SUSTAINABLE MATERIALS | VOLUME 1

BIOREMEDIATION FOR ENVIRONMENTAL POLLUTANTS

Editor:
Inamuddin

Bentham Books

Sustainable Materials

(Volume 1)

Bioremediation for Environmental Pollutants

Edited by

Inamuddin
Department of Applied Chemistry
Zakir Husain College of Engineering and Technology
Faculty of Engineering and Technology
Aligarh Muslim University, Aligarh-202002
India

Sustainable Materials

(Volume 1)

Bioremediation for Environmental Pollutants

Editor: Dr. Inamuddin

ISSN (Online): 2972-4783

ISSN (Print): 2972-4791

ISBN (Online): 978-981-5123-49-4

ISBN (Print): 978-981-5123-50-0

ISBN (Paperback): 978-981-5123-51-7

First published in 2023.

need for a court order if at any point you breach any terms of this License Agreement. In no event will any delay or failure by Bentham Science Publishers in enforcing your compliance with this License Agreement constitute a waiver of any of its rights.

3. You acknowledge that you have read this License Agreement, and agree to be bound by its terms and conditions. To the extent that any other terms and conditions presented on any website of Bentham Science Publishers conflict with, or are inconsistent with, the terms and conditions set out in this License Agreement, you acknowledge that the terms and conditions set out in this License Agreement shall prevail.

Bentham Science Publishers Pte. Ltd.
80 Robinson Road #02-00
Singapore 068898
Singapore
Email: subscriptions@benthamscience.net

BENTHAM SCIENCE

CONTENTS

PREFACE

Modern civilization is experiencing an environmental catastrophe as a result of prevailing pollution issues worldwide. Scientists, researchers, environmentalists, engineers, planners, as well as the developing nations, all need to address this problem to some extent through the introduction of microbes in order to recycle waste into useful forms that other well-beings can utilize efficiently. Varied microbial traits offer a strong substitute to get around the serious issues as they can withstand practically any environmental situation because of their incredible metabolic activity. Hence, the extensive nutritional capacities of microbes can be exploited in the bioremediation of environmental contaminants. Moreover, these microorganisms can be used in bioremediation to eliminate, degrade, detoxify, and immobilize a variety of physical and chemical pollutants. Enzymes are exploited in the destruction and transformation of pollutants like heavy metals, hydrocarbons, pesticides, oil and dyes.

The book *Bioremediation for Environmental Pollutants - Part 1* focuses about the bioremediation of heavy metals, pesticides, textile dyes removal, petroleum hydrocarbon, micro plastics and plastics.

Inamuddin
Department of Applied Chemistry
Zakir Husain College of Engineering and Technology
Faculty of Engineering and Technology
Aligarh Muslim University, Aligarh-202002
India

List of Contributors

Abudukeremu Kadier	Laboratory of Environmental Science and Technology, The Xinjiang Technical Institute of Physics and Chemistry, Key Laboratory of Functional Materials and Devices for Special Environments, Chinese Academy of Sciences, Urumqi, 830000, China Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing, 100049, China
Ankit Kumar	Department of Chemistry, University of Delhi, Delhi 110007, India
Ali Moertopo Simbolon	Research Centre for Environmental and Clean Technology, National Research and Innovation Agency Republic of Indonesia, Kawasan Puspitek gd 820, Serpong, 15314, Tangerang Selatan, Indonesia
Alok Kumar Panda	School of Applied Sciences, Kalinga Institute of Industrial Technology, Deemed to be University, Bhubaneswar-751024, Delhi – 110 042, India
Athar Hussain	Department of Civil Engineering, CBP Government Engineering College Jaffarpur, New Delhi-73, India
Bekti Marlena	Research Centre for Environmental and Clean Technology, National Research and Innovation Agency Republic of Indonesia, Kawasan Puspitek gd 820, Serpong, 15314, Tangerang Selatan, Indonesia
Bhaskarjyoti Gogo	Department of Biotechnology, Assam Royal Global University, Guwahati-781035, Assam, India,
Deepesh Tiwari	Department of Environmental Engineering, Delhi Technological University, Delhi, India
Dongsheng Song	Laboratory of Environmental Science and Technology, The Xinjiang Technical Institute of Physics and Chemistry, Key Laboratory of Functional Materials and Devices for Special Environments, Chinese Academy of Sciences, Urumqi, 830000, China College of Resources and Environment, Xinjiang Agricultural University, Urumqi, 830052, China
Debajit Borah	Department of Biotechnology, Assam Royal Global University, Guwahati-781035, Assam, India,
Evans C. Egwim	Department of Biochemistry, Federal University of Technology Minna, Nigeria
Gargi Dutta	Department of Biotechnology, Assam Royal Global University, Guwahati-781035, Assam, India,
Geetanjali	Department of Chemistry, Kirori Mal College, University of Delhi, Delhi – 110 007, India
Gokul Ram Nishad	Department of Chemistry, Govt. Digvijay PG Autonomous College, Rajnandgaon-491441, Chhattisgarh, India
Grace N. Ijoma	Institute for the Development of Energy for African Sustainability (IDEAS) Research Unit, University of South Africa (UNISA), Florida Campus, Private Bag X6, Johannesburg 1710, South Africa
J. Ranjitha	CO_2 Research and Green Technologies Centre, VIT University, Vellore-14, Tamilnadu, India

Japhet G. Yakubu	Department of Microbiology, Federal University of Technology Minna, Nigeria
Joshua Gorimbo	Institute for the Development of Energy for African Sustainability (IDEAS) Research Unit, University of South Africa (UNISA), Florida Campus, Private Bag X6, Johannesburg 1710, South Africa
Kamlesh Kumar Nigam	Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi 221005, UP, India
Lakshmi Unnikrishnan	CIPET : School for Advanced Research in Polymers (SARP) - APDDRL - Bengaluru 7P, Hi-Tech Defence and Aerospace Park (IT Sector), Jalahobli, Bengaluru North, Near Shell R&D Centre, Devanahalli, Bengaluru - 562 149, India
Mohd. Wajahat Sultan	Department of Geology, Aligarh Muslim University, Aligarh, India
Mohd. Imran Ahamed	Department of Chemistry, Aligarh Muslim University, Aligarh, India
Manish Kumar Singh	Krishi Vigyan Kendra, Rajnandgaon-491441, Chhattisgarh, India
Nanik Indah Setianingsih	Research Centre for Environmental and Clean Technology, National Research and Innovation Agency Republic of Indonesia, Kawasan Puspitek gd 820, Serpong, 15314, Tangerang Selatan, Indonesia
Oluwafemi A. Oyewole	Department of Microbiology, Federal University of Technology Minna, Nigeria
Priti Gupta	Department of Chemistry, Manav Rachna University, Faridabad, Haryana – 121001, India
Praveen Kumar Yadav	Chemical and Food BND Group, Indian Reference Materials Division, CSIR-National Physical Laboratory, Dr. K.S. Krishnan Marg, New-Delhi 110012, India Academy of Scientific and Innovative Research (AcSIR), Ghaziabad, U.P 201002, India
Peng-Chen Ma	Laboratory of Environmental Science and Technology, The Xinjiang Technical Institute of Physics and Chemistry, Key Laboratory of Functional Materials and Devices for Special Environments, Chinese Academy of Sciences, Urumqi, 830000, China Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing, 100049, China
Priyanka Singh	Department of Chemistry, Govt. Digvijay PG Autonomous College, Rajnandgaon-491441, Chhattisgarh, India
R. Gayathri	CO_2 Research and Green Technologies Centre, VIT University, Vellore-14, Tamilnadu, India
Rustiana Yuliasni	Research Centre for Environmental and Clean Technology, National Research and Innovation Agency Republic of Indonesia, Kawasan Puspitek gd 820, Serpong, 15314, Tangerang Selatan, Indonesia
Rupesh Kumar	Department of Biotechnology, Assam Royal Global University, Guwahati-781035, Assam, India
Ram Singh	Department of Applied Chemistry, Delhi Technological University, Delhi – 110 042, India

S. Swarupa Tripathy	Chemical and Food BND Group, Indian Reference Materials Division, CSIR-National Physical Laboratory, Dr. K.S. Krishnan Marg, New-Delhi 110012, India
Salman Ahmed	Department of Geology BFIT Group of Institution, Dehradun, India
Setyo Budi Kurniawan	Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, National University of Malaysia (UKM), 43600 UKM Bangi, Selangor, Malaysia
Shamima Begum	Department of Biotechnology, Assam Royal Global University, Guwahati-781035, Assam, India,
Shishir Kumar Singh	Academy of Scientific and Innovative Research (AcSIR), Ghaziabad, U.P 201002, India Environmental Science and Biomedical Metrology Division, CSIR- National Physical Laboratory, Dr. K.S. Krishnan Marg, New-Delhi 110012, India
Siti Rozaimah Sheikh Abdullah	Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, National University of Malaysia (UKM), 43600 UKM Bangi, Selangor, Malaysia
Sonalee Das	CIPET : School for Advanced Research in Polymers (SARP) - APDDRL - Bengaluru 7P, Hi-Tech Defence and Aerospace Park (IT Sector), Jalahobli, Bengaluru North, Near Shell R&D Centre, Devanahalli, Bengaluru - 562 149, India
Soumyaranjan Senapati	School of Applied Sciences, Kalinga Institute of Industrial Technology, Deemed to be University, Bhubaneswar-751024, India,
Sreelipta Das	School of Applied Sciences, Kalinga Institute of Industrial Technology, Deemed to be University, Bhubaneswar-751024, India,
Sunil Kumar Tiwar	Department of Mechanical Engineering, CBP Government Engineering College Jaffarpur, New Delhi-73, India
Telli Alia	Laboratoire de protection des écosystèmes en zone aride and semi aride, Université de KASDI Merbah, BP 511 la route de Ghardaia, Ouargla 30000, Algérie
Tonderayi S. Matambo	Institute for the Development of Energy for African Sustainability (IDEAS) Research Unit, University of South Africa (UNISA), Florida Campus, Private Bag X6, Johannesburg 1710, South Africa
Younus Raza Beg	Krishi Vigyan Kendra, Rajnandgaon-491441, Chhattisgarh, India,
Vikram Singh	Department of Chemistry, NREC College, Khurja, Uttar Pradesh – 203131, India,
Vijayalakshmi Shankar	CO_2 Research and Green Technologies Centre, VIT University, Vellore-14, Tamilnadu, India
Weiz Nurmahomed	Institute for the Development of Energy for African Sustainability (IDEAS) Research Unit, University of South Africa (UNISA), Florida Campus, Private Bag X6, Johannesburg 1710, South Africa

CHAPTER 1

Microbial Remediation of Heavy Metals

R. Gayathri[1], **J. Ranjitha**[1] and **V. Shankar**[1,*]

[1] *CO_2 Research and Green Technologies Centre, VIT University, Vellore-14, Tamilnadu, India*

Abstract: Chemical elements with an atomic mass unit ranging from 63.5 – 200.6 (relative atomic mass) and a relative density exceeding 5.0 are generally termed as heavy metals. Since they are non-biodegradable inorganic contaminants, physical and chemical methods of degradation are ineffective. Heavy metals cannot be degraded easily due to their physical and chemical properties, such as the rate of oxidation & reduction reactions, rate of solubility, formation of complexes with other metal ions, *etc*. They are flexible, and easily accumulated in the environment. In the case of bioaccumulation, they are highly lethal to the organisms. The process of removal of toxic and hazardous material from the environment using plants and microorganisms is termed bioremediation. The disposal of toxic contaminants using plants is termed phytoremediation. Microbial bioremediation consists of the removal of toxic elements with the application of microorganisms during which the toxic substance is converted into either end products or nontoxic and non-hazardous forms or recovery of metals.

Keywords: Bioremediation, By-products, Hazardous, Heavy metals, Microbe.

INTRODUCTION

Environmental pollution is currently a major problem on a global scale. The ecosystem is severely contaminated due to the rise in industries and increased population. Urbanization with improved standard of life resulted in the reduction of quality of the ecosystem with high pollution within the past 100 years [1]. Air, water, the soil has been contaminated heavily nowadays due to the usage of pesticide, fertilizers, mining, tannery effluents, smelting, electronic appliances, electroplating, paper industries; large scale production of chemicals including solvents, chemical feedstocks, petroleum products, additives, synthetic polymers, pigments and dyes, *etc*., resulting in the release of heavy metals at a large scale [2]. These contaminants are accumulated in the soil, water, and air resulting in a life-threatening situation for all living organisms [3]. Elevated CO_2 levels in the air, fall in natural resources, degradation and release of pollutants such as heavy

* **Corresponding Author Vijayalakshmi Shankar:** CO_2 Research and Green Technologies Centre, VIT University, Vellore-14, Tamilnadu, India, E-mail: vijimicro21@gmail.com

Inamuddin (Ed.)

metals, xenobiotics, toxic gases and chemical substances, *etc*., into the ecosystem are the primary after-effects of technological & industrial modernization [4]. When compared to various environmental pollutants heavy metals are lethal to biotic factors of the ecosystem. Heavy metals easily tend to accumulate in the soil, & water hence this type of pollution is a major ecological issue. They remain in an unstable form - ionic state and readily react with the surrounding elements [5].

HEAVY METALS

Chemical elements with an atomic mass unit ranging from 63.5 – 200.6 (relative atomic mass) and a relative density exceeding 5.0 are generally termed as heavy metals. They possess high density. Even the lowest concentration of heavy metal shows the highest level of toxicity [6]. They are non-biodegradable inorganic pollutants hence, physical and chemical methods such as are not applicable for their decomposition. Heavy metals cannot be degraded easily due to their physical and chemical properties such as the rate of oxidation & reduction reactions, rate of solubility, formation of complexes with other metal ions, *etc*. they are flexible, easily accumulated in the environment, in case of bioaccumulation they are highly lethal to the organisms [7].

List of Heavy Metals

Aluminum (Al), Antimony (Sb),, Arsenate (As (V)),Arsenic (As), Arsenite (As (III)),Barium (Ba), Bismuth (Bi),Cadmium (Cd), Chromium (Cr), Cr(VI), Cr(III)Cobalt (Co), Copper (Cu), Gold (Au), Iron (Fe), Lead (Pb), Manganese (Mn), Mercury (Hg), Molybdenum (Mo), Nickel (Ni), Selenium (Se), Silver (Ag), Titanium (Ti), Zinc (Zn) are the heavy metals present in both contaminated soil and aquatic environment [8]. The adverse effects of heavy metals on plants & human health are listed in Tables **1** and **2**.

Table 1. Impacts of heavy metals on plants [8].

S. No	Metal Ions	Effects
1.	Zn	Reduced growth, development & senescence, inhibition of metabolism, induced oxidative damage, modifications in enzyme functions, leaf-chlorosis, purple-red leaf, lead to Mn, P deficiencies.
2.	Cd	Injuries similar to chlorosis, growth is inhibited, roots become brown resulting in death, interrupts the transport of other mineral nutrients & inhibits enzyme activity, water imbalance, reduces ATP synthesis, inhibits CO_2 incorporation & chlorophyll functions.

(Table 1) cont.....

S. No	Metal Ions	Effects
3.	Cu	Exhibits cytotoxicity in plants, induction of stress, resulting in tissues injuries, chlorosis of leaves, retarded growth, interruption of metabolism, excess oxidation, influences germination, roots & seed morphology
4.	Hg	Interruption of H_2O flow in plants increased oxidative stress, inhibits functions of mitochondria, influences metabolism & rupture of plasma membrane
5.	Cr	Reduced rate of seed germination & root development, reduced CO_2 incorporation & transportation of electrons, enzymatic functions & ATP synthesis, modification in pigmentation, induced synthesis metabolites & with modified structure
6.	Pb	Inhibition of germination, interference in enzymatic function, retardation & abnormalities of growth in various plant parts, chlorosis, interruption in carboxylation reactions. Inhibition of enzymatic functions. Alterations in H_2O balances, modified membrane permeability. high oxidative stress.
7.	As	Competes with P carrier, leads to P deficiencies, transformed into dimethylarsinic acid (DMA), mono methyl arsenicacid (MMA)
8.	Co	Inhibits the growth of shoots & biomass, impedes the concentration of Fe, chlorophyll, protein, enzyme activity, reduced transpiration, other mineral elements get translocated.
9.	Ni	Necrosis & chlorosis, nutrient imbalance, altered cellular membrane &activities, altered ionic concentration in cytosol, and reduced water absorption.
10.	Mn	Reduced rate of photosynthesis, necrosis, leaf colour change to brown resulting in death. Reduced internodal length, chlorosis,
11.	Fe	Excess free radical formation, irreversible changes in cell morphology, injuries to the plasma membrane, protein & DNA damage, reduced photosynthesis & elevated ascorbate peroxidise function & oxidative stress

Table 2. Impacts of heavy metals on the human health [7].

S, No	Metals	Minimum Threshold Level	Toxic Effects
1.	Ag	0.10	Body parts exposed to Ag (skin & tissues) change into grey or blue-grey colour, breathing difficulties, irritation in throat & lung, and stomach ache
2.	As	0.01	Alters the cellular activities including oxidative phosphorylation and ATP synthesis
3.	Ba	2.0	Results in increased blood pressure, respiratory failure, muscle twitch cardiac arrhythmia and gastrointestinal dysfunction
4.	Cd	5.0	Carcinogenic, mutagenic, endocrine disruptor, lung damage and fragile bones, affects calcium regulation in biological systems
5.	Cr	0.1	Severe Hair loss
6.	Cu	1.3	Renal failure, Brain damage, and high concentration lead to anaemia, chronic gastrointestinal irritation & abnormalities, and liver cirrhosis.

CHAPTER 2

Removal of Heavy Metals using Microbial Bioremediation

Deepesh Tiwari[1], **Athar Hussain**[2,*], **Sunil Kumar Tiwari**[3], **Salman Ahmed**[4], **Mohd. Wajahat Sultan**[5] and **Mohd. Imran Ahamed**[6]

[1] *Department of Environmental Engineering, Delhi Technological University, Delhi, India*

[2] *Department of Civil Engineering, CBP Government Engineering College Jaffarpur, New Delhi-73, India*

[3] *Department of Mechanical Engineering, CBP Government Engineering College Jaffarpur, New Delhi-73, India*

[4] *Department of Geology BFIT Group of Institution, Dehradun, India*

[5] *Department of Geology, Aligarh Muslim University, Aligarh, India*

[6] *Department of Chemistry, Aligarh Muslim University, Aligarh, India*

Abstract: The unorganized dumping of effluents along with different wastes directly into the water and soil has resulted in the rise of the concentration of many harmful metals, chemicals, and other gases in the environment. Widely known heavy metals triggering pollution issues are Lead (Pb), Chromium (Cr), Mercury (Hg), Cadmium (Cd), Copper (Cu), Arsenic (As) and Selenium (Se), as these heavy metals are generally found in the effluents of fertilizers, metallurgy, electroplating, and electronics industries. A number of physical-chemical reactions such as acid-base, oxidation-reducing, precipitation- dissolution, solubilization and ion-exchange processes occur and affect metal speciation. The physical methods used for heavy metals removal include magnetic separation, electrostatic separation, mechanical screening method, hydrodynamic classification, gravity concentration, flotation, and attrition scrubbing. The chemical methods used for eliminating heavy metals are chemical precipitation, coagulation and flocculation processes and the heavy metals are therefore removed as sludge. Electro-deposition, membrane filtration, electro-flotation and electrical oxidation are the various electrochemical treatment methods that are used to remove heavy metals from wastewater. Bioremediation is a biological method of eliminating toxins from the environment by using biological microbial bacteria such as *Pseudomonas* and *Sphingomonas*. Examples of bioremediation technologies include field farming, bioleaching, phytoremediation, bioventing, bioreactor, bio-stimulation and composting. Bioremediation is a natural process and is quite applicable as a waste treatment process for contaminated soils. The microbes present in the solution or soil can degrade the pollutants. It can also prove to be less expensive than

[*] **Corresponding author Athar Hussain:** Associate Professor, Department of Civil Engineering, CBP Government Engineering College Jaffarpur, New Delhi-73, India; E-mails: salmanahmed.alig@gmail.com, athariitr@gmail.com and deep1212001@gmail.com

Inamuddin (Ed.)

other technologies that are used for clean-up of hazardous waste and are also useful for the destruction of a wide variety of contaminants as many hazardous compounds can be transformed into harmless products.

Keywords: Bioremediation, Floatation, Hazardous, Heavy metals, Membrane filtration.

INTRODUCTION

The industrialization has grown at a faster rate since the 1950s and is considered as the growth of the economy with pollution on the earth increasing at a higher rate than the threshold predictions of WHO [1]. The knowledge of its adverse impact on health and the ecosystem leading to the unorganized dumping of effluents and waste directly into the water and soil was negligible. It resulted in the rise of the concentration of many harmful metals, chemicals, and gases that are exposed to the environment, and later on, also causes some global pandemics. After the first Global Environmental Summit in 1995, awareness of the environment and its safety had increased. Still many small and medium-size manufacturing units are not following any norms for waste disposal that are issued by the government. The problem of the rising concentration of pollutants appears to be growing for many years. Heavy metal is one of such pollutants, majorly for water and soil. Heavy metal is found naturally in the earth's crust and so it still exists in the water and soil around us but within limits [3]. Sometimes their exposure to the environment increases naturally. But after the rapid growth in industrialization and mining activities, exposure of these heavy metals to our surroundings has been increased and some of these also crossed the safety limits at various places. For example, in the case of the Bengal epidemic, there was a rise of Arsenic (As) due to the direct discharge of industrial waste in the river, causing an increase in its concentration in drinking water and soil resulting in the chronic disease Arsenicosis in the residents of that town [2].

Mining and manufacturing activities are major causes of an increase in heavy metal concentration on the surface in most of the regions. Rock weathering plays the second most abundant role. These two factors take around 97% contribution to heavy metal pollution. Other sources can be fertilizers, pesticides, and waste discharge [1]. To overcome this problem, the disciplines for waste disposal from manufacturing industries, mining activities, construction works, and others, must be regulated by the government [4]. There is a need for recycling and bioremediation of heavy metals that are one of the highly toxic pollutants. This article will cover heavy metals and their remediation processes and will mainly focus on the bioremediation process.

HEAVY METALS: SOURCES AND EFFECTS

The metals that possess a high density of approximately greater than 4000 kg.m^{-3}are termed as heavy metals and have high molecular weight with respect to other metals with their capability of forming colorful complexes (Cotton S., 2013; Pourret, 2018). Widely known heavy metals triggering pollution issues are Lead (Pb), Chromium (Cr), Mercury (Hg), Cadmium (Cd), Copper (Cu), Arsenic (As), Selenium (Se), *etc.* These heavy metals are generally found in the effluents of fertilizers, metallurgy, electroplating and electronics industries [5]. Mercury and lead are also used in laboratories, batteries and other scientific equipment. Some of the heavy metals like iron, zinc in a fixed concentration, are essential to our body for growth and immunity; but after a certain limit, or indifferent oxidation state, they can start interfering with regular functions in the body of a living entity and may cause serious health diseases. The heavy metals originating from the solid waste landfill leachate disposed of sewage, min tailing leachate, liquid wastes disposed of in deep wells, seepage of industrial effluents through lagoons or leakages ultimately join the groundwater reservoirs and contaminate the groundwater.

Distinct physical-chemical reactions such as acid-base, oxidation-reducing, precipitation- dissolution, solubilization and ion-exchange processes, occur and affect metal speciation and also typically influence the mobility of these metal pollutants. Abnormalities with other dissolved elements, pH, Eh, sorption and ion exchange capability, and the quantity of organic matter, usually accelerate the rate and intensity of these reactions. The availability of Eh, pH, temperature and moisture also influence the environmental toxicity, stability, and reactivity of heavy metals that eventually affect the speciation of these toxic metals. The diffusion of some heavy metals in soils can be decided by the use of special solvents, which solubilize the various phases [6].

The detrimental characteristics of such toxic metals are to eliminate the critical structure of cells of almost any living creature, decrease the rate of functions in that organism and modify the transport structure or work of enzymes, proteins or membranes [7]. Continuous exposure to these heavy metals can affect the various parts of the human body such as exposure to arsenic affects the human skin. Exposure to mercury affects the bones and similarly, the presence of lead affects the central nervous system and liver. Similarly, continuous exposure to cadmium affects blood and enzymes. Therefore, the presence of these heavy metals causes toxicity in some states or at higher concentrations. There is a need to get an understanding of the eco-friendly process that can eliminate these heavy metals from the food chain or the environment. Various sources of heavy metals as mentioned in the literature are summarized in Table **1**.

CHAPTER 3

Bioremediation of Heavy Metal in Paper Mill Effluent

Priti Gupta[1,*]

[1] *Department of Chemistry, Manav Rachna University, Faridabad, Haryana – 121001, India*

Abstract: The pulp and papermaking industry, being a large consumer of natural resources, *i.e.*, wood and water, has become one of the largest sources of pollution to the environment. Wastewater generated during various stages of the pulp and paper-making process continues to be toxic in nature even after secondary treatment. The effluent water contains not only various toxic chemicals such as volatile organic compounds but also heavy metals like copper, mercury, iron, zinc aluminium, *etc.* Even at very low concentrations, most of the heavy metals are toxic and deadly in nature. Prolonged exposure to heavy metals causes various diseases in humans and animals either through skin contact, inhalation, or *via* consuming food materials.

Treatment of pulp and paper industry wastewater by conventional methods is not efficient due to its complex nature. These conventional methods, either physical, biological, chemical or a combination of these methods are also not environmentally safe and economically viable. Complete degradation of heavy metals is not possible by the application of a single method. The generation of a huge volume of toxic sludge is an ongoing and major problem. Therefore bioremediation methods are preferred as they are highly efficient, cost effective, eco-friendly in nature, there is no secondary waste created in the environment and metabolize the highly toxic heavy metals into degradable, less toxic components with the help of microbes.

This chapter focuses on Micro-Bioremediation methods using algae, fungi, yeasts and bacteria as the most preferred medium to treat wastewater generated by the pulp and paper industry. These are further also used to reduce toxic organic compounds.

Keywords: Accumulative, Adsorption, Anaerobic, Bioaccumulation, Biosorbents, Bioremediation, Carcinogenic, Chelation, Degradation, Efficiency, Effluent, Genetic engineering, Hazardous, Heavy metals, Organic halides, Persistent, Physicochemical, Phytoremediation, Substrate, Transformation.

* **Corresponding author Priti Gupta:** Assistant Professor, Department of Chemistry, Manav Rachna University, Faridabad, Haryana – 121001 India; E-mail: me.pritigupta@gmail.com

Inamuddin (Ed.)

INTRODUCTION

Urban industrialization has long been identified as a major source of aquatic environment contamination through atmospheric deposition as well as wastewater discharge. All types of manufacturing industries contribute to this. The paper and pulp industry being one of the most volatile and important industries in the world, is by-far the sixth largest polluting industry (after cement, oil, textile, leather, and steel industries). The process of producing paper from pulp produces various discharges of a variety of pollutants including organic and inorganic pollutants like gases, liquid, and solid wastes into the environment [1]. The global volume of toxic effluent released into the water bodies by paper and pulp industries is approximated to be around 178 – 303 m^3.

The process of wood pulping and paper products production generate a considerable amount of pollutants. When these effluents are discharged in either an untreated condition or in the poorly treated conditions in the water bodies, this causes a severe problem of water pollution. Usage of a higher quantity of water between 20,000 and 60,000 gallons per ton of product results in the generation of a large amount of water [2].

The process of pulping and bleaching are energy intensives and consume a considerable volume of chemicals and fresh water. Usage of raw material, pulping method, bleaching process as well as the size of Paper and Pulp mills decide the extent of wastewater production and, therefore, the level of pollution and toxicity [3].

The distribution of wastewater generated by the Paper and Pulp mills encompasses the whole of the surrounding ecosystem. In aquatic life, it may lead to reproductive irregularities and damage the genetic and immune system in invertebrates and zooplankton, which are a source of nutrients and food for fish [4]. Such polluted water when released into the water bodies also causes slime growth, thermal impacts, scum formation, colour problems, and loss of aesthetic beauty in the environment [5].

Paper mill generated waste water contains significantly higher concentrations of BOD (biological oxygen demand), COD (chemical oxygen demand) as well as phosphorous. Electrical conductivity, temperature and colour value also increases in such water [6]. The effluent water not only contains volatile organic compounds like alcohols, phenols, methanol, acetone, surfactants, dyes, acids and alkalies but also carries heavy metals such as zinc, mercury, iron, copper and aluminium [7]. These heavy metals are highly toxic, carcinogenic as well as mutagenic in nature even though present in very low concentrations [8, 9]. They are commonly present in paper mill effluents and being hazardous in nature causes serious problems to the sewage network pipelines. Hazardous impact of heavy metals on biological processes is complex in nature and depends upon various factors such as species, solubility and concentration of the metal as well as on various characteristics such as pH of the influent [10]

Given the intensity of the hazards posed, various methods have been studied and reported for the remediation of wastewater. Physical methods such as adsorption, microfiltration, *etc.* and chemical treatment methods such as coagulation, sedimentation, oxidation, ozonation, *etc.*, or combinations of these methods are prevalent, however, these methods are not cost-effective. Additionally, these also increase the BOD, and COD level of the treated effluent along with the generation of a large amount of sludge [11].

It is therefore essential to develop not only a cost-effective as well as eco-friendly and efficient method for the remediation of the paper pulp mill effluent. Biological methods provide popular and attractive alternative methods that utilize the metabolic potential of microbes to clean up the environment [12, 13]. These include various aerobic and anaerobic treatments using bioreactors.

PAPER & PULP INDUSTRY: GLOBAL OUTLOOK ON UTILITY AND GROWTH

There has been a widespread application of paper products for packaging. With the increasing awareness of long term use of plastic, and increased use of hygiene products that include toilet papers for sanitation, paper towels during travel, and disposable wipes for babies the use of paper products has further elevated the consumption of paper products many folds. Increased demand along with increase in spending capacity of middle class across the globe adds to it. The paper & pulp market was valued at USD 518.83 Billion in 2019 and is expected to reach USD 679.72 Billion by 2027 [14].

Increased e-commerce leading to packaging and shipment will also drive the global paper & pulp market with increased demand for packaging. The paper & pulp industry continues to engage professionals in various areas of research activities such as - maximizing yield, increase in efforts to reduce the use of energy, ways to attain sustainable environmental goals, *etc.* The industry is also shifting focus towards replacing the larger share of products that are currently made out of plastic materials.

PAPER & PULP INDUSTRY: GLOBAL OUTLOOK ON HAZARDS

Unlike many other production units or manufacturing industry, the paper and pulp industry is a heavy consumer of energy and emits an equally large amount of

CHAPTER 4

Bioremediation of Pesticides

Praveen Kumar Yadav[1,2,*], **Kamlesh Kumar Nigam**[3], **Shishir Kumar Singh**[2,4], **Ankit Kumar**[5] and **S. Swarupa Tripathy**[1]

[1] *Chemical and Food BND Group, Indian Reference Materials Division, CSIR- National Physical Laboratory, Dr. K.S. Krishnan Marg, New-Delhi 110012, India*

[2] *Academy of Scientific and Innovative Research (AcSIR), Ghaziabad, U.P 201002, India*

[3] *Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi 221005, UP, India*

[4] *Environmental Science and Biomedical Metrology Division, CSIR- National Physical Laboratory, Dr. K.S. Krishnan Marg, New-Delhi 110012, India*

[5] *Department of Chemistry, University of Delhi, Delhi 110007, India*

Abstract: Increasing population has raised the demand for food grains, which compels the producers for the heavy use of pesticides to meet the demand for sufficient production of food grains. Heavy utilization of pesticides polluted soil, water, plant, animal, food grains, *etc*. Additionally, that much utilization of pesticides has also created several legal and illegal contaminated sites across the world, which are continuously polluting the environment. There are several methods available for pesticide treatment, but the bioremediation method has been more promising than the others. Bioremediation of pesticides is carried out through either *ex situ* or *in situ* methods using different organisms like bacteria, fungi and higher plants. The pesticides degradation using bacteria, fungi and higher plants is called bacterial degradation, mycodegradation and phytodegradation, respectively. Present review discusses different methods, mechanisms and recent tools used for the bioremediation of pesticides.

Keywords: Bacteria, Bioremediation, Food grains, Fungi, Mycodegradation and phytodegradation, Pesticides.

INTRODUCTION

In this contemporary world, increasing population, rapid industrialization, and advancement in technologies have increased the productivity of agricultural activity. But it is well said that every development needs a cost, so, this proverb

[*] **Corresponding author Praveen Kumar Yadav:** Chemical and Food BND Group, Indian Reference Materials Division, CSIR- National Physical Laboratory, Dr. K.S. Krishnan Marg, New-Delhi 110012, India & Academy of Scientific and Innovative Research (AcSIR), Ghaziabad, U.P 201002, India; E-mail: kpraveen.yadav414@gmail.com

Inamuddin (Ed.)

exactly fits modern agriculture. For example, these days, millions of tons ofpesticides are being produced to improve agricultural productivity, to control the harmful effects of various organisms (bacteria fungi, insects) as well as the effect of some herbs on the economical crop's productivity [1].

Though the use of pesticides is not new for the world, it has been utilised for pest control for centuries. For example, Romans, Greeks, and Sumerians also used different types of chemicals like mercury, copper, sulphur, arsenic or plant extracts to control the pests. Though, at that time, these chemicals were not very effective due to primitive chemistry and poor application methods. However, after World War II, several chemical compositions such as aldrin, endrin, DDT (dichlorodiphenyltrichloroethane), 2,4-D (2,4-dichlorophenoxyacetic acid), BHC (benzene hexachloride), and dieldrin were introduced which triggered their rapid use in agriculture due to their certain properties like low cost, effective application and easy to use which made these pesticides more popular [2].

So, the extensive production and application of pesticides have made them the most broadly distributed pollutant in the environment. It is estimated that more than 95% of these pesticides are waste and accumulate in the environment and only 5% reach the target organisms. Therefore, the high leaching capacity of pesticides into the groundwater and accumulation in the soil is the main environmental concern. Additionally, the disposal of outdated pesticide stocks is a major source of pesticide contamination in the environment that has left many long-term contaminated sites in the world. There are several officially recognized sites of pesticides that have been reported from the different parts of the world *e.g.* Poland [3], Argentina, Chile [4], USA [5], Spain [6], Brazil, The Netherlands [7], India [8], China [9], Canada, *etc.* In spite of these sites, several illegal disposal sites are reported. For example, the Santiago del Estero, Argentina [10, 11] has been reported as a known illegal pesticide disposal site where more than 30 tons of pesticides (chlordane (CLD), DDT, lindane (g-HCH), aldrin, methoxychlor (MTX)) along with several heavy metals [Cd(II), Cr(VI), Cu(II)] disposal is carried out. However, there are several studies which report the residues of pesticides in water [12], air [13], food commodities [14], fishes [15], milk [16], soil [11], and even in human blood and adipose tissue [17] as well. Therefore, the availability of pesticides from the environment to human beings could directly affect the plants, animals, microorganisms and human health as well [18, 19] (Fig. **1**).

Hence, in order to reduce the various pollutants and pesticides from the environment, several new techniques such as recycling, landfills, pyrolysis of pesticides, *etc.* have been developed. But these techniques were not completely successful because they also produced some toxic intermediates [20].

Additionally, these techniques were very expensive and sophisticated, especially in the case of pesticide treatment [21].

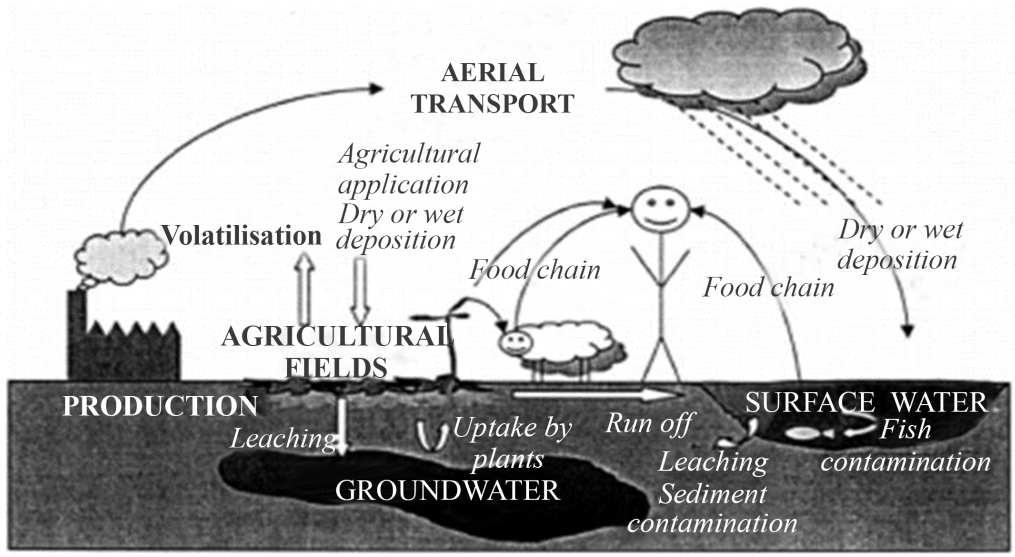

Fig. (1). Environmental fate of pesticides [19].

In the early decades, research has been focused on the development of eco-friendly and cost-effective methods for the cleaning of environmental pollutants using various microbial species and the process of pollutant treatment using microbes called bioremediation. This approach has shown the upper hand over the traditional physicochemical methods due to its low invasive and soil curative property [22]. Bioremediation has been proven as a sustainable technology that is utilised for the tracking of the environmental release of anthropogenic pollutants.

Pesticides

A pesticide is any substance either chemical, biological or herbal constituents that can be utilised to control, destroy or mitigate pests *e.g.* weeds, insects, nematodes, mites, *etc* [23]. Though in different periods, different definitions have been explained for the pesticide but its crux remains unchanged. Pesticides include herbicide, insecticide, fungicide and several other constituents utilised for pest management [24].

Basically, on the basis of the composition, pesticides are of three types *i.e.* chemical and biological and botanical pesticides (Table **1**). The structure-based classification of pesticides is also made which included carbamates, organochlorine, nitrogen-based pesticides, organophosphorus, *etc* [25, 26]. The

CHAPTER 5

Biosurfactants for Biodégradation

Telli Alia[1,*]

[1] *Laboratoire de protection des écosystèmes en zone aride and semi aride, Université de KASDI Merbah, BP 511 la route de Ghardaia, Ouargla 30000, Algérie*

Abstract: The low toxicity, biodegradability, powerful surface activity, and the functionality under extreme conditions (pH, salinity and temperature) make the surfactants produced by micro-organisms (bacteria, fungi, and yeasts) best surface-active molecules that can replace hazardous and non degradable chemical surfactants in different industries and fields. In recent decades, there has been growing interest in the use of biosurfactants for bioremediation of environmental pollution and biodegradation of various categories of hydrophobic pollutants and waste due to their eco-friendly and low-cost properties. This chapter presents the classification, the characteristics, and the potential uses of biosurfactants in the solubilization and enhancing the biodegradation of low solubility compounds.

Keywords: Biosurfactants, Surface-active, Biodegradation, Application, Environmental pollution, Micro-organisms.

INTRODUCTION

Rapid development, industrialization, urbanization, as well as increased demand for energy and various products, cause the depletion of natural resources and environmental pollution. Different kinds of pollutants and contaminants are released into the environment, such as petroleum products, pharmaceutical compounds, pesticides, organic dyes, and heavy metals [1]. These hazardous compounds lead to serious problems and are a major threat to all living organisms and ecosystems [1, 2].

In order to reduce the harmful effect of these contaminants, environmental pollution requires efficient strategies that would lead to the removal of hazardous compounds from contaminated areas. Several physical and chemical techniques were adopted for reaching a suitable solution [3]. However, these conventional

* **Corresponding author Telli Alia:** Laboratoire de protection des écosystèmes en zone aride and semi aride, Université de KASDI Merbah, BP 511 la route de Ghardaia, Ouargla 30000, Algérie;
E-mails: telli.alia@univ-ouargla.dz and alia.telli@gmail.com

Inamuddin (Ed.)

methods have many drawbacks, especially their high cost, ineffectiveness, and being unsafe for the environment by generating toxic by-products [3 - 5].

There are many problems associated with the use of surfactants. These substances are the main components in different products (pharmaceutic, cosmetic, household detergents, food, lubricating agents, *etc.*) and are used by several industries (paper, textiles and fibers, pharmaceutical industry, agriculture, and petroleum industry) [6 - 8]. These tension-active molecules are also used in soil and water remediation techniques [9]. Industries discharge a wide range of chemical surface-active agents to wastewater treatment facilities [10]. Most of them end up dispersed in different environmental compartments such as soil, water, or sediment [7, 11].

The biological approaches of remediation have recently attracted more attention for the removal and detoxification of diverse pollutants and contaminants from soils and water. These techniques consist of the use of living organisms (plants and micro-organisms) or biological compounds (enzymes, polysaccharides, secondary metabolites of plants and micro-organisms) in the elimination and degradation of contaminants [12 - 15]. These techniques are economical, non-invasive and provide an enduring solution [16]. One of the most deeply driven approaches in recent years is the employment of biological synthesis surfactants. These molecules are secondary metabolites fabricated by micro-organisms that interact with an interface and alter the surface properties such as wettability and other properties in order to use the hydrophobic substrates as a source of carbon [17].

In recent years, biosurfactants have paid more attention because of their many advantages in comparison with their chemically synthesized equivalents. They are environmentally friendly, biodegradable, less toxic, active under extreme conditions and have exceptional surface properties [18], which make them good candidates for enhanced oil recovery [19], controlling oil spills [20, 21], biodegradation and detoxification of oil- [22] and metal-contaminated soils [23 - 27], enhanced degradation of pesticides [28] and organic dyes [29, 30]. In addition to their biotechnological applications, biosurfactants also have therapeutic actions. Indeed, they are used as antimicrobial agents against bacteria, fungi and viruses [31, 32]. They have exhibited anti-cancer and immunomodulatory activities and drug delivery [33 - 35].

This chapter discusses the use of biosurfactants as an efficient and safe alternative to remove and enhance the biodegradation of some kinds of pollutants and hazardous wastes.

BIOSURFACTANTS

Definition and Importance

Surfactants are amphipathic molecules that can decrease surface and interfacial tensions by assembling at the interface of immiscible liquids and elevate the solubility, mobility, bioavailability and ulterior biodegradation of lipophilic or insoluble organic molecules [36].

Emulsion is a heterogeneous medium consisting of two immiscible liquid phases, one of which is dispersed in the form of very fine particles in the other (dispersing phase) [37].

Biological surfactants or biosurfactants are tensio-active metabolites manufactured by a broad range of micro-organisms (bacteria, fungi and yeast) [38, 39].

The chemical and bio-surfactants are surface-active molecules possessing hydrophobic (tail group), and hydrophilic (head group) portions which divide themselves in the middle of two immiscible liquids, with the action of decreasing the surface/interfacial tensions causing the solubility of non-polar molecules in polar solvents [40, 41]. These compounds aggregate at higher concentrations into micelles, minimizing the system's free energy [11]. The hydrophilic moiety of biosurfactants can be carbohydrates, amino acids, a protein, a phosphate group or other substances, while the hydrophobic portion is a long carbon saturated, unsaturated or hydroxylated chain fatty acids or fatty alcohols [42, 43].

The chemical surfactants are still preferred and used because of their availability in commercial quantities [40]. These petroleum-derived compounds have generated environmental pollution, putting public health at risk [44]. The biosurfactants are bio-emulsifiers produced from low-cost substrates (e.g. agro-industrial wastes) by diverse micro-organisms that may be considered a safe and green alternative to chemical surfactants due to their less hazardous effect and biodegradability [45].

Surface Activity

Surface tension is a measure of cohesive forces between liquid molecules presented at the surface [46]. Interfacial tension means tension at the interface of two immiscible liquids like oil and water. At the interface of two dissimilar liquids, the forces acting on the molecules of each of these fluids are not the same as within each phase and form interfacial tension [47]. The surface and interfacial

CHAPTER 6

Potential Application of Biological Treatment Methods in Textile Dyes Removal

Rustiana Yuliasni[1], Bekti Marlena[1], Nanik Indah Setianingsih[1], Abudukeremu Kadier[2,3,*], Setyo Budi Kurniawan[4], Dongsheng Song[2,5] and **Peng-Cheng Ma[2,3]**

[1] *Research Centre for Environmental and Clean Technology, National Research and Innovation Agency Republic of Indonesia, Kawasan Puspitek gd 820, Serpong, 15314, Tangerang Selatan, Indonesia*

[2] *Laboratory of Environmental Science and Technology, The Xinjiang Technical Institute of Physics and Chemistry, Key Laboratory of Functional Materials and Devices for Special Environments, Chinese Academy of Sciences, Urumqi, 830000, China*

[3] *Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing, 100049, China*

[4] *Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, National University of Malaysia (UKM), 43600 UKM Bangi, Selangor, Malaysia*

[5] *College of Resources and Environment, Xinjiang Agricultural University, Urumqi, 830052, China*

Abstract: The most problematic issue related to textile wastewater is dyes. The occurrence of toxic and carcinogenic compounds in textile dyes creates aesthetic problems and affects the aquatic ecosystem. Dyestuff removal methods include physical, chemical, and biological-based technology. For a more environmentally friendly process that is low cost, produces less sludge, and needs a lesser amount of chemicals, biological treatment is preferable technology. To get maximum effectiveness and efficiency, integrations/ hybrids consisting of several technologies are commonly used. This chapter is dedicated to exploring the potential of biological technology to remove dyes from wastewater, especially dyes used in textile industries. This chapter briefly discusses dyes' characteristics, their utilization, and toxicity. Deeper reviews about the biodegradation potential of dyes are elaborated, along with a discussion about biodegradation mechanisms and reviews of either lab-scale or full-scale applications of biological-based technology for dyes treatment. Lastly, this chapter also gives future insight into the biological treatment of dyes.

[*] **Corresponding author Abudukeremu Kadier:** Laboratory of Environmental Science and Technology, The Xinjiang Technical Institute of Physics and Chemistry, Key Laboratory of Functional Materials and Devices for Special Environments, Chinese Academy of Sciences, Urumqi, 830011, China; Tel: +860991-3677875;
E-mail: abudukeremu@ms.xjb.ac.cn

Inamuddin (Ed.)

Keywords: Biological treatment of dyes, Dyes wastewater treatment technology, Gye biodegradation, Textile wastewater, Wastewater containing dyes.

INTRODUCTION

Fresh water pollution from industrial, agricultural, and domestic activities has raised major concern due to its severe impacts on the environment niche [1]. Industrial pollution, especially from textile industry wastewater, has caused a negative impact on both environment and human health [2]. A wet textile industrial process consists of scouring, bleaching, dying, printing, and finishing (Fig. **1**). All these phases need a high quantity of water, chemicals, and energy. Hence, textile wet process commonly generates a large volume of wastewater containing toxic chemicals [3], characterized by concentrated pollutant parameters such as: color, salinity, biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solids (TDS), total nitrogen (TN), total phosphorus (TP), and heavy metals, such as chromium (Cr) [4].

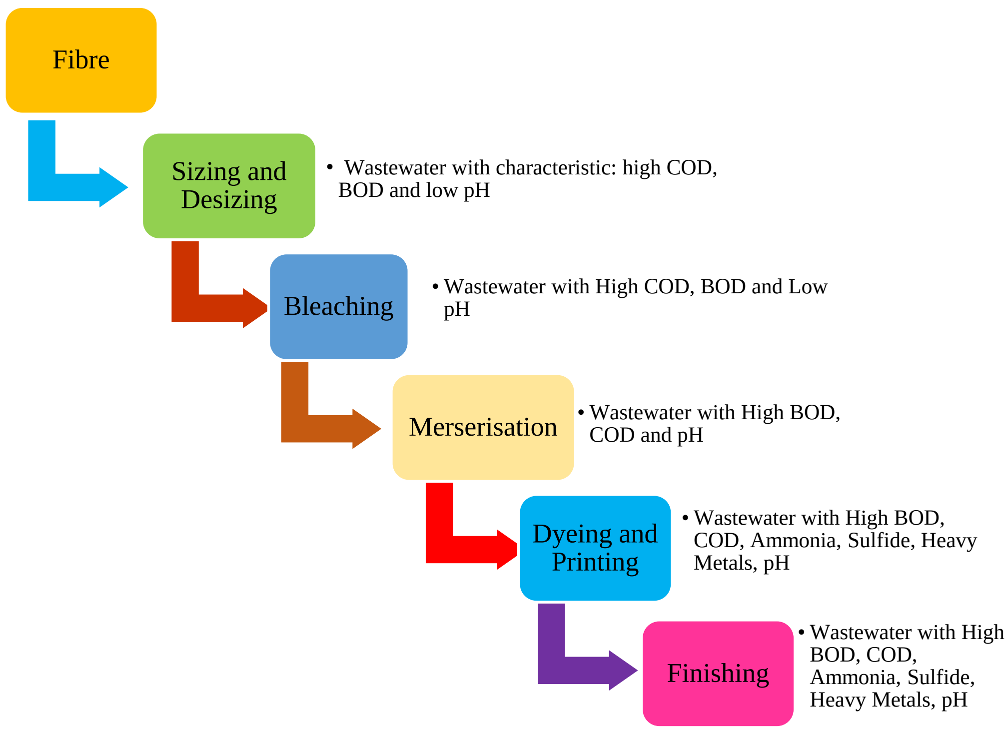

Fig. (1). Textile wet industrial process.

The most problematic issue related to textile wastewater is dyes. The occurrence of toxic and carcinogenic compounds in textile dyes creates aesthetic problems and affects the aquatic ecosystem [5, 6]. For more than 150 years, natural dyes were typically used in textile dyeing [7]. However, since the discovery of synthetic dyes by Henry Perkin in the 17th century, the 21st century has been occupied by many producers in synthetic dyes industry [8]. Dyes are described as complex organic substances (aromatic compounds) that absorb light and give color to the visible range (350 – 700 nm) [7 - 9]. The largest class of dyes is acid dyes. Other types of dyes include reactive, metal complex, direct, basic, mordant, disperse, pigment, vat dyes, anionic, sulphur, solvent, *etc.* Based on dyes consumption data, dyes discharged by the textile processing industry belongs to the class reactive dyes (±35%), acid (±25%), and direct (±15%), all of which are classified as azo dyes [10].

Dyes are highly persistent in the environment and possess the eco-toxic hazards of bioaccumulation. Thus, the release of dyes into the environment can affect man *via* the food chain. The degree of bioaccumulation is normally determined by Bio-concentration values (BCF's). Water soluble dyes, which have log BCF values of <0.5 and low K_{ow} (*i.e.*: acid, reactive and basic dyes), do not bio-accumulate. Bioaccumulation of water soluble dyes increases as they become more insoluble in water (higher K_{ow}) [11]. The acute toxicity of dyes is generally low. However, the chronic effects of dyes, especially azo dyes, are relatively high [12]. Under anaerobic condition, Azo dyes may release aromatic amines that are considered to be carcinogenic [12].

Dyestuff removal methods include physical, chemical and biological based technology. Adsorption and filtration are examples of physical treatment. These methods can achieve 86.8-99% dyes removal [13]. Chemical based technology is considered the most common technology for dyestuff removal. The oldest chemical technique that is still being used is coagulation-flocculation, while advanced oxidation process (AOP) and electrochemical technology are considered to be more advanced methods [14, 15]. AOP and electrochemical technology have short retention time, less sludge production and high removal efficiency [13]. However, the disadvantages of these technologies are high costs in terms of energy and chemicals requirement. For more environmentally friendly processes that are low cost, produce less sludge and need a lesser amount of chemicals, biological treatment is preferable technology [16, 17]. To get a maximum effectivity and efficiency, in terms of pollutants removal performance and costs, integration/ hybrid of physical, chemical and biological treatments is commonly used, *i.e.*: hybrid technology between sequencing batch reactor (biology) and ultrafiltration (physic) or integration technology between electrochemical oxidation/bio-treatment (chemistry/biology) [14 - 18].

CHAPTER 7

Fungal Bioremediation of Pollutants

Evans C. Egwim[1,*], **Oluwafemi A. Oyewole**[2] and **Japhet G. Yakubu**[2]

[1] *Department of Biochemistry, Federal University of Technology, Minna, Nigeria*

[2] *Department of Microbiology, Federal University of Technology, Minna, Nigeria*

Abstract: Advancement in industrialization and urbanization has caused an influx of contaminants into the environment polluting the soil, water, and air. These contaminants come in various forms and structures, including heavy metals, petroleum hydrocarbons, industrial dyes, pharmaceutically active compounds, pesticides, and many other toxic chemicals. The presence of these pollutants in the environment poses a serious threat to living things, including humans. Various conventional methods have been developed to tackle this menace, though effective, are however not safe for the ecosystem. Interestingly, bioremediation has offered a cheap, effective, and environmentally safe method for the removal of recalcitrant pollutants from the environment. White-rot fungi (WRF), belonging to the basidiomycetes, have shown class and proven to be an excellent tool in the bioremediation of the most difficult organic pollutants in the form of lignin. White-rot fungi possess extracellular lignin modified enzymes (LMEs) made up of laccases (Lac), manganese peroxidase (MnP), lignin peroxidase (LiP), and versatile peroxidase (VP) that are not specific to a particular substrate, causes opening of aromatic rings and cleavage of bonds through oxidation and reduction among many other pathways. The physiology of WRF, non-specificity of LMEs coupled with varying intracellular enzymes such as cytochrome P450 removes pollutants through biodegradation, biosorption, bioaccumulation, biomineralization, and biotransformation, among many other mechanisms. The application of WRF on a laboratory and pilot scale has provided positive outcomes; however, there are a couple of limitations encountered when applied in the field, which can be overcome through improvement in the genome of promising strains.

Keywords: Basidiomycetes, Bioaccumulation, Biodegradation, Biomineralization, Bioremediation, Biosorption, Biotransformation, Fungi, Heavy metals, Industrial dyes, Laccases, Mycoremediation, Peroxidase, Pesticides, Petroleum hydrocarbons, Pharmaceutical products, Pollutants, Oxidation, Synthetic pesticides, White-rot fungi.

* **Corresponding author Evans C. Egwim:** Department of Biochemistry, Federal University of Technology Minna, Nigeria; E-mail: evanschidi@gmail.com

Inamuddin (Ed.)

INTRODUCTION

Man's effort to provide an easy and comfortable life for himself through industrialization and urbanization has become a threat to him and the ecosystem at large [1 - 4]. Infrastructural construction, mining, transformation of raw materials, electroplating, smelting, extraction of petroleum, and farming, among many other anthropogenic activities have caused and is still causing deleterious effects on the ecosystem [5]. Most of these anthropogenic activities, release harmful substances into the environment (air, soil and water), which if not properly cleaned or disposed of effect biotic activities in the ecosystem [6]. These harmful substances include polymers, cyanide compounds [7], papers and pulp [8], heavy metals [9 - 11], pesticides, industrial dyes, pharmaceutically active compounds (PhACs) [12], petroleum hydrocarbons [13, 14], chlorendic acids [15] among many others. Some of these pollutants such as heavy metals (*i.e.* mercury, cadmium, arsenic, chromium, copper, selenium, and lead), when present in the environment in large amounts impair the metabolism of living organisms including man [11, 16]. Some of these heavy metals cause cancer, skin inflammation, nausea, dizziness, and headache [17]. Other pollutants such as pesticides have caused chronic illnesses leading to the global loss of about 1 million lives annually [18]. This event of loss of lives and resources is no exception to petroleum pollutants, which arises as a result of oil spills during drilling of oil wells, leakage of underground tanks, vandalization of storage tanks among many more occurrences. This eventually affects the diversity of biological niches, deaths of aquatic organisms, affects the productivity of plants and causes starvation in man [14].

The debilitating effects of pollutants in the environment cause a man to respond rapidly through conventional methods in a bid to alleviate the damages it causes [19, 20]. Some of these conventional methods developed include; soil flushing, land filling, burning, vitrification, electroreclamation/electrokinetics, solidification and stabilization, removal and containment among many others, though rapid but do not eradicate the pollutants, rather they change their location and state from one form to another [4, 19, 21]. The disadvantage of conventional methods is that they are not environmentally friendly, they are expensive, require more labor and expose more surfaces to pollutants. The use of conventional chemicals to treat a polluted environment also has adverse effects in the long run [2]. Some of the methods applied in the treatment of soils affect the soil structure and quality, and the efficiency of some of the methods is limited to certain depths [2, 9, 19]. As a result of all these setbacks, man has searched for a means to alleviate the environmental problems posed by pollutants, out of which biological methods have proven to be environmentally friendly, with little or no adverse effects on the environment [2, 20]. A process where biological materials are used in the cleanup of pollutants from the environment is known as bioremediation [2, 4].

Bioremediation involves the transformation or degradation of hazardous pollutants from a toxic form to a less toxic absorbable form [2]. Among the natural bioremediation processes, microbial bioremediation has stood to be the most effective in the removal of pollutants from the environment [4]. Microorganisms remove pollutants either by biodegradation, bioaccumulation, biosorption, biotransformation or biomineralization [10]. Bioremediation strategy could either be *in-situ* (*i.e.* treatment of pollutants in the site of contamination) or *ex-situ* (*i.e.* taking the pollutants away from the contamination sites for treatment) [2, 4, 20, 22]. However, the former is safe and cheap unlike the latter, which is expensive and a potential threat to the health of laborers involved and exposes the pollutants to more surfaces [2, 4]. Among the bioremediation technologies, the use of fungi, particularly those belonging to the basidomycetes has distinguished themselves as an effective tool in the remediation of an environment polluted by recalcitrant xenobiotics, a technology known as mycoremediation [2, 23, 24]). Their metabolites and body structures coupled with the fact that they can withstand toxic compounds and still perform in an environment depleted of nutrients have made them cheap and effective for a safe and sustainable strategy in alleviating polluted environment [23, 25].

Pollutants and Their Classification

There are different types of pollutants that are generated by various industries. These pollutants could come in the form of solid, liquid, or gases. Their nature, chemical composition and structure could vary from simple monomers to a complex polymer of aromatic rings. They include petroleum hydrocarbons, chemical compounds (*i.e.* industrial dyes and pesticides), and heavy metals [26].

Petroleum Hydrocarbons

The use of petroleum based products is almost inevitable in the world we live today. Aside from being used as a form of energy to power machines, vehicles, trains, aeroplanes, generators, heating mantles, and cookers; some components of petroleum are also used in the production of various forms of plastics, chairs, rubbers, fibbers for reinforcement of concretes, fittings in electric appliances, cutleries, among many other uses [13, 27]. Right from the exploration of petroleum to its conversion (refining), down to its transportation and storage, the environment one way or the other gets polluted by harmful substances present in petroleum [13, 28, 29]. Petroleum is composed of a various complex mixture of hydrocarbons [28], which is distinguished mainly into aromatic hydrocarbon, saturated hydrocarbon and non-hydrocarbon compounds [30, 31]. Aromatic hydrocarbons are complex with high melting and boiling point due to the presence of benzene ring(s), which makes them difficult to degrade away from the

CHAPTER 8

Antifouling Nano Filtration Membrane

Sonalee Das[1,*] and **Lakshmi Unnikrishnan**[1]

[1] *CIPET : School for Advanced Research in Polymers (SARP) - APDDRL - Bengaluru 7P, Hi-Tech Defence and Aerospace Park (IT Sector), Jalahobli, Bengaluru North, Near Shell R&D Centre, Devanahalli, Bengaluru - 562 149, India*

Abstract: In the recent decade, membrane technology has gained immense interest in water purification, wastewater treatment, and water desalination. However, the major drawback which destroys the efficiency of membrane technology is fouling. Membrane fouling arises due to the non-specific interaction between fouling species and membrane surface. This major drawback can be overcome by preparation of antifouling membranes. Although there are various techniques involved in water filtration *i.e.* microfiltration, ultrafiltration, and nanofiltration. However, in this book chapter, we shall emphasize antifouling nanofiltration membranes, recent developments and future prospects. Further, we shall discuss the various fouling types, its consequences, mechanisms affecting fouling, challenges, and modification approaches in the antifouling membrane technology.

Keywords: Antifouling, Membrane fouling, Membrane technology, Nanofiltration, Water treatment.

INTRODUCTION

The major global challenge faced in this 21st century is safe drinking water and its scarcity which arises due to water pollution. The various factors which account for such crisis include urbanization, growing population, the imbalance between demand & supply, inefficient water treatment process and unsustainable economic practices [1]. It has been estimated that in 2050, the worldwide water demand would go up to 40% 2050. As a consequence, 1.8 billion people will be facing problems in water-deficient regions [1]. India too is facing a huge crisis in the sector of water pollution. As per the reports by World Economic Forum (2019) it has been reported that in India about 70% of surface water is unhealthy for intake [2]. Further, World Bank Report suggests that water pollution can lower economic

* **Corresponding author Sonalee Das:** CIPET: School for Advanced Research in Polymers (SARP) - APDDRL - Bengaluru7P, Hi-Tech Defence and Aerospace Park (IT Sector), Jalahobli, Bengaluru North, Near Shell R&D Centre, Devanahalli, Bengaluru - 562 149, India; E-mail: das.sonalee31@gmail.com

Inamuddin (Ed.)

growth as well as GDP growth in the downstream areas [2]. In India, the impact of water pollution would lead to a reduction of GDP growth by almost half a factor [2]. In addition, to economic loss, lack of water sanitation would also lead to the loss of more than 4 million lives in India per year [2]. Hence, to meet the demand for clean drinking water there needs to be a technological transition approach from a traditional to a modern aspect.

Membrane technology for the treatment of waste water has gained immense research interest over the last 2 decades. As per the reports the global membrane filtration market is estimated to grow at a CAGR of 6.4% and reach USD 19.6 billion by 2025 [3]. For the water treatment process membranes are being used as filters for various applications which includes water filtration (desalination), water purification as well as in industries (food and beverage) [4]. The major advantages of this technology are low energy consumption, continuous separation and simple up-scaling [5]. This technology is capable to treat various water streams with different salinity and feed compositions [6, 7]. However, different membrane technology processes *i.e.* microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) with varying pore sizes of the membranes are involved in treating the fluid stream. Fig. (**1**) depicts comparative effectiveness of different filtration processes [8]. Fig. (**2**) shows the broad spectrum of different filtration technologies [9]. Although RO technology is the most accepted one amongst the various membrane technology for absolute purified water, however, it requires more energy to produce it and also removes some of the minerals from water that are considered to be beneficial for human consumption [8, 10]. On the other hand, NF technology allows these minerals to pass through it and also requires less energy to produce higher fluxes at low pressure *i.e.* (6-15 bar/ 600-1500 kPa) [8, 10]. In addition, it works best for applications that do not require a feed stream completely free of dissolved solids [10].

The major drawback, however, in the membrane technology is membrane fouling which arises due to different kinds of foulants in fluid stream resulting in blockage of pore, gel formation, adsorption of organic substances and inorganic precipitates, *etc.* resulting in temporary/ permanent decline of flux [1]. As a consequence, water permeation is reduced thereby restricting the process efficiency, deteriorating water quality, and increasing the energy consumption [11 - 14]. Various strategies have been adapted to mitigate membrane fouling like feed water pre-treatment [15], development of foul resistant membranes [16, 17] and membrane cleaning [18]. However, the design and development of intrinsic antifouling membrane surfaces can be a candid approach towards addressing membrane fouling since it reduces the post and pre-treatment frequency, cleaning cycles and replacement of membrane [19]. Hence, the preceding sections will discuss the fouling mechanism, a brief description regarding nanofiltration, antifouling nanofiltration membranes and their applications.

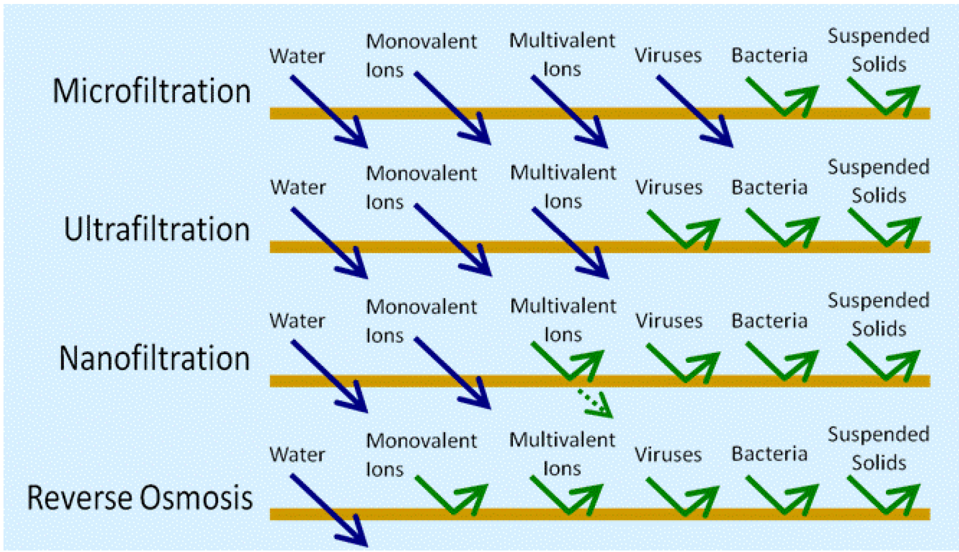

Fig. (1). Comparative effectiveness of different filtration processes [8].

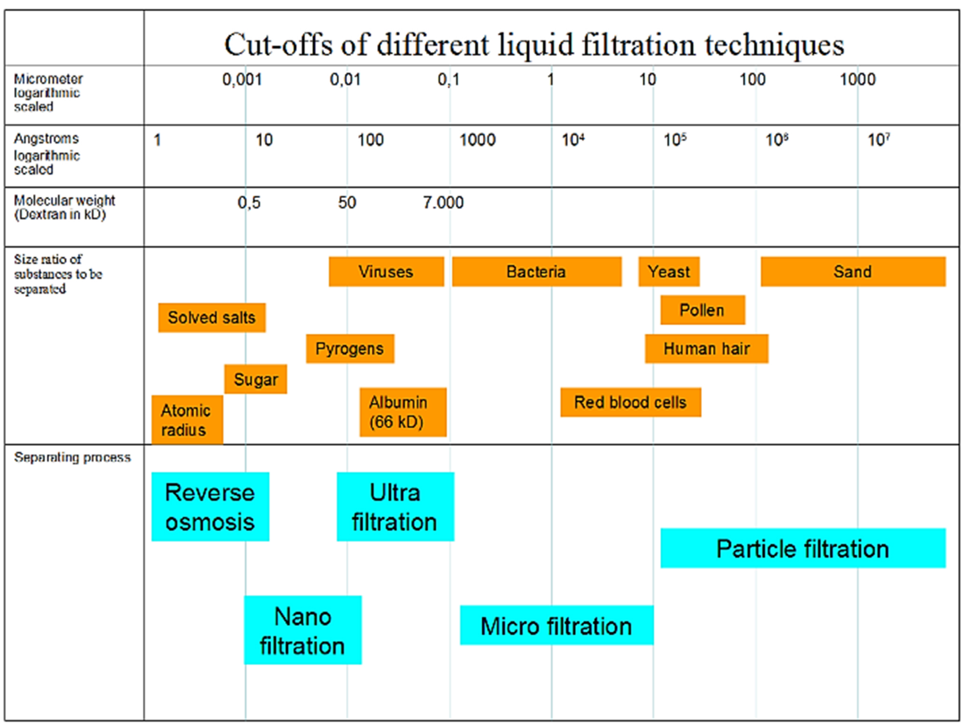

Fig. (2). Broad spectrum of different filtration technologies [9].

CHAPTER 9

Microbes and their Genes involved in Bioremediation of Petroleum Hydrocarbon

Bhaskarjyoti Gogoi[1], **Indukalpa Das**[1], **Shamima Begum**[1], **Gargi Dutta**[1], **Rupesh Kumar**[1] and **Debajit Borah**[1,*]

[1] *Department of Biotechnology, Assam Royal Global University, Guwahati-781035, Assam, India*

Abstract: The catastrophic effect of petroleum contamination on the environment is a severe problem of global concern. Bioremediation is probably the easiest and most cost-effective way to treat the contaminants. Several microorganisms ranging from bacteria, fungi, yeast, algae, *etc.*, are known for their ability to biodegrade different hydrocarbons. Hydrocarbon degrading microorganisms are largely known for the release of biosurfactants and other surface-active biopolymers, which decrease the surface tension of oil particles into smaller entities for their easy degradation throughout the respective metabolic cycle. Such biopolymers are encoded by several genes and operon systems which are discussed briefly in this chapter. Information on such genes help in better understanding the molecular events involved in the microbial bioremediation of petroleum hydrocarbon.

Keywords: Bioremediation, Biosurfactant, Enzymes, Genes.

INTRODUCTION

Due to the massive use of fossil fuel and the derivatives of various petroleum-based products, environmental pollution has become a global issue of public concern that requires immediate attention from the scientific community to develop ways to solve the problem. Deliberate or accidental release of petroleum oil into soil and water largely affects the health of aquatic as well as terrestrial life forms, including human health in the form of chiefly respiratory diseases, kidney ailments, and even cancer [1]. A vast majority of the constituents of petroleum oil are polycyclic aromatic hydrocarbons (PAHs) which are mostly recalcitrant in nature and remain for a prolonged duration of time in the environment [1]. Petroleum contaminants are mostly treated by chemical methods, which involve surfactants, and physical methods involving burning, skimming, *etc.* [2]. However, skimming of petroleum is easier but the major problem with skimming

* **Corresponding author Debajit Borah:** Department of Biotechnology, Assam Royal Global University, Guwahati-781035, Assam, India; Tel: +91-9706394994; E-mail: dborah89@gmail.com

Inamuddin (Ed.)

is the clogging of the suction pipe due to clogging by debris and also solidification of waxy petroleum under ice-cold environment makes it even more difficult [3]. On the other hand, the open burning of petroleum products emits a huge amount of toxic gases into the environment which is more harmful [4]. Even though chemical surfactants are also used as a bioremediation agent but they release toxic non-biodegradable components into the environment [2].

Therefore, bioremediation proves itself as a future scope for solving such issues that involve the use of microorganisms such as various bacteria, fungi, algae, plants, *etc.* without releasing harmful residues to the environment [5, 6]. However, microorganisms including bacteria and fungi are chiefly used for their least requirements for maintenance and implementation nature. They release many surface active molecules which reduce the surface tension of oily substances for the initiation of hydrocarbon degradation and are governed by several independent or cascades of genes.

TYPES OF BIOREMEDIATION STRATEGIES

The pollution of soil, sediments, and both surface, as well as groundwater by petroleum hydrocarbon, possesses a risk to human health. The contaminants can be spread to a broad area from the site of their origin and affect the flora and fauna of the polluted area. Depending upon the various factors like contamination site, nature of contaminants and environmental conditions of the contaminated site, the remediation treatment methods are different. Also, the mechanism of the treatment procedure, regulatory requirements along with the time constraints, costs and the remediation process are chosen. The success of the use of any remediation methods depends on the design and adjustment of the system operation. The integration of two or more remediation processes in combination or in a sequence gives better efficacy in the removal of contaminants from the site of pollution [1].

PHYSICAL METHOD FOR BIOREMEDIATION OF PETROLEUM HYDROCARBON

The physical method is the most perceptible source of contamination that is removed from the oil spill in soil and the water body may involve mechanical removal methods such as skimming, manual removal (wiping), water gushing, *etc* [2]. A great component of the oil pollution problem results from the fact that the major oil-manufacturing countries are not the main oil consumers. It follows that huge transfers of petroleum must be made from areas of high production to those of high consumption [7]. Although physical removal of oil spillage is a primary response of treatment, it rarely achieves complete clean-up due to the usual blockage of the transporting pipes with debris.

CHEMICAL METHOD FOR BIOREMEDIATION OF PETROLEUM HYDROCARBON

To convert the toxic form of the hydrocarbon pollutants into less toxic forms, several chemical agents can be used. The chemicals change the physical and chemical properties of the pollutants. Dispersants and solidifiers are the two different classes of chemicals that are used to treat oil spills. Dispersants break the oil slicks by the activities of surface-active agents and converted them into smaller droplets. Then, the smaller droplets are transferred into the water column and finally undergo degradation. Solidifiers interact with oil and change the physical state of the oil which in turn reduces the release of hydrocarbons into the environment [8]. Several chemical remediation processes such as chemical leaching, chemical fixation, chemical oxidation, *etc.* are available to reduce the load of toxic pollutants in the surroundings of the spillage area [9].

BIOLOGICAL METHODS

Bioremediation is the most effective and proven remediation method for restoring polluted sites by removing the pollutants. In the bioremediation process, micro-organisms play a crucial role. The diverse enzymatic profile, micro-organisms are widely used to degrade petroleum hydrocarbons into less toxic forms. In comparison to the other conventional remediation processes, bioremediation is a more efficient process with relatively low cost. The use of bioremediation causes minimal site disruption with no additional nutrient requirements. Due to these advantages, bioremediation is a widely accepted popular remediation technique [10, 11].

The process of bioremediation can be achieved by any of the two treatments, *ex-situ* and *in-situ* treatment. The remediation strategies are considered based on the treatment cost, type of the pollutants, the severity of the pollution, and site of the pollution. In *ex-situ* bioremediation method, the pollutants are excavated from the polluted site and transferred to another site where the treatment is done. Whereas, the *in-situ* method of remediation involves no excavation of the pollutants; instead, the treatments are done on the site of the pollution. Several treatment methods are being used for the process of bioremediation. Fig. (**1**) shows the schematic representation of the different strategies for bioremediation techniques. Based on the age and the degree of a spill along with the physicochemical properties of the spillage matrix, the treatment procedures may be different [12].

EX-SITU BIOREMEDIATION

As shown in Fig. (**1**), the different *ex-situ* bioremediation methods are biopiling, windrows, bioreactor, and land farming.

CHAPTER 10

Application and Major Challenges of Microbial Bioremediation of Oil Spill in Various Environments

Rustiana Yuliasni[1], **Setyo Budi Kurniawan**[2], **Abudukeremu Kadier**[3,4,*], **Siti Rozaimah Sheikh Abdullah**[2], **Peng-Cheng Ma**[3,4], **Bekti Marlena**[1], **Nanik Indah Setianingsih**[1], **Dongsheng Song**[3,5] and **Ali Moertopo Simbolon**[1]

[1] *Research Centre for Environmental and Clean Technology, National Research and Innovation Agency Republic of Indonesia, Kawasan Puspitek gd 820, Serpong, 15314, Tangerang Selatan, Indonesia*

[2] *Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, National University of Malaysia (UKM), 43600 UKM Bangi, Selangor, Malaysia*

[3] *Laboratory of Environmental Science and Technology, The Xinjiang Technical Institute of Physics and Chemistry, Key Laboratory of Functional Materials and Devices for Special Environments, Chinese Academy of Sciences, Urumqi, 830011, China*

[4] *Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing, 100049, China*

[5] *College of Resources and Environment, Xinjiang Agricultural University, Urumqi, 830052, China*

Abstract: Oil spill contamination occurs due to exploration activities in the deep sea and downstream activities such as oil transportation *via* pipelines, oil-tankers (marine and terrestrial), re-fineries, finished product storage, distribution, and retail distribution setup. Physico-chemical technologies are accessible for oil spill clean-up, but oil bioremediation technologies are proven to be more affordable and environmentally friendly. The aim of this book chapter is to give deeper knowledge about the bioremediation technology of oil spills. This chapter discusses the nature and composition of crude oil, bioremediation agents and strategies, bioremediation on different matrices (water, soil sludge), application strategy, and future prospect of bioremediation technology.

Keywords: Bioremediation of oil spill, Biostimulation, Bioaugmentation, *ex-situ*, *in-situ*, Biosurfactant, Total Petroleum Hydrocarbon (TPH).

* **Corresponding author Abudukeremu Kadier:** Laboratory of Environmental Science and Technology, The Xinjiang Technical Institute of Physics and Chemistry, Key Laboratory of Functional Materials and Devices for Special Environments, Chinese Academy of Sciences, Urumqi, 830011, China; Tel: 860991-3677875; E-mail: abudukeremu@ms.xjb.ac.cn

Inamuddin (Ed.)

INTRODUCTION

Fossil fuel (FF) is a significant source of energy. Industries and transportation will collectively share approximately 75% of the total energy consumption from fossil fuels by 2040 [1]. The exploitation of petroleum hydrocarbon (HC) has been complemented by accidental oil spills and severe marine pollution [2]. The release of oil from various sources also causes severe effects on deep ocean organisms. Other than environmental problems, oil spill has also resulted in economic loss. For example, 250 000 seabirds were killed during the Exxon-Valdez oil spill in 1989, and the DWH disaster cost more than US$ 61 billion [2]. Another example was 407 spills of petroleum products that occurred annually in Alaska between 1996 and 1999 [3], caused shrinkage in microbial populations, soil stress, thermal and moisture unbalance as well as soil pH and nutrient unavailability [3]. A more recent case is the 2007 Hebei Spirit oil spill (HSOS) that severely disturbed the entire ecosystem along the western coast of South Korea [4]. The oil spill contamination occurred not only because of exploration activities in the deep sea/ marine, but also during oil transportation *via* pipelines, oil-tankers (marine and terrestrial), re-fineries, finished product storage and distribution, and retail distribution setup [5]. Oil spill pollution in the marine ecosystem could also transfer to the coastline and contaminate soil because of weather and the formation of tar-ball [1].

Physico-chemical technologies are accessible for oil spill clean-up. Despite having many benefits, oils spill remediation techniques also have many limitations, such as low pollutant removal efficiency and by-product disposal challenges [6]. For instance, skimmers are only effective when oil is concentrated in the surface layer, while *in-situ* burning is influenced by weather, oil type, and slick thickness [7]. Burning could also cause localized air pollution. Dispersants break oil into small droplets but could enhance toxicity to aquatic organisms [8]. An alternative technology such as biological remediation then becomes a solution because it is feasible yet effective and environmentally friendly in comparison to several physical and chemical approaches [3]. Bioremediation techniques are based on two different methods. Bio-stimulation is bioremediation method where natural indigenous microorganisms are enhanced, while bio-augmentation is where oil-degrading microorganisms are induced [9, 10]. Bioremediation is affected by several factors such as the presence of suitable microorganisms, concentration of oil, pH, temperature, the presence of electron donors and acceptors and the bioavailability of nutrients [9, 11]. These reasons make biological removal relatively slow [6]. Furthermore, bioremediation is also limited by our lack of knowledge about environmental factors, such as hydro-static pressure, temperature and dispersant toxicity [2].

Present abundantly in nature, many microorganisms have the ability to use hydrocarbons as their sole carbon [12]. Researches related to the utilization of hydrocarbon utilizing, sulphate-, nitrate- and iron- reducing, fermenting, syntrophic and methanogenic bacteria and archaea for hydrocarbon contaminated sites bioremediation have been done [3, 13]. The most used microorganisms species are firmicutes, *Gammaproteo-bacteria, Deltaproteo-bacteria,, Epsilonproteo-bacteria, Betaproteo-bacteria*, *Bacteroidetes*, and *Methanogenic archaebacterial* members (*Methanosarcina, Methanosaeta*, *etc.*) [12]. Phytoremediation, using plants and rhizospheric microorganisms. also quite popular as a bioremediation strategy [14].

As already mentioned earlier, hydrocarbon contamination could not only take place in the deep ocean or marine ecosystem but also could transfer to the coastline and contaminates soil *via* transportation and distribution. The difference in geochemical characteristic between soil, aquatic, or sludge creates a variation of bioremediation techniques [15 - 17]. For instance, only about 33% of moderately contaminated soil has been successfully treated. The limitation of bioremediation application in contaminated soil was because of the toxic inhibitory effect of hydrocarbon metabolites that harm oil-degrading microorganisms in highly contaminated soil [18]. Another bottlenecks were groundwater contamination during the bioremediation process due to various water-soluble oxidized hydrocarbon metabolites being mobile in soil [18].

The aim of this book chapter is to give deeper knowledge about the bioremediation technology of oil spills in water, soil and sludge. In detail, this book chapter discusses the nature and composition of petroleum hydrocarbon, oil bioremediation agent, oil bioremediation methods, matrice to be bioremediated (that include: water, soil and sludge), application strategy and future prospects of bioremediation technology.

NATURE AND COMPOSITION OF PETROLEUM CRUDE OIL

Petroleum crude oil is containing simple to complex mixture of various hydrocarbon compounds in form of aliphatic saturated compounds or paraffins including straight and branched chain alkanes (n-alkanes), cycloalkanes, unsaturated alkenes, alkynes; aromatics including polycyclic aromatic hydrocarbons (PAHs) such as naphthalene, monoaromatic such as benzene, toluene, ethylbenzene, xylene (BTEX); asphaltenes including phenols, fatty acids, ketones, esters, porphyrins; resins including pyridines, quinolines, cardaxoles, sulphonates, amides. While the non-hydrocarbon components of petroleum oil consist of sulphur compounds such as sulphides, thiols, cyclic sulphides, disulphides, dibenzothiophene, and naphthobenzothiophene; oxygen compounds

CHAPTER 11

Bioremediation of Hydrocarbons

Grace N. Ijoma[1], **Weiz Nurmahomed**[1], **Tonderayi S. Matambo**[1], **Charles Rashama**[1] and **Joshua Gorimbo**[1,*]

[1] *Institute for the Development of Energy for African Sustainability (IDEAS) Research Unit, University of South Africa (UNISA), Florida Campus, Private Bag X6, Johannesburg 1710, South Africa*

Abstract: Hydrocarbons are a common contaminant in both terrestrial and aquatic ecological systems. This is most likely due to the widespread use of hydrocarbons as everyday energy sources and precursors in the majority of chemical manufacturing applications. Because of their physical and chemical properties, most hydrocarbons in the environment are resistant to degradation. Although several derivatives are classified as xenobiotics, their persistence in the environment has induced microorganisms to devise ingenious strategies for incorporating their degradation into existing biochemical pathways. Understanding these mechanisms is critical for microbial utilization in bioremediation technologies. This chapter focuses on recalcitrant and persistent hydrocarbons, describing the reasons for their resistance to biodegradation as well as the effects on ecological systems. Furthermore, aerobic and anaerobic degradation pathways, as well as ancillary strategies developed by various microorganisms in the degradation of hydrocarbon pollutants, are discussed.

Keywords: Biodegradation, Fortuitous degradation, Anaerobic degradation, Bioattenuation, Biostimulation, Bioaugmentation, Bioavailability.

INTRODUCTION

The most commonly occurring forms of hydrocarbons in nature are crude oil, coal, and natural gas, which are referred to as fossil fuels. Additionally, there are seemingly limitless variations of saturated and unsaturated hydrocarbons derived from these natural hydrocarbons. Other hydrocarbons arise from processing naturally occurring hydrocarbon forms into domestic, agricultural, and industrial end products. Hydrocarbon processing generates hydrocarbon derivatives and modifies chemical structures by introducing elements such as sulfur, chlorine, bromine, and many more, with the intention of improving structural bonds, incre-

* **Corresponding author Joshua Gorimbo:** Institute for the Development of Energy for African Sustainability (IDEAS) research unit, University of South Africa (UNISA), Florida Campus, Private Bag X6, Johannesburg 1710, South Africa; E-mail: joshuagorimbo@gmail.com

Inamuddin (Ed.)

asing compound saturation, and transforming aromatic branched hydrocarbons. Examples of such derivative compounds include asphaltenes (phenols, fatty acids, porphyrin, ketones, and esters) and resins (pyridines, quinolones, sulfoxides, amides, and carbazoles). Other notable examples include benzene, toluene, alkyl ketones, halogenated heterocyclics, nitroaromatics, styrenes, chorophenols, chloroaromatic hydrocarbons, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and several pesticides. Although these compounds are applied in several aspects of human endeavors, their persistence in the environment and recalcitrance to degradation [1] prove detrimental to all ecological systems. More concerns have been raised, especially with established data that demonstrate that hydrocarbon derivatives exhibit various carcinogenic, teratogenic, and neurotoxic properties [2, 3].

The impact of environmental pollution from these hydrocarbon-derived compounds (HCs) is dependent on the location, concentration, and composition [4]. In the terrestrial environment, mobile and viscous HCs tend to absorb into the soil, often penetrating several strata and contaminating groundwater [5, 6]. These compounds are also capable of mixing with the soil, affecting permeability and porosity [1], thereby changing the structure and composition of the soil with impacts readily demonstrated in the changed ratios of C/N, C/P. Moreover, there are increased concentrations of toxic elements (lead, nickel, and vanadium), as well as changes in pH, salinity, and conductivity of the soil [7]. These changes damage the soil and environment [8]. Several studies have also shown that HCs impact the microbial population, often causing irreversible changes to the community composition and consequently the enzyme systems of the soil usually, through substrate stimulation, catabolite repression, and inhibitory actions [5]. Crops that are cultivated on these contaminated soils and water are exposed to deleterious conditions, including a reduction in germination rates and fertility. Furthermore, growing plants, through biosorption and bioaccumulation, experience toxemia and sometimes mutagenic effects that can be passed onto their off springs [9]. Interactions along the food chain imply that these effects are later transferred to humans with other health consequences. Moreover, in terrestrial environments, the burning of hydrocarbons as fuels pollute the air, causing inhalation and skin-related health challenges [10, 11]. Combustion of HCs increases the atmospheric concentrations of nitrous oxides and sulfur dioxide which are precursors of acid rain. Acid rain in the aquatic environment reduces the water pH (acidification) which negatively affects organisms present in this ecosystem, such as fish and coral reefs [12].

Hydrocarbon pollution in the aquatic environment, although to a certain extent is mitigated by dilution, is no less consequential in comparison to the terrestrial environments. Pollution in aquatic environments is exacerbated by HCs cleaning and recovery difficulties arising from several factors. A typical factor is tidal wave movement which promotes the mobility of HCs and their rapid spread from the original location of contamination [13]. Often it takes years if ever, to restore the environment to near-pristine conditions.

The microbial population is by far the greatest in number in all environments, and their role in all food chains and the geochemical cycles is considered the most important. When contaminants such as HCs are introduced to an ecosystem, there is an immediate change in concentrations of several elements, generally reaching toxic levels for some. Microorganisms present in the polluted site, respond to these toxic stressors, in a variety of ways. Their most important characteristic that aids in the development of tolerance and adaptation along the food chain, is the rapid generational times common to bacteria, fungi, and algae. Moreover, they perform the important function of biodegrading contaminants and nutrient recycling that ensures an effective and efficient ecosystem [14]. Pollutant degradation is achieved using basically two alternative routes, aerobic and anaerobic pathways. However, these pathways have adaptive variations that have been evolved to cope with substrate changes and availability. Microorganisms have also developed strategies to handle substrates, especially within consortia interactions. This chapter will review the fundamental microbial pathways as well as the strategies including fortuitous degradation, synergistic, multi-phasic kinetics, cometabolism, and genetic exchange, applied by these microorganisms in the degradation of HCs pollutants.

The understanding of microbial mechanisms and strategies in the degradation of pollutants in general has been exploited in the development of bioremediation programs. The overarching goal of bioremediation is to effectively reclaim polluted soil and waste water using sustainable processes that apply organisms and their enzymes. In particular, the reclamation process for wastewater ensures a reduction in pressure on freshwater resources and maintains aquatic biodiversity. This chapter will further review recalcitrant and emerging xenobiotic hydrocarbons, with a focus on how microorganisms have evolved mechanisms to degrade these compounds as well as the exploitation of this knowledge in both *in situ* and *ex situ* bioremediation programs and the future of prospects in the treatment of these pollutants.

Hydrocarbon Pollution Effects on Macrobiota

Hydrocarbons penetrate the plant through the leaves, stomata and roots and adversely affect various metabolic activities including transpiration, respiration and photosynthetic rates. Moreover, the heavy metals often present in crude oil and petroleum derivatives affect the porphyrins in the pyrrolic structure of

CHAPTER 12

Microbial Bioremediation of Microplastics

Manish Kumar Singh[1], **Younus Raza Beg**[2], **Gokul Ram Nishad**[2] and **Priyanka Singh**[2,*]

[1] *Krishi Vigyan Kendra, Rajnandgaon-491441, Chhattisgarh, India*

[2] *Department of Chemistry, Govt. Digvijay PG Autonomous College, Rajnandgaon-491441, Chhattisgarh, India*

Abstract: Plastic is being used over the entire globe in the form of capsules, microbeads, fibers or microplastics. The waste thus generated has gained concern due to the loss of aesthetic value, the presence of various toxic chemicals such as plasticizers, antioxidants, *etc.*, and the release of greenhouse gases. The small size and slow degradability of microplastics are responsible for their accumulation in the environment and organisms. Plastic degradability can be improved by altering its chemical and physical structure or using better degrading agents. Different types of microorganisms and enzymes are being designed and employed for degrading plastic waste. This chapter gives an overview of the degradation mechanism along with different microbial, plant and animal species responsible for this process.

Keywords: Microplastics, Microbial degradation, Animal-mediated degradation, Plant-mediated degradation, Environmental pollutants.

INTRODUCTION

Plastic has become essential evil due to their indispensable necessity. Heaps of plastic waste are continually being added and accumulated in spite of its ill effects. Plastic gets accumulated in the form of macroplastics, mesoplastics, microplastics and nanoplastics in the environment. Generally, several additives such as plasticizers, antioxidants, UV stabilizers, curing agents, *etc.* are added to plastics during their processing which further increases environmental pollution. Moreover, dumping plastics in landfills leads to aesthetic degradation and the release of toxic chemicals and greenhouse gases [1].

* **Corresponding author Priyanka Singh:** Department of Chemistry, Govt. Digvijay PG Autonomous College, Rajnandgaon-491441, Chhattisgarh, India; E-mail: priyankasingh121@yahoo.com

Inamuddin (Ed.)

Microplastics are extremely small and harmful plastic pieces or fragments produced from industrial and consumer products. They can be commonly observed all around the globe and can be in the form of microbeads, capsules, fibers or pellets or may be produced from larger plastic items through their breakdown. This term was coined by a marine biologist, Richard Thompson. Polymers like phthalates, polybrominated diphenyl ethers, tetrabromobisphenol A, polyvinyl chloride, polystyrene, polyvinyl alcohol, *etc.* are common examples of microplastics [2, 3].

They have a size less than 5 mm and pose danger to the environment, flora and fauna. Degradation of plastics is a very slow process that may exceed a period of over hundreds or thousands of years. During this process, their ingestion and incorporation into the environment and living organisms are highly probable. They possess a large surface-to-volume ratio and therefore, interact with organic pollutants like polycyclic aromatic hydrocarbons, polychlorinated biphenyls, *etc.* depending on the properties of the latter [4, 5]. Ingestion of microplastics leads to oxidative stress, reduced growth and reproductive ability, false satiation, *etc* [6, 7]. Toussaint *et al.* (2019) have reviewed the contamination of microplastic and nanoplastic in the food chain. They have studied about 200 animal species and food products forming an element of the human food chain [8]. Zhang *et al.* (2020) have reviewed the direct human exposure to microplastics through the air, table salt and drinking water consumption [9]. Moreover, microplastics act as carrier for toxic chemicals in the environment [10].

New technologies and strategies need to be developed in order to combat the issue of ever-increasing plastic waste. Various methods have been utilized for the physical and chemical degradation of plastics. Different types of microorganisms and enzymes are being designed and employed for degrading plastic waste. Experiments are carried out all over the world in order to increase the catalytic efficiency of these enzymes. Canada, the United States of America, the United Kingdom, *etc.* have banned products containing microbeads [11]. Jenkins *et al.* (2020) and Masia *et al.* (2020) have reported the microbial degradation of plastics and bioremediation of microplastics, respectively [12, 13]. Functional groups capable of affecting the hydrophobicity, molecular weight, morphology, chemical and physical structure, structural complexity, molecular composition and density of polymers affect their degradability [14]. This review deals with microbial, plant and animal or their combinations mediated degradation of microplastics. The mechanism of biodegradation of some polymers has also been discussed briefly.

Types

On the basis of source, microplastics are mainly classified as primary and secondary microplastics.

Primary microplastics: They are the plastic pieces or fragments having size less than 5.0 mm. Microbeads, microfibers and plastic pellets are some of its examples. They are used in face washes, toothpaste, cosmetics [15], scrubbers [16], air blasting technology, biomedical research, *etc.* (Fig. **1**). Polyethylene, polyethylene terephthalate, polypropylene and nylon are generally used in these formulations or technologies.

Secondary microplastics: They are produced through the breakdown of larger macroplastic materials such as water bottles, plastic bags, plastic furniture, tyres, nets, *etc.* (Fig. **1**). UV radiations, wind and wave action, *etc.* may be held responsible for such breakdown.

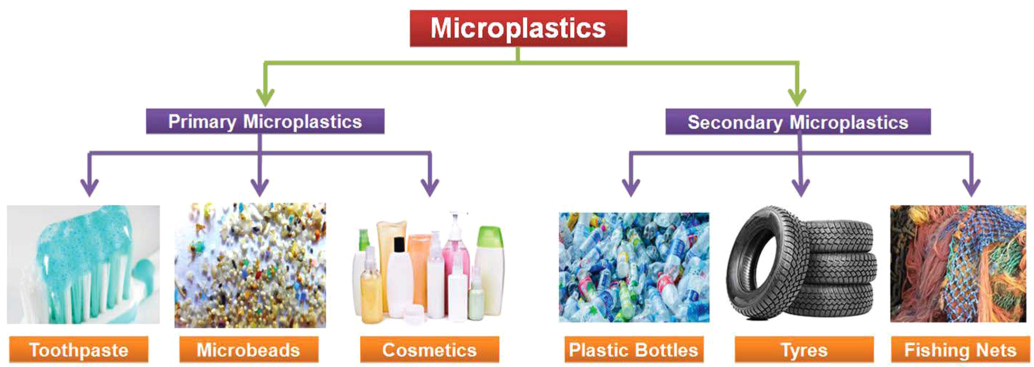

Fig. (1). Classification of plastics.

Sources: There are several sources of microplastics, some of which are being discussed here.

- Microplastics have been identified in primary as well as secondary water treatment stages which are subsequently added to the oceans and surface water bodies.
- Sewage sludge containing microplastics also contaminates the water bodies.
- Automobile tyres undergo wear and tear, thus adding microplastics into the surroundings.
- Natural exfoliating materials have been continually replaced with microplastics in cosmetic industries.
- Microfibers are released during handling and washing of clothing made up of

CHAPTER 13

Microbial Degradation of Plastics

Geetanjali[1], **Vikram Singh**[2] and **Ram Singh**[3,*]

[1] *Department of Chemistry, Kirori Mal College, University of Delhi, Delhi – 110 007, India*

[2] *Department of Chemistry, NREC College, Khurja, Uttar Pradesh – 203131, India*

[3] *Department of Applied Chemistry, Delhi Technological University, Delhi – 110 042, India*

Abstract: The essentiality of plastics in our daily life is inseparable. Almost all industrial sectors utilize plastics either directly or indirectly. But the downside of plastics also increased simultaneously. These materials increased water and soil pollution due to unmanaged discharge. Hence, plastic waste treatment becomes essential for a sustainable and efficient environment. Plastic recycling and degradation are two processes to deal with plastic waste. Out of the three degradation processes, physical, chemical, and biological, biological degradation is near to a sustainable environment. Recent studies revolve around the use of micro-organisms for the degradation of plastics. The present chapter reports the microbial degradation of plastic waste using bacteria and fungi. The discussion also includes the impact of plastic properties and environmental factors on biodegradation.

Keywords: Plastics, Plastic waste, Degradation, Microbes, Bacteria, Fungus, Waste management.

INTRODUCTION

Plastics are derived from petrochemicals or synthetic monomers and possess high molecular weight. These polymeric materials have valuable industrial applications for all walks of life due to user-friendly properties like low cost, high durability, lightweight, and relatively better strength [1 - 5]. Their production has increased manifolds in the last few decades [6, 7]. According to Statista, the global production of plastic has increased from 245 million metric tons in 2008 to 359 million metric tons in 2018 [8]. This huge production, low circular use, long period of degradation or no degradation, and poor recycling lead to the accumulation of plastics in the environment, especially marine and terrestrial causing adverse effects in all ecosystems [3, 9]. The plastics are present in the environment in three main fractions: mismanaged plastic waste, post-consumer

* **Corresponding author Ram Singh:** Department of Applied Chemistry, Delhi Technological University, Delhi – 110 042, India; E-mail: ramsingh@dtu.ac.in

Inamuddin (Ed.)

managed plastic waste and plastic in use [10, 11]. The first one, mismanaged plastic waste, is mainly responsible for environmental pollution. The packaging-related and urban litter plastics are mostly mismanaged category which also include open dump plastics. The last two categories are mostly accountable.

The land and soil environment are directly affected by the pollution of plastics [6, 12]. According to a study by the UN Environment Programme, in the current scenario, we are generating about 300 million tonnes of plastic waste every year [13]. This has been estimated that till now, about 8.3 billion tonnes of plastic have been generated, and approximately 60% of them are mismanaged plastic waste. As per the data on plastic waste management, only 9% has been recycled, and about 12% are incinerated and the rest 79% have been put to the natural environment as landfills or dumps [13]. The ocean receives about 8 million tonnes of plastics every year, either through rivers or human activities at beaches, *etc* [13]. The countries like Philippines, Vietnam, Indonesia, Thailand, and China are some of the major plastic contributors to the ocean [14]. The plastic pieces are entering the marine food chain and further to humans causing several diseases [15].

There have been reviews and reports published regarding the degradation and recycling of plastic materials with their limitations and advantages [16 - 20]. The recycling efforts started after 1980 with only non-fiber plastics whose recycling and incineration in 2014 reached 18 and 24%, respectively of total non-fiber plastics waste generated worldwide [3]. Plastic degradation takes place using different paths (Fig. **1**) and leads to chemical or physical changes in plastic causing deterioration of functionality, discolouration, reduction in strength, changes in optical and electrical properties, and so on [21]. The changes mainly take place due to the formation of new functional groups, changes in bond properties, and chemical transformations [22]. The degradation processes such as UV-treatment, heating, hydrolysis, trans-esterification, ammonolysis, *etc.* require severe conditions and also produce toxic by-products [23 - 25].

The biological method of degradation is better for the sustainable environment. The present chapter discusses the microbial degradation of plastic waste using bacteria and fungus. This chapter also includes the impact of plastic properties and environmental factors on biodegradation.

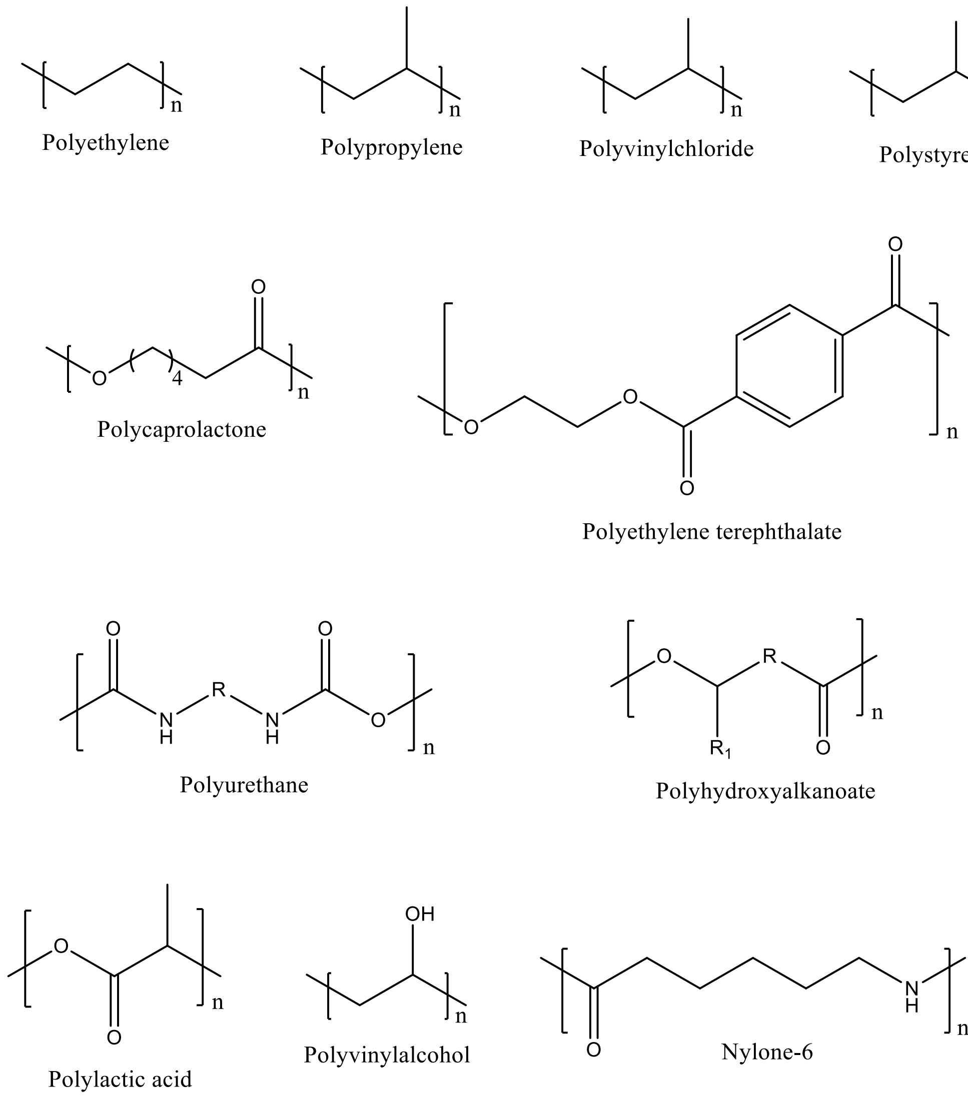

Fig. (1). Methods of plastic degradation.

MICROORGANISM FOR PLASTIC DEGRADATION

The degradation of plastics with the help of microbes is known as microbial degradation. The microbes mainly include bacteria and fungi which transform the structure of plastics and are released into the environment [26 - 28]. This is an environmental-friendly procedure that destroys the gathering of harmful

CHAPTER 14

Characteristic Features of Plastic Microbial Degradation

Soumyaranjan Senapati[1], **Sreelipta Das**[1] and **Alok Kumar Panda**[1,*]

[1] *School of Applied Sciences, Kalinga Institute of Industrial Technology, Deemed to be University, Bhubaneswar-751024, India*

Abstract: The increase in the amount of plastic waste, especially microplastics and the environmental pollution caused by it has diverted the research focus of the world into plastic recycling and degradation. Hence in the last decade, different strategies have been adopted to combat this problem. Albeit many physiochemical technologies are there for the degradation of plastics, they give rise to harmful chemicals as by-products. This has shifted the priority of our research to the biodegradation of plastics by microbes. In fact, in the last decade, many microorganisms have been discovered with the ability to degrade many conventional plastics with moderate efficiency but longer duration. The initial part of this chapter discusses the various kinds of plastics present and the methods adopted for the degradation of plastics, with special emphasis on the factors affecting plastic degradation. In the subsequent section, the microbial degradation of different plastics by bacteria and fungi, along with a mechanism, has been outlined. Furthermore, this chapter also briefly discusses the role of enzymes in the degradation of different plastics by microbes and the future of plastic biodegradation.

Keywords: Plastics, Plastics biodegradation, Microbes, Bacteria, Fungi, Microbial consortia, Microbial biofilm, Biodegradation mechanism, Enzymes, PETase.

INTRODUCTION

Polymers have been associated with human society since 1600 BC, when natural rubber was processed to form different items [1]. The first synthetic plastic was revealed by Alexander Parkes in the year 1862 and Leo Hendrik Baekland in the year 1907, who accidentally discovered a new synthetic polymer that came to be known as Bakelite. Two years later, Baekland coined the name "plastics," which represented a new material [2]. Plastic, derived from the Greek word "plastikos,"

* **Corresponding author Alok Kumar Panda:** School of Applied Sciences, Kalinga Institute of Industrial Technology, Deemed to be University, Bhubaneswar-751024, India; E-mail: alok.pandafch@kiit.ac.in

Inamuddin (Ed.)

means things that can be molded into different shapes. Polyvinyl chloride or PVC was the first plastic to be patented and registered in 1914. However, the boom in plastics started just after World War II, when polyurethane, silicones, polypropylene, polyester joined the race with polyvinyl chloride and polystyrene. It is estimated that there is an increase in plastic production of about 30-40% worldwide due to the application of plastic for different packing purposes, as a result of which the increase rate in the garbage production would rise by around twelve percent per annum [3]. In 1950, the production of plastic per year was 2 million tonnes worldwide. Since then, the annual production of plastic has increased nearly 200-fold and reached 381 million tonnes in 2015 [4]. Due to this large increase in the production of plastic, there is a persistent accumulation of plastics in the environment, which causes severe water and land pollution. A large amount of plastics is found littering the agricultural lands than in the ocean waters, which causes land pollution and hampers agricultural productivity. The plastics released from the household activities end up in the waste treatment plant, which is then accumulated in the agricultural soils, which leads to the transportation of the invasive species [5]. Apart from this, the swallowing of the disposed of plastic materials by both terrestrial and marine animals leads to entanglement which may result in the death of these species [6]. While landfilling is a short-term solution for managing plastic waste, the long-term solution for the disposal of plastic waste needs a lot of work and still has a long way to go. In addition to this, many chemical and physical degradation processes such as hydrolysis, ammonolysis, oxidants, physical and UV stress have been employed to degrade plastics, but these processes lead to the production of toxic substances [7]. Conventional plastics like polyethylene terephthalate (PET) and polyethylene (PE), are very resistant to degradation as they are made of a highly stable carbon backbone and hence are durable and consumer-friendly plastics. The plastic waste generation per person per day in India in 2010 was about 0.01 kilograms, which is less than 10 times as compared to the United States, Kuwait, Germany, the Netherlands, *etc.* In recent times the average per capita plastic usage in India is eleven kg which is less than half of the global consumption which stands at 28 kg [8]. Albeit the consumption of plastics in India is less as compared with that of the world, but India faces a lot of problems in recycling or degrading these plastics in an eco-friendly manner. Therefore, biodegradation is one of the major solutions which can be employed to deal with the plastics wastes from both the world and Indian perspectives.

As conventional plastics are difficult to degrade and generate a lot of pollution, biodegradable plastics are being used in many fields [9 - 13]. But due to the high cost and less durability of biodegradable plastics, their commercial application is limited [14]. Hence, in recent times a lot of efforts and research has been directed to the biodegradation of conventional plastics which is eco-friendly and negates the release and accumulation of toxic and harmful by-products [15]. The biodegradation of plastics is mainly carried out by various micro-organisms, but the degree of biodegradability by different microbes depends on various properties of the plastic especially the chemical and the physical properties [16]. The polymer bonds in the plastic are mainly degraded by the microbes with the aid of enzymatic hydrolysis and the biofilms generation on the plastic surface [17]. In this chapter, the various kind of plastics used and their present method of disposal and degradation has been outlined. Thereafter, the various methods adopted for the biodegradation of selected conventional plastics and the factors affecting their biodegradation and the extensive list of the microbes utilized for the degradation of various plastics have been discussed in detail. Finally, the biodegrading enzymes, their molecular aspects, and the future scope of biodegradation of plastics have been summarized.

CLASSIFICATION AND CATEGORIES OF PLASTICS

Polymers are synthesized by the polymerization of the monomers which may be derived from fossil fuels or nature. In general, there are around twenty different types of polymers and within each group, there are numerous grades. Plastics are divided into thermosetting, elastomers, and thermoplastics and the classification is based on their physical characteristics. But the majority of the plastic that we use is thermoplastic *i.e* it can reform repeatedly. In context to the biodegradability of the plastics, it can be classified as follows:

1. Natural Plastics
2. Biodegradable Synthetic Plastics
3. Non-biodegradable Synthetic Plastics

Natural Plastics

Natural plastics are easily available in nature in the form of biopolymers and dry materials and are named natural bioplastics. These types of plastics are mainly synthesized by plants, fungi, crustaceans, insects or algae, *etc* [18, 19]. The cell wall of different plants have a variable composition and usually, lignin, cellulose and hemicellulose are the main constituents of dry material that endows rigidity to the plant cell wall [18]. So, these lignin, cellulose, and hemicellulose, are the building block of natural polymers [20]. Chitin is another most important and abundant natural polymer [19]. It is the structural element in many organisms, like fungi, insects and algae, *etc* [21].

Biodegradable Synthetic Plastics

Biodegradable synthetic polymers are those which can be degraded by using

SUBJECT INDEX

A

B

C

D

P

Q

R

S

T

U

V

W

X

Z

Inamuddin

Dr. Inamuddin is an assistant professor in the Department of Applied Chemistry, Zakir Husain College of Engineering and Technology, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh, India. He has extensive research experience in the multidisciplinary fields of analytical chemistry, materials chemistry, electrochemistry, renewable energy, and environmental science. He has worked on different research projects funded by various government agencies and universities and is the recipient of awards, including the Department of Science and Technology, India, Fast-Track Young Scientist Award and Young Researcher of the Year Award 2020 from Aligarh Muslim University. He has published about 200 research articles in various international scientific journals, 18 book chapters, and 165 edited books with multiple well-known publishers. His current research interests include ion exchange materials, a sensor for heavy metal ions, biofuel cells, supercapacitors, and bending actuators.