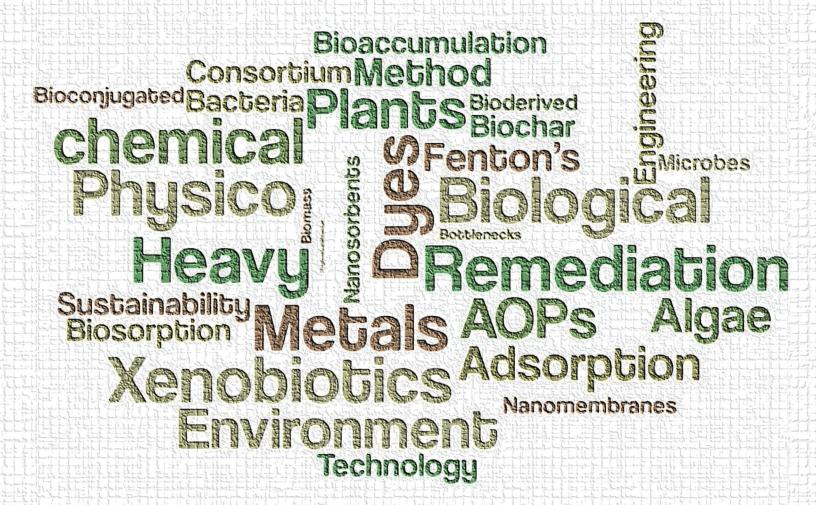
RECENT TRENDS AND INNOVATIONS IN SUSTAINABLE TREATMENT TECHNOLOGIES FOR HEAVY METALS, DYES AND OTHER XENOBIOTICS



Editors: **Biswanath Bhunia Muthusivaramapandian Muthuraj**

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Recent Trends and Innovations in Sustainable Treatment: Technologies for Heavy Metals, Dyes and Other Xenobiotics

Edited by

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CONTENTS

FOREWORD	i
PREFACE	ii
LIST OF CONTRIBUTORS	iii
CHAPTER 1 WASTEWATER TYPES, CHARACTERISTICS AND TREATMENT	
STRATEGIES	1
Uttarini Pathak, Avishek Banerjee, Subham Kumar Das, Teetas Roy and Tamal	
Mandal	
1. INTRODUCTION	2
2. CHARACTERIZATION	4
2.1. Coke Oven Wastewater	4
2.2. Rice Mill Wastewater	4
2.3. Pharmaceutical Wastewater	5
2.4. Leather Industry Wastewater	
3. TREATMENT STRATEGIES	
3.1. Coke Oven Wastewater	6
3.2. Rice Mill Wastewater	
3.3. Pharmaceutical Wastewater	
3.4. Leather Industry Wastewater	
CONCLUSION	
CONSENT FOR PUBLICATION	
CONFLICT OF INTEREST	
ACKNOWLEDGEMENT	
REFERENCES	
CHAPTER 2 HIGH GRAVITY TECHNOLOGY FOR IMPROVING EFFICIENCY OF WASTEWATER TREATMENT PROCESSES Sudhanya Karmakar, Avijit Bhowal, Papita Das and Abhijit Mondal	1
1. INTRODUCTION	1
2. CONVENTIONAL WASTEWATER TREATMENT PROCESS AND EQUIPMENT	
2.1. Adsorption	1
2.2. Air Stripping	
2.3. Liquid-liquid Extraction	
2.4. Emulsion Liquid Membrane	
2.5. Advanced Oxidation Process	
2.6. Fenton Oxidation	
2.7. Ozonation	
2.8. Photocatalytic Treatment	
3. PROCESSES IN HIGH GRAVITY EQUIPMENT	
3.1. Rotating Packed Bed	
3.2. Micromixing	
3.3. Gas and Liquid Mass Transfer Coefficient	
3.4. Allowable Throughput	
3.5. Spinning Disc Reactor	
CONCLUSION	
CONSENT FOR PUBLICATION	
CONFLICT OF INTEREST	
CONFLICT OF INTEREST	2
CONFLICT OF INTEREST ACKNOWLEDGEMENT REFERENCES	

CHAPTER 3 RECENT TRENDS IN ADVANCED OXIDATION AND CATALYTIC PROCESSES FOR REMOVAL OF HEAVY METALS, DYES, AND XENOBIOTICS	45
Rupak Kishor, Suneeta Kumari, Muthusivaramapandian Muthuraj and	. 15
Narayanasamy Selvaraju	
1. INTRODUCTION	45
2. ADVANCED OXIDATION PROCESS (AOP)	
1.1. Ozone Assisted AOPs	
1.2. Ultraviolet Assisted AOPs	
1.3. Fenton Assisted AOPs	
1.4. Sonolysis Assisted AOPs	
1.5. Photocatalysis Assisted AOPs	
1.6. Sulfate Radical-based AOPs	
2. REMOVAL OF DYES BY AOPS APPLICATION	
2.1. Removal of Dyes Using Ozonation Assisted AOPs	
2.2. Removal of Dye Using UV-assisted AOPs	
2.3. Removal of Dye Using Fenton Oxidation	
2.4. Removal of Dye Using Sonolysis	
2.5. Photocatalytic Removal of Dyes	
3. REMOVAL OF XENOBIOTICS BY AOPS APPLICATION	
3.1. Removal of Xenobiotics by Ozonation-based AOPs	
3.2. Removal of Xenobiotics by UV-based AOPs	
3.3. Removal of Xenobiotics by Fenton and Photo-Fenton Process	
3.4. Removal of Xenobiotics by Sonolysis	
3.5. Removal of Xenobiotics by Photochemical Degradation	
4. REMOVAL OF HEAVY METAL USING AOPS	
4.1. Heavy Metal Removal Using Ozonation-based AOPs	
4.2. Heavy Metal Removal Using UV-assisted and Photocatalytic AOPs	
4.3. Heavy Metal Removal Using Fenton Oxidation-based AOPs	
CONCLUSION	
CONSENT FOR PUBLICATION	
CONFLICT OF INTEREST	
ACKNOWLEDGEMENT	. 73
REFERENCES	. 73
CHAPTER 4 DEVELOPMENTS IN ADSORPTION TECHNOLOGIES FOR REMOVAL OF	. 81
HEAVY METALS, DYES, AND XENOBIOTICS	. 01
1. INTRODUCTION	. 81
2. PREPARATION, CHARACTERIZATION, AND MECHANISM OF VARIOUS	. 81
2. PREPARATION, CHARACTERIZATION, AND MECHANISM OF VARIOUS ADSORBENTS	02
2.1. Activated Carbon (GAC, PAC, Biochar)	
2.2. Zeolites and Clay Materials	
2.3. Biosorbent (Agricultural Residue and Microbial Biomass)	
2.4. Carbon Nanotubes	
2.5. Graphene	
2.6. Hybrid	
3. INFLUENCE OF PROCESS PARAMETERS	
4. MODELING OF ADSORPTION PROCESS	
4.1. Adsorption Isotherm	
4.2. Adsorption Kinetics	
4.2.1. Surface Reaction Models (SRM)	. 98

4.2.2. Mass Transfer Models (MTM)	
4.3. Example of Unconventional Mathematical Modeling	
CONCLUSION	
CONSENT FOR PUBLICATION	
CONFLICT OF INTEREST	
ACKNOWLEDGEMENT	
REFERENCES	
CHAPTER 5 BIODERIVED AND BIOCONJUGATED MATERIALS FOR	DEMEDIATIO
OF HEAVY METALS AND DYES FROM WASTEWATER	•••••
S.R. Joshi and Debajit Kalita	
1. INTRODUCTION	
1.1. Heavy Metals from Mining, Processing and Industrial Effluents	
1.2. Heavy Metals Used in Agriculture	
1.3. Air Mediated Sources of Heavy Metals	
1.4. Sources of Dyes	
2. REMEDIATION AND RELATED TECHNOLOGY	
2.1. Phytoextraction	
2.2. Phytostabilization	
2.3. Rhizofiltration	
2.4. Phytovolatilization	
2.5. Phytotransformation/ Phytodegradation	
2.6. Plant-based Remediation of Heavy Metals and Dyes	
2.7. Whole Plant for Dye Removal	
2.8. Plant Derived Material for Heavy Metal	
2.9. Plant Derived Material for Dye	
2.10. Plant Synthesized/Conjugated Material for Heavy Metals	
2.11. Plant Synthesized/Conjugated Material for Dye Removal	
3. MICROBIAL BASED REMEDIATION	
3.1. Whole Cells for Heavy Metals	
3.2. Whole Cells for Dye Removal	
3.3. Microbial Derived/Conjugated Remediation of Heavy Metals	
3.4. Microbial Derived/Conjugated Remediation of Dye	
3.5. Microbial Synthesized/Conjugated Material for Heavy Metals	
3.6. Microbial synthesized/conjugated Material for Dye	
CONCLUSION	
CONSENT FOR PUBLICATION	
CONFLICT OF INTEREST	
ACKNOWLEDGEMENTS	
REFERENCES	
CHAPTER 6 TRENDS IN BIOREMEDIATION OF DYES FROM WASTE	WATED
Chapter 6 TRENDS IN BIOREMEDIATION OF DYES FROM WASTE Chandrani Debnath, Biswanath Bhunia, Bikram Basak and Muthusivaramap	
	unutun
Muthuraj	
1. INTRODUCTION	
2. BIOLOGICAL TREATMENT OF DYES	
2.1. Biosorption of Dyes	
2.1.1. Biomaterials for Adsorption	
2.1.2. Factors Influencing Biosorption of Dyes	
2.2. Bioaccumulation and Degradation of Dyes	
2.2.1. Factors Affecting Biodegradation	
2.3. Biochar, and Biochar-based Nanocomposites	••••••

2.4. Porous Materials and Metal-organic Frameworks (MoFs)	
2.5. High-performance Forward-osmosis Membrane	159
3. SUSTAINABLE STRATEGIES FOR BIOREMEDIATION OF DYES	
4. BOTTLENECKS & FUTURE PROSPECTS	162
CONCLUSION	
CONSENT FOR PUBLICATION	
CONFLICT OF INTEREST	164
ACKNOWLEDGEMENT	164
REFERENCES	164
CHAPTER 7 BOTTLENECKS IN SUSTAINABLE TREATMENT OF WASTEWATERS	,
USING PHYSICO-CHEMICAL PROCESSES AND FUTURE PROSPECTS	
Nibedita Mahata, Biswanath Bhunia, Muthusivaramapandian Muthuraj and Ramesh	175
Kumar Kumar	
1. INTRODUCTION	175
2. BOTTLENECKS OF PHYSICO-CHEMICAL WASTEWATER TREATMENT	175
2. BOTTLENECKS OF FILISICO-CHEMICAL WASTEWATER TREATMENT PROCESS	176
2.1. Membrane Filtration	
2.1. Memorale Futuation	
2.2. Activated Carbon Fination	
2.3. Adsorption	
2.4. Advanced Oxidation Processes	
2.5. Dissolved All Floatation (DAF)	
2.7. Electrocoagulation (EC) Process 3. CRITERIA FOR SUSTAINABLE WASTEWATER TREATMENT TECHNOLOG	
3.1. Performance	
3.2. Cost	
3.3. Sustainability	
3.3.1. Resource Recovery	
3.3.2. Energy Management	
3.3.3. Solid Volume Reduction	
3.4. Prospects in Physico-chemical Remediation	
CONCLUSION CONSENT FOR PUBLICATION	
CONFLICT OF INTEREST	
ACKNOWLEDGEMENT	
REFERENCES	188
CHAPTER 8 SUSTAINABLE MITIGATION OF WASTEWATER ISSUES USING	
MICROBES: HURDLES AND FUTURE STRATEGIES	191
Bidhu Bhusan Makut, Mayurketan Mukherjee, Gargi Goswami and Debasish Das	
1. INTRODUCTION	
2. BIOLOGICAL TREATMENT	195
2.1. Bacterial Treatment	195
2.1.1. Challenges Associated with Bacterial Bioremediation	197
2.2. Treatment of Wastewater Using Microalgae	197
2.2.1. Challenges Associated with Microalgal Bioremediation	
2.3. Mycoremediation of Wastewater Treatment	
3. CONSORTIUM AIDING ENHANCED BIOREMEDIATION	
3.1. Pivotal Role of Microalgae-Bacteria Consortium in Wastewater Treatment	
3.1.1. Mutualistic Association	204
3.2. Microalgae-Bacteria Based Wastewater Treatment	206

3.3. Confrontation Associated with Microalgae-Bacteria Consortium Towards	
Bioremediation	
CONCLUDING REMARKS	
CONSENT FOR PUBLICATION	
CONFLICT OF INTEREST	
ACKNOWLEDGEMENT	
REFERENCES	
SUBJECT INDEX	

FOREWORD

Over the decades, the environment and sustainable development have become major alarms in the engineering industry. The goal of environmental engineering is to ensure that societal development and the use of all resources such as water, land, and air are sustainable. In other words, environmental engineering can ensure the protection of the environment and understand and improve the interactions between human beings and natural environments. The effort to make such challenges effective and economically viable involves substantial interaction among chemical engineers, biochemical engineers, biotechnologists, biochemists, microbiologists, and geneticists. Environmental engineers are mainly associated with water, soil and air pollution problems, and develop technical solutions needed to solve, attenuate or control these problems in a manner that is compatible with legislative, economic, social, and political concerns. Chemical and civil engineers are particularly involved in such activities as water supply and sewerage, management of surface water and groundwater quality, remediation of contaminated sites, and solid waste management. Over the past few decades, biological scientists have produced vast amounts of quantitative information. The life sciences are now seeking a unified basis, with exact knowledge replacing the descriptive approach. Many biological phenomena are now understood and can be employed for the benefit of mankind. While in many cases it has been possible to achieve spectacular reductions in microbiological treatment costs, the risk involved in starting a microbiological venture has never been small, primarily due to a lack of knowledge and talents. Once the problem is recognized for what it is, a realistic solution may be seen which lies in breaking down barriers to communication. This will attract new talents to contribute to environmental engineering research and thereby help advance biotechnology.

This book is a multi-author book concerned with the engineering aspects of environmental science. It is intended to serve the established professionals and also to encourage students to take up careers in this field. The text is organized into areas important to environmental engineers who are working in the field of Sustainable Treatment Technologies for heavy metals, dyes, and other xenobiotics. Any text on environmental engineering is somewhat dated by the time of publication, because the field is moving and changing rapidly. Authors have included those fundamental topics and principles on which the practice of environmental engineering is grounded, illustrating them with contemporary examples. Additionally, chapters on bottlenecks in sustainable treatment of wastewaters using physicochemical processes and future prospects are included. Furthermore, the topic on sustainable mitigation of wastewater issues using microbes: hurdles and future strategies is also included. The analysis of bioprocesses as well as chemical processes has been given prominence in this book. The book deals with some hitherto neglected areas such as sustainable treatment technologies of heavy metals, dyes, and xenobiotics. It is expected that these contributions will stimulate many more talents to contribute through basic research and dissemination of knowledge to the "yet to emerge" hybrid discipline of environmental engineering.

> Prof. (Dr.) Tarkeshwar Kumar Professor of Petroleum Engineering Formerly, Director IIT(ISM) Dhanbad & NIT Durgapur India

PREFACE

Industrial inflations and demographic expansions resulted in incessant pollution of water resources with hazardous chemicals and complex xenobiotic compounds that challenge environmental sustainability. With the high cost and high energy requirements, complex plant designs, less efficiency in recovery, the conventional wastewater treatment strategies fail to support a feasible large-scale process resulting in the release of untreated wastewater into the environment. These serious concerns must be addressed with a feasible and sustainable technology that can remediate contaminated wastewater with scope for reutilization and recycling. Over the past decade, the research in this field keeps producing new processes and techniques to overcome the deficiencies encountered in these technologies. Several innovative green technologies are being outlined to address these issues with environmental sustainability and wastewater treatment such as nano-sized membrane-based treatment strategies, microalgae-based pollution management, commercial-scale fuel cells, inverse fluidization technology, etc. However, commercial-scale feasibility and applicability of these technologies are still far from realization. The present book 'Recent Trends and Innovations in Sustainable Wastewater Treatment Technologies' aims to address all these issues by integrating the knowledge of innovation technologies that have been developed predominantly in the past decade and the available commercial-scale processes altogether to understand the path ahead in reaching sustainability and high efficiency in wastewater treatment.

The book has been compiled into eight chapters. Chapter 1 details the various types of prevailing wastewater, its characteristics, and the major commercial-scale strategies employed to treat those types of wastewater. Chapter 2 details predominantly the different types of physicochemical methods utilized for the remediation of heavy metals, dyes, and xenobiotics. Chapters 3 and 4 highlight the innovations in the advanced oxidation process and adsorption for remediation of such complex molecules respectively. Chapters 6, and 7 individually address the recent innovations in the bioremediation of heavy metals, and dyes respectively. Finally, chapters 8 and 9 discuss the latest technologies, prevailing bottlenecks, and the path ahead towards commercial viability and environmental sustainability in both physicochemical and biological treatment processes.

We are obliged to the authors for their contributions and to the reviewers for their comprehensive comments on shaping up the chapters and improving their quality.

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iv

Wastewater Types, Characteristics and Treatment Strategies

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Abstract: One of the most important issues in recent times is the remediation of wastewater discharged from different industries. Several of the growing economies have been investing heavily to reduce the discharged waste content for economic and environmental sustainability. The wastewater when discharged into natural water bodies harms the flora and fauna of the surrounding environment, which in turn disrupts the ecosystem and affects the food chain. It also increases and possesses a variety of health risks to human beings. To eliminate the potential threats, a critical analysis of the past research and upcoming remediation technologies is necessary. Over the years, a lot of advancements have been made to curb the disruption of the natural ecology from effluent discharges by different industries like the leather industry wastewater, Rice mill wastewater, pharmaceutical industry wastewater and Coke Oven wastewater. The common characterization techniques that are employed in all of them are to measure the COD and BOD levels, pH, odor, TSS, organic and inorganic materials. Subsequently, the common technologies that are in use to treat these wastewaters are mainly physicochemical treatments like adsorption, electrocoagulation/flocculation, nanofiltration, Fenton's oxidation or biological treatments like aerobic/anaerobic microbial degradation. An important requirement is to understand the situation currently prevalent in wastewater treatment to develop better and advanced methods for increased efficiency and waste removal. The aim of this chapter is to give a detailed account on the composition, characterization, and treatment strategies of the discharged effluent to enhance the knowledge of available resources and instigate ideas of future improvements.

Keywords: Industries, Treatment, Dyes, Pharmaceuticals, Heavy metals.

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1. INTRODUCTION

The world's population is continuously increasing along with rapid industrialization which highlights the environmental concerns that arise from industrial wastes [1]. Industrial waste and pollution have become major contributing factors to the degradation of the environment over the years. It was observed through various investigations that almost half of the medium and small-scale industries contribute greatly to water pollution by waste discharge in natural water bodies [2]. The environmental, economic, and societal implications of waste discharge give rise to unavoidable discord between industrialization and environmental sustainability [3, 4]. Due to the mobile nature, detrimental impacts are observed on biodiversity from effluents if discharge is from different industries like chemical, pharmaceutical, leather, textile, *etc.*, which influences the characteristics of the discharged wastewater making it difficult to predict the composition. Hence, the treatment of these wastewaters has attracted more investigation to preserve the environment [7].

Tannery industry earns a large amount of foreign exchange through its leather export and is also one of the most important industries in India. After tanning, the effluents released contains high amount of trivalent chromium, BOD and COD levels, NaCl, sulfides, Mg, Ca, organics, and other toxic ingredients. These effluents affect the natural ecosystem and subsequently possess a variety of health risks to human beings [8, 9]. For example, in Dhapa, Kolkata (India), wastewater from nearby tanneries is disposed of that affects the food chain of human beings [8]. The standard methods of treating tannery wastewater are by adsorption [10, 11], coagulation/flocculation [12], oxidation by Fenton's reagent [13], nanofiltration [14, 15]. Recently, bioremediation technologies are being used by the industries to degrade the generated waste either aerobically or anaerobically [16]. One of the major elements for the toxic hazardousness of the wastewater is chromium [17]. The tanning process using chrome releases about 40% of unutilized Cr salts that are often released through the wastewater, giving rise to serious environment implications [18 - 20]. Exposure to common tannery waste like pentachlorophenol, chromium, and other toxic pollutants increases the risk of ulcer nasal septum perforation, dermatitis, and lung cancer [21, 22].

Rice is the main staple food in India and around the world and its production has a significant role in the world economy. Huge quantities of water are required for the soaking of parboiled rice and thus a significant amount of wastewater is generated from rice production which is approximately 1–1.2 L/kg of paddy [23]. One of the most common concerns is its disposal on land that causes soil contamination and consequently results in surface and groundwater quality

Wastewater Types

degradation [24]. Algal blooms that cause odor problems due to eutrophication and many other adverse effects are the outcomes of discharging untreated effluents into natural water bodies [25, 26]. Rice mill effluent has a pungent odor that is mainly yellowish in color and consists of toxic organic materials along with other impurities. Rice mill wastewater consists of COD elements like cellulose, lignin, phenol, and other humic substances that disrupt the environmental sustainability [27]. The most common technologies that are studied for remediation are physicochemical treatments like adsorption [28] and electrocoagulation [29], microbial treatment [30] and phytoremediation [3].

Human health is becoming a subject of prime importance that is leading to the rapid growth of the pharmaceutical sectors, but at the same time, these industries produce a lot of wastewater effluents that are responsible for the degradation of the environment [31]. Various microbial and toxic elements along with virulent pharmaceutical ingredients (API) are released untreated into natural water bodies. The pollutant load in municipal waste is often increased by the improper disposal of unutilized medicine along with metabolic excretion due to drugs by humans and animals, which in turn could affect the ecology and increase health hazards. Various research works have established that the presence of pharmaceutical compounds in aquatic systems often arise from pharmaceutical manufacturing plants [31 - 35]. Thus it affects the food chain as well as plant and animals [36, 37]. Current techniques employed to treat this wastewater in different industries are biochemical treatment [38 - 40], membrane filtration treatment [46 - 51] for the removal of waste from industrial wastewater.

Coke ovens are used extensively in the steel and coal industries. Compounds like phenol and cyanide are released with the coke oven wastewater which affects the entire ecosystem, harming the flora and fauna along with the human respiratory system [52, 53]. Thus, a permissible limit of 0.5 mg/L for phenol and 0.2 mg/L for cyanide has been set by different industries for the industrial effluent according to various environmental organizations (WHO, USEPA, and CPCB, India) [54]. Different waste treatment technologies have been used in recent times that focus more on biofilm or fluidized bed reactors [55 - 58], membrane-based bioreactors [59], granular activated carbon [60], and immobilized spent tea activated carbon [61, 62]. Since there exists several factors like public hazards, economic feasibility of upscaling and complexity of the wastewater, the approach towards treating this water have been changed from incineration or chemical decomposition. Bioremediation has been a popular technique for remediation of phenol and cyanide with some of the major degrading organisms being *Escherichia coli* [63], *Pseudomonas* sp [64, 65], *Acinetobacter* sp., *Bacillus* sp [66, 67], Serratia odoriferra MTCC 5700, etc. Also, immobilization technique

CHAPTER 2

High Gravity Technology for Improving Efficiency of Wastewater Treatment Processes

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Abstract: Conventional technologies such as stripping, liquid-liquid extraction, chemical precipitation, adsorption, and the advanced oxidation process among others have been applied for the treatment of wastewater. The imposition of stricter regulations on discharge limits has led to a search for novel technologies to make the conventional wastewater treatment technologies efficient and cost-effective. High gravity technology uses centrifugal force to create artificial gravity which is hundreds of times the terrestrial gravitational force. Equipment working in high gravity environment intensifies the rate of mass transfer, micromixing and allows a higher amount of fluid to flow through the devices. The usefulness of high gravity technology for enhancing the performance of wastewater treatment processes has been discussed.

Keywords: Air stripping, HIGEE, Liquid-liquid Extraction, Micromixing, Reactors.

1. INTRODUCTION

Industrial activity results in the generation of wastewater. Numerous chemical industries like pesticides, pharmaceuticals, paints and dyes, detergent, petrochemicals *etc.*, [1], contaminate water by releasing feedstock materials, byproducts, solvents, cleaning agents and value-added products. Food industry, mines and ores, iron and steel industry, nuclear industry, pulp and paper industry, dairy industry, and breweries also play a significant role in water pollution [1].

In case of mines and ore recovery plants, the water released will inevitably be contaminated with minerals present in the ores. Wastewater from food industry

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High Gravity Technology

has high concentrations of biological oxygen. In breweries, the values of BOD (biological oxygen demand) and COD (chemical oxygen demand) are in the range of 1000-1500 mg/L and 1800-3000 mg/L respectively [2]. Waste water of iron and steel industry contains gasification products (phenols, cresols, ammonia, benzene *etc.*) and mineral acids [3]. The differences in pollutant characteristics in waste water discharge by industries suggest that different techniques have to be employed to treat the wastewater to reduce the pollutant level below the discharge limit. Some of these techniques are discussed below.

2. CONVENTIONAL WASTEWATER TREATMENT PROCESS AND EQUIPMENT

2.1. Adsorption

Adsorption is a surface phenomenon where molecules of a solution (known as adsorbate) come in contact with an adsorbent and become attached to its surface [4 - 5]. The reason for this is the physical forces or chemical bonds between the adsorbate and adsorbent molecules. Adsorbents are classified as natural and synthetic. Natural adsorbents are classified as organic and inorganic adsorbents. Organic adsorbents include peat, sawdust, vegetable fibers, straw, feathers, milkweed, *etc.* whereas inorganic adsorbents include ores, clays, clay minerals, volcanic ash [6]. Synthetic adsorbents are made from agricultural products and wastes, industrial wastes, household wastes, sewage sludge and polymeric materials, *etc.* [7]. Activated carbon is one of the most popular adsorbents in industries due to its higher surface area, large porous structure, nonpolar characteristics and economic viability [7]. These have been derived from several agricultural and industrial waste materials.

Most of the adsorbents are in the form of granules or in powder. The removal of pollutant occurs as it diffuses through the waste water onto the surface of the adsorbent. Granular adsorbents are commonly used in fixed bed adsorbers. The design of these adsorbers is based on time required to achieve breakthrough point. A typical breakthrough curve is generally S shaped. But sometimes it may be steep or flat in nature and also distorted in some cases. The bed needs to be regenerated after the breakthrough point is reached. Efficient use of adsorbent bed would increase the breakthrough time, reduce the chemicals required for regeneration and the solid waste generated when the adsorbent bed is disposed and hence reduce the cost [8 - 9].

Adsorbent bed will be efficiently utilized in case of infinitely rapid adsorption process. The breakthrough curve would be a straight vertical line. The mechanism of adsorption, resistance to mass transfer in the solution through which the particle diffuses and the intraparticle resistance dictate the adsorption rate. For a

20 Recent Trends and Innovations in Sustainable Treatment

given adsorbate-adsorbent system, the adsorption rate can be increased if the intraparticle resistance is reduced by using small adsorbent particles and it ensures negligible mass transfer resistance [10]. However, decreasing the particle size also reduces the void fraction in the bed. Therefore, when liquid flows down the adsorbent bed under gravity, the minimum particle size that can be used is restricted by the required flow rate. Powdered form of adsorbent can be used as an alternate. It is added directly to the waste water or in the form of slurry. The continuous adsorption process using powdered form can be carried out in stirred tank contactors or can be added as the wastewater flows in a pipeline. In this process, the maximum utility of adsorbent takes place when the adsorbent leaving the equipment is in equilibrium with the solution.

2.2. Air Stripping

This process has received considerable attention for removal of substances such as ammonia and VOCs from waste water that have reasonable equilibrium vapor pressure at ambient temperature. Wastewater comes in contact with air in order to remove undesirable substances by the air stream [11]. Common gas-liquid contactors that can be used for this process are bubble column, mechanically agitated tanks, packed tower, plate/tray column, spray towers, venture scrubber [12]. A schematic of these equipment is depicted in Fig. (1). Each contactor type has a variety of configurations with numerous possible modifications. Packed bed is widely used for stripping. The equation used to determine the height of a stripping tower is given by

$$Z = NTU x HT U$$
(1)

The height of a transfer unit (*HTU*) is defined as

$$HTU = \frac{v_L}{K_L a} \tag{2}$$

The value of HTU depends on overall liquid mass transfer coefficient (K_L) , the specific interfacial area (*a*) and the liquid velocity (v_L) . The height of an air stripping tower can be decreased by increasing K_L and *a*. The magnitude of overall volumetric liquid side mass transfer coefficient, $K_L a$ reported for a few gas-liquid contactors [12] is given in the Table 1. The desired flow rate of air determines the diameter of the air stripping column which is in turn is controlled by flooding considerations. For a given equipment volume, air stripping efficiency would be increased if the magnitude of $K_L a$ can be increased and higher air flow can be used.

CHAPTER 3

Recent Trends in Advanced Oxidation and Catalytic Processes for Removal of Heavy Metals, Dyes, and Xenobiotics

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Abstract: Heavy metals, dyes and xenobiotic compounds are the primary environmental contaminants that are accumulating at higher rates attributed to increased industrialization and uncontrolled release without treatment. These pollutants have also raised serious concerns about life on earth, attributed to their recalcitrance and tenacity in the environment. The treatment strategies currently utilize chemical methods, such as advanced oxidation processes (AOPs) and catalytic processes, whereas biological processes such as adsorption and accumulation are also predominant. However, AOPs and catalytic processes are proven to be the potential methods for heavy metals, dyes, and xenobiotic pollutant remediation in large-scale applications. Identification and synthesis of novel molecules/ materials that can effectively recover and remediate heavy metals, dyes and xenobiotic compounds from wastewater remain one of the key approaches. This chapter highlights the success of AOPs and catalytic processes in the degradation of dyes, pharmaceuticals compounds, and heavy metal ions from different water environments and possible future prospects.

Keywords: Advanced oxidation process, Dyes, Fenton process, Heavy metals, Xenobiotics.

1. INTRODUCTION

Over 70% of the global land is covered with water, however, only 2.5% of the

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46 Recent Trends and Innovations in Sustainable Treatment

Kishor et al.

total is freshwater suitable for the survival of life [1]. In the current state of demographic expansion and industrial developments, this 2.5% freshwater will be insufficient to meet the needs of life on earth. In the next 50 years, over 40% of the world-wide population is estimated to suffer from water scarcity. To meet the demands, the reuse of wastewater after remediation remains one of the feasible options. Wastewater recycling and reuse in irrigation and industrial activity may also augment the scope towards the expansion of water resources. However, the quality of treatment can be affected by several parameters, such as source, the way it has been collected, and the treatment strategy employed prior to discharge [2]. Wastewater from different sources comprises water, dissolved solids, and colloidal solids at varying concentrations. In industrial wastewaters, the presence of novel emerging contaminants and known pollutants such as halogenated compounds, polyaromatic hydrocarbons (PAH), heavy metals, dyes, pesticides, xenobiotics, phthalates, halogenated compounds, pharmaceutical compounds, and endocrine disruptors are prominently based on the type of industry. These compounds, on release into the environment, lead to irreversible damage to the living systems and affect the ecological system.

The conventional strategies comprise different physical, chemical, and biological processes [3], and are largely categorized as primary, secondary, and tertiary treatment stages along with a separate pretreatment process. The pretreatment involves the removal of large floating particles, sediments, and heavy solids, such as grits, etc. Further, primary treatment involves the removal of grease, oil, and scum based on gravity settling and variations in density. The treated wastewater flows to the secondary treatment process, which principally involves biological degradation. Under certain conditions, the requirement for an additional tertiary treatment becomes necessary to get rid of hazardous microorganisms, or toxic chemical derivatives which were not removed via two stages of the treatment process. The tertiary treatment process predominantly involves chlorination, ozonation, adsorption, and filtration-based techniques. Chlorination targets to remove the pathogenic infectious microorganisms from infecting the environment, whereas filtration and ozonation are well known for their high-efficiency removal of pathogens but with high cost and energy requirements. However, such conventional technologies have resulted in increased waste production and salting issues that affect freshwater resources. Even today, a large number of pollutants could be detected in the wastewater treated with conventional treatment technologies, which shows the efficiency of those processes. Thus, the search for a novel, economically feasible and sustainable technique for remediating wastewater without harming the environment continues. Among prevailing several techniques, the use of advanced oxidation processes (AOP) with and without catalysts have gained significant interest attributed to their low-cost requirements, robust nature, and effectiveness in decontaminating organic

Advanced Oxidation

components, heavy inorganic metals, dyes, and other xenobiotics. The use of AOP and associated techniques have been proven to be efficient in the removal of heavy metals, dyes, xenobiotics, pesticides, herbicides, and organic pollutants from various waste resources, food, textile and tannery industries, and municipal sewage. This chapter targets to consolidate the information on the success story of AOP in treating heavy metals, dyes and xenobiotics with prevailing bottlenecks and prospects.

2. ADVANCED OXIDATION PROCESS (AOP)

The utilization of ozone (O_3) in the disinfection of drinking water commenced in the year 1906 at the Eon Voyage plant located in France. After that, several plants with this particular facility have been created worldwide [4]. Later, Hoigné and Bader [5] explained the involvement of hydroxyl radicals which are formed during ozonation, in the degradation of various organic contaminants. A similar analysis was executed by Glaze *et al.* [6] in 1987and confirmed the presence of such intermediate that strongly influence the degradation process. Thus, the process involving oxidation of contaminants *via* reactions involving the generation of strong oxidants (intermediates) such as hydroxyl ion radicals (OH[•]) or sulfate radicals (SO₄²⁻) at ambient conditions of temperature or pressure is named as Advanced oxidation process or AOP. The effectiveness of oxidation is dependent on the type of ion radical intermediate or oxidant formed and their oxidation potential. Table **1** depicts the differences in the oxidation potential (eV) of various such oxidants.

Oxidizing Agent	Oxidation Potential (eV)
Nascent oxygen	2.42
Chlorine	1.36
Chlorine dioxide	1.57
Fluorine	3.06
Hydrogen peroxide	1.78
Hydroxyl radical	2.8
Hypochlorous acid	1.49
Oxygen	1.23
Ozone	2.07
Permanganate	1.68

Developments in Adsorption Technologies for Removal of Heavy Metals, Dyes, and Xenobiotics

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Abstract: Anthropogenic activities have led to widespread pollution in aquatic bodies due to extensive dissemination of refractory contaminants such as heavy metals, dyes, and xenobiotics. Adsorption is well recognized as a suitable technology for the removal of these pollutants. The major objective of this book chapter is to summarize recent advancement in this field. Accordingly, the book chapter starts with a brief introduction explaining the potential of the technology as compared to other competitive operations, followed by the identification of thrust areas to work on and the construction of a "template" to evaluate the progress in the technology. Next, recent developments in the preparation of various types of adsorbents (activated carbon-based traditional adsorbents, zeolites and clay minerals, adsorbents of biological origin, composite adsorbents having nanoparticles impregnated in a suitable matrix) have been elaborated. The chapter then focuses on how different process parameters may affect the efficiency of these adsorbents in removal of heavy metals, dyes, and xenobiotics. Finally, a comprehensive discussion has been made about how different mathematical models have been applied in recent times to fit experimental equilibrium and kinetic data obtained from the batch adsorption experiments, along with a critical evaluation of frequently used models. The chapter ends with a recommendation regarding future trends in adsorption technology.

Keywords: Adsorption, Biochar, Isotherms, Models, Nanomaterials.

1. INTRODUCTION

Heavy metals are ubiquitously used in medical, agricultural, and industries, such as metallurgy, electroplating, energy and fuel production, fertilizer and pesticide,

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82 Recent Trends and Innovations in Sustainable Treatment

Chatterjee et al.

electric appliance manufacturing among others [1]. Dyes are extensively used in the textile industries, leather tanning, paper, and colouring paper and fabric [2]. Polychlorinated biphenyls (PCB's) are useful as dielectric fluids, lubricants, plasticizers and heat transfer fluids. Increasing commercial application of heavy metals, dyes and other xenobiotic chemicals led to their widespread mobilization in the environment, mostly *via* the discharge of effluent without adequate treatment. Once mobilized, they continue to be accumulated in the ecosystem due to the non-biodegradable nature of these pollutants. These pollutants are toxic (mutagenic, carcinogenic, teratogenic) for human beings, even at a very low dose (in the order of parts per million), causing various health problems in the kidneys, lungs, and central nervous system and reproductive system [1]. Since fresh water is becoming limited in supply due to rapid urbanization, the use of wastewater for agriculture and irrigation is often encouraged. The bioaccumulation and bioaugmentation of these persistent contaminants by food chain could be most damaging for human beings who are present at the top of the food pyramid.

Conventional technologies for the removal of these pollutants include coagulation, membrane filtration, adsorption, oxidation, electrodialysis, biological treatment, ion exchange, and photocatalysis. But adsorption technology is advantageous due to its high effluent quality (compliance to regulatory criteria), environmentally benign operation (low sludge generation), and low operative cost (moderate requirement of reagent and energy) [3]. All of these factors become more prominent in the treatment of high-volume dilute discharge, usually encountered in effluent containing heavy metals, dyes and xenobiotics. Accordingly, adsorptive removal of these contaminants has become a thrust area of research in recent days.

The objective of this article is to focus on recent progress in adsorption technology in development of novel adsorbents capable of binding pollutants such as dyes, heavy metals and xenobiotics. The article will review all different aspects of the technology: a) laboratory synthesis of an adsorbent b) to elucidate the mechanism of adsorption c) parameters to consider in a batch adsorption process d) mathematical modeling of equilibrium and kinetic data obtained from batch experiments. For biosorbents, *i.e.*, adsorbents of biological origin, "synthesis" implies the identification and isolation of proper material through extensive screening. Besides good uptake capacity for target pollutant, stability and rigidity are two important criteria for the selection of biosorbent material. If it disintegrates or is not sufficiently rigid to be applied in a fixed-bed column reactor, additional processing (immobilization within a suitable matrix or granulation through cross-linking) may be required. Spent adsorbent may be desorbed using a suitable eluent for recovery of precious metal and regeneration of adsorbent for the next cycle of adsorption-desorption operation.

Developments in Adsorption Technologies Recent Trends and Innovations in Sustainable Treatment 83

If promising results are obtained in a batch reactor, continuous operation may be tried using a fixed-bed reactor which is commercially preferred. In a fixed bed reactor, high adsorbent saturation can be achieved where the saturated adsorbent is in equilibrium with the incoming concentration. This review, however, will be limited to the batch study.

2. PREPARATION, CHARACTERIZATION, AND MECHANISM OF VARIOUS ADSORBENTS

2.1. Activated Carbon (GAC, PAC, Biochar)

The most frequently used adsorbents for binding heavy metals, dyes and other xenobiotics are activated carbon-based materials, zeolites and clay minerals, and biomaterials. Adsorbents based on activated carbon are well recognized due to their porous structure. Commercially available AC, such as granular activated carbon (GAC) (particles of size 0.5-1.5 mm) and powdered activated carbon (PAC) (particle size<0.2 mm), are generally prepared from coal, wood and coconut shell through pyrolysis [4]. Biochar refers to the thermal conversion of different biomass types into AC in oxygen-depleted atmosphere at temperatures ranging from 300 to 900°C. In a recent study, the FTIR and XRD data revealed that biochar prepared from switchgrass at a higher temperature (900 °C) was more graphitized than the one prepared at normal pyrolysis temperature ($600 \,^{\circ}$ C). The former was also found to have higher adsorption capacity for all three dyes tested (Methylene Blue, Orange G, and Congo Red) [5]. However, the carbon content for both biochars was similar. In a similar study investigating the effect of variation of temperature (from 400 °C to 800 °C) on biochar characteristics, the highest uptake of malachite green (5306.2 mg/g) by macroalgae-derived biochar produced at 800 °C was observed [6]. Biochar prepared from cladodes of Opuntia ficus-indica cactus was found to remove the malachite green dye, Cu(II) and Ni(II)through chemisorption [7]. Another biochar produced by direct pyrolysis of Palm petiole at 700 °C showed high carbon content (87%) with 209 mg/g of crystal violet dye uptake at neutral pH through pi-pi interaction, pore filling, and hydrogen bonding [8]. Typically, "activation" refers to an increase in pore volume and surface area done by physical (two step pyrolysis) or by chemical means. In a recent study, kelp seaweed (KE), owing to its higher ash content, was utilized to "activate" spent mushroom substrate (SMS) via co-pyrolysis [9]. The maximum adsorptive capacity for crystal violet, a cationic dye, was found to increase 2.2 folds for biochar prepared from 10%-KE added SMS compared to the one prepared from SMS only. However, biochar from KE-extract added SMS was found to have the highest carbon content (70.60%). Another study showed that both electrostatic interaction and chemical reactions with oxygenated functional

CHAPTER 5

Bioderived and Bioconjugated Materials for Remediation of Heavy Metals and Dyes from Wastewater

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Abstract: The present review draws on a wide range of resources available on bioderived, bioconjugated, chemisorption technologies and strategies known for degradation of heavy metals. The prevalent escalation in application of heavy metals, chemically synthesized dyes and xenobiotic compounds has created major environmental disruptions. Industries, mining, vehicles, and household activities release heavy metals and their derivatives into a multitude of water resources. Contaminated water provides an easy ingress of these contaminants into human and animal system resulting in exposure related disorders like mutagenesis, carcinogenesis and other serious health issues. Minimization and management of such chemicals demands high end technology, equipment, time, effort and cost. Thus, the less demanding but more effective strategy would be adoption of biosorption, using whole plant/microbial cells, components, derived and/or synthesized materials to convert toxic compounds/metals into less toxic forms. This review documents, critically analyses and collates heavy metals from mining, processing and industrial effluents followed by remediation technologies based on plants and microbes. Each section in the latter is discussed in detail with relevant examples that illustrate biosorption, bioderived, bioconjugated, chemisorptions, and bioremediation strategies. In the final analysis, though plant materials exhibit efficient removal strategies, particularly when augmented by nanomaterial conjunction, the commercial scale and viability remain to be validated.

Keywords: Biosorption, Bioderived, Bioconjugated, Bioremediation, Chemisorptions.

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1. INTRODUCTION

"When the wells dry, we know the worth of water" [1] is a hard fact of life, even in the 21^{st} century, with all its technological prowess and progress. While, clean and fresh water resources have nurtured the evolution of civilizations, the industrial revolution on the other hand has escalated the degradation of global environment and resource depletion [2]. The rapidly growing human population, urbanization, and technological developments continue to exert untold stress on the aquatic ecosystems, with the concomitant loss of aquatic species at an alarming rate. This humungous loss negatively impacts the entire ecosystem, causes irreplaceable depletion in a spectrum of valuable resources that can be used in food, medicines and other applications [3]. Consequently, if the pollution level in a given water supply system (*e.g.*, domestic or industrial), exceeds levels recognized by various agencies/authorities, the water is demarcated unsafe or unhygienic for use, in a specific application [4]. The commonly adopted measures of resolution are point source pollution reduction and treatment of polluted water prior to use [4].

Heavy metals are major hazardous pollutants disseminated world wide by anthropogenic, geogenic and pedogenetic processes. Various natural phenomena like volcanoes, weathering of rock, flood, geochemical cycles, wind, industrial transportation, and excessive use of household products accelerate the pollutant levels in natural sources of water, air and soil [5].

1.1. Heavy Metals from Mining, Processing and Industrial Effluents

Kabata and Pendias [6] reported the pedogenic process of the parent material breaking down to ultimately form trace material (<1gm/kg), which is rarely toxic by nature. Various metal binding solids can originate from the wide variety of anthropogenic activities such as tailing, disposal of metal wastes and their leachate, leaded gasoline and paints, fertilizers, biosolids (sewage sludge), pesticides, coal combustion residues, petrochemicals, and atmospheric deposition [7 - 9]. Mercury is utilized in the electrical industry (switches, thermostats, batteries), dentistry (dental amalgams), and numerous industrial processes including the production of caustic soda, in nuclear reactors, as antifungal agents for wood processing, as a solvent for reactive and precious metals, and as a preservative of pharmaceutical products [10]. The adverse ecological fall out of soils contaminated by heavy metals have become critical environmental concerns. Toxic metals are considered as contaminants due to their widespread existence, and their acute and chronic toxic effect on plants [11].

Joshi and Kalita

A simple mass balance of the heavy metals in the soil can be expressed by the formula mentioned below [12, 13]:

$$M_{total} = (M_p + M_a + M_f + M_{ag} + M_{ow} + M_{ip}) - (M_{cr} + M_i)$$

where, M - heavy metal, p - parent material, a -Atmospheric deposition, f -fertilizer source, ag - agrochemical sources, ow - organic waste sources, ip - other inorganic pollutant, cr - crop removal, l - losses by processes like leaching, and volatilization.

1.2. Heavy Metals Used in Agriculture

The first major human intervention on the soil was agriculture [14]. Crops require macronutrients like N, P, K, S, Ca, and Mg, besides essential micronutrients such as Co, Cu, Fe, Mn, Mo, Ni, and Zn, that are all essential for plant growth [15]. Application of fertilizers to crop fields increases crop efficiency, productivity, and product quality. The fertilizer industry is a significant source of chemicals containing toxic levels of heavy metals like Hg, Cd, As, Pb, Cu, Ni, and Cr [16]. *Ad libitum* application of chemical fertilizers in agriculture processes has resulted in release of toxic heavy metals, and created a large number of related environmental problems (Table 1). Several arsenic-containing compounds produced industrially have subsequently been used to manufacture products with agricultural applications such as insecticides, herbicides, fungicides, and algicides [17].

Type of Threat	Causes
Water Regime	Flooding; reclamation; water diversion; erosion/siltation; roads; irrigation; water works (floods)
Water Pollution	Solid waste refuse; siltation; sewage/fecal; mining; pesticides; fertilizers; salinization of soils
Physical Modification	Erosion; flooding; clearance and fire; sedimentation; infrastructure/housing; quarrying and sand mining; hunting; recreation

Table 1. Environmental threats and the their causes.

1.3. Air Mediated Sources of Heavy Metals

In the air, heavy metals can accumulate from the sources such as mining process, fossil fuel combustion, metallurgical process, incineration activities, industrial plants and even from windblown soil and dust [18]. Han and Naeher [19]

Trends in Bioremediation of Dyes from Wastewater

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Abstract: Over 100 tons of dyes are released per year into the wastewaters without prior treatment which adds to the contamination of freshwater resources globally. Thus, the development of economical, and sustainable control measures to avoid the pollution of natural resources remains imperative. In the present scenario, recent advancements in biological approaches have escalated bioremediation as a potential strategy for treatment of dyes and associated derivatives. These biological approaches utilize simple to complex microorganisms, plants, and wastes generated from different animal products as tools to remediate and remove dye molecules from wastewater. This particular chapter targets to address the recent advancements in the past three to four years in the sustainable treatment of dye molecules from wastewater using bioremediation approaches. The study also includes the prevailing hurdles, and research prospects in the bioremediation techniques utilized for the reduction of dyes from wastewater.

Keywords: Biodegradation, Biomaterials, Composites, Dyes, Nanosized compounds.

1. INTRODUCTION

In the present scenario, contamination of freshwater resources remains a major problem attributed to the unsupervised discharge of industrial wastewaters without prior treatment [1]. To worsen, uncontrolled increase in industries under different sectors which are not limited to printing, food, pharma, cosmetics, textiles, leather, *etc.*, in order to meet the demand chain was evidenced in the past few decades [2]. These industries predominantly utilize over a million tons of

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Bioremediation of Dyes

dyes per year and release about 10% i.e., ~100 tons of dyes per year into wastewater [3]. Among them, over 50% of the total dyes released are from textile industries which utilize over 1000 different varieties of dyes and pigments. Dyes possess strong structural stability and are certainly non-biodegradable in many cases which make them more harmful to the environment when released without proper treatment. The chemical nature of dyes can vary from simple, biodegradable, natural pigment molecules to complex polyphenols, paranitrophenol, pyrene, etc., which are carcinogenic in nature. These dyes can be classified based on their mode of applications, and based on their structural complexities. For instance, moderate dyes, vat, acidic, disperse, reactive, direct, sulfur, and basic dyes are the categories based on their application whereas azo, xanthene, nitrated, polymethinic, indigo, and many more are categorized based on their structural complexities [2]. Thus, the removal or degradation/ neutralization of all these complex color molecules remains one of the major tasks to be addressed. Conventional chemical-based treatment strategies such as adsorption, flocculation, filtration, precipitation, photocatalytic process, membrane dependent process, oxidation, etc., are utilized for the treatment of effluents containing dye molecules. In addition, novel treatment strategies involving combinatorial approach are being developed to either neutralize the dye or to remove the dye from effluent and reuse them. However, the task remains breath-taking for dves with complex structures. In addition to that, these physico-chemical methods generate large volumes of sludge which must be dumped at a different site and requires high cost to meet the needs of chemicals involved in the treatment process and maintenance. Alternately, biodegradation strategies are gaining increased attention attributed to the availability of variety of microorganisms (bacteria, fungi, algae), biocatalysts (enzymes), and plants that are capable of mineralizing the complex dye molecules thereby generating reduced volumes of sludge. Thus, with growing environmental contaminants, reliance on biological treatment systems makes the process sustainable and ensures the non-generation of xenobiotic derivatives. This chapter targets to review the recent trends and advancements over the past three to four years in the field of bioremediation of dyes with various life forms, while highlighting the prevailing strategies, bottlenecks, and future prospects.

2. BIOLOGICAL TREATMENT OF DYES

Unlike physico-chemical treatment strategies involved in remediation of dyes, the biological treatment strategies are considered to be economically feasible and sustainable attributed to the reduced release of sludge. In case of biological treatment, a wide variety of treatment options could be opted which generally comprise techniques such as accumulation, sorption, degradation, and

142 Recent Trends and Innovations in Sustainable Treatment

Debnath et al.

mineralization. In biosorption, the dye molecules are allowed to passively bind to the surface of dead or live microbes or agricultural residues or biological polymers, *etc.* which results in the removal of color from the wastewater. On the contrary, bioaccumulation is an active process that involves living cells of microbes or plants or animals that can accumulate the dye molecules in to their biomass composition through different uptake mechanisms. Usually, these assimilated dye molecules further undergo a serious of metabolic reactions within the biomass resulting in complete degradation or neutralization. Thus, the removal of dye molecules from wastewater through sorption, and accumulation techniques results in the discoloration of the wastewater effectively. The other technique involves the mineralization phenomena in which the dye molecules are converted into metallic crystals or precipitated through the metabolic reactions either in the active living organisms or through catalytic reactions mediated by enzymes derived from living organisms. Fig. (1) depicts the various mechanisms involved in the biological treatment of dyes from wastewater.

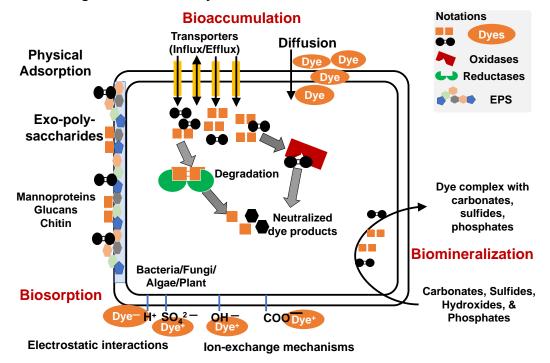


Fig. (1). Various mechanisms involved in bioremediation of dye molecules from wastewater through biosorption, bioaccumulation, biomineralization, and biodegradation.

2.1. Biosorption of Dyes

Adsorption with biological materials remains one of the attractive techniques in

Bottlenecks in Sustainable Treatment of Wastewaters Using Physico-Chemical Processes and Future Prospects

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Abstract: This chapter covers bottlenecks in various sustainable physio-chemical processes including membrane filtration, activated carbon filtration, adsorption, advanced oxidation processes, dissolved air floatation, coagulation-flocculation and sedimentation, and electrocoagulation process for removing heavy metal ions, dyes, and xenobiotics from the aquatic environment. The approach taken in this chapter is to give a quick overview of each phase before focusing on the bottlenecks that these processes face when it comes to removing metal ions and organic matter from wastewater. Performance, cost, and sustainability criteria for sustainable wastewater treatment technologies are also covered in this chapter for each process.

Keywords: Bottlenecks, Economic feasibility, Physico-chemical process, Resource recovery, Sustainability.

1. INTRODUCTION

Wastewater is one of the most serious environmental challenges today, posing serious health and environmental risks to humans, animals, and the environment [1]. Inadequate management and technologies are too accountable for the aforementioned issues. Domestic, commercial, industrial, and agricultural discharges all contribute to wastewater. Pollutants and contaminants in waste water include nutrients, microbes, chemicals, and other poisons. When wastewater is inappropriately discharged into body rivers, these pollutants can cause health

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176 Recent Trends and Innovations in Sustainable Treatment

and environmental hazards [2]. Wastewater, on the other hand, contains reusable resources such as water, carbon, and nutrients, all of which can be collected and reused [3]. As a result, adequate pollution removal processes are required in order to meet effluent regulatory limits. Furthermore, resource recovery should be a priority in order to reduce carbon emissions and make the processes self-sustainable [4].

Wastewater treatment is a procedure that involves the use of a combination of physical, chemical, and biological treatments to help return healthy water to the environment. Because the wastewater problem is so serious, many engineers and scientists have been working on new technologies to come up with a viable solution. Treatment procedures that can eliminate dissolved organic material and hazardous compounds have been developed due to technological advancements. At this time, advances in scientific understanding and awareness of the global environment have led to the development of new technologies and systems that can minimize pollution in wastewater and recycle energy, with the ultimate objective of zero pollutant discharge. There is a lot of wastewater created every day in many developing countries because of their rapid growth. However, wastewater contamination is still an issue in developing countries. Weak regulations, poor management, the current economic condition, and the use of inadequate technologies are all contributing factors to the problem. It is critical to choose the right technology to tackle the problem. Wastewater treatment plants are frequently ineffective at removing heavy metals, dyes and xenobiotics from wastewater, allowing them to enter public sewers and the food chain, directly affecting humans and contributing to micropollutant pollution of aquatic bodies [5 - 7]. Activated sludge is typically not specialized enough for this activity, despite the fact that populations of bacteria and other microorganisms have been demonstrated to be successful in degrading/accumulating them [8 - 10]. Communities would have to adjust to the wastewater treatment conditions, which are economically unviable in traditional plants. Biological or physicochemical procedures that are more successful at removing them from water are being studied and improved substantially. As a result, the primary goal of this book chapter is to explain the bottlenecks of new approaches and sustainable techniques that can be employed to improve overall wastewater treatment.

2. BOTTLENECKS OF PHYSICO-CHEMICAL WASTEWATER TREATMENT PROCESS

The goal of a traditional physico-chemical wastewater treatment process is to remove solids such as colloids, organic matter, nutrients, and soluble pollutants (metals, organics, and so on) from effluents. As a result, the procedure to be Bottlenecks in Sustainable Treatment Recent Tre

utilised will be determined by the properties of the effluent. Each treatment has its own set of constraints, including cost, feasibility, efficiency, practicability, dependability, environmental impact, sludge production, difficulty of operation, pre-treatment needs, and the formation of potentially harmful by-products. However, just a few of the different wastewater treatment procedures now identified are commonly used by the industrial sector for technological and economic reasons.

2.1. Membrane Filtration

Membrane processes are a crucial technology for advanced wastewater reclamation and reuse techniques because they provide a reliable advanced treatment. They have several advantages, including the need for less space, the ability to act as a physical barrier against particle material, and the ability to keep microorganisms without generating resistance or the generation of by-products. Membranes are used in a number of large-scale advanced treatment schemes that are used around the world for artificial groundwater replenishment, indirect potable reuse, and industrial process-water generation. Ultrafiltration membranes (UF) filter out colloids, proteins, polysaccharides, bacteria, and even viruses, resulting in high-quality treated effluents. To separate ions and dissolved particles from water, nanofiltration (NF) and reverse osmosis (RO) are effective methods. In Singapore, as part of the NEWater project, NF/RO membrane technology was successfully used to recover water from wastewater for indirect potable reuse. The method involves multiple treatment phases and produces large amounts of reclaimed water, which is used to replenish natural drinking-water reservoirs in the city.

The membrane process, in combination with the activated sludge process, has been widely used for large-scale solid-liquid separation in wastewater treatment. In the process, separate management of sludge and hydraulic retention durations, as well as increased mixed liquor-suspended solids concentrations, could be beneficial. Kim *et al.* (2009) investigated the effects of granular activated carbon (GAC) on microfiltration (MF) performance in terms of permeate flux. When utilizing simply MF, the efficiency of pollutant removal with GAC was around 60%, compared to 30% when using only MF [11]. Hammami *et al.* (2017) used a hybrid technique that combines adsorption using powdered activated carbon (PAC) and ultrafiltration to remove color (*i.e.*, acid orange 7) from aqueous solutions. It was found that the use of hybrid processing reduced UF membrane fouling and PAC dose, increased permeate flux, and improved color removal [12]. To remove levofloxacin (LEV) from effluents, Ullah *et al.* (2019) created a magnetic carbon nanocomposite (MCN). Then, by combining MCN with

Sustainable Mitigation of Wastewater Issues Using Microbes: Hurdles and Future Strategies

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Abstract: Exponential growth in population associated with changing lifestyle patterns and industrial upheaval has led to the degradation of the most valuable renewable resource *i.e.* water. Contamination of water bodies of varying sizes across the world has resulted in mass-scale deterioration of health and environmental adversaries. Uninhibited disposal of domestic, municipal and industrial effluents onto water bodies has severely impacted the flora and fauna, in turn affecting human health globally. If unchecked, this would lead to an unmitigated disaster, which would be detrimental to the very existence of humans on the planet. Wastewater remediation, therefore, is of paramount importance to safeguard water bodies and prevent them from excessive pollution. To that end, novel, sustainable technologies for elevated nutrient removal from wastewater are the need of the hour. Bioremediation of wastewater is one of the most prolific and novel approaches directed towards the efficient elimination of contaminants coupled with their subsequent conversion into value-added products. Over the last few decades, microbial treatment processes have gained increasing momentum due to their ease and high efficiency compared to conventional treatment technologies. The chapter provides a detailed overview of various biological wastewater treatment methodologies such as bacterial, fungal, microalgal and microalgae-bacteria consortium-mediated bioremediation.

Keywords: Bioremediation, Bottlenecks, Microalgae-bacteria consortium, Mycoremediation, Wastewater treatment.

1. INTRODUCTION

Scientists have been searching for decades for another suitable planet to inhabit both in our galaxy and beyond. However, their expeditions have not been fruitful

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Makut et al.

mainly due to the absence of suitable environmental conditions on other planets similar to earth. One of the key factors pertinent towards thriving sustenance of any life form on earth is the presence of water. Water is reported to constitute more than three quarters of our planet, which has been instrumental in maintaining environmental balance to support flora and fauna. Water is one of the utmost key renewable sources which are essential for thriving existence of all life forms, nutrition, socio-economic advancement and maintenance of overall climatic health [1]. The importance of fresh water is widely accepted and acclaimed, yet, the exponential increase in population associated with industrialization and economic flourish has adversely impacted the quality and availability of fresh water on a global scale [2]. Water pollution is a man-made phenomenon owing to the unwanted and inadvertent discharge of excess inorganic, organic and xenobiotic compounds into aquatic bodies [2]. The continual dissemination of untreated nutrients into water bodies results in eutrophication and detrimentally impacts its beauty, and biological and pecuniary values. The ever-rising fear over degrading water quality has resulted in the formulation of more strict regulatory policies towards the dissemination of wastewater into the environment. To that end, there has been a conscious move directed towards the development of bioremediation tools that permit improved removal [3]. Anthropogenic activities and industrial operations have directly resulted in the magnification of toxic substances in the environment, negatively impacting the global health [4]. Statistically, the world is poised to encounter a water deficit of 40% by the year 2030 due to the exponential usage of water, its contamination, and a lack of suitable and sustainable technologies for treatment [5]. Decades of urbanization and industrialization have resulted in 80% rivers being contaminated by organic resources, nitrogen, phosphorous and heavy metals [6]. Humanity in the present century is concerned with quality water and alternate energy supply [7]. Pollution of the surface and groundwater resources has become a key environmental hazard affecting both humans and animals alike. This is a grave issue in developing countries, where human is at risk due to the compounding and continual increase of water pollution due to uninhibited release of heavy metals, organic substances, sewage, municipal waste dumping, etc [7].

Wastewater may be conventionally distributed into three categories depending on their source of their origin such as: (i) municipal wastewater which contains low amounts of toxicants and poisonous substances, (ii) agricultural wastewater is comprised mostly of animal manure, fertilizer and high concentrations of inorganic and organic nutrients and (iii) industrial wastewater arising as effluent streams is heavily laden with complex and toxic heavy metals with an inadvertently high COD content. The presence of organic and inorganic nutrients in municipal and agricultural wastewater renders them feasible and suitable options towards treatment and recovery whereas the presence of complex and

Wastewater Issues

toxic components in industrial effluents poses a major challenge in designing physical, chemical and biological treatments [5]. Wastewaters exuding from different sources have typical physico-chemical properties such as nutrient concentration, pH, temperature of substances, chromaticity, toxic heavy metals, and phenolic which are essential in understanding and designing suitable treatment strategies. The wastewater treatment is majorly accomplished with the following goals: (a) Transforming substrates present into valuable products that are suitable for disposal, (b) ensuring health of the society, (c) conferring efficient handling of wastewaters on a trustworthy basis, (d) reimagining and recycling wastewaters, (e) development of sustainable treatment processes and dissemination techniques and (f) adhering to governing regulations and policies for discharge and disposal [8]. The ultimate objective of wastewater control and management is to safeguard the environment which, in turn will offer a positive influence on human health.

Physical treatment of wastewater is amongst the first methods to be successfully demonstrated towards wastewater treatment using physical unit operations deploying mechanical forces [9]. Physical treatment processes are still prevalently used coupled with chemical treatments in which certain catalysts are used to lower the toxicity of the wastewater. However, there is an inherent disadvantage of the overall chemical treatment strategies that they are always used in conjunction with physical processes and they often add constituents into the wastewater, rendering them significantly infeasible for further reuse [9]. Treatment through biological means is currently gaining traction as the processes involve the use of microbial communities which successfully remove toxic pollutants and subsequently produce value-added chemicals. The three treatment processes have been used in combination to enhance treatment efficiency (Fig. 1). These combinations have been denoted as primary, secondary and tertiary wastewater treatment [10]. These methods are employed for achieving maximum contaminants' and organic removal from wastewater, making it suitable for dissemination and recycling [11]. Primary treatment is mainly focussed on the physical separation of the heavy solids, lighter solids, oil and grease by gravitational settling [9]. The decanted liquid is further processed *via* secondary treatment where the soluble and remaining suspended matter is removed by the action of indigenous water-borne microbes [12]. Furthermore, tertiary treatment involves purification, coupling, biological digestion, and physicochemical flocculation / purification for nutrient removal before discharging it onto freshwater bodies.

SUBJECT INDEX

Alcaligenes 7

A

Absorption 25, 28, 61-63, 96, 118, 120 Acceptors 93 Acclimatization 10 Accumulation 45, 66, 86, 118, 125, 141-42, 153-54, 194, 201, 203 Acetamide 199 Acetaminophen 84, 90 Acetate 54, 126, 149 Acetogenic 197 Acetonitrile 207 Acid 7-8, 32, 35, 37, 47, 53-54, 56-58, 62-64, 69, 72, 85, 87-88, 102, 119, 123-26, 146, 148, 151-52, 154, 161, 177, 181-82 Acid-treated 121 Acinetobacter 3, 126 Acrvlamide 87 Acrylic 28, 147 Actinomycetes 154 Adenine 198 Adenosine 199 Adsorbate 19, 86-91, 93, 96-99 Adsorbent 7-8, 10, 13, 19-20, 25, 31, 33, 57, 82-83, 86-98, 100, 103-5, 144, 149-50, 157-58, 163, 165, 178-80, 189 Adsorption 1-3, 8, 10-12, 18-20, 25, 31-35, 38-39, 45-46, 54, 58, 61, 68, 81-113, 118, 121, 124, 126, 141-45, 149-50, 156-59, 161, 175, 177-81, 187, 194, 197, 199 Adsorption-desorption 82 Advanced Oxidation Process (AOPs) 3, 7, 10-12, 18, 23-24, 38, 40, 45-57, 59-63, 65-67, 70-73, 75, 162, 175, 181 Aerobic 1, 62, 85, 123, 143, 151–52, 155, 164, 196-97, 201, 204-5 Aerogels 87, 91, Agar-agar 125 Agitation 22, 27, 150 Agriculture 5, 82, 116, 186 Agrobacterium 120-21, 124 Air-saturated 183

Aldehydes 84 Algae-bacteria 204, 207-8 Algicidal 205 Aliphatics 196 Alkanes 196 Alkynes 84 Aluminium-ferrous 55 Aluminum 183-84 Ambient 20, 47, 80, 87, 196, 201 Amidation 160 Amine 68-70, 85, 143 Amine-based 54 Aminobenzoic 154 Ammonia 6, 8, 19-20, 29, 35, 162 Amoxicillin 31, 36, 38, 62-64, 66 Amphiphilic 158 Anaebaena 161 Anaerobic 1, 15, 123, 143, 151-52, 154-55, 164, 183, 186, 194, 196–97, 200–201, 204, 207 Anaphylaxis 54 Anions 159 Anoxybacillus 126, 155 Anthraguinone 55, 124–25, 151–52 Anthropogenic 81, 115, 192, 195 Antibacterial 160, 205 Antibiotic 5, 63, 91, 99, 205 Anti-cancerous 64-65 Antidepressants 5 Antifouling 160 Antifungal 115 Antihistamines 5 Anti-inflammatory 62 Antimicrobial 194 Antipyrine 64 Aquaculture 196, 205 Arabidopsis 120 Arsenic-contaminated 125 Aseptic 203 Aspergillus 122-23, 125, 146, 151-52

Biswanath Bhunia and Muthusivaramapandian Muthuraj (Eds.) All rights reserved-© 2022 Bentham Science Publishers 215

Bhunia and Muthuraj

Atmosphere 83, 118, 184, 186–87, 200 Azodyes 117, 120–21, 123–24, 126 153 Azoreductase 119–20, 123–25, 152–54 *Azospirillum* 205

B

Bacillus 3, 121-22, 124-26 145, 152-53, 188, 196, 208 Bacteria 9-11, 85, 119, 122-24, 126, 141-43, 145, 150, 152, 154-55, 160, 162 176-77, 181-82, 195-97, 200, 204-8 Bacteria-based 206 Basic 32, 54-55, 62, 66, 87, 93, 98, 125, 141, 146, 151, 155, 163, 179 Batch 7-8, 10, 22, 27, 72, 81-83, 93, 96, 98, 100, 104, 144-45, 188, 199, 201 Bentonite 84, 87-88, 90, 104 Benzaldehyde 154 Benzene 4, 19, 154, 162 Benzidine 117, 153-54 Benzopyrene 207 **Bicarbonates 63 Bimetallic** 121 Binding 48, 54, 82-83, 85, 91-93, 97-99, 103-4, 115, 118, 120, 124-25, 143-45, 158, 180, 183, 199-200 Bioaccumulation 82, 85-86, 122, 124, 142, 150, 156, 199-200 Bioactive 202-4 Bioadsorb 125 **Bio-adsorption** 121 Bioaugmentation 82, 125 **Bioavailability 118** Bio-based 163, 198 **Biocatalysts** 141 Biocathode 161 Biochar 7, 61, 81, 83, 88, 90, 144, 147, 150, 156-57, 162, 164 Biochar-based 156-57, 164 Biochemical 3, 10-11, 202, 204 **Biocomposites 161** Bioconjugated 114-15, 117, 119, 121, 123, 125, 127, 129, 131, 133, 135, 137, 139 Biodegradability 7, 48

Biodetoxification 123 Biodiversity 2 Bioelectrochemistry 14 **Bioenergy** 194 **Biofilms** 124 Biofuels 194, 198 Biogas 186 **Biohazardous** 195 **Bioimmobilization 123 Biomagnification** 198 Biomass 83, 85, 103, 121, 124, 142-52, 156-57, 162, 197, 199-204 **Biomethanation 9 Biomethylation 123** Bio-nanocomposite 161 **Biopolymers** 194 **Bioprecipitation 123** Bioreactor 3, 126, 196, 203 **Biorecalcitrants 52 Biorefineries 163** Bioremediation 2-3, 7, 86, 114, 122, 140-3, 145, 147, 149, 151, 153, 155, 157, 159-63, 191-92, 194-97, 201-4, 206-7 Biosorbent 31, 82, 85, 97, 102, 104, 143-49, 161 Biosorption 31, 42, 85-86, 92, 114, 122-26, 142-45, 149-50, 152, 154, 199 **Biostimulation 189** Biosynthesis 126, 144 Biotransformation 120, 122 Biotreatment 16, **Biovolatilization 123 Biphenyls 82** Bipolar 184 **Bisphenol 89** Bottlenecks 47, 141, 162, 175-77, 179, 181, 183, 185, 187, 191, 195 Breweries 18-19, 39 Bromate 182 Bromide 182 Bromophenol 121, 123, 151 Bulk 5, 70, 98

С

Cadmium 60, 67-68, 72, 119, 122 Calcification 181 Calcium 7, 67, 120, 157 Cancer 2, 54, 154 Cancer-causing 182 Carbamazepine 61-62, 89-90 Carbonaceous 156, 179 Carbonate-bicarbonate 201 Carbonates 63, 142 Carbon-based 81, 83, 93, 180 Carbon-centered 48 Carbonization 156 Carcinogenesis 114 Carcinogens 54, 82, 117, 141, 153 Carprofen 62 Casing 25-26, 32 Catabolized 124, 152 Catalyst 36, 51, 54, 57, 59-60, 66, 68, 72, 84, 90.180 Catalyst-based 72 Cathode 80, 161, 184 Cations 53-54, 83-84, 92-93, 124, 126, 156, 158-59, 199-200 Cellular 151 Cellulose 3, 54, 87, 91, 126, 144, 149, 158 Centrifugal 18, 25-26, 29-33, 37 Cetrizine 5 Charges 61, 84, 126, 143, 159-60, 183, 199 Cheaper 84, 203 Chelating 66 Chemical-based 141, 187 Chemisorption 83, 98, 114, 199 Chemosphere 80, Chitosan 8, 11, 87, 92, 126, 143-44, 149, 154, 181, 202 Chlamydomonas 125, 147, 166, 205 Chloramphenicol 91 Chlorella 124, 147, 153, 161, 206-8 Chloride 6, 68, 84, 124, 151, 157, 183 Chlorinated 152, 196 Chlorination 46 Chlorine-based 117

Chloroaniline 154

Recent Trends and Innovations in Sustainable Treatment 217

Chlorohydrate 183 Chromium 2, 6, 10-11, 30-31, 33, 54, 71-72, 117, 119, 122, 158, 161 Chromophoric 119 Chrysosporium 123, 151 Ciprofloxacin 64-65, 89 Cladosporium 126 Classification 53-54 Classified 19, 90, 97, 141, 195 Clavibacter 125 Clostridiales 124 Clostridium 152 Coagulants 183-84 Coagulation 2, 82, 184, 197 Coal 3-4, 83, 85, 115, 117, 179 Coal-based 85 Cobalt-EDTA 70 Coliforms 185 Colloidal 46, 54, 60, 176-77, 183 Color 3, 10-11, 53, 55-56, 58-60, 117, 119, 125-26, 141-43, 151, 163, 177 Combinatorial 52-53, 59-62, 65-66, 71, 141, 161 Combustion 115-16 Commensalism 204-5 Commercial 60, 82, 85, 114, 150, 157, 160, 175, 178, 180, 197-98, 203 Community 188, 194, 203 Complexation 91-92, 143, 199 Composites 7, 12, 39, 59-61, 72, 80-81, 90-92, 100, 125, 140, 144-45, 149, 157, 161-62, 180 Compost 120 Conductivity 6, 155 Congo-red 161 Consortium-mediated 191 Consumption 10, 51, 71, 155, 159, 163, 205 Continuous 9, 20-21, 23, 30-31, 33, 83, 144-45, 158, 188-89, 199 Conversion 25, 83, 158, 182, 191, 198, 201 Copper-ethylenediaminetetraacetic 67-68, 70-71,80 Co-precipitation 34, 90, 157 Co-pyrolysis 83 Co-remediate 120

Bhunia and Muthuraj

Corynebacteria 125 Cosmetics 53, 140 Cost-effective 18, 61, 91, 154, 164, 182 Co-substrate 161 Covalent 54, 90, 97, 143 Cr-citrate 70 Crops 116 Crystal 83, 86–88, 92, 120, 125, 147–48 Cyanide 3–4, 6–8 Cyanobacteria 147 Cytoplasm 200 Cytotoxic 160

D

Dairy 18 Deactivation 55 Deaminated 154 Decarboxylation 69-70 **Dechlorination** 194 Decoloration 37, 123. Decolorization 31, 33, 55-60, 123-24, 126, 152-53, 155, Decolorize 54, 57, 126, 151-52 Decomplexation 71, 80 Decomposed 70 Decomposing 156 Decomposition 3, 24, 36–37, 49–52, 59, 62, 66, 68,70 Decontaminating 46 Degradable 53 Degradation 1-3, 7, 9-12, 23, 31, 35-37, 45-49, 51, 55-60, 62-68, 70-72, 80, 114-15, 118-21, 123-26, 141-42, 150-56, 161-64, 180, 191, 194, 196, 203-4, 207-8 **Deionization 178** Demobilizes 118 Demographic 46 Deprotonation 97 Desalination 162, 182, 188 Desmodesmus 124-25, 152 Desmolyticum 124 Desorption 144-45, 161, 181 Desulfovibrio 122 Desulfuricans 122

Detergent 18, 117 Detoxification 80, 86, 153 Dewatering 197, 203 Dextrose 151 Diameter 7, 20-21 Diatoms 143 Di-azo 55-56 Di-bromide 154 Diclofenac 62-63, 65, 89, 110 Dictyostelium 123 Dielectric 82 Diffusion 32-34, 88-89, 96, 98, 100-104, 142, 153.199 Diffusion-controlled 101 Dimethylpthalate-copper 67 **Disassociation 68** Discoloration 54-57, 59, 124, 126, 142, 153-54 **Disinfectants 182** Disinfection 47, 61, 80, 181-82, 190, 194 Donor 153 Donor-acceptor 93 Dosage 8, 33, 55-56, 62, 68, 184 Drugs 3, 5, 10, 62, 64-65, 160 Dye-based 119 Dve-degrading 155 Dyestuffs 53, 125 **Dynamics 39**

Е

Eco-friendly 12, 66, 119, 187, 199, 206 Ecology 1, 3, 39, 61 Economics 199 Ecosystem 1–3, 39, 82, 115, 190, 197 Effluent 1–3, 5–8, 10, 12, 21, 25, 53, 82, 106, 114–15, 117, 119–20, 123–26, 141, 144– 45, 151, 154–55, 164, 176–79, 181–82, 185–86, 191–93, 197–201 Efflux 142, 200 Electrocatalysis 70 Electrochemical 24, 49, 52, 54, 70–71, 163 Electrocoagulation 3, 11, 175, 184, 190, 197 Electrode 9, 48, 52, 184 Electro-deionization 178

Electrodeposition 80 Electrodialysis 82, 178 Electro-fenton 49 Electro-generated 80 Electrolysis 162 Electrolyte 84 Electromagnetic 50-51 Electron 24, 48–49, 53, 71, 93, 161, 199, 204 Electron-hole 51, 61 Electrooxidation 71 Electroplating 66-67, 80-81 Electrospun 159 Electrostatic 83-84, 91-92, 124, 142-44, 158-59, 199 Emissions 176, 186 Emulsion 21–23, 157–58 Encapsulated 109-10, 121, 124 Endocrine 46, 61 Endocrine-disrupting 86 Endophytic 126 Endosulphan 207 Energy-intensive 56, 157 Energy-rich 200 Energy-saving 187 Enterobacter 122, 125, 154 Enterococcus 152, 154 Enthalpy 92, 150 Entrapment 120 Entropy 150 Environment 1-3, 8, 10-11, 18, 25, 45-46, 53-54, 61, 82, 115, 117, 141, 150-51, 154, 158, 164, 175-76, 179, 187, 192-94, 196-98, 201, 204 Enzymatic 55, 123-25, 152 Enzyme 119-21, 123-26, 141-42, 151-55, 162, 196, 198, 203 Epidermidis 121 Equations 24, 29, 48, 50, 52, 93-94, 98-99, 102 Equilibrium 20, 22, 81-83, 90, 93-95, 97-99, 104.167 Eriochrome 87, 107, 157 Ernofloxacin 5

Error 104

Escherichia coli 3, 123, 125, 145 Ethanol 148 Ethers 180 Ethylbenzene 162 Ethylene 64, 154 Ethylene diamine tetra-acetic 80 Ethyl hexyl phosphoric acid 35 Eutrophication 3, 192, 197-98 Evaporation 200-201 Evolution 115 Excitation 52, 60 Exopolysaccharide 124, 126 Exothermic 92 Exponential 191–92 Extracellular 123, 143, 149, 151, 155, 202-3, 205 Extract 121, 125-26, 149, 152, 155, 161-62, 178, 186 Extractor 21, 30-31 Extremophilic 124 Exudates 119

F

Facilitated 124, 194 Fauna 1, 3, 191-92 Feedstock 18, 156, 204 Fenton 1-2, 7, 10, 24, 31, 35-36, 38, 45, 48, 50, 57-59, 63-64, 67, 71-72, 80, 162 Fenton-chemical 80 Fenton-Ozone 58 Fermentation 85, 196, 207 Ferredoxin 198 Ferric 50, 53, 64-65, 71-72, 183 Ferrioxalate 64 Ferrite 80.90 Ferrocene 57 Ferrocene-catalyzed 57 Ferrous 36, 50, 53, 57-58, 64, 71-72, 183 Fertilizers 115-16, 162, 198, 204 Fibers 19, 53-54 Filamentous 151, 203, Filtration-based 46 Fixed-bed 82-83, 93 Flavonoids 32

Bhunia and Muthuraj

Floatation 175, 182 Flocculants 183 Flocculation 1-2, 54, 141, 184, 193-94 Flooding 20-21, 26, 28, 116 Fluidized 3 Fluoride 159 Fluorine 47-48 Flux 159-60, 177 Foam 28, 158 Footprint 183, 188 Formaldehyde 117 Formate 55 Forward-osmosis 159, 164 Fourier 100 Freshwater 46, 140, 193, 195, 198 Freundlich 34, 86-90, 94-95, 97, 101-2, 156 Fungal-based 203 Fungi 85-86, 119, 122-23, 126, 141-43, 145, 150-51, 195, 202-3 Fungicides 116 Fuschin 146

G

Gas 4, 22, 25-29, 48, 55, 97, 158, 184, 186, 194, 205-6 Gasification 19, 156 Gas-liquid 20-22, 25-26, 28, 36 Gasoline 115 Gas-phase 38 Gas-side 29 GCMS (Gas chromatography mass spectrophotometer) 8 Gelatinous 160 Gel-based 180 Gene 123, 125-26, 153, 162 Genetic 8, 125, 152-53, 162, 164, 168-69 Geochemical 115 Geogenic 115 Glucans 142, 202 Glucose 155 Glucuronic 126 Glutaraldehyde 144, 154 Glycogen 202 Glycols 180

Glyoxylic 69 Gradient 98 Gram-positive 205 Granular 3, 83, 85, 177, 179 Graphene 12, 86–87, 90–92, 156, 180 Graphene-based 86–90 Graphitized 83 Growth-promoting 205

H

Half-life 52 Halogenated 46 Hardness 182 Harmful 48, 53, 141, 154-55, 177, 208 Harvesting 201-2 Harzianum 123, 151 Hazard 2-3, 46, 61, 66, 80, 115, 163, 189-90, 192 Herbicides 47, 116 Heterogeneous 24-25, 48, 52, 71-72, 80, 92, 94-95, 97, 101, 103, 156 Heterotroph 195 Heterotrophic 195, 197-98, 204-6 Heterotrophs 195 Hexadecyl 84 Hexavalent 30-31, 33, 71 Hibiscus 120 High-efficiency 46 High-energy 52 Homogeneous 31, 37, 56, 69, 72, 98, 100 Homogenization 27 Husk 4, 8, 10-11, 34, 85, 156 Hybrid 49, 57, 60-61, 72-73, 90-91, 177-78, 188,200 Hydro-carbonated 117 Hydrocarbon-containing 151 Hydrocarbons 46, 196, 203 Hydrogel 87, 92, 144 Hydrolysis 51, 92, 158 Hydrophilic 53-54, 85 Hydrophobic 93, 143, 159 Hydrothermal 85, 156, 161-62 Hydroxides 66, 142 Hydroxylase 152-53

Hyperaccumulator 118 Hyphae 151 Hypochlorous 47

Ι

Ibuprofen 89 Ice-templating 91 Imidazole 84 Imidazolium 84 Immobilization 3, 7, 59, 82, 118, 125-26, 145, 149, 154, 206 Impeller 27 Incineration 3, 116 Indigenous 193, 195, 202, 208 Indomethacin 61-62 Industrialization 2, 45, 192 Infectious 46 Insecticides 116 Intensification 205 Intermediates 10, 47–48, 51, 68–70 Intracellular 86, 150, 153, 200 Intraparticle 19-20, 32, 34, 88-89, 98, 100-103 Ion 36, 47–48, 50–51, 64, 67–68, 72, 82, 84, 97, 102-3, 149, 184, 197, 199, 207-8 Ion-exchange 84-85, 142-43 Iron-containing 72 Iron-oxide 126 Irradiance 201 Irradiation 24-25, 49-50, 56, 59, 64, 181-82 Isotherm 34, 86–90, 93–99, 101–2, 104

K

Kerosene 30, 35 Ketone 154 Ketoprofen 62 Kinetic 7, 33, 37, 81–82, 86–90, 93, 95, 98– 104, 163 *Klebsiella* 152

L

Laboratory 12, 60, 73, 82, 93, 114, 153, 191 Lab-scale 54, 178 Laccase 119, 123-26, 151-54 Lactobacillus 122 Lagoon 194 Landfills 186-87 Langmuir 34, 86-90, 94-95, 97, 99, 101-4, 156 Large-scale 45, 62, 65, 73, 121, 163, 177-78, 188 Leachate 115 Leaching 116 Lead 7, 46, 61, 67-68, 72, 93, 117, 119, 122, 191.197 Lead-based 117 Lead-EDTA 68 Leather 1-2, 5-6, 10-11, 53, 66, 82, 140 Lecythophora 123 Levofloxacin 65, 177 Levosulpiride 5, 9 Lifecycle 179 Ligands 64, 92, 124, 158 Lignin 3-4, 6, 9, 120, 123, 125-26, 151 Lignite 117 Ligustilide 158 Lipids 143 Liquefaction 161 Liquid-liquid 18, 21, 25-26, 29-30, 32, 35 Liquid-solid 182 Liquor 196-97, 203 Liquor-suspended 177 Lithoautotrophs 195 Low-cost 46, 52, 104, 157-58, 180 Lysinibacillus boronitolerans 154

Μ

Macroalgae 147, 149, 161, 201 Macroalgae-derived 83 Macrolides 91 Macronutrients 116 Magnaporthe 122

Bhunia and Muthuraj

Magnetic 90, 92, 144, 157, 177, 180-81 Magnetite 90 Magnetization 90 Magnification 192 Malachite 55, 83, 87-89, 120, 125-26, 145-46, 154, 158, Malt 148 Mangifera 148 Mangrove 122 Man-made 192 Manure 192 Marine 117, 151, 163 Mass-scale 191 Materialization 60 Mathematical 34, 81-82, 97-101 Mechanical 84, 91, 185-86, 193, 197 Mechanistic 93 Mediators 203 Medicine 3, 9 Membrane-adsorption 178 Membrane-based 3, 162, 178-79 Membranes 3, 21–23, 35, 38, 82, 85, 141, 156, 159-60, 162, 164, 175, 177-80, 182, 187, 195.198-99 Membrane-technology 178 Mercury 56, 90, 115, 120, Mesoporous 178 Mesospheric 196 Metabolism 155, 196-97, 199, 205 Metabolism-dependent 85 Metabolites 124, 144, 152, 202, 205 Metal-based 181 Metal-binding 103, 200 Metal-contaminated 118, Metal-EDTA 68 Metallothionein 200 Metal-organic 157-58 Methane 186, 196 Methanogenic 197 Methylococcus 208 Methylotrophs 196 Microalgae 102, 147, 194-95, 197-200, 202, 204 - 6Microalgae-bacteria 191, 204, 206-7 Microalgae-based 200

Microalgal-bacterial 208 Microbe 155, 204, 207 Microbe-based 154 Microchannel 32 Micrococcus 122, 125 Microelectrolysis 80 Microfiltration 177 Micronutrients 116 Microorganisms 11, 46, 119, 121, 141, 154-55, 176-77, 182, 185, 195 Micropollutant 176 Micropores 156, 181 Microprecipitation 85 Microwave 49, 51, 156 Mineral-based 180-81 Mineralization 36, 58, 60-62, 70, 142 Mineralize 70, 123 Mitochondrial 199 Mixed-order 99 Model 33-34, 85-90, 92-104, 151, 160, Modeling 82, 93, 98, 101-2, 104, Molecular-weight 119 Momentum 191 Monobasic 84 Monocrotophos 207 Monolayer 94 Monooxygenase 196 Monopoly 184 Morphological 203 Multifunctional 160, 163 Multi-ion 162 Multilayered 159 Mutagenesis 114 Mutagenic 82 Mutations 54 Mutualism 204 Mycelia 203 Mycelium 151 Mycobacterium 153, 196 Mycoremediation 191, 202-3

Ν

NaCl 2, 123–24, 155 NADH 125

NADH-DCIP 125 **NADPH 198** Nanocatalysts 80 Nanocomposite 60, 66, 72, 87-88, 90, 156-57, 164, 177 Nanoconjugates 161 Nanofiltration 1-2, 162, 177-78 Nanomaterial-based 180, 188 Nanomaterials 12, 81, 90, 157 Nanoparticles 65, 81, 100-101, 104, 117, 121, 124, 126, 144, 149, 157-58, 190 Nanoplates 87 Nanoporous 85, 91, 101 Nanorods 180 Nanosheets 91 Nano-sorbent 91, 100 Nanosorption 118 Nanotechnology 159 Nanotubes 86, 88-90, 125, 159, 180-81 Naphthalene 59, 89, 207 Naproxen 89–90 Nasal 2 **NCIM 124** Negatively-charged 160 Nerium 119 Nervous 82 Neurophora 149 Neurospora 125, 145 Neutralization 141-42 Newtonian fluid 26 Nickel 28, 67, 71-72, 80, 145 Nickel-EDTA 70-72, 80 Nickel-zinc 90 Nitrates 68, 117, 162 Nitrites 117 Nitrobenzene 36, 38 Nitrogen 4, 6, 155, 159, 161-62, 183, 185-86, 192, 197-98, 201, 203, 208 Nitrogen-containing 91 Nitrogenous 198 Nitrosamines 180 Non-biodegradable 23, 82, 117, 141, 180-81, 188.198 Non-biological 104 Non-corrosive 60

Non-covalent 90, 158 Non-disinfected 182 Non-electrostatic 93 Nonmagnetic 144 Non-Newtonian fluid 26 Non-porous 98, 159 Non-woven 144, 159 Nonylphenol 86 Non-zero 101 Nostoc 124, 153 Nuclear 18, 66, 115 Nutrients 162, 175–76, 183–84, 186, 192, 195, 197–98, 204–6, 208

0

Ochrobactrum 122, 125 Odor 1, 3, 6, 186 Oil 22, 46, 148, 183-84, 193, 207-8 Ondansetron 5, 10-11 Operons 125 Optimization 7, 33, 71, 91, Organisms 3, 123-24, 142-43, 150, 152-53, 155, 163, 195–97, 200, 202 Orthophosphates 199 Osmosis 159, 162, 177-78 O-toluidine 74 Oxacillin 64 Oxadiazole 160 Oxalate 64, 69, 85 Oxidation 1-3, 7, 10-12, 18, 23-25, 36-38, 45-55, 57-61, 63-71, 80, 82, 141, 153, 155, 162, 175, 180-81, 197, 199, 203 Oxidation-based 71 Oxidation-coagulation 80 Oxide-based 91 Oxide-cerium 72 Oxide-chitosan 92 Oxide-cobalt 72 Oxidoreductase 125 Oxygenase 152 Oxytetracycline 63 Ozonation 24-25, 36-38, 46-49, 54-62, 66-67, 152, 162, 180, 182 Ozonation-based 61, 66

Bhunia and Muthuraj

Ozone 7, 9–11, 24, 31, 35–38, 47–49, 52, 55– 58, 61–62, 67, 180–82 Ozone-assisted 72 Ozone-Fe 37 Ozone-Fenton 38

P

Packed-bed 42 Paddle 201 Paddy 2, 4 Paint 18, 53, 66, 115, 117 Para-aminophenol 54 Paralicheniformis 126 Paramagnetic 65 Parameters 6, 8-9, 21, 33-35, 46, 56, 58-59, 61-63, 67, 81-82, 91-94, 97-98, 100, 104, 145, 149-50, 152, 154, 178, 180, 196, 201 Paramorphogenic 123 Paramycoides 126 Para-nitrophenol 141 Para-phenyldiamine 54 Parasites 206 Parasiticus 146 Paspalum 121 Pathogens 46, 185, 197-98, 201, 205 Pathways 24, 68-70, 153, 163, 180 p-chlorophenol 90 Peanut 161 Penicillium 123, 150, 152 Pentachlorophenol 2 Peptides 200 Permanganate 47, 150 Peroxidase 119-20, 123, 125-26, 151, 153 Peroxy-di-sulfide 63 Peroxymonosulfate 52 Persulfate 36, 52-53, 68 Pesticides 18, 46-47, 104, 115-16,180-81, 196, 207 Petrochemicals 18, 115 Petroleum 1, 179, 196 Phaeobacter 205 Phanerochaete 151 Pharmaceutical 1-3, 5, 9-11, 46, 60-66, 115 pH-based 64

pH-dependent 62, 92 Phenibacillus 196 Phenol 3-4, 6-9, 31, 34-36, 38, 93, 146, 207 pH-independent 92 Phormidium 208 Phosphodiester 85 Phosphorus 6, 155, 183, 185-86, 197, 199, 208 Phosphorylation 199 Photo-assisted 80 Photoautotrophs 195 Photo-bioreactor 200 Photocatalysis 16, 25, 32, 48-49, 51, 60-61, 65-66, 70, 82 Photocatalyst 51-52, 60, 71 Photochemically-assisted 182 Photodecoloration 157 Photo-Fenton 7, 50, 58-59, 63-64, 72, 80 Photolysis 50, 56, 63, 65-68, 70 Photo-oxidation 67, 201 Photosynthesis 200, 204 Phragmites 125 Phthalates 46 Phycoremediation 161, 197-98, 201-2 Physico-chemical 49, 141, 164, 175-76, 180, 187-88.193 Physisorption 98, 150 Phytoaccumulation 119 Phytochelatin 120, 200 Phytodegradation 119 Phytoreactors 121 Phytoremediation 3, 9, 118, 120, 163 Phytostabilization 118-19 Phytostimulation 119 Phytotransformation 119-20 Phytovolatilization 118-20 Pichia 123 Piggery 208 Pigments 54, 141 pi-pi 83 Piroxicam 65 Planktonic 123-24 Plant-based 118-19 Plasmid 153 Plasticity 84 Plasticizers 82

Platforms 195, 207 Platinum 36 p-nitrophenol 154 Pollutants 2, 7, 12, 21, 23-24, 31, 45-52, 55, 59, 72, 81-82, 84-86, 104, 115, 117-19, 156-57, 175-76, 179-81, 185, 187, 193, 197-98, 202-4, 207 Polyacrylamide 160 Polyacrylamide-modified 92 Polyacrylonitrile 159 Poly-aluminum 183 Polyamide 159 Polyaromatic 46, 196 Polycaprolactone 125 Polychlorinated 82 Polycyclic 151, 203 Polyelectrolyte 183, 199 Polyester 54 Polyethersulfone 159 Polyethylene 162 Polylactic 125 Polymer 88, 142-43, 160, 181, 183 Polymer-based 180-81 Polymer-supported 80 Polyphenol-Cr 80 Polyphenols 141 Polyphosphate 199-200 Polypyrrole 87 Polysaccharides 143, 177, 199, 202 Polysulfone-based 85 Polyvinylidene 159 Porosity 93, 156, 158-59, 179 Porous 19, 83, 98, 157-59, 163-64 Potable 5, 177, 179 Precipitation 18, 25, 54, 66, 68, 80, 92, 118, 141, 143, 183, 194 Proteins 143, 177, 196, 198-99, 202 Proteus 125, 152 Protonated 149, 158-59 Protonation 69, 97 Protozoa 181-82, 195 Pseudo-first 99 Pseudomonas 3, 122-25, 152-53, 161, 196, 205-6 Pseudo-nth-order 88

Recent Trends and Innovations in Sustainable Treatment 225

Purification 4, 25, 193 Pyrolysis 4, 83, 156, 158 p-π 91

Q

Quantum 63, 65 Quenching 4 Quinol 36, 91, 203

R

Raceway 200-201 Radiation 24, 36, 48-53, 56-60, 62-68, 181-82, 201 Radiation-based 62, 67 Radical 7, 23-25, 47-48, 50-53, 55-59, 62-73, 158, 180-82 Radical-based 52 Radioactive 91-92 Radionuclides 119 Raschig 28 Rate 7, 10, 18-20, 24-25, 27-28, 31-38, 48-49, 51, 54, 56, 58–61, 65–67, 90, 96–100, 102-4, 115, 152, 155, 159, 163-64, 181, 185-86, 199 Rate-controlling 98, 102 Rate-determining 100 Rate-limiting 100 Ratios 57, 70, 150 Reactants 27, 50, 68, 71, 179 Reaction 7-8, 24-25, 27, 32, 35-37, 47-55, 57-59, 61-62, 64, 67-71, 80, 83-85, 92, 97-98, 100, 102-3, 142-43, 153-55, 160, 180-82, 198, 203 Reactivation 182 Reactor 3, 18, 27, 29-32, 36-38, 54, 82-83, 93, 100, 115, 123, 178, 183, 188 Reagent 2, 10, 31, 35, 58, 82, 183 Realization 73, 202-3 Real-time 68, 188 Recalcitrant 23, 52, 104 Reciprocal 99

Bhunia and Muthuraj

Reclamation 116, 177, 181 Recombinant 151 Recovery 70-72, 80, 82, 123, 159-60, 162-63, 175-76, 186, 188, 192, 203 Redox 23, 52, 80, 92, 198 Reductase 120, 125-26, 142, 152, 198 Refining 201 Refractory 81, 84 Remediation 1-3, 12, 45-46, 54, 72-73, 91, 104, 114, 117-20, 122, 124-26, 141, 151, 154, 162-64, 180, 187, 190-91, 194, 199, 202 - 3Renewable 187, 191-92, 208 Replenishment 177 Reservoirs 177 **Resilient 48** Rhizodegradation 118 Rhizofiltration 118 Rhizogenes 120 Rhizophora 148 Rhizopus 122, 124, 146, 152 Rhizosphere 122 Rhodamine 60, 86, 89, 144, 149, 157 Rhodococcus 196, 208 Rhodopseudomonas 145 Rhodotorula 123-24 Riboflavin 126 Robustness 151 RSM 91-92 **RSM-fitting 38 RSM-optimized** 92

S

Saccharides 199 Saccharomyces 123, 125 Safranin 121 Salinity 6, 123 Salt 2, 54, 57, 85, 154–55, 159–60 Sardinella 149 Sargassum 124, 147, 149–50, 152, 161 Sawdust 19, 34, 121 Scales 4, 27, 31, 33–34, 60, 84, 92, 114, 126, 143–44, 149–50, 178, 180–81, 192, 198, 203 Scarcity 46 Scenedesmus 161, 207-8 Scheffersomyces 123 Seawater 182 Seaweed 83, 85, 147 Second-order 99 Secretory 153 Sedimentation 116, 175, 183, 194 Sedimentibacter 124 Sediments 46, 122, Seed 104, 120, 143, 148, 167 Selenium 123 Self-sustainable 176 Semi-anaerobic 155 Semi-arid 200 Semiconductive 49 Semi-conductor 51, 60 Semi-continuous 145 Semi-synthetic 204 Septum 2 Sequestering 200 Sequestration 118 Serratia 3 Sesuvium 120 Settling 46, 183, 193, 197, 200 Sewage 5, 19, 47, 115-16, 184, 186, 190, 192 Shewanella 123, 125 Shrimp 143, 149 Simulated 10, 25, 80, Single-step 21 Single-treatment 162 Small-scale 2, 163 Socio-economic 192 Solid-liquid 102, 177 Solid-phase 96, 102 Solids 46, 115, 152, 176-77, 193, 195-96, 201, 203 Solubility 53-54, 160, 179 Solute 21, 23, 96, 159-60 Solution 8-10, 12, 19-20, 22, 30-31, 33-34, 36, 49-50, 56-57, 63, 68-70, 72-73 84-85, 90, 96, 99, 102, 121, 150, 156-57, 159-60, 176-78, 183, 188, 199-200, 202-3 Solution-based 91 Sonication-assisted 85

Sonolysis 48, 51, 59-60, 64-66 Soybean 158 Spectrometry 68, 96 Spectrophotometer 96 Spectrum 115 Sphingomonas 126, 196 Spillage 23 Spirogyra 124, 152 Spirulina 147, 166 Sporosarcina 122 Stabilization 118, 194, 200 Stainless-steel 28 Staphylococcus 121 Stichococcus 208 Stoichiometry 85 Streptomyces 122, 124, 154 Succinic 119 Sucrose 125 Sugarcane 124 Sulfamethoxazole 160 Sulfapyridine 63 Sulfasalazine 63 Sulfate 47, 52-53, 55, 64, 67-68, 125-26, 143 Sulfate-reducing 122, 126 Sulfide 2, 6, 10–11, 51, 60, 85, 117, 142 Sulfonamides 91 Sulfur 54, 117, 141, 152, 154, 162 Sunflower 131 Sunlight 117, 195 Super-adsorbent 90 Superoxide 24 Superparamagnetic 121 Surfactants 22, 35, 84, 106, 157, 163 Sustainability 1-3, 160, 162, 175, 185-87, 190 Switchgrass 83 Symbiosis 200 Symbiotic 204, 206 Synergistic 121, 163, 204, 207 Synthesis 45, 48, 82, 91, 120-21, 126, 157

Т

Taguchi 33 Tanneries 2, 5, 47 Tannins 71, 152 Teratogenic 82 Terephthalate 158-59 Terrestrial 18, 29 Tertiary 46, 193, 197 Tetracycline 65, 90 Tetrahedral 84 Textile 2, 37, 47, 53-54, 59-61, 66, 82, 117-21, 123–26, 140–41, 144, 151, 155–56, 164 Thermochemical 156 Thermodynamic 92, 150 Thermophilic 155 Thermostability 163 Thermostats 115 Thiobacillus 10 Thiocyanate 6, 207 Titanium 25 Titanium-di-oxide 48, 51-52, 60-61, 63, 65 Toluene 4 **Topologies 158** Toxic 2-3, 8, 11-12, 46, 52, 66, 72-73, 82, 114-17, 119, 121, 144, 181, 190, 192-93, 196-99, 205 Toxicants 192 Toxicity 7, 10, 61, 163, 180, 193, 203 Toxicological 190 Transformation 104, 118, 153, 199 Transition 53 **Transpiration 118** Trees 124 Triazole 160 Triazole-co-oxadiazole-co-hydrazine 160 Trichloroethylene 196 Trichoderma 123, 125, 151, 154 Trickling 194 Trimethoprim 61-62, 64, 77, 160 Triphenylmethane 120 Tri-phosphate 199 Trivalent 2, 33 Trichloroethylene 29 Tumorigenic 117 Tungsten-trioxide 60 Turbidity 57, 59, 182, 196-97 Tyrosinase 120, 126

U

Ultrafiltration 177-78 Ultrasonication 51, 65, 71 Ultrasound 24, 49-51, 53, 59, 64-66 Ultra-violet 48-50, 52-53, 56, 58-60, 62-64, 67-68.181 Unicellular 151 Upstream 180 Uptake 31, 82-83, 85, 90-93, 97, 99-100, 102, 118-19, 142, 144, 151, 199 Uranium 123 Urbanization 82, 115, 192 UV-A 56, 63 UV-assisted 50, 55, 67, 73 **UVB 56** UV-based 62-63 UV-C 56, 62-63 UV-dependent 70 **UV-radiations 58** UV-region 62 UV-Vis 72, 96

V

Vacuoles 120, 200 Valency 52, 68, 72, 84, 161 Valorization 12, 194, 197 Value-added 18, 161, 191, 193–94, 197, 199, 202, 204 Vapour 20, 90, 186 Viability 19, 114, 155, 207 Violet 83, 86–88, 92, 120, 125, 144, 147–48, 158 Virulent 3 Viruses 177, 181–82, 184 Viscosity 26, 29, 53, 150, 179 Visible 49–50, 56, 58, 60 Vitamin 205 Volatilization 116

W

Wastewater 1-22, 25-26, 32, 35-40, 42, 44-46, 48-52, 54-56, 59-62, 64-68, 71-80, 82, 84, 90-92, 100, 104-8, 110-11, 114, 117-19, 123-25, 128, 130, 132, 135-36, 138-45, 151, 154–57, 160–65, 168–71, 173–79, 181-214 Wastewaters 1-2, 46, 57, 60,140, 175, 179, 184, 190, 193, 195, 198-99 Water-based 158 Water-borne 193 Water-oxygen 28 Waveform 29-30 Wavelength 52, 56-57, 63 Wetland 197 Wheat 124 White-rot 203

X

Xanthene 141 Xenobiotics 45–47, 61–66, 72–73, 81–83, 86, 93, 104, 114, 141, 175–76, 178–80, 192 X-ray 158 XRD 83 Xylene 31, 35

Y

Yeast 123-25, 151, 155, 161

Z

Zanthoxylum 121 Zeolite 81, 83–85, 91, 144, 149, 163 Zerovalent 24, 33 Zeta 84 Zinc 51, 59–60, 67–68, 72, 119, 122 Zingiber 121 Zirconium 60



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