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ISBN 978-3-319-64500-1 ISBN 978-3-319-64501-8 (eBook)
DOI 10.1007/978-3-319-64501-8

Library of Congress Control Number: 2017950048

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Printed on acid-free paper

This Springer imprint is published by Springer Nature
The registered company is Springer International Publishing AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Preface

Modern age environmental problems are arising from the extreme desire of the modern human population for more efficient and comfortable life. To amplify the quality of life is coupled with the industrial revolution and pollutant generation. Since the beginning of the nineteenth century, rapid industrialization and urbanization has produced huge amounts of waste materials, thereby creating an extra burden to our environment. Every year, the global pollutant budget is increasing multiple fold by means of natural (e.g. natural release of methane gasses, volcano eruption, acid rain, rock weathering and releasing toxic metals) as well as anthropogenic activities (domestic waste, carbon emission from fossil fuel burning in automobile and energy generation, radioactive materials from nuclear reactors, polycyclic aromatic compounds from oil industries and other xenobiotic compounds, heavy metals). Environment pollution is a worldwide issue and its capability to affect the human health is great. It is unavoidable and influences somehow almost everybody and everything. Exposure of human to pollution is accepted to be more intense now than at any other time in human existence. Pollution can be made by human exercises as well as by natural forces. Human exercises adversely affect the environment directly or indirectly. Undoubtedly extreme level of pollution is causing a lot of harm to human and animal health, plants and trees, as well as the wider environment. Developmental activities, for example, transportation, manufacturing and construction, exhaust the natural resources as well as produce a large amount of wastes that contaminate water, air and soil and lead to global warming and acid rains. Improperly treated or untreated waste is a noteworthy reason for contamination of waterways and environmental degradation creating problem to health and crop productivity. Increasing globalization has also negative impact on environment. Due to increasing globalization, consumption of products has increased that leads to an increase in the production of goods, which in turn puts burden on the environment. Therefore, an important challenge in the present times is to supply the sufficient energy per person to the increasing world population. Today, this energy supply principally relies on fossil fuels that have numerous shortcomings, like emission of greenhouse gasses, effect of environmental change and the exhaustion of these assets. So, we have to think for alternate sources of energy that are renewable as well as sustainable. Renewable energy, for instance, hydro energy, wind energy, geothermal energy, solar energy or bioenergy, might be important energy sources in the future. Bioenergy is renewable energy from organic material (biomass).

An extensive number of technologies exist for generating bioenergy, heat and power, like biogas digesters, large-scale biomass gasification plants, microbial fuel cell for bioelectricity, etc. Producing energy from biomass can be cost competitive. Bioenergy is the main renewable source that can supplant fossil fuels and can be used in the production of electricity, heat and fuels for transport. Bioenergy is now making a generous contribution to meet worldwide energy demand. This contribution can be extended fundamentally in the future, giving reduction in emission of greenhouse gasses and other natural advantages and in addition adding to energy security, giving chances to social and financial improvement in rural areas and improving the resource and waste management.

For sustainable development, promotion of greater access to bioenergy is essential. Bioenergy has a definite contribution to make to sustainable development as with other potentially interesting renewable energy sources. Bioenergy can possibly be modernized around the world. Bioenergy contributes to all essential components of the nation or local development, economic growth, energy security, environmental security, food security, income and employment generation, poverty alleviation, etc., and it can increase access of poor people to improved types of energy. Attention on bioenergy production is increasing and the trend will continue.

A number of studies have been conducted and reported in the literature, but they are not sufficient to cope with the growing problems of pollution and clean energy supply. Thus, there is an urgent need to develop new, innovative and wise strategies to control pollution in a sustainable manner along with the generation of energy. This book deals with several current issues relating to environmental problems and further focusses on newer technologies (e.g. bioelectrochemical systems) for the generation of renewable and sustainable energy.

We are highly grateful to our internationally renowned contributor from different countries for providing their reliable, progressive and cutting-edge scientific information to accomplish this book. All chapters in this book are well illustrated with appropriately arranged images and tables and enriched with most recent references of related literature. A generous support provided by the authority of Center of Excellence in Environmental Studies (King Abdulaziz University) and research scientists who have contributed in the designing of this book is highly acknowledged. We are undeniably very thankful to our family members for their constant support during the period of book preparation. We highly appreciate the great efforts of book publishing team at Springer Nature, who always replied promptly with solution of queries during the whole book project. Finally, this book may have some basic mistake, printing errors and inaccuracies for which we feel regret in anticipation. However, if found out at any stage, we will certainly try to improve them in the subsequent print/edition. Readers are most welcome to provide critical analysis and suggestions related to the content presented in this book.

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Chapter 1
Chemical Contaminants for Soil, Air and Aquatic Ecosystem

Tesfalem Weldeslassie, Huma Naz, Balwant Singh, and Mohammad Oves

Abstract Chemicals from fossil fuel use, domestic and industrial waste products, mining and agriculture contaminate air, water and soil. Contaminant chemicals may have considerable implications for human health and safety, welfare and the value of nature. Air contaminants include carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), nitrogen oxides (NO_x), hydrofluorocarbons (HFC_s), perfluorocarbons (PFC_s) and sulphur hexafluoride (SF_6). These gases brings climate change by increasing the temperature of the earth's atmosphere and oceans. Climate change is responsible for unpredictable changes in precipitation, rising sea level and extreme climate events. Air contamination can be controlled by passing a law against harmful chemicals production, introducing special devices that reduce green houses gases, and making use of alternative sources of energy. Major water contaminants include sewages, petroleum products (like polychlorinated biphenyls), nitrates, insecticides, sediments and excess organic matters. Harmful chemicals may reach water bodies from outlet of pipes in industries; leakage of pipe line or storage tanks, mining operations, improper application of fertilizers and pesticides in agricultural fields and some leakage from ships. Water contaminants inflict vital body organs, nervous systems, and cause different types of cancers and cardiovascular effects. Soil contamination is caused by dispersion of toxic compounds, acidification, salinization and sodification, enhanced soil erosion, chemical fertilizers, pesticides, fungicides, and the accumulation of heavy metals and other inorganic contaminants. Like air and water contaminants, soil contaminants, if they enter into our body, are also causative agents of many diseases. There are many

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M. Oves et al. (eds.), *Modern Age Environmental Problems and their Remediation*,
DOI 10.1007/978-3-319-64501-8_1

tangible mechanisms to control soil contaminants such as landfills, incineration or burning, composting and recycling.

Keywords Contaminant chemicals • Contamination control • Contaminant sources • Impacts and implications

1.1 Introduction

Environment is the physical (non-living and living) surroundings of human society. Interactions between society and the environment are inevitable. These interactions include the effects of society on the environment and the value of the environment for society (Fig. 1.1).

Environmental problem, most of the time, is caused as a result of the disturbance of the interactions between society and the environment. Such disturbance may have several impacts such as air, water and soil contaminations. In turn, these environmental impacts will have diverse implications for human society, including implications for human health and safety, welfare and the value of nature. Pollution, contamination of earth's environment, afflicts not only the health of human but the quality of life along with the ecosystems (IPCC 2014). Thomas (2012) and IPCC (2014) clearly stated that it is out of question to say the cause for relentless rise of global warming is the consequences of human-induced increases in heat-trapping gases. Nowadays there is no a question on the credibility and maturity of climate science (Carlton et al. 2015). The reason why climate change is dreadfull is its vital power to shape the human planet in a different way so that life becomes very hard. Industrial activities may have environmental impact on water contamination due to disposal of heavy metals such as mercury, lead, copper and selenium and this contaminated water will have implications for human health, for example after ingesting or dermal contact with contaminated soil (Hannah et al. 2009). The risk of climate related impacts is becoming more greater for those disadvantaged societies in any country (IPCC 2014). Many people could understand the negative impacts of air and soil contaminations on human's health, but that of soil is still not fully understood (Science Communication Unit 2013). However, many studies agreed that increased level of soil contaminants affect soil chemisty, microbial activities and health of the animals and plants living in the soil significantly (Hannah et al. 2009; Science Communication Unit 2013).

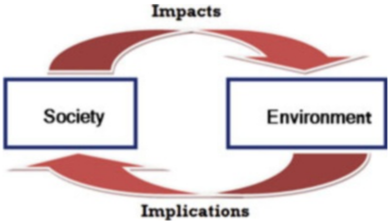

Fig. 1.1 Interactions between society and environment

Environmental problems can be assessed at global or continental or local level (WHO 1982). Global problems include environmental problems caused by pollutants that usually stay in the environment for a long time, and that are transported over long distances. People focus more on atmospheric pollutants as they have large-scale and long-term effects. It does not matter where on earth the emissions take place, because the pollutants spread into earth's entire atmosphere within a few years, while the effects may last for decades or centuries (GISS 2017). Therefore, global problems, for example climate change and stratospheric ozone depletion, are international problems that need urgent global solutions.

Continental problems are caused by pollutants that are transported at a continental scale. These problems are international and need to be solved at the continental level. Continental problems include acidification, eutrophication; tropospheric ozone; dispersion of toxic compounds and the like.

The impact of local environmental problems is limited to more or less the location where the causes of these problems are found. Therefore, these problems need local solutions. Local problems include heavy metals, waste production and disposal, excess use of agricultural chemicals (fertilizers and pesticides), domestic wastes and industrial effulients.

Pollutants can be categorized into biodegradable and non-degradable. Biodegradable pollutants are those materials that are decomposable simply by natural phenomena. They may pose a problem if their rate of addition is greater than their rate of decomposition. The second types of pollutants are those of non-degradable. Non-degradable pollutants decompose at a rate more slowly than their decomposition so that it is needless to say that their removal from the environment is very difficult if not impossible.

1.2 Air Contaminants

Many human activities including fossil fuel use, industry, mining and agriculture are sources of air pollution. Emissions of green house gases (GHG) like carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrofluorocarbons (HFC_s), perfluorocarbons (PFC_s) and sulphur hexafluoride (SF_6) affect the radiative balance of the atmosphere (so-called radiative forcing). As a result of the radiative forcing, the temperature of the earth's atmosphere is increasing and the climate is being changed. Climate change means occurrence of abnormal precipitation events and rise of sea level. In addition, weather patterns will become less predictable and the incidence of extreme climate events, such as storms, floods, and droughts, will increase. Climate scientists clearly understand the suitation may reach to the level whre nature and human society may not be capable of responding rapidly enough to these changes.

According to IPCC (2006), many processes in the ecosystem are definitely affected by management of land use which will directly affect fluxes of GHGs, to mention some of them are combustion, respiration photosynthesis, enteric fermentation, decomposition and nitrification or denitrification.Within these processes carbon, sulphur and nitrogen are exposed to complex transformations. Biological (activity of microorganisms, plants, and animals) and physical processes (combustion, leaching, and run-off) involve in the transformation of these elements. Troposphere, 16 km wide atmospheric layer, is frequented with continuous change of climatic variables due to change in the fluxes of GHGs. Almost all local and global pollutions are observed in this layer.

The common air pollutants inside any house can be mentioned as tobacco smoke, invisible radioactive gas, radon, synthetic chemicals of carpets and tools, pesticides and chemicals that are used in cleaning household. It is realized that the most harmful component of air pollution is the polluted air inside the homes and buildings as in one way it is hardly identified and on the other way people particularly children, without recognizing the pollution, spend most of their time being exposed to polluted air (Moya et al. 2004). For example, many people suffer from a lung disease known as asbestosis. The main cause of this disease is airborne fibers of asbestos. Asbestos which are easily accessible in every house are used in insulation of many electrical tools. If there is a lack of appropriate air ventilation inside the house, it is possible that pollutants may concentrate to the level much higher than outside. Hence, the pollutants may threaten the life of many residents of a house at one go. Equipments which can cause unanticipated accumulation of air pollutants are heaters which lack efficient and proper vents.

1.2.1 Major Air Contaminants and Their Sources

IPCC (2014) reported that CO_2, carbon monoxide (CO), nitrogen oxides NO_x, sulphur dioxide (SO_2), and tiny solid particles-including lead from gasoline additives-called particulates are the main known results of anthropogenic GHGs emisions. Human's injudicious and continuous use of resources like burning coal and oil (fossil fuels) to obtain energy for operating industries, fabrics and vehicles, incarnation of domestic wastes, agricultural processes, is referred as the firsthand and unparalleled sources of the major air contaminants. May be sometimes air pollutants can be the outcomes of natural occurring forest fires, aerosols, volcanic ash and the list is many.

Carbon Dioxide It the is one of the most important heat traping gas. Climate scientists show that the major cause of greenhouse effect is high concentration of CO_2 in the atmosphere. Greenhouse effect is the causative agent of global warming, increase of global temperate. Comparing with other air contaminants in terms of its abundance, CO_2 holds the first level. It constantly circulates in the environment through a variety of natural processes known as the carbon cycle. CO_2, released from respiration of animals, combustion or oxidation of fossil fuels including gasoline, coal, manure, soil organic matter, dead organic matter, fermentation of sugars, chemical decomposition of carbonates and urea, and eruptions of volcanoes.

Oxidation of soil organic matter provides energy for the soil organisms. CO_2, the product of respiration, is released into the atmosphere. But it is also removed from atmosphere as it is absorbed into water bodies and by plants by the processes of photosynthesis, conversion of CO_2 and water into simple sugars using the energy of light. However, deforestation, human activity that leads to creation of bare land by cutting trees mercilessly, tremendously reduces the processes of photosynthesis which is the ultimate increase the concentration of CO_2 in the atmosphere. It plays many roles in domestic uses like manufacture of washing soda, baking soda, and effervescence of carbonated beverages. It also helps as fire extinguisher, refrigerant and anesthesia.

With advancement of new technologies the life of human being has been improved drastically. Paradoxically, an increase in concentration of CO_2 in the atmosphere due to human activities is becoming much faster than its removal, which can not be imagined with normal human mind. The problem is becoming more severe due to the ability of CO_2 to stay for more than tens of century in the atmosphere without being disposed naturally. If you look at the history of the concentration of CO_2 in the atmosphere, there were only about 280 ppm molecules of CO_2 before industrial revolution began in the mid 1700s (Michael and Schneider 2009). However, in 2017 the concentration was risen up to 406 ppm due to global wide spread of industrial sectors and increased consumption of fossil fuel for vehicle transportation and electricity generation (GISS 2017).

Methane (CH_4) and Other Volatile Organic Chemicals CH_4 also known as natural gas is emitted from livestock enteric fermentation, from manure management systems, and largely from rice cultivation. About 43% of the emission of CH_4 into the atmosphere is from natural wet lands and paddy fields (Wild 1993). Mining of coal and other fossil fuels also some times aggravate the emission of methane particularly during their production and transportation. Methane also is emitted from decomposition of garbage in landfills, solid waste disposal sites and household products. Comparing CH_4 with CO_2 in terms concentration in the atmosphere, CO_2 is far greater than CH_4. However, the problem with CH_4 is that because it stays in the atmosphere for longer period of time than CO_2. CH_4 is more effective in rising atmospheric temperature as it traps heat more efficiently than CO_2. If we compare CH_4 with CO_2, for example, molecule of CH_4 is nearly 30 times more efficient at trapping infrared radiation radiated from the earth's surface than a molecule of CO_2.

People use CH_4 mainly as a source of fuel energy by burning it. But it has also wide application in different industries to produce different types of chemicals. In kitchens it helps to heat furnaces, stoves, heaters etc. Industries which produce construction materials also use natural gas in large amount to burn wooden materials. Food and glass processing factories also use natural gas to get heat. CH_4 is also very essential for generating chemicals, called petrochemicals, which can be employed for manufacturing commodities that can be used to enrich soil fertilities, to make plastic materials and drugs.

Volatile organic chemicals (VOCs) come in to the atmosphere due to lack of inefficient burning of fossil oils. Volatile organic compounds (VOCs) include organic compounds like ethylene, propylene, benzene, or styrene. VOC_S evaporate at a relatively low temperature and contribute to air pollution.

Nitrous Oxide and Nitric Oxide N_2O has a long residence time in the atmosphere of about 150 years. It absorbs infrared radiation but because of its low concentration it has only a small effect on global warming. Because of its long residence time it has, however, more serious effects in the stratosphere where it reacts with excited atomic oxygen to give nitric oxide, NO, which destroys ozone.

Soil temperature and water content affect the production of N_2O after application of ammonium nitrate as fertilizer. N_2O is produced mainly by the biological reduction of nitrate, a process known as denitrification. Most of the time, this process occurs under anaerobic conditions. It takes place most rapidly when the soil is warm and contains readily decomposed organic matter. Microorganisms use $NO^-{}_3$ instead of O_2 as an electron acceptor, producing NO, N_2O and N_2. Many studies indicate that the highest values of N_2O are from irrigated and fertilized soils high in organic matter (Havlin et al. 2005).

Carbon Monoxide CO enters into the atmosphere from industrial activities and from vehicles which consume fossil oil. If the concentration of CO in the atmosphere is greater than 10 mgm^{-3} over 8 h or 40 mgm^{-3} over 1 h, it will be dreadful for health (Engelking 2009). As the concentration of CO in the atmosphere increases, oxygen will not reach the lungs adequately so that the accident of asphyxia, death due to failure of blood to be oxygenated in the lungs. During the time when CO is inhaled, it is immediately assimilated with haemoglobin in the blood so that no more adsorption of oxygen, asphyxiation. Children/infants are more vulnerable to the poisonousness of CO in a given confined environment (WHO 2005). Formation of CO is prevailed if there is incomplete of burning of fossil fuels. In fact it is difficult to get a situation free of CO even with the presence of excess oxygen. Almost all moving vehicles are the main producers of these poisonous gases.

CO is very fatal to life; even 1% may lead death in less than min. The major sources of CO are urban industries, automobile exhaust and cigarette smoke. The main symptoms of this poisoning include headache, nausea, or fatigue, followed by unconsciousness and finally death. An automobile engine, leaking furnace and fuel gas are the main sources of CO.

Sulphur Dioxide SO_2 emits to atmosphere from generators and from oil or coal mining containing sulphuric acids. Nowadays, it becomes a common experience to have the incident of acid rain as their industries deposit huge amount of SO_2 to the atmosphere. If the maximum concentration of sulphuric acid is greater than 80 μgm^{-3} over a year or 365 μgm^{-3} over 24 h, it is detrimental to the life of human being (Engelking 2009).

Particulate Matter Particulate matter, collection of individual particles, may also be the cause of air pollution. Its composition differs from place to place depending on the type of industrial processes, type of vehicles, method of incineration and type of heat and power generation. Generally, it composes of carbon, nitrates, sulphates, and many harmful metals including lead, copper, iron, and zinc (Engelking 2009). The health standard recommends below 50 μgm^{-3} over a year or 150 μgm^{-3} for 24 h.

Nitrogen Dioxide NO_2 contributes to contamination of air after reacting with hydrocarbons and sunlight to form photochemical oxidants. There are many ways which lead the accumulation of NO_2 in the atmosphere. To mention some of them are improper application of fertilizers, use of nitric acid, operation of all types of generators, during mobility of vehicles and make use of explosives to break rocks and others. Acceptable level of this gas is less 100 μgm^{-3} over a year (Engelking 2009).

Ozone O_3 is formed in the lower part of the atmosphere as a result of a reaction among nitrogen oxides, hydrocarbons and sunlight. That is NO_x and VOCs may affect the chemical composition of the air in such a way that O_3 is formed under the influence of sunlight in the troposphere. O_3 is toxic at low concentrations for many organisms and may cause damage to vegetation and crops. In addition it may cause health problems to humans. According to WHO air quality guideline (2005) concentration of O_3 in the air should not be greater than 120 μgm^{-3} with in 8 h duration of exposure.

Chlorofluorocarbons (CFC_s) These types of compounds are derived from industrial by-products. Increased concentrations of CFCs and halons in the atmosphere are the major causes of stratospheric O_3 depletion. Because O_3 is a natural “filter” for ultraviolet (UV) radiation from the sun, O_3 depletion may result in increased UV-radiation, which in turn may increase risks for skin cancer and disturbances of ecosystems. People have used these compounds as a cooling agent, blowing agent, cleaning agent, aerosol propellant and fire extinguishers. Many studies realized that O_3 is being severely attacked by different pollutants. CFCs are among the pollutants which are responsible for the attack of O_3 layer. CFC molecules are virtually durable until they reach the stratosphere. But when they reach in the stratosphere, they are broken by intense UV radation and chlorine atoms will result in. Subsequently, these atoms react with O_3 to break the bond between oxygen atoms. Finally, the absorbing power of the O_3 for UV-B will be reduced tremendously and the earth will be then liable to direcr UV radiation. During the reaction the chlorine remains unchanged and hundreds of thousands of O_3 molecules can be destroyed by a single chlorine atom, reacting again and again. Some reports indicate that pollutants like N_2O from fertilizers and methyl bromide from pesticide also attack atmospheric O_3. In the Montreal Protocol on substances, countries agreed to stop using CFC_s to avoid O_3 layer depletion by this chemical. Even the use of hydrochloroflurocarbons ($HCFC_s$) will be abolished in the coming decades completely.

Waste The main sources of air contamination due to wastes are landfills, incineration and composting. Incineration and composting may result in emissions of pollutants to the environment. Possible solutions are waste prevention, recycling and making more efficient use of resources.

1.2.2 Consequences of Air Contaminants

Air pollution occurs inside laboratories, technical schools, rooms and offices, in cities, across continents, and even globally (WHO 2005). Increasing the concentration of contaminating substances in the atmosphere, air pollution, not only afflicts human health but environment and quality of life as well. Particularly, air contaminants affect the health of human being. Major problems associated with air pollution are cancer and respiratory systems. Also, all living organisms together with their ecosystems are the main victims of these harmful pollutants. Some air pollutants (oxides) combine with water vapour and return to earth in the form of acid rain and snow, which corrode statues and buildings, damage crops and forests, and make lakes and streams unsuitable for fish and other plant and animal life.

Pollution is feared to cause ineffective atmosphere to reflect dangerous radiations (UV-B from the sun). At the same time the atmosphere acts as barrier so that no way of escaping of heat in to the atmosphere. Therefore, the absorbed heat in the atmosphere increases dramatically. As the result the average temperature of the globe increases so that the global warming phenomenon prevails. It is belived that sudden rise of sea level, wide spread of contagious diseases etc will prevail due to global warming.

A mixture of smoke and fog forms a smog which causes irritation in eyes, throat and lungs as well as it damages plants. Smog containing O_3 in the lower atmosphere is poison which can damage any living thing and spoil artifacts and statures. The Parthenon temple in Athens, Greece, and the Taj Mahal in Agra, India are some of the victims of smog acids. Environmental officials measure O_3 to determine the severity of smog. With increasing the level of O_3, pollutants like CO intends to increase so that the condition going on even more worse.

Smog also has the potential to spoil the beautifulness of cities and towns. All outdoor activities are becoming unpleasant and their efficiencies are highly affected. It becomes harsher for those who have respiratory, headache and heart problems. Some times smog can be fatal to mass death due to high concentration of CO. For example, in 1952 about 4000 people were killed in Landon due to incidence of thick smog (Ware et al. 1981).

Air pollution is not restricted only at regional level but expands to effect globally. The stratosphere, a zone of O_3, which is between 16 and 50 km above sea level, is the most liable atmospheric layer to air contaminants.This lever saves the earth from penetration of UV-B. If these radiations reach the earth surface, definitely, they will damage the genetic molecule (DNA) of any living cell. This problem then can impose cancer in human being. Thus, we can say that O_3 layer is the saver of the whole lives of our planet.

According to the report of IPCC (2006), if the control measures of air contaminants are not implemented on the ground, there is high possibility that a rise of global temperature between 1.4 and 4.8°C and sea level between 20 and 88 cm will be occurred by the year 2100. If the sea level rises by this magnitude, costal cities will be part of the sea, high social crisis will occur, and spread of communicable diseases will be beyond control.

1.2.3 Control of Air Contamination

For controlling air contamination, a law should be passed against those responsible for polluting materials and activities. However, the law will not be practical unless it clearly specify type and level of these harmful substances.Though there are many ways of specification of air contaminants, the common one is just sampling ambient air and testing it for the presence of the pollutants. Generally, materials like lead, CO, SO_2, $NO_{x,}$ O_3, VOCs, particulate and other polluting materials. Efforts are needed to publicise and enforce acceptable population standards.Then, investigation of the existing and the newly entering pollutants in the atmosphere will be carried smoothly.

It is the best strategy to control air contamination by decreasing the emission of pollutants locally and globally. However, once the pollutants are formed the contaminants should be controlled using special devices. These are fixed in any vehicle (as catalytic converter) and industrial plants (as filters and scrubbers). The function of catalytic converter is to reduce the harmfulness of the gasses. Protecting air pollution is much more feasible than cleaning the polluted air. Many attempts have been made to achieve clear air. For example let's take the case of gasoline. It has been tried to formulate many times to burn it without polluting the air. Another way is using alternative sources of energy like electricity, solar energy, wind energy etc. for automobiles. Improvement has been made in the design of buildings so that to utilize the sun during cold times and shade and breezes during hot time in stead of using artificial heating and cooling. If more people use public transportation rather driving individually, the number of automobiles will be reduced significantly. Special buildings equipped with proper ventilation should be constructed to avoid indoor pollution. Smoking in public rooms must be prohibited. Never use asbestos in insulation. Construction of tight foundations avoids seeping of pollutants into buildings.

1.3 Water Contaminant Chemicals

Water has unparalleled necessity to all lives existing in the human planet. But contaminated water resources such as streams, lakes, underground water, bays, or oceans by chemicals are harmful to living things. Pollution even makes streams, lakes, and coastal waters unpleasant to look at, to smell, and to swim in. Water pollutants can be in the forms of chemical, biological, or physical materials.The ultimate consequence of these materials is to degrade the quality of water. In this chapter more focus is given on chemical pollutants of aquatic ecosystem.

1.3.1 Types and Sources of Chemical Contaminants

There are two types of sources of water contaminants. These are point pollution and non point pollution. Point pollution is the type of pollution in which the sources of chemical contaminants are clearly identifiable. An example of point pollution includes factories, processing plants etc. But non point pollution is the second type of pollution in which the sources of chemical contaminants are not easily identifiable. Generally, the main cause for water pollutants is thought to be human activities. Chemical may reach water bodies from outlet of pipes in industries, leakage of pipe line or storage tanks. Mining operations is also responsible for significant water pollution either through the use of chemical contaminants during ores processing in the mining area or through leaching of water through chemical rich rocks. Large amounts of sewage are produced in cities and carried to water bodies either through canals and flowing streams or other mechanisms. Chemical pollutants are also produced in industries, agricultural sources like pastures, ranches, feedlots etc. The major source of sea pollutants includes processing plant and mining activities in the adjacent shorelines, offshore oil platforms, some leakage from ships etc. Plastics are the most harmful materials to marine animals if thrown and swallowed.

Significant oil is added to oceans during the flushing of tanks. There are other sources of water pollution. The outlet of a given chimney transfer chemicals, for example SO_2, from the plant to the atmosphere. As SO_2 in the air starts to mix with moisture in the atmosphere, sulphuric acid is produced and rain to the earth. This acid will get a way to reach the water bodies by runoff and then it will harm many animals living in the water bodies or drinking from that water. The materials in the garbage may be toxin so that during raining times the toxic substances can be carried with percolating water and hence pollution of underground water will be there.

In agricultural fields, nutrients like nitrates and phosphates from applied fertilizers and sewages are carried into rivers, streams and lakes. This leads to the formation of eutrophication which causes the death of many fish and other aquatic lives. Runoff also sometimes carries toxic algae like *Pfiesteria piscicida* and pesticides together with industrial wastes into water bodies. Fine sediment which has been carried by soil erosion is also responsible for the killing of mass aquatic lives.

Petroleum Products People use crude oil to produce chemicals which are used for many purposes such as lubrication activities, fuel energy, plastics and others. As a result of improper use and handling of these chemicals, however, they reach water bodies and reduce the quality of water. To mention some of human activities which lead to water contamination are leakage from perforated pipeline system, above and underground oil containers, vehicles, ships and others. Almost all oil products are lethal if they taken by animals in large amount. Polychlorinated biphenyls (PCBs) are harmful substances that contaminate water bodies.

Pesticides The chemical agents called pesticides include herbicides (for weed control), insecticides (for insects control), and fungicides (for fungus control). Chemicals used to kill unwanted animals and plants, for instance on farms or in suburban yards, may be collected by rainwater runoff and carried into streams, especially if these substances are applied too lavishly. Some of these chemicals are biodegradable and quickly decay into harmless or less harmful forms, while others are non-biodegradable and remain dangerous for a long time.When animals consume plants that have been treated with certain non-biodegradable chemicals, such as chlordane and dichlorodiphenyltrichloroethane (DDT), these chemicals are absorbed into the tissues or organs of the animals. When other animals feed on these contaminated animals, the chemicals are passed up the food chain. With each step up the food chain, the concentration of the pollutant increases. This process is called biomagnification. An excess of glyphosphate, a widely used ingredient in herbicides, kills susceptible beneficial insects that prey on insect pests, and it is extremely toxic to fish.

Nitrates Use of uncontrolled pesticides and fertilizers in the farm area contaminate drinking water supplies with nitrates. The NO_3^- ion, being negatively charged, is not adsorbed by most soils. It remains in the soil solution until it is either taken up by plant roots or leached out of the soil in drainage water, or denitrified. Nitrate analysis of drinking water are reported as concentrations of nitrate in milligrams per litre, or the amount of nitrogen possessed by nitrate (NO_3^-N) in milligrams per litre. The most recent guideline from the European Commission set the ‘Maximum Admissible Level’ for nitrate in drinking water to be 50 g of NO_3 per litre of water. The health risk from nitrate in drinking water free of faecal contamination is very small.

Heavy Metalloids Lead, mercury, copper, and selenium are some of the harmful heavy metals. They pollute water bodies if they get the way from their sources like mining, factories and industries, vehicles and parent materials having these chemicals (Oves et al. 2016). Animals can acquire these heavy metals from plants and other animals which already consumed these chemicals.

Hazardous Waste Generally, hazardous wastes are categorized into toxic, reactive, corrosive, and flammable. Most of the time the materials can reach the water bodies due to lack of appropriate storage or treatment. The wastes can get into the water by oil spills or any other mechanisms. Or animals can also be victims of these wastes if they scavenge polluted dead or alive organisms. Animals can also be toxic by their nature if they are eaten by other animals.

Excess Organic Matter Excess application of fertilizers, organic matter and other nutrients can get a way to pollute water. These leads to the high growth of algae and aquatic plants which when die in the water leads to prevalence of high decomposition processes- eutrophication phenomena, depletion of oxygen to a deadly level. Eutrophication causes many deaths of oxygen dependent organisms like fish and others. Pollutants used to promote plant growth on farms and in gardens, may find their way into water. Landfills may result in landscape deterioration, and pollutants may leach from the landfills to the groundwater.

Sediment In the absence of good vegetation cover and appropriate soil water conservation measures too many soil particles are discharged into water bodies from agricultural lands, mining areas and roads. This sediment may impose water contamination not only because of having high nutrient matter but it may be laden with harmful contaminants. Wildlife living in wells, lakes, rivers and streams are extremely vulnerable to contaminant chemicals. Pollutants that reach sea may kill and disturb aquatic ecosystem. Though the oceans are vast, but they are vulnerable to pollution. Polluted water is not only responsible for health problems for humans but cause the deaths of unimaginable amount of wildlife.

1.3.2 Consequences of Water Contamination

Human beings at the top of food chains may, as a result of these chemical concentrations, suffers cancers, reproductive problems, and death. High intake of water and food contaminated with high concentration of nitrates can lead to methemoglobinemia or blue baby syndrome in infants, a potentially lethal form of anemia. This disease is not caused by nitrate but by nitrite, produced in the gastro-intestinal tract by nitrate-reducing organisms. Highly consumption of nitrate also leads to gastric cancer.

Like pesticides and herbicides heavy metals can result in long-term health problems as they reach high levels in the body. That is, if humans eat crops and vegetables, which already absorbed cadmium excessively from organic fertilizers particularly sewages, can lead to the damage of essential body organs. Consumption of Lead is also responsible for mental retardation (Morgan 2013). Fish and shellfish harvested from polluted waters may be unsafe to eat. People who ingest polluted water can become ill, and, with prolonged exposure, may develop cancers or bear children with birth defects. Industrial pollutants that run into streams, rivers, or lakes can have serious effects on wildlife, plants and humans.

A change in the nutrient status in soils and sediments may have an effect on species distribution in terrestrial and aquatic ecosystems; increased nitrate levels in ground water may result in toxic nitrate levels in drinking water, health hazards. Eutrophication is one of the common consequences of water contaminated with nutrients. It is an enrichment of lake, river and sea waters with nutrients (such as nitrogen, phosphorous and sulphur) that increase the growth of aquatic plants. It is due to agricultural and industrial activities underlying losses of nitrogen, sulphur and phosphorus to the environment. That is, though it is a natural process, but it is accentuated by human activities like discharge of industrial wastewaters, sewage effluent, runoff, leaching from heavily fertilized or manured agricultural land and deposition from atmosphere. Eutrophication is always underway if the levels of nitrogen and phosphorus in natural ecosystems and groundwater have increased.

There are some events in which acid rain or acid snow can have disturbance of the aquatic ecosystems. Moreover, spilled oil from ship and industries in coastal waters may cause the poisoning of fish and the loss of feathers and furs. If the animals swallow the chemicals in large amount, there is high possibility of death.

1.3.3 Control of Water Contamination

Governments, policy makers, and managers should give priority to reduce water contaminants coming from eroded soils, agricultural chemicals and wastes, pesticides and excessive fertilizers. Increasing vegetative covers help being as barriers against to those harmful chemicals which come along with eroded soils. To reduce the amount of sediments, well planned soil and water conservation should be implemented in the water shed and along the river banks. Farmers and foresters should work to stabilize the banks of rivers and streams by increasing the vegetation cover. Farmers should be aware of not tilling their land up and down along the slope to reduce the accumulation of sediments in water bodies. Animals should be confined in a certain places so that their wastes can be controlled and treated conveniently. If possible wet land area should be reserved to help for retaining sediments and nutrients.

1.4 Soil Contaminants

Wild (1993) defined soil pollution in his book as a build-up of toxic chemical compounds, salts, pathogens (disease-causing organisms), or radioactive materials that can affect plant and animal life. Soil is a mixture of mineral, plant, and animal materials that form during a long process that may take thousands of years. It is the growing house of plants and microorganisms. These living things get their nutrients with the help of chemical processes. Shortly soil is a source of food for most living things and without which agricultural production is impossible. Therefore, the chemical situations like pH, structure of organic compounds and minerals, soil ventilation system, and liquid phase affect the growth of plants and organisms living in the soil (Havlin et al. 2005).

1.4.1 Types and Sources of Soil Contaminants

In addition to metallurgical activity and addition of sewage sludge to the soil, there are several possible causes of soil contamination such as dispersion of toxic compounds, acidification, salinization and sodification, enhanced soil erosion, chemical fertilizers, pesticides, fungicides, and the accumulation of heavy metals and other inorganic contaminants (Meerschman et al. 2011).

Dispersion of Toxic Compounds Human activities, for example the use of biocides, are the main sources of toxic compounds which pollute air, soil and water. Dispersion of these compounds may result in toxic levels in the environment. Toxicity may cause health problems for many organisms.

Acidifying Compounds Soil acidification is accelerated by deposition of acids and acid forming substances from the atmosphere, fossil fuel use, industry and traffic, excessive use of agriculture fertilizers containing ammonium salts or Urea, by biological nitrogen fixation and nutrient removal by crops.

The most common types of acidifying compounds are SO_2, various NO_x that include NO, nitrogen dioxide (NO_2), and N_2O, and ammonia (NH_3).These compounds (SO_2 and NO_x) after making some transformation in the atmosphere they come down to the earth surface in the form of acid rain. The main chemical compounds which cause soil acidifications are carbonic acid (H_2CO_3), nitric acid (HNO_3), sulphuric acid (H_2SO_4), hydrochloric acid (HCl) in precipitation falling on to soil, direct absorption of gases like CO_2, SO_2 and SO_3 from the atmosphere by soil and deposition of aerosols onto soils. In Europe, North America and some Asian countries, deposition of acidifying compounds is becoming common for causing acidification of soil and aquatic systems. Soil acidification can cause problems to natural ecosystems with respect to diversity and distribution of species. As a result of an inappropriate use of agricultural fertilizers, ammonium involves in the acidifying processes after being nitrified in soils to NO_3^-.

Salt Buildup The accumulation of salts particularly sodium (Na^+), chlorine (Cl^-), and boron (B), is an existing danger in irrigated agriculture of arid and semiarid regions (Havlin et al. 2005). Significant buildup of these salts in the upper soil can be toxic enough to inhibit crop yields. Na^+ is particularly determinant because of both its toxic effect on plants and spoiling effect on soil structure. The sources of salts can be from the weathering of minerals and accumulation of such salts in areas where the precipitation is too low to provide leaching. Salinization (buildup salts) of land is particularly prevalent in areas with high water tables and poor lateral drainage that experience high evaporation rates and lack opportunities for leaching excess salts. Salinization affects not only agriculture but also structure and living standards of society particularly women and children, emigration, collapse of metropolitan cities, and health problems (including stomach diseases, breathing difficulties and skin conditions).

Heavy Metals and Radionuclides Any element can be harmful to plants or animals if it presents in a soil in excess concentration. Heavy metals and radionuclide (also called radioactive nuclides or radioactive isotopes which decay with time, in contrast to stable isotopes) are known to contaminate soils. Generally, their path into the soil is through mining and smelting activities, deposition from the atmosphere, seepage from disposal sites, and application of sewage and sludge, pig manure and certain fertilizers and pesticides.

During mining operation the contamination of adjacent soils with metal mined (blown or washed), low grade ore, solid waste and associated heavy metals is inevitable. Metal mining particularly during purification processes emits harmful particles and gases, especially SO_2. Blown particles are deposited on the soils around the mining activities. However, those very fine particles are removed by rain. Deposition of metals is greatest near the smelter and decreases exponentially with distance. Sewage and sludge is the organic material produced from domestic and industrial wastewater and direct run-off from roads. If not properly treated, sewage will have bad smell and may pollute the environment. Globally, billions of tons of solid wastes including resistant plastics, animal products, metal and wood pieces and unwanted papers are disposed into water bodies and agricultural area annually. More solid wastes per capita are observed in the cities of developed countries than in economically developing countries. Moreover, waste from developed countries typically contains a high percentage of synthetic materials that take longer to decompose than the primarily biodegradable waste materials of developing countries. Hazardous wastes are solid, liquid, or gas wastes that may be deadly or harmful to people or the environment and tend to be persistent or nondegradable in nature. Such wastes include toxic chemicals and flammable or radioactive substances, including industrial wastes from chemical plants or nuclear reactors, agricultural wastes such as pesticides and fertilizers, medical wastes, and household hazardous wastes such as toxic paints and solvents.

Hazardous wastes of particular concern are the radioactive wastes from the nuclear power and weapons industries. To date there is no safe method for permanent disposal of old fuel elements from nuclear reactors. Most are kept in storage facilities at the original reactor sites where they were generated. With the end of the Cold War, nuclear warheads that are decommissioned, or no longer in use, also pose storage and disposal problems.

Organic substances such as pesticides like atrazine (chloroethylaminoisopropyla), Bordeax mixtures (solutions of copper sulphate and calcium hydroxide), herbicide (2, 4-dichlorophenoxyacetic acid), DDT (dichlorodiphenyltrichlorothane) and others can also contaminate soil. Pesticides reach the soil in drip from plants, as seed treatments, root dips, spray which does not contact the target organism, and in the tissues of plants and insects that have been killed. Some pesticides are applied directly to the soil.

Heavy metals which are considered as hazardous elements to plants or animals include arsenic, As; cadmium, Cd; chromium, Cr; copper, Cu; lead, Pb; mercury, Hg; nickel, Ni; and zinc, Zn (WHO 2013). However, the most common known hazardous elements in soil are Cd, Pb, Zn, and F. Heavy metals are more strongly held as complexes on the surfaces of clay aluminosilicates, hydrated oxides and humus. They also occur in solution as cations and are adsorbed by the negatively charged soil particles.

Soil is usually regarded as the ultimate sink for heavy metals discharged into the environment, yet relatively little is known about the way that heavy metals are bound to soils and the ease with which they may be released. The concentration of heavy metals in soils can be influenced by variation in their texture, composition, reduction/oxidation reactions, adsorption/desorption, and physical transport or sorting in addition to anthropogenic metal input (Hannah et al. 2009). Metal concentrations in time and space and metal bioavailability from soils fluctuate due to the above processes. Researchers have studied metal inputs to soil from and/or around various industrial sources such as mining, smelters, cement factories etc.

Several elements have caused fatalities of animals and humans due to the ingestion of excessive amounts, although very few of these fatalaties have been caused by contamination of soils, and hence of food, by metals of anthropogenic origin. The four elements to be discussed here include cadmium, lead, zink and fluorine, which is not a heavy metal.

Cadmium This is relatively rare metal, its concentration in the earth's crust and in soils is very low. Generally, it is found in zinc sulphide ores, and in lesser concentration in zinc carbonates and silicaes and in lead and copper sulphides. It is covered as a byproduct during the processing of zinc ores, but its removal is often incomplete. Its increasing industrial use in batteries, alloys and pigments, as stabilizing agent for polyvinyl plastics, and electroplating metals, has caused concern about its effects in the environment.

One of the most widespread sources of cadmium in soils is phosphatic fertilizer, which has an average concentration of about 7 μg Cd per gram fertilizer, although this varies with the source of the phosphate rock from which the fertilizer is manufactured. However, much more cadmium is added in one application of sewage sludge than in a normal application of fertilizer. Cadmium and solutions of its compounds are highly toxic, with cumulative effects similar to those of mercury poisoning.

Lead The distribution of lead over the world is in the form of its sulphide called lead sulphide (PbS), the ore galena. Waste materials, such as battery scrap, recovered from various industrial processes, are also smelted and constitute an important source of lead. Uses of lead are many viz. in storage batteries, in sheathing electric cables, in industry for lining pipes, tanks, in paints and pigments, X-ray apparatus and as protective shielding for radioactive material.

Contamination occurs near to, and downstream from, old lead mining areas and by deposition from the atmosphere of particulate material released from smelters. The toxicity of lead to humans has long been recognized. With wider use of alternative materials, exposure to lead from water pipes, house paints, children's toys and food containers is becoming less; the use of unleaded petrol is also becoming more common. The lead is added to petrol as lead tetraethyl and tetramethyl and is emitted from car exhaust as PbBrCl in particulate form. Most of the suspended particulates are deposited within 50 m of highways but small particles can be transported several kilometres. The greatest hazard to humans from this source of lead occurs through inhalation of the particles and consumption of leafy vegetables grown in urban gardens on which the particles have been deposited. Analysis of contaminated soils shows that lead is concentrated near the soil surface, very little moving down the soil profile. The low mobility is due to adsorption onto the surfaces of iron and manganese oxides and clay aluminosilicates.

Zinc Zinc plays many roles in making coatings, galvanizers, alloys, wood preservatives, soldering fluid, paint pigment, filler in rubber tires, screens of television tubes and fluorescent coatings, and antiseptics. At high concentrations in soil zinc can be phytotoxic, reducing the growth of plants or killing them at tissue concentrations that would not be toxic to animals. The principal hazard with zinc is therefore with plants, and the problems are associated with the mining and smelting of zinc ores, the application of sewage sludge, which usually contains more zinc than other metal known to harm plants, and sites beneath galvanized wire netting and electric cables.

Fluorine Fluorine compounds have many applications. Toxicity is not limited to heavy metals only. High concentrations of fluorine or its compounds are toxic to plants and animals. Various industries, especially aluminium smelters, cement and brick kilns, and phosphate fertilizer factories emit fluorine compounds to the atmosphere in both in particulate and gaseous forms. The particulate emissions are deposited close to the source and although they do not damage plants, they may harm animals grazing affected pastures. Gaseous fluorides, principally hydrogen fluoride (HF) and silicon tetrafluoride (SF4), can harm plants and grazing animals, even present in very low concentrations. Fluorine compounds are also emitted from some volcanoes, giving high concentrations in drinking water.

Radionuclides The radionuclides in soil that have concern have come from the testing of nuclear weapons, accidents at nuclear power stations, and poor waste disposal and storage. Three most important radionuclides of caesium, iodine and strontium, will be discussed below. An elevated level of each radionuclide causes considerable environment hazard.

Caesium It is one of the most reactive elements. It is produced in nuclear reactors; it can be present in the discharging liquid of the reactors. It was released in large amounts to the atmosphere from the accident of Chernobyl reactor and was deposited over much of Europe and contaminated soil and pastures. Caesium ions (Cs^+) are adsorbed by soils. When they displace more hydrated ions, e.g. Na^+, Ca^{2+}, Mg^{2+}, from the interlayer spaces of clay minerals like smectites and illite, the layers collapse and trap the caesium ions in cavities. The adsorption of small amounts of Cs^+ by these clay minerals and especially by illite is difficult to reverse. It is difficult to remove the adsorbed caesium from top few centimetres. However, it is taken up from the soil by plants and passes into the food chain.

Iodine Escape of this radionuclide happened as a result of accidents to nuclear reactors in UK (1957) and in Ukraine (1986). Contamination of soils with ^{131}I is less hazardous than with ^{134}Cs and ^{137}Cs because most will decay during the course of a growing season. But if contaminated herbage is eaten by diary cows, it can be transferred to milk (Hannah et al. 2009). In the soil solution iodine is present as I^-. The ions are retained by soils by reaction with organic matter, oxides of iron and aluminium and clay aluminosilicates. An other isotope, ^{129}I, is present in waste from reprocessing plants, and as it has a half-life of 1.7×10^7 years its retention in soil can be a long-term hazard.

Strontium It has been released into the atmosphere from the testing nuclear and from accidents at nuclear power stations. It has been a cause of great concern because it behaves like calcium in the food chain, the radionuclides passing into bones from milk and other foods. In solution strontium is present as Sr^{2+} and undergoes cation exchange reactions in a similar way to Ca^{2+}. It is readily taken up by plant roots and translocated to leaves, fruit and seeds. Uptake can be reduced, especially in soils low in calcium by the application of gypsum or lime.

1.4.2 Consequences of Soil Contaminants

Increase or decrease of pH beyond optimum level may affect the soil's natural processes. Acidic soils cause toxicity of aluminium and manganese, deficiencies of basic elements like calcium, phosphorus, magnesium and reduction of nitrogen mineralization as affected by microbial activity (Havlin et al. 2005). It also leads to reduction of boron, zinc, molybdenum and copper availability. Alkaline soils damage the health of physical properties of soils through surface sealing and crusting. More importantly, availability of iron, manganese, zinc, phosphorus and copper is reduced due to the presence of excessive sodium on the exchange complex of the colloids. Many cities like ancient Sumerian cities in Mesopotamia were collapsed due to extreme soil alkalinity.

Applying chemical fertilizers, pesticides, and fungicides on the soil for unlimited period of time will have negative influences soil physical and chemical properties (Hannah et al. 2009). Contaminated soil also kills soil fauna which are beneficial to soil fertility (Science Communication Unit 2013). For example, soil treated with methyl bromide totally damage strawberry seedlings. If the application of these chemicals continues, important microorganisms will be damaged. In the long term the soil will be sterile and finally the soil's potential productivity will be highly dependent up on the application of chemical fertilizers. Excessive application of fertilizers also leads to lakes and streams pollution.

Soil contaminants have high health risks during their use, storage, transportation, and disposal. They also pose serious environmental risks. Long term exposure to these harmful materials, in the long term, they may cause cancer, disorders of nervous system, sexual dysfunction and birth defects and even death (Science

Communication Unit 2013). If the hazardous materials are released in large amount due to weak controlling mechanisms, they will cause thousands of deaths of people. The chemicals also will last for many years contaminating air, water and soil. It will take long time and unbearable cost to reclaim such contaminated soil (European commission 2012)

According to Beckett and Davis (1988) *phytotoxicity* can be defined as the accumulation of harmful substances in the plant tissue so that optimal growth and development of that plant is highly affected. This is mainly because the response of the plant to phytotoxic materials varies from plant to plant. Additionally, the intensity of heavy metals and nature of soil type are the key factors which affect the phyototoxic effects in soils (Science Communication Unit 2013).

Wild (1993) listed three mechanisms of plants to fight the phytotoxic effects. Plants can tolerate the effects of heavy metals by excluding from the roots by forming mycorrhizas, restricting their translocation from roots to shoots and forming complexes with organic acids inside the plant to avoid the metals interferences with metabolic processes.

1.4.3 Control of Soil Contaminants

There are many tangible ways to control soil contaminants such as landfills, incineration or burning, composting, recycling etc.

- **Landfills**: solid wastes can be disposed and buried. However, careful preparation and management are often required to avoid unnecessary contamination of air, soil and water from landfills.
- **Incineration or burning**: this is mainly done to reduce the volume of solid waste. But here well planned activity of burning is required to avoid the production of airborne dense ashen wastes which can have hazardous materials like heavy metals and toxic compounds.
- **Composting**: it is essential natural processes to decompose the organic wastes instead of burning. Compost is natural fertilizer which has several benefits in agricultural.
- **Recycling**, **extracting and reusing**: countries should develop a mechanism to recycle the solid wastes so that the materials can be used as raw materials in different industries as part of waste management strategies. The by-products also can be utilized in agriculture as organic fertilizers. Every country, particularly developed countries, should get help to expand recycling programs worldwide so that pollution due to solid wastes will be reduced significantly.
- **Waste prevention**: the best practice in the management of solid wastes is waste prevention. During the manufacturing of goods and commodities injudious use of resources has to be reduced systematically, such as altering the way products are designed or manufactured to make them easier to reuse and reduce the high costs associated with environmental pollution.

- **Law and Legal regulations**: law should be enforced to protect or to restrict the dumping of potentially hazardous materials into water bodies and soils. The law and regulation should state the way how to dump and bury the hazardous materials safely. In addition, the law should fight against the waste trade, enforcing poorer countries to accept shipment of solid and hazardous wastes after getting nominal payments from developed countries.
- **Contaminated soils** with heavy metals can be limed so that to reduce the availability of these metals to plants. Addition of organic matter has the same effect as that of liming. Improved drainage can also be remedial because the most oxidized forms of iron (Fe^{3+}) and manganese (Mn^{4+}) oxides adsorb the metals. Where contamination is extreme new topsoil should be added. Tolerant plant species should be grown, if necessary using genotypes transferred from metalliferous sites.

1.5 Conclusion and Future Prospects

All developmental activities such as agriculture, mining, construction, industrial processes, energy generation plants, transportation facilities directly or indirectly and knowingly or unintentionally have vital contribution in producing contaminant chemicals for air, water and soil. The consequence of air contamination is becoming evident as the earth experiences abnormal precipitation patterns, relentless increase of global temperature and melting of polar ices, ever increasing ocean acidity and sea level, and frequenting of unpredictable and exteme change of weather events. In turn this climate change reflected back against human being interms of health and safety of societies and the value of the whole ecosystem. Generaly, both soil and water contaminats have being produced in a large amount with the advancement of industrial processes. Many studies confirmed that contaminant chemicals are the causative agents of many chronic and acute diseases. In addition to the effects of contaminant chemicals on health aspects, they (chemicals) are affecting the environment negatively.

Many assessments reported that surface temperature is projected to rise even beyond our expectation. It is very likely that heat waves will occur more often and last longer, and that extreme precipitation events will become more intense and frequent in many regions. The ocean will continue to warm and acidify, and global mean sea level to rise. Despite increasing awareness of climate change, our emissions of GHGs continue on a relentless rise. In 2017, the daily level of CO_2 in the atmosphere recorded more than 406 ppm. Though the effects of soil and water contaminants on health and environment is not fully understood, we are already beginning to see the implications of chemical contaminants.

Climate change can be responded using two approaches: mitigation and adaptation. Heat trapping gases can be reduced by decreasing the use of their sources or enhancing sinks of the gases. It is also the right time to think on how to reduce our vulnerability to the harmful effects of climate change. The major source of all chemical contaminations is the fight to get energy in commodities productions, transportation and other necessary requirements. Therefore, it is vital and timely to boost the alternative sources of energy: solar, hydropower and wind energy. If proper and efficient use of agricultural chemicals, recycling of domestic and industrial effulents are introduced, contamination hazards of soil and water can be stepped down.

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Chapter 2
An Insight to Atmospheric Pollution- Improper Waste Management and Climate Change Nexus

Bhavisha Sharma, Barkha Vaish, Vaibhav Srivastava, Sonu Singh, Pooja Singh, and Rajeev Pratap Singh

Abstract Urbanization and industrialization along with expansion of the cities, extract resources indiscriminately in order to provide better access to food security, education, health and employment. However, accompanying this urbanization and industrialization, there is an increase in generation of vast amount of waste. Per capita waste generation is closely related to high quality life style, consumer pattern and economic development. Municipal Solid Waste (MSW) is affected by many drivers (socio-economic, political, environmental, etc.) and its impact differs from country to country. The scenario is worse and complicated in developing countries due to negligence in waste management sector. Improper waste management has emerged as one of the potent source of series of air pollutants that arises concerns over ambient air quality, environmental degradation and public health. Overall waste sector is estimated to contribute around 3–5% of global greenhouse emission. But, this estimate does not include the emission from the uncollected waste that decays anaerobically and is the main cause of methane generation which has not yet been quantified. Therefore, it is imperative to integrate proper waste management technologies especially for developing economies. Thus, this chapter attempts to relate the nexus between improper management of municipal solid waste and climate change and to reduce greenhouse gas emissions through proven technologies and existing policies.

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M. Oves et al. (eds.), *Modern Age Environmental Problems and their Remediation*,
DOI 10.1007/978-3-319-64501-8_2

Keywords Atmospheric pollution • Waste management • Climate change • Greenhouse gases • Policies

2.1 Introduction

The rapid pace of urbanization and industrialization along with technological advancement has ended up in generation of huge volume and quantity of municipal solid waste (MSW) around the globe (Singh and Sarkar 2015; Srivastava et al. 2015, 2016; Singh et al. 2017). Presently, more than 52% of the global population resides in urban and sub-urban areas which is expected to increase upto 64–69% by 2050 (World Bank 2013). As per provisional figures of World Energy Outlook (IEA 2008), urban areas accounted for 67–76% of global energy use whereas the urban energy related to carbon dioxide (CO_2) emission ranged between 71–76%. It is a bitter truth that only about 20% of the MSW is recycled and around 14% is utilized for energy conversion while the rest is disposed off in open dumps or landfills (IPCC 2014). Also, 47% of wastewater from domestic and industrial sectors remains untreated. Therefore, a proper waste management system is required to overcome the negative impact of economic growth and technical development throughout the world (Singh and Sarkar 2015). During the process of MSW management several kinds of air pollutants are released into the environment. Also, when wastes are heaped up in open dumps/landfills, some organic substances are decomposed and discharge noxious gases. In most of the developing countries improper waste disposal and treatment processes are being used for managing MSW, that leads to production of a series of air pollutants like greenhouse gases (GHGs), Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), particulate matter, odorous gases, etc (Vaish et al. 2016a). Consequently, waste has been recognized as a new significant emerging source for air pollutants that pose threat to the ambient air quality and public health (Tian et al. 2013). Nowadays, emission of GHGs from MSW disposal and treatment practices is considered the most significant anthropogenic sources of GHGs and is getting attention of environmental scientists and policymakers (Singh et al. 2017).

Although, post-consumer waste generated is a diminutive contributor to the global GHG emissions ($<5\%$) with total emission of approximately 1300 $MtCO_2$-eq in 2005, but this sector could play a major role in GHG mitigation at low cost and help in sustainable development (IPCC 2007). Jeon et al. (2007) reported that methane produced from waste landfill sites has a contribution of 3–4% to the annual global anthropogenic GHG emissions. The waste sector considerably contributes to the atmospheric GHGs emission (e.g. CH_4, CO_2 and N_2O) through emission from landfills, sewage and wastewater treatment, incineration, anaerobic digestion, etc. The anaerobic decomposition of organic matter/biodegradable portion of MSW in open dumps/landfills generates landfill gases (LFGs), composed of methane (CH_4) (50–60%) and CO_2 (~40%) along with trace amount of non-methane volatile organic compounds (VOCs) (Hegde et al. 2003; Vaish et al.

2016b). This percentage may differ and largely depend on waste composition, moisture content and the hydrogen/oxygen availability. Being GHGs both CH_4 and CO_2 have global warming potential, which is 25 times higher for CH_4 than global warming potential of CO_2 with atmospheric residence time of 12 ± 3 years (IPCC 2007). Fang et al. (2012) demonstrated the emission of odorous substances like ammonia, acetone, acetic acid, n-butanone, n-butaldehyde, dimethyl sulfide, styrene, toluene and xylene from landfill site situated in Shanghai, China. However, the formation dynamics and dispersion of these pollutants in landfill sites basically depend on their own characteristics, waste composition and existing atmospheric conditions (Nolasco et al. 2008; Tian et al. 2013). In general, the air pollutant types, their characteristics and GHGs emission may vary among different MSW disposal methods (Tian et al. 2013). It is believed that emission of both solid and gaseous pollutants takes at least three decades or even centuries to end from an abandoned landfill site (Ritzkowski et al. 2006). Therefore, in order to reduce the GHGs emissions an integrated approach for waste management should be adopted from the beginning of the process (i.e. waste collection), since it has significant effect on subsequent waste treatment processes. Apart from this, socio-economic, environmental and public health standards should be achieved.

The present chapter is planned to highlight the existing air pollution problems related with waste management sector. Furthermore, authors have tried to establish a connection between improper waste management and its contribution to the global climate change. Also, some comprehensive control proposals to reduce GHGs emission for this sector in the future are proposed.

2.2 Emission of GHGs from Waste Sector

During last few decades anthropogenic GHG emissions have increased sharply. From 2000 to 2010, GHG emissions raised on average by 1.0 $GtCO_2eq$ per year as compared to 0.4 $GtCO_2eq$ per year throughout the entire period of 1970–2000 and reached to 49 (±4.5) $GtCO_2eq$ per year in 2010 (JRC/PBL 2013). In 2010, more than 52% of global direct GHG emissions from industrial and waste/wastewater sectors were reported from Asian region, followed by Organisation for Economic Co-operation and Development in 1990 (OECD-1990), Economies in Transition (EIT), Middle East and Africa (MAF), and Latin America (LAM) (Table 2.1).

Total global GHG emissions from different sectors are shown in Fig. 2.1. Although, the global emissions from waste sector has doubled from 1970 (734 $MtCO_2eq$) to 2010 (1446 $MtCO_2eq$) but there was a significant increment of 13% during 2000–2010 (from 1278 $MtCO_2eq$ to 1446 $MtCO_2eq$) reflecting the rapid pace of urbanization (JRC/PBL 2013). In 2010, GHG emissions from waste represented 3% of the total GHG emissions from different sectors compared to 2.6 % in 1970 (JRC/PBL 2013). The main source of waste GHG emissions are open dumps/landfills (43%) and wastewater handling (54%), whereas incineration and other sources are of less importance (JRC/PBL 2013). On a global scale,

Table 2.1 GHG Emission pattern from waste/wastewater in different world regions

Region	GHG emission ($GtCO_2eq$)		
	1990	2005	2010
Asia	0.35	0.54	0.60
Latin America	0.10	0.14	0.14
Middle East and Africa	0.10	0.16	0.17
Economies in Transition	0.12	0.13	0.15
OECD-1990	0.50	0.40	0.39
World	1.17	1.37	1.45

Source: IEA (2012a, b, c) and JRC/PBL (2013)
Adapted from IPCC (2014)

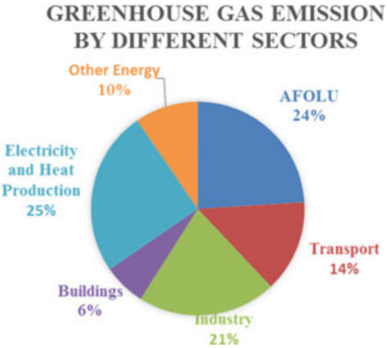

Fig. 2.1 GHG emissions from different sectors (IPCC 2014)

approximately 653 Tg per year of waste is open dumped/landfilled, whereas landfill CH_4 emission ranges from 16 to 223 Tg (Bogner and Matthews 2003; Simpson et al. 2006). Monni et al. (2006) indicated that developing nations shared 29% of the global GHGs emission in the year 2000, which is expected to reach up to 64% in 2030 and 76% by 2050 with major contribution from landfills. Waste sector has a significant contribution to the global anthropogenic CH_4 emission accounting for about 18%. Furthermore, landfills generate approximately 10–19% of annual global CH_4 emissions (Kumar et al. 2004a; USEPA 2006). In the developed nations, landfill CH_4 emission is stabilizing due to increased landfill gas recovery, recycling, rich economy and policy initiatives.

On the other hand, in the developing nations, an exponential increase in population and urbanization resulted in large quantum of solid waste, which is usually open dumped/landfilled or incinerated. Consequently, it produces large amount of GHGs particularly CH_4 followed by CO_2 and nitrous oxide (N_2O). Similarly, wastewater treatment generates greater amount of CH_4 and N_2O compared to the landfilling and other treatment options (Fig. 2.2).

Also, it is expected that CH_4 emission from wastewater alone will be increased by 50% between 2010 and 2020, particularly in developing countries of South-East Asia (USEPA 2006; IPCC 2007). As per report of IPCC (2014), since 1990, Asia (41%) is the greater emitter of waste GHG emissions and has surpassed the OECD-1990 (27%). Skovgaard et al. (2008) reported that waste sector represented 2.6% of

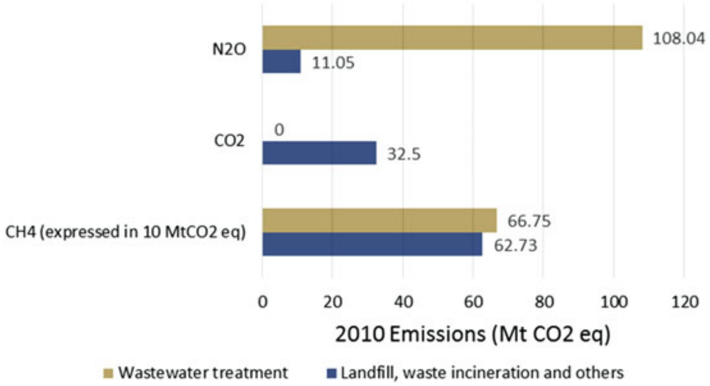

Fig. 2.2 Waste GHG emissions in 2010 (IPCC 2014)

the total GHG emissions in the EU-15. Similarly, in the United States, landfill CH_4 accounted for 23% of the total anthropogenic emissions in 2006. Also, US landfills generated around 5135 Gg in 2010 (USEPA 2012). In Europe, landfills are the second largest source of anthropogenic CH_4 emission with an estimated amount of 3373 Gg from waste disposal in 2006 (EEA 2008). Likewise, in China landfill CH_4 accounted for 26.3% of the total emission from waste management in 1994 and was estimated to be approximately 2.03 Tg (National Development and Reform Commission, China 2004). Qu and Yang (2011) reported that in China waste GHGs emission have increased significantly over a period of 1981 to 2009 that will raise to 33.2 $MtCO_2eq$ by 2024. In addition to this, GHGs emission (CO_2, CH_4 and N_2O) from composting process in Beijing was estimated by Lingyang et al. (2010) and speculated that release of CO_2 was much higher as compared to CH_4 and N_2O emissions. These GHG emissions were lower than that of landfill emissions. In India, waste sector contribution to the total national CO_2 emission is around 3%, of which 40% is shared by domestic wastewater which is followed by industrial wastewater (38%) and open dumps/landfills (22%) (INCCA 2010). Domestic wastewater is the main source of CH_4 emission in India. Two landfill sites at Chennai were quantified for GHG emissions and the emission flux ranged from 12.3 to 964.4 mg CO_2 m^{-2}/h, 2.7 to 1200 μg N_2O m^{-2}/h and 0.9 to 433 mg CH_4 m^{-2}/h at Perungudi and 39 to 906 mg CO_2 m^{-2}/h, 6 to 460 μg N_2O m^{-2}/h and 1.0 to 23.5 mg CH_4 m^{-2}/h at Kodungaiyur (Jha et al. 2008). Similarly, Kumar et al. (2004a) examined total CH_4 emission during the span of 8 years i.e. from 1994–2001 at Okhla dumping site, Delhi and reported that around 102.006 Gg CH_4 was released from 3311.867 Gg of waste piled up till 2001. Trends of waste GHG emissions are shown in Fig. 2.3.

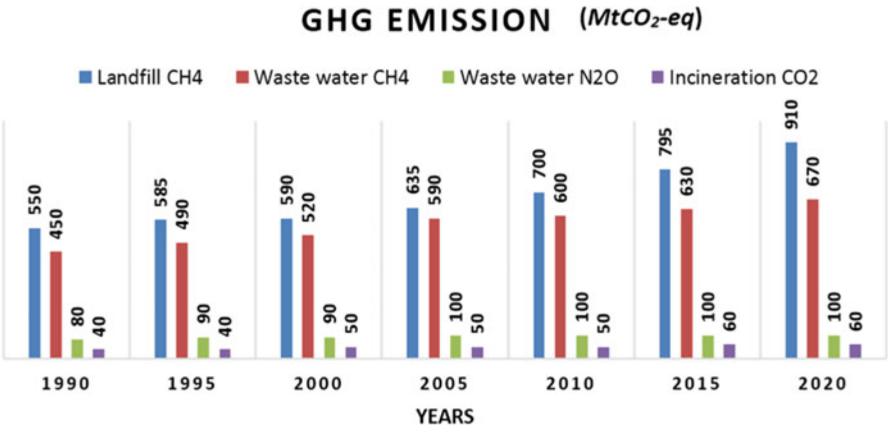

Fig. 2.3 Trends for GHG emissions from waste (Based on 1996 and 2006 UNFCCC inventory guidelines, extrapolations and business-as-usual projections) Source: IPCC (2007), Adapted

2.3 MSW Management Practices

MSW management is a multidimensional issue comprising of social, economic, political and environmental considerations. It is a complex and challenging set of processes with differing strategies and methodologies employed by developed and developing countries of the world. Rapid surge in population and urbanization along with industrial revolution in the past few decades have played a pivotal role in increasing waste generation rates worldwide (Seo et al. 2004; Singh et al. 2014, Sharma et al. 2017). However, the challenges or problems associated with waste management are more evident in developing countries of the world due to severe lack of proper waste management practises (Ahmeda and Alib 2004; Al-Khatib et al. 2010; Singh et al. 2017; Singh and Sarkar 2015). With an accounted emission of 1.5 $GtCO_2eq$ from waste and wastewater during 2010 (IPCC 2014) it is important to look for ways through which mitigation of GHGs emission from waste management sector can be achieved. Following the 3R principal of waste reduction, reuse and recycle along with use of technologies to recover energy thereby reducing fossil fuel consumption can lead to direct reduction in emissions from wastes of different types and waste management practices. Some of the most popular and widely adopted MSW management practices in both developed and developing countries of the world are listed as following: (a) landfilling, (b) incineration, (c) composting, (d) recycling, and (e) open burning.

2.3.1 Landfilling

Landfilling of MSW is the most common practice of disposing waste in both developed and developing countries of the world. A landfill is a waste disposal facility designed and constructed to ensure safe disposal of solid wastes. Generally, it is a land area where solid wastes are dumped or deposited. Landfilling is the most simple and economical method of waste disposal especially for developing countries (Barrett and Lawlor 1995; Gupta et al. 2015) wherein most of the low to medium income level countries dispose nearly 100% of their generated wastes in landfills (Singh et al. 2011a). Landfills can be divided into three broad categories viz. (a) Open dumps or open landfills (b) Sanitary landfills (c) Bioreactor landfills.

2.3.1.1 Open Dumps or Open Landfills

Landfilling of MSW by means of open dumping is the most regular waste management practice widely adopted in developing countries (Narayana 2009; Singh and Sarkar 2015). Open dumping involves uncontrolled, unscientific and non-engineered disposal of solid waste in the low-lying areas or open grounds situated in the outskirts of the urban centres (Vij 2012). These dump sites are not lined and also no compaction and covering with soil after dumping of waste is done. There is absence of leachate and gas collection systems and waste picking is a common sight at these open dumps (Gupta et al. 1998; Sharholy et al. 2008). Poorly developed open landfills are no less than an unhygienic hotspot associated with several environmental and health hazards (Ambulkar and Shekdar 2004) such as groundwater and surface water contamination of nearby water bodies due to leachate production (Zanoni 1972; Mor et al. 2006a; Gupta et al. 2015), degradation of air quality due to open burning, emission of GHGs such as CH_4, breeding ground for vectors like flies and mosquitoes rodents (Anon 2001) etc, health effects on rag pickers actively involved in waste picking and wandering stray animals like cows and dogs on these open dumps. More than 90% of solid waste generated in urban centres of India is disposed off in open dumps (Sharholy et al. 2008; Ojha et al. 2012; Srivastava et al. 2015). Often, there is also mixing of infectious biomedical waste and hazardous wastes in MSW without any segregation being done and it is deposited at these open landfill sites (Kumar et al. 2009). This common practice of waste disposal in open dumps in most of the developing countries across the world results in emission of biogas primarily CH_4 and CO_2 from these sites which are responsible for global warming. It is important to note that 3–19% of the CH_4 emissions from anthropogenic sources come from emission from landfills (IPCC 1996).

2.3.1.2 Sanitary Landfills

Sanitary landfills are final or ultimate disposal facility for dumping of solid waste in a planned, safe and scientific manner involving proper site selection, construction design and management incorporating principles of engineering (Zanoni 1972; Singh et al. 2011a). Sanitary landfills are designed to eliminate or reduce to a great extent, risks associated with waste disposal to environment and human health (Vasanthi et al. 2008). Sanitary landfills are mostly used for waste disposal in developed countries of the world, which go for compaction and covering with layer of soil, to reduce the volume of waste dumped and also to act as a barrier for entrance of surface water, escape of landfill gases generated and access of insects, pests and stray animals. These landfills are lined with different liners and have a top cover (Gupta et al. 2015) aimed to prevent any contact of waste disposed with the adjacent environment, particularly groundwater. In contrast to open landfills, sanitary landfills are well equipped with leachate and gas collection and treatment systems which help in regulating and minimizing the adverse environmental effects of toxic leachate and obnoxious gases generated due to waste decomposition at landfills (Tchobanoglous et al. 1993). These landfills also have an advantage of being a potential source for energy generation from landfill gases generated due to anaerobic waste decomposition at these sites (Zamorano et al. 2007). However, the landfill gases generated from landfills can be linked to the air pollution and climate change as landfill gas produced is mainly composed of GHGs like CH_4 (50–60%), CO_2 (40%) and air pollutants such as CFCs, benzene, toluene etc (El-Fadel et al. 1997; Newman et al. 2009). In a qualitative assessment of CH_4 emissions data from a landfill site located in Okhla, Delhi done by (Kumar et al. 2004a), estimated emissions were found to be ranging from 7.667 Gg to 14.206 Gg using modified triangular method and default method respectively during 2001. However, the field investigation CH_4 emissions from the site were found to be of value 1.776 Gg. According to a survey conducted in Beijing from 2001 to 2007, total CH_4 and CO_2 emission from landfilling of MSW has increased from 143 kt and 400 kt during 2001 to 477 kt and 1331 kt till 2007 (Pan et al. 2010).

2.3.1.3 Bioreactor Landfills

Increase in scientific knowledge and technological advancement in the area of waste management have been instrumental in the development of Bioreactor Landfill. It is an upgraded version of conventional sanitary landfill that uses improved microbiological processes to accelerate the decomposition of organic waste (Warith 2002). To maintain optimum moisture content for microbial digestion, these landfills are designed to utilize rain water, sewage and recirculation of leachate. Enhanced microbial degradation helps in rapid reduction of waste volume, increase in production of CH_4 for energy recovery (Attal et al. 1992) and lowered cost of leachate management due to leachate recirculation being practised in bioreactor landfills. In comparison to sanitary landfill, the bioreactor landfill is based mainly on increasing the process efficiency and conversion of complex organic compounds at a faster rate (Pacey et al. 1999). Bioreactor Landfill employs controlled conditions to increase the generation rate of landfill gas and minimize the migration of leachate into the subsurface environment (Warith 2002). However, prolonged leachate recirculation in bioreactor landfills can lead to production of N_2O, a strong GHG having a global warming potential of 310 times more than CO_2 (Lee et al. 2002; Watzinger et al. 2005; Lou and Nair 2009). Hence to minimize the negative impact of bioreactor landfills on climate change, recirculation of leachate needs to be properly regulated.

2.3.2 Incineration

Incineration is the most common thermal treatment process in which controlled combustion of waste takes place in the presence of oxygen with temperatures ranging from 980 to 2000 °C (Sharholy et al. 2008). The by-products of incineration process are mainly carbon dioxide, water vapour and ash (Zaman 2009) and this method can be utilized to recover energy for heating purposes or the supply of electricity. Incineration is a widely practiced and popular waste disposal method, mostly followed by the developed countries of the world (Cheng and Hu 2010). This process comes with various advantages such as significant reduction in volume of waste by 85–90% along with the potential of energy recovery (Singh et al. 2011b). Reduction in volume of waste is rapid and immediate in contrast to biological decomposition of wastes, which is a time-consuming process along with reduced GHG production. Incineration also results in significantly lesser transportation costs (Cheng and Hu 2010) if such facilities are constructed in the vicinity of MSW generation or collection points. In addition, it is more economically viable as energy recovered can be used in operation of incineration plants and also much less much land is required which is a very costly and valuable resource. However, incineration would not be a suitable method of waste disposal especially for developing countries characterized by high moisture content and low calorific value of wastes generated, comprising of mostly organics (Bhide and Shekdar 1998; Kansal 2002; Narayana 2009). Incineration results in emission of mainly three types viz. fly ash, bottom ash and stack emissions. Out of which, the stack emissions result in atmospheric discharge of GHGs like CO_2 & N_2O, along with a variety of air pollutants like PAHs, PCBs, SO_2, NO_x, particulate matter, heavy metals and PCDD/Fs (Tian et al. 2013) leading to both air pollution and climate change. Similarly, in Japan, incineration of waste is the largest contributor of CO_2 emissions resulting from the waste sector (Takaoka et al. 2011). Approximately 8% of total anthropogenic mercury emissions result from waste disposal mainly through incineration (Pirrone et al. 2010). Also, China accounts for approximately 1/4th of global mercury emissions with about 700 tons/year (Wu et al. 2006).

2.3.3 *Composting*

Composting is the method of biological treatment of waste in which biodegradable organic matter is decomposed in controlled aerobic conditions through the action of microorganisms and small invertebrates resulting in nutrient and humus rich compost that can be utilized for agricultural purposes (Singh et al. 2011a). This biodegradable organic portion of the waste stream is one of the largest sources of GHG emissions of anthropogenic origin (Tian et al. 2013). Various factors affecting the rate of compost formation are Carbon/Nitrogen (C/N) ratio, the temperature, the moisture content and the amount of air supplied. Maintaining the apt C/N ratio i.e. between 26 and 35, is very significant for composting process to be efficient as the decomposers use carbon as an energy source and require nitrogen for protein synthesis (Kumar 2011). Optimum moisture levels are also required to carry out efficient composting process as microorganisms require moisture for their metabolic functions. Too less (below 25%) or too much (above 70%) (Encarnación et al. 1995) moisture can disrupt composting process (Lu et al. 2009) as high moisture levels may deprive the microbes of oxygen by displacing air in the composting heap. Similarly, optimum temperature levels in the range of 45–55 °C need to be maintained for proper composting to take place. High temperature levels, i.e. more than 55 °C are required for eliminating pathogenic microbes (Kumar 2011), however temperatures higher than 75 °C or above may kill the microorganisms required for composting process. Since composting is an aerobic process, aeration is another very important parameter to be taken into account for efficient composting to take place. Insufficient oxygen in composting pile would lead to death of aerobic microbes and anaerobes will begin to thrive producing undesirable odours and inflammable methane gas, therefore over turning of composting pile is recommended to maintain aeration.

Composting has its implications for air pollution and climate change resulting from production of these odorous gases and generation of GHGs. According to an estimate, based on 42.7% of total organic carbon (TOC) and 40.8% of organic matter in Chinese waste, nationwide emission of CO_2, CH_4 and N_2O were estimated to be 56.6 × 104 t, 3000 t and 221 t, respectively along with a total of 69.5 × 104 tCO_2-eq (Tian et al. 2013). All these above-mentioned parameters are required to be maintained and monitored for microorganisms to carry out decomposition and produce quality compost from solid wastes such as MSW. There are different types of composting techniques such as in vessel composting, windrow composting, static pile composting and vermicomposting. Composting as a waste management practice is recommended for MSW with significant levels of organic matter, which is mostly a characteristic of wastes from developing countries (Narayana 2009).

2.3.4 Recycling

Recycling can be defined as removal of items from the waste stream to be sold, given away for reuse or to be used as raw materials in the manufacturing of new products. The most common items for recycling in a MSW stream are plastics, paper, metal and glass (Kumar et al. 2009). Recycling of wastes involves three types of processes (i) sorting of waste (ii) collection of recyclables (iii) processing of recyclables to create raw materials for manufacturing of new products. Methods of recycling and material recovery from waste are an important and preferred option in management of solid wastes. Both, developed and developing countries recycle their wastes, however they differ in their ways, as in developing countries recycling is done mainly through the informal sector i.e. waste pickers at the garbage collection points or at open dumps sites (Wilson et al. 2006), after some pre-sorting is done at source, for example in households.

Segregation of wastes such as paper, plastics, metal and glass is done by the informal sector engaged in recycling in the developing countries (Kumar et al. 2009) with around 2% population of certain Asian and Latin American cities depending on waste scavenging as their source of income (Medina 2000), whereas in developed countries at source segregation of recyclables through collection in different bins is a common practice. Recycling of wastes encompasses multiple economic and environmental benefits viz. reduction in volume of wastes therefore less demand for landfill space, reduction in greenhouse gas emissions and pollutants discharge to surrounding environment, reduction in cost incurred on waste management practices, conservation of energy and resources, and regeneration of raw materials and material recovery that have potential industrial use and application (Hui et al. 2006).

2.3.5 Open Burning

The practice of burning solid wastes or discarded materials in the open surroundings, wherein resulting smoke and other emanations are released directly in the atmosphere is referred to as open burning. The practice of open burning doesn't involve smoke or emission control equipment's such as stack or chimney or any other pollution control devices. Open burning of waste is a common practice in urban centres in the low-income countries, as it greatly reduces the volume of the dumped waste and provides extended lifetime to the dumping site as well, and is cheap, rapid and highly convenient method for waste disposal. To avoid paying for waste disposal, people in certain countries practice open burning to rapidly reduce the volume and odours resulting from uncollected or dumped MSW. Countries like Burkina Faso and Nepal openly burn 25 to 12% of their total MSW generated (McKay 2002). There are several drawbacks associated with the practice of open burning such as release of pollutants and toxic gases like dioxins, particulate matter, furans, PAHs, VOCs, carbon monoxide (CO), hexachlorobenzene and ash into the atmosphere posing serious health effects like cancer, hormonal disruption, respiratory disorders (asthma or bronchitis) and neurological problems etc (Viel et al. 2000). Negative effects of uncontrolled burning of wastes on environment can be seen due to release of oxides of carbon and nitrogen where NO_X contributes to formation of smog, ozone (O_3) depletion and global warming. Particulate matter released due to open burning severely deteriorates the air quality causing smoke and hazy conditions.

2.4 Impacts of Improper Waste Management

With the current scenario of increasing MSW generation rates worldwide, effective and proper management of solid wastes has become a major issue of environmental, economic and social concern especially for the developing countries of the world. Due to lack of sufficient funds, infrastructure and technology, developing countries fail severely to manage their wastes (Ngoc and Schnitzer 2009) posing threat to the environmental and human health. There are various negative impacts of improper waste management on the surrounding environment.

2.4.1 Impact on Surface and Groundwater

Lack of proper MSW management leads to significant negative impact on the water resources present in the vicinity of any solid waste disposal site. Decay of solid wastes in open dumps or sanitary landfills results in production of toxic leachates containing heavy metals, organic compounds like PAH, benzene, toluene, phenols etc. (Vasanthi et al. 2008). Discharge of these leachates in the absence of proper drainage and leachate collection and treatment systems, into the groundwater aquifers present near the dumping site or surface runoff to nearby rivers or streams leads to contamination of these water bodies (Mor et al. 2006a). Semi-treated or untreated leachates pollute the water by causing undesirable changes in the water quality of the receiving water bodies (Kathiravale and Yunus 2008). Consumption of this polluted water leads to severe public health issues and is also toxic to the aquatic life in these water bodies.

2.4.2 Impact on Soil Quality

Landfilling of MSW is the most common method of waste disposal that leads to the deterioration of soil quality and degradation of a very valuable resource. Landfilling and open dumping involves decomposition of solid waste resulting in production of toxic leachates that contaminate the soil with toxic compounds and heavy metals (Vergara and Tchobanoglous 2012). Since waste at the dump sites is not covered by soil or any inert material, direct contact between soil and MSW leads to contamination of the land area with pathogenic microorganisms and toxic organics like PAH, PCBs. Incineration and open burning residues such as fly ash and slag also lead to contamination of soil in the vicinity (Giusti 2009).

2.4.3 Impact on Air Quality

Different waste management practices such landfilling, open dumping and burning and incineration of MSW have grave impact on air quality of the surrounding environment. Solid waste decay at poorly managed open dumps and landfills results in emission of GHGs such as CH_4 and CO_2 (Kumar et al. 2004a) and also foul odours degrading the air quality. Open burning of solid wastes results in air pollution due to emission of particulates, CO, CO_2, SO_2, dioxins, furans (Vergara and Tchobanoglous 2012), toxic metals, PAH, VOCs, NOX, fly ash and slag. The smoke and hazy conditions result in deterioration of the air quality of the surrounding areas.

2.4.4 Impact on Human Health

Improper waste management has direct impact on public health. Open burning of waste leads to emissions of various toxic substances which affect human health badly causing diseases like cancer (Sever 1997), hormonal disruption, respiratory disorders (asthma or bronchitis) (Ray et al. 2005) and neurological problems (Misra and Pandey 2005) etc. Open dump of solid wastes are potential breeding grounds for disease vectors, flies and mosquitoes which are responsible for spreading diseases like malaria (Giusti 2009), diarrhoea, encephalitis, dengue etc. Inappropriate management of wastes affects the health of poor people and informal sector more as they live in the vicinity of the waste disposal sites and are more susceptible to unhygienic conditions that prevail leading to infectious diseases and congenital birth defects (Johnson 1999; Wilson et al. 2006).

2.4.5 Impact on Climate Change

Inappropriate waste management shows its impact on the phenomenon of climate change by directly contributing to the emission of GHGs like CO_2, CH_4 and N_2O. Due to the anaerobic environment created in landfills, they happen to be the biggest contributor of GHG emission resulting from any waste management practice (Mor et al. 2006b; Vergara and Tchobanoglous 2012). 50 to 60% of CH_4 of methane by volume is released in the form of landfill gas from landfill sites. Also, CH_4 has a global warming potential 25 times more than that of CO_2. Other waste management practices like incineration, open burning and composting also have their share in contributing to emission of GHGs. Apart from these listed sources, emissions resulting from vehicular fuel combustion involved in transportation of solid wastes also contribute to GHGs emission leading to global warming and climate change.

2.5 Improper Waste Management-Climate Change Nexus

Urbanization along with industrialization coupled with economic growth and increase in consumption pattern leads to generation of huge quantity of waste. In the majority of the developing economies, waste produced is openly dumped in low lying areas or land filled unscientifically as the usage of waste to energy treatment processes like gasification, incineration, pyrolysis or anaerobic digestion etc. are not actively promoted to effectively remove solid waste (Park and Shin 2001). Thus, a large amount of the waste is openly dumped and causes secondary pollution like ground water pollution by leachate, leakage of GHGs, bad odors etc. (Allen et al. 1997; Ham et al. 1993). Organic portion of waste during decomposition generates CH_4, CO_2 and trace amount of toxic gases.

CO_2 and CH_4 highly potent GHGs that contribute to global warming and CH_4 in particular is 25 times more potent than CO_2 (He et al. 1997).

Inspite of waning shares of industry in global GDP, GHG production from waste/wastewater and industry extended from 10 $GtCO_2eq$ to 13 $GtCO_2eq$ within the year 1990 to 2005 and reached upto 15 $GtCO_2eq$ in 2010 (for which waste/waste water contributed to 1.4 $GtCO_2eq$) (IPCC 2014). Similarly, solid waste produced in Indian metropolitan cities expanded from 6 Tg to 48 Tg in time span of 1947 to 1997 (Pachauri and Sridharan 1998), including per capita increase of 1–1.33% per year (Rao and Shantaram 2003). Around 0.5–0.7 kg $capita^{-1}$ day^{-1} MSW is produced from urban centers of India (Kameswari et al. 2003) along with 10–30% of volatile matter content (Rao and Shantaram 2003). In Asia 90% of the open dumps are without any scientific measures. About 70–90% of landfills in India are open dumping grounds. CH_4 generated by these landfill sites adds to global emission in the range of 10–70 Tg/y (Cerminara 2014). In India, about 500 t CH_4 and CO_2 are produced daily from the open dumps (Hebbliker and Joshua 2001). The quantity of GHG generations varies spatially due to waste quantity, composition, moisture content, hydrogen/oxygen ratio available during decomposition process.

Similarly, Themelis and Ulloa (2007) attempted to estimate the prospects of municipal solid waste to generate CH_4 for heat and electricity. United States (US) mount up about 2.6 million tonnes of CH_4 gas per year (70% of that gas is used for production of heat or electricity) from landfills. Theoretical and experimental studies speculated that if complete biomethanation of municipal solid waste is allowed, it generates around 100–200 Nm^3 of CH_4 per dry tonne of waste (Verma and Themelis 2004). Nonetheless, the production rate of CH_4 in industrial anaerobic reactor ranges from 40–80 Nm^3 per tonne of organic wastes. Numerous reports on US landfills indicate that 100 Nm^3 of methane per ton of MSW is land filled in an individual year. These reports led to a conclusion that CH_4 production is about 50 Nm ^{3} per ton of MSW landfilled. Hence, for every 1.5 billion tonnes of MSW, global landfills will generate CH_4 at the rate of 75 billion Nm^3. However, only 10% of this potential is utilized. Similar publication by Barlaz et al. (2002) accounted that CH_4 production rate at landfill receiving 286,000 tonnes of waste per year ranged from 0 to 90 Nm^3/min.

Effective utilization of CH_4 release is crucially important and will ultimately lead to environmental and economic benefit. Likewise, Noor et al. (2013) reported that in 2010, CH_4 emission from the landfill was 310,225 tonne and is speculated to reach 345,000 and 370,000 t by 2015 and 2020, respectively in Malaysia. These reading are equivalent to 2.20 * 109, 2.44 * 109 and 2.63 * 109 kW h of electricity. This will generate revenue of around US $219.50, 243.63 and 262.79 million, respectively. This will signify huge potential for Malaysian economy. However, in developing economies like India, inventory estimations of methane from open dumpsites and landfills have huge uncertainties because of insufficient data on solid waste generation, management and emissions of gases. Before reaching to the landfill site, solid waste goes through a variety of intermediate stages like sorting of recoverable and recyclable materials, composting etc. This changes the physico-chemical properties and quantity of waste that ultimately makes its way to the dump sites and consequently influences GHG emissions (Jha et al. 2008). Therefore, reduction in uncertainties is necessary for estimation from these sources. Estimate suggests that quantum and complexity of waste will increase in near future and so will the GHG emissions, if current practices prevail in urban economies. Action must be taken to ensure that waste management sector is more focused for climate change mitigation.

2.6 Mitigation Policies

This section delivers an outline of policy framework that impacts waste management provisions. Mitigation policies aim at reducing risks by mainstreaming national risk management policy framework for reducing GHG emissions and sequestering carbon that will curb emissions over the long term. Policy framework includes pre-event preparedness, early warning systems, innovative mitigation strategies and risk financing instruments. These elements are applicable both for rural, sub-urban and urban population contained in an ecosystem. The main aim of mitigation policies is to reduce exposure of risk and lessen negative outcomes. The process involves risk mapping, analysis of types of risk involved, and estimating height of risk exposure to various groups and places depending on their risk absorption capacity.

2.6.1 Global Context

Generation of GHG emanating from waste are indirectly or directly affected by number of policies and strategies which promotes waste-to-energy, correct choices for waste disposal methods, encourage waste minimization through recycling and reuse (Pan et al. 2015). In developed economies like Japan and EU, waste management policies are integrated with climate policies. Although, mainly regulations are covered within policy instruments, nonetheless there are economic measures also to promote waste minimization through different technologies. However, in developing economies the main policies are intended to restrict the unscientific dumping of waste.

2.6.1.1 Landfill Directive to Reduce Landfill Methane Emissions

Two major strategies are followed to reduce landfill emissions: standards implementation for CH_4 recovery from landfill and to curtail the amount of organic waste reaching landfills (Sadef et al. 2016). In US, Clean Air Act (CAA) Amendments/ New Source Performance Standards (NSPS) regulates landfill CH_4 emissions by using landfill-gas production model, by mixing ratio of NMOCs i.e. total non-methane organic compounds and their restrictions (Saquing et al. 2014). Annually, huge amount of CH_4 is recuperated to comply with air quality standards and offers energy, supported by renewable energy initiatives and national tax credits (Omer 2016). European Legislative has primarily notable Landfill directives (Council Directive 1999/31/EC on the Landfilling of Waste) which has now been transposed in Great Britain that aims at reducing negative environmental effects by landfilling of waste through introduction of uniform standards. Ambitious targets are being set for organic portion of waste being disposed off in landfill. It imposed strict controls on how waste is managed and dumped in landfills. This contributes safeguarding of human well being and environment by lessening the quantity and hazardousness of waste generated. In addition to this, co-disposal of non-hazardous and hazardous waste is strictly banned which was a regular practice in UK. Similarly, landfilling of tyres is also banned under this directive (Bebb and Kersey 2003). As discussed previously, the landfill directive instructs phased reduction in waste upto 50% of 1995 levels by 2009 and 35% by the year 2016 (UN 1993; Zorpas et al. 2017).

2.6.1.2 Directive on Packaging and Packaging Waste

England implemented the Directive on Packaging and Packaging Waste (94/62/ EEC) by two sections of legislation: The Producer Responsibility Obligations (Packaging Waste) Regulations 1997 and the Packaging (Essential Requirements) Regulations 1998. They set targets on recycling and packaging of waste, placing responsibility on packaging chain. All companies are restricted to arrange recycling and recovery of handling of packaging. In Wales and England, recovery and recycling targets set by government for 2002 were 59% and material specific recycling targets were 19% (Calaf-Forn et al. 2014).

2.6.1.3 Waste Incineration Directive (2000/67/EC)

In Europe, two Council Directives (89/369/EEC and 89/429/EEC) were implemented in 1989 to control certain emissions commencing from waste incinerators. This directive has made considerable reduction in emission of GHG gases and other toxic substances but its scope was limited to MSW only. To substitute this, Directives and the Hazardous Waste Incineration Directive (Council Directive 94/67/EC), a new Waste Incineration Directive (2000/76/EEC) has been implemented. These directive aims at integrating technical progress that has been accomplished in recent years for controlling emissions from incinerators and extending its measures to control air pollution, water pollution and land pollution that was earlier not covered under Hazardous Waste Incineration Directive (HWID). Their objective will contribute in safeguarding of human well being and atmosphere by achieving their set goals.

2.6.2 Indian Context

In the year 1969–74, fourth 5-year plan was declared by Government of India (GoI), that commenced attempts to set better facilities for disposal of solid waste by giving loans and grants for setting up of vermicomposting/composting facilities. GoI assigned a committee to assess the problem of solid waste management in India. Seventy six recommendations were made by this committee that covered eight areas of waste management (GoI 1995; Vishwakarma et al. 2015).

In the year 1990, Ministry of Environment, Forests and Climate Change constituted NWMC (National Waste Management Council) with management of municipal solid waste as one of its objectives (UNEP 2001). It recommended 22 municipalities to estimate the amount of solid waste and its transportation and disposal. In 1993, National Plastic Waste Management Task Force was constituted by NWMC to reduce health impact and undesirable environmental problems arising out of plastic (Banerjee et al. 2014). Based on the suggestion, in the year 1998 MoEFCC drafted Recycled Plastic Usage Rules, which puts a ban on carrying, storing and packing of food articles in plastic bags and specified standards for making plastic bags.

According to MSW Rules 2000, local municipal bodies are accountable for implementing these rules and provisions for collecting, storing, segregating and disposing of solid waste. These rules direct that appropriate technologies (composting/vermicomposting, anaerobic digestion, pelletisation, etc.) must be adopted for organic faction of waste. While for inorganic fraction of waste, incineration or land filling must be adopted. In the year 2000, a manual by CPHEEO (Central Public Health Environmental Engineering Organisation) was published on managing MSW for guiding urban local bodies (ULBs) under Ministry of Urban Development (CPHEEO 2000). Several other acts and rules have been formulated to deal with solid waste management. Under these rules it was made mandatory that all cities to develop waste processing and treatment technologies by 2003 (Asnani 2006).

The Government of India (GoI), The Ministry of Environment, Forests and Climate Change (MoEFCC), has commenced a project for preparation of India's Initial National Communication (NATCOM) to the United Nations Framework Convention on Climate Change (UNFCCC) which is funded by Global Environment Facility (GEF) underneath United Nations Development Programme, New Delhi (GoI 2002). Estimation of GHGs inventories are source for specific areas like land use change pattern a forestry, energy and transformation, industrial and agricultural processes etc. However, GHG inventory emission from waste sector has been allotted to NEERI, Nagpur (Kumar et al. 2004b).

Developing economies like India lacks finances that are the major obstruction to proper solid waste management practices (Srivastava et al. 2015). Thus, Joint Implementation (JI) and Clean Development Mechanism (CDM) are useful mechanism for getting investments from developed countries. Often, developing countries do not have proper infrastructure for collection, transportation and treatment of waste. Hence, the advantage of JI and CDM are improvement in waste management practices and GHG emission reduction (Sreekanth et al. 2014). For validation of landfill gas CDM projects, emission reductions (CERs, with units of tCO_2-eq) are verified directly by quantification of methane captured and combusted (Yulkin et al. 2013). Mitigation policies are key requirement that impact on development of future waste management sector. Therefore, it is possible that the waste management practices which are now being developed are in accordance with changes in legislation so as to adequately address climate changing scenarios.

2.7 Recommendations and Conclusion

Change in climate because of inappropriate waste management practices has not yet featured prominently within environment and economic policy schemes of developing economies. Particularly low income countries are disproportionately affected by the changing climate. Despite getting limited attention from policy makers, climate change policies regarding waste management segment may have significant ancillary benefits for local government. Local and national policies that address air quality, proper waste management, and incorporation of clean energy services will definitely limit GHG emanations into the atmosphere. Recognizing how changing climate is liable to influence developmental activities, therefore, priority must be to build cost-effective, integrated and institutional capacity especially in developing economies so as to retort to climate change (Beg et al. 2002). Opportunities prevail in developing nations for designing of integrated responses and exploit synergies amid climate change and waste management policies. Few recommendations for abating climate change are listed below:

1. To finance waste abatement plans via Clean Development Mechanism (CDM) and carbon markets (Aggarwal et al. 2017).
2. To promote 4R's hierarchy (Reduce, Reuse, Recycle and Refuse)
3. To encourage local administration for establishing central solid waste removal facilities with integrated concept of innovative technology and best utilization of waste by compost material or energy recovery.
4. To promote area clustering approach intended for establishing Central MSW Management Facilities
5. Waste management policy makers must have an effective link with climate change policy makers so as to make certain that appropriate waste management policies are adopted to retort towards changing climate.
6. An industry forum must be established for waste management companies so that they are capable of having a good understanding of potential climate change impact on their operations.
7. Waste collection and disposal authorities must be aware of any concerns occurring from potential impact of changing climate that could affect their functional role or responsibilities.
8. To develop robust and vigorous set of climate change indicators specifically for waste management like temperature, precipitation, site damage, storms and floods incidences, occupational health and safety appraisals etc. that will facilitate in monitoring climate change at site level and in assessing likely consequences.
9. To adapt various options for waste management processes like engineering, operational, land use planning and costs etc. (Andersson-Sköld et al. 2016). These options must be identified by managers, policy regulators and researchers so as to assist in successful planning of waste management practices.
10. It must be ensured that measurement of GHG emission is only the initial step intended for addressing the predicament of climate change. However, it is the basis for adopting emission reduction targets, preparing mitigation plans, implementation of policies, monitoring and verifying of results so as to curb the crisis of GHG emissions through waste management division.

The environmental and economic policy schemes of developing economies do not envisage climate change policies firmly. There are evidences that developing nations are more prone to the outcome of climate change and least adaptable to climate change (IPCC 2001a, b). Moreover, the understanding of inappropriate waste management and its potential impact on climate change is also in preliminary stage. There is lack of understanding, information exchange, knowledge, training and research in this area. Therefore, from the developing country perspective, it is imperative that developing countries participate actively and globally for adapting and mitigating climate change scenarios (Munasinghe and Swart 2000). Broad participation will open the likelihood to limit damage costs. Therefore, range of actions must be addressed for this issue that must include research, training along with information dissemination. These combined efforts will confer significant co-benefits for mitigating GHG emanations from waste and achieving sustainable development.

Acknowledgement The authors gratefully acknowledge the Head, Dean and Director, Institute of Environment and Sustainable Development, Banaras Hindu University for providing the necessary help. RPS is thankful to Department of Science and Technology, India, University of Nebraska–Lincoln, Indo- US Science and Technology Forum (IUSSTF) and Robert Daugherty Water for Food Institute (DWFI) – University of Nebraska for support. RPS is also thankful to Dr. Alan S. Kolok, Director, Nebraska Watershed Network, University of Nebraska-Omaha (UNO), and Dr. Shannon L. Bartelt-Hunt, Civil Engineering, University of Nebraska–Lincoln, US for their constant support and guidance. BS is thankful to University Grants Commission for awarding Junior Research Fellowship.

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Chapter 3
Pesticide Contamination and Human Health Risk Factor

Ngangbam Sarat Singh, Ranju Sharma, Talat Parween, and P.K. Patanjali

Abstract The use of pesticide has become an integral part of modern agricultural practices. Majority of pesticides applied in agriculture are not target specific and during their application they also affect non-target organisms. Repetitive use of pesticide leads to loss of biodiversity. Continuous and non-judicious use of pesticide has leads to increase pesticide contamination in the environment. It is associated with various ecological and health problems. It leads to over three million poisoning cases annually and up to 220,000 deaths, primarily in emerging countries. Pesticides may present instantaneous danger to the user if applied inadequately or without appropriate knowledge of their toxic effects. Occupational exposure to pesticides repeatedly occurs in the case of agricultural workers in open fields and greenhouses, workers in the pesticide industry, and exterminators of house pests. Some are highly toxic and may cause serious illness and even death if spilled on the skin, inhaled, or otherwise used imprecisely. Potential future hazards to human health can be created by pesticide residues that may cause accumulation in the food chain and widespread contamination of the environment. Acute and chronic effect of pesticide contamination cause various carcinogenic, oncogenic, genotoxic and teratogenic effect on the human being. This chapter explores the different types of pesticide, their mode of action, various ways through which pesticide enters our environment (soil, air and water) lead to pesticide contamination. We also learn about the way that how pesticides enters the human body and causes various health effects and also discuss about their future perspectives.

Keywords Pesticide • Environmental contamination • Human health • Risk factor • Acute effects • Chronic effects

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M. Oves et al. (eds.), *Modern Age Environmental Problems and their Remediation*,
DOI 10.1007/978-3-319-64501-8_3

3.1 Introduction

Any chemical that either occurring naturally or synthetically used to destroy, supress or alter the life cycle of any insect pest is categorise as pesticide. These are officially known as economic poisons and include insecticides, fungicides, herbicides, rodenticides and nematicides and many other chemical like antibiotics, chemosterilants, disinfectants, defoliants, and juvenile hormones etc. Many of these chemicals are highly poisonous not only to the particular organisms but also for non-target organisms, including human. Target pests include insects, plant pathogens, weeds, mollusks, birds, mammals, fish, nematodes (roundworms) and microbes that destroy property, cause nuisance, or spread disease, or are disease vectors. Some of these pesticides can be accumulated by lower organisms like aquatic microorganisms, plant life and increase in concentration continuously in the food chain until toxic concentrations are consumed by the higher animals. This increase in concentration along the food chain is called biomagnification.

Classification of pesticides: Pesticides can be classified on the basis of

I. Toxicity
II. Mode of entry
III. Mode of action
IV. Chemical nature

I. ***Based on toxicity***

- Extremely toxic (LD_{50}<5 ppm) Example: Parathion
- Highly toxic (LD_{50} 5–50 ppm) Example: Eldrin
- Moderately toxic (LD_{50} 50–500 ppm) Example: DDT
- Slightly toxic (LD_{50} 500–5000 ppm) Example: Malathion
- Practically non-toxic (LD_{50} 5000–15,000 ppm) Example: Pyrethrum
- Relatively harmless (LD_{50}>15,000 ppm)

II. ***Based on mode of entry***

- **Stomach poisons** – These pesticide enters in the body of pests via their mouth part and digestive system and causes death by stomach poisoning. Example: *Bacillus thurigiensis.*
- **Contact poisons** – These pesticides enter in the body of pests via their epidermis upon contact and causes death. Example: Fenvalerate.
- **Fumigants** – Such pesticides are in gaseous form and enter the body via respiration system. Example: Aluminium phosphide.
- **Systemic poisons** – These pesticides are consumed by a host organism and remain in its body fluids. Pests feeding on the body fluids of the host organism will then be killed by poisoning. Example: Metasystox.

III. ***Based on mode of action***

- **Physical poison** – These pesticides kill insect by exerting physical effect like desiccation. Example: Diatomaceous earth.

- **Protoplasmic poison** – These chemical kill the insect by protoplasmic destruction. Example: Arsenic compound.
- **Respiratory poison –** These chemicals block the cellular respiration by inhibiting the catalytic action of cytochrome oxidase. Example: HCN.
- **Nerve poison –** These chemicals causes the death of an insect by affecting the nervous system through blocking of acetylcholinesterase. Example: Organophosphates and carbamates.
- **Chitin inhibitors –** These chemicals affect the chitin synthesis by inhibiting chitin synthetase. Example: Diflubenzuron.

IV. ***Based on chemical nature***

- Inorganic pesticides
- Organic pesticides
- Synthetic pesticides
- Miscellaneous compounds

1. ***Inorganic pesticides***
   (a) Arsenicals: Lead arsenate.
   (b) Fluorine compounds: Sodium fluoride.
   (c) Other inorganic compounds: sulphur, zinc phosphide.
2. ***Organic compounds***
   (a) Oils and soaps: kerosene, diesel, natural oil, crude oil.
   (b) Pesticide of animal origin: Nereistoxin in marine annelid, Lumbrinerisheteropoda. It is a nerve poision.
   (c) Pesticide of plant origin:
      - **Pyrethrum –** Flower of *Chrysanthemum cinerifolium* and *c. coccineum.*
      - **Nicotine –** leaves of *Nicotianatabacum* and *N.rustica.*
      - **Rotenone –** Roots of *Derris elliptica*
      - **Neemproduct –** Neem seed oil and neem seed kernel extract.
3. ***Synthetic organic pesticides***
   (a) **Organometal compounds**: These are the metal salt of organic compound. They have their toxicity effect due to inhalation, skin absorption, or ingestion. They occur in the environment either because they are naturally formed, or direct anthropogenic inputs. Example: Tetraethyl lead.
   (b) **Organochlorine Pesticides**: They are broad-spectrum, long residual stability and relatively low toxicity. Chemically they are stable in nature, so hard to break down in the natural environment. Continuous use in large quantities will easily lead to environmental pollution and accumulation in mammals, resulting in cumulative poisoning or damage. Therefore, they are banned under general circumstances and

gradually replaced by other pesticides. Example: DDT and Endosulfan.

(c) **Organophosphate Pesticides**: These pesticides are characterised by their multiple functions and the capacity of controlling a broad spectrum of pests. They are nerve poisons that can be used not only as stomach poison but also as contact poison and fumigant. These pesticides are also biodegradable, cause minimum environmental pollution and slow pest resistance. Example: Monocrotophos and DDVP.

(d) **Carbamates**: These are synthetic derivative of physostigmine. They affect the transmission of nerve signals resulting in the death of the pest by poisoning. They can be used as stomach and contact poisons as well as fumigant. Moreover, as their molecular structures are largely similar to that of natural organic substances, they can be degraded easily in a natural manner with minimum environmental pollution. Example: Propoxur.

(e) **Synthetic-pyrethroid**: They are synthetic derivative of natural pyrethrins. They are comparatively more stable with longer residual effects than natural pyrethrins. They are highly toxic to insects but of only slight toxicity to mammals. Example: Cypermethrin and Decamethrin.

4. ***Miscellanoous compound***

(a) **Neonicotinoids**: They inhibit nicotinic acetylcholine by binding with nicotinic acetylcholine receptor. Example: Imidacloprid and acetamiprid.

(b) **Thionicotinyl compound**: These are broad spectrum insecticide. Example: Thiomethaxam.

(c) **Phenyl pyrazoles**: It is a broad spectrum insecticide. They block the GABA regulated chloride channel in neurons. Example: Fipronil.

(d) **Oxadiazine compound**: It affect the sodium ion channel and lead to paralysis and death. Example: Indoxacarb.

(e) **Spinosyns**: It is isolated from actinomycetes *S. spinosa* and has both fumigant and stomach action. Example: Tracer.

(f) **Avermectins**: It is isolated from *S. avermitilis*. They inhibit transmission of neuromuscular junction. Example: Abamectin.

(g) **Fumigants**: These are in gaseous form, heavier then air and highly penetrating. Example: HCN and Aluminium phosphide.

3.2 Pesticide contamination

The major part of the pesticides applied in any area for a specific reason (about 99%) remain unused and it gets mixed with air, soil, water and causes harmful effects on the people, pets, and the environment (Aktar et al. 2009). Many pesticides are not easily biodegradable and they remain persistent in the environment either remain on the soil surface i.e. soil contamination or leaching through the soil to the ground water i.e. water contamination. Through soil it may get into the air through wind and contaminate larger area i.e. air contamination.

Pesticides contamination depend on the interactions between the physicochemical properties (vapour pressure, stability, solubility, pKa) of the pesticide, soil adsorption and soil persistence, the soil factors (pH, organic components, inorganic surfaces, soil moisture, soil microflora, soil fauna), the plant species, and the climatic variation (Eleftherohorinos 2008). Also, the toxicity and dosage application of pesticide, the weather conditions prevailing after application, and persistency of pesticide in the environment could account for its adverse effects on the environment. Soil factors and weather conditions are the most important factors that affect the providence of the pesticide in the environment and consequently the selectivity, activity, and adverse effects on the environment (Monaco et al. 2002).

3.3 Soil Contamination

Soil contamination occurs when use of chemical pesticide exceeds the threshold level. It endures for decades and possesses risk for soil conservation as well as soil health by declining the population of beneficial micro-organisms. The famous soil scientist Dr. Elaine Ingham says “If we lose both bacteria and fungi, then the soil degrades. Overuse of chemical fertilizers and pesticides have effects on the soil organisms that are similar to human overuse of antibiotics. Indiscriminate use of chemicals might work for a few years, but after a while, there aren’t enough beneficial soil organisms to hold onto the nutrients” (Savonen 1997).When these pesticides are applied into the soil, they undergo following reactions (Kalpana 2016):

(a) Chemicals may vaporize and lost to the atmosphere without any chemical changes.
(b) They may absorbed by soil colloids.
(c) They may leach through the soil.
(d) They may undergo various chemical reactions or may undergo microbial degradation by soil microorganisms.

Soil acts as a natural sink for various accumulating and concentrating contaminant which culminate in soil from various sources. With time, the amount of accumulated pesticides reaches considerable concentration and release persistent toxic compounds either through microbial degradation or photo-degradation resulting in **soil pollution**. It alters the physical, biological and chemical characteristics of soil, thereby reducing its productivity.

3.3.1 Factor Affecting Soil Contamination

3.3.1.1 Increase in Soil Organic Matter

Increase in soil organic matter increases the pesticide contamination. Pesticides bound to soil organic matter are less mobile, bio available but also less accessible to microbial degradation and thus more persistent.

3.3.1.2 Haphazard Use of Fertilizer

Fertilizers generally used to overcome the soil deficiencies. They contaminate the soil with impurities, which come from the raw materials used for their manufacture. Mixed fertilizers often contain ammonium nitrate (NH_4NO_3), phosphorus as P_2O_5, and potassium as K_2O.

For instance, arsenic (As), lead (Pb) and cadmium (Cd) present in traces in rock phosphate mineral get transferred to super phosphate fertilizer. Since the metals are not degradable, they accumulate in the soil above their toxic levels due to excessive use of phosphate fertilizers and become an everlasting poison for crops.

During harvesting, a large amount of macro and micronutrients are removed with the crops. If the same crop is grown again, depleted levels of the nutrients can result in decreased yields. Application of fertilizers can obscure the nutrient level but on the other side over use of NPK fertilizers reduce quantity and protein content of crops (wheat, maize, grams, etc,) grown on that soil over the years.

Excess potassium content in soil declines vitamin C and carotene content in vegetables and fruits. The vegetables and fruits grown on over fertilized soil are more susceptible to attacks by insects and disease.

3.3.1.3 Indiscriminate Use of Insecticides, Pesticides and Herbicides

Insecticides are used to control insect populations. The first widespread insecticide use began at the end of World War II and included DDT (dichlorodiphenyltrichloroethane) and gammaxene. Insects soon became resistant to DDT and as the chemical did not decompose readily, it persisted in the environment. Since it was soluble in fat rather than water, it biomagnified and enter in to the food chain and disrupted calcium metabolism in birds, causing eggshells to be thin and fragile. As a result, large birds of prey such as the brown pelican, ospreys, falcons and eagles became endangered. DDT has been now banned in most western countries but many of them including USA still produce DDT for export to other developing nations whose needs outweigh the problems caused by it.

Pesticides not only bring toxic effect on human and animals but also decrease the fertility of the soil. Some of the pesticides are quite stable and their biodegradation may take weeks and even months. The most important pesticides are DDT, BHC, chlorinated hydrocarbons, organophosphates, Aldrin, Malathion, Dieldrin, Furodan, etc. The remnants of such pesticides may get adsorbed by the soil particles, which then contaminate root crops grown in that soil. The consumption of such crops causes the pesticides remnants to enter human biological systems, affecting them adversely. For example, Endosulfan when accumulate in the soil converted into more toxic compound Endosulfan sulphate through microbial degradation.

An infamous herbicide used as a defoliant in the Vietnam War called Agent Orange (dioxin), was eventually banned. It had caused cancer, skin conditions and infertility in soldiers.

3.4 Water Contamination

Water is essential for our life on earth. No living being can survive without it. Water quality is important to support physiological activities of any biological cell. Water contamination is the impairment in its native characteristics by addition of contaminants to the extent that it either cannot serve for drinking purposes or to support the biotic communities, such as fish. It is a major cause of global concern as it leads to the commencement of numerous fatal diseases which is responsible for the death of over 14,000 people everyday (Oerke and Dehne 2004). Environment Protection Agency (EPA) reported in 1990 that more than 50% of the water pollution occurs due to leaching and mixing of chemicals from the agriculture practices (Damalas 2009)

There are five major routes through which pesticides reaches the water (Papendick et al. 1986):

- It may drift outside of the intended area when it is sprayed.
- It may leach through the soil.
- It may be carried to the water as runoff.
- It may be spilled accidentally.
- By eroding soil.

3.4.1 Pesticide in Ground Water

Pesticide contamination in groundwater is a matter of national importance because groundwater is used for drinking water by about 50% of the world population

(Agrawal et al. 2010). Especially in agricultural areas where pesticides are more frequently used, as about 95% of the population relies upon groundwater. Before the mid-1970s, it was thought that soil acted as a protective layer that filter and stopped the pesticides from reaching groundwater (Perlman 2016). Now studies have shown that pesticides can reach the ground water aquifers from applications onto crop fields, seepage of contaminated surface water, accidental spills and leaks, improper disposal, and even through dumping waste material into water bodies. According to the U.S. EPA, 46 pesticides were found in groundwater in 26 states as a result of normal agricultural applications (Trautmann et al. 2012).

3.4.1.1 Pesticide Properties Concern with Groundwater Contamination

There are some specific properties of pesticides that influence its ability to reach the groundwater (Trautmann et al. 2012):

Solubility: Pesticide that dissolve readily in water are said to be highly soluble. As water moves downward through soil, the pesticide with a higher solubility moves readily through the soil and possibly leaching to groundwater. For example, EDB and DBCP have been detected in groundwater in several states.

Volatilization: Volatilization is a function of both vapour pressure and solubility of a pesticide. Vapour pressure is a measure of the propensity of a compound to become a gas. The higher the vapour pressure of a pesticide, the faster it is lost to the atmosphere and the less that remains available for leaching. However, this does not necessarily mean that pesticides with high vapour pressures pose no threat to groundwater. Few pesticides, such as soil fumigants, are injected into the soil and therefore have limited exposure to the atmosphere.

Adsorption: The affinity of a pesticide to leach also depends on how strongly it adsorbs to soil. Adsorption refers to the attraction between a pesticide and soil particles. Pesticides that are strongly adsorbed onto soil are not likely to leach, regardless of their solubility. They are retained in the root zone where they are taken up by plants or eventually degraded. On the other hand, pesticides that are weakly adsorbed will leach in varying degrees depending on their solubility.

Degradation: The process of breakdown of toxic compound in to its non-toxic form is called degradation. Degradation of pesticide occur through various ways

- **Photodegradation**: Breakdown caused by exposure to sunlight.
- **Hydrolysis**: Breakdown occurs due to reaction of pesticide with water. It occurs in the root zone and at slower rates in groundwater.
- **Oxidation**: Breakdown of pesticide in the presence of oxygen.
- **Biodegradation**: Breakdown occurs due to reactions mediated by microorganisms in the soil. The natural distribution of microbes in the soil has important implications for managing pesticides. The vast majority of microbes live in the uppermost parts of the soil.

Half-life provides a useful empirical measure of pesticide degradation in soil. It is the time taken for a certain amount of a pesticide to be reduced by half. It takes into account physical, chemical, and biological degradation, plant uptake and volatilization. Higher the value of half-life of a pesticide, longer the length of time it remains in the soil and, hence, greater the opportunity to leach. It is difficult to predict because it varies widely for each pesticide and in different soil condition. Factors affecting half-life includes soil type, soil temperature, soil moisture content, concentration of the pesticide, method of application, chemical structure of pesticide, amount of sunlight and microbial populations

Half-lives in sub-soils are generally much longer than those in the root zone because of the less microbial populations and the changes in physic-chemical conditions. Once a pesticide gets into groundwater, its degradation is likely to proceed at a slower rate than that in the root zone.

3.4.1.2 Site Conditions

Besides the pesticide properties, site conditions also affect the potential for leaching of pesticides (Trautmann et al. 2012). These include:

Depth to Groundwater: Depth of ground water depends on climate and geologic conditions. Ground water with shallow depth has low opportunity for degradation or adsorption of pesticides. In such cases we need much precaution. In high rainfall areas, soils are permeable and water carrying dissolved pesticides may take only few days to permeate downward to groundwater. While in summer, ground water level tends to fall due to increase in plant uptake and evaporation.

Geologic Conditions: Groundwater quality is most vulnerable in areas where permeability of geologic layers is rapid. Highly permeable materials like gravel allow water and dissolved pesticides to penetrate freely downward to groundwater. On the other hand, clay is much less permeable and thus inhibits the percolation of water. Limestones are particularly highly susceptible to groundwater contamination because water with dissolved pesticides can move rapidly through cracks in the bedrock underlying the soil, receiving less filtration and very little chance to pesticide degradation.

Topography: Whether water runs off the surface or infiltrates into the soil depends on topography, plant cover, and soil type. Surface run off is maximum on land with steep slopes, sparse vegetation, and moderately impermeable soils. Water that runs off hilltops and hillsides tends to collect in depressions, where it sits until it evaporates or infiltrates into the soil. In flat areas soils are permeable and water will infiltrate into the ground rather than run off. Due to this, susceptibility to leaching is highest in flat or depressed areas.

Climate and Irrigation Practices: In high rainfall areas, soils are more susceptible to pesticide leaching. If high rainfall or heavy irrigation occurs during or shortly after the application, pesticide can be rapidly leached from the root zone and become potential groundwater contaminants.

Management Practices: Another factor determining leaching potential is the way in which a pesticide is applied. The rate and timing of a pesticide's application also are critical in determining the leaching potential. The larger the amount of pesticide used and the closer the time of application to a heavy rainfall or irrigation, the more likely it is susceptible to leaching and will be lost to groundwater. During chemigation, the risk of pesticide leaching can be minimized by using the lowest amount of water needed to activate the pesticide.

Pesticide in Drinking Water

Drinking water comes from two main sources i.e. **surface water** and **ground water**. Surface water includes water reservoirs either occur naturally like lakes, and river bodies or artificial constructed like ponds. In surface water pesticide usually comes either through direct application of pesticide to control aquatic weeds, insects or fish or through air moving from application site to surface water.

3.5 Air Contamination

The atmosphere is a complex system of natural gases which are essential to support life on Earth. Pesticide contamination in atmosphere is an aspect of air pollution that remains less documented than that of other environments. Air quality is a measure of the amount of pollutants in our atmosphere. Pesticides used in agriculture have the potential to contaminate our atmosphere which directly affects human, animal and plant health. **Pesticide drift** is the main cause of air contamination. During this pesticide remain suspended in the atmosphere. Some pesticides remain in the atmosphere for only a short period of time, while others can last longer. Pesticides released into the atmosphere either settle to the ground, dissociate by sunlight and water in the atmosphere, or dissipate into the surrounding air and contaminate them (NPS 2016). During the time of applications, weather conditions like temperature and relative humidity affect the spread of pesticide in air. Low relative humidity and high temperature result in more spray evaporating. During the pesticide spray, high wind velocity increases the spray drift and exposure. Also, pesticide applied as dust may travel with wind to other areas as a dust particle (http://ipm.ncsu.edu/wildlife/peanuts_wildlife.html). Ground spraying produces less pesticide drift than aerial spraying. Farmers can surround their crop by a buffer zone, consisting of empty land or non-crop plants such as evergreen trees to serve as windbreaks which absorb the pesticides and preventing their drift into other areas. Pesticides that are used to fumigate soil can give off chemicals called volatile organic compounds, which can react with other chemicals and form a pollutant called tropospheric ozone. Pesticide accounts for about 6% of total tropospheric ozone levels (https://researchnews.osu.edu/archive/evrgreen.htm).

3.6 Pesticide and Human Health

Pesticides can be considered as an economic and efficient tool of pest management. Due to their mode of action, they not only kill the specific target organism, but often kill or harm non target organism including humans. According to the WHO (World Health Organization) estimates, there are 3 million cases of pesticide poisoning each year and up to 220,000 deaths, primarily in developing countries. The application of pesticides is often not very specific, and unintentional exposures occur to other organisms. Young and developing organisms, are particularly susceptible to the harmful effects of pesticides. Even very low levels of exposure during development may have adverse health effects (Lah 2011).

3.7 Human Exposure to Pesticide

When a pesticide comes in contacts to an organism, it is called a pesticide exposure. About 97% of all the body exposure that happens during pesticide spraying is through skin contact. The toxic effect of a pesticide exposure depends on the amount of pesticide involved and the time of its persistence i.e. how long it remain there. In our daily routine we expose several times to pesticides either directly or indirectly (USEPA 2016).

- **Indirect exposure** occur either through dietary products such as food and drinking water, or application of insect repellents in our house or on our skin.
- **Direct exposure** occur through occupational exposure such as farmers working in open fields and greenhouses, workers in the pesticide industry, and exterminators of house pests.

However, irrespective of the occupation, the presence of such pesticides in the working environment also contributes for possible occupational exposure. Workers who mix, load, transport and apply formulated pesticides are considered to receive the greatest exposure because of the nature of their work and therefore are at highest risk for possible acute intoxications (Valenzuela et al. 2009). In some cases, exposure may occur from accidental spills of chemicals, leakages, or faulty spraying equipment. The pesticide exposure also increases if farmers do not follow instructions carefully about the application of pesticides. Particularly when they ignore basic safety guidelines about the use of personal protective equipment and fundamental sanitation practices such as washing hands after the handling and application of pesticide or before eating (Fenske and Day 2005).

Several factors can affect pesticide exposure during handling (Fenske and Day 2005). Various form of pesticide formulation may affect the degree of exposure. Liquid formulations are easily susceptible to either direct contact through splashing and occasionally spillage or indirect skin contact through clothing contamination. Solid formulations like dust resulting in exposure to face and eyes and also cause respiratory hazards while being loaded into the application equipment. Depending on the type of packaging, some extent of pesticide exposure also occur during the opening of bag. The size of packaging container such as cans, bottles etc. may have the risk of spillage and splashing. Sometime adjuvant chemicals which are used in the preparation of formulations to enhance their activity and also facilitate application to get reaching target species may show toxicity themselves, thus contributing to the overall effect of exposure to a commercial pesticide product (Surgan et al. 2010).

Route of Pesticide Exposure

Oral Exposures
- Not washing hands before eating and drinking.
- Mistaking the pesticide for food.
- Accidently splashing of pesticide.

Inhalation Exposures
- Prolonged contact with pesticides,
- Vapours of fumigants, dust or mist
- Use of old or inadequate pesticide application equipment.

Dermal Exposures
- Not washing hands after handling of pesticides or their equipment.
- Splashing of pesticides on unprotected skin.
- Wearing pesticide contaminated clothes.
- Applying pesticides during windy weather.
- Wearing inadequate personal protective equipment while handling pesticides,
- Touching pesticide-treated surfaces.

Eye Exposures
- Accidently splashing of pesticides in eyes.
- Applying pesticides in windy weather without protection.
- Rubbing body with contaminated gloves.
- Pouring dust, granule, or powder formulations without any protection.

3.8 Human Health Risk factor

According to The Stockholm Convention on POP's, among the 12 most dangerous and persistent chemicals, 9 are pesticides (Gilden et al. 2010). Risk factor arise due to pesticide exposure may be acute or chronic. Some pesticides are highly toxic to humans; only a few drops in the mouth or on the skin can cause extremely harmful effects. Other pesticides are less toxic, but too much exposure to them also will cause harmful effects. A good equation to remember is:

Hazard is the risk of harmful effects from pesticides Hazard = Toxicity × Exposure. It depends on both the **toxicity** of the pesticide as well as **exposure**.

Pesticides Can Cause Three Types of Harmful Effects

1. **Acute Effects**: These may appear immediately or within 24 h after exposure to a pesticide. They can be measured more accurately and easily diagnosed than delayed effects. These effects are usually observable and often curable if appropriate medical treatment is given on time. For example nerve, skin, and eye irritation and damage, headaches, dizziness, nausea, fatigue, vomiting, abdominal pain and systemic poisoning. Because these symptoms are similar or identical to those caused by other illnesses, so often misdiagnosed and even occasionally cause fatal death. Major acute effects can cause respiratory problems, nervous system disorders, and aggravation of pre-existing conditions such as asthma.

   For example: Cases of fetal paraquat poisonings in Costa Rica presented either renal or liver impairment, followed by adult respiratory distress syndrome (ARDS) or pulmonary edema (Wesseling et al. 1997).

   In 1997, 88,255 endosulfan exposure emergencies were reported to the national network of Poison Control Centers (Jamal 1997). Fourteen fatalities were attributed to pesticide poisoning during the same period. Over 50% of all reported pesticide poisoning cases involved children under six years of age (Lifshitz et al. 1999).

(a) **Respiratory problems**

Asthma: It is a serious life-threatening disease, of the lungs characterized by recurrent attacks of bronchial constriction, which cause breathlessness, wheezing, and coughing. Risk of developing asthma increases by increasing bronchial hyper-responsiveness. Pesticide directly damaging the bronchial mucosa, and in turn making the airway very sensitive to allergens. Pesticides such as Paraquat, OC, OP, Carbamate and Pyrethroid insecticides showed strongest association with asthma for occupational, domestic and environmental exposures (Amaral 2014).

Neurotoxic effect: Pesticides such as organochlorines, OPs and carbamates are capable of producing acute and chronic neurotoxic effects in mammals (Tanner and Langston 1990). Both acute and chronic alterations in sensory, motor, autonomic, cognitive, and behavioural functions have been observed in people exposed occupationally to relatively high levels of these pesticides. These neurobehavioral effects and chemical-induced changes in behaviour may be a relatively sensitive indicator of nervous dysfunction (NAS 1975). Organochlorine compounds have effects on motor, sensory, or cognitive function that are detectable using functional indicators of neurotoxicity to assess neurotoxicity risk. (Duffard and Duffard 1996).

2. **Chronic effects** are those which do not appear even within 24 h after exposure to a pesticide. These effects from pesticides are problematic to study in humans because most people are exposed to low doses of pesticides and have delayed health effects. **Different types of chronic effects:**

   Carcinogenic effect: It includes many types of cancer in humans. **For example**: Leukemia, Non-Hodgkins lymphoma, Brain, Bone, Breast, Ovarian, Prostate, Testicular and Liver cancers (Asghar et al. 2016).

   Bladder and colon cancer: Heterocyclic aromatic amines are found in several cases of bladder and colon cancer (Weisburger 2002). The cancer incidence depends upon the intensity and time of exposure. **For example**: Imazethapyr is extensively used in agricultural increased the risk of bladder cancer by 137% and colon cancer by 78% (Stella et al. 2009; Koutros et al. 2009). Research showed that from total 20,646 applicator of this pesticide, 2907 develop cancer. Thus use of aromatic amine is restricted to prevent bladder and colon cancer.

   Brain cancer: Meningioma is a type of brain cancer which is caused due to extensive use of herbicide (Claudine et al. 2008). A study conducted on the pesticide exposure and childhood brain cancer show that, exposure before during or after pregnancy can greatly increase the brain cancer incidence. The risk of brain cancer is twofold increased in professional applicators by exposure to pesticide which is used to control the termites, then exposure to other pesticide. The risk of brain cancer is 30% by other pesticides, and 50% by termites controlling pesticides (Kathryn et al. 2013).

   Breast cancer: It is a kind of cancer that develops from breast cells. It usually starts off in the inner lining of milk ducts or the lobules that supply them with milk. A malignant tumor can spread to other parts of the body. A breast cancer that started off in the lobules is known as *lobular carcinoma*, while one that developed from the ducts is called *ductal carcinoma*. It is the most common cancer among women in the United States while in male, it is relatively rare (Siegel et al. 2012). Pesticides that were predominately found in the milk samples were p,p′- DDE, p,p′-DDT, α-chlordane, heptachlor epoxide, heptachlor, β-HCH, and γ-HCH. In 1993, Wolff et al observed that the risk of breast cancer was higher among women with high serum concentrations of DDE, the major metabolite of DDT, compared with women with low levels (Wolff et al. 1993). Cohn et al**.** conducted a nested case-control study among a cohort of female members of the Kaiser Permanente Health Plan in Oakland, California. They found that that increasing serum *p,p′*-DDT concentrations were positively associated with breast cancer risk, but only among those women exposed prior to 14 years of age (Cohn et al. 2007).

   Leukemia: It is a type of cancer which causes abnormal production of white blood cells. Several researches show that risk to childhood leukemia increases threefold by the parental exposure of pesticides. According to Children’s Cancer Study Group the basic reason of acute non-lymphoblastic leukemia is parental exposure to pesticides and those children which are regularly exposed to household pesticide have 3.5 times great chance of leukemia (Lawrie et al. 1997).

Pesticide also cause leukemia in children whose mothers are exposed to them during the period of their pregnancy, small children less than one year have seven time more chances of leukemia if they are exposed to **permethrin pesticide**. It alter the nervous system and also consider as a carcinogenic. Childhood leukemia is due to alteration in the DNA of infants. By research it is found that time from pregnancy to 11 month of nursing is very critical for children and if they exposed then they have two times more chances of leukemia (Ferreira et al. 2009).

Non-Hodgkin Lymphoma: It is a heterogeneous group of over 20 different B- and T-cell neoplasms affecting the immune system/lymphatic system and arising primarily in the lymph nodes (Dreiher and Kordysh 2006; Campo et al. 2011). Exposure to pesticides, particularly phenoxy acid herbicides, has been cause of NHL (Dich et al. 1997). In Sweden, Hardell et al observed a sixfold increased risk of NHL among those who used phenoxy acid herbicides (Hardell et al. 1981). In Kansas, Hoar et al observed a significant twofold increased risk among those who used phenoxy acid herbicides and the risk was highest for those who used 2,4-dichlorophenoxyacetic acid (2,4-D) for 21 days or more during the course of one year (Hoar et al. 1986).

Mutagenic effects: These effects can lead to permanent genetic change. Lax and colleagues in 2000 examined the presence of mutations at codon 12 of the ras gene in 61 patients with pancreatic cancer that were environmentally exposed to organochlorine pesticides (Lax et al. 2000). The results showed mutation in K-ras codon in patients with higher serum levels of DDEs (Lax et al. 2000). Porta et al. in 1999 reported significant associations in a case control study of 51 subjects with exocrine pancreatic cancer between serum concentrations of p-p –DDT (Porta et al. 1999).

Teretogenic effect: These effect cause birth defect. It is a pathetic situation for the next generation. When a pregnant woman is exposed to pesticides, the baby inside her is also exposed and can be damaged. These babies will have a higher risk of having learning difficulties, allergies, and other health problems. There are many evidences for the pesticide exposure to birth defects, fetal death and altered fetal growth. It occur due to the application of pesticides to kill and control garden insects, ants, mosquitoes and insects (Pimentel 2005; Power 2010; Raja and Masresha 2015). These chemicals indirectly affecting fetus and leads to increase the risk for oral clefts, neural tube defects, heart defects and limb defects (Oerke and Dehne 2004; Ortega and Carmona 2012).

Oncogenic effect: It has been proven that pesticides activate oncogenes in vitro and in vivo. They have ability to induce tumor growth. Long term exposure to organochlorine and organophosphate pesticides cause oncogenic effect (Vakonaki et al. 2013). Atrazine is one of the most heavily used pesticides in the United States and have been detected in groundwater at very high level. It rapidly metabolized to polar metabolites that are readily excreted in the urine in humans. However, its major quantitative metabolite, dialkylchlorotriazine, covalently modify proteins both in vitro and in vivo and has the potential to alter protein and cellular function. In addition, it also cause neuroendocrinedisrupting effects. Glutathione conjugation of methyl bromide is the primary mechanism of its detoxification and this reaction is catalyzed by the glutathione S-transferase theta- 1 (GSTT1) isoform. Individuals who cannot express GSTT1 due to methyl bromide exposure would be predicted to have a higher prostate cancer risk (Alavanja et al. 2013).

Prostate cancer: Cancer of the prostate, a gland of the male reproductive system is the result of oncogenic effect of pesticide exposure. It is the second most common cancer among American men, with one in six men diagnosed during their lifetime. It is the second leading cause of death. In 2003, *International Journal of Cancer* shows that individuals who have worked in agriculture have 40% increased risk of having prostate cancer over the general population. Other studies suggest that endocrine disruption is likely to be a mechanism for developing this type of cancer (Owens et al. 2010).

Liver damage: Long term exposure to Bipyridyl pesticides cause death of liver cells. They damages the liver over many years can lead the liver to form scar tissue. Fibrosis is the first stage of liver scarring. When scar tissue builds up and takes over most of the liver, this is a more serious problem called cirrhosis.

Reproductive disorder: Pesticides exposure also have reproductive health effects as other toxic chemicals. They can enter a woman's body and appear in her breast milk later. There are so many pesticides in use all over the world that even mothers who have never used pesticides have some toxic chemicals in their breast milk. (Conant and Fadem 2008)

For example: **Sterility**: Many male farm workers have become unable to have children after they worked with certain pesticides because they can no longer make sperm.

Damage to hormone-producing glands: Hormones control many of our body activities, such as growth and reproduction. When pesticides damage the glands that produce hormones, this can cause problems with childbirth and reproduction. Even if a woman is exposed to pesticides before she is pregnant, she can have a miscarriage or the baby may be born dead because of the exposure.

Neurotoxicity: Many pesticides including organophosphates, organochlorine and carbamates affect central and peripheral nervous system by their toxic effects. High or low-level exposure during adult, childhood or in utero exposure leads to very chronic nervous disorders like **Alzheimer and Parkinson disease** (Keifer and Firestone 2007).

Alzheimer disease: Dementia, decrease in brain capacity, increased in recent years due to increase in pesticide exposure. Pesticide affect neuron function at molecular level by distrusting microtubules and hyperphophorylation which lead to Alzheimer diseases (Zaganas et al. 2013). Organophosphate and organochlorine pesticides are found to effect acetylcholineestrase regulation at synaptic junction in nervous system and may lead to the Alzheimer disease especially in exposed person during their late life (Hayden et al. 2010). Some herbicides like rotenone and paraquat will disrupt the bioenergetical activities of mitochondria, oxygen metabolism and redox function which also lead to Alzheimer disease (Thany et al. 2013).

Parkinson disease: This disease occur when dopamine is not produce by the substania nigra neuron (dopaminergic) in brain, which leads to lack of coordination, trembling and loss of muscles control. Some pesticides like rotenone and paraquat will disrupt these dopaminergic neuron which causes the inhibition of dopamine production and disruption of chemical synapse in peripheral nervous system thus causes Parkinson disease (Qi et al. 2014). Pesticide and it's metabolites effects mitochondria and modulate xenobiotic metabolism which lead to Parkinson disease (Couteur et al. 1999). In a separate research it is found that if rats are exposed to the rotenone then with the passage of time there is neurodegenration is found in the peripheral nervous system, there is decrease in motor nerve conduction velocity especially in sciatic nerves. It is due to absence of dopamine and disruption of chemical synapse in peripheral nervous system (Binienda et al. 2013).

Multiple Chemical Sensitivity (MCS) is a medical condition characterized by the body's inability to tolerate relatively low exposure to pesticides. Symptoms of this condition include dizzying, including everything from cardiovascular problems to depression to muscle and joint pains. Individuals suffering from MCS will begin to react adversely with time to substances that formerly did not affect them. The only way to relieve their symptoms is to avoid those substances that trigger adverse reactions. For some individuals, this can mean almost complete isolation from the outside world (Miller and Mitzel 1995).

3. **Allergic Effects**: These are harmful effects that some people develop in response to some pesticides. These effects are not to be supposed to occur during a first exposure to a pesticide. The first exposure causes the body to develop repelling response but the later exposures result in the allergic response. This process is called **sensitization**, and the pesticides that cause allergic reaction are known as **sensitizers**. **For example**: Asthma or even life threatening shock, skin irritation, such as rash, blisters, or opensores, and eye and nose irritation, such as itchy, watery eyes and sneezing. Unfortunately, it is quite difficult to tell which person may develop allergy to which pesticide. However, certain people seem to be more sensitive than others. They develop an allergic response to many types of pesticides in their surrounding environment. These persons may be more likely to develop allergies to pesticides (Owens et al. 2010).

3.9 Future perspectives

The easiest way to prevent the inappropriate use of pesticides is through education. If more farmers, especially in developing countries, educated about the risks of pesticides, they would be more cautious about use the pesticides and the protection taken during the application. Another way is to implement the Integrated Pesticide

Management program which "*Emphasizes non chemical and cultural pest control strategies such as removal of diseased plant parts, crop rotation that may disrupt the life cycle of pests, and biological control such as the use of insect predators*" (Emily 2011).

Non-government organizations providing the best prevention strategies through various educational sessions, telephone hotlines, and safety classes. The UN Food and Agriculture Organization and the convention on Persistent Organic Pollutants are making global efforts to decrease the presence and abundance of the harmful pesticides (Emily 2011).Thus, new techniques with better consistency are needed to predict the potential hazards of pesticides and thus contribute to reduction of the adverse effects on human health and the environment.

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Chapter 4
Genetic Engineering and Environmental Risk

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Abstract Genetic engineering in today's world is gaining much importance. It provides plant varieties with good agronomic characteristics, superior quality values and expressing traits of agricultural interest such as insect resistance and herbicide tolerance. The production and use of genetically modified organisms (GMO's) is increasing steadily. There are various techniques by which genetic modified crops can be developed. But the issue still remains; whether altering genetic structure of any organism is ethical, will it create any problem to the people who consume it. Therefore, it is important to examine both pros and cons of genetic engineering and to determine whether this technology have place in a future. There are lots of controversies regarding the safety issue of GM crops and labeling of GMO products. Environmental risk assessment is a structural approach use to analyze the risk associated with GM crops. The goal of the risk assessment is to identify, characterize and evaluate risks by considering a wide range of potential pathways through which harm might occur. The assessment evaluates any risks posed by the genetic engineered (GE) plant in comparison to the risks posed by non-GE plant.

Keywords Genetic modified crops • Insect resistance • Environmental risk assessment • Genetic engineering

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M. Oves et al. (eds.), *Modern Age Environmental Problems and their Remediation*,
DOI 10.1007/978-3-319-64501-8_4

4.1 Introduction

Introducing genes from various organisms into crops and livestock has long been regarded as a promising way to ensure the productivity of agriculture and forestry (Beringer et al. 1992; Lehrman 1992). Genetic engineering technology has dramatically reduced the time required for the development of new commercial varieties of crops. Genetic engineering or recombinant DNA (r-DNA) technology offers many opportunities for improving agriculture and public health (Gulfishan et al. 2015). This technology transcends classical plant and animal breeding by permitting the rapid transfer of genetic traits between entirely different organisms. Potential benefits include higher yields and enhanced nutritional value from crops and livestock, reductions in pesticide and fertilizer use and improved control of soil and water pollutants. Nevertheless, some releases of GMO's may have ecological, social and economic effects. During the course of time there have been rapid developments in genetic engineering techniques. Plant breeding techniques have been used for generations to both improve existing crops, like rice and to produce entirely new crops, like modern maize. Overtime, plant breeders have adopted new tools and technologies to accelerate the development of crops with greater yields, better nutritional value and the ability to withstand diseases, pests and other environmental stresses. For example, plant breeders have artificially changed plants chromosome numbers, induced mutations using chemicals and radiation and used tissue culture and embryo rescue to recover the offspring of crosses between distantly related species (Carpenter et al. 2002; Lemaux 2008).

The concept of genetic engineering as direct transfer of DNA from one organism to another was given by Herbert Boyer and Stanley cohen in (1972). The first genetically modified animal was a mouse created in (1974) by Rudolf Jaenisch. An antibiotic resistant gene was inserted into tobacco in (1983) leading to the first genetically engineered plant which was developed by Michael W. Bevan, Richard B. Flavell and Mary-Dell Chilton. The golden rice a vit-A enriched rice was developed with increased nutritive value. Genetech the first GE company produced the Humulin a human insulin in (1982) and later on many genetically organisms were produced like GloFish, Zebra fish, Flavr Savr (National Research Council (NRC) 2004).

According to ISAAA (International Service for the acquisition of Agri-biotech applications) in (2015) the country with largest growing genetically modified (GM) crop is USA followed by Brazil and Argentina. The major GM crops cultivated are maize, soyabean, cotton, canola, sugarbeet, alfalfa, papaya, squash and potato. India has the fourth largest area planted under genetically modified organisms (GMO). The area under cultivation is 11.6 million hectare and crops include cotton only. Only four GM crops account for 99% of worldwide GM crop hectarage which is soyabeans, corn, canola and cotton. GM soyabean are planted on half of all the hectares in the world (50%), corn accounts for 30%, cotton for 14% and canola 5% of the total global GM hectarage. These are the only GM crops that have been grown in any significant quantities over the past 20 years. Minor GM crops which account for just 1% are alfalfa, sugarbeet, papaya, squash and eggplant.

On the large scale only two GM traits have been commercialized, herbicide-tolerant (HT) and pest resistant crops (BT crops). They are mainly grown in North and South America and mostly used in animal feed and biofuels. Pest resistant GM cotton (Bt cotton) is widely grown in India. The production and use of GMO's is increasing steadily. Although there are many potential benefits to humans from this process, the risks have not been adequately defined. There are many people and organizations that are completely against GMO's. It is important to thoroughly examine all of the statements both in favor of and against genetic engineering to determine whether it should have a place in our future. It is equally important to ensure that the public has access to this information, as they are the ones using or consuming the modified products.

4.2 Difference Between Conventional Breeding and Genetic Engineering

The aim of any breeding practice is to obtain plant varieties with good agronomic characteristics. With conventional breeding there is little hope to obtain plant with desirable genes as it allows limited exchanges between the same or very closely related species. Large number of crosses is done for any particular trait which has to be transferred, still success is limited. Sometimes there is a chance of linkage drag means some undesirable genes can be transferred along the desirable genes. Another drawback is conventional breeding is time consuming and laborious thus making the process unfit for today's need to obtains plants with good quality traits.

In contrast, genetic engineering allows the transfer of one or more genes between the closely related organisms or distantly related organisms. Comparatively shorter time is required to obtain GMO's using genetical engineering (GE) technique and there is no linkage drag (Fig. 4.1).

4.3 Importance of Genetic Engineering

GE is a field of biotechnology that deals with genes. Genes from one organism are taken and inserted into another organism to make various changes. It can be used to introduce specific traits into plants like resistant to disease, insect, high yielding and high nutritional value etc. It also has the potential to slow the aging process and extend the shelf life of a fruit. Ananda Chakrabarty in (1971) developed first genetically engineered organism and granted patent protection. He genetically engineered a common bacterium into *Burkholderia cepacia* which is a variant that digests petroleum products. This bacterium cleans up oil spills and has proven to be both safe and useful. According to Koepsell (2007) the first genetically engineered mouse to be patented for use as a model organism for cancer research

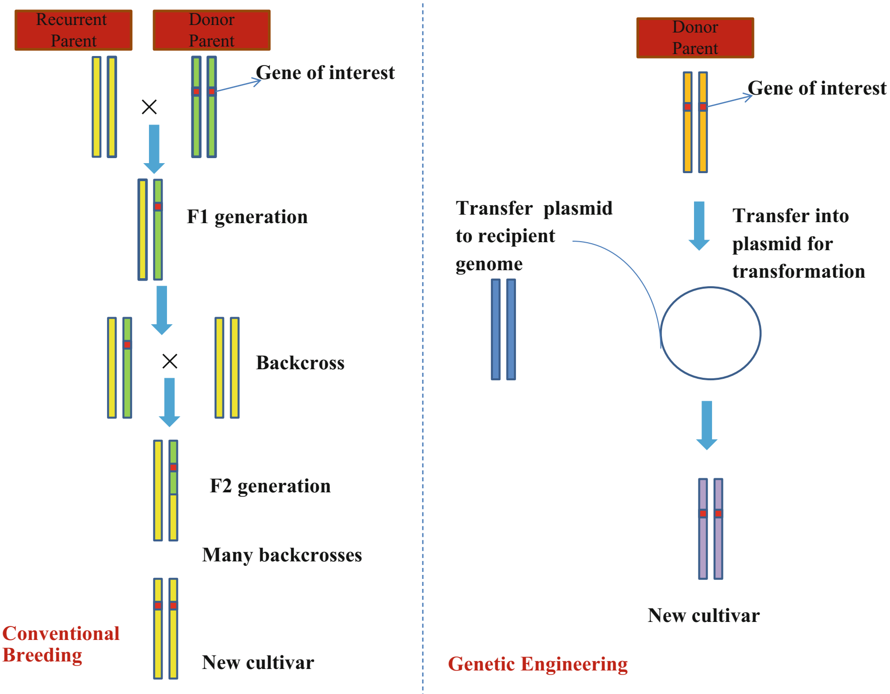

Fig. 4.1 Difference between conventional breeding and genetic engineering (Modified from Nielsen KM, 2003)

was *The OncoMouse*. Genetically engineered foods reduce the need for pesticides and fertilizers as they produce pest-resistant, and drought-resistant crops and increase yields. According to Liao (2004) there are two kinds of GE known as somatic and germline. Somatic engineering targets the genes in specific organs and tissues of the body of a single existing person and it do not affect the genes in their eggs or sperm. Germline engineering targets the genes in eggs, sperm or very early stage embryos. Given the rapid advances in the human genome project and GE, it seems that GE can be used as an alternative method for sex selection. Another ambitious goal of GE is reducing the susceptibility of livestock to pests and diseases. Bottom line to understand the objectives of the GE is that it is helpful in duplication of DNA fragments and there manipulation, for agricultural, industrial, medical and research purposes.

4.4 Techniques of GE and Advancement

GE is the important tool and various techniques are used for transferring genes from one organism to another. These techniques include: *Agrobacterium* mediated, microinjection, macroinjection, electroporation mediated, PEG/liposome mediated,

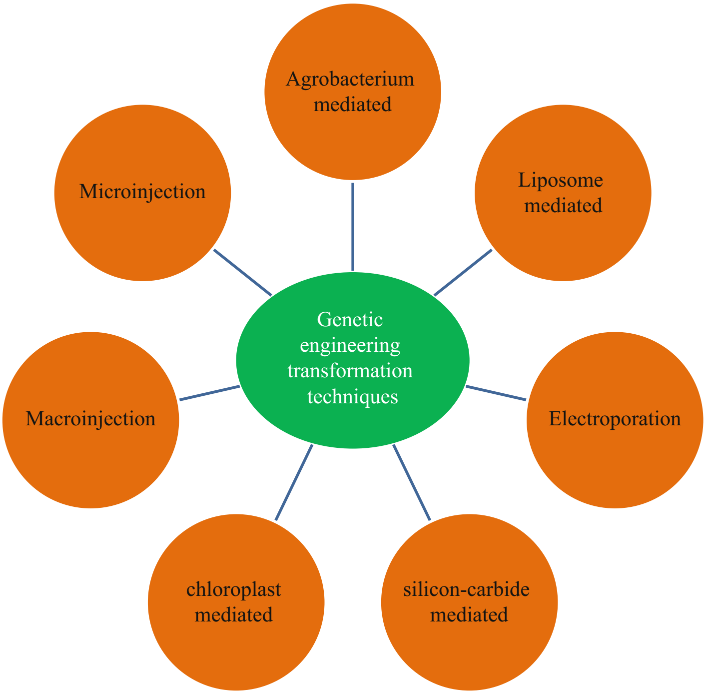

Fig. 4.2 Different techniques used in genetic engineering for transformation

silicon-carbide mediated, chloroplast mediated etc (Fig. 4.2). Over the last few years there has been rapid development in GE techniques. Currently there is a list of seven new GE techniques before the European commission. But there is a debate whether the product of these techniques when applied to plants cover the EU GMO laws. The seven new GE techniques referred to as (New Breeding Techniques) NBT's each bring their own set of risks and uncertainties. These seven techniques include: Zinc finger nuclease technology, oligonucleotide directed mutagenesis, cisgenesis/Intragenesis, reverse breeding, grafting, agroinfiltration (Ricarda 2015).

4.5 Clustered Regularly Interspaced Short Palindromic Repeats System (CRISPR/Cas)

Clustered regularly interspaced short palindromic repeats system (CRISPR/Cas) The CRISPR/Cas system is part of the immune system of bacteria, which confers resistance to foreign genetic material by cutting them out of the organism's DNA. CRISPR/Cas9-based technologies contains two components, CRISPR-associated protein 9 (Cas9) and a single guide RNA (sgRNA), to carry out genome-editing.

The sgRNA typically is designed to have a 20-nucleotide DNA sequence complementary to a target sequence directly in front of a protospacer adjacent motif (PAM). The Cas9 can then interact with the sgRNA and target DNA creating a double strand break in the target DNA 3 to 4 base pairs upstream of the PAM site. The PAM is an essential targeting component (not found in bacterial genome) which distinguishes bacterial self from non-self DNA, thereby preventing the CRISPR locus from being targeted and destroyed by nuclease.

CRISPRs have been now been used experimentally in a wide variety of species, including a variety of plant species, zebrafish, mice, chickens and mosquitoes. CRISPR/Cas9 is becoming the gene editing method of choice due to its versatility and ease of use. By delivering the Cas9 nuclease and appropriate guide RNAs into a cell, the cell's genome can be cut at a desired location, allowing existing DNA to be removed and/or new DNA to be added. However, RNA-guided endonucleases have demonstrated off-target effects, which can cause collateral damage in the genome. Further, CRISPR/Cas may be used to develop a wide variety of genetically engineered traits in many different organisms, some of which might have adverse effects on human health and the environment. Proposals to use CRISPR/Cas to create a "gene drive" mechanism, potentially allowing a genetically engineered trait to spread throughout the entire population of a species (e.g. plants or insects), have led to debate about the need for strict regulation, to avoid potential adverse effects to entire ecosystems.

Zinc Finger Nucleases Zinc finger nucleases are genetic engineering techniques that aim for deliberate changes to the genetic makeup and traits of an organism. Zinc finger nucleases technique involves changes in the sequence of the DNA in order to delete, substitute or insert DNA sequences at specific position in the genome. Zinc finger contains *FokI* enzyme which cut at specific position in the genome and zinc finger component recognize a short stretch of DNA (9–12 bases). The construct of Zinc finger nucleases is made and then transformed into the plant cell. Later plant lines are selected that do not carry transgene for the zinc finger protein.

Oligonucleotide Directed Mutagenesis (ODM) The aim of this method is to create small and predesigned changes within very specific sites in genes to either change the function of the gene product or to stop its production. Oligonucleotide consists of short stretch of single stranded nucleic acids composed of a small number of nucleotides which is synthetically produced. It is designed to be almost identical to the DNA sequence of the target gene, except for one-four nucleotides. This will create a sequence mismatch when the oligonucleotide binds to the target gene, inducing a site-specific DNA change once the cell's own DNA repair mechanism is triggered, preserving the sequence of the oligonucleotide rather than the original sequence.

Cisgenesis and Intragenesis In this method the sequence of DNA inserted will be sourced from the same or closely related species. In 'Cisgenesis'the DNA inserted will have been made according to the exact sequence of a gene found in a related donor organism. In ‘Intragenesis’ the inserted gene sequence is a composite, made up of sequences and elements from different genes of one or more closely related species.

Reverse Breeding is a GM technology intended to reconstitute genetically uniform and pure (homozygous) parental lines from an existing hybrid whose parental lines are no longer available or do not exists now. In this technology individual resulting gametes are used to reconstitute plants with two sets of the same chromosomes. At the last stage the GM gene is deselected and parental lines are selected.

Agroinfiltration In this method gene are not stably inserted and integrated in the plant genome but rather such genes are present within the plant cell transiently for maximum of just one generation.

Grafting Grafting in this method desired traits of two organisms are combined into one without having to cross breed them (Ricarda 2015).

4.6 Uses of Genetic Engineering

Crops Resistance to Pests Insect attack is a serious agricultural problem leading to yield losses and reduced product quality. Every year insects destroy 25% of food crops worldwide. Researchers have used genetic engineering approach to take the bacterial genes needed to produce *Bt* toxins and introduce them into plants. If plants produce *Bt* toxins on their own they can defend themselves against specific types of insects. By using GE technique farmers no longer have to use chemical pesticide to control insect disease. Bt crops are widely planted commercially (Ranjekar et al. 2003).

Crops Resistance to Herbicide Weeds are constant problem in farmer’s field. Weed not only competes with crops for water and nutrients but also harbor insect pests and diseases. Weeds can reduce crop yields significantly. Herbicide tolerant (HT) crops offer farmers a vital tool in fighting weeds. Several crops have been genetically modified to be resistant to non-selective herbicides. These transgenics crops contain gene that enable them to degrade the active ingredients in a herbicide, rendering it harmless. Farmers can thereby easily control weeds during the entire growing season and have more flexibility in choosing time for spraying.

Crops Resistance to Virus Plant virus diseases cause severe damage on the productivity of a wide range of economically crops worldwide. Generally strategies which are used for management of viral diseases include control of vector propagating material, appropriate cultural practices and use of resistant cultivars. However, with due course of time the methods show certain drawbacks. With the advances in GE a new approach towards controlling plant virus diseases were developed. There are mainly two approaches for developing genetically engineered resistance depending on the source of the genes used. The genes can be either from the pathogenic virus itself or from any other source (Dasgupta et al. 2003).

Crops Resistance to Drought As we all know that water availability is considered the main constraint for crop production. Although conventional breeding also has contributed a lot to develop drought tolerant plant but genetic transformation contribute to widen still more the water stress tolerance range of plants. Plant response to drought stress has been analyzed at the ecological, cellular, physiological and molecular levels. After gaining the knowledge in these levels, the technological basis is utilized for increasing the drought tolerance of plants by genetic manipulation. If molecular biology is to really put in to improvement of water stress tolerance of plants, a coherent framework for revealing basic parameters of stress tolerance should be followed. Firstly, water stress responsive genes can be identified by means of all the expression analysis techniques that are available. Latter, isolation of these genes can be done and followed by differential hybridization techniques and their function evaluated in transgenic plants using model species as receptor organisms. Transgenic crop performance can be finally evaluated under field conditions or the identified genes used for marker assisted selection (MAS). Although modern and high throughput technologies such as expression profile analysis by DNA microarray technology and analysis of protein profiles by one- and two-dimensional gel electrophoresis are permitting us to know the genes (and proteins) that are up-regulated, down-regulated or newly expressed in response to stress. In consequence, determining those which are central to drought tolerance and genes that are unique to particular strategies for water deficit tolerance, the function of only a limited number of gene products have been established (Bartels and Sunkar 2005; Hasegawa et al. 2000; Ramanjulu and Bartels 2002).

Metabolic Engineering Metabolic engineering is referred to as the directed improvement of cellular properties through the modification of specific biochemical reactions or the introduction of new ones, with the use of recombinant DNA technology (Stephanopoulos 1999). This multidisciplinary field draws principles from chemical engineering, computational sciences, biochemistry and molecular biology. In short, metabolic engineering is the application of engineering principles of design and analysis to the metabolic pathways in order to achieve a particular target. This target may be to increase process productivity, production of antibiotics, biosynthetic precursors or polymers, or to extend metabolic capability by the addition of extrinsic activities for chemical production or degradation. Previous strategies to attain these goals was tedious and error prone. The scientific approach for metabolic engineering would involve the use of recombinant DNA technology and a better understanding of cellular physiology to modify intermediary metabolism (Bailey 1991; Stephanopoulos and Vallino 1991).

Biopharmaceuticals Plants and their extracts have long been used as remedies for a variety of health conditions and many modern pharmaceuticals are still derived from plants. With rDNA technology and the introduction of efficient transformation technologies for plant cells it is now possible to extend the use of plants for pharmaceutical purposes by using them as production platforms for biopharmaceuticals. The enormous numbers of biopharmaceuticals are proteins of human or animal origin and include enzymes, blood factors, monoclonal antibodies, cytokines, hormones and growth factors. These proteins are currently produced mainly in bacterial, yeast or animal cell cultures. Therefore, plants and plant cells have been investigated as alternative production hosts.

The first successful production of a monoclonal antibody in transgenic tobacco plants was done two decades ago (Hiatt et al. 1989) a great variety of proteins with potential pharmaceutical applications have been produced in plants (Basaran and Rodríguez-Cerezo 2008; Fischer et al. 2004; Schiermeyer et al. 2004; Twyman et al. 2005). These proteins are collectively referred to as plant-made pharmaceuticals (PMPs) and a large number of plant species have been evaluated as production platforms for these molecules (Sparrow et al. 2007). These include food crops such as maize, barley, potato and tomato, non-food crops such as tobacco and others such as duckweed and moss. As well as intact plants, certain types of plant tissue cultures (e.g. hairy roots) and cell suspension cultures from various species have been investigated (Hellwig et al. 2004).

Biopolymers Naturally occurring polymers (e.g. polysaccharides, polyamides, polyesters) are produced by bacteria or plants. The most widely used polysaccharide is cellulose which is a main component of plant cell wall. Cellulose is used in making paper, cardboard or other textiles. So, they have to be isolated from wood, cotton, corn etc. But it has some limitations like its costly and environmentally damaging processes. Likewise polyamides are polymers containing monomers of amides joined by peptide bonds. They occur naturally as wool or silk. The widely and best known silk is obtained from cocoons made by the larvae of the mulberry silkworm *Bombyx mori,* used for textile manufacture (Tirrell 1996). However to obtain large quantities of silk lot of labour and money is utilized. So, in order to overcome the drawbacks and to exploit the potential of plants as producers of cheap biomass, new technologies have to be introduced to improve the plant made polymers. GE technology provides us the tools to add new facilities to plant metabolic pathways which should lead to either high quality or even new polymers in plants.

4.7 Ecological Issues

1. **Genetic transfer**: It has been found that few bacteria has the capability of transferring novel DNA sequences to bacteria of other species and genera (Trevors et al. 1987). So it is the possibility that genetic exchange may occur between closely related plants as well as in microorganisms. For example, important weed species have originated through the hybridization of two intrageneric species, such as the crosses of *Raphanus raphanistrum* × *R. sativus* (radish) and *Sorghum halepense* (Johnson grass) × *S. bicolor* (Sorghum corn) (Colwell et al. 1986).

2. **Threat to soil ecosystem**: Many *Bt* crops secrete their toxin from their roots into the soil (Saxena et al. 2002). These toxins are sometimes very harmful and effects soil ecosystem.
3. **Threat to biodiversity**: The introduction of GM plants into the environment may have devastating effects on biodiversity. Certain birds, insects or animals are dependent on crops for their survival but may find themselves unable to eat GM crops due to introduction of genes in those varieties (Epstein 2001). This may somehow affect the food chain and predator-prey relationship.
4. **Non target effects**: Effects on non-target organisms have been demonstrated for a number of GMOs. The effects of *Bt*-maize pollen on non-target Lepidopteran species have been reported by (Jesse and Obrycki 2000; Losey et al. 1999; Sears et al. 2001; Wraight et al. 2000).
5. **Threat to human**: There is certain that problems could arise for humans who eat GM food. Some scientists have reported that if people are constantly eating food with antibiotic resistance genes in them they could develop a resistance to antibiotic as well. But these are just possibilities.
6. **Increased weediness**: One way of thinking generally about the environmental harm that GE plants might do is to consider that they might become weeds. In agriculture, weeds can severely inhibit crop yield. In unmanaged environments, like the Everglades, invading trees can displace natural flora and upset whole ecosystems.

4.8 Approaches to Environment Risks Assessment

According to Indian law and Cartagena protocol on biosafety it is mandatory that a risk assessment be performed prior to the commercial release of a GE plant in India. India approach to environmental risk assessment is described in the guidelines. The main objective of the risk assessment is to identify risks associated with the health and safety of people and environment from the cultivation of the GE plant in comparison with the non- GE plant.

4.8.1 Goal of Risk Assessment

The goal of the risk assessment is to identify, characterize and evaluate risks to the health and safety of the environment from the cultivation of the GE plant that resulted from the genetic engineering process (OGTR 2013). All the parameter and potential pathways are considered through which harm might occur. Risks are then characterized by considering how serious the harm could be.

Table 4.1 Scale for severity of harm

Consequences assessment	Degree of potential harm
Marginal	Minimum effect on the people and environment.
Minor	Minor increase in illness to people and minor increase in damage to environmental components. But can be easily treated.
Intermediate	Significant increase in illness to people and increase damage to environmental components. Requires treatment.
Major	Increase in illness, large number of people affected and generally not treatable.

4.8.2 Risk Assessment Process

The assessment of GE plant for risk includes four steps (Hill 2005; Kaplan and John Garrick 1981; Keese et al. 2013; NRC 2008).

Risk identification: The first thing should be identification of risk and for identification, all parameters and pathways should be consider through which harm may occur. This process should be comprehensive and rigrous. Certain points should be taken in mind that the harm that is occurring is it really from use of gene technology (Hayes et al. 2004; Keese et al. 2013).

Risk characterization (consequences assessment): Once risk has been identified now it is important to assess the severity of the potential harm. The severity of harm is dependent on the scale at which impacts are considered (Table 4.1). Assessing the seriousness of harm to people or to the environment may include consideration of the following points:

(a) Magnitude of each potential adverse impact
(b) Spatial extent or scale
(c) Temporal component of the impact

Risk characterization (likelihood assessment): It's called likelihood assessment. Regulators examine the causal link between the cultivation of the GE plants and a particular harm and determine how likely it is that the harm will occur (Table 4.2).

Risk evaluation: Once all the above steps have been completed the next step is to evaluate whether the risk is negligible, low, moderate or high. Risk is evaluated against the objective of protecting the health and safety of people and environment to determine the level of concern. In addition to this risk evaluation includes to reconsider the proposed genetically modified organism/crops whether additional data must be collected or it requires further assessment. To help inform the regulator decision making process and make the process more transparent, it is useful to define discrete level of risks (Table 4.3).

Table 4.2 Likelihood of harm

Likelihood assessment	Nature of likelihood
Highly unlikely	Harm may occur only in very rare circumstances.
Unlikely harm	Could occur in some limited circumstances.
Likely harm	Could occur in many circumstances.
Highly likely	Harm is expected to occur in most circumstances.

Table 4.3 Level of risks

Level of risk	Risk level definition
Negligible	Risk is of no noticeable concern and there is no present need to invoke actions for mitigation.
Low risk	It's of minimal concern, but may invoke actions for mitigation beyond standard practices.
Moderate risk	Its of marked concern and will necessitate actions for mitigation that need to be demonstrated as effective.
High risk	It's of considerable concern that is unacceptable unless actions for mitigation are highly feasible and effective.

4.9 Conclusion

Genetic engineering technology holds exceptional promise for improving agricultural production and keeping it environmentally sound. The commercialization of transgenic plants is likely to expand in future and will include a much larger variety of plants and traits than those that have been assessed to date. These include plants with (1) increased stress tolerance; (2) alterations to improve post-harvest processing such as lower lignin content in trees; (3) modified food quality, novel products and increased nutrient content for human consumption; and (4) phytoremediation abilities. New plant species will include turfgrass, pasture and tree species, and aquatic plant. Along with the potential benefits for agriculture come some risks. In essence, the release and regulation of GMO's into the environment should be similar to the release and regulation of exotic plant and animal species into a new environment. Therefore, time and effort must be devoted to laboratory and field testing before the release of GMO's. The public must be informed about the risks and benefits of GE, in order to make decisions about whether to use modified products or not. Furthermore, it is essential that all genetically modified foods be labeled clearly with what genes have been added. In conclusion, genetic engineering research should proceed slowly, and only by following codes of environmental and professional ethics. The precautionary principle should be employed, and GMO's should not be produced, sold, or consumed until the effects are completely known.

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Chapter 5
Effect of Air Conditioning on Global Warming and Human Health

Mohammad Nawaz Khan, Mazhar Ali Khan, Sumbul Khan, and Mohammad Mamoon Khan

Abstract With rapid growth of industrialization, deforestation and cleaning of land over a last few decades causes a considerably rise in temperature of environment and due to this air conditioning becomes a basic need to achieve a thermal comfort for people. However, in accompanying this thermal comfort it also causes an adverse effect on human health and also increases the risk of global warming. The regular or prolonged use of air conditioning results into dry skin, illness and constant fatigue, breathing problem and also the central air conditioning units causes indoor air contamination which results into cardiovascular diseases. Air conditioning also have a bad impact on global warming, after the Montreal Protocol in 1987 the HFCs replaced CFCs and HCFCs in lieu of the protection of ozone layer but HFCs are having high global warming potentials causes global warming. Due to the anthropogenic activities greenhouse gas emissions and their concentrations are rapidly increasing. Therefore it is necessary to find out the replacement of HFCs to reduce the global warming. Thus chapter explain the effect of air conditioning on global warming and human health and also their remedies.

Keywords Air conditioning • Global warming • Greenhouse gases • Human health • HFCs

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M. Oves et al. (eds.), *Modern Age Environmental Problems and their Remediation*,
DOI 10.1007/978-3-319-64501-8_5

5.1 Introduction

The conditioning of air according to the human comfort irrespective to the environment is known as air conditioning process. Air-conditioner technology has come into existence in 1902 by Willis Carrier who invented the first modern air-conditioner in New York, America. Air conditioning system based on the vapour compression system which uses the refrigerant as its working fluid.As the temperature of the environment increases in India, use of room air conditioners (ACs) is rapidly growing, straining India's electric grids. Air conditioning units also contribute to increasing greenhouse gas pollution. As India phases out ozone-depleting hydrochlorofluorocarbons (HCFCs) to comply with the international Montreal Protocol treaty but the refrigerants causing global warming are still in use.

5.2 Global Warming

Global warming refers to elevatein the average temperature of the Earth's atmosphere globally so that it causes changes in the global climate. The temperature of the atmosphere and surface has grown significantly during recent years (Hartmann et al. 2013). Greenhouse effect enhance the global warming by increasing the amount of greenhouse gases in the earth's atmosphere due to which more and more solar radiations are trapped, and hence the overall temperature of the earth's increases. According to the United Nations Intergovernmental Panel on Climate Change (IPCC) since the mid-twentieth century anthropogenic activities is the main cause of the global warming (IPCC Climate 2013). The effect of global warming include Elevation in global temperature and sea levels and expansion of deserts are the some consequences of global warming (Lu et al. 2007). But now the rapid warming in recent decades has mainly caused by the non-CO_2 greenhouse gases (GHGs), such as chlorofluorocarbons, Methane, NO_2 etc. (Hansen et al. 2000) (Fig. 5.1).

Chart above shows the temperature anomaly of ten top warmest year. The blue colour shows the global temperature anomaly in °C while the orange colour shows the temperature anomaly in °F. Over the past 150 years the temperature of the earth increases in two stages. An average temperature rise of 0.35 °C was recorded from 1919 to 1940, and 0.55 °C rise in between from 1970 to 2000 (Hansen et al. 2000; Jones et al. 1999) and in this century it is projected to further increase by 1.5 to 4.5 °C (Houghton et al. 1995). In the last five centuries the past 25 years was the warmest time recorded ever (Hansen et al. 1999). The global warming is the consequences of heating up of the oceans, melting of glaciers, rising of the sea levels. The map illustrates how much warmer temperatures of earth surface is and the maximum temperature of earth's surface was recorded in 2016 since modern record keeping began in 1880 (NOAA 2016). The Arctic regions were very warm

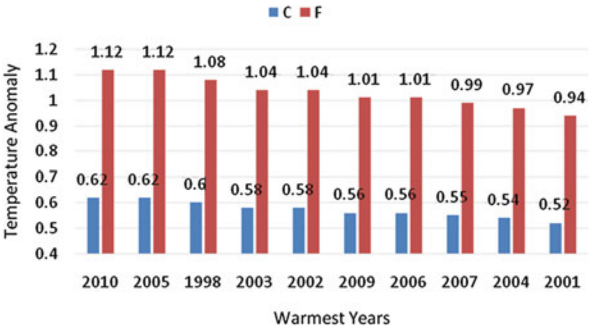

Fig. 5.1 Global temperature anomaly (Hansen et al. 2000)

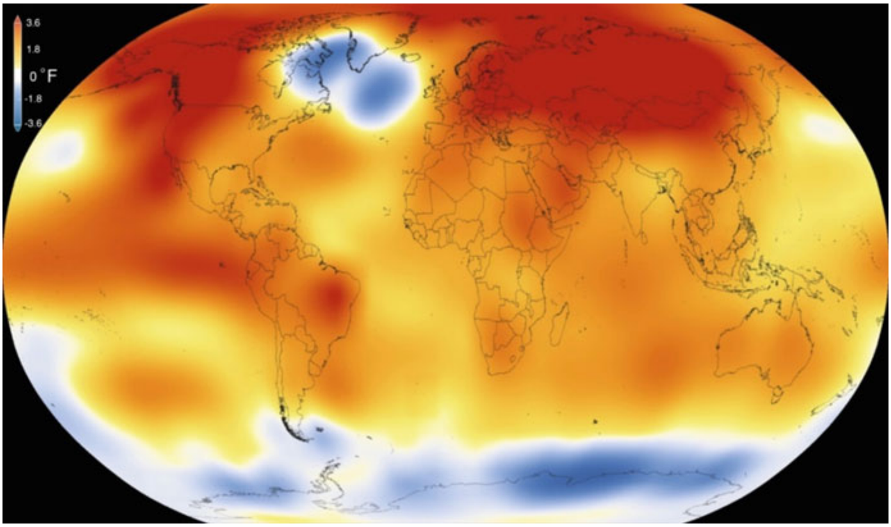

Fig. 5.2 Colours show the temperatures anomalies (Adopted from NOAA 2016)

and shows in red colour and the blue colour represents the areas which have lower than normal temperature (Fig. 5.2).

5.2.1 Types Of Air-Conditioning System

(i) **Window Air Conditioner**

The most commonly known air conditioner is window air conditioner which is used for single rooms. Window ac is more energy efficient than central air conditioning plant. The main components of window air conditioner are the compressor, condenser, expansion valve or coil, evaporator and cooling coil and all of them are consists in a single box. Window air conditioner is fixed in a slot made in the wall of the room.

(ii) **Split Air Conditioner**

This type of air conditioner are made up of two parts namely the outdoor unit which is placed at outside the space to be conditioned and comprises of the components like the compressor, condenser and expansion valve. The evaporator or cooling coil and its fan are comprises by the indoor unit which is fixed on the wall of the room. This type of air conditioner is suitable to condition small spaces such as single or double room.

(iii) **Packaged Air Conditioner**

When our requirement is to condition more than two rooms or big space then packaged air conditioner is suitable for this purpose. Packaged units are classified into two types. In the first one, in single housing all the components, compressor, condenser, expansion valve and evaporator are placed. The cooled air is thrown by the high capacity blower through the ducts into the various rooms. In the second arrangement, the compressor and condenser are housed in one casing. The compressed gas passes through individual units, comprised of the expansion valve and cooling coil, located in various rooms.

(iv) **Central Air Conditioning System**

It is very expensive to put individual air conditioner in each room for big buildings, malls, offices, entire hotels, gyms etc. Hence for this type of buildings central air conditioning system is used. A central air conditioning system is high capacity air conditioning system and for the sake of high capacity a big compressor is used to produce large amount of air conditioning. Air is cooled in the chiller and then supplied through the air handling unit and by ducts to the required space. Applications of the central air conditioning are cooling big halls, malls, huge spaces, galleries etc.

5.2.2 Refrigerants

A refrigerant is a working fluid used in air conditioning system and refrigerator to carry the heat directly or indirectly from the space to be cooled and rejects it to the atmosphere. During the process refrigerant changes its state from liquid to gas and then again gas to liquid. In sixteenth and seventeenth century the study of state change and their fundamentals results in the invention of artificial refrigerants. Evan was the first who proposed to freeze the water into ice by using volatile fluid as a refrigerant in a closed cycle (Evans 1805). Jacob Perkins used volatile fluids for cooling and freezing without the wastage of fluid in his patent (Perkins 1834). For the first 100 years mostly all of the refrigerants were flammable, toxic or both and some of them were also very reactive (Calm 2008). The practical design with better performance for a refrigerant came into existence in 1920(Carrier and Waterfill 1924). Dielene (R-1130) was the first refrigerant which is selected for the first centrifugal machine (Ingels 1952).

5.2.3 *Effect of Refrigerants on Global Warming*

Total Equivalent Warming Impact (TEWI) of the refrigerants system on environment considers the amount of leakage and the energy used by a system. Montreal and the subsequent protocols to contain ozone depletion were aimed at the reduction in HCFCs production culminating into its complete phasing out by 2020. Significant efforts are already made in search of R-22 alternatives, including HFCs, Hydrocarbons, CO_2, Ammonia, etc. Different "green" products with new technologies and refrigerants are introduced in several countries while others are yet to fall in line. The search for new refrigerants is still going on. Propane (R290) is one of the hydrocarbons, which has many advantages as a refrigerant also has several major disadvantages also like it is flammable. In the following paragraphs some of the refrigerants and their effects on global warming are discussed.

The non-hydrofluroethers are like CFCs, HCFCs and PFCs. These refrigerants act as blowing agents, and cleaning solvents with a desired effect on environment, safety, toxicity etc. The number of these refrigerants runs into hundreds. However, some of them are selected for future development as refrigerants. Al-l these refrigerants are having great potential to deplete the ozone layer and therefore these should be replaced with friendly alternative compounds which neither deplete the ozone layer nor increase the global warming. Among these hazardous refrigerants perfluorocarbons (PFCs) are also supposed to add to substantial global warming.

The Kyoto Framework Convention on Climate Change (1997) selected and listed six compounds including CFCs, HCFCs, PFCs, together with carbon dioxide as restricted compounds which are fluorinated ethers exerting low environmental effects as well as no flammability and low toxicity, and also have other physical properties similar to those of CFCs. It is also found that these ethers would have high potential to replace CFCs, HCFCs, and PFCs as refrigerants. A brief description of CFCs, HCFCs, HFCs, HCs are given below:

(i) **Chlorofluorocarbon**

For the safety and durability CFCs came into existence. Midgley et al. shows the variation in toxicity, flammability and boiling point by the chlorination and fluorination in hydrocarbons (Midgley and Henne 1930).

Dichlorodifluoromethane is the well-known CFC. Freon 12 consists up of only carbon and halogens such as chlorine, and fluorine, produced as volatile derivative of methane, ethane, and propane. Commercial production of R12 was started in 1931. The CFCs have high ODP (Ozone Depletion Potential) as well as GWP (Global Warming Potential) value (ASHRAE 2004) and hence this is the reason

CFC has been phased out in between 1990 and 2000 under the Montreal Protocol which was agreed on 26th August 1987 (Montreal Protocol 1987) and entered into force on 26 August 1989, followed by a first meeting in Helsinki.

It was assumed that chlorine atom would be split off by the action of sunlight, and the free chlorine will react with ozone in the stratosphere to form oxygen molecule.

$$\begin{gathered} CCl_2F_2 \rightarrow CClF_2 + Cl \\ O_3 + Cl \rightarrow ClO + O_2 \end{gathered}$$

(ii) Hydrochlorofluorocarbons

Due to high ozone depletion potential CFCs were replaced by hydrochlorofluorocarbon (HCFC) because of its low ODP value compare to CFCs but still it have high global warming potential which causes global warming. The replacement of HCFCs is also in progress. The Montreal Protocol limits the consumption of HCFCs in step in 1996, 2004, 2010, 2015 and 2020 and fully phase out by 2030 in non- Article 5 countries. While the Article 5 countries sets the reducing limit in 2015, 2020, 2025, 2030 and completely phased out in 2040 (UNEP 2007). The most commonly used HCFC are R-22 (chlorodifluoromethane) and still approximately 50% of Indian Air Conditioners use HCFCs. According to Indian Government's strategy, HCFCs will be phased out from India by the year 2030 (Ozone Cell 2009).

(iii) Hydro fluro carbons

The successful response to ozone depletion leads to change in temperature of environment globally (Perkins 1834). In order to remove the chlorine from the refrigerants and to get zero ODP value manufacturers created another set of refrigerants called HFCs which are better than HCFCs because they do not deplete ozone layer however they have high value of global warming potential to cause global warming. The change in temperature of environment is shown in the (Brohan et al. 2006; Rayner et al. 2006) (Fig. 5.3).

The most common HFC used in air conditioner are R-410a. A few more HFCs that are commonly used are: R-32 in Air Conditioners and R-134A in refrigerators. About 20-30% of the air conditioners in India still (in 2016) use HFCs. R-32 is better than R-410a in terms of global warming potential, but then it is still an HFC. The Kyoto Protocol is an International Treaty set the goal of the United Nations Framework Convention on Climate Change and sets the binding target byreducing green house gas emission to a level sothat it could stopharmfulhuman involvementto the climate system (Kyoto Protocol 1997).

This international treaty was first accepted in Kyoto, Japan on 11 December 1997 and came into existenceon 16 February 2005. Presently there are 192 countriesinvolved in this treaty (EEA 2012). The protocol first amendment period was started in 2008 and ended in 2012 and the Doha Amendment was agreed on 2012 in which 37 countries have set their targets (Fig. 5.4).

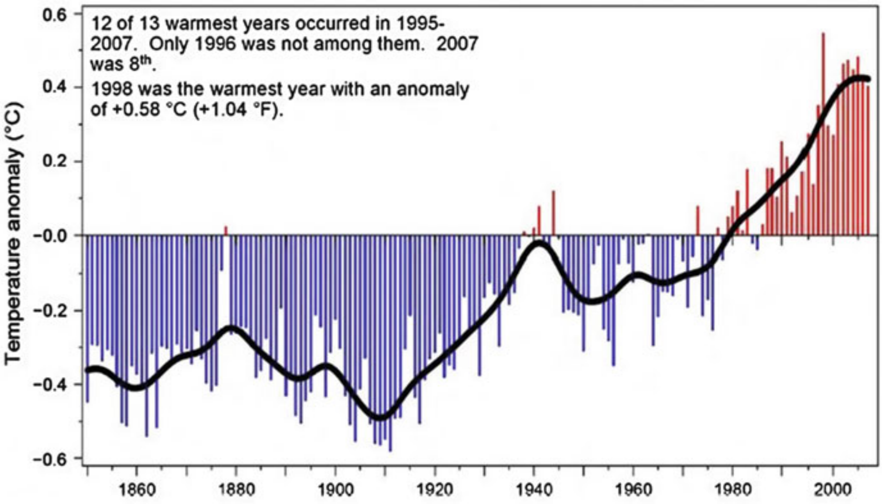

Fig. 5.3 Global temperature rise (Depicted by Calm (2008), based on Brohan et al. (2006), Rayner et al. (2006))

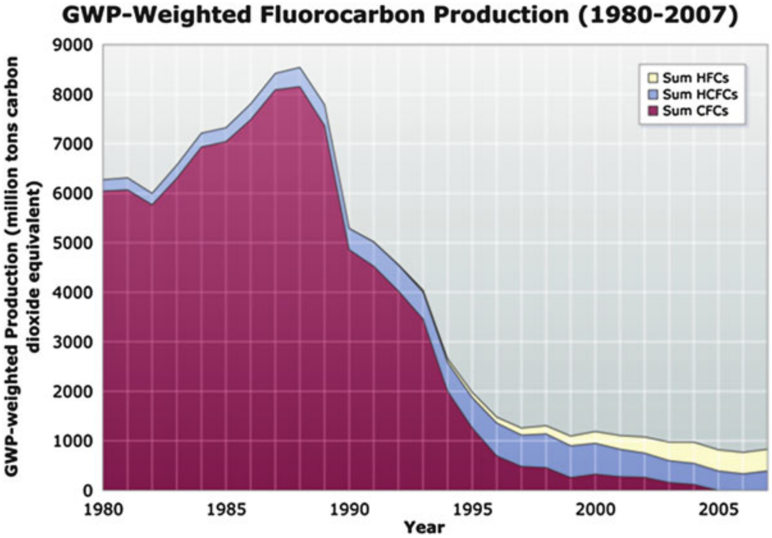

Fig. 5.4 GWP weighted Fluorocarbon Production

After the amendment of Kyoto Protocol the weighted production of CFCs, HCFCs & HFCs has decreased by 90% between the year 1988 and 2005 (Didier Coulomb).

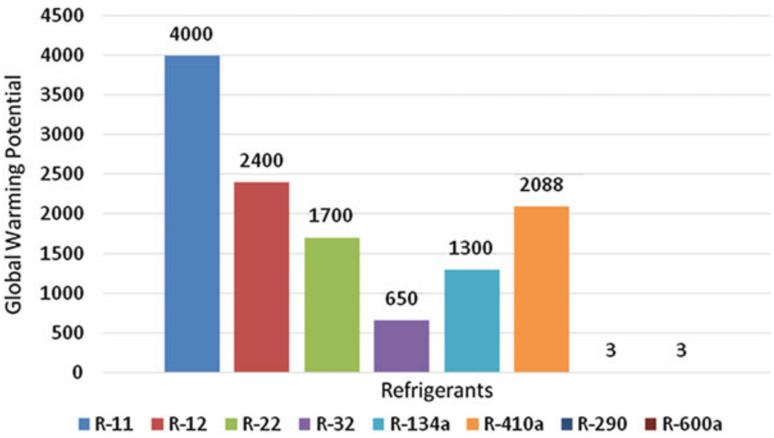

Fig. 5.5 Refrigerants with Global Warming Potential (ASHRAE standard)

Table 5.1 Refrigerants with ozone depletion potential (ASHRAE standard)

Refrigerant	Ozone depletion potential
R-11	1.0
R-12	1.0
R-22	0.05
R-32	00
R-134a	0
R-410a	0
R-290	0
R-600a	0

(iv) **Hydrocarbon**

HC or Hydrocarbons are the most environment-friendly refrigerants available in Indian market and have high-energy efficiency. They are “R-290” (Propane) and “R-600A” (Iso-Butane). Halogen molecules are completely absent in hydrocarbon so it have zero ozone depletion potential and are lowest in terms of global warming potential (James et al. 1997). They are the greenest refrigerants in the market but are highly flammable as they are hydrocarbons but manufacturers, who use these refrigerants, claim that they have taken good care in using these refrigerants and the appliances are absolutely safe but for the sake of safety of domestic refrigeration system a standard has been formed, IEC Technical Sheet TS 95006 in Europe and the approval of the refrigerator are done according to the procedure of TS since 1994 and is also transferred to an emendation to IEC/EN 60 335-2-24 (Danfoss 2000). In fact, most refrigerators in the Indian market are now on R-600A and there are no reported incidents of any accidents due to the same. So we can comfortably believe that they are safe (Fig. 5.5 and Table 5.1).

5.3 Effect of Air Conditioning on Human Health

It feels very comfortable in a cool room in the hot sunny day and to achieve this comfort a large number of population have installed air conditioners in their houses and over the last decade after a significant rise in temperatures people spending more and more time in an air conditioned environment not only in the offices but are also in their houses. This continuous use of air conditioners to achieve comfort causes more harm and health issues related with these systems and the quality of indoor air unfold more repeatedly (Yu et al. 2009).

Below are some of the health disorders which are caused by the prolonged use of air conditioners.

(i) Hypersensitivity pneumonitis

In the case of hypersensitivity pneumonitis, symptoms may develop 4–6 h including fever, chills, chest tightness, dyspnea, rash, malaise, cough, swelling and headache. The Symptoms of Hypersensitivity pneumonitis cured out when the presence of antigen is completely vanished in 12 h to several days (Sharma 2006). Banaszak et al in their study reported about hypersensitivity pneumonitis which found in 4 out of 27 workers of an office. A reduction in vital capacity is found in thespirometric tests of the affected workers and the cause is continuous exposure of thermophilic actinomycete to the air which is conditioned by the air conditioning system installed in their office (Banaszak et al. 1970).

(ii) Legionnaires' disease

Legionella bacteria is the main cause of this disease. The indication of Legionnaires' disease are high fever, muscle pains, headaches etc. Patient also suffers from diarrhea during this disease (CDC 2016). Lester et al. reported about Legionnaires' disease spread at an Atlanta, Georgia, country club, where golfers contracted the illness (Cordes et al. 1980). Tran Minh et al. reported about the same occurred in Pas-de-Calais, France, in November 2003–January 2004 and the Legionelia pneumophila was isolated by the cooling towers, waste water and covers a distance of 6 km from the plant (Nguyen et al. 2006). In August and September 1978 this disease was occurred in Memphis also (Dondero et al. 1980).

(iii) Skin Problems

Xerosis is caused by various factors such as use of diuretics, intrinsic changes in keratinization and lipid content, similar medications, and continuous use of heaters or air conditioners (White-Chu and Reddy 2011). In order to control the humidity of air in summer, air conditioners extract the moisture from the air and room become as dry as desert. Along with air AC also pulls out the moisture from the skin and the consequences of continuous reduction of moisture from the skin without any compensation of water in the skin tissues result in flaking and chapped skin and leaving it dry and stretched. Water is very essential for skin to maintain its elasticity. Facial skin is also very affected by this sudden change in temperature and all this hastens the ageing process.

(iv) **Sick Building Syndrome (SBS)**

Now a day's sick building syndrome is growing common issue (Redlich et al. 1997). Occupants who spent a large amount of time in the over air-conditioned building experience various problems related to comfort. Indication of the sick building syndrome is headache, dizziness, nausea, itching, problem of asthma and lack of concentration etc. (Hodgson 1999; Stolwijk 1991; Burge 2004). Finnegan et al. in his work study the random samples of the fully air conditioned and naturally ventilated offices and the outcome of his study was, the occupants of building having a problem of allergies of nasal and eye, headaches and lethargy are the symptoms associated with the sick building syndrome (Finnegan et al. 1984). According to World Health Organization, SBS appear in 30% of new or renovate buildings although 10 to 30% occupants of this building are affected by SBS (Lyles et al. 1994).

(v) **Heat Intolerance**

Spending more time in an air conditioned room makes human body intolerant with heat of outside at summer. It is very stress full for the body when we moves from coldair conditioned room to hot environment or from the hot environment to the cold room. This cause to the increasing death rate by hot waves in summer.

(vi) **Joint Pain**

For the arthritis joint pain air conditioning is one of the main factor. There are two types of arthritis patients Rheumatoid Arthritis Patients and Osteo Arthritis Patients those who are affected by the air conditioning. Direct circulation of cold air from Air conditioner increases Arthritis joint pain inflammation (Helen Aikman 1991). Air Conditioner controls humidity and temperature of the room. When AC pulls out the moisture from the room and there is no humidity in the room then the intensity of pain in joints increases and also the pressure of the room elevated by the air conditioner which increases arthritis joint pain. Air conditioning has more effect on rheumatoid arthritis, hence for the proper care of arthritis continuous use of air conditioner should be avoided.

(vii) **Diseases due to commercial air travel**

Infectious diseases caused by the commercial air travel are an important health issue (Mangili and Gendreau 2005). In mid-1990 many study have been done on transmission on tuberculosis in aircraft (Mangili and Gendreau 2005; Kenyon et al. 1996). Joel in his study reported about the spreading of Mycobacterium tuberculosis by an inefficient air conditioning system. The persons those who don't have direct contact with the patient have been infected due to the lack of high-efficiency filters (Ehrenkranz and Kicklighter 1972).

5.4 Conclusion

Air conditioner is now a basic need but also one side AC have many drawbacks on human health and global warming. After Montreal Protocol CFC were replaced by HCFC followed by HFC because of its zero Ozone Depletion Potential but still have high Global Warming Potential. In India still approximately 50% AC used HCFC. However after the treaty of Kyoto Protocol the production of Fluorocarbon has decreased but in order to achieve healthy global environment we must move towards the environment friendly refrigerants such as hydrocarbons because they have zero ODP and lowest in terms of GDP so it is necessary for manufacturer to take safety precaution while using hydrocarbon as refrigerant. A part from the global warming the continuous use of AC also have bad impact on health and become the cause of headache, muscles pain, skin problem and sick building syndrome etc.

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Chapter 6
Water Contamination by Organic-Pollutants: TiO_2 Photocatalysis

Khalid Umar

Abstract Water sources are polluted continuously by a variety of organic compounds (PPCPs, Pesticides drugs, dyes). This contaminated water should be purified before using it. Among various techniques for the removal of these pollutants AOPs proved a promising technique in which redox reaction occurs that leads the formation of degraded products. Various nanomaterials have been used for this purpose. Titanium dioxide is used extensively. But, due to band large band gap energy it worked only in UV region that consume more energy. For making Titanium dioxide suitable in visible region, the doping of metal/non metal can be done. This chapter reveals mechanism of TiO_2 as well the doped-TiO_2 particle, changing of properties after doping and generation of new energy bands in the particles and also few combination of doped TiO_2 in visible/UV region.

Keywords Co-doping • Dopants • Nanoparticles • Photocatalysis

6.1 Introduction

In recent years, the worldwide intensive use of organic compounds (Pharmaceutical and personal care products, industrial chemicals, surfactants, pesticides, and combustion products etc.) in various commercial fields as well as in daily life is the cause of contamination of soil water sources. These organic compounds, due to their chemical stability, resistant to biodegradation and with sufficient water solubility penetrate deep in both surface and ground water in different localities all over the world (Knee et al. 2010; EPA 1988; Székács et al. 2015). Textile dyes is another group of organic compounds, which have been used to color paper, plastic, natural and artificial fibers. During dyeing process, some amount of dye released as effluents, which poses a major problem to the environment (Khan et al. 2013; Holme 1984; Zollinger 1987; Umar et al. 2013). The water polluted by these

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M. Oves et al. (eds.), *Modern Age Environmental Problems and their Remediation*,
DOI 10.1007/978-3-319-64501-8_6

organic pollutants is not of any use, either for irrigation or for domestic purpose. The existence of these residues in large quantities in the environment has received great attention as new emerging contaminants. The conventional wastewater treatment methods (physical, chemical and biological) are unable to completely remove them because of complex nature and non-biodegradable character of these compounds (Daghrir et al. 2013). Therefore, destruction of these pollutants is essential before the water be used for any useful purposes.

There are several methods which have been used suggested by the researchers for the removal of these compounds from waste water such as biodegradation, coagulation, adsorption, filtration and treatment with ozone (Blake 2001). Among these methods, biodegradation has received the greatest attention. But all of these methods have some limitations. Therefore, development of an appropriate and economical method is necessary which can be utilized for the degradation of contaminated drinking, ground, surface and wastewater containing toxic or non-biodegradable compounds.

Advance oxidation processes employing heterogeneous catalysis have emerged as potential technology in the destruction of these organic pollutants. In heterogeneous catalysis, various types of photocatalyts have been used extensively during past few decades (Blake 2001; Umar et al. 2012a, b; Akpan and Hameed 2009). Among various semiconductors (ZnO, CdS, SnO_2 etc.), TiO_2 is one of the most efficient and widely used photocatalyst for the degradation of pollutants in aqueous suspension. The reason behind this superiority of TiO_2 is that it is chemically and biologically inert, photo-catalytically stable, relatively easy to produce and use, able to efficiently catalyse reactions, cheap and devoid of risks to human beings as well as to environment. It is pertinent to mention here that TiO_2 photocatalysts can only be excited by UV light due to its large band gap energy (3.2 eV) which is not suitable to catch visible light or sunlight for transition of electrons from valance band to conduction band. To overcome this problem, the research groups working in the area of photocatalysis are trying to extend the its optical property from UV region to visible region by doping it with metal or nonmetal into the TiO_2 lattice, co-doping, fabrication of nanocomposite with various materials, to utilize a large fraction of the solar spectrum and to realize the indoor applications of this photocatalyst (Umar et al. 2012a, b; Kanmani and Ramachandran 2012; Devi 2009; Fan et al. 2008; Zhang and Zhu 2012; Liu et al. 2009).

On the other hand, the particle size plays a critical role in altering the properties of materials. For example, a conventional insulator material converted into semiconductor by changing the particle size down to nano scale (Khan et al. 2014). During the past decades, a number of methods are being developed to synthesize these materials in nanoscale range. Among them metal oxide showed huge potential in bringing nanotechnolohgy to next level, as they are widely used various field such as catalysis, transistors, energy storage and conversion, biomedicine and sensors etc. (Fierro 2006; Chaudhuri and Paria 2012). The various methods used for doping of TiO_2 involve ion implantation, sol-gel reaction, chemical vapor deposition, sonochemical method, solvothermal and hydrothermal method, etc

(Akpan and Hameed 2009; Zhao et al. 2016; Srilakshmi et al. 2016; Chen and Mao 2007).

6.2 Mechanism of Photocatalysis

6.2.1 Mechanism of Photocatalysis Process (TiO_2 Particle)

The molecular orbital of semiconductor has a band structure. The bands in photocatalysis are valance band and vacant conduction band, which is commonly characterized by band gap energy. The semiconductor may be photoexited to form electron-donor site (reducing site) and electron-aceeptor sites (oxidizing sites) providing great scope for redox reaction. When semiconductor is illuminated with light of greater energy than that of the band gap, an electron is promoted from valance band to conduction band. Due to this promotion of electron, the generation of hole in valance band takes place as shown in Fig. 6.1.

If charge separation is maintained, the electron and hole migrate to the catalyst surface where they participate in redox reactions. Specially hole may react with surface-bound water molecules to produce hydroxyl radical (•OH) and electron is caught by oxygen to generate superoxide radical anion (O_2•$^-$) as illustrate in following Eqs. 6.1, 6.2 and 6.3;

$$TiO_2 + hv \rightarrow e^-_{cb} + h^+_{vb}. \tag{6.1}$$

$$O_2 + e^-_{cb} \rightarrow O_2^{\bullet -} \tag{6.2}$$

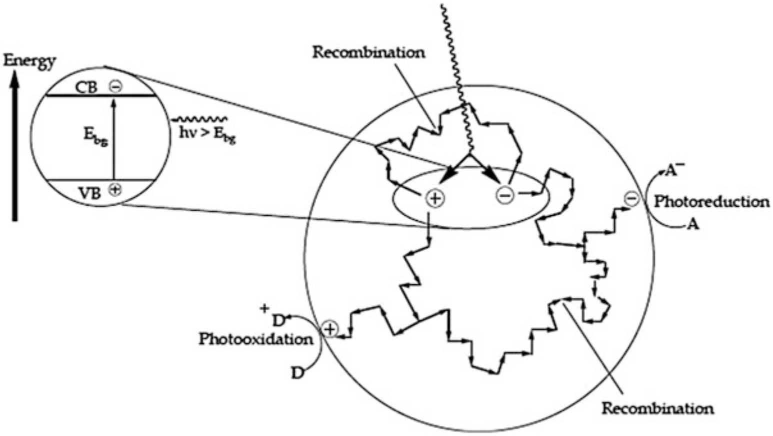


Fig. 6.1 Mechanism of photocatalysis (TiO_2) Haque et al. 2012

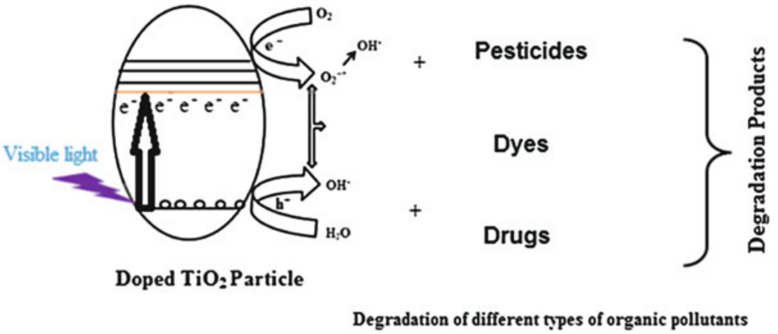


Fig. 6.2 Mechanism of photocatalysis (Doped TiO_2) Umar et al. 2016

$$H_2O + h^+_{vb} \rightarrow {}^{\bullet}OH + H^+ \tag{6.3}$$

It has been suggested that the hydroxyl and superoxide radical anion are the primary oxidizing species in photocatalytic oxidation processes.

6.2.2 *Mechanism of Photocatalysis Process (Doped TiO_2)*

The mechanism for the photocatalytic degradation of organic pollutants in the presence of metal doped TiO_2 could be envisaged as follows. As shown in Fig. 6.2, doping of TiO_2 with metal ion launches a new energy level in TiO_2 matrix which acts as an electron catcher (Ni et al. 2007). Due to catching of these electrons, the inhibition of electron-hole recombination takes place. This delay in recombination increases the lifetime of charge carriers. The doping of TiO_2 with dopants get better the separating efficiency electrons and holes which was induced by light, it also increases the visible light absorption due to shortening of band gap. This shortening of band gap is suitable for working in visible region.

6.3 Methods for TiO_2 Nanoparticle Synthesis

6.3.1 *Sonochemical Method*

Using ultrasound, a wide range of materials (alloys, oxides etc.) have been synthesized. There is no direct contact between molecular species and chemical effect of ultrasound but this chemistry starts from the formation of acoustic cavities. Due to collapse of these bubbles, high pressure and enormous heat etc are produced. The sonochemical method has been applied to synthesis TiO_2 nanomaterial by different research groups.

6.3.2 Hydrothermal Method

This type of synthesis is generally conducted in steel pressure vessels known as autoclaves. These hydrothermal reactions take place in presence of water under controlled temperature and/or pressure. The autoclave is designed with or with Teflon liners. The temperature can be increased above the boiling point of water so that the pressure of vapor saturation can be achieved. The internal pressure is entirely depends on the amount of added solution as well as on temperature. This process have been used for the synthesis of TiO_2 nano-particles, nano-tubes/nano-rods/nano-wires by many research groups successfully and generally applied in ceramic industry for the production of different articles.

6.3.3 Solvothermal Method

This method is almost similar to hydrothermal method except one variation, i.e. the solvent used in this process is nonaqueous. In this method, the reactions take place at high temperature as compared to hydrothermal process so high boiling point's solvents can be chosen. In terms of size, shape and crystallinity of TiO_2 paprticle, solvothermal process has normally better results that hydrothermal. These parameters are largely affected by the amount of surfactant/solvent weight ratio/starting material. It is also used to prepare nanoparticles/nanorods with or with adding surfactant.

6.3.4 Sol-Gel Method

For making a number of materials, a versatile process exist known as sol-gel method. In this process, inorganic metal salts/metal organic compounds usually used as starting material. Sol is formed by the hydrolysis and polymerization reactions of the starting material while the loss of solvent and complete polymerization lead to the formation of solid gel phase. Using this method, TiO_2 particle with different size/shape and highly crystalline in nature could be obtained.

6.3.5 Chemical Vapor Deposition

The deposition of material in vapor form takes place and solid phase is obtained in this method. This technique usually used for coating on materials. These coatings are responsible for the modification of their properties. In CVD Process, thermal energy is accountable for heating the gases in coating chamber where the deposition reaction occurred. It is used to synthesis fibres, composite materials etc.

6.3.6 Physical Vapor Deposition

There is no direct chemical reaction in this method. The evaporation of materials take place first and later solid material is obtained. The primary PVD methods are consist of laser vaporization, laser surface and thermal deposition processes. Nanowires are synthesized by this method more perfectly than other methods of synthesis.

6.4 Properties of Undoped/Doped TiO_2 Photocatalyst

6.4.1 Optical Property

Fig. 6.3 shows the absorption spectra of undoped/doped TiO_2 with different dopant concentration (Mn metal ion). The result from this figure shows that the absorption band shifts towards visible light region. The incorporation of dopants into TiO_2 lattice has been resulted to shift the fundamental absorption edge towards the longer wavelength known as red shift. Due to the red shift, a decreases in band gap energy occurred.

The transition between the d-electrons of the metal ion and the CB or VB of TiO_2 may responsible for this red shifting. The red shifting differs for different metal ions as well as the concentration of metal ions. In few studied, where the red shifting does not occur with the doping of metal ion, a new absorption band formation takes place.

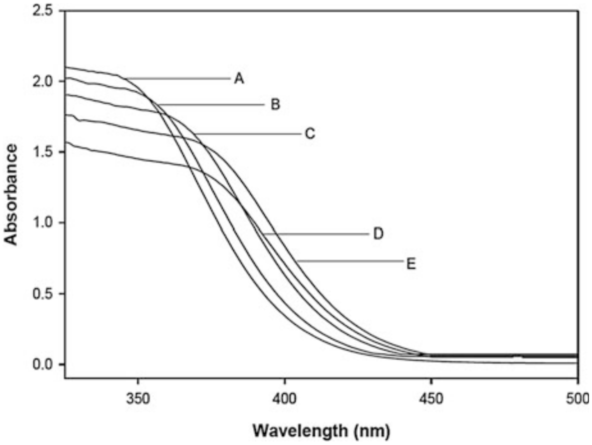
6.4.2 X-Ray Diffraction

Using this technique, the determination of crystal structure and the crystallinity can be done easily. The estimation of the crystal grain size according to the scherrer equation may also calculated by Debye Scherrer formula (Eq. 6.4)

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{6.4}$$

where, K = shape factor, D = Crystallite size, λ = wavelength, θ = diffraction angle, β = Full width at half maximum.

Fig. 6.3 Absorption spectra of Mn-doped TiO_2 ((*A*) Undoped TiO_2, (*B*)–(*E*) 0.25% Mn-doped-1.0% Mn-doped TiO_2 respectively)



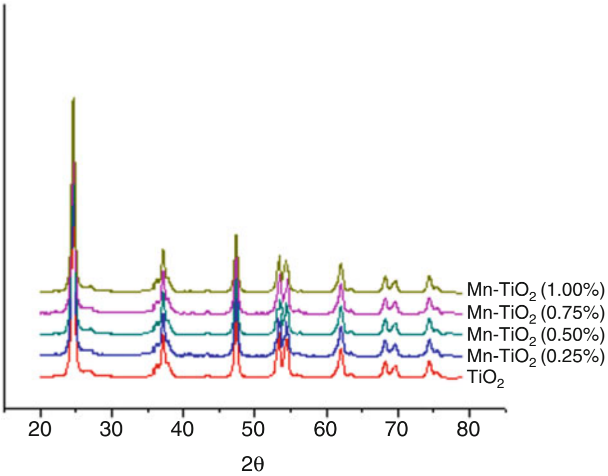


Fig. 6.4 XRD patterns of Mn-doped TiO_2

The periodicity of the cryatallite areas highlights the diffraction of X-ray beam, resultant in a tall narrow peak. A broader peak will be obtained if the crystals have low degree of periodicity or they are randomly arranged. The diffraction peak is also related to the size of the nanomaterials, as the nanoparticle size increased, the diffraction peaks became narrower.

The XRD patterns of undoped/doped TiO_2 with different concentration of Mn are shown in Fig. 6.4. The partial crystalline nature and anatase phase can be seen in figure. There are two ways for dopant firstly, it can enter into the TiO_2 lattice either interstitially and secondly it can act as substitutional impurity. The properties of dopants such as (electronegativity, relative valency etc.) decides substitution. In the present example, if the ionic radii of Mn^{2+} (0.080 nm) and Ti^{4+} (0.068 nm) are considered, the radius of metal ion is bigger than Ti. Therefore, it will not enter into lattice of TiO_2 but it may be present on the surface layer.

6.5 Synthesis of Doped TiO_2 Nanomaterials

6.5.1 Metal-Doped TiO_2 Nanomaterials

In literature, TiO_2 materials have been doped with different metals (Yildizhan et al. 2016; Waseem et al. 2016; Wang et al. 2015; Pongwan et al. 2016; Momeni and Ghayeb 2016). There are few general methods for the preparation of doped TiO_2, i.e. wet chemistry, ion implantation and high temperature treatment on TiO_2 nanomaterials. Li et. al. produced Fe-doped TiO_2 with particle size of 09–13 nm using hydrothermal process (Li et al. 2008) while Devi et. al. synthesized Mn-doped TiO_2 by sol-gel method (Devi et al. 2009a, b). Mo-doped TiO_2 has been synthesized using thermal hydrolysis (Stengl and Bakardjieva 2010) and sol-gel method (Devi and Murthy 2008). In another study, the modified sol-gel process has been implementing for the synthesis of Mn-doped TiO_2 (Papadimitriou et al. 2011). On the other hand, synthesis of La-doped TiO_2 using different methods (Jin et al. 2008; Cheng et al. 2013; Stengl et al. 2009; Raza et al. 2015) has been reported in the literature. The synthesis of La-doped TiO_2 reported by Li et. al. and demonstrated that the doping of lanthanum could hinders the phase transformation and inhibits the crystallite size of TiO_2 particle (Lin et al. 2013). Choi et al. doped with 21 metal ions by sol-gel method. This study show that the introduction of these metal ions dopants significantly affect the activity of photocatalyst. The charge carriers recombination and interfacial electron transfer rate also influenced by these doping (Babu et al. 2015). The doping of different metal ions such as V, Ce, W, Zr, Fe and Cu by different methods have been reported in literature (Inturi et al. 2014; Liu et al. 2013). Bessekhouad et al. studied the doping of alkaline metals, which was prepared by sol-gel technology (Yildizhan et al. 2016).

Using Sol-gel method, the synthesis of Cu doped TiO_2 nanoparticles, (Yang et al. 2015a, b) (Cr, V, Fe, Co)-doped TiO_2 by CVD and Fe-doped TiO_2 nanoparticle by oxidative pyrolysis (Wang et al. 2005) conducted respectively by different researchers.

The results of the above study showed that for making the charge carrier photocatalyst ideal to visible light, the selection of doping of metal ions into titania matrix has been proven to be an efficient route. At lower pH, all three types of TiO_2 coexisted. The delay in recombination of charges is responsible for the working of photocatalyst under visible light (Patel et al. 2015; Pelaez et al. 2012; Yu et al. 2009a, b; Bouras et al. 2007; Bharti et al. 2016). The doping with a transition metal ion increases the formation of Ti^{3+} ions, leading to the enhancement in the photocatlytic activity (Siddhapara and Shah 2014).

6.5.2 Non-metal Doped TiO_2 Nano-materials

Non metal ion doping is a promising way to improve thermal stability of the TiO_2 material. Various non-metal elements, such as Carbon, Nitrogen, Boron, Fluorine, Sulphur etc have been successfully doped into TiO_2 nanomaterials. For instance, the synthesis of nitrogen doping in TiO_2 lattice prepared by the solvothermal route showed violet color. On calcination for some time in air at high temperature the powder changes to different colors but not in white color. This shows the thermal stability of titanium and nitrogen bonding in TiO_2 powders (Nolan et al. 2012). For the first time, Khan et al. reported that on incorporation of carbon the band gap reduces from 3.0 to 2.32 eV and also splitting of water (Shaban and Khan 2010). There are different processes such as heating, annealing (high temperature) or direct burning of Ti metal sheet by which the C-doped TiO_2 nano material was obtained (Goriparti et al. 2015; Yang et al. 2015a, b; Lu et al. 2012). The hydrolysis of TTIP in a water/amine mixture and the post treatment of the TiO_2 sol with amine lead the synthesis of Nitrogen-doped TiO_2 nano materials (Ansari et al. 2016; Asahi et al. 2014; Cheng et al. 2012). Nitrogen-doped TiO_2 can also be obtained directly from a Ti-bipyridine complex, by ball milling of TiO_2 in a ammonia/water solution (Asahi et al. 2014). N-doped TiO_2 nanomaterials were also obtained by different reaction condition, using different precursors, various methods and at different calcinations temperature (Bakar et al. 2016; Polo et al. 2014; Zhang et al. 2013). Sulphur-doped TiO_2 nano material were synthesized by different techniques and using different precursors (Yu et al. 2009a, b; Xianzhong et al. 2015). F-doped TiO_2 nano-material were prepared by heating TiO_2 under hydrogen fluoride (Dozzi et al. 2013).

6.5.3 Co-Doped TiO_2 Nanomaterials

The addition of two or more heteroatom (metal/Nonmetal) to the TiO_2 particle has been also reported in literature (Shi et al. 2007; Shi 2009; Xu 2008). Co-doping of metal/nonmetal has proven more significant as compared to their single ion doped (Ling et al. 2008; He et al. 2008; Tan et al. 2010).

Some studies on co-doping of TiO_2 (silver and Indium oxide co-doped, Sulphur, Indium co-doped, N-F Co-doped) with enhanced photocatalytic activity have been reported in literature (Yang et al. 2008; Yu et al. 2010; Li et al. 2005). Due to co-doping of metals/non-metals to TiO_2 alters the charge carrier transfer recombination. The combination of one dopant with another dopant has been proposed to enable a reduction in the number of carrier recombination centers and also enhance the absorbance of visible light by increasing the maximum solubility of dopants (Shi et al. 2007; Shi 2009; Xu 2008). Shi et. al. reported that in co-doped composite Fe-Ho-TiO_2, ferric ions enhanced the photocatalytic activity of TiO_2. On the other hand, Ho^{3+} doping is responsible for the increase of grain growth and reducing the recombination charge carriers. As a result, the faster degradation of methyl orange as compared with single ion doping or undoped TiO_2 under UV light takes place (Shi 2009; Xu et al. 2008).

6.6 Application of TiO_2 in Photocatalysis Process

The different class of organic pollutants (Pesticides, Dyes, Drugs) photodegraded by researchers in different conditions (Visible/UV-light, doped/undoped, doped with metal/non-metal etc.) are shown below in Table 6.1.

The results of these studies clearly indicate that doped-TiO_2 can efficiently catalyse the photodegradation of the organic pollutants. Table also shows that the performance of doped-TiO_2 photocatalyst in presence of UV light is better than the doped-TiO_2 photocatalyst in the presence of visible light. Secondly, co-doping has also proven a promising method to get better degradation efficiency in the photocatalysis process because in most of studies codoped TiO_2 worked more efficiently than single doping in presence of visible or sunlight.

Table 6.1 The degradation efficiency of different nano-doped-TiO_2 using the photocatalytic degradation process in presence of UV/Visible/sunlight on various organic pollutants

Types of dopant (TiO_2)	Destroyed organic pollutants	Light source	Degradation efficiency (%)	References
Fe	Methyl Orange	UV	99.7	Deng et al. (2009)
Fe	Phenol	Visible	20	Ambrus (2008)
Ce	Rhodamine B	UV	90	Bettinelli et al. (2007)
Fe	Methylene Blue	UV	72	Li et al. (2008)
Mo	Acid Red 88	Visible	77	Umar et al. (2013)
Sn	Orange-G	UV	99.1	Sun et al. (2006)
P	Rhodamine B	Sunlight	93	Lv et al. (2009)
Ag	Crystal violet	UV	100	Sahoo et al. (2005)
Mn	Gentian violet	Visible	84	Umar et al. (2013)
Ba	4-Chlorophenol	UV	100	Venkatachalam et al. (2007)
W	Dodecyl benzenesulfonate	Visible	98	Setiawati and Kawano (2008)
Sm, N	Salicyclic acid	Visible	67	Wei et al. (2008)
La	Ramazol Brilliant Blue	Visible	72	Umar et al. (2013)
N, S	Formaldehyde	Sunlight	65	Yu et al. (2006)
S, I	Methylene Blue	Visible	90	Yu et al. (2010)
Cu	Methylene orange	Visible	100	Hamadanian et al. (2010)
Mn	Glyphosate	Visible	80	Umar et al. (2016)
Mn	Methylene Blue	Visible	75	Umar et al. (2015)

6.7 Conclusion

The detailed study of Doped-TiO_2 nanomaterials as photocatalyst in this chapter indicates that a number of efforts put into TiO_2 nanomaterials for the modification in properties (photocatalysis). The results of these studies also clearly indicate that these nano-photocatalyst are capable in the removal organic pollutants from water in presence of UV light as well in visible light upto a good level. Secondly, codoping has also proven a promising method to get better degradation efficiency in the photocatalysis process because in most of studies codoped TiO_2 worked more efficiently than single doping in presence of visible or sunlight. Further studies are needed to increase the degradation efficiency of doped TiO_2 photocatalyt especially in the presence of visible or sunlight by which conservation of energy sources occurs. It has also been observed that all the papers describe the photocatalytic activities of these doped materials with quite good results, but no one at large scale, which is required urgently.

Acknowledgements The author gratefully acknowledged the postdoctoral financial support by the Research University Grant, Universiti Teknologi Malaysia and the Ministry of Education Malaysia for providing LRGS Grant on Water Security entitled Protection of Drinking Water: Source Abstraction and Treatment (203/PKT/6720006).

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Chapter 7
Bioelectrochemical Systems for Transforming Waste to Energy

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Abstract In recent years, BES has emerged as a new and promising approach for wastewater treatment. BES use microorganisms to convert chemical energy to electric energy and other value added chemicals. Compared to the conventional techniques available, it has evolved as a low energy intensive technology with an approach of integrated management of wastewater and recovering energy. This chapter presents a review on the different types of BESs with a brief discussion of their principle and anodic and cathodic reactions involved. Further, an overview is presented of recent work with different types of wastewater used as substrate, utilising different donors and acceptors of electrons involved and the various kind of electrodes used in various BES setups. BES is still a relevantly new and emerging field that deals with harnessing energy from wastewater with the potential to change the wastewater remediation techniques in future with gross positive energy recovery.

Keywords Bioelectrochemical system • Desalination • Energy generation • Wastewater remediation

Nomenclature

AEM	Anion Exchange Membrane
BES	Bioelectrochemical System
CEM	Cation Exchange Membrane
DCMEC	Dual chambered Microbial Electrolysis Cell
DCMFC	Dual Chambered Microbial Fuel Cell
IEM	Ion Exchange Membrane
MFC	Microbial Fuel Cell
MEC	Microbial Electrolysis Cell

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M. Oves et al. (eds.), *Modern Age Environmental Problems and their Remediation*,
DOI 10.1007/978-3-319-64501-8_7

MDC	Microbial Desalination Cell
MSC	Microbial Solar Cell
PEM	Proton Exchange Membrane
PMFC	Plant Microbial Fuel Cell
SCMEC	Single Chambered Microbial Electrolysis Cell
SCMFC	Single Chambered Microbial Fuel Cell
TEA	Terminal Electron Acceptor

7.1 Introduction

Rapid industrialization and urbanization of the world has increased concerns for more energy demand, clean water supply and fresh and healthy environment for the better sustenance. The maximum portion of this energy comes from the non-renewable sources (e.g. fossil fuels) but the ever decreasing supply and increasing cost of fossil fuels has rendered researchers thinking lately of developing and discovering the sources of energy that are ever sustaining and are not going to end. These sources are the non-renewable sources like sun, water, wind and geothermal energy. The depleting fossil fuel however, is not the only concern. Global warming is also growing as a concern as the climate is changing abruptly that may be damaging to humans and other living forms alike. According to NASA, the global surface temperature has risen dramatically since year 2000 with year 2016 recorded as the warmest year (NASA 2016).

The increasing population and advancement in the lifestyle has lead to an increased development of different types of waste like industrial waste, municipal waste, agricultural and dairy waste. The conventional chemical methods of wastewater treatment such as ozonolysis serve the purpose but are cost intensive and not stable (Robinson et al. 2001). Other methods like chlorination tends to add an additional requirement of removing chlorine before disposing water into water bodies as chlorine affects the aquatic life. The traditional biological methods of water treatment like activated sludge process leads to a lot of sludge production (Wei et al. 2003), disposal of which is again a great issue.

With the rapid development of various sectors and increasing population, the demand for fresh water has increased tremendously. Even though the Earth is 75% water, most of it is saline and unfit for drinking and only 1% is available as fresh water. Most of this fresh water is trapped as glaciers and snowfields. It is estimated that by 2025, the population as high as around 1.8 billion people will be living in water-scarce areas with around 67% of the world’s population living in water-stressed regions as a result of excessive usage, over population, and climate change (FAO-WATER 2017). To tackle this global menace, different methods are being employed like wastewater recycling, desalination. However, these methods are highly energy intensive (Al-Karaghouli and Kazmerski 2013). Thus, there is a high need for the development of methods that not only produce fresh water but uses lower energy expenses.

Energy is the driving force of the future global economy. To lift the world out of poverty, enormous energy is required to fulfill the need of the growing population. According to EIA, the energy consumption of the world is expected to increase by 48% by the year 2040 (U.S. Energy Information Administration 2016). To match the need of energy production and also making it more sustainable and environmental friendly, the renewable sources can serve as a better alternative to the non-renewable sources. In recent years, the method of producing energy from waste electrochemically is gaining a lot of focus from the researchers around the world. The electrochemically produced energy can not only alleviates the global energy crisis but at the same time help reducing pollution by treating waste. Unlike the traditional method of water treatment, bioelectrochemical systems (BESs) treats the wastewater with no or minimal expense of energy with the help of microbes.

7.2 What Is BES?

BES is a technology that combines the biological and electrochemical processes for waste remediation and side by side generation of value added products like electricity, hydrogen and other useful chemicals (Pant et al. 2012).

The basic principle of BES is the reduction of electron donor at anode by electrochemically active microbes, transferring the generated electrons from anode to cathode thereby generating electrical current (Harnisch and Schröder 2010). The output power efficiency of the BES depends upon the number of electrons recovered and transferred to anode.

7.3 Types of BES

BES is a combination of different types of technologies that involve the same basic principle of waste remediation with the help of microbes. But, the output of different BES technologies can be different. There are four major types of BESs namely Microbial Fuel Cell (MFC) wherein the final product is electricity from wastewater, Microbial Electrolysis Cell (MEC) wherein hydrogen is mainly generated at cathode, Microbial Desalination Cell (MDC) where desalination of saline water can be effectively performed, Microbial Solar Cell (MSC) where solar energy is utilised to produce electricity.

7.3.1 Microbial Fuel Cell (MFC)

MFC is a type of BES (Fig. 7.1) where microorganisms catalyse the oxidation of electron donors anaerobically at anode producing electrons and protons. These

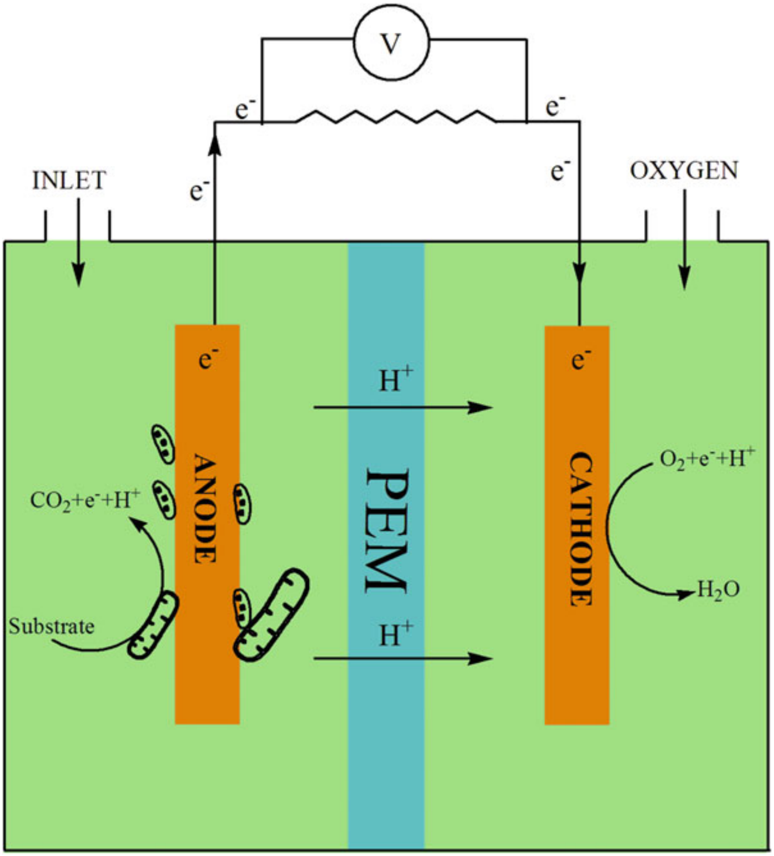

Fig. 7.1 Microbial Fuel Cell (MFC)

electrons flow across the external circuit reaching cathode and thus producing electric current. The electron acceptors in turn accept these electrons at the cathode (Logan et al. 2006; Khan et al. 2017). It has potential to substitute fossil fuels for generating electricity.

7.3.1.1 Components and Configuration of MFC

The main components of MFC include an anaerobic anodic compartment, an aerobic cathodic compartment, electrodes and a proton exchange membrane (PEM) separating the electrodes connected through an external circuit. The materials used as anode and cathode vary widely from graphite rods (Khan et al. 2015), carbon cloths (Elmekawy et al. 2014) to MWCNTs (Mehdinia et al. 2014), and other polymeric electrodes (Yong et al. 2012). However, carbon-based electrodes are most common. The most commonly used PEMs are NAFION, ULTREX and ZIRFON (Elmekawy et al. 2014; Khan et al. 2015).

There are two main configurations of MFC viz. Single Chambered Microbial Fuel Cell (SCMFC) and Dual Chambered Microbial Fuel Cell (DCMFC).

SCMFC

In a SCMFC, anode is contained in an anaerobic compartment and cathode is directly in contact with the air either with or without a PEM. The anaerobic microbes release electrons and protons as they oxidise the substrate in the anodic chamber. The flow of these electrons through the circuit generates current.

DCMFC

DCMFC consists of an anaerobic chamber for oxidation of the substrate and an aerobic chamber where reduction of electron acceptors takes place. PEM separates the two chambers. Microbes oxidise the substrate at anode releasing electrons and protons. The movement of these released electrons across the circuit generates current. The charge balance is maintained by protons diffusing through PEM to cathode where they are accepted by terminal electron acceptors (TEA) like ferricyanide (Rabaey et al. 2005). DCMFC has the advantage of simultaneous treatment of two different waste streams (ter Heijne et al. 2010).

7.3.1.2 Different Types of Anolyte and Catholyte in MFC

Various types of substrates can be utilised in MFC both as anolyte and catholyte. Anolyte may vary from glucose (Khater et al. 2015), acetate (Liu et al. 2005), cellulose (Rezaei et al. 2009), to phenol (Luo et al. 2009), synthetic and real wastewater (Elmekawy et al. 2014). However only oxygen can act as catholyte in case of SCMFC but in case of DCMFC, many different types of electron acceptors can be utilised as catholyte like copper (ter Heijne et al. 2010), chromium (Tandukar et al. 2009; Gupta et al. 2017), dyes (Han et al. 2015) and sulphate (Zhao et al. 2008) etc.

7.3.1.3 Anodic and Cathodic Mechanism Involved in MFC

Since MFC is a BES, its mechanism simply involves redox reaction taking place at anode and cathode. Microorganisms under anaerobic conditions provided in the anodic chamber of both single and dual chambered MFC catalyse the reduction of substrate added to release electrons and protons. This can be represented as:

$$\boldsymbol{substrate} \xrightarrow{\boldsymbol{microorganisms}} \boldsymbol{CO_2 + electrons + proton} \tag{7.1}$$

E.g. If acetate is present as electron donor,

$$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^- \tag{7.2}$$

At cathode, reduction of oxygen or TEA takes place. This can be represented as:

$$\boldsymbol{terminal\ acceptor + protons \xrightarrow{electrons} reduced\ form + water} \tag{7.3}$$

E.g. If oxygen is TEA:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{7.4}$$

If ferricyanide is taken as TEA:

$$Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-} \tag{7.5}$$

7.3.2 Microbial Electrolysis Cell (MEC)

Hydrogen is considered as a source of green energy with zero pollution. Hydrogen is basically obtained by three main methods: from fossil fuels by thermochemical processes, by water electrolysis and by biological process like dark fermentation. However the energy recovery from dark fermentation is rather low while the other two processes are costly. MEC is considered an advanced version of MFC and can serve as an alternative to cleaner hydrogen production.

MEC (Fig. 7.2) can be defined as a technique that utilises wastewater and produce hydrogen by the catalytic action of microorganisms in the presence of external power and fully anoxic conditions. The microbes oxidise the substrate at anode releasing protons which undergo reduction to release hydrogen at cathode. Cucu et al. suggested there can be two modes of hydrogen production in MEC by either applying negative polarisation on anoxic cathode or by applying negative polarisation on microbial biofilm at anode (Cucu et al. 2013). An external voltage of over 0.14 V is ideally required for hydrogen production (Rozendal et al. 2006).

7.3.2.1 Composition and Configuration of MEC

MEC, just like MFC is composed of two chambers but unlike MFC, here both chambers are maintained under anaerobic conditions. It also contains an anode, a cathode, a PEM separating the two chambers. The electrodes used can be graphite felt (Escapa et al. 2012b), graphite granules (Batlle-Vilanovaa et al. 2014), graphite brushes (Cheng and Logan 2011) beside many others.

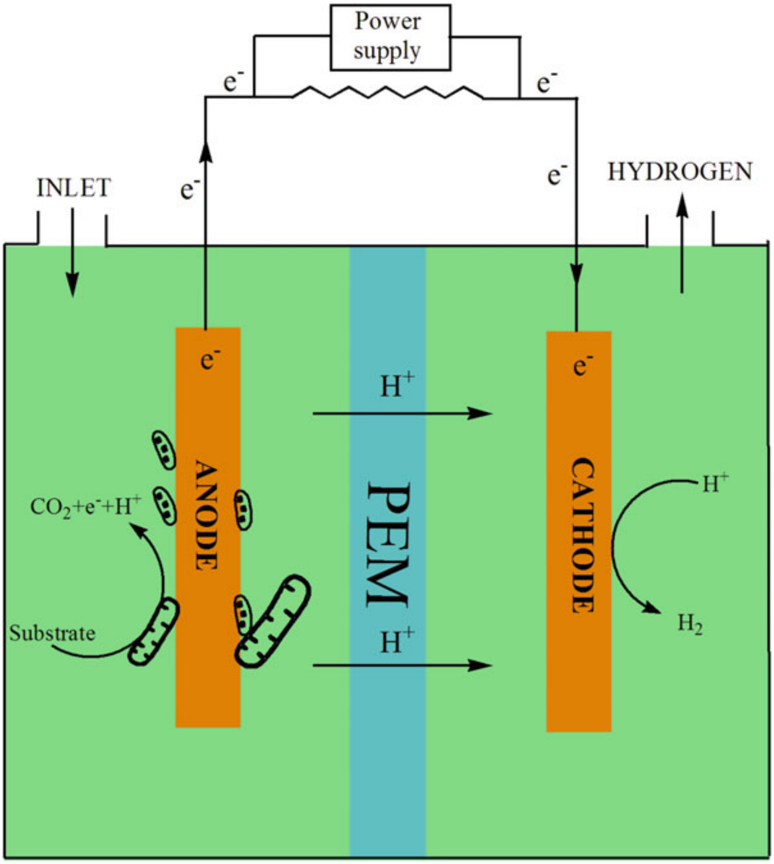

Fig. 7.2 Microbial Electrolysis Cell (MEC)

Just like MFC, the two main configurations of MEC are:

SCMEC

In this type of setup, a single chamber lacking a membrane encloses both anode and cathode under anaerobic conditions. The microbes act on substrate producing protons and electrons at anode. These generated protons are reduced to hydrogen at cathode by the application of external potential over it.

DCMEC

DCMEC is composed of separate anodic and cathodic chambers connected through PEM, both under the anaerobic conditions. The microbes in the anodic chamber act on substrate librating electron and protons at anode. The released protons are diffused to cathodic chamber via PEM and electrons through external circuit where protons get reduced to hydrogen.

Both SCMEC and DCMEC can utilise variety of substrate to produce hydrogen but SCMEC is considered more economical for high hydrogen production rates as suggested by Call and Logan (Call and Logan 2008).

7.3.2.2 Different Types of Anolyte and Catholyte in MEC

Variety of substrates can be utilised in MEC as anolyte like acetate (Cheng and Logan 2011), glycerol (Escapa et al. 2009), domestic wastewater (Escapa et al. 2012b) etc. Unlike MFC, MEC contains anaerobic cathode where catholyte can be abiotic with only hydrogen being produced by reduction of proton in the presence of metal catalyst like platinum on cathode or it can be biotic where substrate like sulphate (Luo et al. 2014a), sodium bicarbonate (Jeremiasse et al. 2010) and metal ions like Cd (II) (Chen et al. 2016) can be reduced along with hydrogen production.

7.3.2.3 Anodic and Cathodic Mechanism Taking Place in MEC

At anode, oxidation of electron donor takes place. This step is similar as MFC.

$$\boldsymbol{substrate \xrightarrow{microorganisms} CO_2 + electrons + protons} \tag{7.6}$$

E.g. If acetate is present as electron donor:

$$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^- \tag{7.7}$$

At cathode, under anoxic conditions reduction of protons generated at anode takes place.

$$\boldsymbol{protons \xrightarrow{electrons} Hydrogen} \tag{7.8}$$

$$\mathrm{H}^+ + \mathrm{e}^- \rightarrow \frac{1}{2}H_2 \tag{7.9}$$

7.3.3 *Microbial Desalination Cell (MDC)*

With the growing population and industrialisation, the demand for fresh water has increased drastically and this calls for the need to desalinate the sea water or brackish water. The techniques available for desalination e.g. reverse osmosis, electrodialysis and distillation are highly energy exhaustive. A new method has evolved from the so called BESs, which is popularly known as Microbial Desalination Cell (MDC) as shown in Fig. 7.3.

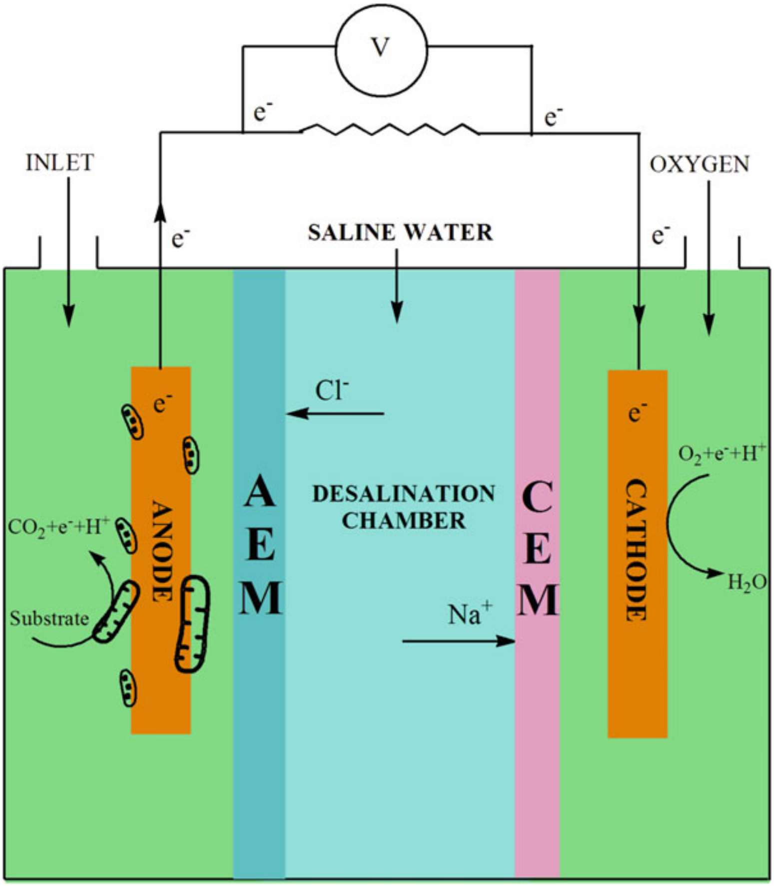

Fig. 7.3 Microbial Desalination Cell (MDC)

MDC is a modification of MFC. It is an electrochemical technique of desalination where microbes act on the organic matter generating electric potential which drives the ion transport through ion exchange membranes (IEMs) thereby removing dissolved salts present in saline water (Cao et al. 2009).

MDC involves the basic principle of creating across the electrodes a sufficient electric gradient. This gradient drives the anions towards anode and cations towards cathode thus desalinating the water in the middle chamber (Kim and Logan 2013). MDC serves three main goals viz decomposition of organic waste, energy generation and desalination.

7.3.3.1 Components and Configuration of MDC

Since MDC is the modification of MFC, the basic components are similar consisting of anodic and cathodic chambers. The cathodic chamber can be kept under both anaerobic and aerobic conditions thereby reducing either protons to release hydrogen gas at cathode or oxygen to form water. It also contains anode, cathode, anion exchange membrane (AEM) and cation exchange membrane (CEM) (Cao et al. 2009).

The two basic configurations of MDC are three chambered MDC and Stacked MDC.

3-CHAMBERED MDC

This is the most basic configuration of MDC first designed by Cao and coworkers in the year 2009 (Cao et al. 2009). It consists of three separate chambers linked together through IEMs. The three chambers are anodic chamber, cathodic chamber and a middle desalinating chamber. On the anodic side, AEM separates the middle chamber while the middle and the cathodic chamber are connected through the CEM. As the electric potential is generated between anodic and cathodic chamber the desalination of the saline water in the middle chamber takes place (Brastad and He 2013).

STACKED MDC

Stacked MDC also consist of separate anodic and cathodic compartment linked through a series of IEM pairs forming multiple cell pairs with concentrate and desalinates chambers. As the number of IEMs increases, the magnitude of filtration also increases. However, the system's internal resistance is also increased. Therefore it is necessary to monitor the resistance and apply the appropriate number of membrane to improve the performance of the system (Chen et al. 2011).

7.3.3.2 Anodic and Cathodic Mechanism Taking Place in MDC

At anode, oxidation of organic substrate takes place

$$\boldsymbol{substrate \xrightarrow{microorganisms} CO_2 + electrons + protons} \tag{7.10}$$

The most common substrate taken in MDC is acetate

$$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^- \tag{7.11}$$

At cathode, reduction of either oxygen or proton takes place to form water or hydrogen

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{7.12}$$

$$H^+ + e^- \rightarrow \frac{1}{2} H_2 \tag{7.13}$$

In middle chamber, the ions present in the saline water move towards anode and cathode under the effect of electric potential gradient. As the electrons and protons are generated at anode, AEM prevents the positively charged species from escaping the anodic chamber causing the negative charge carriers from the middle chamber to move into the anodic chamber to maintain the charge balance. At the same time the consumption of protons in the cathodic chamber lead to the movement of positive ions towards the cathodic chamber thereby causing desalination in the middle chamber.

7.3.4 Microbial Solar Cell (MSC)

MSC (Fig. 7.4) is a collection of biotechnologies that integrates the photosynthetic and electrochemical activity of microbes to harvest electricity directly from solar

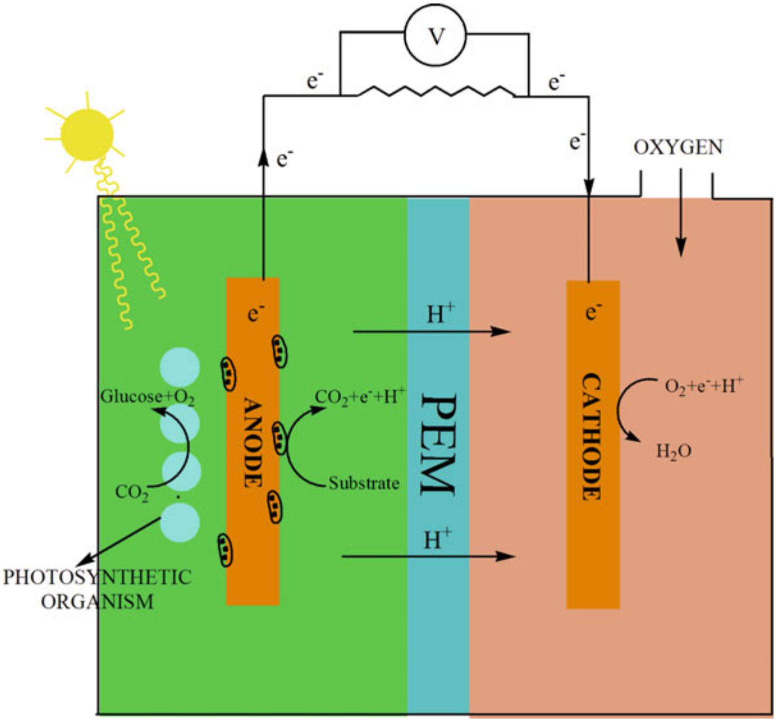

Fig. 7.4 Microbial Solar Cell (MSC)

energy. The technology establishes a synergic relationship between photosynthetic organisms and electrochemically active microbes (Kadier et al. 2016).

MSC works on the basic principle of oxidation of organic substrate transferred to anode that is produced by photosynthesis and thus producing electricity by flow of electrons to the cathode for the reduction of electron acceptor usually oxygen (Strik et al. 2011)

7.3.4.1 Component and Configuration of MSC

The basic components of MSC are same as MFC composing of an anode, a cathode and an IEM. However, MSC are different from typical MFC in the involvement of photosynthetic organisms either at anode or cathode.

The organisms involved in the fixing solar energy into electricity are higher plants, photosynthetic bacteria and algae on basis of which MSC can be divided into 3 categories of plant MSC, algal MSC, MSC with phototrophic biofilm.

Plant MFC
PMFC is the most commonly investigated MSC. In PMFC, plants perform photosynthesis to synthesis organic matter that is excreted by the roots of the plants in form of rhizodepositions onto the anode where exoelectrogens oxidise the matter to release electrons thereby generating electricity (Timmers et al. 2010). The proof of concept for PMFC was demonstrated by Striks and co-workers in 2008 (Strik et al. 2008a).

Algal MSC
Algal MSC is a growing field of harvesting energy from algae either by growing algae in the anodic chamber and allowing the exoelectrogenic oxidation of the organic matter synthesised (Xu et al. 2015) or by utilising the photosynthetic nature of algae to produce oxygen insitu for reduction at cathode (Kakarla and Min 2014). The biomass produced can either be directly fed as substrate in the anode of MFC or it can be utilized to synthesise other value added products (Gouveia et al. 2014). Cui et al. fed anode with dead algae and grew live algae at cathode and harvested current (Cui et al. 2014). A photosynthetic algal MFC was developed by Strik et al. by integrating photobioreactor with the anode of MFC to derive electricity by the direct feeding of living algae (Strik et al. 2008b).

MSC with Phototrophic Biofilm
An autotrophic biofilm can be generated at anode to fix solar energy into substrate that can be further oxidised to release electrons leading to the flow of electric current (Pisciotta et al. 2010).

7.3.4.2 Anodic and Cathodic Mechanism Taking Place in MSC

(a) when photosynthetic organisms are present in the anodic chamber

(i) solar energy fixed to form organic substrate

$$\boldsymbol{Carbon\ dioxide + water \xrightarrow{sunlight} organic\ substrate + oxygen} \tag{7.14}$$

e.g.

$$CO_2 + H_2O \xrightarrow{sunlight} CH_2O + O_2 \tag{7.15}$$

(ii) At anode,

$$\boldsymbol{substrate \xrightarrow{microorganisms} CO_2 + electrons + protons} \tag{7.16}$$

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^- \tag{7.17}$$

(iii) At cathode

$$\boldsymbol{terminal\ acceptor + protons \xrightarrow{electrons} reduced\ form + water} \tag{7.18}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{7.19}$$

(b) when photosynthetic organisms are present in the cathodic chamber

(i) At anode,

$$\boldsymbol{substrate \xrightarrow{microorganisms} CO_2 + electrons + protons} \tag{7.20}$$

e.g. If acetate is present as electron donor:

$$CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^- \tag{7.21}$$

At cathode, algae consume carbon dioxide to produce organic matter and oxygen. The organic matter can be further utilised to produce value added products while oxygen is utilised as TEA.

$$CO_2 + H_2O \xrightarrow{algae} biomass + O_2 \tag{7.22}$$

$$\boldsymbol{terminal\ acceptor + protons \xrightarrow{electrons} reduced\ form + water} \tag{7.23}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{7.24}$$

Table 7.1 presents the summary of the work done in recent years on different bioelectrochemical systems.

Table 7.1 Summary of work done on different types of BES

Type of BES	Anode/cathode	Electron donor/acceptor	Output	References
Plant MFC	Graphite anode/graphite felt cathode	*A.anomala, S. anglica, A. donax* grown in graphite felt	Electricity+ biomass	Helder et al. (2010)
Plant MFC	Graphite granule anode/carbon felt cathode	Ryegrass grown at anode/Cr(IV)	Electricity + Cr (IV) removal	Habibul et al. (2016)
Biofilm MFC	Gold electrode/graphite carbon cloth	Algal biofilm grown at anode	Electricity	Lin et al. (2013)
Algal MFC	Carbon fibre brush/Pt coated carbon cloth	Dead microalgae biomass/live algae	Biomass + electricity	Cui et al. (2014)
Algal MFC	Carbon fibre veil electrodes	Acetate/algal feed from bioreactor	Biomass + electricity	Gajda et al. (2015)
Algal MFC	Graphite rods	Live algae/ferricyanide	Electricity	Xu et al. (2015)
Stacked MDC	Carbon felt/Pt coated carbon cloth	Sodium acetate/phosphate buffer with NaCl solution in middle chamber	Desalination + electricity	Chen et al. (2011)
Photosynthetic MDC	Graphite paper electrodes	Glucose/microalgal biocathode with NaCl in desalination chamber	Electricity + biomass	Kokabian and Gude (2013)
Tubular MDC	Carbon fibre brush/Pt coated carbon cloth	Sodium acetate/tap water with NaCl and boric acid in desalination chamber	Simultaneous desalination and boron removal + electricity	Ping et al. (2015)
MDC	Carbon graphite electrodes	Municipal wastewater/tap water with Ni, Pb containing water in desalination chamber	Removal of heavy metal + electricity	Mirzaienia et al. (2016)
SCMEC	Graphite brush/Pt coated carbon cloth	Sodium acetate/proton	Hydrogen	Call and Logan (2008)
Continuous flow MEC	Graphite/Ni based GDE	Domestic wastewater + proton	Hydrogen	Escapa et al. (2012a)
DCMEC	Graphite brush electrodes	Sodium acetate/sulphate and proton	Sulphate removal + hydrogen	Luo et al. (2014b)

(continued)

Table 7.1 (continued)

Type of BES	Anode/ cathode	Electron donor/acceptor	Output	References
DCMEC	High density carbon fibre/ stainless steel	Dilute sugarbeet juice/ proton	Hydrogen	Ranjan et al. (2015)
SCMEC	Graphite brush/Ni foam based graphene	Acetate/proton	Hydrogen	Cai et al. (2016)
DCMFC	Carbon paper electrodes	Rice straw/ferricyanide	Electricity	Hassan et al. (2014)
SCMFC	Carbon paper/Pt coated carbon paper	Cadmium chloride and zinc sulphate with sodium acetate /oxygen	Electricity + heavy metal removal	Abourached et al. (2014)
DCMFC	Graphite rod electrodes	Dyes/oxygen	Electricity + dye removal	Khan et al. (2015)
DCMFC	Carbon felt/ stainless steel	Sodium acetate/sodium bromate	Bromate removal + electricity	Dai et al. (2016)
DCMFC	Graphite electrode	Soak liquor/ferricyanide	Electricity	Rajeswari et al. (2016)

7.4 Merits of BES:

1. BES is an energy efficient technology that does not require heavy external power to operate.
2. Wastewater can be treated efficiently including toxic chemicals and recalcitrant xenobiotic compounds.
3. In BES, the recovery of energy can be in the form if electricity, hydrogen, potable water (through desalination) and other value added chemicals.
4. The technology has the potential to decrease the pre-treatment cost of the conventional treatment of solid waste.
5. Very low secondary pollution in form of sludge and harmful gases is an added advantage.

7.5 Conclusion

BES is a novel technology of harvesting energy from waste without any external assistance. BES has broad application of pollutant removal, energy generation and desalination. BES is one of the few technologies that combine the applications of catalysts of different nature like chemical, microbial and enzymatic origin. It can treat recalcitrant pollutants and toxic chemicals present in wastewater as suggested by reports with synthetic and real substrates. It has a unique ability to not only treat toxic pollutants but also at the same time generate electric power that makes it a potent future technology. The results of extensive ongoing research and studies in this field suggests that the technology still lags in power generation especially with real waste stream as compared to synthetic waste stream. It is crucial to shift the focus of research to treat real wastewater for generating power. It is also necessary to work in the direction of upscaling the technology for better power production with large volume and heavy loadings of waste for real time assessment of performance on large scale.

Acknowledgement Authors are thankful to Department of Chemistry, Aligarh Muslim University, Aligarh for providing necessary research facilities. Authors are also thankful to Science and Engineering Research Board (SERB), University Grants Commission for departmental research support in the form of DRS II Grant.

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Chapter 8
Microbial Fuel Cell: Waste Minimization and Energy Generation

Mohammad Danish Khan, Nishat Khan, Saima Sultana, Mohammad Zain Khan, Suhail Sabir, and Ameer Azam

Abstract Microbial fuel cells (MFCs) have gained a recent attention as a mode of converting organic waste into electricity using variety of biodegradable substrate as fuel. Different designs of MFCs are available for different purposes, however dual and single chamber MFCs are common used for energy generation. Type of electrode materials, membrane, pH, electron transfer rate, reactor design and operating conditions affects the performance of MFC. Microbes actively catabolize substrate and transform their chemical energy into electrical energy. MFCs could be utilized as power generator in small devices such as biosensor, pacemakers and by doing small modification (Microbial Electrolysis Cell) can produce hydrogen a potential fuel in cathodic chamber. Besides the merits of this technology, it is still immature and faces practical limitations such as low power and current density. The construction and analysis of MFCs requires knowledge of different disciplines ranging from microbiology and electrochemistry to materials and environmental engineering. This article presents various aspects of MFC technology for proper understanding of the readers. This article present an extensive literature survey of some selected papers published on MFC technology in the last decade. Various practical solutions have been suggested to overcome the practical challenges of this technology.

Keywords MFC • Bioelectricity • Wastewater treatment • Power density • COD

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M. Oves et al. (eds.), *Modern Age Environmental Problems and their Remediation*,
DOI 10.1007/978-3-319-64501-8_8

8.1 Introduction

Energy has been universally recognized as one of the most important inputs for economic growth and human development. In recent decades, consumption of energy has increased tremendously. Energy sources are classified into three groups: renewable sources and non-renewable sources which includes fossil fuels, and nuclear sources (Akdeniz 2002; Rahimnejad et al. 2015). Fossil fuels have shared a major part of total non-renewable energy sources and depleting day by day. Combustion of fossil fuels has badly influenced the environment because carbon dioxide (CO_2) emissions. It has been estimated that 70–75% of all CO_2 emissions are due to combustion of fossil fuels (Hoel and Kvemdokk 1996). Therefore, there is a need to explore new energy sources that are cheap and eco-friendly. Many countries around the world have made amazing and interesting efforts to find a solution for scarcity of energy such as wind energy, solar energy, geothermal energy, waste to energy etc. MFC is an excellent, novel and renewable source of energy that converts chemical energy stored in the bonds of organic matter into electricity through biocatalysis of microorganisms (Khan et al. 2015b; Zhu et al. 2016; Society 2016). The idea of obtaining energy from bacteria had begun in 1911 with M. C. Potter, a professor of botany at the University of Durham. In his studies of how microorganisms degrade organic compounds, he discovered that electrical energy can also be produced. Potter had the idea of trying to harvest this new found source of energy for human use. He was able to construct a primitive microbial fuel cell, but not enough was known at that time about the metabolism of bacteria for the design to be improved upon. Figure 8.1 shows a schematic diagram of MFC reactor along with the redox processes occurring in the system. Figure 8.1 shows that anodic and cathodic chambers are separated by proton exchange membrane (PEM) that allows transfer of proton while blocking oxygen and other compounds. In the anodic chamber, microorganisms degrade organic matter into electron, proton and carbon dioxide. The electrons and protons thus produced are then transported to cathodic chamber through external circuit and PEM respectively. Since the terminal electron acceptor (i.e. oxygen) is kept away from anodic chamber, electrons are allowed to pass through external load to generate electricity (Logan et al. 2006; Khan et al. 2017). Typical electrode reactions are shown below using sugar (sucrose) as an example:

Anodic reaction:

$$C_{12}H_{22}O_{11} + 13H_2O \rightarrow 12CO_2 + 48H^+ + 48e^-$$

Cathodic reaction:

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$$

There are different types of electron acceptors and donors (substrates) used in MFC. The substrates not only have impact on the integral composition of the

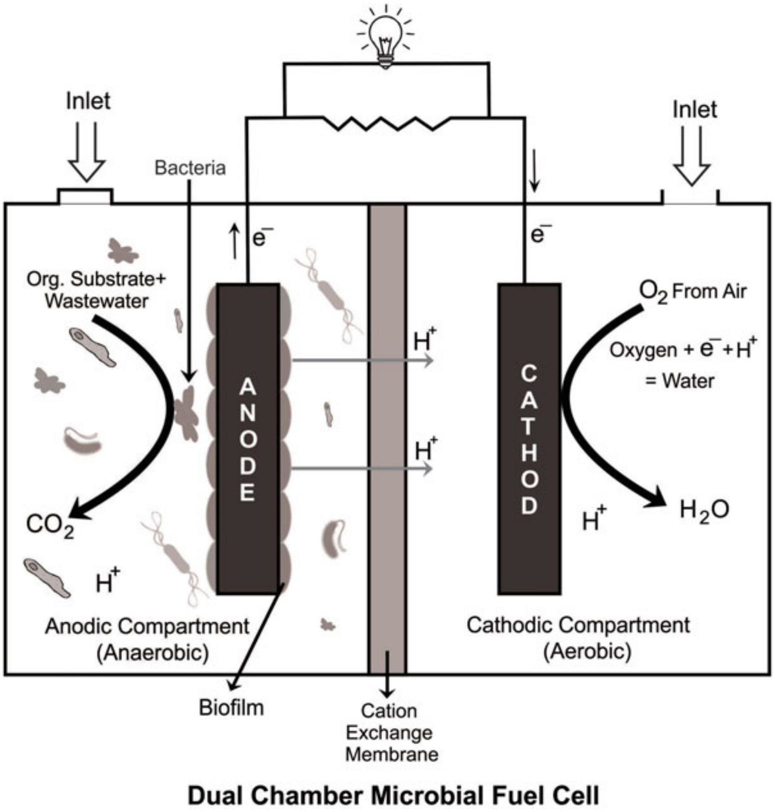


Fig. 8.1 Schematic diagram of microbial fuel cell

bacterial community in the anodic biofilm, but also on the MFC performance including power density (PD) and columbic efficiency (CE) (Chae et al. 2009). In the initial stage of MFC development, low molecular weight (simple) substrates were employed i.e. carbohydrates (such as glucose, fructose, sucrose) organic acids such as acetate, propionate, butyrate, lactate, alcohols (such as ethanol, methanol) (Pandey et al. 2016) and inorganic sulfate (Rabaey et al. 2006). Later, complex substrates such as starch, cellulose, molasses, wastewater coming from food processing industry, dye industry, petroleum industry, dairy industry, organic wastewater, distillery wastewater were also employed (Pandey et al. 2016; Khan et al. 2017). Different electron acceptors used in MFC can be nitrates (Clauwaert et al. 2007), oxygen (Liu and Grot 2005; Logan and Liu 2004), ferric ion (Ringeisen et al. 2006), sulphide (Rabaey et al. 2006) and chromium (Tandukar et al. 2009). However, because of the easy availability and sustainability oxygen can be used as preferred electron acceptor (Luo et al. 2011).

In his work Potter employed *Saccharomyces Cerevisiae* and *Escherichia coli* for electricity generation in MFC. Studies have showed that pure microbial cultures have limits for technical application because of need for sterile conditions, which leads to high cost, whereas mixed cultures or microbial consortia have been more productive than pure strains (Chaturvedi and Verma 2016). The most impressive breakthrough of MFCs was made near the end of twentieth century when some microbes were found to be capable of transferring electrons directly to anode (Biotechnology 1999). e.g. *Shewanella putrefaciens* (Pandit et al. 2014), *Geobacter sulfurreducens* (Bond and Lovley 2003), *Rhodoferax ferrireducens* (Chaudhuri and Lovley 2003), *Geobacter metallireducens* (Min et al. 2005). These exoelectrogenic microbes could form a biofilm on anode and transfer the electrons produced from oxidation organic carbon to anode. The operational cost can be reduced and the worry for environmental pollution caused by artificial electron mediators is (Ieropoulos et al. 2005). Furthermore, mediator-less MFCs containing exoelectrogens are operationally more stable, yields a high CE and thus more suitable for wastewater minimization and power generation.

8.2 MFC Configurations

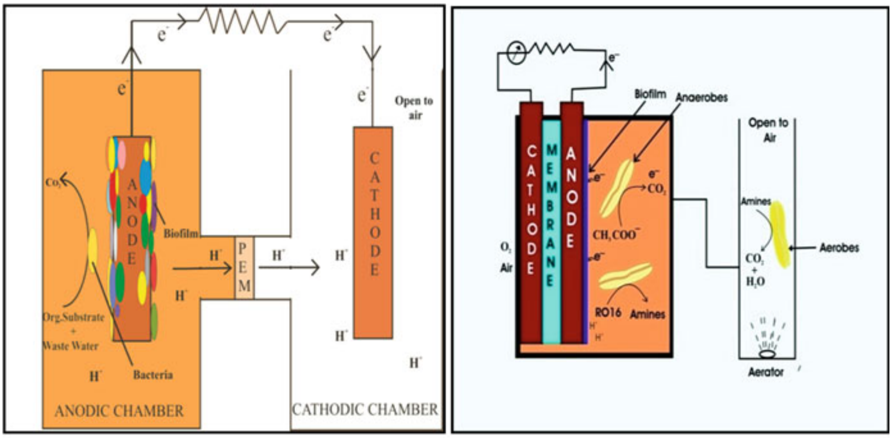
Different configurations of MFCs are used for different purposes; however, two of them are very common viz dual chambered and single chambered MFC. They are discussed given below.

8.2.1 Dual Chamber

Dual chamber MFCs are often built in H-shape design (Fig. 8.2a). Dual chambered MFC consist of anode and cathode is connected by a PEM. Substrate along with sludge is placed in anodic chamber while oxygen is made available in cathodic chamber. The purpose of membrane is to support ionic transfer. H-shaped MFCs have high internal resistances with corresponding low power densities and are limited to laboratory use only (Khan et al. 2015b; Society 2016; Logan et al. 2006).

8.2.2 Single Chamber

In this type of MFC, the cathode is placed in direct contact with air either in presence or absence of membrane (Fig. 8.2b). In the simplest form the anode and cathode are placed on either side of tube with anode sealed against a flat plate and the cathode exposed to air (Logan et al. 2006; Pant et al. 2010). Larger power densities are usually achieved since the internal resistance of single chambered MFCs is quite low.



(a) (b)

Fig. 8.2 Common MFC configurations (**a**) Dual Chamber MFC (**b**) Single Chamber MFC

8.3 Materials Used for Construction of MFCs

8.3.1 Anode Materials

In MFCs, exoelectrogenic bacteria form biofilm on the surface of anode which support efficient electron transfer. Therefore, it is ideal to look up for an anode that is non- corrosive, fully conductive, having high specific surface area, pure, inexpensive and easily available (Logan et al. 2007). A variety of materials have been used as anode including carbon-paper, carbon-cloth, graphite rod, graphite felt, graphite fiber brush, conducting polymers and metals etc (Guo et al. 2012).

8.3.2 Cathode Materials

Most of the materials used for anode and cathode are same however a MFC cathode should have high mechanical strength, excellent catalytic activity and superior ionic and electronic conductivity. MFC cathodes are generally used with and without metal (generally platinum) based catalyst. If MnO_2 or ferricyanide is used as final electron acceptor, no catalyst is needed for cathodic reaction (Logan et al. 2006). Since graphite and carbon materials are poor catalysts for oxygen reduction, therefore, if oxygen is used as the final electron acceptor, it is necessary to employ a catalyst (Guo et al. 2012).

Because of higher cost of metal catalysts and their limited availability, many researchers are working to find an alternative catalysts which is comparable in activity and cheaper than metal catalysts. Chemically modified carbon based materials including carbon nanotubes, graphite foam, graphene can be used as catalyst for oxygen reduction reactions (Matter et al. 2006; Su et al. 2010). Moreover, high cost, toxic nature and complexity in the fabrication of metal catalysts lead to the development of biocathodes where microorganisms themselves act as catalyst. The biofilm formed over the cathode catalyzes reduction reaction (Harnisch and Schroder 2010).

8.3.3 Membrane

Nafion is the most commonly used cation exchange membrane (CEM) to allow passage for ion exchange while separating the anode chamber and the cathode chamber. Alternative to Nafion, such as Ultrex CMI-7000 also are well suited for MFC application (Rabaey et al. 2004). Besides CEM, anion exchange membrane (AEM), bipolar membrane (BPM), charge mosaic membrane (CMM), ultrafiltration membrane (UFM) may play the role of facilitating the transport of ions through the membrane in order to maintain electrical neutrality in MFC systems.

8.4 Factors Affecting the MFC Efficiency

Electrode Material
Type and quality of electrode material used in electrode fabrication as well as the area of electrodes affect the performance of MFCs to a great extent. Better electrode materials will always improve the efficiency of MFC.

pH Buffer and Electrolyte
Since proton transfer inside the cell (diffusion) is slower than its production rate in anode and its consumption rate in cathode, a pH difference between two electrodes occurs without buffer. The pH difference increases the driving force for the diffusion of proton from the anode to the cathode chamber and finally a dynamic equilibrium is attained.

Proton Exchange System
Proton exchange system can affect the internal resistance as well as the concentration polarization loss in a MFC which in turn influence the output power density of the MFC. Nafion is most popular proton exchange system because of its highly selective permeability for protons but still a number of problems associated with the use of nafion including oxygen transfer rate, cation transport as well as accumulation in addition to membrane fouling and substrate loss (Rahimnejad et al. 2014).

Operating Conditions in the Anodic Chamber
Concentration and type of substrate and feeding rate are vital factors that affect the performance of a MFC. Power density varies significantly with different substrates

using same given microbe or microbial consortium. Electricity generation is dependent on substrate concentration both in batch and continuous flow mode MFCs.

Operating Conditions in the Cathodic Chamber
Oxygen is the most commonly used electron acceptor in MFCs for the cathodic reaction. Power output of an MFC strongly depends on the concentration of electron acceptors. Rate of aeration in the cathodic chamber also controls the operating cost and performance of MFC.

8.5 Electron Transfer in a MFC

Electrochemically active bacteria (EAB) transfer electrons from inside of the cell to electrode (Schröder 2007; Rozendal et al. 2008) (Fig. 8.3). Organisms utilize the electron transport chain to generate electrochemical gradients which enable the formation of energy rich adenosine triphosphate. Microbes have strong and diverse mechanisms to conduct or transfer electrons for the energy generation process

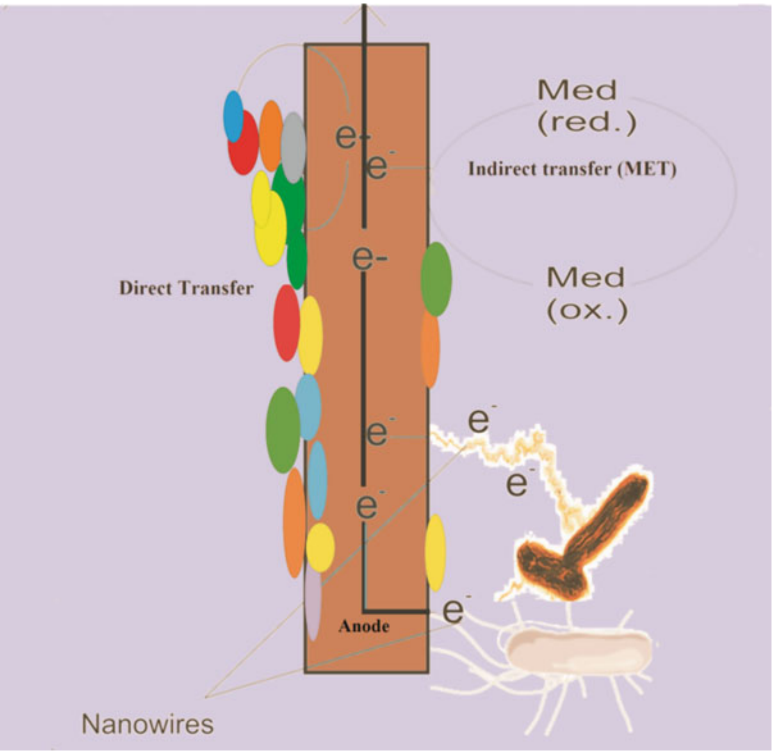


Fig. 8.3 Electron transfer in MFC

(El-Naggar and Finkel 2013). Better knowledge of such mechanisms can be useful for further development of MFCs. Three main possible strategies have been identified for facilitating electron transfer (Aelterman et al. 2008; Song et al. 2015). These are

1. direct electron transfer (DET),
2. electron transfer through mediators and
3. electron transfer through electrically conductive appendages known as microbial or bacterial nanowires

Direct electron transfer requires a physical contact between bacterial cell membrane and anode surface. This electron transfer mechanism was reported with *Geobacter* species, *Rhodoferax, Shewanella* or mixed culture (Huang et al. 2011). In direct electron transfer microbes form a biofilm on the surface of the anode and support electron transfer indicating that the microbial layer only in direct contact with the anode is taking part in transport of electrons i.e. only single layer not all layers which is a limitation of direct transfer thereby restricting the PD and CE.

Mediators or electron shuttle are soluble molecules which can reversibly oxidized and reduced. Mediators such as humic acid, sulphur species, thionine, benzyl viologen, 2,6-dichlorophenol, 1,4- naphthoquinone and various phenazines, iron chelates etc offer the possibility for microorganisms to generate reduced products that are more electrochemically active than most fermentation products. These mediators can accept electrons from cellular electron carriers and then, transfer these electrons to the electrode (Harris et al. 2009).

While some bacteria perform direct electron transfer and some uses chemical mediators, there are certain classes of microorganisms that can excrete redox-active compounds to carry out indirect electron transfer with electrodes. This mechanism does not need a physical contact between bacterial cell membrane and electrode surface. For example *Geobacter sulfurreducen* and *Shewanella* species can produce a special type electrically active structure for transfer of electrons. These are known as nanowires or pili (Logan et al. 2006; Lin et al. 2014; Babanova et al. 2011).These nanowires help in formation of efficient electroactive layer instead of single layer which ultimately increase the PD and CE.

8.6 Key Microorganisms Used in MFC

In general, all the microbes carry out their metabolic activities either in the presence or absence of oxygen . However, all microbes utilize the available substrate generating the reducing equivalents (protons (H^+) and electrons (e^-)) and help in generating energy.

The direct transfer of electrons to an anode by microorganisms was until recently thought to be impossible and the production of useful current was only possible through the use of exogenous (artificial) mediators, which can be expensive, toxic, and unstable (Gil et al. 2003). Several microorganisms have been discovered to have developed physiological processes allowing them to utilize an anode as a terminal electron acceptor without the addition of an exogenous mediator (Gil et al. 2003). The microorganisms described here do not, however, provide a complete list of potentially electricigenic bacteria, and are meant simply to provide examples of key microbes utilized in electron transfer. Some common species are-

8.6.1 Geobacteraceae *spp.*

Several members of the family *Geobacteraceae*, including *Geobacter sulfurreducens* and *Geobacter metallireducens* have the capability of transferring electrons to an anode through direct contact. The exact mechanism by which this transfer occurs is not fully understood, but it is thought that they utilize some form of electrochemically active protein present on outer surface of the cell, and some groups have confirmed the involvement of electrically conductive pili in the process of electron transfer (Yi et al. 2009).

8.6.2 Shewanella *spp.*

Few strains of *Shewanella* spp. *e.g.* (*Shewanellaoneidensis*) produce endogenous electron mediators, which are reversibly reducible molecules with activity very much similar to exogenous mediators, except that the bacteria biosynthesizes them (Du et al. 2007).

Some important bacteria strains generally employed in MFCs are are *Shewanellaoneidensis*, *Actinobacillus succinogenes*, *Escherichia coli*, *Pseudomonas aeruginosa*, *Streptococcus lactis*, *Klebsiella pneumoniae*, *Proteus mirabilis* etc. and Mediator-less electricity-producing bacteria are *Geobacter metallireducens*, *Geobacter sulfurreducens*, *Rhodoferax ferrireducens*, *Shewanella putrefaciens IR-1*, *Geopsychrobacter electrodiphilus*, *Thermincola* sp. *Strain JR*, *Escherichia coli*, *Aeromonas hydrophila* etc.

8.7 Biochemical Cell Reactions in MFCs

In MFCs, organic molecules such as acetate and glucose are oxidized to produce electrons, which are transferred to an external circuit, producing electric power. The EMF produced by a MFC can be calculated according to the following equation:

$$E_{emf} = E_{cathode} - E_{anode} - \eta \quad (8.1)$$

where, $E_{cathode}$ and E_{anode} are the half cell potential at the cathode and anode respectively while η is a term associated with voltage loss (Logan et al. 2006; Hoogers 2014). This loss term 'η' includes ohmic losses (which are more dominant), activation losses and mass transfer losses. The oxidation reaction for sodium acetate at anode with corresponding oxygen reduction at cathode can be written as:

$$CH_3COO^- + 2H_2O \rightarrow 2CO_2 + 7H^+ + 8e^- \quad (8.2)$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (8.3)$$

The half cell potential can thus be calculated in accordance to Nernst equation as:

$$E_{half\ cell} = E_0 - \frac{RT}{nF} ln Q \quad (8.4)$$

where, E_0, R, T, Q are the standard half cell potential, gas constant, temperature (Kelvin) and the activity constant, respectively.

The feasible energy produced by the electrochemical system can be calculated using the Gibbs free energy equation as:

$$\Delta G = -nFE \quad (8.5)$$

where, n is number of electrons, F is Faraday constant and E is the electromotive force of the cell (Worrell 1997). If the overall reaction is thermodynamically favored, the electricity is generated in the MFC following the Gibb's free energy equation.

8.8 Wastewater Treatment and Energy Recovery Through MFCs

Researchers across the globe have treated wastewater using different MFC designs and operational conditions (Khan et al. 2015a, b; Najafabadi et al. 2016; Zhang et al. 2014; Song et al. 2016) and calculated various parameters such as Chemical oxygen demand (COD) removal rate, CE, effects of substrate concentration on maximum output voltage and PD (Elmekawy et al. 2015). Various organics can be utilized in MFCs for electricity generation. Some simple or defined substrates are carbon source wastewater & substrates (such as glucose, fructose, ribose), nitrogen source wastewater & substrates (like amino acids) and organic acids and miscellaneous substrates (e.g. acetate, mixed volatile fatty acids, mixture of naphthalene and benzidine) and complex or undefined wastewater substrates are food-processing wastewater, beverage industry wastewater, dairy industry wastewater, agro-processing industry wastewater, pharmaceutical industry wastewater, domestic and municipal wastewater, refinery and distillery industry wastewater etc (Pandey et al. 2016). A summary table (Table 8.1) has been given for providing comparative information on performance of MFC with simple and complex substrates.

The removal of reducing equivalents (electrons) from the anode chamber is basically similar to decreasing the chemical oxygen demand (COD) from the wastewater. Therefore, the CE for a given organic substrate in the anode chamber is related to the amount of Biological oxygen demand (BOD) or COD removed by the mixed culture in the anode chamber and the electric current generated over a period of time.

During last two decades, the PD has increased from less than 1 mW/m^3 to 2.87 kW/m^3 (or 10.9 kA/m^3) in MFC (Fan et al. 2012), mainly due to the better advancements in reactor design, material, and operation, which relaxes the physical and chemical limitations of the system. The projected wastewater treatment capacity of MFCs can reach 7.1 kg chemical oxygen demand (COD)/m^3 reactor volume/day, which is even higher than conventional activated sludge systems (~0.5–2 kg COD/m^3 reactor volume/day) (Rozendal et al. 2006, 2008). However, there are still many challenges that need to be tackled before the technology can be applied on commercial scale. The overall benefit to be realized from MFC is that it provides greater incentives for advance innovations and create sustainable future for wastewater treatment. The world's population is increasing day by day and concentrating in urban areas. This trend is particularly intense in developing countries, where an addition 2.1 billion people are expected to be living in cities by 2030 (Tables 2013). These cities produce billions of tons of waste every year, including sludge and wastewater. Municipal wastewater contains a multitude of organic compounds that can fuel MFCs. The amount of power generated by MFCs in the wastewater treatment process can potentially reduce the electricity needed in conventional treatment.

MFCs using certain microbes have a special ability to remove sulfides as required in wastewater treatment. MFCs can enhance the growth of bioelectrochemically active microbes during wastewater treatment thus they have good operational stabilities as well. Continuous flow and single-chamber MFCs and membrane-less MFCs are favored for wastewater treatment due to concerns in scale-up. Sanitary wastes, food processing wastewater, swine wastewater and corn stover are all great biomass sources for MFCs because they are rich in organic matters. It can even break the organic molecules such as acetate, propionate, and butyrate to CO_2 and H_2O.

MFC can remove upto 90% of the COD and BOD of wastewater. MFCs yield 50–90% less sludge, which eventually reduces the sludge disposal cost. This shows effectiveness of MFC in wastewater treatment. Table 8.1 shows various strategies adopted by researchers for wastewater treatment with high energy recovery.

Table 8.1 Summary on performance of MFCs with simple or complex wastewater substrates

Wastewater/ substrate	Inoculum	Type of MFC	Electrode	Power density	References
D-Glucose	Mixed bacterial culture	Two chamber	Anode & cathode-carbon cloth	2160 mW/m^2	Catal et al. (2008)
D-Fructose	Mixed bacterial culture	Two chamber	Anode & cathode-carbon cloth	1810 mW/m^2	Catal et al. (2008)
Sucrose	Anaerobic sludge	Single chamber	Anode-carbon fiber veil cathode-carbon cloth	1.79 W/m^3	Beecroft et al. (2012)
Mannitol	Mixed bacterial culture	Single chamber mediatorless	Anode & cathode-carbon cloth	1490 mW/m^2	Catal et al. (2008)
L-Glutamic acid	Domestic wastewater	Single chamber air cathode	Anode & cathode-carbon cloth	686 mW/m^2	Yang et al. (2012)
Acetate	Domestic wastewater	Single chamber	Anode-Toray carbon paper cathode-carbon paper	506 mW/m^2	Liu et al. (2005)
Butyrate	Domestic wastewater	Single chamber	Anode-Toray carbon paper cathode-carbon paper	305 mW/m^2	Liu et al. (2005)
Pyridine	Anaerobic sludge	Two chamber	Anode-carbon paper cathode-Pt coated carbon paper	142.1 mW/m^2	Hu et al. (2010)
Phenol	Anaerobic sludge	Single chamber	Anode-carbon felt cathode-Pt coated carbon paper	31.3 mW/m^2	Wu and Zhou (2014)
Bad wine	Glucono bacterroseus and Acetobacteraceti-	Two chamber	Anode-carbon felt cathode-graphite	3.82 W/m^3	Rengasamy and Berchmans (2012)
Food processing	Activated sludge	Catalysts and mediator-less	Anode & cathode-graphic sheets	230 mW/m^2	Jafari et al. (2013)
Domestic wastewater	Domestic waste-water	Single chamber with double air-cathode	Anode-carbon yarn cathode-Pt coated carbon paper	621 mW/m^2	Sonawane and Marsili (2014)
Crude glycerol	Anaerobic sludge	Two chamber	Anode-graphite brush cathode-graphite cloth	90 mW/m^2	Chookaew et al. (2014)
Azo-Dye (acid navy blue r) wastewater	Anaerobic sludge	Single chamber	Anode & cathode-graphite rod	2236 mW/m^2	Khan et al. (2015a)
Distillery wastewater	Isolated broth culture	Two chamber	Anode & cathode-graphite plate	202 mW/m^2	Samsudeen et al. (2015)
Azo-Dye (reactive orange 16) wastewater	Anaerobic sludge	Single chamber	Anode & cathode-graphite rods	60 mw/m^2	Sultana et al. (2015)
Petroleum refinery wastewater	Activated sludge	Dual chamber GC-packing type	Anode-graphite plate cathode-graphite flake	330.4 mW/cm^3	Guo et al. (2016)
Organic wastewater	Activated sludge	Up-flow constructed wetland MFC	Anode & cathode-activated carbon	184.75 mW/m^3	Oon et al. (2017)
Dairy industry	Activated sludge	Dual chamber	Anode & cathode-carbon sheet	5.1 W/m^3	Faria et al. (2016)
Lemon peel (synthetic) wastewater	Anaerobic sludge	Dual chamber	Anode-carbon felt cathode-carbon cloth	371 mW/m^2	Miran et al. (2016)

8.9 Advantages and disadvantages of MFC

Comparing MFC technology with traditional technologies used for energy generation, MFC hold many advantages and offer wide spread applications:

- MFCs have a wide range of substrates, such as carbohydrates, proteins, lipids and even the organic matters in the wastewater (Pandey et al. 2016).
- MFCs possess a high energy transformation efficiency, since it converts the chemical energy stored in substrates into electricity directly.
- Single-chamber MFC do not require energy input for aeration, which lowers operational costs (Rabaey et al. 2005).
- By proper modification in designing, MFCs have greater potential for widespread applications such as wastewater treatment, biological oxygen demand (BOD) sensors, bioremediation, hydrogen production and more and more sustainable electricity generation (Logan and Regan 2006).
- MFC technology is an alternative to other energy intensive techniques such as activated sludge system, trickling filters and offers advantages by reducing sludge production (since a part of COD is converted to electricity), improving odour control and eliminate aeration requirements, all at the cost of waste treatment for electricity production. For instance, according to Electric Power Research Institute, US, the median energy usage for activated sludge plants is 1322 kWh per million gallons treated and 955 kWh per million gallons treated for trickling filter plants but in MFC there is no external energy requirement for running the process in fact it can produce electricity itself.
- It can serve the dual purpose of treating waste and producing electricity (Khan et al. 2015a, b).

The major drawback of MFC is the high cost of membrane and electrode materials used that shoots up the price of MFC to be practically installed on a commercial scale. Another problem is the low waste to energy conversion efficiency. The electrode materials used in MFC are also very limited as in MFC, biological catalysts are used and it is crucial to use electrode materials that are biocompatible.

8.10 Challenges and Future Perspectives

- Cost is the most important challenges with MFC. Currently, expensive PEM (like Nafion) and costly metals (like platinum) are generally used in lab-scale. This account for more than 80% of construction cost. High cost of these materials makes MFCs uncompetitive against energy production from wind, solar, biofuels and methane digesters (Khan et al. 2014). Construction cost MFC must be reduced so it is necessary to look for the materials that are not only cost effective but simultaneously biocompatible as well (Guo et al. 2012).

- Another challenge is to produce maximum conversion of COD into energy by preventing the side reactions and thereby increasing the CE and PD (Mink et al. 2012) which will make the technology stand on a larger scale. This can be achieved by using electrodes of high surface area to volume ratio.
- The reduction of various types of losses like ohmic losses can be done by decreasing the electrode distances, increasing conductivity of solution by ensuring efficient electron transfer, developing natural mediators that can conduct electrons and reduce activation losses and optimizing reactor conditions (Logan et al. 2006).
- Researchers are successfully trying to develop micro and nanosized MFCs for powering miniature sensors in remote locations or in space and for implanting into human body as pacemakers but it needs to tackle the need of stable power production even at low quantities.
- The exact mechanism of transfer of electrons from bacteria to electrodes is still not fully known and needs to be investigated further (Oh et al. 2010).
- The side reactions (methanogenesis or acetogenesis), oxygen reduction leading to the current losses needs to be minimized to increase the CE and PD (Liu et al. 2005).

8.11 Conclusion

The increasing demand for energy in the near future has created strong motivation for environmentally clean alternative energy resources. The simultaneous production of clean water and energy makes this technology exclusive in its own way. This chapter provides types of MFC setup that have been developed by researchers across the world using different types of substrates/wastewater, electrode materials and inoculums and their corresponding COD removal efficiency and PD to improve the performance of MFC for practical and commercial applications. The mechanism of electron transfer should be clearly understood for improving the performance of MFC. The attainable power output from MFCs has increased remarkably over the last decade, which was obtained by improving their designs, such as optimization of the MFC configurations, their physical and chemical operating conditions, and their choice of biocatalyst.

A major disadvantage of MFCs is their reliance on biofilms for mediator-less electron transport, while anaerobic digesters such as up-flow anaerobic sludge blanket reactors eliminate this need by efficiently reusing the microbial consortium without cell immobilization. Another limitation is the inherent naturally low catalytic rate of the microbes.

Although some basic knowledge has been gained in MFC research, there is still a lot to be learned upon in the scale up of MFC for large-scale applications. However, the recent advances might shorten the time required for their large-scale applications for both energy harvesting and wastewater treatment systems. Even though the idea of harnessing the energy produced by bacteria has been around for almost

100 years, researchers have just begun to fully understand the concept of MFC and how to bring out its true potential. In the past decade, rapid progress has been made in MFC research and the number of publications has increased exponentially in this area. Most of the studies focused on MFC design, exoelectrogenic bacteria and cost-effective electrode materials. The power densities of MFCs have increased from less than 0.1 to 6860 mW/m^2 over the past decade. Researchers have realized that understanding the roles of different bacteria in a synergetic biofilm consortium and the electrons transfer mechanisms by key microorganisms is needed to improve MFC power output (Logan and Regan 2006b). Researchers are working to optimize electrode materials, types and combinations of bacteria and electron transfer in microbial fuel cells.

Acknowledgement Authors are thankful to Department of Chemistry, Aligarh Muslim University, Aligarh for providing necessary research facilities. Authors are also thankful to Science and Engineering Research Board (SERB), University Grants Commission for departmental research support in the form of DRS II Grant.

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Chapter 9
Recent Advancement in Membrane Technology for Water Purification

Faraziehan Senusi, Mohammad Shahadat, Suzylawati Ismail, and Shazlina Abd Hamid

Abstract The present chapter deals with the recent advances in the fabrication of polymer supported nanocomposite membranes for water purification. Fabrication of compositing membrane using conducting polymers in the form of polymer-matrix or surface based thin-film open an innovative way to used nanocomposite materials in diverse field. The improvement of PANI based nanocomposite membranes should be designed by tailored their morphological and physico-chemical properties, thus introducing unique functionalities in order to meet the specific wastewater treatment applications. This review provides a brief description of the current status of PANI nanocomposite membrane which projected higher demand to be applied in water purification systems owing to the significant enhancement on permeability, antifouling and mechanical properties.

Keywords Composite membrane • Fabrication • Characterization • Water purification • Separation of protein • Removal of contaminants

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M. Oves et al. (eds.), *Modern Age Environmental Problems and their Remediation*,
DOI 10.1007/978-3-319-64501-8_9

9.1 Introduction

Water is one of the most important sources of living beings and is used in daily life. Rapid growth in industrialization has been severally affected natural water resources. According to the progress of World Health Organization (W.U.J.W. Supply, S.M. Programme 2014) on drinking water and sanitation estimated about 748 million people still lack of safe drinking water (WHO and UNICEF 2014), and 3900 children die every day due to the communicated diseases by using polluted water or poor hygiene. These statistics can become worsen further as water contamination by various pollutants increases day by day. Therefore, effective water purification technologies must be developed to increase water resources and to tackle the water pollution issues. In this regard, membrane process technology is playing an important role in the water industry (including drinking water treatment, brackish water desalination and wastewater treatment as well as reuse of wastewater) in order to provide the effective technology to purify water at lower cost using less energy and minimizing the environmental impact. Recently, polymeric based membrane is the commonly applied for treatment of industrial effluent and wastewater treatment owing to its straight forward pore forming mechanism, higher flexibility, smaller footprints required for installation and cost effective contrasted with inorganic membrane equivalents. The improvement of membranes with high permeability and rejection rate, together with great antifouling property is require in the treatment wastewater under the context of energy efficiency and cost effectiveness (Yin and Deng 2015). The main aim of present chapter is to focus on the advancement of water purification systems and emphasizes primarily on the membrane technology.

9.2 Water Purification Systems

Contamination of freshwater scarcity is a severe problem in many regions of the world and a number of people living in highly water-stressed areas is predicted to increase throughout the twenty-first century. The demand of fresh water is increasing due to the rapid urbanization and industrialization, population growth, and climate disruption (Galiano et al. 2015; Manawi et al. 2016). At present, global water resources can be divided into two resources, either conventional water resources including natural freshwater resources (e.g., rivers and lakes) or unconventional water resources such as wastewater, seawater and brackish water which are not available for direct use (Zhang et al. 2016). Currently, various technologies such as coagulation and flocculation, air flotation and advanced oxidation processes have been developed for sustainable water purification as summarized in Table 9.1.

The processes of water purification are quiet efficient, however, these are associated with some drawbacks. Therefore, to improve water treatment processing system, attention has been paid to develop advance environmental friendly, energy efficient and low cost treatments technology for sustainable water purification.

Table 9.1 Treatment methods for water purifications

Treatments	Methods for purification	Applications	Remarks	References
Coagulation and flocculation	Coagulation with combination of ferric chloride and poly aluminium chloride (PAC)	Removal of turbidity and DOC (dissolved organic carbon)	Coagulation efficiency for blended coagulants was improved and 40.7% low molecular weight organic matters were removed.	Lee et al. (2008)
	Coagulation with biological flocculants produced from strain *Bacillus* sp. F6	Turbidity removal	The removal efficiency was increased up to 97% with the combination of chemical flocculants compared to single biological flocculants.	Ma et al. (2008)
	Electro-coagulation	Removal of bacteria, water turbidity, and chemical contaminants	The new method for treating the surface raw water and suitable for small scale water treatment plants.	El-Masry et al. (2004)
Air flotation	Micro bubble clarifier	Removal of CODCr, BOD5, SS, T-N, T-P, DO and Chlorophyll-a	Micro bubble clarifier used for on-site water purification without treatment facility and added chemical which are natural and environmental friendly concepts.	Kim et al. (2014b)
	Counter flow co-flocculation flotation (CC-FF)	Removal of trihalo methane (THM)	The counter flow co-flocculation flotation technique have three major advantages compared to the conventional flocculation-flotation process which are produces low-density, however, high shear-force-resistance flocci as well as increases the stability of the blanket of bubble-microfloc.	Guo et al. (2003)
Advanced oxidation processes	UV and UV/H_2O_2 treatment processes.	Removal of organic micro pollutants (OMPs)	Eighty percent of diclofenac and triclosan oxidation was accomplished using UV (below 200 mJ cm^{-2}). While, atrazine and Carbamazepine recorded on 80% UV degradation (dose; 740 and 990 mJ cm^{-2}).	Rozas et al. (2016)

Many researchers have focused on suitable and economical treatments for water purifications including water remediation, reclamation and desalination to meet the demand of clean water. Among various treatment technologies, adsorption of contaminant through polymeric nanocomposite membrane is considered as an advanced tool in water treatment technology (Yin and Deng 2015; Jhaveri and Murthy 2016). The demand of membrane technology is witnessing an era of rapid growth due to the continuous effort and collaboration research among the private industry and academia.

9.3 Polymer Based Nanocomposite Membranes

In membrane separation technology, especially porous material is used which plays an interception role to trap contaminants. It is characterized according to the particle size membrane molecular weight cut-off (MWCO) and the process is not involved phase change. In addition, reprocessing cost is found low. This advanced technology has potential to produce superior water quality beyond the current regulatory requirements. Therefore, membrane technology can be adopted to serve as an alternative to conventional clarification and filtration water treatment process. These advantages hence account for the growing interest in membrane technology.

In general, several types of membranes with different pore sizes employed in water treatment process including microfiltration, ultrafiltration, reverse osmosis and nanofiltration membranes which depend on their common materials that would be filtered out through each process. Most of the material made up of synthetic organic polymers; poly(vinylidenefluoride) (PVDF) (Zhang et al. 2013), polysulfone (PSf) (Chakrabarty et al. 2008), polyetehersulfone (PES) (Pasaoglu et al. 2016) and poly(acrylonitrile) (PAN) (Ulbricht and Belfort 1996) and they are prepared under different membrane formation conditions. Besides this, inorganic materials such as ceramics (Richard et al. 2003) or metals (Ho et al. 2011) can also be used for the preparation of membranes. Ceramic membranes which widely applied for microfiltration and utilized in gas separation applications possess properties such as microporous, thermally stable and chemically resistant. However, ceramic membranes associated with some drawbacks namely; high cost and mechanical fragility which slowed down their wide-spread use.

Recent advances in nanotechnology have offered the development on the new generation of membrane application for water purification and wastewater treatment. A progressive recent trend in research has been seen progress in the fabrication of polymeric membranes. Incorporation of inorganic nanomaterials in to polymeric matrix produces nanocomposite membranes with excellent surface properties compared to the conventional membranes to meet the harsh requirements in wastewater treatment processes. A recent trend in the fabrication of polymeric nanocomposite membranes is shown in Fig. 9.1.

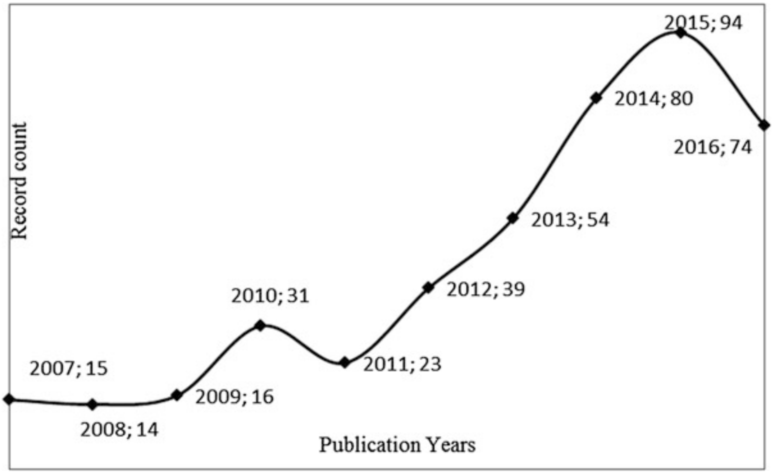

Fig. 9.1 Fabrication of polymers based nanocomposite membrane

Basically, the PES is a polymeric material; it is widely used for the development of ultrafiltration (UF) membranes. However, the hydrophobic properties of PES itself lead to poor membrane performance and low anti-fouling during filtration process. Vatsha et al. (2014) reported the ability of PES membrane to prevent antifouling in water purification system by using polyvinyl pyrrolidone (PVP) as an additive for the modification purpose. Different concentrations of PES and PVP were used to obtain better performance of membrane. Due to good chemical resistance, excellent thermal stability and high pH tolerance, PES polymer was chosen for membrane preparation. The PES membrane was prepared by using nonsolvent-induced phase separation method (where NMP was used as solvent). In the fabrication of composite membrane, six casting ratio of PES/PVP were prepared by fixing the amount of PES (16 and 18%) and varied PVP amount (0, 2, 4, 6, 8, 10%). The solution mixture was stirred for 18 h and left for 3 h for complete liberation of bubble. The mixture was then casted using automated steel knife with 250 μm air-gap and immersed in coagulation bath filled with deionized water at 23 °C. Fabricated membrane was kept in deionized water before being used for experimental purpose. The membrane was characterized by SEM, contact angle, ATR-FTIR, AFM, and testing on dead-end membrane filtration unit. The SEM analysis result showed that the pore size of 16% PES increased along with PVP concentration, meanwhile pore size was found reduced as the PVP concentration increased for 18% PES. The AFM results established the enhancement in the roughness of membrane surface by enhancing the content of PVP. This membrane showed good ability in rising water flux by rejecting BSA protein at the flow rate of 112 to 418 L m^2h^{-1} using 16% PES. Thus, the PES membrane modified with PVP has water purification potential.

The progressed nanocomposite membranes on their morphology and physico-chemical properties such as hydrophilicity, porosity, charge density as well as thermo-mechanical stability need to be developed to meet the specific requirements in water treatment applications. In addition, establishing exclusive functionalities is needed (e.g. antibacterial, antifouling, photocatalytic, photodegradation, self-cleaning or adsorptive behaviour) in order to improve membrane mechanical strength and thermal stability (Yu et al. 2009b; Yan et al. 2006). Thus, in order to improve the physico-chemical properties of polymeric membranes for water purification, a number of nanocomposite membranes have been developed by the incorporation of nanoparticle of metal oxides. Some important polymeric nanocomposite membranes together with several types of nanomaterial and their prospective applications are shown in Table 9.2.

A study regarding the performance of PES membrane was carried out by the modification of PES with Al_2O_3 particles to reduce activated sludge (Maximous et al. 2010). Five different composite membranes were prepared by varied the ratios of Al_2O_3 (0.01, 0.03, 0.05, 0.1, and 0.2) and keeping fixed amount of PES. In order to obtained homogenous and uniform membrane. The mixture of PES/Al_2O_3 was dissolved in NMP solution and sonicated for 72 h at 60 °C prior the addition of 18% (by wt.) PES and the mixture were sonicated for 7 days. The membrane was casted using knife of 100 μm and evaporated at room temperature (25 ± 2 °C) for 15 s before being immersed into deionized water coagulation bath for 2 min. The excess solvent on the membrane was removed by immersing it in the water bath for 15–17 days at 25 ± 2 °C before used. The composite membrane was examined using SEM analysis which confirmed introduction of the Al_2O_3 caused aggregate formation and pore plugging. The fouling performance of membrane increased by increasing content of activated sludge and reached optimum limit. The optimum performance of PES-Al_2O_3 composite membrane was achieved in terms of lowest fouling rate and the highest membrane permeability for the PES loaded with 5 wt.% of Al_2O_3.

In another study, Muhamad et al. examined the rejection rate of BSA using PES polymer membrane modified with silicon oxide (SiO_2) nanoparticles (Muhamad et al. 2015). In order to improve the membrane properties in advanced water treatment, various SiO_2 loading was investigated. The initial step involved modification of SiO_2 particle with sodium dodecyl sulfate (SDS) to reduce SiO_2 agglomeration. A series of modified SiO_2 loading (0, 1, 2 or 4 wt.%) is added together with 6 wt.% PVP and solution was mixed with 18 wt.% PES and N, N-dimethylacetamide (DMAc) solvent. The PES/SiO_2 composite membrane was prepared by phase version techniques and characterized using SEM, FTIR/ATR, TGA analyses and contact angle analyser. The FTIR result established the presence of SiO_2 functional group was improved the water flux and rejection of BVA. The PES/SiO_2 membrane successfully improved the water flux from 44.2 L m^2 h^{-1} to 87.2 L m^2 h^{-1} and BVA rejection from 81 to 94%. Hence, prepared membrane can be effectively applied in wastewater treatment.

Similarly, PVDF has been chosen as a membrane material in ultrafiltration and microfiltration due to its good mechanical properties, chemical resistance and thermal stability. However, the hydrophobic characteristic of PVDF causes fouling nature of membrane. Recently, possibility of coupling membrane filtration and

Table 9.2 Polymer nanocomposite membranes for water purification

Polymer	Solvent	Filler	Nanomaterials	Fabrication method	Applications	References
PES	NMP	PEG	Fe_3O_4	PI	Removal of salt	Alam et al. (2013)
PES	DMF, DMAc, NMP, DMSO	–	TiO_2	Electrospinning	Bacteria removal	Khezli et al. (2016)
PES	DMAc-DegOH	–	TiO_2	Vapor induced phase separation + immersion precipitation process	Water purification	Li et al. (2009)
PES	DMAc	PVP, H_2O	TiO_2	PI	Protein (BSA)	Wu et al. (2008)
PES	DMAc	PVP	TiO_2	PI	Protein (BSA)	Razmjou et al. (2011)
PES	NMP	–	Al_2O_3	PI	Activated sludge	Maximous et al. (2010)
PES	DMAc	–	SiO_2	PI	Protein (BSA)	Muhamad et al. (2015)
PSf	NMP	PVP	Ag	PI	Remove virus	Zodrow et al. (2009)
PSf	DMAc, DMF	PEG	Ag	PI	Silver removal	Taurozzi et al. (2008)

(continued)

Table 9.2 (continued)

Polymer	Solvent	Filler	Nanomaterials	Fabrication method	Applications	References
PSf	DMF	–	Graphene oxide (GO)	PI	Arsenate removal	Rezaee et al. (2015)
PSf	NMP	PEG 400	Exfoliated graphite nano-platelets (xGnPs) decorated by Au NPs	PI	Gold removal	Crock et al. (2013)
PSf	DMAc-NMP	–	TiO_2	PI	Removal of emulsified oil	Yang et al. (2007)
PAN	DMF	PVDF particles	–	Electrospinning	Water purification	Elkhaldi et al. (2016)
PAN	DMF	–	Calcium hypochlorite ($Ca(OCl)_2$)	Electrospinning + blending	Bacteria removal	Kim et al. (2014a)
PAN		PEGDA and MBAA	Cellulose nanofibers (CNF)	Coating	Removal of heavy metal ions	Wong et al. (2012)
PVDF	DMAc	PEG 200	TiO_2	PI	Organic compounds removal	Méricq et al. (2015)
PVDF	DMAc	PEG	TiO_2	PI	Protein (BSA)	Moghadam et al. (2015)
PVDF	NMP	–	TiO_2	PI	Casein	Oh et al. (2009)
PVDF	DMAC	PEG	TiO_2	PI	PEG and pepsin removal	Song et al. (2012)
PVDF	DMF	–	TiO_2	PI	Blood serum albumin (BSA)	Cao et al. (2006)

PVDF	DMAc	$LiCl \cdot H_2O$	TiO_2	PI	TiO_2	Yuliwati and Ismail (2011)
PVDF	NMP	PEG 400	TiO_2	PI	BSA	Bian et al. (2011)
PVDF	DMAC	–	TiO_2	PI	Methylene blue	Ngang et al. (2012)
PVDF	DMAc, NMP	PVP	TiO_2	sol gel method + blending	Pure water	Yu et al. (2009a)
PVDF	NMP	–	TiO_2	PI	Antibacterial, removal of Reactive Black 5 (RB5) dye and fouling of BSA	Damodar et al. (2009)
PVDF-sulfonated PES	DMAc	PVP	TiO_2	Blending	Bacteria	Rahimpour et al. (2011)
PSf, PVDF, PAN	NMP	–	TiO_2	PI	Activated sludge	Bae and Tak (2005)

photocatalytic activity of TiO_2 has been investigated since this membrane can mitigate membrane fouling. Titanium dioxide (TiO_2) is a type of photocatalyst that has a high stability, a low environmental impact together with good performance of photocatalysis activity under UV irradiation. Thus, PVDF is found very suitable for such coupling as its high resistance to UV degradation and photocatalytic activity (Table 9.2).

In most of the studies, TiO_2 has been synthesized by the combination of PVDF to form nanocomposite which was extensively used as photocatalyst used (Yuliwati and Ismail 2011; Yu et al. 2009a; Yang et al. 2007) as TiO_2 enhance hydrophilicity of composite membrane surface and its permeability as well (Oh et al. 2009; Bian et al. 2011; Damodar et al. 2009). A very few finding demonstrated decline in hydrophilicity by increasing concentration of TiO_2 more than 6–10 by wt.% (TiO_2/PVDF) (Yuliwati and Ismail 2011; Yu et al. 2009a; Damodar et al. 2009). In addition, self-cleaning capacity during the filtration process was also improved (Ngang et al. 2012). Meanwhile, no effect of TiO_2 was found on pure water flux (Song et al. 2012).

9.4 Polyaniline (PANI) Based Nanocomposites Membranes

PANI based nanostructures (nanofibers, nanowires and nanotubes) have gained great interest because of their successful applications in various fields (Hui et al. 2016; Khan et al. 2016; Sharma et al. 2014; Hojjat Ansari and Basiri Parsa 2016; Shyaa et al. 2015; Shendkar et al. 2016; Bushra et al. 2014b, 2015). A number of findings related to the synthesis of PANI nanocomposite membranes and their application in water purification for water purification are shown in Fig. 9.2.

The increasing of intrinsically conducting polymers (ICPs) as an attractive subject of research was initiated due to interesting properties and a number of possible applications of ICPs (Huang et al. 2014; Shahadat et al. 2014). Among the available ICPs; polyaniline (PANI) is observed to be the most encouraging due to its ease of synthesis, cost effective monomer, tunabile behaviour, and better stability (Bhadra et al. 2009). Other than achieving the high degree of conductivity, the properties of ICPs in processing either alone or in a matrix of a suitable host polymer need to be considered in order to exploit them as promising candidates in development of membranes.

Since past decades, PANI supported nanocomposite membrane has attracted much attention to be applied in membrane water purification systems by reason of the significant enhancement on permeability and antifouling as well as mechanical property. The improvement on membrane permeability, hydrophilicity and antifouling property were reported by the mixing of PANI nanomaterials and these material have been applied for various applications in membrane separation such as ultrafiltration, (Jhaveri and Murthy 2016) gas separation membranes (Zhao et al. 2012; Nimkar et al. 2015), pervaporation membranes (Vijayakumarnaidu et al. 2005) and proton exchange membranes (Gharibi et al. 2006). An outline for the

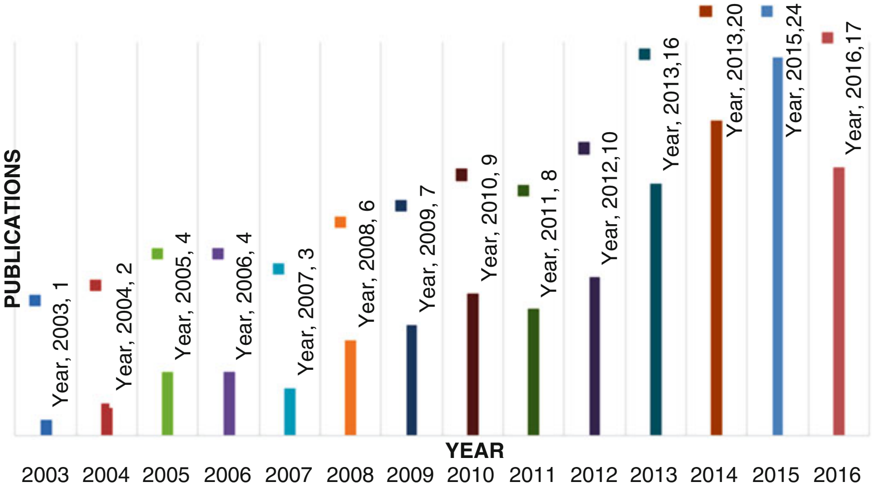

Fig. 9.2 Bibliographic data of PANI based membrane

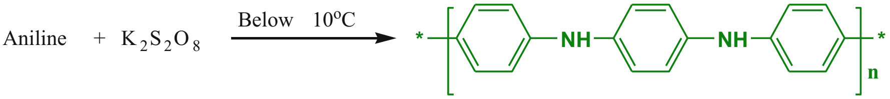

Fig. 9.3 Synthesis of polyaniline (PANI)

synthesis PANI from aniline (monomer) is shown in Fig. 9.3. Polymer of PANI consists of two structural units (as shown in Fig. 9.3) resulting from the oxidative polymerization of aniline, which are reduced (B–NH–B–NH) and oxidized (B–N–Q–N^{-}) (where B denotes benzenoid and Q denotes a quinoid ring. Both units can transform into each by redox).

9.5 Applications

The application of PANI as an additive in the development of polymer composite membranes have received much attention due to the improvement in process ability and good combination in terms of mechanical and conductivity properties (Huang et al. 2014). The successful utilization of PANI is found through blending or surface modification of commercial available polymers (e.g. PSf, PES and PVDF etc.) during the membrane preparation. In addition, the combinations of nanoparticles (such as TiO_2 and Fe_3O_4) with PANI improve surface area, functional groups and surface morphology. This functional membranes not only filter solute particles from water, but also adsorbing, degrading or deactivating. A proposed scheme for the

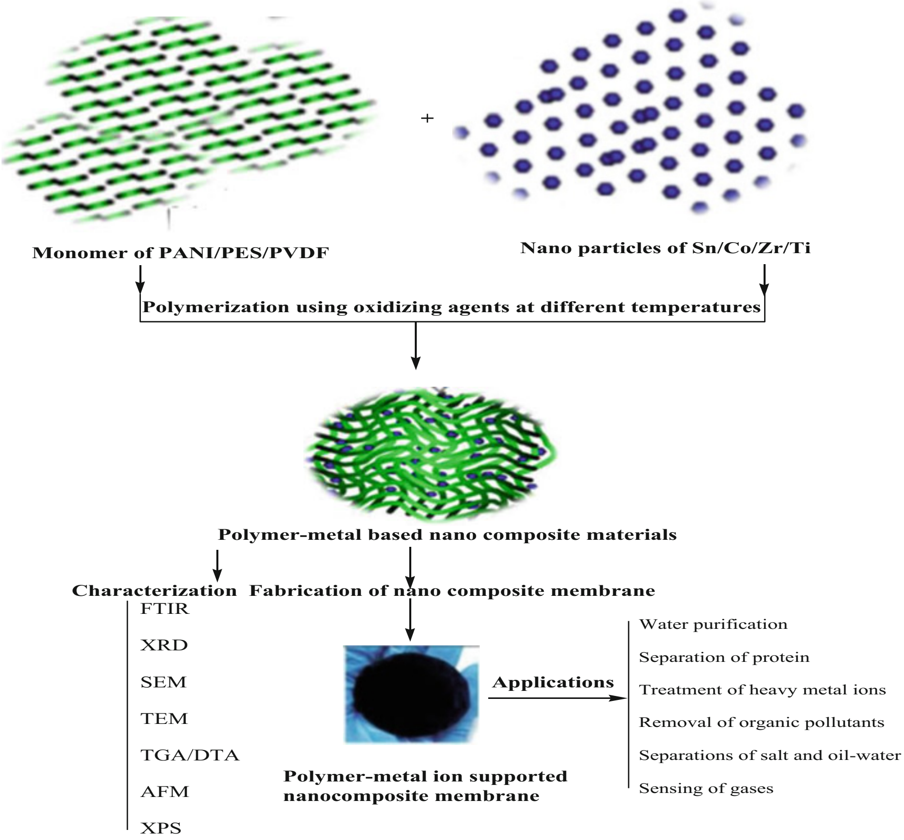

Fig. 9.4 A proposed scheme for the synthesis, characterization of PANI supported nanocomposite together with fabrication of membrane and their applications

synthesis, characterization of PANI supported nanocomposite together with fabrication of membrane and their application is shown in Fig. 9.4.

The fabricated or modified PANI nanocomposite membranes have potential to apply various fields; water purification for removal of proteins, heavy metal and salt rejections and oil-water separation systems as summarized:

9.5.1 Removal of Protein

Fan and co-workers developed PANI/PSf nanocomposite membrane through the filtration of PANI nanofibers in aqueous dispersion (Fan et al. 2008a). PANI nanofiber layer was fabricated on the surface of PSf which improved the permeability flux and showed better antifouling performance during the removal of bovine serum albumin (BSA). The composite membrane demonstrated better performance as compared to the native PSf membrane due to the strong electrostatic repulsion (under acidic condition). However, the rejection performance was almost same as PSf substrate membrane. The improvement of this work were continued by Fan and co-researchers (Fan et al. 2008b) throughout the phase inversion by using blended PANI nanofibers membranes in order to improve the hydrophilicity and permeability for the rejection of BSA and albumin eggs. In addition, to obtain better porosity and membrane properties, different PANI-PS mass ratios was studied and reported that the blended membranes showed better performance in term of permeability, flux decline rate, mechanical and thermal stability compared to the PS membrane. Similar studies on the BSA ultrafiltration has also been investigated by Zhao et al. 2011 on the preparation of PSf/PANI nanocomposite using in situ blending method via immersion phase inversion process using a solvent; N-methyl-2-pyyrolidone (NMP) and oxidant with ammonium peroxydisulfate (Zhao et al. 2011a). The behavior of PANI in the form of oligomers and nanospheres demonstrates that the improvement in membrane porosity along with surface size, hydrophilicity, strength and thermal stability were contribute by using large portion of PANI oligomers and small portion of PANI nanospheres. Experimental results established that pure water fluxes were found 1.7–4.1 times higher compared to the PSf membranes and BSA rejections were above 96% with the slower flux decline rate. The hydrophilic surface, higher porosity, larger pore size as well as wider pores beneath the skin layer, less acicular pores, thicker skin layer, better vertically interconnected finger-like pores and less macrovoids than PSf membranes were analysed using characterization studies.

Another emeraldine base polyaniline (PANiEB) as the additive has been used to synthesize PSf-PANiEB membrane using immersion precipitation technique. The prepared composite membranes showed stable pure water flux at 0.30 MPa TMP and slower pure water flux decline at 0.5 MPa TMP than PSf-polyvinylpyrrolidone (PVP) membranes (1.7–2.8 times pure water fluxes) compared to the PSf membrane. The rejections of BSA, EA and trypsin were also studied and demonstrated superior antifouling performance as compared to PSf membrane (Zhao et al. 2011b). To enhance antifouling property, the ultrafiltration PES membrane of (PANI)/phosphor molybdic acid (PMA) nanoparticles was developed on the protein rejection followed by protonation method (Teli et al. 2012). The effect of various concentrations of PANI-PMA nanoparticles (0–7 wt.%) together with a solvent (DMAc) were studied during the preparation of membranes. The studies of physic-chemical properties confirmed the improvement in contact angle, water flux and flux with rejection of protein in all membranes by increasing nanoparticle concentrations (in the range of 0, 2, 3, 5 and 7 wt.% into casting solution). The prepared PES–PANI/PMA membrane thus, exhibited better antifouling performance along with high protein rejection rate (>98.8%).

9.5.2 Treatment of Heavy Metal Ions

Water pollution through heavy metal pollutants (e.g. arsenic, zinc, lead, copper, mercury, nickel, cadmium and chromium etc.) has become a burning issue of the world. The metal ions not only affected human being but also flora and fauna (Long et al. 2002). The main cause of environmental contamination in industrializations and urbanization is due to all these contaminants discharged to the water bodies (e.g. sea, river and lack etc.) and severely disturbing the aquatic environment (Pereira et al. 2010; Chen et al. 2006; Barbieri et al. 2000; Rawat et al. 2009). Even a trace concentration of metal pollutant is risky to living beings (Jamil et al. 2010; Khan et al. 2008; Singh et al. 2010; Peng et al. 2004). Therefore, it became a challenging task to pay attention towards the analysis of heavy metal ions in bodies and industrial effluents. A number of methods have been applied for removal and recovery of metal pollutants (Kurniawan et al. 2006; Fu and Wang 2011; Nabi et al. 2010, 2012b; O'Connell et al. 2008). Among them methods membrane filtration is considered the best method for the treatment of heavy metal ions (Wernisch et al. 2013).

Pereira et al. developed UF membrane by the reaction of polystyrebe-co-maleic anhydride (H-PSMA) and PANI nanofibers (Pereira et al. 2014). Several concentrations of PANI nanofibers were used during the synthesizing the composite membrane to enhance the hydrophilicity of PVDF. The increasing on the properties such as hydrophilicity, porosity, water uptake and permeability and the rejection of toxic metal ions (specifically for Pb^{2+} and Cd^{2+}) was effectively performed which demonstrated better performance with 1.0 wt.% of PANI nanofibers and has good rejection potential 98.25% and 97.38%, respectively for Pb^{2+} and Cd^{2+} ions.

The coating of TiO_2 nanotubes with PANI was prepared using oxidative polymerization to produce the PSf UF membrane (Pereira et al. 2015). The study on the effect TiO_2 concentrations (0–1.5 wt.%) was carried out to observe the improvement in membrane structure and performance. The membranes revealed better hydrophilicity, improved permeability, enhanced porosity, water uptake and good antifouling ability compared with neat polysulfone membranes. Based on the heavy metal ions studies, it showed 83.75% and 73.41% rejection during the filtration process while, 68% and 53.78% rejection rate using polyethyleneimine (PEI) for Pb^{2+} and Cd^{2+}, respectively. Similar study was also reported by the synthesis of PANI/Fe_3O_4 nanoparticles to prepare the PES membrane for removal of copper (Cu^{2+}) ions (Daraei et al. 2012). The prepared membrane covered 75% removal efficiency of Cu (II) ions in low concentration of feed solution. The results of characterization studies suggested the adsorption mechanism was dominating during rejection of ions and the regeneration results established the reusability and durability of nanocomposite membrane during filtration.

9.5.3 Separations of Salt and Oil-Water

Composite membrane are playing key role in the separation of salt and oil-water from industrial effluents and wastewaters. The optimisation of blended PES/PANI membranes was predicted by using response surface method (RSM) via central composite design (CCD) to improve the PES structure and performance during salt rejection (Razali et al. 2013). Under reported optimal conditions with 18.33 wt.% PES and 0.75 wt.% PANI, 1.34 min of evaporation time was achieved which showed strong interaction between the variables of PES concentration, PANI concentration and evaporation time. On other hand, mixing of nanoparticles evidently improved membrane surface roughness and showed the highest charge at low and high pH with iso-electric point at pH 3. Thus, optimized membrane demonstrated an enhancement in the membrane structure. Mixed matrix of PES-PANI-co-MWCNTs composite membrane was fabricated using casting solution technique (Bagheripour et al. 2016). The effect of membrane structure and performance of PANI was examined for the different concentrations of PANI-co-MWCNTs. The modified composite membrane showed better improvement in the performance of salt rejection and water flux.

Liu et al. studied the surface modification of PVDF commercial membranes by one-step dilute polymerization at low temperature of PANI (Liu et al. 2016). The rough micro-nano structures was uniformly and firmly developed onto the membrane surface and leads to be underwater superoleophobicity with low oil adhesion characteristic once coated with PANI nanofibers. The results showed that the PANI grafted PVDF membranes was effective for the removal of surfactant-stabilized emulsions which demonstrated the high oil rejection, and stable even after ultrasonication and immersing in oils and several cycles of harsh conditions. Some important PANI based nanocomposite membranes and their applications in diverse fields including on water purification together with the treatment methods are listed in Table 9.3.

9.6 Conclusions and Outlook

Current investigations indicate successful removal of various pollutants from aqueous solution using nanocomposites membrane. The uses of PANI as one of the conducting polymers as nanocomposite membranes were predominantly produced by physical blending with conventional polymeric membranes (such as PSf, PES and PVDF). In comparison to the extensive used of PANI as conjugated polymer in adsorption and ion exchange treatment methods, different types PANI based nanocomposites membranes are required to develop novel composite membrane for membrane process in wastewater purification. Thus, PANI supported nanocomposite materials can also be effectively used in the form of membrane to

Table 9.3 Treatment methods applied for different PANI based nanocomposite for water purification

Treatment methods	Composite material	Pollutants	References
Adsorption	PANI salt/silica	Anionic dye (acid green 25)	Ayad and El-Nasr (2012)
	PANI/SBA-15	Polycyclic aromatic hydrocarbons	Gholivand and Abolghasemi (2012)
	PANI/Cobalt-Prussian blue analogues (Co-PBA)	Rb^+ ions	Moazezi and Moosavian (2016)
	PANI zirconium (IV) silicophosphate (PANI-ZSP)	Methylene blue dye	Gupta et al. (2014)
	PANI/γ-Fe2O3	Cr (VI) and Cu (II) ions	Chávez-Guajardo et al. (2015)
	PANI/Ti (IV) arsenophosphate	Toxic metal ions and organic contaminants	Bushra et al. (2014a)
Ion exchange	PANI/α-zirconium phosphate (α-ZrP)	Pb^{2+} ions	Du et al. (2016)
	PANI/Sn (IV) tungstomolybdate	Pb^{2+} ions	Bushra et al. (2015)
	PANI/Cobalt hexacyanoferrate (CoHCNF)	Cs (I) ions	Yousefi et al. (2015)
	PANI-Cl^-, PANI-ClO^{4-}, PANI-SO_4^{2-}	Nitrate ions	Hojjat Ansari and Basiri Parsa (2016)
	PANI/zirconium (IV) arsenate	Toxic metal ions	Nabi et al. (2012a)

treat industrial wastewaters systems especially for the heavy metal ions and dyes removal.

Acknowledgments The authors wish to thank Universiti Sains Malaysia (Research University Grant) (1001/PJKIMIA/814269) for the financial support throughout this study. Faraziehan Senusi gratefully acknowledges the generous financial support from Ministry of Higher Education (MOHE) and Universiti Teknologi MARA (UiTM) for her study leave.

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Chapter 10

Plant-Bacterial Partnership: A Major Pollutants Remediation Approach

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Abstract Environmental pollution due to global industrialization and urbanization has become a serious matter of concern for human inhabitants throughout the world. As safety point of human health and environmental issues, it required an efficient removal for the sake of minimized inlet of these hazard materials into the food chain generated by organic and inorganic pollutants. The physical and chemical means need specialized equipment, labor intensive and highly costs inputs which make less familiar to remove the pollutants, but it seems biological methods especially phytoremediation, gaining comprehensive remedial measure approach. The green technology based Phytoremediation carried out the process with the help of altogether action of plants and their specific attached microbial communities to remove, transform, degrade or immobilize various toxic organic and inorganic contaminants deposits in soil and polluted water and air pollutants could be treated well with this approach which is nowadays publicly high acclaimed, less disturbance to the environment remediate various form of pollutants and lower cost investment input. The symbiotic nature of plants combination with related beneficial bacteria (rhizobacteria or endophytic) offers tremendous potential as bacteria possess set of catabolic genes which produce catabolic enzymes to decontaminate complex organic compounds and inorganic pollutants with an effective way and in return of these bacteria increase plant growth promoting activities and gain more biomass in the plants. This chapter highlighted the remediation approach of major pollutants by phytoremediation with the main focal point on rhizoremediation and plant-bacterial partnerships and discuss how to improve the efficiency of phytoremediation by various approaches.

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M. Oves et al. (eds.), *Modern Age Environmental Problems and their Remediation*,
DOI 10.1007/978-3-319-64501-8_10

Keywords Phytoremediation • Plant growth promotion • Biodegradation • Rhizobacteria • Endophytic bacteria

10.1 Introduction

The parsimonious nature of human activities, such as exploration, extraction, refining, storage and transportation of a wide range of chemicals, etc. to meet his full desire at the cost of our polluted environment which indirectly adversely affect the biosphere of our planet system (Ololade 2010; Khan et al. 2013a, b). Somehow, it is estimating approximate 30% of the terrene environment threatened to contaminate which directly adverse our agricultural production land and the surrounding environment, and this figure is still rising on (Alloway and Trevors 2013; Valentín et al. 2013). Along with the widespread dispersal of the latest version of persistent organic pollutants (POPs) such as polybrominated diphenyl ethers, polychlorinated naphthalenes and per fluorooctanoic acid, etc. paid to us alert attention (Lohmann et al. 2007).

The higher toxicity and bioaccumulation factor of these anthropogenic environmental contamination concerned adverse effects on environmental and human health hazards which are our prime duty to arrange another alternative way so that it recede up to some levels of entered these toxics components into our food chain network. The conventional way to remediate heavily polluted sites by categorized under chemical and physical methods shown the successful result in smaller areas but in addition to need special machinery and more labor requirement further added more costly approach (Segura et al. 2009). However, the various types of bioremediation which are based upon the utilization of living organisms and their bi-products to clean up or stabilize various forms of inorganic/organic contaminants present in our ecosystem. Among them phytoremediation seem to be promising remedial strategies, higher public acceptance, an eco-friendly and cost-effective approach that utilizes selected or genetically engineered plants which are capable to customize the major pollutants present in the biosphere (Salt et al. 1998; Chigbo and Batty 2014; Samardjieva et al. 2015; Susarla et al. 2002; Khan et al. 2013a, b). As we know Plant work like as a "green liver" to produce various types of contaminant-degrading enzymes that digest, transform and overcome these pollutants prevails in the environment into less toxic form and thus restore the quality parameters of soil medium which directly benefits to enhance biomass, bio-fuel production, and biodiversity of our ecosystem. (Dietz and Schnoor 2001; Pilon-Smits 2005; Couto et al. 2011; Basumatary et al. 2012). The manipulation and handling nature of the bacteria culture are easier than plants system and former one the natural way transfer of beneficiary genes among closely related to bacteria species is commonly occurrence process. The plant has always remained burning issue about ethical concern matter for consumption of genetically modified crop, but with respect to bacteria, till date, there is no issue with it. Additionally, the availability of vast knowledge of information for metabolic pathways employed in microbes as well as plant system and feature of microorganism-plant cross-talk interaction gives us an opportunity for valuable tools to assist phytoremediation. Therefore in this chapter, the authors addressed the current knowledge of the plant–bacteria partnerships and its utilization for phytoremediation basic processes with special stress upon rhizobacteria and endobacteria so that it enhanced the removal of various contaminants and toxic metals exist in the polluted environment to revitalize the ecosystem.

10.2 Mechanism of Phytoremediation of Various Pollutants in Soil

There is sequential process involve in Phytoremediation for removal of organic and inorganic contaminants from soil. Firstly the involvements of the phytoimmobilization process take place with the help of plant's roots zone in which they absorb these contaminants present in the soil. Secondly, the phytoextraction/accumulation process involves that transporting and concentrating the contaminants in the aerial part of the plant. In some cases it undergoes phytovolatilization process depend upon the nature of pollutants to allow transpired to the atmosphere through leaf stomata. Thirdly phytodegradation process involves in which contaminants metabolized inside the plant in three sequential phases such as transformation, conjugation, and compartmentalization. The chemical modification takes place with the help of oxidation, reduction, and hydrolysis reactions converted into hydrophilic and water soluble of these contaminants with the help of involvement of various enzymes such as cytochrome P450, carboxylesterases, peroxidases, and flavin-dependent monooxygenases, etc. in the transformation phase. It further modify to add small molecular weight endogenous molecules like sugars or peptides with the help of enzymes such as glycosyltransferases and glutathione S-transferases to make contaminant less phytotoxic, followed by compartmentalization phase where destiny of the treated contaminant take positioned in the various compartments such as vacuole, peroxisomes, Golgi apparatus, mitochondria, cell wall or excretion from the cell of the plant system. The properties of the contaminant compound like its level of solubility in the water, octanol-water partition coefficient, molecular mass, optimum temperature, pH level, content of organic matter, moisture level and finally features of the target plant i.e., configuration of root structure and catalytic active site on enzymes etc decide the success level of these sequential process (Suresh and Ravishankar 2004; Susarla et al. 2002).

10.3 Advantages and Limitations of Phytoremediation

The attractive advantage of phytoremediation technology is that it is less expensive in term of a cost factor as it requires low inputs needs such as sunlight, water and carbon dioxide and negligible zero maintenance for their optimum growth and development (Dzantor 2007; Olson et al. 2008). It is highly acceptable in public places due to its minimum site disturbance factor and more aesthetically pleasant as a comparison to other conventional remediation methods like excavation and removal or chemical stabilization (Schnoor et al. 1995; Glass 1999; Weyens et al. 2010a, b; Nesterenko-Malkovskaya et al. 2012). The result of synergetic effects cause by uses of pioneer plants in phytoremediation process not only in environmental cleanup but also make to us a way to restore the ecosystem up to some level (Hao et al. 2014a, b).

The constraints associate with this large scale field application of phytoremediation technology as it is time-consuming process, lower biomass of hyperaccumulator species, the sensitiveness of plant involved in remediation to high concentrations of environmental pollutants present, abiotic stressors including salinity, drought, flooding etc and in the rarest case, an unacceptable tolerance the increment level of evaporated harmful and poisonous volatile organic contaminants escaped to our surrounding atmosphere (Huang et al. 2004; Chaudhry et al. 2005; Peng et al. 2009; Gerhardt et al. 2009; Zhang et al. 2012). Moreover, it is considered as slow and incomplete due to limitations in plant metabolic capacities, rooting depths, and the seasonality of plant growth (Abhilash et al. 2012). The efficacy of phytoremediation varies with environmental conditions, physicochemical properties of the soil system, bioavailability of the contaminant due to its small molecular weight and hydrophobic properties and the variation of seasonal temperature (Segura et al. 2009; Wyszkowski and Ziolkowska 2009). Moreover, these bottlenecks may be a solution by growing depth plantation in the soil as well as an amendment with adding materials like lime, compost, chelators, surfactants, etc. to make the pollutant more bioavailable which further make it expensive.

10.4 Transgenic Approach for the Solution of Phytoremediation

Nowadays developed candidate transgenic plants by transferring genes involved in the catabolise and mineralization of xenobiotic pollutants, obtained from other sources of an organism like bacteria/fungi/animals/other organisms has alleviated some problems associated with phytoremediation measure (Eapen et al. 2007). It reported the successful upregulation of those metabolic pathway genes involved in the degradation of pollutants in a transgenic plant like tobacco, rockcress, mustard, poplar, rice, potato etc which further enhanced the process of phytoextraction, phytovolatilization and phytodegradation of heavy metals and organic contaminants like explosives, chlorinated solvents, various herbicides and atrazine (Van Aken et al. 2004; Cherian and Oliveira 2005; Rylott and Bruce 2009; Panz and Miksch 2012). Hybrid poplar (*Populus* sp.) and Yellow poplar (*Liriodendron* sp.) known as rapid in growth rate, higher in transpiration rate and pollutants tolerant tree which has a tendency to translocate the pollutants from soil to the shoot, consider emerging genetically engineered species for phytoremediation. However, the norms and conditions designed by the European Union don't allow commercialization for *in situ* applications of genetically modified organisms. Thus, till date, most of the promising results obtained from the study had done only in the experiments performed in laboratory and greenhouse conditions.

10.5 Assisted-Phytoremediation

To efficacy, the performance of plant-based phytoremediation, the utilization of plant-microorganisms partners relationship played the nature-based method for the cleanup and prevention of environmental pollution. This relationship uses natural way to disintegrate, transform or bioaccumulate these pollutants that prevent their entry into food chain network, increased the plant biomass level, better management practice and improve plant growth (Weyens et al. 2009a, b, c; Chen et al. 2013; Afzal et al. 2013). The combined use of suitable plants and various forms of pollutants degrading bacteria has promised advanced approach to enhance the phytoremediation efficiency (Afzal et al. 2014b; Arslan et al. 2014; Khan et al. 2013a, b; Shehzadi et al. 2014). As plants provide residency area space and free available nutrients to their associated bacteria for their growth, proliferation, and colonization (Yang and Crowley 2000; Zhang et al. 2014). In turn of it, the pollutant-degrading pathways type of bacteria promotes the growth of the plant and its development by the degradation and detoxification of these pollutants as well as enhanced the innate plant defense system without causing any pathogenicity effect (Naveed et al. 2014; Sessitsch et al. 2005). Therefore, this type of Phytoremediation that need minimal site disturbance for work, lower maintenance cost input and no harm to environment reflect the valuable and effective alternative for the treatment of diffuse pollution of large contaminated areas. To improve the phytoremediation of soil contaminated with different organic and inorganics pollutants, recently, the extensively studied on plant–bacteria partnerships focused on the diversity level of bacteria present in the rhizosphere and endosphere zone of different plants (Siciliano et al. 2001; Yousaf et al. 2010a). It reported the successful fixation of inhabitants RB and EB in different compartments of the plant has considering an emerging technology to promote the efficient of phytoremediation process (Nie et al. 2011; Yousaf et al. 2011; Afzal et al. 2012; Wang et al. 2012).

10.6 Effectiveness of Phyto- or Microbial-Remediation

The mutual plant-microbe partnerships always remain the successful journey for remediation of various form of contaminants which had evidenced by lot of work done on the rhizosphere (Ma and Burken 2003; Ma et al. 2004), the phyllosphere (Eapen et al. 2007) and inside the plant (Schröder and Collins 2002; Burken and Schnoor 1998; Kuiper et al. 2004; Cherian and Oliveira 2005). Among microbes, the bacteria always prefer for the phytoremediation as these are commonly found in the environment and plays crucial role in the substantial degradation of pollutants present in the soil, water and air system (Yergeau et al. 2009; Yousaf et al. 2010a; Al-Awadhi et al. 2012; Ali et al. 2012). The growth rate and elicitation of responses in host plants of a bacterial culture very fast as compare with fungal cultures (Wang et al. 2015). In addition, the bacteria decrease the toxicity up to some level and also prevention the escape of the pollutants to the environment. Therefore, the scale of effectiveness for phyto- or microbial-remediation in toxic and devoid of nutrient rich environments depends upon various factors which are following:

10.6.1 Soil Physio-chemical Properties

The optimum conditions for the growth and development of the plant as well as conducive environment for the survival, multiplication and modulate upregulate the expression of genes involve in the degradation pathways present in the inoculated bacteria, need the physical and chemical properties of the soil like pH value, the shape, size and texture of soil particle, cation exchange capacity, surface tension and humus content present to obtain efficient phytoremediation (Labana et al. 2005; Kaimi et al. 2007; Sun et al. 2010; Schulz et al. 2012). Afzal et al. (2011) observed loamy soil decide the significantly higher level of colonization and also induced maximum levels of gene expression concerned with two Hydrocarbons based pollutants degrading bacterial strains inhabitant in the different compartments of Italian ryegrass. The functional characteristics and elevate the expression levels of HC-degrading genes residents in the rhizosphere is highly influenced by the soil salinity. This study reflects that type of soil acts as a detrimental factor to decide the proportionate of bacterial colonization and metabolic activities and henceforth the biodegradation of pollutants.

10.6.2 Availability of the Toxic Contaminants

The solubility and bioavailability of hydrocarbons (HC) highly depend upon the content of humic substances and clay minerals present in the soil composition (Richnow et al. 1995; Sijm et al. 2000; Chung and Alexander 2002; Parrish et al.

2005). In addition to it, the level of bioavailability of HCs extends up to some levels if added some organic amendments to HC contaminated soils that directly affect microbial population so that we get effective phytoremediation treatment. (Cheng et al. 2008; Williamson et al. 2009; Wang et al. 2012). To remediate the problems of heavy metals, there are metal- resistant microbes which has a tendency to increment the plant development along with suppressing the metal toxicity in the plant, involve in the metal translocation from soil and accumulate to the organelle compartment of the plant cell (Li et al. 2012).

10.6.3 Bacterial Inoculation Approach

The level of optimal remediation obtain by bacterial colonization in the plant grow in the polluted soil of hydrocarbon contaminant highly correlate with what type of bacterial inoculation approaches such as seed inoculation and soil inoculation we follow. Afzal et al. (2012) reported the soil inoculation found more desirable than seed inoculation for effective phytoremediation of HC contaminated soil. Furthermore, the selection of effective contaminant-degrading bacteria is often affected by a variety of factors, including competition for the space of microbial population, temperature variation and scarcity of nutrients level (Chen et al. 2005). The bacteria residents in the plant system lead to increase the biomass production, improve the soil structure and plant resistance power against contaminant stress. In turn of it, plant gifted the enhancement of favor bacteria population and increased the potency of HC pollutants (Susarla et al. 2002; Abhilash and Yunus 2011; Ma et al. 2011).

10.6.4 Plant Species and Traits

Some plants like grasses have tendency to cope up the surmount level of hydrocarbon type of pollutants as they possess extensive surface area of root system and greater penetration level into the soil surface (Tesar et al. 2002; Cofield et al. 2008; Yousaf et al. 2011; Afzal et al. 2012). During the vegetative growth stages of ryegrass (*L. multiflorum* L.), it observed the greater numbers of HC-degrading bacteria possessing *alkB* and *tol* genes (Nie et al. 2011). The phylogenetic related closely different strains of plants species, different developmental stages of plant and different compartments of plant decide the extent of survival level and metabolic activities of HC-degrading bacterial strains. For example Leguminous species generally known as heavy metal accumulator, removal the significant levels of organic pollutants i.e. polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and amide herbicides (Aprill and sims 1990; Narasimhan et al. 2003; Fan et al. 2008; Hamdi et al. 2007; Li et al. 2013; Hao et al. 2014a, b).

10.6.5 The Diversity of Microbial Communities

The diversity and richness of the indigenous soil microbial communities are highly variable, depending mainly on the plant genotypes, plant development stage, inoculums density, contaminant amount, and soil physicochemical properties (Segura et al. 2009).

10.6.6 Physicochemical Characteristics of Pollutants Compounds

The uptake of pollutants compounds in plants depends on various physicochemical characteristics such as octanol–water partition coefficient (log K_{ow}), acidity constant (pKa), aqueous solubility (Sw), octanol solubility (So), and the levels of the pollutant (Admire et al. 2014; Alkorta and Garbisu 2001; Zhan et al. 2015). Out of these characteristics, the role of log K_{ow} value is an important determine of the compound whether it is hydrophobic or lipophilic. Mostly, the plants took up the compounds having the range the value of log K_{ow} from 0.5–3.0.

10.6.7 Bioavailability of Mineral Nutrients

The presence of organic pollutants causes the limited availability of mineral nutrients like nitrogen, phosphorous and iron content in the soil which directly affected the growth of the plant (Kirk et al. 2005; Kechavarzi et al. 2007; Nie et al. 2011). Zhou et al. (2009) reported Maximum HC degradation observe if the higher presence of phosphorous and water contents in the soil. Furthermore, the exogenous supply of organic manure and NPK fertilizer supplement in HC polluted soils increased the growth of the plant and speed-up the process of HC degradation (Bordoloi et al. 2012; Jidere et al. 2012; Song et al. 2012). It observed the presence of nitrogenase enzyme in plant-associated bacteria reduced the atmospheric nitrogen into ammonia form, which support plants growth under a lower level of nitrogen content in the site of contaminated soil (Doty 2008; Weyens et al. 2009b, c).

10.7 Remediation by Plant-Associated Bacteria

The tendency of those bacteria that associated with plant like rhizobacteria (RB) and endophytic bacteria (EB), have involving in the optimum level of biodegradation process of toxic organic compounds present in the polluted infested soil and could have emerging scope to extent the level of improved phytoremediation (Siciliano et al. 2001; Germaine et al. 2006, 2009; McGuinness and Dowling 2009; Weyens et al. 2009c; Yousaf et al. 2010a; Afzal et al. 2012). RB target the root environment and take shelter where they active participation in the biodegradation process of various contaminants (Alkorta and Garbisu 2001; Glick 2003; Abhilash and Yunus 2011; Afzal et al. 2011). EB residents in the internal tissues of the plant confer no pathogenic issue to their host (Compant et al. 2010).

10.7.1 Rhizoremediation

Genus *Rhizobium* is considering the most abundant member of the degrading microcosm that prefers habitat to the close vicinity of the root surface of the host plant and helps to maintain the proper functioning of the ecosystem. The famous characteristic of these *Rhizobia* bacteria has nitrogen fixation and promoting the growth feature of the plant that enhances the plant biomass, maintain the fertility of soil, bioavailability of contaminants, the uptake, and transfer of pollutants from soil to plant and degradation of contaminants to non-toxic/less-toxic compounds. These rhizobia traits could fill the gap associated with plants based remediation known as Rhizoremediation for the effective destruction of contaminants residue that involves the synergetic effects of multiple interactions obtained from roots, root exudates, soil of residential rhizosphere and microbes (Gaskin and Bentham 2010; Hao et al. 2014a, b). The plant root exudates released exoenzymes and nutrients for the stimulation of colonized rhizosphere microbial population as well as protection covered against various abiotic and biotic stresses (Kuiper et al. 2004). In return of it, rhizospheric microorganisms enhance the growth rate of the plant through nitrogen fixation cycle, immobilization of nutrients, promote the key pathways involve in the production of plant growth regulators and suppress the negative impact of toxic pollutants on the plant growth (Chaudhry et al. 2005; Segura et al. 2009). Apparently, these symbiotic mutual interactions in the close vicinity of roots compared to bulk soil cause escalated the diversity of those microbes that it can express key metabolite pathways for degradation of the complexity of contaminants (Ramos et al. 2000; Kent and Triplett 2002).

The rhizosphere microbes remain the attractive approach for degradation process as it is generally aware that the mineralizations of hydrocarbon skeleton come from various form of contaminant during bioremediation significantly raise the deposition level of organic carbon in the soil which create imbalance of C/N level (Moreto et al. 2005; Dashti et al. 2010). But the present rhizobia bacteria at root surface of specific plant exert direct or indirect impacts in the multiplication of specific contaminant degrading microbial communities in the rhizosphere to facilitate the restoration (Smalla et al. 2006; Hartmann et al. 2008; Cebron et al. 2011; Li et al. 2013). The prevail competition exist with localized indigenous microorganisms cannot survive and not succeed in the bioremediation of existing pollutants in the soil environment. However, potential benefits of Rhizobacteria

(RB) able to degrading organic and inorganic pollutants and promote the growth of plant-specific family that could provide lower budget, eco-friendly, efficient and non-invasive Rhizoremediation technology for the twenty-first century (Weyens et al. 2009c; Glick 2010; de-Bashan et al. 2011; Turan et al. 2012).

10.7.2 Rhizosphere Colonization

The plant roots secreted large amounts of exudates which are photosynthetically derived lower molecular weight organic compounds consisting of lactic acid, oxalic acid, succinic acid, fumaric acid, malic acid and citric acid, amino acids, enzymes, simple and complex carbohydrates etc in the vicinity of roots and make suitable condition for the attraction of beneficial contaminant degrading bacteria to aggressively colonize the root surface (Jones 1998; Knee et al. 2001; Shim et al. 2000; Reichenauer and Germida 2008). Phillips et al. (2012) reported certain compounds (acetate, alanine) present in the composition of root exudates responsible for enhanced mineralization capacity, which directly affect the success of a given phytoremediation treatment of a HC contaminated soil while malonate decreased mineralization process. The amount and composition of root exudates is specific to plant family or species which also depends on the properties of the soil (Paterson and Sim 2000; Bais et al. 2006).

Beside root exudates, plants also releases secondary derive metabolite including terpernes, flavonoids and some lignin-derived components in which their motif structure similar to those HCs cause shifts in microbial metabolism of HC and elicit the over expression of HC-degrading genes in bacteria anchorage at rhizosphere zone (Tesar et al. 2002; Singer et al. 2003; Sun et al. 2010). These flavonoids also involve in the signals cascade pathway involve in the plant–microbe interactions (Steinkellner et al. 2007). Normally, the plant derive secondary metabolite also biodegraded by RB produce organic intermediate compounds, such as resorcinol, phloroglucinol phenylacetic acid, cinnamic acid and protocatechuic acid through the β-ketoadipate pathway (Parke et al. 2000) and also degrade HCs (Kim et al. 2008). Similarly, salycilate, which enhances plant defense system against phytopathogens, has been associated to the microbial degradation of PAHs (naphthalene, fluoranthene, pyrene, chrysene) and PCB (Chen and Aitken 1999; Master and Mohn 2001; Singer et al. 2000), while terpenes induce the microbial degradation of toluene, phenol, and TCE (Kim et al. 2002).

10.7.3 Reclamation of Contaminated Soil by PGPR

The colonized RB exerts a beneficial effect on the plant termed as ‘plant growth promoting rhizobacteria’ (PGPR) which promoted the plant growth and biological disease control. However, some of the bacteria residing on rhizoplane can penetrate into plant roots, and some of them may migrate to aerial plant parts (Compant et al. 2010). To reclaim the polluted agricultural land with contaminated HCs, the application of PGPR is an appropriate approach of phytoremediation as it reduced the contaminant-induced stress level and promoted host plant growth (Weyens et al. 2009c). The enzyme *ACC deaminase* expressed in these PGPR functionally to decrease the stress level generated by the presence of contaminants (Glick 2003; Arshad et al. 2007; Glick et al. 2007). Teng et al. (2011) inoculated *Rhizobium meliloti* culture with alfalfa and observed stimulate the growth of indigenous HC-degrading rhizosphere microorganisms and increased plant biomass production. Hong et al. (2011) found positive correlation established in HC degradation, ACC deaminase activity and siderophore production by inoculation of a *Rhizobacterium gordonia* sp. S2RP-17 with *Z. mays* which grew on the diesel-contaminated soil. Recently, rhizoengineering has paid attention in which support the population of rhizobacteria by adopting many feasible strategies including nutrient adjustments, flavonoid regulations, and facilitating degradation by the inoculation of transgenic strains for removal of persistent organic contaminants (Fu et al. 2012).

10.7.4 Rhizodegradation of Hydrocarbons

The synergistic effects between the plants and inoculated bacteria make rhizodegradation of HCs more efficient as compared to alone microbial remediation and phytoremediation (without bacterial inoculation) (Gurska et al. 2009; Afzal et al. 2012). The plant has own regulatory machinery to select certain bacteria in their rhizosphere colonization by physical, chemical and biological properties of the soil to attract beneficial bacteria for efficient degradation of contaminants and rejection to other (Hartmann et al. 2008; Afzal et al. 2011; Hong et al. 2011; Yousaf et al. 2011). However, the intensity of relationship varies with other rhizospheric microorganisms and environmental conditions. The plant–rhizobacteria interactions enhance the abundance and expression of catabolic genes in the rhizosphere, leading to an increase in mineralization, degradation, stabilization, and/or sequestration of variety of organic compounds including POPs (Jha and Jha 2015; Passatore et al. 2014; Sprocati et al. 2014; Yateem 2013). The hydrophobic nature of hydrocarbons reduces the availability of nutrients to the plants and microorganisms. It enhances the competition for available nutrients such as nitrogen, phosphorus, and potassium between plants and their associated microorganisms for plant growth and microbial proliferation. To explore the effects of nutrients on survival and metabolic activity of an alkane degrading rhizobacterium *Pantoea* sp. strain BTRH79 inoculated in Annual ryegrass (*Lolium multiflorum*) grown in diesel-contaminated soil, it observed improved plant growth and hydrocarbon degradation and these were further enhanced by exogenous supply of nutrients application (Arslan et al. 2014). It found the effects of two different nutrient levels directly associated with the abundance and expression of CYP153 gene in the rhizosphere of ryegrass.

Beside bacterial abundance in the rhizosphere, it provide a suitable condition for horizontal transfer of gene and gene rearrangements that lead to increase the diversity levels of variety of catabolic enzymes which can metabolize and detoxify the ranges of complex xenobiotics as well as organic pollutants (Hong et al. 2015; Singer et al. 2003; Xun et al. 2015). Till date, it reported many successful examples of RB application for the phytoremediation of crops grown in the HC contaminated soil. Such as alfalfa, ryegrass, birdsfoot trefoil, sorghum, maize, Bermuda grass, legumes and beggar ticks (Kaimi et al. 2007; Shirdam et al. 2008; Tang et al. 2010; Yousaf et al. 2010b; Hall et al. 2011). For example, root activities of alfalfa and perennial ryegrass enhanced the population of RB possessing HC degradation capability (Kirk et al. 2005; Schwab et al. 2006; Sorkhoh et al. 2010). Similarly in the rhizosphere of goosegrass (*Eleusine indica*), vegetated in HC contaminated soil observed 72 times greater bacterial numbers than in the unvegetated soil (Lu et al. 2010). The colonized microorganisms survived at plants of reed (*Phragmites australis*), bulrush (*Scirpus tripueter*), galingale (*Cyperus rotundus*) and wild rice (*Zizania latifolia*) grow in the soil polluted with diesel observed increase the tolerance capacity and biodegradation activity (Cao et al. 2012). Villacieros et al. 2005 reported the degradation of a variety of PCBs enhanced when alfalfa made partner with *Pseudomonas fluorescen*ce sp. strain F113 and Arabidopsis with *Pseudomonas putida* strain Flav1-1. If alfalfa inoculated with a symbiotic N_2-fixing rhizobacterium, *Sinorhizobium meliloti* strain A-025, it enhanced the biotransformation of many aroclor compounds (e.g., 1242, 1248, 1254, and 1260) (Mehmannavaz et al. 2002). To date, many successful cases of phytoremediation of various organic contaminants using rhizospheric bacteria are mentioned in Table 10.1.

10.8 Legume-Rhizobia Symbiosis Relationship

To the removal of heavy metal and metalloid ions and increased in the plant biomass, phytoremediation aided by legume-rhizobia symbiosis seems promising capacity for its removal (Chen et al. 2008). The collaborative system of this rhizobial metabolism increased: (i) the bioavailability and shifting of metals from soils to plants (ii) microbial extracellular secretion of siderophores and enzyme that actively involve in the transform the higher toxic redox state of metals to lower level (Hao et al. 2014a, b; Wani et al. 2007); and (iii) the excessive production of the leguminous biomass and bioaccumulation of lower toxicity of metals in plants (Carrasco-Gil et al. 2013). Hao et al. (2012) attempted to identify the metalloid resistance genes so that it promotes host plant growth as well as aiding phytoremediation in a draft genome sequence.

Table 10.1 Successful remediation of hydrocarbon pollutants by combined use of plants and rhizobacteria

Plant named	Rhizobacteria	Bacterial characteristics	References
Maize (*Z. mays* L.)	*Pseudomonas* sp. UG14Lr	Hydrocarbon degradation	Chouychai et al. (2012)
Italian ryegrass (*L. multiflorum* var. Taurus)	*Pantoea* sp. strain BTRH79	Hydrocarbon degradation and ACC deaminase activity	Afzal et al. (2012)
Sesbania cannabina	*Microbacterium foliorum*,*Gordonia*, *alkanivorans*, and *Mesorhizobium*	Hydrocarbon degradation	Maqbool et al. (2012)
Alfalfa (*M. sativa* L.)	*R. meliloti* (strain ACCC 17519)	Hydrocarbon degradation	Teng et al. (2011)
Maize (*Z. mays* L.)	*Rhizobacterium gordonia* sp. S2RP-17	Hydrocarbon degradation, ACC deaminase and siderophore synthesizing activities	Hong et al. (2011)
Sorghum (*S. bicolor*)	*Sinorhizobium meliloti*	Hydrocarbon degradation, auxin production	Golubev et al. (2011)
Ryegrass (*L. multiflorum*)	*Acinetobacter* sp. strain	Hydrocarbon degradation	Yu et al. (2011)
Italian rye grass (*L. multiflorum* var. Taurus) and birdsfoot trefoil (*L. corniculatus* var. Leo)	*Pantoea* sp. strain BTRH79, *Pseudomonas* sp. strain ITRH76	Hydrocarbon degradation	Yousaf et al. (2010b)
Winter rye (*Secale cereale* L.), alfalfa (*M. sativa* L.)	*Azospirillum brasilense* SR80	Hydrocarbon degradation, indole-3-acetic acid production	Muratova et al. (2010)
Italian rye grass (*L. multiflorum* var. Taurus)	*Rhodococcus* sp. strain ITRH43	Hydrocarbon degradation	Andria et al. (2009)
Sorghum (*S. bicolor* L. Moench)	*S. meliloti* P221	Phenanthrene degradation, indole-3-acetic acid production	Muratova et al. (2009)
Maize (*Z. mays* L.)	*P. putida* MUB1	Hydrocarbon degradation	Chouychai et al. (2009)
Annual ryegrass (*L. perenne*), tall fescue (*F. arundinacea*, var. Inferno), barley (*Hordeum vulgare*)	*Pseudomonas* strains, UW3 and UW4	ACC deaminase production	Gurska et al. (2009)
Rice (*Oryza sativa* L.)	*Acinetobacteria* sp.	Hydrocarbon degradation	Li et al. (2008)
Barley (*H. sativum* L.)	*P. putida* KT2440	Hydrocarbon degradation	Child et al. (2007a)

(continued)

Table 10.1 (continued)

Plant named	Rhizobacteria	Bacterial characteristics	References
Barley (*H. sativum* L.)	*Mycobacterium* sp. strain KMS	Hydrocarbon degradation	Child et al. (2007b)
Wheat (*Triticum* spp.)	*Pseudomonas* sp. GF3	Phenanthrene degration	Sheng and Gong (2006)
Wheat (*Triticum* spp.)	*A. lipoferum* sp.	Hydrocarbon degradation and indole-3-acetic acid production	Muratova et al. (2005)
Common reed (*P. australis*)	*P. asplenii* AC	ACC deaminase production	Reed and Glick (2005)
White Clover (*T. repens* L.)	*R. leguminosarum*	Hydrocarbon degradation	Johnson et al. (2004)
Barley (*H. sativum* L.)	*P. fluorescens*, *P. aureofaciens*	Hydrocarbon degradation	Anokhina et al. (2004)
Barmultra grass (*L. multiflorum*)	*P. putida* PCL1444	Naphthalene degrading bacteria	Kuiper et al. (2001)

10.9 Shortcomings of the Rhizoremediation

Despite rhizobial remediation represents a low-input technology without requiring repeated inoculations of microbial agents, it has some pitfalls are as follows:

1. It is a slower process of remediation measure than *ex situ* treatments due to the fluctuation of various environmental conditions present in the field sites area such as the presence of competitive weed species, retarded plant growth in case of heavily polluted soil, phytopathogens effects and other biotic and abiotic stress.
2. It is suitable only in rooting zone and not responded at deeper subsurface layers of the soil.
3. Some toxic by-products compounds of microbial degrading contaminant bioaccumulate in plants, which make it unfit for consumption of that plant.
4. The compositions of root exudates fluctuate depend on plant growth stage, plant species as well as pollutant level which ultimately vary the level of remediation.

10.10 Endophytic Bacteria

Endophytic bacteria (EB) define as non-pathogenic plant growth promoting bacteria that naturally shelter inside the tissues of plants. It belongs to genera such as *Pseudomonas*, *Burkholderia*, *Bacillus* and *Azospirillum* commonly which is isolated from a variety of healthy plant species ranging from herbaceous crop plants and different grass species to woody tree species. The primary site for entry of endophytic bacteria into plants is the roots system. Hence they established the symbiotic, mutualistic and commensalistic relationships with their host plant (Ryan et al. 2008). Once penetrate into the plant, endophytes survive in specific plant tissues like the root cortex or the xylem or colonize the plant systematically by transport through the vascular system or the apoplast. It is considering seem as effective remedial measure over rhizospheric bacteria to improve phytoremediation and detoxification of contaminants as any toxic organic compound when traveled inside plant tissues after absorption, lead to decrease its phytotoxicity. The previous one rhizospheric bacterial population is difficult to control that lead to decrease the number of the desired strains which had selected for the metabolism of the pollutant. There is no problem of competition for nutrients and space exist between bacterial strains by the use of endophytes as it colonized the internal tissues of plants that interact more closely with their host without the eruption of any infection and are physically defend from abruptly changes in the environment conditions (Schulz and Boyle 2006). Along with pollutant degradation pathway, these bacteria have capability to promote directly plant growth mechanisms involving production of plant growth hormones such as auxins, cytokinins and gibberellins, suppression of ethylene production by 1-aminocyclopropane-1-carboxylate (ACC) deaminase activity cause lower stress level, siderophore production, stimulation of plant resistance mechanisms, synthesis of hydrolytic enzymes, nitrogen fixation and nutrient solubilisation such as phosphorus and other mineral nutrients that bring to efficient phytoremediation respond (Kloepper et al. 2004; Krechel et al. 2002). The indirectly benefit of these endophytic bacteria support the better survival of plant by preventing the downregulate of plant pathogens due to competition for space and nutrients, production of hydrolytic enzymes, antibiosis, activation of plant defense mechanisms and inhibition of enzymes and toxins secreted through plant pathogen. Many studies revealed that these bacteria could be used to supplement the metabolic potential of their host plant through direct degradation (Germaine et al. 2006; Phillips et al. 2008, 2009) as well as transfer of degradative type plasmids into other endophytes (Taghavi et al. 2005; Wang et al. 2007).

10.10.1 Endophytic Bacteria with the Capacity to Enhance HC Phytoremediation

The remediation measure for the wide range of xenobiotics by Plant–endophyte partnership have contributed significant level of effects on plant growth-promoting activities in the contaminated soil and water (Afzal et al. 2012; Ryan et al. 2008; Shehzadi et al. 2014).The plant absorbed toxic pollutants protected due to the innate immune system of colonized endophytic bacteria in root and shoot system and provide nutrients and residency to these bacteria (Afzal et al. 2014a, b; Rylott

2014). The characterization of isolated endophytes bacteria from different plants possess degradation potential of several organic contaminants including HCs (Siciliano et al. 2001; Germaine et al. 2006; Phillips et al. 2008; Yousaf et al. 2011).

Germaine et al. (2006) conducted the first laboratory study of the endophytic bacterium *Pseudomonas putida* VM1450 in the pea plant for the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D). To efficiently colonized towards the interior of root and shoot of the host plant and enhanced plant growth, a naphthalene-degrading endophytic bacterial strain, Pseudomonas putida VM1441, has been reported for naphthalene degradation (Germaine et al. 2009). Porteous Moore et al. (2006) studied the several endophytic strains of diverse bacterial communities found in poplar tree grow on a BTEX degraded contaminated site. Furthermore, Barac et al. (2009) demonstrated on the same site after remediation, it observed the detection limit of BTEX-concentration became meager low and the degradation capacity of the endophytic community disappeared during the normal original situation. Recently, the investigation proceeds for the diversity of the cultivable bacteria associated with English oak and common ash grown at the TCE-contaminated site and observed some of the strains showed increased tolerance to TCE and TCE degradation capacity. It is said in the literature that trees species like Poplar (*Populus* spp.) and willow (*Salix* spp.) are known famous for both biomass production and phytoremediation measure and the isolated endophyte bacteria from these trees had a tendency to fix nitrogen (Taghavi et al. 2005). The exposures of various compounds present in the plant/soil niche make some EB in different plants to tolerate and mineralize various organic pollutants as this organic pollutant-degrading capacity naturally exists in the EB (Barac et al. 2004; Germaine et al. 2006; Phillips et al. 2008; Weyens et al. 2009b; Afzal et al. 2011; Yousaf et al. 2011). The host Italian ryegrass shelter large number of phylogenetically distinct HC-degrading EB as compared to birdsfoot trefoil did not host such large number of EB. The reason is that hosting endophyte bacteria of ryegrass able to degrade alkanes release alkanes in the rhizosphere and plant absorb alkanes from the soil as sole carbon source (Marseille et al. 1999; Rojo 2009). Yousaf et al. (2010a) isolated different EB bacteria from the root and stem tissues of host Italian ryegrass and birdsfoot trefoil, capable of degrading HCs present in the HC contaminated soils. Sessitsch et al. (2012) isolated EB from the roots of rice grown in uncontaminated soil, has the potential to degrade the HCs contaminant site as these bacteria able to degrade alkanes as the sole source of carbon for its survival. Although RB-assisted phytoremediation of HCs has been extensively studied, but it reported on application of plant–endophyte partnerships for the phytoremediation of HC-polluted soils are comparatively less (Johnson et al. 2004; Peng et al. 2009; Cai et al. 2010; Afzal et al. 2011; Yousaf et al. 2011). Afzal et al. (2013) inoculated the endophytic bacterium, *Burkholderia* sp. strain PsJN, a plant growth promoting bacteria to three different plants species (*Acacia ampliceps, Eucalyptus camaldulensis, and Leucaena leucocephala*), vegetated in soil irrigated with secondary treated textile wastewater for one year and it observed the production of plant biomass and effective soil remedies measured in the treatment of *A. ampliceps* inoculated with *Burkholderia* sp. strain PsJN.

To date, many successful cases of phytoremediation of various organic contaminants using endophytic bacteria are mentioned in Table 10.2.

10.11 Plant Growth-Promoting Bacteria (PGPB)

The potential of bacteria having both pollutants degrading quality as well as plant growth promoting activity known as Plant Growth-Promoting Bacteria (PGPB) is recently paid attention for the effective remedial measure (Glick 2010). The genomes of bacteria have expressed pollutant degrading pathway and metabolic activities which tolerant the capacity of the plant to expose these type of pollutants by degrading these organic compounds (Escalante-Espinosa et al. 2005; Robert et al. 2008). Following are the points we discuss the impacts of Plant Growth-Promoting Bacteria (PGPB) and their advantages associate for the remediation of pollutants contaminated soils:

10.11.1 Reclamation of Polluted Environments

The close association of plant with pollutants degrading as well as growth-promoting bacteria (PGPB) offers dual benefits for the remediation of different environmental pollutants (McGuinness and Dowling 2009; Afzal et al. 2011; Teng et al. 2011; Yousaf et al. 2011). Beside exploration of plant–bacteria associations for the reclamation of polluted environments, bacterial application to plants vegetated in contaminated soil enhances biomass production, for its use in different industries (Weyens et al. 2010a, b). Recently, Cowie et al. (2010) reported that plant growth-promoting bacteria (PGPB) enhanced HCs removal from the soil, mainly due to improving plant growth, and bacterial population and activities.

10.11.2 The Composition of Root Exudates

The organic compounds present in the root exudates released by plant roots act as signaling agents to enhance the plant–bacteria interactions and consequently bacterial survival, their persistence and metabolic activities in the endosphere. The different plants secreted a variety of different root exudates and chemicals in the plant which decides the level of diverse bacterial population shelter in HC contaminated soil (Siciliano et al. 2003; Smalla et al. 2001).

Table 10.2 Successful remediation of hydrocarbons by combined use of plants and endophytic bacteria

Plant used	Endophytic bacteria.	Bacterial characteristics	References
Agrostis	Consortium CAP9	2,4,6-Trinitrotoluene	Thijs et al. (2014)
Willow	*Burkholderia* sp. HU001, *Pseudomonas* sp. HU002	Production of siderophores, organic acids, and indole acetic acid and showed increased Cd resistance	Weyens et al. (2013)
Cytisus striatus	*Rhodococcus erythropolis* ET54b, *Sphingomonas* sp. D4	Hexachlorocyclohexane	Becerra-Castro et al. (2013)
Poplar (hybrid)	*Enterobacter* sp. strain PDN3	TCE degradation	Kang et al. (2012)
Italian ryegrass (*L. multiflorum* var. Taurus)	*Pseudomonas* sp. strain ITRI53, *Pseudomonas* sp. strainMixRI75	Hydrocarbon degradation	Afzal et al. (2011, 2012)
Italian ryegrass (*L. multiflorum* var. Taurus), birdsfoot trefoil (*L. corniculatus* var. Leo) and alfalfa (*M. sativa* var. Harpe)	*E. ludwigii* strains	Hydrocarbon degradation and ACC deaminase activities	Yousaf et al. (2011)
Italian rye grass (*L. multiflorum* var. Taurus) and birdsfoot trefoil (*L. corniculatus* var. Leo)	*Pantoea* sp. strain ITSI10, P*seudomonas* sp. strain ITRI15	Hydrocarbon degradation	Yousaf et al. (2010b)
Wheat (*Triticum* sp.) and maize (*Z. mays*)	*Burkholderia cepacia* strain FX2	Toluene degradation	Wang et al. (2010)
Poplar	*P. putida* W619-TCE	Trichloroethylene degradation	Weyens et al. (2010c)
Yellow lupine	*B. cepacia* VM1468	Trichloroethylene degradation and Ni resistance	Weyens et al. (2010a)
Pisum sativum	*P. putida*	Naphthalene degradation	Germaine et al. (2009)
Italian rye grass (*L. multiflorum* var. Taurus)	*Pseudomonas* sp. strain ITRI53	Hydrocarbon degradation	Andria et al. (2009)
Wheat (*Triticum* sp.) and maize (*Z. mays*)	*Enterobacter* sp. 12J1	Pyrene degradation, indole acetic acid (IAA), siderophore production and inorganic phosphate solubilization	Sheng et al. (2008)

10.11.3 Mitigate Plant Stress Responses

PGPB increase the expression of 1-aminocycloprpane-1-carboxylate (ACC) deaminase activity which played an important role to decrease the levels of ethylene hormone generated in the plants under stress condition and consequently enhances plant growth, particularly root growth and development that expected effective phytoremediation (Weyens et al. 2009c; Afzal et al. 2012; Glick et al. 2007).

10.11.4 Phytotoxicity and Evapotranspiration of Volatile Pollutant Residue

It is known that Phytoextraction is a time-consuming process and not efficient for the removal 100% of the contaminant from the site due to poorly availability, limited intake capacity and higher toxic ceased the plant growth. To degrade HCs, EB produces various enzymes to degrade them, and consequently, it reduced both the phytotoxicity and evapotranspiration of volatile HCs (Germaine et al. 2009; Yousaf et al. 2011; Li et al. 2012).

10.11.5 Monitor Gene Abundance and Gene Expression

The breakdown of complex organic pollutants largely depends upon the survival and activation of metabolic rates of enzymes carrying exogenous bacteria involve in the plant–bacteria partnerships. Quantitative PCR (qPCR) given us a reliable proof for monitoring gene expression and functional activity of the applied microorganisms involve during phytoremediation of contaminated soil (Juhanson et al. 2007). It reported the expression profile of genes such as alkane mono oxygenase (*alkB*), alkane hydroxylase and cytochrome P450 (CYP153) present in isolated HC-degrading bacteria monitored through Quantitative PCR (qPCR) (Andria et al. 2009; Panicker et al. 2010; Afzal et al. 2011).

10.12 Endophyte in Phototoxicity of Heavy Metals

Phytoextraction a time consuming, also does not remove 100% of the contamination and applicable only in some metals. In a plant-endophyte relationship, it offers promising result for phytoremediation of metals pollution because endophytes possess a metal-resistance/sequestration system able to produce natural metal chelators that can lower metal phytotoxicity as well as translocate these metals into the aerial part of the host plant. To improve phytoremediation regarding heavy metals present, there are some endophyte which has a tendency to hyperaccumulator these metals, detoxified the soil surface and alter the reactive form of metal in the soil. Some endophytic bacteria isolated from plants grown at the soil of heavy metal deposition have shown on the host like cope-up with metal stress condition, stimulatory effects on the plant growth and developments and acts as a biocontrol agents of phytopathogens agents (Ma et al. 2011; Shin et al. 2012). Therefore, selection of such isolated beneficial endophytic bacteria could apply to assist phytoremediation for soil contaminant with metal contents (Rajkumar et al. 2009). Ma et al. (2016) isolated multi-metal resistant endophytic bacterial strain E6S which is homologous to *Achromobacterpiechaudii* from plant *Sedum plumbizincicola* which is hyperaccumulator in nature growing in mine soils of metals, showed promoted plant growth and the translocate of metals from soil to accumulate in the organelle of the plant. This Strain E6S exhibited increase resistant to various heavy metals (Cd,Zn, and Pb), prompted beneficial plant traits, such as solubilisation of phosphate and production of indole-3-aceticacid which can be used *in situ* metal rhizoaccumulation in plants.

Xu et al. (2016) isolated endophytic bacteria from *Pteris vittata* which is Arsenic –resistant in nature and exhibited plant growth promoting characteristics including IAA synthesis, siderophore production, and Phosphorous solubilisation. Mesa et al. (2015) isolated endophytic bacterial strains such as *Micrococcus yunnanensis* SMJ12, *Vibrio sagamiensis* SMJ18, and *Salinicola peritrichatus* SMJ30 from *Spartina maritime* tissues, a heavy metal bio-accumulator cord grass growing in the most polluted areas. These strains resistant toward numerous heavy metals such as As, Cu, and Zn and also expressed various industrial value enzymes such as amylase, cellulase, chitinase, protease and lipase. It also participates in the promotion of plant growth properties like nitrogen fixation, phosphates solubilization, and production of indole-3-acetic acid (IAA), siderophores and 1-aminocyclopropane-1-carboxylate (ACC) deaminase. To reduce phenanthrene contamination, Sun et al. (2015) inoculated Rye grass plants (*Lolium multiflorum* Lam.) with the endophytic bacterium *Pseudomonas* sp. Ph6 isolated from the interiors of clover (*Trifolium pratense* L.) grown at the PAH-contaminated site. It provides an optimized method to endophytic bacteria reduce plant PAH residues, which may be applied to agricultural production in PAH-contaminated soil.

10.13 Engineering Endophyte

Recombinant technology offers greater prospects for the design of constructed endophytic bacteria with appropriate metabolic pathways fitted to improve phytoremediation. If desired metabolic degrading pathways not present in naturally occurring endophytes, the isolated endophytic bacteria could be rectified with the appropriate catabolic pathways present in many other soil bacteria encoded on autonomous replicate plasmids or transposons and subsequently again inoculated to the host plant. This approach evidenced by inoculating yellow lupine plants and poplar with endophytic bacteria able to decreased toluene phytotoxicity and significantly lowered toluene evapotranspiration (Barac et al. 2004; Taghavi et al. 2005). To determine the potential of the phytoremediation technology, the monitoring technique is useful for quantitative gene expression of genes involve in metabolic degrading pathways inside the plant. (Afzal et al. 2011; Yousaf et al. 2011). It found that the longer time of contaminants resides in the xylem generate great havoc to the plant. To escape this type of circumstances, the engineered endophytes consider the perfect candidate to lower phytotoxicity and avoid evapotranspiration of rescue contaminants or their intermediates into the environment so that it reduced the residual levels of agrochemicals in food crops as well as for as protection of the food chain. Recently, the Inoculation of pea plants (*Pisum sativum*) with a poplar endophyte able to successfully reduce the toxic level of 2,4-D herbicide residues in crop plants as well as degrade from the soil (Germaine et al. 2006).

10.14 Advantages over Plant–Rhizobacteria Partnership

Recently, plant–endophyte partnership has earned familiarity over plant–rhizobacteria partnership during the remediation of organic pollutants which are easily taken up by plants. Due to its less time spend in the rhizosphere and optimum lipophilicity, the pollutant is not available to the rhizospheric microflora. Consequently, endophytic bacteria has a tendency to degrade the contaminants by the action of intracellular dioxygenases enzymes before the contaminants get evaporated (Trapp et al. 2000; Weyens et al. 2009b). The main advantage of endophytic bacteria over free-living rhizobacteria is that they shelter inside the tissues of the host plant and there is no fear for competition for nutrients and space, whereas rhizobacterial population faced hard competition due to present of soil microbes which cause reduction of the desired species.

10.15 Conclusions and Future Perspectives

Assisted phytoremediation is emerging new and growing technology for cleanup and prevention of environmental pollution. This green technology based upon natural process has dominated advantages over chemicals based methods as plant-associated microbes are much more efficient for effective removal of pollutant. They produce the beneficial secondary metabolites practically at the plant surface or inside the plant by quorum-sensing dependant principle while exogenously applied chemicals don't properly contact with the plant surfaces which cause more chances escaped to the environment and polluted them. It already confessed from the earlier work done on assisted phytoremediation for the remediation of pollutions contaminated soils in which inoculation of plants with rhizobacteria or endophyte bacteria showed different growth promoting traits.

Application of plant growth promoting bacteria is lower in the investment cost and easy to apply and also increase plant biomass production and remediation of various organic and inorganic contaminants. But till date many basic questions need to be answered like: why and how do plants select specific rhizosphere bacteria to become endophytic? What does the endophytic microbiome do for the plant? Which bacterial and plant traits are involved in colonization and persistence within plant tissues? How do plants tolerate the 'invasion' of beneficial endophytes? How do endophytic bacteria modulate plant defense responses to be considered as nonharmful? What are the driving forces operating to build up endophytic communities? How do environmental, physiological, developmental stages and genetic factors influence indigenous microbiomes? How will these processes affect the interactions among organisms in the ecosystem? Most of the researches have been carried out in laboratory conditions, yet no work done reported on field trials in contaminated sites.

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Chapter 11
Carbon Nanotube/Polyaniline-Based Nanocomposite Anode for Microbial Fuel Cells

Satyaranjan Bairagi, Abebe Teka, Mohammad Shahadat, S. Wazed Ali, and Zia A. Shaikh

Abstract It has been described in this chapter that the potentiality of an anode in the Microbial Fuel Cells (MFCs), prepared by Carbon Nanotube/Polyaniline (CNT/PANI) supported nano-composite material. The nanocomposite materials were also characterized based on various advance analytical techniques namely; Fourier Transform Infrared Resonance spectroscopy (FTIR), X-ray Diffraction (XRD), and Scanning Electron Microscopy (SEM) analyses to investigate the chemical composition and morphology of the composite materials. The electrochemical impedance spectroscopy (EIS) and ions discharge experiments are used to evaluate electro catalytic behaviour of the anode in the MFCs. In contrast with the announced execution of various anodes utilized as a part of MFCs, the CNT/PANI composite anode is discovered superb and is found a promising material for the application as an anode material in MFCs. The significant potential of CNT/PANI based anodic electrode is established owing to the conducting behaviour of PANI. On the basis of good conductivity of CNT/PANI nanocomposite, in upcoming years that the fabrication CNT/PANI based anode electrode are expected to open an innovative ways for demonstrating their exceptional application of MFC.

Keywords Synthesis • Characterization • Electrode fabrication • Microbial cell • Electrical conductivity

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M. Oves et al. (eds.), *Modern Age Environmental Problems and their Remediation*,
DOI 10.1007/978-3-319-64501-8_11

11.1 Introduction

Recently, the utilization and transformation of energy has been increased tremendously worldwide (Bhogilla et al. 2017). The different forms of energy sources have been classified as; renewable and non-renewable sources. Non-renewable sources of energy consisting of enormous portion of the total energy consumption which could be further categorized into two main groups; nuclear and fossil energy (Akdeniz et al. 2002; Koroneos et al. 2003). The releasing of carbon dioxide and other toxic gases form fossil fuels have severely affected to the environment which brutally jeopardised human life through its drastic consequences in terms of global warming and atmospheric pollution (Veziro and Barbir 1992). To prevail over the drawbacks associated with fossil fuels researchers in the world have made a radical shift from fossil fuel based to renewable energy sources to control energy consumption.

One of the fruitful results of these efforts is fuel cell (FC), the best alternative energy sources, which produces energy using high value metal catalysts. FCs technology has numerous advantages over other kinds of energy generation sources; no discharge of hazardous gases to the environment such as SOx, NOx, CO_2 and CO, better energy converting efficiency, lower sonic pollution since there is no mobile parts in MFCs, however, it also has some limitations such as, high cost and high mass generation (Peighambardoust et al. 2010). Nowadays, different types of Fuel cells are available among them microbial fuel cell (MFC) is considering a potential technology to generate bioelectricity by using an active microorganism (as a biocatalyst) in an anaerobic anode compartment (Tardast et al. 2012). The electrical energy obtained by the microorganism (bacteria) was observed by Potter in 1911 (Potter 1911) and very studies were found by the next 50 years (Lewis 1966). In the early 1990s, FCs became far more appealing devices; consequently, MFCs were considered as promising technology (Allen and Bennetto 1993). In microbial fuel cells (MFCs) bacterial biomass is used in the form of catalyst to degrade (oxidize) organic and inorganic stuff for getting energy. The performance of MFC is affected and depends on a number of parameters including proton exchange membrane, microbial biomass, involving chemical species, ionic strength of solution resistance of cell (internal and external) and the material of electrode etc (Qiao et al. 2007; Rabaey and Verstraete 2005). These entire factors play significant role to obtained higher electrical energy, however, the performance of MFCs depend on the electrode. To improve the output power efficiency of MFCs, attention has been paid to anodic and cathodic materials (Chaudhuri and Lovley 2003). As compare to cathode, anode plays a key role to achieved high power efficiency. The attachment of bacterial biomass depends on the nature and structure of electrode material to transfer electrons. Different types of materials have been used for anode electrode in MFCs such as carbon based materials (carbon cloth, carbon paper, graphite), platinum, Teflon treated carbon fibrous paper and graphite and PTFE based composite. These materials provide stability to the inoculums of biomass and enhance stability and surface area of the electrode. In other words, carbon based anodic electrode materials increase catalytic property of electrode which increases the performance of MFC. However, besides the significant advantages, carbon supported anode electrode associated with some drawback: as the electric conductivity of carbon electrode vary below two or three orders of magnitude than that of metal (Baudler et al. 2015). The enhancement in electrode resistivity, results decline in cell voltage and decrease the power of system which affects the electrochemical performance of MFCs. Conductivity, chemical stability in the solution and biocompatibility are some of the essential requirements to be best suited for anode material. Graphite rod or plates have attracted attention owing to simplicity, inexpensive and without any handling problem. The anodic material; polytetrafluoroethylene (PTFE) is commonly employed for its chemical stability and hydrophobic property in MFC. However, these materials are associated with some drawback in term of electrical conductivity. To improve the performance or drawback of graphite and PTFE, the CNT/PANI composite anode was fabricated by the mixing CNT/PANI powder with PTFE solution to make pastes which was coated on the surface of nickel foams after through drying the anode electrode was obtained as prepared by Qiao et al. (2007). Therefore, to enhance the efficiency of anode electrode in terms of conductivity and stability, attentions have been paid to fabricate CNT/PANI based nanocomposite material. Carbon nanotubes (CNTs) are considered as the new class of nanomaterials consisting of some special properties in terms of high conductivity and high surface-to-volume ratio together with unique structure (Danilov and Melezhyk 2006). The CNTs have shown superior properties in the form of catalyst for proton exchange membrane fuel cells as compared to carbon blacks material (Wang et al. 2004). The CNTs have also acted as anodic material in enzymatic biofuel cells (Yan et al. 2006). However, cellular toxicity nature of CNTs inhibits the growth of biomass in MFCs (Magrez et al. 2006) which are not found suitable for MFC without any controlling the cellular toxicity CNTs. Thus, CNTs have been incorporated with PANI to develop PANI/CNTs conducting composite material (Zou et al. 2008). The coordination of CNTs with PANI possesses the properties of each component with a synergistic effect.

In various electrochemical devices, conductive polymers have been shown their excellent performance in the form of thermal and chemical stability (Li et al. 2005). Due to its better electrical conductivity, ease to synthesis, thermal and chemical stability, PANI is considered is an important conducting polymer. The electrochemical behaviour of PANI have been studied (Chan et al. 1992). PANI is associated with some disadvantages as it is obtained in the form of electrochemically thin film and insoluble powder form (Nabi et al. 2011a). To remove the drawback of pure PANI and improve its electrochemical properties, PANI has been modified with a number of metal ions and these materials have been effectively used in the treatment of wastewaters (Nabi et al. 2011b, c; Shahadat and Bushra 2015; Shahadat et al. 2015). Thus, the electrochemical properties of PANI can be controlled by the addition of metal entity or protonation process (Zengin et al. 2002). In addition, modified PANI has been employed to detect *Escherichia coli* (*E. coli*) using an enzyme based method (Misra and Angelucci 2001). Platinum modified PANI have been used in the form of anode in MFCs (Schröder et al. 2003). The use of PANI in MFCs not only functionalized the biomass, but also provide high current density (Niessen et al. 2004). Synthesis of CNT/PANI composites material has been accepted as the highest interest because the incorporation of the CNT into the matrix of PANI proven better results in terms of electric properties, mechanical and chemical stability (Qiao et al. 2007). Multilayer of PANI/CNT has been fabricated followed by a layer-by-layer assembly method (Kulesza et al. 2006). The combination of PANI with CNTs enhanced the electrical conductivity of PANI/CNTs which can be employed as anodic materials to improve the performance of the MFCs. This chapter focuses on the recent development characterization and performance of CNT/PANI-based composite anode in MFCs.

11.2 Microbial Fuel Cells (MFCs)

Microbial fuel cells are the good substitute to get electrical energy by the oxidation of industrial effluent with the help of microorganisms (Davis and Yarbrough 1962; Rao et al. 1976). The schematic working presentation of MFC is shown in Fig. 11.1 and the working phenomenon of MFC described as; the obtained electrons from the bacterial biomass are transfer to the negative terminal (anodic) and flow towards the positive terminal (cathode) connected by a conductive wire which contained a resistor. Consequently, the current flows from the positive terminal to negative terminal in the opposite direction of electron. Unlike a bio battery, the MFC assembly should have the potential to oxidize, continuously or intermittently, the substrate at the anode. Electrons produced by the bacteria can be transferred to the anode by electron mediators or shuttles (Rabaey et al. 2004, 2005), by direct membrane associated electron transfer (Bond and Lovley 2003).

There are two types of MFCs, “mediator and mediatorless MFCs”, depending on their supplementary material. Neutral red or anthraquinone-2,6-disulfonate (AQDS) can be used as chemical mediators in MFC to produce electricity using

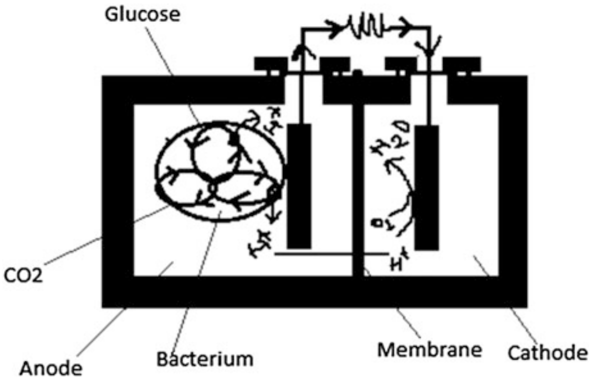


Fig. 11.1 Microbial fuel cell (Logan et al. 2006)

bacteria. (Bond et al. 2002; Logan 2004). The formation of water molecule in most of the MFCs is the electrons transfer from the anode to the cathode are combine with protons, which diffuse from the anode through a membrane, and then react with oxygen which is obtained from air (Kim et al. 2002; Min and Logan 2004). Other oxidizers (ferricyanide or Mn (IV)), can also be used in the form of catalyst (Rhoads et al. 2005). For instance, Mn are reduced from Mn(IV) to Mn (II), with the help of the bacteria's available in the solution the re-oxidation of these metal ions is catalysed using dissolved oxygen. Microbial catalysed electron release at the anode and subsequent utilization of electron at the cathode show the characteristics of an MFC (Rhoads et al. 2005). Therefore, using a Mg based anode does not complete the criteria of MFC because no bacteria are needed for catalyzing the oxidation of the fuel (Shantaram et al. 2005). The use of enzymes or catalysts which are not directly produced in situ by the bacteria are considered to be as enzymatic biofuel cells (Barton et al. 2004). Generally, mixed cultures MFCs achieved more power density as compared to pure cultures (Rabaey et al. 2004). Some pure culture MFCs have shown higher power generation, however, their power generation efficiency was not observed using acclimated mixed cultures (Ringeisen et al. 2006). The physico-chemical parameters such as operating condition; temperature differences, effect of pH, electron acceptance potential, the surface area of electrode and other parameters (e.g. reactor size and time etc) also affect the efficiency of the MFCs (Logan et al. 2006; Rabaey and Verstraet 2005).

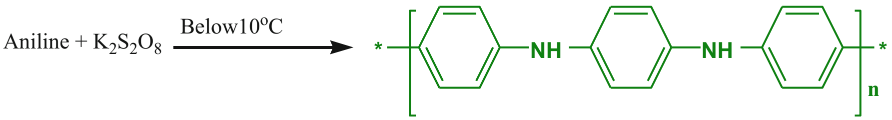
11.3 Synthesis of PANI and CNT/PANI Composite

11.3.1 Synthesis of PANI

The polymerization of aniline has been carried out using oxidative polymerization of aniline monomer in an acidic solution (1.0 M HCl). The polymerization was initiated by addition of 1.0 M oxidizing agent; $K_2S_2O_8$ (drop wise) to the acidified solution of aniline at 0–4 °C under constant stirring for 1 h. After polymerization, green gel was obtained and kept it in refrigerator for 24 h (Shahadat et al. 2014). The resultant product was extracted by filtration and frequent washing using distilled water and acetone until it becomes colourless which shows effective removal of unreacted agents. The proposed scheme of aniline polymerization is shown in Scheme 11.1.

11.3.2 Synthesis of CNT/PANI Composite

Synthesizing CNT/PANI composite show complexity to disperse CNT and control the orientation of CNT in the matrix of PANI due to the strong Van der Waals



Scheme 11.1 Polymerization of aniline monomer using oxidizing agent below 10 °C

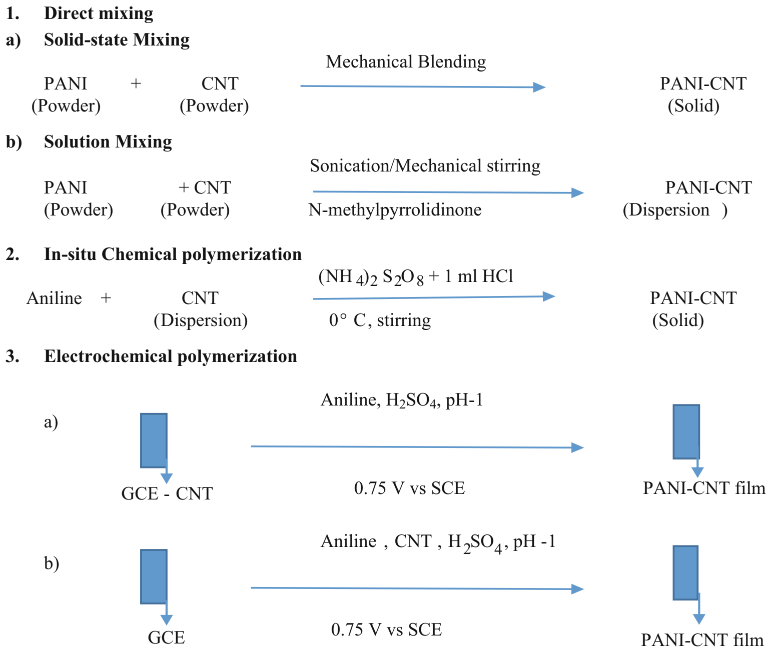
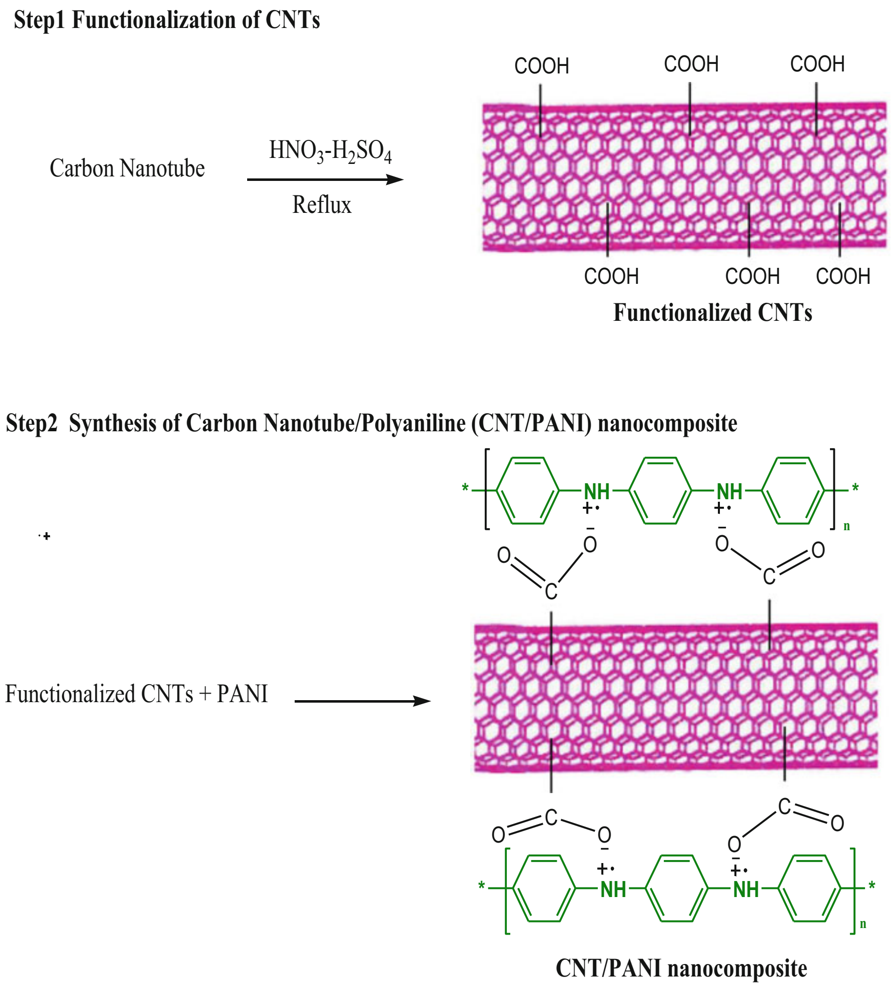


Fig. 11.2 Synthesis of CNT/PANI composite using different chemical routes (Gajendran and Saraswathi 2008)

interaction between CNT molecules unless they functionalized using covalent and non-covalent reactions with organic molecules (Oueiny et al. 2014). First time the synthesis of CNT/PANI was reported in 1999 using electro polymerization of analine on CNT whiskers since then different CNT/PANI composite synthesis methods have been reported based on electrochemical or chemical processing (Gajendran and Saraswathi 2008). These methods were categorized into three main schemes including; direct mixing, insitu chemical polymerization and electrochemical polymerization and in-situ polymerization is branded as the simplest method as shown in Fig. 11.2.

The composite of CNT/PANI has been prepared using in-situ polymerization of aniline on CNT followed by reported method (Wu et al. 2005). The process PANI synthesis was initialled by distilling the aniline monomer under lower pressure. A fixed amount (1 mL) of aniline was mixed with HCl (0.3 mL) in 50mL demineralized water (DMW) in an ice bath followed by the addition of oxidizing



Scheme 11.2 Modification of CNT and fabrication of CNT/PANI composite

agent; ammonium persulphate solution (APS; 2.3 g in 25 mL DMW) to the mixture. It took 6 h at a temperature range of 0 to 5 °C for complete polymerization. After washing several times using DMW a green gel of proton-doped PANI is extracted. On the other hand to synthesise the carboxylic acid modified CNTs, it was ultrasonically treated using a mixture of 3:1 of H_2SO_4:HNO_3 at 50 °C for 24 h so that the CNT converted to hydrophilic due to incorporation of acid functionalities. The proposed scheme for the modification of CNT and development of CNT/PANI composite is shown in Scheme 11.2.

11.4 CNT/PANI Supported Composite Electrode and Their Application in MFC

The CNT/PANI based materials have been characterized using advanced analytical techniques; FTIR, SEM, TEM, AFM, XRD, RAMAN M, EIS and TGA/DTA analyses. The physico-chemical properties and conductivity was also determined to establish the stability of composite anode. The FTIR spectra of pure PANI and composite CNT/PANI is shown in Fig. 11.3. At 835 cm^{-1}, 1500 and 1600 cm^{-1} wave numbers shows sharp and medium picks due to the N–H out-of-plane bending absorption, the stretching vibration of the quinoid ring and benzenoid ring, respectively (Qiao et al. 2007). A prominent C-N bond stretching at 1240 cm^{-1} is observed due to the covalent bond between the polymer chain and the functionalized radical CNT (Qiao et al. 2007). The broad band at 1730 cm^{-1} and 3000 cm^{-1} corresponds to the C–O vibration in C–H stretching PANI and composite material, respectively (Rahman et al. 2014).

SEM micrographs of PANI and CNT/PANI composite are shown in Fig. 11.4. SEM image of CNT/PANI composite demonstrates the network of rod like core-shell nanostructures which are formed owing to wrapping of CNT by PANI. But the pure PANI film is compact and fibrillar structure (Gajendran and Saraswathi 2008).

Mostly Electrochemical impedance spectroscopy (EIS) and impedance meter utilized to assess the MFCs performance. Electrochemical impedance spectra studies can be used to assess the charge transfer and ion transport in the composite. Qiao et al. (2007). described the EIS measurement that well-defined single semicircles followed by short lines over the high frequency range and low frequency range respectively in which the semicircles shows interfacial charge transfer resistance. And the magnitude of Rct found higher for CNT/PANI when it is compared with pure PANI (Fig. 11.5). Beside the EIS, the electrode potential can also be acquired by taking the voltage which is measured against a reference electrode.

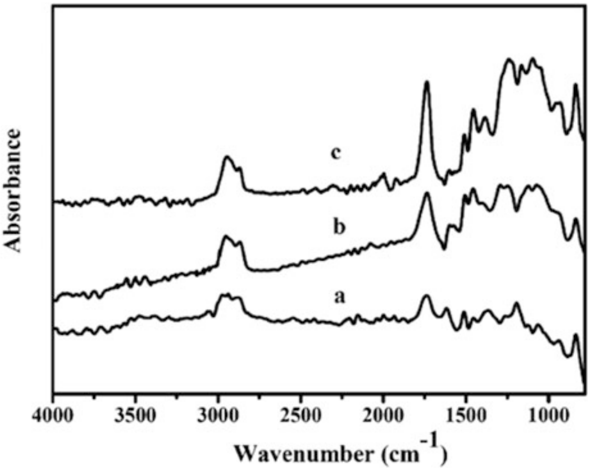


Fig. 11.3 (*a*–*c*) FTIR spectra of PANI (*a*) and composite powders (1 % (*b*) and 20 % by wt. CNT/PANI composite (*c*) (Qiao et al. 2007)

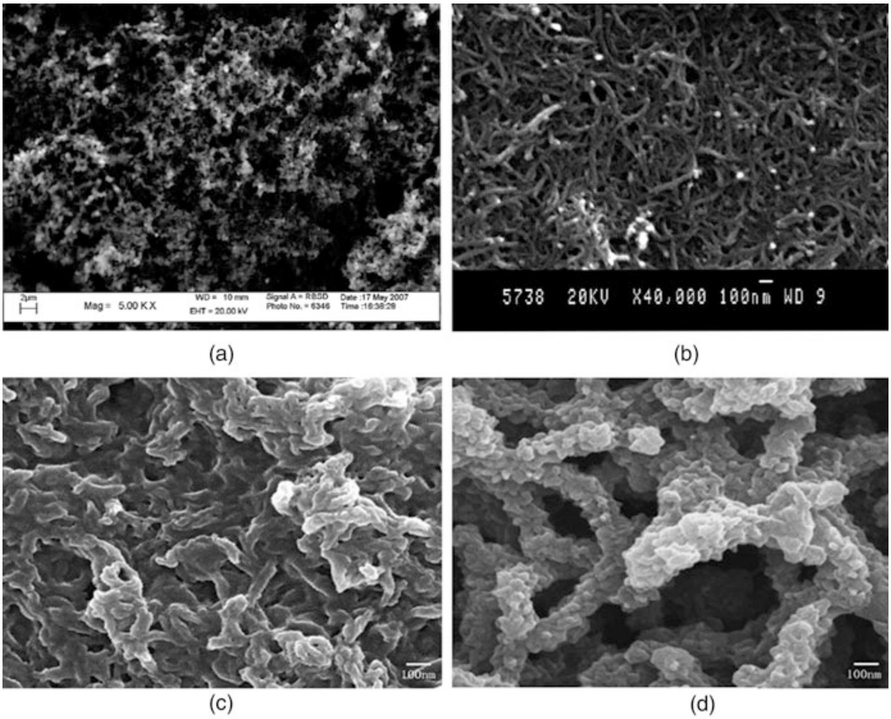


Fig. 11.4 SEM images of electrochemically deposited (**a**) PANI and (**b**) PANI-CNT (**c**) plain PANI; (**d**) 20 wt.% CNT/PANI composite (Qiao et al. 2007)

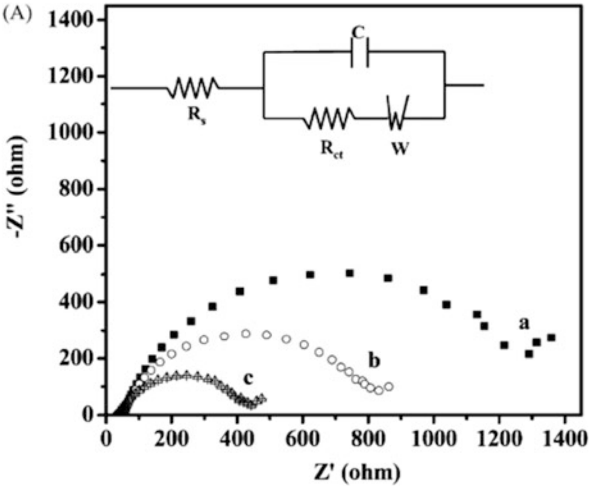


Fig. 11.5 (A) EIS of PANI (*a*), 1 wt.% CNT/PANI (*b*) and 20 wt.% CNT/PANI (*c*) composite electrode in 0.1 M phosphate buffer (pH 7) at open-circuit potential and equivalent circuit used to fit the EIS (Qiao et al. 2007)

MFCs performance can also be determined through power output and columbic efficiency. Power density is also another method to compare different system using the power output against surface area.

Chin-Tsan et.al fabricated CNT/PANI composite electrode for clean energy source from MFC in *E.coli* (Wang et al. 2013). Fabricated electrode produced 1574 mW/m^2 power density by maintaining a voltage of 1.18 V and 12.8 mA current condition which was far better than carbon paper, carbon cloth or NR-woven carbon paper electrodes (Oueiny et al. 2014). Qiao et.al. also claimed to produce a maximum of 42 mW/m^2 power density with a cell voltage of 450 mV for composite containing 20% CNT using *E.coli* as microbial catalyst (Qiao et al. 2007). They have showed that the electro catalytic behaviour of the anode was improved due to advantageous properties of both components. Electrochemical activity of the anode reaction is increased owing to high surface area and enhanced electric conductivity of the carbon nano tube. High power output take place, while PANI allowed the electrons through a continuous matrix.

Another graphene, CNT and PANI supported GNS-CNT-PANI nanocomposite material has been synthesized via oxidative in-situ polymerization (Yan et al. 2010). The material was characterized using XRD, SEM, TEM and CV analyses and it was used as electrochemical supercapacitors. XRD analysis revealed amorphous nature while SEM and TEM studied showed rough agglomerations of GNS-CNT-PANI nanoparticle. The CV study of nanocomposite covered outstanding performance in term of stability which demonstrated enhancement in specific capacitance (11%). In addition, the GNS-CNT-PANI showed only 6% decline in capacitance after 1000 cycles, this established its better cyclic stability. Higher electrical conductivity of nanocomposite was found to be due to the synergic effect of GNS, CNT and PANI which also attributed to higher value of specific capacitance and enhanced mechanical strength of nanocomposite. Thus, by using PANI and CNT in the form of conductive filler, the electrochemical electrode supercapacitors containing higher capacitance and together with high recycling efficiency can be synthesized (Tan et al. 2012).

11.5 Conclusions

For their chemical stability, biocompatibility and optimum cost carbon based electrode materials have shown significant potential in MFCs. However, carbon based anode associated with some draw backs including such as the electric conductivity of carbon electrode vary below two or three orders of magnitude than that of metal. The enhancement in electrode resistivity, results decline in cell voltage and decrease the power of system which affects the electrochemical performance of MFCs. Transition metal oxides (e.g. manganese oxide, nitrogen-doped carbon-based materials etc) have been used in the form of anode, however, these material was not showed sustainable catalytic properties in MFC. The PANI/CNT based anode electrode demonstrated excellent electrical conductivity owing to its high surface area, chemical stability and thermal stability when it is compared with pure carbon based anode which has a significant effect on the performance of MFCs.

Finally, to optimize the performance of the MFCs it should be given a due attention on a microorganism interaction with electrode surfaces. Although, very study was carried out by using CNT/PANI supported nanocomposite as anode electrode in MFC, however, these nanomaterials revealed excellent performance due to their higher electrical conductivity and specific capacitance. Therefore, more extensive research is needed to improve the thermo-chemical stability and electrical conductivity of PANI/CNT based anode. Biocompatibility and electrical conducting nature of PANI/CNT have amplified its interest to develop anode electrode in MFC. In future, it is expected that PANI/CNT electrode materials have prospective to open innovative way in MFCs.

Acknowledgments The authors would like to express their appreciations to [1]Department of Textile Technology, [2]Department of Biochemical Engineering and Biotechnology, Indian Institute of Technology, Delhi, New Delhi-110016, India. One of the authors (Dr. Md. Shahdat) is very much thankful to SERB-DST (SB/FT/CS-122/2014), Govt. of India for awarding Postdoctoral research grant to carry our research at IIT Delhi.

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Chapter 12
Bioremediation: A Sustainable Tool to Prevent Pesticide Pollution

Talat Parween, Pinki Bhandari, Ranju Sharma, Sumira Jan, Zahid Hameed Siddiqui, and P.K. Patanjali

Abstract The revolution in manufacturing of different types of agrochemical has no doubt enhanced yield in our agricultural products and protect crops from diseases and pests. Pesticides at present play an important role in enhancing the yield and provide an economical benefit to our farmers. Environmental contamination is a potential threat to human health.With the advent of agrochemicals there has been enhancement in crop productivity and improved resistance against diseases. To combat economic losses in agriculture sector pesticides plays crucial role in sustaining agro-productivity. Due to indiscriminate use of chemical pesticides together amplified industrialization and urbanization; there has been a parallel increase in environmental pollution. To counterfeit environmental contamination, we need to implement bioremediation. Bioremediation is most effective technology wherein we utilize microbes as a potential contrivance for degradation of environmental pollutants. Bioremediation is eco-friendly, inexpensive, competent and proficient technology for pesticide detoxification. Bioremediation encompasses numerous *in-situ* initiatives for instance bioventing, biosparging, bioaugmentation and *ex-situ* contrivances namely *land* farming, biopiling, bioreactors etc. Detoxification of pesticides via phytoremediation methods like phytodegradation (Phytotransformation), phytovolatilization, rhizoremediation etc., has also been employed. The central theme of this chapter will be summarizing limitations and challenges linked with some widely employed bioremediation techniques and consequently evaluating the impending relevance of these remedial tools to eliminate pesticides from the environment.

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M. Oves et al. (eds.), *Modern Age Environmental Problems and their Remediation*,
DOI 10.1007/978-3-319-64501-8_12

Keywords Bioremediation • Environment • Pesticide • Phytoremediation • Pollution

12.1 Introduction

Annually about 6 × 10^6 synthetic compounds are produced with even more synthetic compounds still in production line (Niti et al. 2013). Conventional techniques viz. landfilling, incineration and chemical decomposition are considered to be effective, but it also associates with some disadvantages such as complexity, improper public awareness, particularly the ignition of contaminants can lead to enormous human loss or impaired health among workers. Decontamination of the environment can have detrimental effects on ecology, including microbes, aerial as well as terrestrial environment by impairing significant life sustaining process thereby imbalancing ecological integrity (Batayneh 2012). In order to combat this problem, scientists and industrialists from all over the world are facing challenges to tackle this issue of environmental decontamination via eco-friendly and economical approach. These substantial approaches include the use of plants and microbes for detoxification of environmental pollutants via phytoremediation and bioremediation respectively (Conesa et al. 2012). These strategies are well known ground breaking technology that utilizes absolutely organic initiative for decontamination of pollutants (Cardenas et al. 2008). Being biologically acceptable and economically feasible, bioremediation has exceptionally towering human approval and can be employed naturally in any place. Bioremediation is being enlisted as top cleaner up strategy. Bioremediation can be effectively carried out through appropriate stabilization of determinants like state of pollutants, pH, nutrient supply in medium, moisture content, microbial diversity of location, temperature and redox potential (Dua et al. 2002). Bioremediation ensures utilization of pollutants as a source of food for microbes (Tang et al. 2007). Bioremediation encompasses most advanced technologies like phytoremediation (plants) and rhizoremediation (plant and microbe interaction). Hence bioremediation together with phytoremediation and rhizoremediation enumerate as major technology intervention for inorganic and organic decontamination from ecosystem.

The most suitable compounds for decontamination via bioremediation include long chain hydrocarbons, complex aromatic hydrocarbons and halogenated pesticides. Pesticides are major pollutants extensively utilized for pest eradication in order to minimize crop loss and declined productivity. Pesticides are significant for intensive farming, hence indispensable for the integrated pest management (Gouma 2009). Indiscriminate use of pesticides leads to ecological imbalance. During recent decades, there has been the indiscriminate use of pesticides leading soil and water contamination (Surekha et al. 2008; Heath et al. 2010). Pesticide seldom hit target, about 90% of pesticides is disseminated to atmosphere thereby leading environmental pollution. Hence pesticide incidence in food, air and water in a consistent manner cannot be ruled out. Further pesticide use for disinfestations of soil pests also leads to accretion of pesticide residues and their metabolites which prove detrimental for the microbial flora of the soil. Among volatile environmental pollutants, 6.3% are from pesticides (Yates et al. 2011). Due to their bioaccumulation capacity, pesticides accrue in living tissues. A pesticide can be effectively cleaned through bioremediation technologies owing to their eco-friendliness and have been used effectively in numerous countries (Mohammed 2009; Mougin et al. 1994). Bioremediation is most effective technology for decontamination of environmental pollutants (Mervat 2009).

12.2 Techniques for Bioremediation

The efficacy of bioremediation is site specific with respect to contaminant. The strategy of bioremediation is determined whether contaminated soil is within an environment or offside from contaminated sites. Fundamentally, bioremediation is classified into two types: In-situ bioremediation, Ex-situ bioremediation.

12.2.1 In Situ Bioremediation

In this technique, living microbes detoxify pollutants via supply of food and oxygen by mingling aqueous solutions in polluted soils. These techniques are economical and employ comparatively lesser harmful microbiome for detoxification of organic contaminants. Because of the lower interruption of the polluted site, it is known to be most advantageous alternative. Microbes exhibiting chemotactic functions are particularly useful for in situ bioremediation. Strobel et al. (2011) illustrated that the efficacy of in situ bioremediation can be further improved via amplifying chemotactic abilities of microbes. In situ treatment could be implemented via varied media as employed for pesticides. Fungi being effective bioremediator, their application, particularly white rot fungi is utilized extensively in pesticide bioremediation. White rot fungi contain lignin degrading enzyme which is effective against lethal and recalcitrant compounds. Following practical evaluation, it has been confirmed that white rot fungi can effectively degrade 45–75% pesticides than control (Fragoeiro 2005). Seech et al. (2008) reported treatment of soil and groundwater with organic carbon and zero-valent iron (ZVI) lead to degradation of organochlorine pesticides. In situ bioremediation of organochlorine pesticides from polluted areas via coupled approaches of biostimulation and bioaugmentation was illustrated by Qureshi et al. (2009) in which field trial of 2–3 months was pre-requisite for final adjustment.

12.2.1.1 Bioventing

It is a technique in which bioremediation is maintained by injecting oxygen and/or nutrients into the soil (Shanahan 2004). The two commonly added nutrients are nitrogen and phosphorous (Rockne and Reddy 2003). Nitrogen and phosphorous are uniformly disseminated all thorough soil matrix. Soils exhibiting lower permeability such as clay avoid biovented oxygen and nutrients from spreading all thorough soil. Due to minute pored and large surface area, it is cumbersome to regulate moisture content in finely textured soil exhibiting lower water retaining capacity, hence averting oxygen from reaching microbes all thorough polluted sites (USEPA 2006). Bioventing is compatible for well drained, medium and coarse-textured soils. The fundamental bioventing organization encompasses well and a blower which forces air into well and soil (Lee et al. 2006). Bioventing system demonstrated 93% decline in phenanthrene concentration following 7 months trial Frutos et al. (2010).

12.2.1.2 Biosparging

This strategy employs amplified levels of oxygen in groundwater, thereby increasing the rate of biodegradation of pollutants via organic microbes which implicates low pressure air injection under the water table. Amplified oxygen enhanced integration in the saturated zone and thus enhanced interaction between soil and groundwater. The simplicity and economically feasible installation of the minute dimension injection system allocate dexterity in design and construction system. Prior to execution of bioventing or biosparging, it is indispensable to resolve scope and kind of pollution together with soil features to evaluate the utility of these methods and accurate placement of air. Prior to implementing bioventing or biosparging, the extent and type of contamination as well as soil characteristics must be determined to assess the applicability of these processes and appropriate air position (Baker 1999). Both these processes are appropriate for instant volatilization. These strategies are not generally employed in pesticide polluted locations. Biosparging system exhibited detoxification of 70% of BTEX from groundwater within 100 month remedial processes (Kao et al. 2008). This signified that biosparging is a potential technology for BTEX remediation of polluted ground water. Biosparging improves both aerobic biodegradation as well as volatilization and is generally implied, to protracted hydrocarbon resource remediation (Lambert et al. 2009). Bioremediation is employed in high energy route to identify resource of gasoline pollution so as to estimate the extent of remediation obtained through mass removal and decline in mass discharge into groundwater. Off gas equipped with CO_2 and O_2 monitoring established specified range of hydrocarbons. Through this approach approximately 80% of pentane, 50% of hexane but only about 4% of the aromatic hydrocarbons is volatilized and eradicated.

12.2.1.3 Bioaugmentation

Bioaugmentation is an approach to amplify degradation, when microbes are translocating to polluted site. But several drawbacks linked with it are (i) Inducted microbes seldom participate with a native population to extend and maintain functional population ranks and (ii) Mainly soils with extensive disclosure of biodegradable waste have native microbes that are also effectual degrades.

Bioaugmentation is generally correlated with biostimulation in which sufficient quantity of water, food resources and oxygen are inducted into the polluted site so as to improve degradation potential of microbes (Couto et al. 2010) or to advance co-metabolism (Lorenzo 2008). Biostimulation strategy is employed to amplify degradation prospective of contaminated site via accretion of nutrients and other restraining determinants utilized for extensive range of xenobiotics (Kadian et al. 2008). However, *in situ* bioremediation has few drawbacks:

1. It is inappropriate for majority of soil types.
2. Inclusive degradation is cumbersome to be obtain and
3. Regulation of ambient temperature for probable degradation is difficult to achieve.

12.2.2 Ex Situ Bioremediation

In this strategy, polluted site is relocated from its original place. It includes various treatments as listed below:

12.2.2.1 Land Farming

It is an ex situ bioremediation strategy wherein polluted soil is combined with nutrients to frame treatment beds which are regularly shifted over or dug to expose the soil matrix. Peadological parameters like moisture content, aeration, pH and addition of nutrients and bulking agents are the main determinants for evaluating efficacy of pollutant biodegradation. It is an effective stratagem for bioremediation of long chain hydrocarbons counting from heavy oils to long carbon fuels and creosote. Pesticide polluted land is specially treated by land farming (Felsot et al. 1992). It is a total bioremediation technology where in magnitude and site of dissemination proccess relies on the relevance of pesticide spray to avert application that is detrimental for atmosphere. Pesticide application rate is equal to pesticide labels, which is anticipated rate of application of pesticide per unit of land or soil. Improper disposal of pesticides for locust control in Africa during the last century posed huge threat. In this context, Africa stockpile program (ASP) instigated by FAO was framed to divest Africa of stockpiles and organize them in Eco friendly order. Cleaning up of contaminated land is intricate and highly lucrative deal even for most advanced countries. Coping with such issues in Mali and Mauritania was probably impossible.

From observations and exaggerated site surveys, proper remediation plan was organized via FAO for every site. Bioremediation was characteristically dependent on organic amendment and land farming to improve restricted pesticide detoxification. The main theory underlying remediation technology was to assist and to increase organic pesticide detoxification in the soil at any site particularly organophosphate and carbamate insecticides. Persistence and sluggish organochlorine detoxification are common. Organophosphate concentration in Mali at Molodo on July, 2008 was declined by two orders magnitude, however, dieldrin concentrations continued to be same.

12.2.2.2 Biopiling

In this technology polluted soil is tilled out and combined with organic additions produced to compost piles and enclosed for treatment. Biopile comprises of treatment bed, ventilation frame, medium matrix and leachate compilation method. All peadological parameters are regulated properly to amplify detoxification. Nutrient system was kept under soil matrix upto 20 ft to surpass air and nutrients via the soil. A soil pile about 20 ft was enclosed in a plastic sheet to manage overflow, evaporation and volatilization in addition to enhance solar heating. Volatile organic compounds are evaporated from soil and air containing VOCs can be disposed off into the air. Clean up takes about 3–6 months following which unearthed matrix is reverted back to its actual site or cleared off (Wu and Crapper 2009).

12.2.2.3 Bioreactors

With this technique, polluted soil is combined with water and nutrients. In order to increase the efficiency of microbes, the assortment was disturbed via automatic bioreactor. This method is instantaneous and more suitable for clay soil (USEPA 2006). Numerous further reactor configurations might be utilized namely bioslurry reactors, fermenters, and ready bed reactors if the likely danger from release and production are severe (Riser-Roberts 1998). Fulekar (2009) demonstrated remediation of fenvalerate via *Pseudomonas aeruginosa* in an upgraded bioreactor and confirmed that this technology would be advantageous to fenvalerate detoxification.

12.3 Bacterial and Fungal Degradation of Pesticides

Even though there are numerous bioremediation technologies. However, below are listed a few techniques with high efficiency

12.3.1 Phytoremediation

Phytoremediation is a stratagem that utilizes green plants for contaminant detoxification in atmosphere. The main characteristics of phytoremediation are: An inexpensive, solar energy driven remediation technology. Mainly advantageous for shallow and low level polluted sites. Applicative for detoxification of extensive range of environmental pollutants. Effectual even in mechanical remediation procedures. Phytoremediation is possible due to utilization of specific abilities of the plant root system. Phytoremediation It includes various methods for instance uptake, phytotransformation (conversion of more toxic metals to relatively lower toxic metals), phytodegradation (metabolizing organic contaminant via plant enzymes), phytovolatilization (volatilization of organic contaminants via plant leaves), and rhizoremediation. At rhizospheric zone, organic compounds are released through root exudation and activate Microbiome leading to improved rhizospheric pollutant detoxification

12.3.2 Pesticides Uptake by Plant

Various plant and soil features are implicated in the pesticide uptake via plants (Dzantor and Beauchamp 2002; Gao and Zhu 2003). Microbial detoxification or foliar uptakes are the main determinants of incidence of pesticides in soil. Further aspects that influence pesticide availability and plant uptake are moisture content, organic carbon, and clay content in the soil (Koskinen et al. 2006). Herbicide triazolinone sorption desorption in clay loam and loamy sand soils was an increased exhibiting sorption (*Kd*) in both soils by a factor of 5–7 after 12 weeks of incubations (Koskinen et al. 2002). Bouldin et al. (2006) reported phytoremediation of atrazine and lambda-cyhalothrin through *Juncus effusus* and *Ludwigia peploides* via hydroponic conditions. This confirmed that *J. effuses* and *L. peploides* are phytoremediators for higher atrazine and lambda-cyhalothrin uptake respectively. Pesticides are transported to the plants through soil and meager fraction through airborne pesticides. An analogous experiment carried out in zucchini (*Cucurbita pepo* L.) illustrated two main courses following exposure to insecticide chlordane (Lee et al. 2003). Grangeot et al. (2006) demonstrated glufosinate and glyphosate in *Ambrosia artemisiifolia about* 80% via foliar uptake, spray retention and translocation with maximum uptake within 6 h. Pesticide uptake by plants and the residue has been illustrated even under controlled and experimental setup (Khan et al. 2011). Organophosphate binds to both organic amendments and antibiotic streptomycin. Antibiotic streptomycin hinders enzyme activity p-nitrophenol 4- hydroxylase produced from the root and shoot. Wheat plants increased uptake/degradation of methyl parathion, p-nitrophenol and hydroquinone in unsterilized soil by 64.85%, 94.7% and 55.8% correspondingly. Methyl parathion hydrolyzes to p-nitrophenol which is extra metabolized to hydroquinone with nitrite release.

The enzyme p-nitrophenol 4- hydroxylase is active as confirmed via disposal of nitrite via leaf and root extracts and production of hydroquinone in the reaction mixture.

12.3.3 Phytodegradation and Phytotransformation

The term "phytodegradation" refers to conversion of organic contaminants into a less toxic, less mobile or more stable form. Phytodegradation is the proccess of dilapidation of pollutants into simpler units via phytoenzymes (Newman and Reynolds 2004) or root exudates as a result of microbial metabolism which facilitate detoxification of contaminants. However, no proccess is entirely effectual in the conversion of intricate and refractory compounds to the basic molecules via phytocompounds. Thus phytotransformation refers to transition to chemical transition without complete breakdown. Xia and Ma (2006) reported elimination of organophosphate ethion by *Eichhonia crassipes* (water hyacinth). Likewise, Chang et al. (2005) illustrated translocation of atrazine and break it to lesser complex metabolites within plants. Garrison et al. (2000) reported dehalogenation of DDT in aquatic plant elodea (*Elodea canadensis).* Phytotransformation is possible due to catalyzation of endogenous enzymes that react with reactive functional groups of pesticides such as NO^{-2}, NH^{-2}, OH^{-}, $COOH^{-}$ or Cl^{-}, Br^{-}, and I^{-} in I phase (Sandermann 1992) via oxido-reduction and hydrolysis reactions (Trapp et al. 1994). This is followed by conjugation of pesticides with variant enzymes that occurs in phase II leading to pesticide detoxification (Hatzios and Penner 1982). Conjugation is induced via adding tripeptide like glutathione or sugar moiety or novel compound (Sandermann 1992). Conjugation of glutathione with pesticides via nucleophilic addition has been reported in the case of pesticides with glutathione-*S*-transferase as catalyst (Dietz and Schnoor 2001; Dixon et al. 2002; Edwards et al. 2000). Pesticides exhibiting conjugation with glutathione include atrazine, simazine, and cyanazine, while 2, 4-D, chloramben, and bentazon favor conjugation with glucose (Hatzios and Penner 1982). In the last phase, plant metabolism is restricted to compartmentation and storage where in plants store soluble metabolites in vacuoles or constitute cell wall.

12.3.4 Phytovolatilization

It is the method by which pollutants are volatilized from plant leaf or any aerial portion. However, there are scarce research reports pertaining to phytovolatilization of pollutant from plants owing to restrained relevance of phytoremediation. Phytovolatilization has significant relevance with respect to highly volatile pollutants for instance ethylene dibromide (EDB), trichloroethylene (TCE), methyl-tert-butyl ether (MTBE) and carbon tetrachloride (CTC). Hong et al.

(2001) reported volatilization of methyl-tert-butyl ether (MTBE) via the leaves, stem and bark. Phytovolatization can occur through rhizodegradation or phytodegradation in breakdown product. Anonymous (2009) illustrated the influence of trichloroethene, or its simpler compounds in poplar for phytovolatilization. Davis and Erickson, 2002 illustrated prospective for phytovolatization of fumigants ethylene dibromide, ethylene dichloride, and carbon tetrachloride. Trichloroethylene (TCE) detoxification in field plants has been illustrated in Florida and Utah. TCE concentration ranged from 10–100 times more at transpiration sites at Utah location while at the relatively lower TCE plant concentrations at Florida site was recorded owing to minimal groundwater contamination as a result of recurrent rainfall (Doucette et al. 2003). Ma and Burken, 2003 confirmed decline in volatile compound in xylem with increase in distance from rhizosphere zone. Hence, highly volatile compounds like TCE are instantly oxidized into the atmosphere through hydroxyl radicals. But phtyvolatilization cannot be successful due to environmental parameters like lower air circulation.

12.3.5 Rhizoremediation

Rhizosphere refers to zone of soil around plant roots which affect plant metabolism. Rhizosphere develops intricate environment around plant ensuring metabolically vigorous microbiome (Capdevila et al. 2004). Plant Growth Promoting Rhizobacteria (PGPR) is a significant group of microbial exhibiting imperial function in plant nutrient cycling, soil formation, pest control and pesticide detoxification (Rajkumar et al. 2009, 2010). Plant root release compounds which provide nutrients to entire microbial hence enhancing anti-microbial potential which in turn increase plant growth and decline chemotoxicity. Plant Growth Promoting Rhizobacteria (PGPR) and Arbuscular Mycorrhizal Fungi (AMF) together constitutes consortium against soil contamination (Ma et al. 2010). Due to pollutants in soil microbes tend to dwell in the chemical rich environment which serve as a food resource for them. Numerous research reports elucidated characterization of microbial gene functions in rhizodegradation of pesticides (Shaw and Burns 2004, 2005). In this strategy, diverse gene pool in the rhizosphere is implicated in rhizodegradation of pesticides. Numerous research reports confirmed parallel gene transfer of degradative genes which might provide soil microbes to detoxify pesticides in soil atmosphere (Boltner et al. 2005). They establish indistinguishable *lin* genes in *Sphingomonas* strains displayed definite confirmation for the parallel relocation of the HCH-detoxifying potential. Miyazaki et al. (2006) illustrated propagation of *lin*B genes for HCH detoxification in the organic surrounding.

12.4 Conclusion

Bioremediation entails diverse clean up technologies to dispose pollutants from the atmosphere. Microbiome harbors richest diversity of living soldiers which could fetch an ecological solution for pesticide detoxification. By proper implementation of phytoremediation initiatives together with the appropriate microbe selection we can develop innovative strategies for contaminant detoxification. Engineering of beneficial microbes to improve detoxifying capacity can provide further advancement in pesticide detoxification. Pesticide detoxification via varied remediation technologies can be implemented to clean the atmosphere. Field trials of different clean up technologies can provide a data set for developing remediation technologies and screen out the feasibility of remediation technology for a particular kind of contaminant.

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Chapter 13
Silver Nanoparticles in Water Purification: Opportunities and Challenges

Rahul R. Gadkari, S. Wazed Ali, R. Alagirusamy, and Apurba Das

Abstract Conventional water purification or disinfection techniques, such as chemical treatment, water purification via ozone or chlorine based components lead to the generation of disinfection byproducts. Antimicrobial activity of nanomaterials has the potential to avoid problems associated with the release of disinfection products. Advances in nanoscale science and engineering have provided solution to many of the current problems involving water purification. Purifying water with silver is known for quite some time and has been traditionally applied in a wide range of applications. Potential use of silver nanoparticles (AgNPs) for water purification and its relative bacterial filtration effectiveness is discussed in this chapter. The section also provides information about the limitations and the current challenges for the effective utilization of AgNPs in water purification.

Keywords Water purification • Nanomaterials • Silver nanoparticles • Antibacterial effects

13.1 Introduction

Water is necessary for the survival of all living beings. However, the presence of various toxic impurities in drinking water generates various health risks, making it extremely important to protect the water from being contaminated. Water should essentially be bereft of toxic chemicals and pathogens to ensure good health of all living beings as well as for preserving of the environment. Existing supplies of fresh water have considerably been decreased due to the extended droughts, increasing

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M. Oves et al. (eds.), *Modern Age Environmental Problems and their Remediation*,
DOI 10.1007/978-3-319-64501-8_13

population and competing demands from a variety of users. Consequently, it has become difficult to meet rising demands of clean drinkable water. The provision of safe drinking water is currently a high priority for many of the nations.

Conventional water disinfection techniques like chemical treatment purify the water via the ozone or chlorine based components, and lead to generation of disinfection byproducts (Gomez et al. 2006). In order to overcome this problem, researchers are actively engaged in exploring the antimicrobial activity of various nanomaterials. Advances in nanoscale science and engineering have provided solution to many of the current problems involving water filtration. The use of nanotechnology for water disinfection has huge potential and has thereby gained importance.

Uses of nanosorbants, nanocatalysts, bioactive nanoparticles, nanostructured catalytic membranes and nanoparticles have been reported to enhance the water purification efficiency (Savage and Diallo 2005). Utilization of specific nanoparticles, either embedded in membrane or in the form of nanofilaments web membranes, or on other structure media, can effectively and economically filter contaminated water to consumable form (Coopera et al. 2013).

Nanomaterials act as superb adsorbents, catalysts and sensors owing to their large surface area and higher reactivity. The advanced research in the stream of polymer science presents several natural and engineered nanomaterials like chitosan, silver nanoparticles, photocatalytic titanium dioxide, aqueous fullerene nanoparticles and carbon nanotubes which can be effectively used in water filtration systems (Savage and Diallo 2005).

Purifying water with silver is known from long time. It has been around for thousands of years. Silver is an extensively studied material due to its antimicrobial effectiveness over a range of microorganisms, low toxicity to human beings, and ease of incorporation on various substrates for disinfection applications. This chapter focuses on the potential use of silver nanoparticles (AgNPs) for water purification along with its challenges.

13.2 Silver as an Efficient Antibacterial Agent

The antimicrobial properties of silver compounds and silver ions have been traditionally recognized and applied in a wide range of applications (Bosetti et al. 2002). Silver and its compounds have shown strong inhibitory and bactericidal effect against various bacteria, fungi and viruses (Lok et al. 2006; Li et al. 2010). However, mechanism of action of the AgNPs to kill the bacteria is still not completely understood.

Several researchers had studied and anticipated few mechanisms for the antimicrobial property of AgNPs. Jung et al. (2008) studied antibacterial activity and mechanism of action of the silver ion against *Staphylococcus aureus* and *Escherichia coli* bacterial cells. They found considerable changes in the bacterial

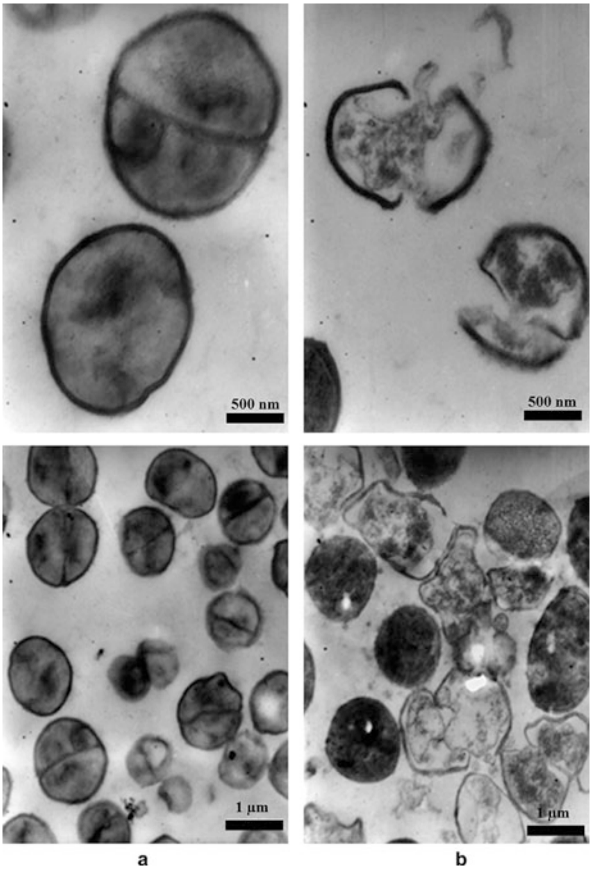


Fig. 13.1 Transmission electron microscopy images of *S. aureus* before (**a**) and after 24 h (**b**) AgNP treatment (Mirzajani et al. 2011)

cell membranes upon silver ion treatment, which might be the cause or consequence of cell death.

Mirzajani et al. (2011) investigated the antibacterial activity of AgNPs using *Staphylococcus aureus* (Gram-positive bacteria). They studied the mechanism of antibacterial action of AgNPs by analyzing the growth, morphology and molecular variations in the cell wall. They reported that for concentration of 4 mg/mL of AgNPs, there was complete inhibition of bacterial growth. The transmission electron microscopy images (Fig. 13.1) show accumulation of AgNPs in the bacterial membrane and bacteria cell wall damage produced.

Antibacterial mechanism of AgNPs on *Escherichia coli* (Gram-negative bacteria) was studied by Li et al. (2010). They reported that AgNPs destroy the permeability of the bacterial membranes by leakage of reducing sugars and proteins and induce the respiratory chain dehydrogenases into inactive state (Fig. 13.2).

Sondi and Salopek-Sondi (2004) reported that AgNPs degrade lipopolysaccharide molecules accumulated inside the membrane by forming “pits”, and cause large increases in membrane permeability. It has also been proposed that silver ions

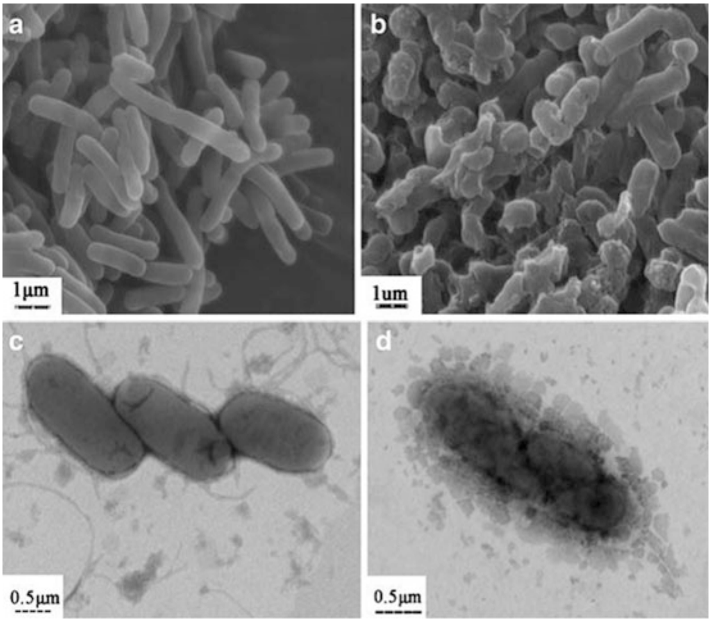


Fig. 13.2 Action of AgNPs on *E. coli* cells observed by SEM (**a**, **b**) and TEM (**c**, **d**). (**a** and **c**) Cell structure of native *E. coli* cells; (**b** and **d**) cell structure of *E.coli* cells treated with 50 µg/mL AgNPs (Li et al. 2010)

prevent DNA replication and affect the structure as well as permeability of the cell membrane (Feng et al. 2000). Some researchers have reported that silver ions are photoactive in the presence of UV-A and UV-C irradiation which boosts the UV inactivation of bacteria and viruses (Rahn et al. 1973; Kim et al. 2008; Li et al. 2008).

13.3 Potential Use of AgNPs in Water Purification System

Nanoparticles are stable on the foam and are not washed away by water; and also retain the morphology of the foam after coating. Jain and Pradeep (2005) studied the potential use of AgNPs-coated polyurethane foam for antibacterial water filter. They used 1.5 L of the nanoparticle solution for the saturated coating of 20 cm × 25 cm foam of 8 mm thickness. The foam was soaked in AgNPs solution overnight. Then this coated foam was tested for its antibacterial filtration activity. The input water which had bacteria concentration about 1×10^5–1×10^6 colony-forming units (CFU)/mL was filtered out; no bacterium was detected in the output water. Moreover there was no bacterial growth below the foam.

Phong et al. (2009) also fabricated an antibacterial water filter by coating AgNPs on flexible polyurethane foams. AgNPs-coated polyurethane foams were prepared by soaking the foam in 10, 20 and 50 ppm of silver colloidal solutions for 10 h. Input water samples, which were received from a well, had total coliforms of 45 Most Probable Number (MPN)/100 mL, *E. coli* density of 30 MPN/100 mL in one sample; and coliforms density of 110 MNP/100 mL, *E. coli* density of 70 MPN/100 mL in another sample. After filtration of these two water samples through fabricated filter, no bacterias were detected in output water. Furthermore, the obtained result reflected that antibacterial efficiency increased with increasing the concentration of silver solutions.

Dankovich and Gray (2011) impregnated AgNPs on paper from the point of use in water treatment. AgNPs were deposited by the in situ reduction of silver nitrate on the cellulose fibres of an absorbent blotting paper sheet having 0.5 mm thickness and weight 250 g/m^2. These AgNPs papers were tested for bacteria inactivation and silver leach out and were found to exhibit antibacterial properties towards suspensions of *Escherichia coli* and *Enterococcus faecalis* bacteria. Moreover, the silver loss from sheets was found to be 0.1 parts per million (ppm).

Zodrow et al. (2009) fabricated polysulfone ultrafiltration membranes impregnated with AgNPs which gave improved biofouling resistance and virus removal efficiency. Biofouling and virus penetration are two important hindrances in water treatment membrane filtration. Biofouling reduces membrane permeability, increases energy costs, and decreases the lifetime of membranes. This fabricated membrane exhibited antimicrobial properties towards a variety of bacteria, including *Escherichia coli K12*, *Pseudomonas mendocina KR1* and *MS2bacteriophage*.

All these studies show the potential of AgNPs, qualifying it to be effectively used for the bacterial filtration of water.

13.4 Enhancement of Antibacterial Effects by Complexing Novel AgNPs with Other Natural Bioactive Agents for Water Purification

Chitosan is a polysaccharide having excellent biocompatibility with noticeable antimicrobial activity along with low level of immunogenicity and toxicity (Rinaudo 2006; Paul and Sharma 2000; Muzzarelli and Muzzarelli 2005; Chandy and Sharma 1990). Owing to its remarkable combination of properties, chitosan is highly potent of being used in several applications like water purification, air filtration, biomedical, etc (Ravi Kumar 2000; Crini 2005).

Wazed Ali et al. (2011) conducted preliminary studies on the synthesis and characterization of chitosan and silver loaded chitosan nanoparticles for bioactive polyester. The silver loaded chitosan nanoparticle showed an increase in activity due to synergistic effect of Ag and chitosan nanoparticles. Several researchers have embedded AgNPs along with chitosan in order to enhance antibacterial performance at lower level concentration of silver and reduce the toxicity associated with silver.

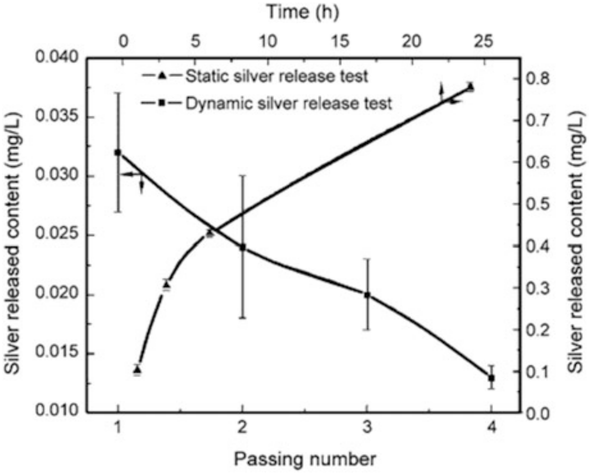
Zhao et al. (2012) manufactured an electrospun web from AgNPs/Polyvinyl alcohol (PVA)/chitosan nanofibres taking $AgNO_3$ concentration as 5 and 10 mol L^{-1}. The AgNPs were formed in-situ in PVA/chitosan blend solution. This resulted in AgNPs/PVA/chitosan nanofibres having smooth surface and uniform diameter. It was also observed that the average diameter of fibres slightly decreased with the decrease in silver content. AgNPs were round in shape with diameter ranging from 4 to 14 nm as observed on the surface of the nanofibers. With approximately 10 mg nanofibres in 50 mL bacteria nutrient solution with an initial concentration of ca. 10^4 CFU mL^{-1}, the AgNPs/PVA/chitosan nanofibres had an inhibition ratio of 98% against *E. coli* up to a contact time of 12 h. These results suggest that silver deposited chitosan electrospun nanofibrous web can be explored as filters for purifying water contaminated with bacteria.

Chitosan is a rigid and brittle natural polymer and has amino groups and hydroxyl groups in the backbone. Hang et al. (2010) found that as the concentration of chitosan increased in the chitosan/PVA blends, it resulted in the production of an electrospun web with higher tensile strength at break. However, the elongation at break falls down for the same. Moreover, they found that addition of $AgNO_3$ to the chitosan/PVA blend solutions enhanced the electrospinning performance as well as led to higher antibacterial activity.

Adibzadeh et al. (2014) studied the leaching behaviour of chitosan/PVA nanofibres containing 4 wt% $AgNO_3$ which was evaluated using static and dynamic methods under same conditions. In case of static method, AgNPs impregnated nanofibres were evaluated by immersing 10 mg of CS/PVA nanofibres containing 4 wt% $AgNO_3$ in 50 mL Phosphate-buffered saline (PBS). The amount of silver leached from the nanofibres at different exposure time was determined by flame atomic absorption spectrophotometry. The amount of silver released increased rapidly during the first 3 h of exposure time during static testing, whereas during dynamic testing it was found to decrease continuously from 6 h to 24 h immersion time. The total Ag^+ content released into the PBS from the CS/PVA nanofibers containing 4 wt% $AgNO_3$ during 24 h time frame was just below 0.8 mg/L, as shown in Fig.13.3.

In case of dynamic leaching test, four consecutive batches of 100 mL PBS were filtered through the CS/PVA electrospun nanomembrane containing 4 wt% $AgNO_3$ and the silver content was determined after each filtration. It was observed that the concentration of the Ag^+ lost during the filtration was rather high at the beginning of the filtration, while this amount dropped upon further filtration. Increase in the Ag^+ in the PBS sample was explained by the release of AgNPs, which had lower stabilization rate on the surface of the nanofibers during the first and second filtrations (Fig 13.3).

Fig. 13.3 Static and dynamic silver release test (Adibzadeh et al. 2014)



13.5 Limitations and Challenges for Use of Silver Nanoparticles in Water Purification Application

Numerous nanomaterials, such as silver, chitosan, titanium dioxide (TiO_2), fullerenes and its derivatives, and zinc oxide (ZnO) have found applications in water treatment systems, as antimicrobial agents. Among all these antimicrobial agents, AgNPs is undoubtedly the most extensively used material for the water treatment. Quite a few challenges exist for efficient application of AgNPs in water disinfection treatment like retention of AgNPs and the sustainability of antimicrobial activity over a period of time. Retention of AgNPs is important mainly because it not only affects the cost of treatment but also gives an adverse impact on human health (Li et al. 2008). The suppliers that can provide large quantities of nanomaterials at economically viable prices is also a critical requirement for the application of nanotechnology for water disinfection on mass scale. Moreover, added investigations are needed in order to integrate the AgNPs into the existing water purification systems.

13.6 Conclusions

Clean water is an essential need for all human beings. The antimicrobial properties of silver compounds and silver ions have been traditionally recognized and applied in a wide range of applications. AgNPs can be effectively used for the bacterial filtration of contaminated water. AgNPs are a promising alternative to traditional chemical disinfectants that are prone to generate harmful disinfection by-products. Wide scope awaits and substantial contributions are needed in order to make use of the AgNPs more scalable, economical, and safer for water purification systems.

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