence of several other heavy metals. Most of the electronic equipment contains hazardous heavy metals such as, lead, copper, mercury, nickel, iron, aluminium, cadmium, arsenic along with brominated flame retardants and polychlorinated biphenyls (Terazono et al., 2006). The heavy metals percolate through ground water and cause acidification in soil resulting in severe soil and water pollution. They eventually reach ponds, rivers and lakes through the groundwater. The heavy metals which are discharged from electronic wastes are assimilated by the roots of plants and accumulated in various parts of the plants which are eventually consumed by humans and animals (Luo et al., 2011). Heavy metals remain unchanged or do not undergo any modifications during natural degradation of organic wastes and thus their toxicity is not decreased with time (Olafisoye et al., 2013). Exposure of living beings to the contaminants released from e-wastes causes serious deterioration of kidneys, lungs, nervous system, brain development, heart and liver (Pandit, 2016). Most of the time, the hazardous metal content of electronic wastes reaches human beings due to their consumption of the contaminated devalued food. However, the heavy metals can also be exposed to humans via working in e-waste recycling areas, absorption through skin and inhalation of residents in and around e-waste dumping zones (Tang et al., 2010). Burning of the electronic wastes is applied at some places as a disposal approach. However, along with burning the wastes, noxious gases and cancer causing dioxins are discharged in air resulting in air pollution (Global, 2018). Increased concentrations of dioxins are responsible for cancer and deterioration in development of growth in infants (Bhutta et al., 2011).

3. Global Status of E-Wastes Pollution

The worldwide business related to electronic waste depends on the intra-regional trade between Americas, Europe and Asia (Lepawsky and McNabb, 2010). The United Nations Environment Programme has reported that in a year around 90% of the electronic waste globally is either traded via illegal means or dumped in open areas. Several countries in Asia and Africa, such as China, India, Pakistan, Vietnam, Nigeria and Ghana are considered as the focal point of illegal electronic waste (Nichols, 2015). The labor cost of electronic waste recycling in developing countries is much lesser than the developed countries. Also, in the developing countries there are no strict regulations in management of electronic wastes. In order to avoid the high labor costs and harsh regulations, developed countries export their generated e-wastes to the developing countries. It has been reported that almost 80% of electronic waste which is produced in western side of the United States of America are transported to Asia for their management, among which, China receives around 90% of the electronic wastes which in turn increases the count of e-waste present in China. Also, 70% of electronic waste found in New Delhi, India, is shipped from the developed nations (Schmidt, 2002; Schmidt, 2006). According to a collaborative effort by the United Nations University, International telecommunication Union along with The International Solid Waste Association, the count of e-waste generation across the world was 44.7 million metric tonnes (6.1 kg/individual) in 2016. In the year 2014, the amount of e-waste was 5.8 kg/individual. Thus, the study assumed that by the end of 2021, the electronic waste will be 52.2 million metric tonnes (equivalent to 6.8 kg/individual) in all countries combined. In comparison to all the continents, Asia is the largest producer of electronic wastes followed by Europe, America, Arica and Oceania. 40.7% of the global production of e-waste is generated from Asia (Balde et al., 2017). The United Nations reported that by the year 2020, electronic wastes generated from old and used computers would increase by 400% and 500% when compared to the e-waste generated in 2007 by China and India respectively. Currently, among the individual countries, United States of America and China are the two leading producers of electronic wastes, generating around 3 million tonnes and 2.3 million tonnes of e-wastes (Secretariat, 2011).

Predominantly found electronic wastes in disposal areas are television panels, computer motherboards, cellular phones, calculators and digital versatile disc, which consists of around 4-62% of iron, 2-15% of aluminium and 3-18% of copper along with trace amounts of gold, silver and palladium (Fornalczyk et al., 2013). Study regarding e-waste contamination and release of potent heavy metals from electronic wastes in Guiyu, e-waste disposal area in Chaoyang District in Southeast zone of China, revealed that soil sediments were contaminated with copper, nickel, lead, zinc and chromium. All the heavy metals were present beyond permissible limits. Concentration of copper in the open burning sites was found in excessive amounts, ranging from 1374 to 14,253 mg per kg of soil sediments (Wong et al., 2007). Copper, iron, nickel and lead are the most commonly found heavy metals in electronic wastes (Gramatyka et al., 2007).

4. STATUS OF INDIA IN E-WASTE GENERATION AND E-WASTE POLLUTION

In the recent past, India is widely exposed to the idea of consumerism leading to application of several electronic goods along with their fast replacement. The constant change in technologies and wide acceptance of the consumers to the newly produced electronic goods results in obsolescence of a product. With the increasing rate of electronic waste across the globe, India ranks as the 5th largest electronic waste producer. National waste electrical and electronic equipment task force evaluated in 2005 stated that, the total count of electronic waste would be around 146,000 tonnes annually. However, the central pollution control board examined the production of e-waste in 2005 and reported it to be 134,700 lakhs metric tonnes (Borthakur and Sinha, 2013). An estimation assessment regarding generation of e-waste revealed that by the end of 2020, India will produce e-wastes from mobile phones 18 folds higher (Perkins et al., 2014). India's production of e-waste might increase to 52 lakh metric tons from 18 lakh metric tons annually after 2020 which is calculated to be a 30% increase in the compound annual growth rate. Among the discarded electronics, 70% of e-waste is computers and their accessories, 12% being telecommunication instruments, 8% of electrical appliances and 7% accounts to medical apparatus. It has been reported that

82% of the unwanted dumped electronic products belong to the group of personal devices (Bandela, 2018). However, most of the e-wastes are not recycled in the country and are dismantled and disposed of by the scrap dealers (Pandit, 2016). According to the Ministry of Environment and Forests, most of the e-wastes are produced from Maharashtra followed by Tamil Nadu and Andhra Pradesh. Uttar Pradesh, West Bengal, Delhi along with Karnataka, Gujarat, Madhya Pradesh and Punjab. Maharashtra is the highest producer of e-waste producing up to 20270.6 tonnes of waste in a year (MoEF, 2008).

According to a survey administered by Environmental Performance Index (EPI) in the year 2014 regarding management of environmental pollution, it declared that among 178 countries across the world, India holds its position at 155. India lacks a proper guideline regarding management of e-wastes. Common citizens including e-waste management laborers are not aware of the basic rules and regulations to be maintained in order to prevent contamination and release of pollutants from e-wastes. Also, the facilities and infrastructure present for recycling the wastes are insufficient for management of huge quantities of e-wastes (Kumar and Karishma, 2016). The formation of a strategy for management of e-wastes is difficult mainly because of the inadequacy of dependable evidence. Due to lack of a proper system, barely 10% of the dumped electronic equipment is destined for the recycling process. Moreover, in India, electronic waste recycling groups are handled by non-governmental administrations for business purposes and not by governmental bodies (Joseph, 2007).

Heavy metal pollution due to extensive exposure of electronic waste in the environment has become a serious threat to nature. According to a report, water and soil in Delhi, India is polluted with hazardous heavy metals like copper, lead, nickel, chromium, cadmium and zinc due to haphazard disposal of used electronic equipment. Copper and lead are present in high concentrations in the soil. Mostly, top soil is contained with a high amount of copper because copper is acquainted with organic compounds and their oxides and thus remains as a superficial layer on the soil rather than percolating. Printed circuit boards (PCBs) are one of the major electronic wastes that are dumped in large quantities in the environment. PCBs contain copper and lead to a large extent which is ascertained by the increased concentration of these two heavy metals in electronic wastes dumped areas (Panwar and Ahmed, 2018). Batteries are also a serious threat to the environment since they consist of large quantities of heavy metals and are readily leached into soil and water bodies (Bajestani et al., 2014).

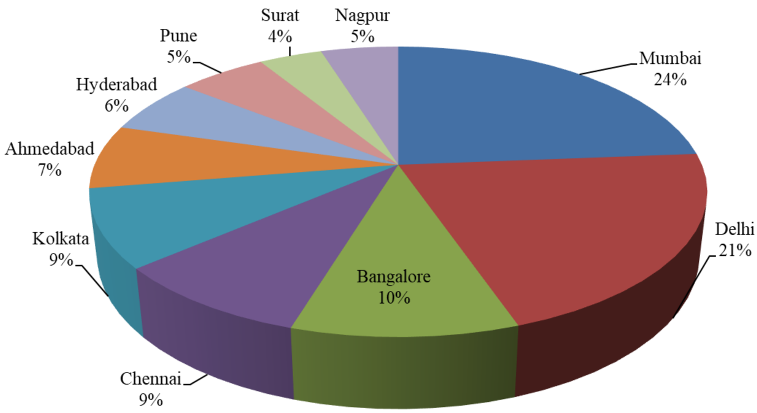

Figure 2. Statistics of E-waste generation in different cities of India.

The predominant problems in reducing the pollution caused by electronic wastes are explained below:

- Immense quantity: The short lifespan of electrical appliances along with rise in demand for the recent technologies result in newer versions of electronic devices thereby increasing the number of devices discarded.
- Heavy metals content: This type of waste is considered to be the most hazardous group due to the presence of large amounts of heavy metals which once dumped in the landfills leach into the surrounding environment thus polluting the entire area.
- Complex designs: Various toxic and non-toxic materials are combined while designing electronic equipment. However, during recycling, it becomes extremely tedious and labor intensive in separating the components.

- Poor financial support: The conventional techniques to recycle electronic wastes require huge amounts of money which many under-developed countries are unable to afford. Thus, the cost of the management procedure plays an important role in the hindrance of recycling electronic wastes.
- Inadequacy of proper regulations: Effective enforcement or appropriate regulations are not applied in most of the countries (Lundgren, 2012).

5. Progress in E-Waste Management through Metallurgical Processes

Metallurgical processing involves pyrometallurgy, hydrometallurgy and electrometallurgy. Among which most frequently implemented for metal recovery is pyrometallurgy and hydrometallurgy. In this section aspects of the metallurgical process are being discussed. A background on the principle is provided. Then a brief comparison to hydrometallurgy and electrometallurgy is detailed and how this can be utilized in e-waste management. E-waste recovery begins with physical separation processes, which includes disassembly, density separation, and magnetic separation, separation of metals and non-metals from e-wastes. This is subsequently followed by metal recovery processes through pyrometallurgy, hydrometallurgy, and biometallurgy which is being discussed in depth.

5.1. Pyrometallurgical Process

Pyrometallurgy is a process of extraction or recovery of metals using high temperatures above 1000C resulting in chemical reactions in the absence of aqueous solutions. This involves heating under high temperature in a plasma arc furnace or blast furnace, dross formation, sintering, melting, and reactions in a gas phase at high temperatures (Cui, Jirang and Roven, 2011). This process occurs entirely from the exothermic nature of the chemical reactions taking place, usually oxidation reactions. However, energy must be added to the process by combustion of fuel or, in the case of some smelting processes, by the direct application of electrical energy. Metals like Cu, Zn, Pb can be extracted by this process. However, metals like Al, Fe cannot be recovered by this method as they are oxidized to metal oxides and form large amounts of slag.

In pyrometallurgy the most important process involving heat are roasting, smelting and refining. Roasting is a process of heating where ores are converted to oxides. Reduction of metal oxide ore is accomplished by the process of smelting. It is a process which involves metal rich phase known as matte along with gangue which is impurities in metal ore. Smelting is used in reducing iron ores, tin copper and lead ores etc. in blast furnaces. Followed by pyrorefining process which involves removal of impurities from the metal.

Anderson (2016) has stated that pyrometallurgy will continue to dominate the field of extractive metallurgy for copper and iron ore. It has also been recorded by Anderson 2016 that a combination of the use of hydrometallurgical processes would be effective in the case of low-grade ores or complex concentrates with abundant impurities.

Pyrometallurgical process is used in E-waste recovery: In e-waste it is mainly used to recover valuable metals which are non-ferrous in nature. As pyrometallurgical method involves application of high temperature, incineration and smelting, printed circuit boards are treated using the application of smelting for recovering copper and gold. Any form of scrap can be treated with pyrometallurgical methods. Pyrometallurgy, when combined with electrolysis, is efficient in recovering copper from electronic wastes (Ghosh et al., 2015). This is an old process of recovery of e-waste, the technique has certain disadvantages. Printed circuit boards contain plastics and other materials which are flammable when exposed to high temperature along with release of toxic, carcinogenic substances (Kamberović et al., 2018). The process requires a high amount of energy for completion.

5.2. Hydrometallurgical Process

This is a process where aqueous solutions are used to extract metals from ores. Hydrometallurgy, also referred to as chemical leaching, is mostly used in recovery of heavy metals. Hydrometallurgical method was first reported in the year 1907 in Serbian mine Bor where 200 tonnes of copper were recovered using this technique (Kamberović et al., 2018). In the hydrometallurgical process there are two main stages called Leaching or lixiviation where there is transfer of metals from the solid matrix to the aqueous phase. But undesired contents are also found in the solution other than the metal of interest. In the second phase the separation of desired metal from the undesired elements leach liquor is removed. Some of the most useful hydrometallurgical methods for separation of metal ions from leachates are solvent extraction, ion exchange, and precipitation.

The principal advantage hydrometallurgical process has over pyrometallurgy is the low capital cost and is more environmentally friendly. When compared to pyrometallurgy only a fraction of hazardous gases are released into the environment. However, there is expulsion of large amounts of wastewater after the desired metals have been removed. One of the major disadvantages is the process time required to recover the metal as it is often carried out at lower temperatures than other extractive processes.

Hydrometallurgical Process of E-waste recovery: Hydrometallurgy involves application of acid, alkalis or ligands to enhance complexation. Three important steps are attempted to extract metals using hydrometallurgy: (i): preliminary treatment of the waste collected, (ii): metals leaching using an appropriate solvent and (iii): purification and recovery of the metals (Tuncuk et al., 2012). Various types of solvents, such as, cyanide, halides, thiourea, thiosulfate, sulfuric acid, hydrochloric acid, aqua regia, nitric acid, sodium hypochlorite, oxalates, ethylenediaminetetraacetic acid, copper chloride and ferrous chloride are used in accomplishment of the hydrometallurgical process (Pant et al., 2012).

5.3. Electrometallurgy

This process is of using electrical energy through electrolysis and producing metals. Metals generally extracted through these processes are copper, aluminium etc. There are four categories to this process, which are: 1. Electrowinning recovery of metals from ores from aqueous solution. Copper and zinc are the main metals extracted by this process. The anode plays as an inert electrical conductor and the metal of interest is placed on the cathode. 2. Electrorefining is removing impurities in the metal in other words, purifying the metal by the process of electrolysis to high purity. Electrorefining is a process which has gained recognition for recycling of metals. Both electrowinning and electrorefining are performed in electrolytic cell. 3. Electroplating is a process of coating an inferior metal over a superior metal, layering one over the other. This is done to mask the inferior metal from corrosion. 4. Electroforming forming thin metal parts.

Among the three types of metallurgy, pyrometallurgical method and hydrometallurgical method are used for metal recovery from e-waste, however hydrometallurgy technique is more advantageous from an environmental point of view.

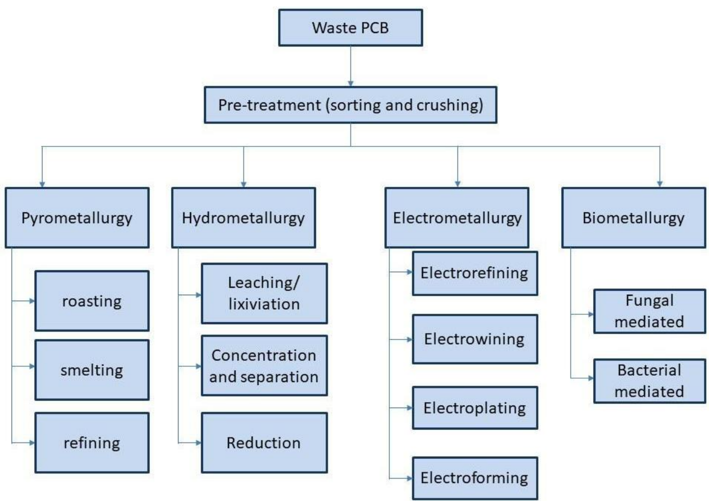

Figure 3. The different processes of electronic waste management.

Table 1. Comparative study among the metallurgical processes of E-waste management

Sl. No.	Factors	Pyrometallurgy	Hydrometallurgy	Electrometallurgy
1.	Principle	When impurities have more affinity to oxygen than metal itself. Uses thermal processes at high temperature	Elecro-positive metal can displace electro-less electropositive metal from aqueous salt solution. Uses aqueous solution	Electrolytic process using electrical energy
2.	Recovery Speed	Fast	Slow	Moderate
3.	Readiness of Technology	Optimal technology readiness	Good technology readiness	Good technology readiness
4.	Relative energy requirement	High energy consumption	Moderate energy consumption	High energy consumption
5.	Level of recovery	Low	High recovery efficiency	Moderate level of recovery
6.	Level of purity	Low	High	High
7.	Initial capital investment	High	Low	Intermediate
8.	Production cost	Low, cost of raw materials and reducing agents is low	Intermediate	High
9.	Waste generated by the process	Hazardous gas emission and dust. Material loss in slag	No gaseous emission, Waste liquor produced, can be recycled	Solid and gaseous waste
10.	Application	Fe, Zn, Pb, Cu, Al, Mg	Zn, Cu, Al, and valuable metals can be recovered	K, Na, Mg, Al, No. of valuable metals can be recovered

5.4. Progress in E-Waste Management Using Biometallurgy

Apart from the above-mentioned traditional techniques, biological techniques (specifically biometallurgical processes and bioleaching) have become a well-established pathway for management of electronic wastes. The application of microorganisms in extraction of metals from their sources is named as bioleaching or biometallurgical process. The solid electronic wastes are converted into simpler forms which are soluble in water and can be recovered later from water. In China, at around 100-200

BC leaching of copper from its ores was achieved using precipitation which was also followed in Europe and Asia in later generations. Although these practices were conducted, utilization of microorganisms in accumulation of heavy metals was not much explored till 1940. There was a gradual increase in the application of heavy metals tolerant microbial cells for recovery of heavy metals from their sources (ores or electronic equipment). However, the appropriate mechanism of the microbes in accumulation of metal ions is continuing to be explored (Mishra et al., 2005). The major advantages of bioleaching are reduced cost and energy requirements, environment friendly nature and ability to extract metal from poor grade electronic wastes (Wu et al., 2018).

Table 2. Heavy Metal tolerant Microorganisms

Sl. No.	**Type of Microorganism**	**Name of the Microorganism**	**Heavy metals able to tolerate**
1.	Actinomycetes	*Streptomyces* sp. MC1	Chromium
2.	Bacteria	*Deinococcus radiodurans*	Lead, cadmium
3.	Bacteria	*Escherichia coli*	Copper, cadmium
4.	Bacteria	*Pseudomonas* sp.	Zinc
5.	Bacteria	*Bacillus cereus* strain RC-1	Copper, Zinc, Cadmium, Lead
6.	Bacteria	*Micrococcus* sp.	Chromium and nickel
7.	Yeast	*Saccharomyces cerevisiae*	Copper, Cobalt, Cadmium, Manganese
8.	Fungi	*Neurospora crassa*	Cobalt, Nickel
9.	Fungi	*Aspergillus versicolor*	Copper, chromium, nickel
10.	Fungi	*Aspergillus* sp.	Chromium and nickel Lead, cadmium, copper, mercury, zinc, manganese
11.	Fungi	*Amanita muscaria*	Chromium and nickel Lead, cadmium, copper, mercury, zinc, manganese Lead, cadmium, copper, mercury, zinc, manganese
12.	Fungi	*Amanita rubescens*	Lead
13.	Fungi	*Amanita vaginate*	Lead, cadmium, copper, mercury, zinc, manganese
14.	Fungi	*Hypholoma fasciculare*	Lead, cadmium, copper, mercury, zinc, manganese
15.	Fungi	*Russula foetens*	Lead, cadmium, copper, mercury, zinc, manganese
16.	Fungi	*Russula cyanoxantha*	Lead, cadmium, copper, mercury, zinc, manganese

Several bacterial and fungal strains have been reported to be used in bioleaching processes. In order to extract metals from electronic wastes, most of the microorganisms follow acidolysis, redoxolysis as well as complexolysis. Sulfur and iron oxidizing bacterial isolates oxidize metal ions from the electronic wastes depending on two different mechanisms (direct and indirect). The bacteria oxidize ferrous form to ferric thus forming a powerful oxidizing agent. Oxidation of sulfur also occurs to produce sulfuric acid which in turn metabolizes the metal ions (Beolchini et al., 2012). Cell-free supernatants of *Leptospirillum ferriphilum* and *Sulfobacillus thermosulfidooxidans* have been used to recover copper from printed circuit boards in a recent study conducted by Wu et al. in 2018. Other acidophilic bacteria, like, *Acidithiobacillus ferrooxidans*, *Leptospirillum ferrooxidans*, *Acidithiobacillus thiooxidans*, *Sulfolobus* sp. etc. are able to dissolve metals from electronic wastes at a pH range of 2-4 (Mishra and Rhee, 2010). Pradhan and Kumar (2012) reported that *Chromobacterium violaceum*, *Pseudomonas aeruginosa* and *Pseudomonas fluorescens* are capable of solubilization of metals from electronic wastes. The organisms were capable of leaching out copper, gold, zinc, iron and silver. The activity of *Sulfobacillus thermosulfidooxidans* in leaching heavy metals from electronic waste proved the organism to be an efficient bioleaching agent which is able to recover nickel, copper, zinc and aluminium along with trace amounts of lead and tin (Ilyas et al., 2007). Apart from bacteria, fungal strains, such as, *Aspergillus niger* and *Penicillium simplicissimum* leaches out copper, tin, aluminium, nickel, lead and zinc from the electronic wastes. The strains were able to lixiviate copper and tin by 65% whereas the other heavy metals were extracted till 95% as reported by Brandl et al. (2001). Along with these metals, several strains of *Aspergillus niger* are reported to extract gold from mobile phones and computer motherboards (Madrigal-Arias et al., 2015). However, efficiency of several other fungal strains is yet to be explored in leaching of heavy metals from electronic wastes. Microorganisms which produce organic acids have a significant role in the bioleaching process. Organic acids bind with the metal ions to form complexes and thus chelate the metals from their sources (Liaud et al., 2014). The acidolysis mode of bioleaching by the microbes is dependent on the production of organic acids by the strains since in this process organic acids protonate the oxygen atoms thereby leaching out the metal ions. Thus, briefly, the fundamentals bioleaching of heavy metals by microorganisms includes three important criteria: (a) reaction involving oxidation reduction, (b) synthesis of organic as well as inorganic acids and (c) discharge of primary and secondary metabolites and chelators by the microbial strain (Priya and Hait, 2017).

5.5. Application of Microbes in Electronic Waste Management: Bioleaching

Bioleaching is the process of heavy metals mobilization from electronic wastes via dissolution of metal ions from the waste; complexation and oxidation reactions are carried out using microorganisms (Jin et al., 2018). Bioleaching has various advantages over the conventional methods of extraction of heavy metals, such as, easy process, no complicated instruments are required, low energy consumption and most predominantly non-hazardous to the environment. However, since the time consumption during bioleaching is more than chemical processes of leaching, more studies are required to be conducted in this field in order to develop a less time consuming process (Karwowska et al., 2014).

Heavy metals present in the e-wastes react to the extracellular enzymes, such as, laccase, manganese peroxidase and lignin peroxidase, produced by microorganisms and are known for their inhibitory activity for enzyme production. The extracellular enzymes are perpetually surrounded by heavy metals in the environment, hence, are capable of existence in presence of heavy metals. These enzymes are not guarded by any metal detoxification arrangement which enhances their tolerance capacity towards heavy metals (Baldrian, 2003).

Microorganisms produce certain proteins and peptides which are capable of metal binding, such as metallothioneins and phytochelatins. Siderophores are also secreted by microbes which enhance the tolerance of microbes towards heavy metals. The primary function of siderophores is to interact with iron and chelate the iron ions. Thus, siderophores aid in the uptake of iron from microbial surroundings. Along with iron, siderophores can also chelate copper, cadmium, lead and aluminium. Some of the siderophore producing bacteria are *Staphylococcus* sp., *Pseudomonas* sp., *Arthrobacter* sp., *Serratia marcescens*, *Agrobacterium tumefaciens*, *Rhodococcus* sp. etc. (Rajkumar et al., 2010). Among fungal groups, *Lichtheimia corymbifera*, *Rhizopus pusillus*, *Rhizopus microspores* and *Rhizopus arrhizus* are reported to produce siderophores (Larcher et al., 2013).

Secretion of organic acids by microorganisms plays a compelling role in remediation of heavy metals. Organic acids are low molecular weight compounds able to solubilize the heavy metal ions (Ojuederie and Babalola, 2017). The solubilization of heavy metal ions by organic acids can be achieved in the following ways: exchange of heavy metal ions with ligands, dissolution of metal oxides and complexation of organic acids with metal ions. In a previous study, the effectiveness of four organic acids, acetic acid, oxalic acid, citric acid and succinic acid were checked for removal of copper, lead and zinc from metals contaminated soil. All the organic acids showed prominent remediation capacity (Kim et al., 2013). Organic acids act as electron donors for reduction of toxic heavy metal ions into soluble forms (Wood et al., 2016).

Table 3. Production of Siderophores by Microorganisms and their Activity in Heavy Metal Remediation

Sl. No.	Name of the Microbe	Siderophore produced	Uptake of Heavy metal	References
1.	*Streptomyces tendae* F4	Desferrioxamine B, Desferrioxamine E, Coelichelin	Cadmium	Dimkpa et al., 2009
2.	*Streptomyces acidiscabies* E13	Desferrioxamine B, Desferrioxamine E, Coelichelin	Aluminium, copper, iron, manganese, uranium, nickel	Dimkpa et al., 2009
3.	*Pseudomonas aeruginosa*	Pyoverdine, Pyochelin and Alcaligin E	Chromium and Lead	Braud et al., 2009
4.	*Pseudomonas putida* KNP9	Pyoverdine	Lead and Cadmium	Tripathi et al., 2005

Bioleaching can be conducted following two modes: direct leaching and spent medium bioleaching. In case of direct mode, the electronic wastes are introduced into the medium at the initial phase, that is, during the inoculation process. However, during the spent mode of bioleaching (indirect bioleaching), the process occurs in two phases. In this process, the electronic wastes are added to the spent medium containing organic acids produced by the organisms to leach out the heavy metals (Valix, 2017). Bioleaching activity of bacteria, such as, *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, *Leptospirillum ferrooxidans* and *Sulfolobus* sp. and fungi, like *Aspergillus* sp. and *Penicillium* sp. have been reported earlier (Kavitha, 2014). Although there are detailed reports with application of bacterial isolates on bioleaching, pertinence of fungal strains for extraction of heavy metals has to be explored.

Table 4. Application of Microbes in Bioleaching of Heavy metals from Electronic Wastes

Sl. No.	**E-waste**	**Type of Microbe**	**Name of the Microbe**	**Heavy metals extracted**	**References**
1.	Printed circuit board	Bacteria	*Acidithiobacillus thiooxidans*	Copper, zinc, nickel, cadmium, lead, chromium	Karwowska et al., 2014
2.	Copper and gold boards	Bacteria	*Chromobacterium violaceum*	Copper and Gold	Natarajan and Ting, 2014
3.	Copper and gold boards	Bacteria	*Pseudomonas fluorescens*	Copper and Gold	Natarajan and Ting, 2014
4.	Printed circuit board	Bacteria	*Pseudomonas aeruginosa*	Copper, Iron, Gold, Silver, Zinc	Pradhan and Kumar, 2012
5.	Scrap television circuit board	Bacteria	*Acidithiobacillus ferrooxidans*	Copper, Iron	Bas et al., 2013
6.	Scrap television circuit board	Bacteria	*Leptospirillum ferrooxidans*	Copper, Iron	Bas et al., 2013
7.	Scrap television circuit board	Bacteria	*Acidithiobacillus thiooxidans*	Copper, Iron	Bas et al., 2013
8.	Printed circuit board of mobile phones	Fungi	*Aspergillus niger*	Copper, gold, nickel, zinc, cadmium, lead	Madrigal-Arias et al., 2015

Conclusion

Detailed information regarding global and national status of e-waste generation has been discussed in the chapter. The availability of the e-wastes and its components in the environment depicts the pollution caused by the e-wastes in recent days. The traditional recovery processes employed for management of e-wastes are observed to have some drawbacks and they are failing to manage the rise in e-waste concentration. Thus, biological methods are suggested to avoid the e-waste pollution. The application of microbes helps in declination of the toxic metals and chemicals thereby resulting in a clean environment. Hence electronic wastes recovery in combination with traditional recovery methods of pyrometallurgical method, hydrometallurgical method with biometallurgy will be more successful in recovery of precious metals.

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Chapter 5

The Application of Electrochemical Technology in VOCs Removal

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Abstract

Volatile organic compounds (VOCs) is a kind of pollutants mainly produced by human production and living. At present, there are many ways to remove VOCs in industry, such as electrochemical method, adsorption, absorption, heat treatment, biological treatment, photocatalysis and so on. Among these methods, electrochemical technology, as a new VOCs treatment technology, has been considered as a god choice for VOCs removal. The electron is used to realize the oxidation and reduction of substances in electrochemical technology, which can easily control electron potential and current density. This method has been applied to VOCs removal by many researchers. Different types of VOCs could be removed due to the difference of electrode materials and catalysts, and the efficiency of removal is also

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different. This chapter is based on research achievements of recent years, and we reorganized the concrete application of electrochemical technology, discussed the influence of electrochemical battery electrolyte, electrodes, the reaction product and current density on the removal of VOCs. The relevant literature data is collected for comparative study. The electrochemical technology is also compared with other treatment methods. This is of strategic significance for the effective and extensive application of electrochemical technology in industrial VOCs removal.

Keywords: volatile organic compounds, electrochemical technology, removal

INTRODUCTION

VOCs is the abbreviation of volatile organic compounds. According to the definition of WHO, VOCs are all kinds of organic compounds with boiling point of 50℃ to 260℃ at room temperature. It mainly comes from coal chemical industry, petrochemical industry, fuel coating manufacturing, solvent manufacturing and application, etc. Most VOCs have uncomfortable special smell, toxicity, irritation, teratogenicity and carcinogenesis, especially benzene, toluene and formaldehyde, which will cause great harm to human health. Therefore, the processing of VOCs has become one of the most popular topics in recent years.

Electrochemical treatment of VOC has been thought as one of the potential means for gases pollution removal, which is widely used in the treatment of VOCs. Electrolytic cell is a device that converts electric energy into chemical energy. Electrolysis is a process in which the current passes through the electrolyte solution (or molten electrolyte) and causes redox reaction at the cathode and anode. The galvanic cell is a device that converts chemical energy into electrical energy. The oxidation and reduction of VOCs in electrolyzers and primary cells are based on the oxidation and reduction of different VOCs. Different types of electrolytic cells have been used to deal with different types of VOCs.

In this article, electrochemical treatment technology for VOCs removal is classified according to electrolysis and other methods. In the same battery structure, different catalysts and electrode materials for different types of VOCs adsorption/absorption were compared. The current period, the application and advantages of electrochemistry in the treatment of VOCs are summarized.

In addition, we also summarized some other methods involving electrochemistry used in the treatment of VOCs, such as spark discharge, plasma and other emerging electrical treatment technologies. We also compared and analyzed these methods horizontally, so as to better understand their application in electrochemical treatment of VOCs.

THE APPLICATION OF ELECTROCHEMICAL TECHNOLOGY FOR VOCS REMOVAL

The Application of Electrolysis in VOCs Removal

In 2021, Yang and colleagues (Yang et al. 2021) used an electrochemical method to treat 10-trichloroethyl phosphate (TCEP). A foamed copper was used as the cathode, and Pt as the anode with an electrolyte of 10 mM Na_2SO_4. It was found that foamed copper has higher catalytic performance and faster TCEP (tris(2-chloroethyl) phosphate) degradation rate compared with other materials. And the author found that electrochemistry is faster and more stable than other methods in removing TCEP. Moreover, the toxicity of reaction products and intermediates was reduced in this process.

In 2020, Safarvand et al. (Safarvand et al. 2020) studied a new technology to strengthen the electron transfer in the photoelectrocatalytic (PEC) degradation process of BTEX (benzene, toluene, ethylbenzene and xylene). The experiments were achieved by using a photoanode, which was a highly active material made of $CuO/Cu_2O/TiO_2$(CCT) nano-hybrid. And the cathode was a MWCNT/GO/Gf (MGGF). The characteristics of the electrode were studied. Tested the mineralization of BTEX through various reactions such as COD (chemical oxygen demand) and specific energy consumption. It was found that when the reaction condition is optimal, the removal rate of COD could reach 81.3%, CCT and MGGF had high activity and strong stability for PEC. Ruan et al. (Ruan et al. 2020) used MgO cathodes and graphene-metal oxide (Mn-Ce bimetallic oxide) to improve the removal performance of toluene in pulsed discharge plasm (PDP). It was found that magnesium oxide cathode can increase the density of high-energy electrons, so it has an enhanced effect on the removal of toluene. Besides, according to the results of experiments, the graphene-metal oxide system has no significant effect on toluene removal, and a large amount of underutilized O_3 was found in the product. Then they introduced the Mn-Ce(8:1)/rGO (reduced graphene oxide) catalyst into the system to crack O3, and found that it is beneficial to the decomposition of residual toluene. In the same year, Lou and coworkers (Lou et al. 2020) researched the electrocatalytic activity of Bi. They took alachlor as the research object and studied the catalytic activity of Bi electrode on it under different experimental conditions. Its properties were characterized by cyclic voltammetry. The results showed that the bismuth electrode showed high electrocatalytic activity and high selectivity.

In 2019, Wan-Cho et al. (Cho et al. 2019) used electrochemical advanced oxidation method to treat VOCs (chloroform, benzene, trichloroethylene and toluene). They studied the removal effect of VOCs by electrochemical advanced oxidation method under static stirring and aeration conditions. Four kinds of stable anodes: Pt/Ti, IrO_2/Ti, IrO_2-Ru/Ti and IrO_2-Ru-Pd/Ti were compared to screen the best removal efficiency. They found that more than 90% of VOCs were removed in sufficient air. Among the four anodes, IrO_2-Ru/Ti anode showed the highest VOCs removal efficiency, which could reach more than 98% within one hour with a lowest volatilization rate (less than 5%). It showed that IrO_2-Ru/Ti anode has excellent electrocatalytic activity and should be a good electrode material. Rodrigo's team (Muñoz-Morales et al. 2019) proposed a new process concept for the treatment of perchloroethylene in gaseous wastewater in 2019. They used methanol solution containing sodium chloride and sodium hydroxide as electrolyte, electrolytic aluminum tetrachloroethylene. The results show that this process could be used to treat gaseous wastewater containing volatile chlorinated hydrocarbons. And the author believes that this technology can be combined with activated carbon adsorption to treat wastewater contaminated by volatile organic compounds.

A new method for toluene degradation was proposed by Yao et al. (Yao et al. 2019) in 2019. They used metal oxides as cathodes (MgO/NiO/Ni and NiO/Ni cathodes), which were modified to emit secondary electrons to ignite corona discharges. The results showed that the discharge current of MgO/NiO/Ni cathode and NiO/Ni cathode is higher than that of Ni. In addition, the secondary electrons emitted by the oxide cathode are more effective for toluene degradation. They believe that the secondary electrons generated by the cathode could significantly increase the current, and discharge the gas, thus improving the degradation performance of toluene.

In 2018, Cho and colleagues (Cho et al. 2018) thought that dimensionally stable anode (DSAs) is an effective method for the treatment of VOCs in industrial wastewater, because the anode can reduce the volatile components in the treatment of liquid VOCs. They applied four kinds of composite materials with high electrocatalytic activity on Ti plate to evaluate the removal effect of each DSA on VOCs. The four materials are Ir, Ir-Pt, Ir-Ru and Ir-Pd, respectively. At the same time, the current density and electrolyte concentration were changed to determine the best catalytic conditions. The electrolyte is the waste water solution containing pollutants such as chloroform, benzene, toluene, trichloroethylene, etc. Ir was added as the basic catalyst to maintain the electrochemical stability of the anode. The results showed that chloroform is the most difficult organic substance to degrade. Compared with the other three materials, Ir-Pd/Ti anode has the strongest oxidation capacity on VOCs, and the oxidation rate of $CHCl_3$ reaches 78.8%. The using of DSAs as the anode is simple and stable, and the volatile fraction of VOCs is less than 5%, which is an impressive number.

In 2019, Zhang and Chen et al. (Zhang et al. 2019) carried out electro oxidation of indoor low concentration gaseous benzene in all solid state battery. Sb-SnO_2/Ti was used as anode and Pt/RGO/CFP as cathode. With the increase of nano coating loading (Sb/Sn¼14.0 mol%), the conversion of benzene increased continuously with a high reaction rate. They provided a method to remove low concentration VOCs indoor effectively. Zhang et al. (Zhang et al. 2018) carried out a work of electrocatalytic treatment of VOCs at the gas-solid interface at room temperature. They used a membrane electrode assembly (MEA) to form an all-solid state battery. Titanium and carbon supported platinum were used as anode and cathode, respectively, and antimony doped SnO_2 was applied as a catalyst on the anode for the treatment of benzene, toluene and o-xylene (BTX). The results showed that most of BTX is converted to CO_2 and some to CO within four to five hours, and no organic by-products are produced. Therefore, MEA was thought a promising equipment to treat low concentration gaseous BTX at room temperature. An's team (Liu, Sun, et al. 2018) used nickel-doped graphene as the cathode, Pt as the counter electrode, and Ag/AgCl as the reference electrode for the electrochemical dechlorination treatment of groundwater containing perchloroethylene (PCE). It was found that the removal rate of PCE after doping with nickel is significantly higher than that before doping.

In 2017, Pillai et al. (Pillai, Muthuraman, and Moon 2017) used carbon as the cathode and platinum as the anode to electro-reduce the epichlorohydrin (ECH) by adding 1 mol/L of $[Ni(II)(hmc)]^{2+}$ to the NaCl aqueous electrolyte. It was found that Ni(II)/Ni(I) redox reaction occurs during this process, forming $[Nickel(I)(hexamethylcyclam)]^{+}$ ($[Ni(I)(hmc)]^{+}$). The results showed that $[Ni(II)(hmc)]^{2+}$ has high catalytic efficiency and good stability for ECH.

In 2016, Wang et al. (Wang et al. 2016) used Ti/IrO_2 as anode and Cu/Zn as cathode to electrolyze chloroform in 0.05mol/L NaH_2PO_4 containing $CHCl_3$, and the characterizations were conducted by cyclic voltammetry and paired electrolysis. The results showed that an environmental pH of 4.6 was favorable to the removal of $CHCl_3$. When the surface area ratio of anode to cathode was 2.0, the reduction effect of chloroform was the most significant. Finally, they found that the electrocatalytic activity of Cu/Zn cathode was not much different from that of Ag electrode, and Cu/Zn electrode had the advantages of low cost and long activity duration compared with Ag electrode. Li et al. (Li et al. 2016) investigated the removal efficiency of BTEX (benzene, toluene, ethylbenzene, xylene) by electrolytic oxidation and Fenton reaction. The experimental results showed that the current intensity and pH of electrolyte have obvious impact on the removal rate of BTEX in the process of electrolytic oxidation, and the removal rate of BTEX could reach 95% within 8 hours under a current intensity of 500 mA. In Fenton reaction, the removal rate of BTEX can reach more than 95% by adding 12 mg/L H_2O_2 at pH 4. The cost of these two reactions is similar to that of electrodialysis, but lower than that of freeze-thaw and evaporation. In the same year, Guillén-Villafuerte et al. (Guillén-Villafuerte et al. 2016) studied the formation of products in the process of ethanol oxidation by an electrochemical mass spectrometry. Acetaldehyde and acetic acid were detected by this method. Besides, in 2015, Lugaresi et al. (Lugaresi et al. 2015) introduced scanning electrochemical microscopy technology as a new method to quickly screen high-efficiency particles.

In 2014, Geneste's team (Fontmorin et al. 2014) studied the electrolysis of 1,3-dichloropropane. They used Ni (TMC) Br_2 as an effective catalyst to dechlorinate 1,3-dichloropropane in aqueous electrolyte. Before starting the electrolysis experiment, it was found that the dechlorination rate could reach 98% within 5 hours with a substrate/catalyst ratio of 2.3. Then the catalyst was fixed on the electrode for the electrolysis experiment. The results showed that in 3.5 hours, when the substrate/catalyst ratio was 100, the dechlorination yield could reach 80%, and the stability of the catalyst was relatively high. Hansen and his team (Ippolito and Hansen 2014) carried out the electro oxidation of propylene in a porous electrochemical reactor. Propylene was treated with $La_{0.85}Sr_{0.15}FeO_3$ (LSF) as working electrode and $Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO) as electrolyte in a wide temperature range. They found that the oxidation rate of propylene was increased, and a layer of $Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO) film formed on the electrode which could promote the polarization oxidation of propylene, and the Faraday efficiency reached more than 70% at 250°C.

Hu and his colleagues (Hu et al. 2014) used a system with two-step process for the removal of BTEX. In the first step, magnetite, hematite and their complexes were used to adsorb BTEX, and their adsorption efficiencies were tested. In the second step, an electrochemical reactor was designed to regenerate iron oxide nanoparticles. The results showed that the performance of electrolyte using NaOH is better. The stripping efficiency of cathode regeneration is higher than that of anode regeneration. Under suitable conditions, the stripping efficiency can reach 85%, and the regeneration rate of iron oxide can reach 90%. Delpeuch and coworkers (Delpeuch et al. 2014) studied the electrocatalytic activity of two electrocatalysts, Pt/C and Pt-Rh/C, for the oxidation of ethanol. Differential electrochemical mass spectrometry (DEMS) was used in a flowing system. They found that during the ethanol oxidation process, when the catalyst is Pt-Rh/C, more CO_2 is produced compared to the catalyst of Pt/C, and the reaction rate is also faster. The author believed that the addition of the third element makes the electrocatalytic performance of catalyst be promoted.

Lin et al. (Lin et al. 2014) applied electrolysis for the treatment of toluene. They used fibrous activated carbon to adsorb Co^{2+} as an electrode. The current density was 0.05 $A\cdot cm^{-2}$, the working voltage was 12V, and the air blasting rate conditions were 80 $L\cdot h^{-1}$. Electrolysis is carried out in an aqueous solution, and the results showed that the final product of toluene is benzoic acid, and the removal rate can reach more than 90%. Durante et al. (Durante et al. 2014) deposited Cu nanoparticles on glass carbon electrode, and then obtained Ag nanoparticles modified Cu nanoparticles electrode (Ag/Cu) by displacement deposition method. Pt was used as auxiliary electrode and DMF + 0.1 M $(C_2H_5)_4NBF_4$ as electrolyte. After analyzing the experimental results, they found that the reduction potential of organochlorides moved forward compared with the unmodified electrode.

In 2012, the electrocatalytic activity and stability of copper electrode were investigated by Isse et al. (Isse et al. 2012). CCl_4, $CHCl_3$, CH_2Cl_2 and CH_3Cl were electrolyzed with dimethylformamide (DMF) as electrolyte. It was found that the main product was methane. The electrocatalytic activity of copper electrode was similar to that of silver electrode, and the dehalogenation mechanism of the two electrodes was similar. Therefore, they thought that copper should be an economic material for the treatment of VOCs by electrocatalysis.

In 2012, Huang et al. (Huang et al. 2012) investigated the electrocatalytic activity of several transition metals for the dechlorination of methyl chloride and ethyl chloride (PECs). They used DMF + 0.1 M $(C_3H_7)_4NBF_4$ as the electrolyte, Pt as the counter electrode, and the glassy carbon electrode as the reference electrode. The electrocatalytic activity of Ag, Au, Pd, Pt, Cu, Fe, Ni, Pb, and Zn for the electrochemical reduction of PEC were explored. The reduction potential of different VOCs was affected by the electrode and the substance itself. The Ag, Cu and Au electrodes showed the highest electrocatalytic activity. The reduction mechanism was also affected by the nature of the pollutant itself. For double-substituted pollutants, dechlorination was occurred step by step, with each step losing one chlorine atom, until completely dechlorinated ethane is obtained. Ortho PCE lost two chlorines at the same time. The whole process was thought the removal of a series of chlorine, and ethane is produced finally.

In 2011, Muthuraman et al. (Muthuraman, Chung, and Moon 2011) explored the oxidation activity of platinum electrodes with Nano-Ag-Nafion coating on VOCs. They conducted an electrochemical analysis of the oxidation activity of acetaldehyde in different electrolytes such as nitric acid, sulfuric acid, potassium, nitrate and potassium hydroxide, and analyzed the stability of the Nano-Ag-Nafion membrane on platinum electrode. By comparison, it was found that Nano-Ag-Nafion coating electrode exhibited higher stability. In 2011, Mascia and colleagues (Mascia et al. 2011) used an advanced oxidation process to treat groundwater contaminating BTEX and METB (methyl tertiary butyl ether). A boron-doped diamond anode (BDD) was used because the oxidation of the anode is caused by hydroxyl radicals generated by water oxidation, which can replace other advanced oxidation processes. Experimental results showed that the removal of pollutants in this process was almost complete. In terms of energy consumption, this method is similar to other advanced oxidation processes.

Scialdone et al. (Scialdone et al. 2010) studied the effect of water on the reduction of aliphatic chlorides using a silver electrode. They conducted cyclic voltammetry experiments in acetonitrile, water and their mixtures. The experimental results showed that the electrocatalytic effect of silver on aliphatic chlorides in aqueous media is stronger than that in aprotic solutions such as acetonitrile. They also electrolyzed 1,1,2,2-tetrachloroethane and 1,2-dichloroethane for a long time, and the reduction rate was higher than 90%. The author believed that the special catalytic effect of silver in water may be due to the fact that water facilitates the resolution process and increases the turnover frequency of catalytic sites. In 2010, Wei et al. (Wei and Yang 2010) treated non-water-soluble gaseous VOCs using a combination of adsorption and electrochemical catalytic oxidation. They studied benzene as the subject and Na_2SO_4 solution as an electrolyte solution. Iron plates and ACF, an adsorption porous conductive material, acted as anode and cathode, respectively. The most optimal experimental conditions were determined, and the removal rate of benzene could reach 93.3%. The authors believed that ACFs are potential cathode materials for VOCs removal.

In 2009, Li et al. (Li and Gaillard 2009) observed the electrochemical promotion of toluene by a silver catalyst on a ZrO_2 (YSZ) solid electrolyte stabilized by Y_2O_3. They found that the catalyst can promote the conversion of toluene into CO_2 and H_2O through cathode polarization, and this catalytic effect is greatly affected by the concentration of toluene and catalyst. As the concentration of toluene increased, the effect of enhancement becomes less obvious. In the same year, S. Rondinini et al. (Rondinini et al. 2009) conducted a research on the catalyst for the electroreduction of organic halides. This catalyst is a silver nanoparticle synthesized under six kinds of stabilizers. Cyclic voltammetry and electrolysis were used to investigate the dechlorination of chloroform. The electrolyte was a liquid medium, and the dehalogenation process of chloroform was tested during the electrolysis process. Experimental result showed that the final product is methane, and the removal effect is great.

Table 1. The current applicable researches of electrolysis in VOCs removal

Electrolyte	Anode	Cathode	Overpotential	Removal rate	References
10mM Na_2SO_4	Pt	Cu	-	-	(Yang et al. 2021)
Na_2SO_4	$CuO/Cu_2O/TiO_2$ ternary hybrid nanorods	MWCNT/ GO/GF	-	81.3% (COD)	(Safarvand et al. 2020)
Wastewater containing VOC	dimensionally stable anodes(DSA): Pt/Ti, IrO_2/Ti, IrO_2/Ti, and IrO_2-Ru-Pd/Ti.	Ti	-	at over 98% in 1 h(IrO_2-Ru/Ti anode)	(Cho et al. 2019)
ethanol medium containing sodium chloride and sodium hydroxide	diamond	stainless steel	-	-	(Muñoz-Morales et al. 2019)
-	nickel plates	High secondary electron emission oxide	10.5-14.0KV	-	(Yao et al. 2019)
Wastewater containing VOC	Four DSAs (Ir / Ti, Ir-Pt / Ti, Ir-Ru / Ti and Ir-Pd / Ti)	Titanium plate coated with Ir, Ir-Pt, Ir-Pd and Ir-Ru	-	78.8% (chloroform)	(Cho et al. 2018)
solid polymer electrolyte	Sb-SnO_2/Ti nano-coating	Pt/rGO/CFP	1.9V	-	(Zhang et al. 2019)
solid	Long-empty Ti foam of antimony-doped SnO_2	Pt/rGO/CFP	-	-	(Zhang et al. 2018)
Add 1 mole per liter of NaCl aqueous electrolyte $[Ni(II)(hmc)]^{2+}$	Pt	carbon	-	-	(Pillai, Muthuraman, and Moon 2017)
$CHCl_3$ solution containing 0.05 M NaH_2PO_4	Ti=IrO_2	Cu/Zn	-	-	(Wang et al. 2016)
0.01 M SO_4^{2-} solution	Ti	stainless steel plate	-	95%	(Li et al. 2016)
$Ce_{0.9}Gd_{0.1}O_{1.95}$ (CGO)	$La_{0.85}Sr_{0.15}FeO_3$ (LSF)	$La_{0.85}Sr_{0.15}$ FeO_3 (LSF)	-	-	(Ippolito and Hansen 2014)
Aqueous solution containing toluene	Fe	Porous solid adsorbent	12V	90% (toluene)	(Lin et al. 2014)
DMF + 0.1 M $(C_2H_5)_4NBF_4$	Cu	Ag/Cu NPs	0.3-0.5V	-	(Durante et al. 2014)

Table 1. (Continued)

Electrolyte	Anode	Cathode	Overpotential	Removal rate	References
Solution containing sodium nitrate and compound	boron doped diamond	stainless steel disc	-	-	(Mascia et al. 2011)
A solution containing 0.1 M $TBABF_4$ and 0.035 M $NaClO_4$ and acetonitrile	Pt	Ag	-	90%	(Scialdone et al. 2010)
Na_2SO_4	Fe	Adsorbent conductive porous material	10V	93.3%(benzene)	(Wei and Yang 2010)
1 M Na_2SO_4	Pt	Ag	-	-	(Fiori et al. 2005)

In 2005, Rondinini's team (Fiori et al. 2005) used silver as cathode material to study the electrocatalytic activity of silver for dehalogenation reduction of chloromethane and chloroethane in a mixed electrolyte. The mixed electrolyte is composed of acetonitrile (ACN), dimethylformamide (DMF) and water. Pt was used as anode in 1M $NaSO_3$. According to the study of cyclic voltammetry, they found that the main product was methane, and the energy consumption of this process was very low. The reduction potential required for this process is at least 500mV lower than other metals. In addition, the existence of a small amount of water is beneficial to improve the stability of silver.

In 2001, Iniesta et al. (Iniesta et al. 2001) researched the effect of chloride ion on the electrochemical degradation of phenol in the presence as well as absence of NaCl in the solution. In separate cells, 0.5 m H_2SO_4 solution was used as cathode electrolyte, and NaOH containing aqueous solution was used as anode electrolyte. They used Bi-doped lead dioxide and pure lead dioxide as anodes and the cathode was titanium plate electrode. Both experiments showed that phenol was almost completely removed regardless of chloride ion in electrolyte, and the partial conversion rate of COD in chloride containing solution was as high as 0.9. The most difficult chloroform was reduced at low current density and low chloride ion concentration. The current applicable researches of electrolysis in VOCs removal are summarized in Table 1.

Application of Other Methods in Electrochemical Removal of VOCs

In recent years, with the rise of some emerging technologies, the processing methods of VOCs have become more and more diversified. Application of gas diffusion electrode, electrochemical desorption, plasma structure system and some new electrode preparation techniques are tried to be used in the electrochemical treatment of VOCs. The efficiency of VOCs treatment is improved by the application of different electrochemical methods as well as the innovation of electrodes and catalysts.

Gas diffusion electrode is a kind of special porous membrane electrode. Because a large amount of gas can reach the inside of the electrode and connect with the whole solution (electrolyte) outside the electrode, a three-phase (solid, liquid, gas) membrane electrode can be formed. With the passage of time, the research of gas diffusion electrode is more in-depth. Some scholars begin to use it in the electrochemical treatment of VOCs.

In 2014, Lugaresi et al. (Lugaresi et al. 2014) used a gas diffusion electrode (GDE) as a working cathode to study the electrocatalytic activity of silver nanoparticles on VOCs. $CHCl_3$ was chosen as the target substance. In the experiment, the concentration of chloride was evaluated by detecting the concentration of chloride ions. Graphite fiber cloth was used as the carrier and electrical collector of GDE for the contact of the GDE and the electrolyte solution. Simple GDE characterization by voltammetric analysis was performed. In the presence of $CHCl_3$, the increase in net current indicated that the substrate undergoes a continuous electroreduction reaction. In 2011, Yang et al. (Yang et al. 2011) passed the gas containing VOCs into an electric scrubber containing a gas diffusion electrode and found that it can effectively remove organic matter. They believed that the gas diffusion electrode is a promising electrode in electrochemistry.

With the development of various treatment technologies, the application of electrochemical technology on the preparation of electrodes or catalysts to treat pollutants has also attracted increasing attention.

In 2018, Liu et al. (Liu et al. 2018) prepared Cu-Ni Bimetallic cathode by electrochemical method to absorb trichloroethylene. It could be seen that the dechlorination rate of trichloroethylene has been significantly improved. In 2016, He and other members (He et al. 2016) prepared PE-Pd/foam-Ni electrode by electrochemical method, and applied it to the reductive dechlorination of 2,4-dichlorophenoxyacetic acid (2,4-D) in aqueous solution. They also used electrodeposition to prepare a catalyst, which is more conducive to chemisorption of active hydrogen than other catalysts. Electrochemically prepared electrodes and catalysts were used by them to treat 2,4-D. The results showed that the removal rate of 2,4-D was 98% in 3 h with a current density of 1.5 MA/cm^{-2}.

The decomposition of VOCs in plasma system has a broad application prospect. In 2018, Zheng et al. (Zheng et al. 2018) supported Mn_3O_4 catalyst on vertically oriented graphenes by constant current method in conventional three electrode electrochemical system. This method showed broad application prospects in the field of VOCs decomposition in plasma system. In the plasma catalytic system, the vertically-oriented graphene loaded with manganese oxide showed a good degradation rate of toluene.

In 2017, Ana Gómez-Ramírez et al. (Gómez-Ramírez et al. 2017) added Fe to a row plate packed bed dielectric barrier discharge plasma reactor to remove methane, chloroform, toluene and acetone. The results showed that the removal rate of organic matter increased: chloroform 22% to 52%, methane 15% to 21%.

The technology of combining electrochemical and biological methods to remove pollutants is becoming more and more mature, with a wide range of application prospects, and has been favored by many researchers.

In 2020, Lin and coworkers (Lin et al. 2020) prepared a kind of composite microbeads by combining other carbon coke and conductive carbon black, and then filled the microbeads into the anode compartment of the microbial fuel cell. This method provided a larger surface area for the attachment of microorganisms, thereby increasing the removal rate of the toluene. And the results showed that this method improved the power generation efficiency of microbial fuel cell (MFC). In 2018, Matteo Daghio et al. (Daghio et al. 2018) studied the degradation of BETX at 0.8V, 1.0V and 1.2V by bioelectrochemical method. The results showed that bioelectrochemical treatment improved the degradation of toluene, m-xylene and p-xylene. When the voltage was 0.8V, the effect was best.

In recent years, electrochemical desorption technology and electrochemical characterization methods have also attracted the interest of researchers. In 2020, Chen et al. (Chen and Liu 2020) combined anodic film diffusion/biodegradation with ultraviolet photodegradation to remove toluene by activated carbon fiber photocathode activated by peroxymonosulfate adsorption oxidation in a reactor system. In this study, they first designed and built a new PMS/pec-mfc system, and proved that it is an effective system for simultaneous power generation (battery voltage: 0.40V (vs. SCE)) to treat gaseous toluene. ACF based CeO_2/TiO_2/ACF and/or PMS/ACF photocathodes were prepared in PMS/pec-mfc system. After the system was successfully integrated with PVDF membrane module, bio anode and catalytic cathode, the removal efficiency of toluene was 95%. In addition, their EPR experiments showed that SO^{4-} could produce ·OH radicals under UV irradiation. The mechanism of toluene removal in this system was the adsorption and oxidation of cathode, the adsorption and diffusion of anode as well as biodegradation.

In 2015, Zhao et al. (Zhao et al. 2016) applied activated carbon fiber to adsorb VOCs, and conducted electrochemical desorption of toluene, isopropanol, ethyl acetate and acetone. The results showed that the desorption efficiency of active carbon activated carbon fiber (ACF) was high, and it still showed good adsorption effect after four times of desorption.

In 2012, Minguzzi et al. (Minguzzi et al. 2012) characterized the electrocatalytic activity of the composite material by electrochemistry. The results showed that the electrocatalytic activity of materials containing silver is good.

In 2012, in Xu et al.'s work, (Xu et al. 2014) toluene waste gas was treated by solution absorption and electrochemical oxidation. The experiment used two kinds of absorbent (NaCl and Na_2SO_4). With the increase of the current density of the electrochemical reactor, the removal rate of toluene increased, and NaCl solution had better removal effect than Na_2SO_4 solution. The experiment also found that acidic conditions are more conducive to the removal of toluene.

In 2006, Subrenat et al. (Subrenat and Le Cloirec 2006) used activated carbon fiber cloth to adsorb VOC in the air. This method used the means of electrochemical desorption. The system worked continuously for more than 18 months (24 hours a day) without any operation problems, and performed well with a low VOC outlet emission concentration. The current application of other methods for electrochemical removal of VOCs are summarized in Table 2.

Table 2. The current application of other methods for electrochemical removal of VOCs

Research method	**Pollutant**	**Effect**	**Reference**
Gas diffusion electrode	$CHCl_3$	-	(Lugaresi et al. 2014)
Gas diffusion electrode	2-ethoxyethyl	-	(Yang et al. 2011)
Electrochemical preparation of electrodes	Trichloroethylene	Increased removal rate	(Liu, Zhang, et al. 2018)
Electrochemical preparation of electrodes	2,4-D	98% removal rate	(He et al. 2016)
Plasma	Toluene	Improved toluene decomposition	(Zheng et al. 2018)
Plasma	Methane, Chloroform, Toluene and Acetone	52%(Chloroform) 21%(Methane)	(Gómez-Ramírez et al. 2017)
Microbial fuel cell	Toluene	Improved power generation efficiency and removal rate	(Lin et al. 2020)
Bioelectrochemical technology	BETX	-	(Daghio et al. 2018)
Combination of ultraviolet light and electrochemistry	Toluene	95%	(Chen and Liu 2020)
Electrochemical desorption	Toluene, Isopropanol, Ethyl acetate, Acetone	The desorption effect is good	(Zhao et al. 2016)
Electrochemical characterization	Composite material	High catalytic activity of silver-containing materials	(Minguzzi et al. 2012)
Absorption and electrochemical oxidation	Toluene	-	(Xu et al. 2014)
Electrochemical desorption	VOCs	The desorption effect is good	(Subrenat and Le Cloirec 2006)

CONCLUSION

VOCs are one of the most important pollutants nowadays. The application of electrochemical technology for VOCs are summarized in this chapter. In brief, there are two main electrochemical treatment methods: electrolytic cell and primary cell. Although the reported treatment effect is relatively good, there are still some problems:

1. In the removal process of liquid VOCs, volatile components may cause secondary pollution. A better way to deal with VOCs is still needed.
2. At present, there is a lack of removal methods and catalysts for the treatment of pollutants with strong chemical bonds such as chloroform, and more catalysts and selective operations are needed.
3. It is still a challenge to remove low concentration BTEX in the room.
4. For non-electrolytic cells and non-primary batteries, most of the VOCs are treated with good results, but there are problems of higher prices and poor practicability.

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Chapter 6

CARBON FOOTPRINT ON MICROALGAE-BASED PROCESSES

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ABSTRACT

In the last 7 decades, microalgae-based processes have been the scene of an incessant duel to try to curb excessive consumption of a wide range of feedstocks and natural resources, working on technologies for the recovery of solid, liquid, and gaseous waste, in order to avoid the global collapse of ecosystems. However, we cannot combat

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environmental problems with emitting devices. It is necessary to use tools that leave no doubt about their applicability and competence. Thus, immersed in the environmental uncertainties generated by biotechnological processes, scientists have deepened their research to bring to the surface the real environmental impacts and their relations with the social and economic triad, providing the true global status of sustainability. Therefore, focused on solving the hottest point of the investigation, that is, the reduction of carbon dioxide emissions, the carbon footprint mechanism has become the key tool of today. In light of this, this chapter will address a brief review of the main microalgae-based processes and their relationship to carbon footprints. In addition, the chapter will provide a compilation of information regarding the main methodologies currently used to quantify the carbon footprints of biological systems, as well as direct the reader to use them appropriately. Finally, the last part of the chapter emphasizes and guides researchers in the area to get to know some general views about the global carbon market and the perspectives to be elucidated and developed on carbon credits involving microalgae-based processes.

Keywords: microalgae, biological carbon capture, environmental assessment, carbon credits, carbon market

1. INTRODUCTION

Since the post-industrialization era, alarming rates of greenhouse gases have been present in the environment. Anthropogenic activities, which include the chemical and petrochemical industries, as well as the pharmaceutical and food sectors, are mainly responsible for these exponentially significant releases to the atmosphere, resulting in deep and direct impacts on the ecosystem (Varbanov et al., 2018; Jha, 2020).

Bearing in mind that carbon dioxide (CO_2) is the main compound responsible for the greenhouse effect, in recent years the mitigation of CO_2 emissions has become a substantial challenge of great concern due to the diverse climatic effects that can cause. Thus, becoming a hot spot for numerous researches worldwide (Barati et al., 2021). Proof of this is the studies that report that the projected trend is for CO_2 emissions to reach an exponential behavior around 51% by the year 2050 compared to 2005

(Zhang and Liu, 2021). As a result, this can initiate unpredictable changes in the climate system, leading to an environmental collapse. Therefore, urgent decisions and measures are needed against this potential increase in the release of carbon dioxide into the environment (Saravanan et al., 2018).

Based on this understanding, efforts are underway, such as government measures implemented, with a focus on carbon reduction and in search of continence alternatives. At the same time, several carbon capture and storage technologies (CCS) have been proposed for combustion gases, including absorption, adsorption, cryogenic, and membrane separation. On the other hand, it is believed that the process of biological carbon capture and utilization (BCCU) is potentially more promising if carried out by microalgae and cyanobacteria (Severo et al., 2020; Patel et al., 2020). In addition, the integration of microalgae cultivation using CO_2 from industries has been employed as an ecologically correct approach (Barati et al., 2021).

As is well known, microalgae are increasingly attracting global attention due to the cost-benefit for their manufacture, they have an exceptional rate of growth speed and their ability to survive hostile environments (Zhang and Liu, 2021). In addition, because they have this potential for capture and storage, they can convert biomass into a broad portfolio of commercial bioproducts, making it of great interest to researchers, private companies, and government agencies (Severo et al., 2020).

Unfortunately, although microalgae have a great prospect of being environmentally friendly, excessive energy consumption becomes the most critical point in the system. And, to make matters worse, what contributes to a substantial part of the global CO_2 emission is in relation to the energy supply, usually in the form of electricity generated by the burning of coal and natural gas (IEA, 2018). Therefore, it is of great relevance to assessing, in fact, whether these biotechnological processes based on microalgae are environmentally friendly for the ecosystem. Thus, the life cycle assessment (LCA) appears, with an auxiliary tool that is the carbon footprint (CF), where it emerges as a promising methodology to quantify metrics and indicators of sustainability. In essence, this tool presents itself as a key point where it assists in the recognition and detection of possible solutions to reduce greenhouse gas emissions, as well as in measuring an environmental load of a product or process throughout its life useful (Deprá et al., 2018; Patel et al., 2020).

In this sense, this chapter will briefly review the main processes based on microalgae and their relationship with carbon footprints. In addition, throughout the chapter, it will provide a compilation of information on the main methodologies currently used to quantify the carbon footprints of biological systems, as well as guide the reader to use them properly. Finally, the last part of the chapter emphasizes and guides researchers in the field to learn about some views on the global carbon market and the perspectives to be elucidated and developed on carbon credits involving processes based on microalgae.

2. Microalgae-Based Processes

Since the geological and chemical processes suffer multiples issues of environmental responsibility related to the capture of CO_2 from the atmosphere and flue gas, the focus of recent research has shifted to use CO_2 as a carbon source to grow microalgae (Mata et al., 2018). Microalgae are the more significant microrganisms for the global carbon balance, performing crucial roles in fixing CO_2 through photosynthesis (Pourjamshidian et al., 2019).

Progress in biological carbon capture and utilization through photosynthesis has become a promising alternative compared to other conversion processes already consolidated (Choi et al. 2017). In this case, the biological assimilation of carbon dioxide in microalgae actively acts in the transport and intracellular accumulation of inorganic carbon transforming them into rich products of interest, beyond presenting an efficient alternative route for CO_2 bioconversion from anthropogenic sources (Severo et al., 2019).

Normally, the photosynthetic process in microalgae occurs in chloroplasts with the use of sunlight as an energy source (Figure 1).

Microalgae contain in their chloroplasts a mechanism singular enzymatic, which catalyzes the conversion of CO_2 into simple (reduced) organic compounds, denominated carbon fixation. In this process, CO_2 is incorporated (fixed) in a three-carbon organic compound, triose-phosphate-3-phosphoglycerate. This simple product of photosynthesis is the precursor to more complex biomolecules, such as sugars, polysaccharides, and the metabolites derived from them, where CO_2 is assimilated by a cyclic pathway and commonly called the Calvin-Benson-Bassham cycle (Masojidek et al., 2013).

During this series of metabolic modifications, familiar as the Calvin-Benson-Bassham cycle (CBB), the acceptor ribulose-1,5-bisphosphate is regenerated, ready to accept another carbon dioxide molecule. The requirements for energy, however, render the conversions during the cycle fully based on the primary photochemical act, which takes place in the organelle membranes. In this stage, the chlorophyll molecules are excited by light energy when it is absorbed by highly organized structures of photosynthetic pigments and by electron transporters, called photosystems I and II, or reaction center (P700) and reaction center (P680), respectively. Their electrons are then transferred to an electron-accepting molecule that flows through a series of membrane-bound transporters in order to generate an electrochemical potential and lead to the reduction of ferredoxin to the formation of the reducing intermediate nicotinamide adenine dinucleotide phosphate (NADPH). Part of the released energy is assimilated during the transport of this electron into adenosine triphosphate (ATP) in the process of photophosphorylation (Brinkert 2018).

Although complex and not always efficient in a few species, the carbon conversion mechanisms (CCM) are beneficial for microalgal cells, as they intensify their photosynthetic productivity (Ghosh and Kiran, 2017). Due to their simple cell structure and rapid growth rate, microalgae are expected to have CO_2 biofixation efficiency of about ten times greater than terrestrial plants (Moreira and Pires, 2016). However, since the mass transfer of CO_2 from the atmosphere is very low (0.04% CO_2), it is essential to provide supplemental CO_2 to the cultivation system, instead of relying only on the diffusion of CO_2 from the air (Kim et al., 2019).

Depending on the microalgae strain, a supplement of 1–20% CO_2 is generally suitable for growing microalgae and achieving higher biomass yields (Bhola et al., 2014).

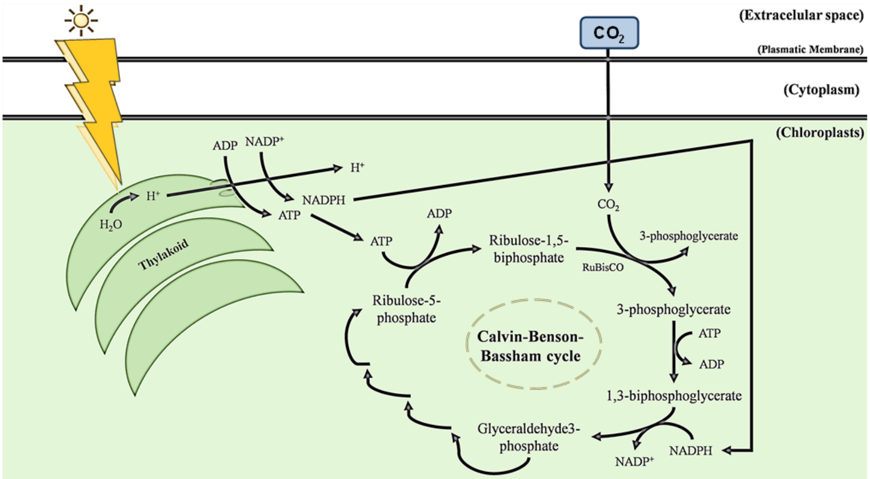

Figure 1. An overview of the photosynthesis process. ADP - adenosine diphosphate, ATP - adenosine triphosphate, CO_2 – Carbon dioxide, H^+ - hydrogen, H_2O – dihydrogen monoxide, NADP - nicotinamide adenine dinucleotide phosphate, NADPH - nicotinamide adenine dinucleotide phosphate.

Consequently, microalgae biomass has been studied for various applications, most of which are particularly food, animal feed, pharmaceutical, and nutraceutical products. In fact, they have a great potential to excrete various substances with unique bioactivities for high-value applications, for example, pigments, polysaccharides, proteins, nucleic acids, and lipids (Xiao and Zheng, 2016). However, the most promising frontiers for microalgae relate to their collaboration in environmental protection and the environment, including carbon dioxide bio-sequestration, waste treatment, and their use for energy purposes, such as biogas production, biohydrogen, bioethanol, and biodiesel (Debowisk et al., 2020). In this case, microalgal Biomass is undoubtedly a promising substrate for the production of energy carriers, characterized by pollutants with lower levels of emission compared to conventional fuels.

Table 1. Some cultivations of microalgae used for biofixation of carbon dioxide (CO_2) and biomass productivity

Microalgae	Experimental setup	Concentration CO_2 (%v)	Productivity rate (mg/L/h)	CO_2 fixation rate (mg/L/h)	References
Chlorella sp.	cylindrical glass reactor	9.45	5.00	155	Pourjamshidian et al. (2019)
Chlorella sp.	cylindrical glass reactor	1.75	7.08	206.25	Pourjamshidian et al. (2019)
Chlorella vulgaris	Fermenter	10	10.41	20.83	Lam et al. (2012)
Chlorella vulgaris	Hybrid PBR	15	26	162.50	Maroneze et al. (2018)
Desmodesmus sp	Polyethylene PBR	10	0.86	1.62	Swarnalath et al. (2015)
Dunaliella tertiolecta	Bio-Floc Fermentor	5	0.007	3.08	Van Den Hende et al. (2011)
Isochrysis galbana	Bubble column PBR	0.038	5.16	9.83	Zhao and Su (2014)
Nannochlorophsis oculata	Tubular PBR	15	9.54	17.95	Zhao and Su (2014)
Scendesmus obliquus	Erlenmeyer flask	10	12.08	76.60	Lam et al. (2012)
Scendesmus obliquus	Tubular PBR	5	0.007	3.25	Tang et al. (2011)
Scendesmus obliquus	Tubular PBR	12	0.75	1.42	Basu et al. (2014)

This approach creates a dubious sustainable carbon cycle view, in which the CO_2 emitted from burning biofuels is absorbed back by the microalgae in order to continuously maintain the level of CO_2 in the atmosphere (Lam et al., 2012; Callegari et al., 2020). As proof that, recently, an increasing number of studies reported in the literature on the use of microalgae in different cultivation have shown a positive effect on the carbon fixation rate and on biomass productivity. Table 1 shows the efficiency of removing atmospheric CO_2 and biomass yield under different strains of microalgae.However, while the potential for carbon biofixation is indeed promising, assessing global emissions from microalgae-based processes is strictly necessary in order to consolidate the environmental advantages of these mechanisms from the perspective of the carbon footprint.

3. Carbon Footprint Assessment

Undeniably, the use of environmental assessment tools has been indispensable to determine the extent to which humanity's demand remains within or exceeds the limits of what global natural capital can provide, beyond detecting early warning signs and potentially predicting the consequences of man-induced pressures on ecosystems (Mancini et al., 2016).

In light of this, assessing carbon footprints gained prominence in the search for environmentally sustainable products and processes. As a consequence, the widespread use of this term by political organizations and the public and private sectors, in addition to industrial facilities, provided a series of challenges and issues that previously need to be addressed (Wright et al., 2011). After all, what does the term carbon footprint actually mean?

Traditionally, the carbon footprint is a segment within the ecological footprint methodology, whose criterion was attributed to quantify the bioproductive demand, through the forest area, necessary to capture the anthropogenic emissions of CO_2 at a rate of sequestration world average in order to avoid the accumulation of CO_2 in the atmosphere. However, the term carbon footprint is a new buzzword that has gained tremendous popularity over the last few years and has been used as a popular measure used to assess the amount of anthropogenic greenhouse gas emissions expressed in tons of CO_2 equivalent (tCO_2eq) (Mancini et al., 2016).

In fact, the increasing popularity of the term has resulted in very divergent approaches, which until now, the scientific community has not been able to establish a standardized methodology capable of quantifying the carbon footprint (Weidema et al., 2008). Thus, the lack of a harmonized methodology can make comparisons between products and processes difficult, in addition to potentially providing publications where there are erroneous or biased results. Thus, the development of harmonized, transparent, and accurate methodologies is, therefore, of great importance (Dias and Arroja, 2012).

Faced with the need to achieve global standardization, associated member bodies and the technical committees of the International Organization for Standardization (ISO) have worked hard to prepare a document that brings together a consistent methodology for the carbon footprint. As a result, the document generated by the ISO 14060 family provides clarity and consistency to quantify, monitor, report, and validate or verify greenhouse gas (GHG) emissions and removals to support sustainable development through a low-cost economy. In addition, the manual also benefits organizations, project proponents, and stakeholders worldwide, providing clarity and consistency in quantifying, monitoring, reporting, and validating or verifying GHG emissions and removals (ISO 14067, 2018).

The methodological structure is based on the LCA tool, whose calculation system is similar to the impact category of global warming potential. Therefore, conducting the carbon footprint assessment requires following the guiding principles of the LCA, that is, it becomes essential that the questions of the definition of the objective and scope are ignored, the establishment of a functional unit, collection of inventory data from the cycle of life, assessment of environmental impacts, as well as the elucidation of the data generated.

Therefore, the carbon footprint of a product or process calculations can be given by the sum of GHG emissions and removals, according to Eq 1:

$$CFP = GHG_E + GHG_R \tag{1}$$

where CFP is the carbon footprint of product or process (kg CO_2 equivalent), GHG_E is greenhouse gas emissions (kg CO_2 equivalent), and

GHG_R is the greenhouse gas removed (kg CO_2 equivalent). It is important to note that the carbon footprint unit must be associated with the pre-established functional unit at the beginning of the quantification of the process inputs and outputs, as defined by the LCA methodology.

On the other hand, the partial carbon footprint assesses only a specific unit operation included within the total process. Generally, this analysis is applied to corrections and process optimization, in order to verify if the changes were, in fact, positive. The main difference is the determination of the functional unit since it only needs to be a clearly stated unit. At the level of exemplification, we can say that the partial carbon footprints are the key pieces of the puzzle, while the total carbon footprint consists of the assembled puzzle. Using technical-applied examples of a microalgal process, the partial carbon footprint can be understood as the assessment of only the upstream process phase - cultivation step - used to quantify carbon emissions and captures during cell culture. However, the total carbon footprint can be understood as the total assessment of the process, including the stages of harvesting, drying, purification, and other steps necessary to obtain the final product.

Besides, the most advanced carbon assessments quantify carbon offset criteria, which can later be converted into financial returns (More details in Section 4). The mechanism of total or partial compensation of the carbon footprint is provided by preventing the release, reduction, or removal of a quantity of greenhouse gas emissions in a process outside the product system under study. For example, in a microalgae biomass production system, the scope of the study delimits the analyzes of carbon quantification, from the beginning of cultivation to the final steps to obtain dried whole biomass. However, outside the process, the power supply for the equipment comes from a renewable energy installation system, where the cultivation relies on the installation of solar panels. Thus, aware that solar energy is considered a cleaner production compared to conventional electricity (coal), avoided carbon emissions are part of carbon offsets. Another relevant common way of installing carbon offsets is through measures of afforestation and reforestation within industrial facilities. Also, some studies suggest that the capture and use of carbon by microalgal processes can also be considered as potential sources for generating carbon offsets (Matthews, 2008; Pandey et al., 2011).

Nonetheless, this quantification is limited only to greenhouse gases and does not consider the environmental charges associated with the soil and oceans. For this reason, some authors suggest that quantifications in addition to emissions and catches should be elucidated in order to consolidate the carbon cycle and truly identify the environmental burdens associated with industrial processes. Conversely, as the carbon footprint is a new procedure, considering that the first official standardization methodology was only published in 2018 (ISO 14067: 2018), it is understandable that there is confusion about the appropriate means and limits to be adopted for these impact analyses. Therefore, regardless of the quantification model to be used, it is imperative that research and development groups, as well as the application of these tools, be implanted and implemented, in order for companies to consider their carbon footprints so that mitigation efforts carbon emissions are, in fact, achieved.

4. Carbon Market: Perspectives for Microalgae Technologies

There is a consensus that urgent actions at an unprecedented level need to be taken to limit global warming to 1.5 °C. According to climate scientists, if the inertia in the reduction of the global greenhouse gas emissions perpetuates, the result will be the triggering of changes that will be irreversible. The central message consists of the need to deconstruct the current economic system to the imposition of limits. The savings are, undoubtedly, the primary source of environmental emissions, and aligning them with sustainability is an imperative action to achieve the goals of combating climate change (Gills and Morgan, 2020). In light of that, investments in production systems and consumption of products and services of low-carbon have been strongly supported, as well as divestments in fossil fuels. Noteworthy, the pressures around climate change have led many institutions to reduce or abandon investments in fossil fuels and transfer them to more sustainable alternatives (Monasterolo and De Angelis, 2020).

In fact, especially in the last decade, genuine efforts to deal with climate change and to confine global warming to below 2 °C have been and are being expended. Many nations, despite being highly dependent on fossil resources, have pledged to reach carbon neutrality by 2050. The promise translated into actions led them to adhere to carbon pricing to decarbonize their economies. The tactic seems clear: become expensive and we will use less. Here, it is important to mention that in many jurisdictions carbon prices are less than USD 10/tCO_2eq. This value is very low considering, for example, the Paris Agreement temperature targets. In order to meet the targets, it is estimated that carbon prices of USD 75 to 100/tCO_2eq by 2030 and USD 125 to 140/tCO_2eq by 2040 are necessary. About this, it is worth mentioning that the pricing policy is and precise to be carefully planned so that it is socially fair (IEA, 2018; World Bank, 2020).

Carbon pricing is a mechanism that will play a central role in the compliance of international treaties. Besides that, it is the trigger for which polluting companies to reduce their emissions and invest in cleaner and low-carbon technologies. Namely, the two main carbon-pricing instruments are: (i) carbon taxation, where is imposed a tax on the emitted carbon emissions, and (ii) the emissions trading system also known as the cap-and-trade system. In the cap-and-trade system, the emissions are limited, i.e., the companies that exceed the permitted emissions limit will need to buy carbon credits or make environmental compensations for that to adjust to the permitted quantity. But, if the limit is not exceeded and there is an economy beyond the expected in the carbon emissions, they receive carbon credits that can be negotiated on the international market. Each carbon credit corresponds by convention to 1 ton of CO_2 equivalent (tCO_2eq) (Entezaminia et al., 2021).

The cap-and-trade system is by far the most opportune instrument for business and has been implemented or programmed for implementation in Europe, China, Australia, New Zealand, and various jurisdictions of the world. In this narrative, it is worth mentioning that there are two groups of countries: (i) those developed, mainly, with emission reduction targets to be accomplished mandatorily and (ii) those in development that have not committed themselves to reduce their emissions; however, have taken the initiative to reduce voluntarily. In the voluntary market, considering the second group, the protagonists are, in truth, companies that voluntarily act in the fight against climate change. These companies neutralize their emissions and, that why, generate carbon credits that can be sold to countries of the first group that wishes to neutralize their residual emissions. Under this scenario, besides the objective of reducing or neutralizing emissions, there is the generation of revenues. It is no wonder that this market is growing and is leveraged mainly by companies that seek to differentiate their products and be in alignment with the sustainability objective (Paiva et al., 2015).

Notoriously, reducing pollutant gas emissions is not an easy task. However, there are a series of actions that can be implemented to achieve the objective and, among them, are activities associated with carbon capture and wastewater treatment. In the field of biotechnology of phototrophic microorganisms, industrially important microalgae producing companies can profit from these activities. This is because microalgae are microorganisms that have the capacity to fix CO_2 and bioremediate a variety of organic and inorganic pollutants (Dias et al., 2021).

Recently, Severo et al. (2020) and Deprá et al. (2020) evaluated the estimate of carbon credits for capture and utilization of CO_2 by microalgae. In the study by Deprá et al. (2020) it was reported that during the seven-day cultivation period of the Scenedesmus obliquus microalgae in a photobioreactor, about 4.36 kg/m^3 of CO_2 was captured. Based on this value, to mitigate 1 ton of CO_2 that corresponds to a carbon credit would be necessary an operational volume of approximately 229 m^3, considering the enrichment of the culture with 1% CO_2. This suggests an important opportunity to generate additional revenues that, ultimately, could be used to reduce other costs of the commercial facility (Singh et al., 2011). The same goes for microalgae-based wastewater treatment. The microalgae are in conformity with new trends of wastewater treatment and the dual application of these microorganisms for wastewater bioremediation and value-added biomass production have been explored (Rawat et al., 2011; Li et al., 2019). Besides, the microalgae biomass can be used as a feedstock for the generation of different biofuels including bioethanol, biomethane, biohydrogen, and biodiesel (Deprá et al., 2018; Sydney et al., 2019). As is known, reducing the burning of fossil fuels can be one of the best ways to mitigate the effects of climate changes and, for this reason; many countries support the production of biofuels through the implementation of policies (Yan, et al., 2021).

Finally, studies are lacking that investigate the potential of coupling these strategies to the production of microalgae-based commercial products bearing in view the generation of carbon credits. What happens is that the microalgae-based carbon mitigation processes as a strategy to contain climate change still not achieved great visibility. However, microalgae biotechnology will play a central role in this issue, once major efforts are being directed towards the development and implementation of green technologies.

CONCLUSION

Effective mitigation of greenhouse gas emissions - mainly carbon dioxide - is only feasible when its exact magnitude is known. However, to date, the number of methods that have been employed to assess the carbon performance of industrial processes remains small, while their scientific merit requires further validation. In addition, this argument requires greater attention, especially when applied to biotechnological processes, since the methodologies employed are based on conventional industrial models. Thus, the carbon footprint approaches of microalgae-based processes must address both the environmental burden associated with carbon emissions and financial savings. So, in the future, improvements ahead of carbon management policies should be reviewed and developed according to biological processes, in order to encourage carbon credit, and consequently, generate financial returns and incentive measures to reduce carbon emissions.

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