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BIOSYNTHESIS, ENVIRONMENTALLY FRIENDLY SYNTHESIS USING PLANTS, BACTERIA, AND FUNGI TO PRODUCE NANOCOMPOSITES AND AS ANTIBIOTICS AND REDUCE WASTEWATER POLLUTION [PART ONE]





Karrar hazim Salim 1 Zahraa F Khudair 2 Iman K. Kadhim 3 Mayada Ahmed Abass 4 Lidia Mohamed 5 Fatima Hiader Kutham 6 Zainab Ahmed Abass7 Muntadher Rafil Hashim 8 Faris J. Alyasiri 9 Heba Haded Rashed 10

# PREFACE

Metal nanoparticles are the basic elements of nanotechnology as they are the primary source used in the design of nanostructured devices and materials. Nanomaterials can be manufactured either incidentally, with physical or chemical methods, or naturally; and the high demand for them has led to their large-scale production by various toxic solvents or high energy techniques. However, due to the growing awareness of environmental and safety issues, the use of clean, nontoxic, and environment-friendly ways to synthesize metal nanoparticles has emerged out of necessity. The use of biological resources, such as microbes, plant parts, vegetable wastes, agricultural wastes, gums, etc., has grown to become an alternative way of synthesizing metal nanoparticles. This biogenic synthesis is green, environmentally friendly, costeffective, and nontoxic. The current multi-authored book includes recent information and builds a database of bioreducing agents for various metal nanoparticles using different precursor systems. This book also highlights different simple, costeffective, environment-friendly and easily scalable strategies, and includes parameters for controlling the size and shape of the materials developed from the various greener methods. In order to exploit the utmost potential offered by the synthesis of metal nanoparticles from different sources, such as agricultural and food waste, flora and fauna, microbes, and biopolymer systems, it is also crucial to recognize the biochemical and molecular mechanisms involved in the production of nanoparticles and their characterization. The contents of other books mainly include the fundamentals of nanoparticles, characterization, mechanisms, and the methods thereof. However, this book more narrowly focuses on the exploration of the green synthesis of metal nanoparticles and their characterization and applications in a specific manner currently lacking in these other available books.



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# Biosynthesis, environmentally friendly synthesis using plants, bacteria, and fungi to produce nanocomposites and as antibiotics and reduce wastewater pollution (Part One)

Karrar hazim Salim<sup>1</sup> Zahraa F Khudair<sup>2</sup>

Iman K. Kadhim<sup>3</sup> Mayada Ahmed Abass<sup>4</sup> Lidia Mohamed<sup>5</sup>

Fatima Hiader Kutham<sup>6</sup> Zainab Ahmed Abass<sup>7</sup> Muntadher Rafil Hashim<sup>8</sup>

Faris J. Alyasiri<sup>9</sup> Heba Haded Rashed<sup>10</sup>

<sup>1&2&3&4&6</sup> Pharmacy Department, Al-Mustaqbal University College, Iraq
<sup>5</sup> Al-Zahrawi University College/ Department of Medical lab-technology
<sup>7</sup>Optics techniques Department, Al-Mustaqbal University College, Iraq
<sup>8</sup> Al-Zahrawi University College Department of Pharmacy
<sup>9</sup> Islamic Azad university science and research branch
<sup>10</sup> Medical Laboratories techniques Department, Al-Mustaqbal University College, Iraq

Optics techniques Department \* Corresponding author E-mail: karar.hazim@mustaqbal-college.edu.iq Preface

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### Preface

Metal nanoparticles are the basic elements of nanotechnology as they are the primary source used in the design of nanostructured devices and materials. Nanomaterials can be manufactured either incidentally, with physical or chemical methods, or naturally; and the high demand for them has led to their large-scale production by various toxic solvents or high energy techniques. However, due to the growing awareness of environmental and safety issues, the use of clean, nontoxic, and environment-friendly ways to synthesize metal nanoparticles has emerged out of necessity. The use of biological resources, such as microbes, plant parts, vegetable wastes, agricultural wastes, gums, etc., has grown to become an alternative way of synthesizing metal nanoparticles. This biogenic synthesis is green, environmentally friendly, cost-effective, and nontoxic. The current multi-authored book includes recent information and builds a database of bioreducing agents for various metal nanoparticles using different precursor systems. This book also highlights different simple, costeffective, environment-friendly and easily scalable strategies, and includes parameters for controlling the size and shape of the materials developed from the various greener methods. In order to exploit the utmost potential offered by the synthesis of metal nanoparticles from different sources, such as agricultural and food waste, flora and fauna, microbes, and biopolymer systems, it is also crucial to recognize the biochemical and molecular mechanisms involved in the production of nanoparticles and their characterization. The contents of other books mainly include the fundamentals of nanoparticles, characterization, mechanisms, and the methods thereof. However, this book more narrowly focuses on the exploration of the green synthesis of metal nanoparticles and their characterization and applications in a specific manner currently lacking in these other available books.

The One Part FUTURE VISION OF GREEN NANOTECHNOLOGY

#### Abstract

Nanotechnology today is moving from one visionary paradigm towards another. Green synthesis and green nanotechnology are a totally integral part of the domain of sustainable nanotechnology. According to the Brundtland Commission Report, sustainability can be defined as that development that meets the needs of the present without compromising the ability of future generations to meet their own needs. Humankind's immense scientific prowess, scientific advancements and futuristic vision will all lead to a long and visionary way towards the true realization of sustainable development. The challenges, vision, and intricacies of scientific endeavors in green nanotechnology are opening new windows of innovation in nanoscience and nanotechnology. Nanotechnology for green innovation-green nanotechnology-aims for products and processes that are safe, energy efficient, reduce industrial wastes and lessen greenhouse gas emission. This chapter delves deep into the murky depths of scientific vision and scientific innovation in green synthesis and green nanotechnology. Green nanotechnology veritably and addresses global water shortage and drinking water issues. The authors repeatedly address the issue of drinking water provision and heavy metals and arsenic groundwater contamination. Other areas of scientific endeavors are nanotechnology-based water treatment problems, better and more efficient renewable energy technologies, environmental and waste remediation, and the application of nanotechnology in sustainable production. This chapter targets the wide and visionary domain of environmental sustainability and its vital and pivotal need in a nation's growth.

Keywords: Nanotechnology, green, synthesis, sustainability, process, advance

#### **1.1 Introduction**

Science and technology are moving at a rapid pace today. Environmental engineering science is witnessing drastic changes. In a similar manner, nanotechnology and green nanotechnology are moving from one visionary paradigm towards another. Environmental regulations, frequent environmental catastrophes and loss of ecological biodiversity have urged the scientific community to move forward towards a newer vision and newer innovations. Green nanotechnology is the frontier of science and engineering today. Human civilization's immense scientific prowess, wide futuristic vision, and vast scientific and academic rigor all lead along a long and visionary path towards the true realization and emancipation of green nanotechnology. In this chapter, the authors focus deeply on recent scientific endeavors and scientific advances in the field of green nanotechnology with the sole objective of furthering science and engineering. Today the domain of nanotechnology needs to be re-envisioned and redefined with scientific rigor. The vision and challenge of environmental engineering science and nanotechnology are broadly

combined in the evolution of a new branch of scientific endeavor known as green nanotechnology. Thi chapter also focuses on global water issues mainly heavy metal groundwater contamination and subsequent remediation. Scientific research pursuit today is replete with vision and scientific profundity. The authors in this chapter have strived to open new windows into innovation in the field of green nanotechnology, which will continue to take place in decades to come.

#### **1.2 The Purpose of the Study**

Today the scientific vision of nanotechnology, green nanotechnology and green synthesis are surpassing wide and visionary scientific frontiers. Technological vision and scientific validation are today's foundation stones of scientific endeavors in the field of nanotechnology and green nanotechnology. The endeavors in this chapter are replete with deep scientific contemplation and scientific introspection. Global nanotechnology applications and their health risks are challenging the scientific landscape, hence the importance of green synthesis, green nanotechnology, and green chemistry. This chapter pointedly focuses on the recent scientific research pursuits in green nanotechnology, especially on the vast domain of groundwater remediation and its vision for the future. Today global nanotechnology initiatives are targeted towards green chemistry, sustainable chemistry, and green engineering. The vast scientific potential of green nanotechnology is delineated with scientific precision in this chapter. Deep scientific understanding, wide scientific contemplation and the vision of green science and technology are the basic foundations of this well-observed chapter [1, 2].

# 1.3 What Justifies This Study?

The rationale for this study surpasses vast scientific imagination and deep scientific discernment. Technology is moving at a rapid pace today. The global water shortage, frequent environmental disasters and stringent regulations have urged the scientific and engineering communities to be geared towards a newer visionary era of green technology. Today, humankind stands during a global water crisis. Heavy metal and arsenic groundwater contamination are the vexing issues of this century. Thus, the need for this well-observed study. Technological vision and scientific motivation are greatly needed as civilization wearily trudges a scientific path in this century. Scientific comprehension, the deep scientific avenues of this century and a futuristic vision are the forerunners of the recent emancipation of green nanotechnology today. Groundwater remediation and prevention of arsenic and heavy metal drinking water contamination are the futuristic vision of this chapter. Scientific success, scientific potential and wide scientific forbearance are of utmost importance as science and engineering moves into the second half of this visionary century. The rationale of this study goes beyond scientific imagination and scientific fortitude. Humankind and scientific endeavor today stand during deep vision and contemplation. Today green

nanotechnology is a burgeoning area of science. This study pointedly focuses on the vast applications of green nanotechnology with the sole aim of furthering science and engineering.

## 1.4 What Exactly Does "Green Nanotechnology" Mean?

Today, nanotechnology can alleviate major sustainability issues. Sustainable development is the utmost need of the hour. The framework of green nanotechnology involves the production and processes to make nanomaterials, green chemistry, green engineering, direct and indirect environmental applications; and encompasses the production of nanomembranes, nanocatalysts and the greater emancipation of harnessed energy. Broadly speaking, green nanotechnology refers to the use of nanotechnology to enhance the environmental sustainability of processes, producing veritable negative externalities [1, 2]. It also encompasses the use of products of nanotechnology to enhance sustainability. It includes green nanoproducts and using nanoproducts in support of sustainability. Technological challenges, deep scientific vision and scientific insight are the pivotal elements of scientific rigor in green nanotechnology today. Green nanotechnology has been described as having a major pivotal role in the development of clean technologies.

## **1.5 The Doctrine and Reality of Science**

Nanotechnology Applications Today, nanotechnology needs immense scientific vision and deep scientific forbearance. Green engineering and green science are the order of today's scientific research pursuits. Scientific doctrine, scientific truth and futuristic vision are all forerunners to a greater emancipation of green nanotechnology. The water shortage crisis is challenging the scientific fabric of today. Heavy metal and arsenic groundwater contamination are changing the face of civilization and the scientific endeavor of humans. The doctrine of the science of green nanotechnology and nanotechnology needs to be re-envisioned and redefined with every step of human life today. Technological vision and scientific validation are reframing the world of green nanotechnology and sustainable chemistry. The vision of environmental and energy sustainability and its immediate needs are forerunners to a greater realization of environmental engineering science today. Environmental engineering and green nanotechnology are the two opposite sides of the visionary coin. Today scientific doctrine and scientific cognizance are the pathway to newer scientific regeneration and rejuvenation. Global water challenges and environmental engineering issues are veritably changing the face of scientific research pursuits today. Arsenic and heavy metal groundwater contamination are the vexing issues of scientific empowerment today. Technological validation and scientific vision are the definite rules of today's scientific research pursuit. Human civilization's immense scientific rigor, the academic rigor behind today's environmental engineering research and path towards the true emancipation and realization of green nanotechnology and green chemistry. Scientific innovation and scientific advancements are on the pathway to immense rejuvenation and forbearance. This chapter emphasizes the success of application of green nanotechnology with the sole objective of furthering science and engineering [1, 2].

#### 1.6 Nanotechnology research projects recently undertaken

Nanotechnology and nanoscience are the revolutionary avenues of scientific endeavor. The challenge and vision of science and engineering need to be redefined and re-envisioned in relation to scientific history and scientific vision with the passage of time. Today nanotechnology is the visionary domain of scientific research pursuit. The vision and challenge of this domain will be to open new windows of innovation in the field of nanotechnology in years to come. The European Commission Report of 2011 [3]. clearly discusses successful European nanotechnology research. According to the report, nanotechnology is an outstanding science and technology endeavor which matches the future needs of society. The fruits of nanotechnology are vast and versatile and cross visionary scientific frontiers. Nanotechnology is the new frontier of science and technology in Europe and around the world. Validation of nanoscience and nanotechnology are of utmost importance in the future of scientific and academic rigor. Setting up appropriate methodologies is a relevant and uphill task in the future of nanotechnology [3]. This report gives a sharp glimpse into the application of nanotechnology in energy and the environment, electronics and ICT, industrial applications, textiles, nanomaterials, nanomedicine, and a wider approach towards ethical, legal, and social aspects [3]. The avenues of nanotechnology are far-reaching and wellresearched today. Technology barriers need to come down as nanoscience enters a newer era [3]. The United States Environmental Protection Agency White Paper of 2007 [4] provides a deep insight into mainly the environmental benefits of nanotechnology. Technology and engineering science are surpassing vast scientific boundaries. Humankind's immense scientific prowess is redefined as engineering and technology that ushers in a newer era in the field of nanotechnology. The authors touch upon the environmental benefits of nanotechnology, risk assessment of nanomaterials, EPA's research needs for nanomaterials and future recommendations [4]. The vision of and scientific rigor will lead to the true realization of environmental protection and nanotechnology. The science of nanotechnology according to this report needs to be veritably reenvisioned and readdressed with the passage of scientific history and time.

#### 1.7 Efforts to Advance Green Nanotechnology in Science

Green technology and sustainability engineering are the path to immense scientific regeneration and scientific forbearance. Today, the avenues of scientific endeavor are ushering in a newer visionary era in green nanotechnology. Global water issues, global drinking water crisis and groundwater contamination by heavy metals are challenging the wide scientific frontier. This chapter pointedly focuses on the immense scientific vision and forbearance needed in the pursuit of green technology research. Nanotechnology for green innovation was widely redefined by OECD Science, Technology, and Industry Policy Paper No. 5 (2013) [5]. This paper brings together widespread and vital information collected through discussions and projects undertaken by the OECD Working Party on Nanotechnology (WPN), which is relevant to the development and use of nanotechnology for green sustainable development and vast innovation [5]. The aim and objective of this paper is to provide background information for future work by the WPN on the application of nanotechnology for green engineering and innovation. Green nanotechnology is today ushering in a new era in the furtherance of science and technology [5]. Technological vision, scientific motivation and vast academic rigor are forerunners to a greater emancipation of nanoscience and nanotechnology. Humankind today is in a state of immense scientific distress due to vast challenges. In their paper, the authors gleaned the tremendous challenges, deep scientific crisis and the success of nanoscience and nanotechnology today. The entire treatise is divided into three sections; 1) a thorough introduction to nanotechnology, 2) strategies for green innovation and green engineering through nanotechnology, and 3) the impact of green nanotechnology [5]. The immediate need for sustainable development of affordable and safe methods of addressing global challenges in areas, such as energy, the environment and health, has never been so pressing as in this century. Energy and environmental sustainability are the pillars and pivotal elements of today's scientific and engineering endeavors [5]. The global demand for energy is expected to increase by more than 30% between 2010 and 2035 [5]. More than 800 million people throughout the world are currently without proper access to drinking water. Such challenges have changed the scientific mindset of scientists, engineers, policymakers, and politicians in developed and developing economies. Scientific self-control and deep insight are the supports of a larger vision for a greater emancipation of green nanotechnology [5]. Green innovation targets the reduction of environmental impacts by increasing energy efficiency, reducing waste or greenhouse gas emissions and by minimizing the consumption of nonrenewable raw materials. Scientific research pursuits in green nanotechnology are today ushering in a new era of sustainable development and green engineering. The technology and science of green nanotechnology and engineering are highly advanced today. Scientific success, a visionary path and overcoming obstacles will all go a long way towards environmental sustainability and environmental engineering science today. Since it began its work in 2007, the OECD Working Party on Nanotechnology (WPN) developed several feasible projects addressing emerging and far-reaching policies of science, technology and innovation related to the cogent development of nanotechnology [5]. Nanotechnology of green innovation, or green nanotechnology, aims for wide-ranging scientific products and processes that are immensely safe, energy efficient, reduce waste and deeply lessen greenhouse gas emissions. Technological validation is of utmost importance in the progress of scientific and academic rigor. The WPN treatise widely researches the success of green nanotechnology and the authors pointedly focus on the immense scientific potential and deep scientific vision behind green engineering [5]. Karn and Bergeson [6] clearly present thoughtful insights into the immense promises and uncertainties in the vast world of green nanotechnology today. The technology and engineering science of nanoscience and nanotechnology are highly advanced today, ushering in a new technological era [6]. Green nanotechnology today is redefining the world of success in the field of application of nano-enabled products to human society. The article of Karn and Bergeson describes green nanotechnology and discusses the many feasible reasons why traditional chemical assessment and management approaches may not be enough in the pursuit of scientific research [6]. A project report by the Woodrow Wilson International Center for Scholars [7] describes green nanotechnology with immense clarity. Technological advancements, the vision to move forward and the targets of science will all lead towards the true realization of nanotechnology for green innovations [7]. In this report, clean and green nanotechnology, nano-enhanced green technology and the global green nanopolicy are well observed. According to this report, the principles of green chemistry encompass prevention of waste, design of safer chemicals, design of less hazardous materials and less hazardous process syntheses. Also, this wide scientific frontier involves use of catalysts, avoids chemical reagents, maximizes atom economy, and visualizes reuse of used products. Green chemistry also involves the minimization of the potential of accidents and the success of chemical process safety. This paper rigorously points out the scientific success and the deep scientific forbearance behind green nanotechnology [7]. Scientific vision is in a state of immense distress today as science and technology moves forward. The challenge of this research pursuit goes beyond scientific imagination and opens new areas of endeavor and vision. This insightful report investigates the endeavors of research and educational institutions in North America [7]. Nath and Banerjee [8] provide clear insight into the success of green nanotechnology and its interfaces with medical biology. The development of eco-friendly technologies in material synthesis is of vital importance to extend their biological and biomedical applications. Today, technological splendor and depth are in a state of immense regeneration due to newer thoughts [8] Their review highlights the classification of nanoparticles, giving vital emphasis to the biosynthesis of metal nanoparticle by viable organisms [8]. The science of nanoparticles is always growing and crossing visionary boundaries. Biomedical engineering is also surpassing farreaching scientific frontiers today. Technological validation and profundity are of utmost need as green nanotechnology ushers in a new era in the field of nanoscience and nanotechnology. This treatise also focuses on the applications of the biosynthesized nanoparticles in a wide spectrum of potential areas of medical biology, including catalysis, targeted drug delivery, cancer treatment,

antibacterial agents and as biosensors [8]. Nanomaterials, with characteristic dimensions in the range of 1–100 nm, are at the leading edge of the scientific research pursuit in nanotechnology [8]. Nano vision and nanotechnology, especially metal nanoparticles, have received immense scientific interest in diverse fields of applied science, ranging from materials science to biotechnology. Because of the extremely small size and high surface volume ratio of nanoparticles, the physicochemical properties of nanoparticles-containing materials are quite different to those of the bulk materials. Scientific vision and scientific forbearance are the pillars of scientific research pursuit today. The authors touched upon classification of nanoparticles such as liposomes, superparamagnetic nanoparticles, fullerenes such as buckyballs and carbon nanotubes, dendrimers, quantum dots and liquid crystals [8]. The authors rigorously dealt with synthesis of metal nanoparticles by traditional physical and chemical methods. The methods encompass laser ablation, inert gas condensation, sol-gel method, hydrothermal synthesis, and a wide range of colloidal methods. The authors also described bio-inspired green nanomaterial synthesis [8]. Virkutyte and Varma [9] intently discussed green synthesis of metal nanoparticles with more research forays into biodegradable polymers and enzymes in stabilization and surface functionalization. Engineering science and technology of green synthesis are ushering in a new era of scientific vision and scientific sagacity. Current scientific breakthroughs in green nanotechnology are intensely capable of transforming many of the existing processes and diverse products that enhance environmental quality, reduce pollution, and conserve natural resources. Science is moving through difficult terrains today. Scientific research avenues, the futuristic vision and the intense academic rigor of metal nanoparticles and biodegradable polymers are opening new avenues of scientific and engineering research pursuit today [9]. Schwarz [10] presented a clear discussion of green nanotechnology with its tremendous vision and scientific forbearance. Nanotechnology has recently been identified along with principles of sustainability and with "green agenda" [10]. Schwarz's paper discusses and argues that deeper lying societal and cognitive structures are at work to target the true realization and true emancipation green nanotechnologies [10]. Green nanotechnology is today understood as a boundary concept in which wide and disparate discourses are dealt with immense scientific vision. This treatise also pointedly focuses on green nanotechnology and sustainability with the sole objective of furtherance of science and engineering. His paper gives a wider view of the relevance of green nanotechnology in the Germanspeaking countries in Europe. Green nanotechnology today is replete with scientific vision and encompasses technological validation and scientific fortitude [10]. Yehia et al. [11] dealt with immense lucidity the structural and magnetic properties of nanocrystalline spinel ferrite powders. These are synthesized by a novel green nanotechnology derivative of the sol-gel method. Nickel ferrite (NiFe2O4) has an inverse spinel structure. The science of nanotechnology and its wide scientific vision are documented with forbearance and deep scientific understanding in this treatise [11]. Shawkey et al. [12] presented an immensely insightful discussion of green nanotechnology and the anticancer activity of silver nanoparticle using Citrullus colocynthis aqueous extracts. Green nanotechnology and biotechnology are the two opposite sides of the visionary coin today. Green synthesis of metal nanoparticles is a growing research avenue because of their potential applications in nanomedicines [12]. The science of nanomedicines is wide-ranging and farreaching. The green synthesis of silver nanoparticles (SNPs) is a comparatively convenient, cheap and environmentally safe approach compared to chemical synthesis [12]. Technology is highly advanced today, crossing wide scientific frontiers. The engineering science of green nanotechnology today is replete with scientific vision and deep scientific cognizance. In their study, the authors synthesized SNPs from AgNO3 using aqueous extracts (AEs) of fruits, leaves, roots and seeds of C. colocynthis as reducing and capping agents [12]. Nanoparticles of free metals have been extensively investigated because of their unique physical properties, chemical reactivity, biological labeling, biosensing, drug delivery, antibacterial activity, antiviral activity, detection of genetic disorders, gene therapy and DNA sequencing [12]. Green nanotechnology is opening new windows of scientific innovation today and deep scientific instinct in years to come. The present study explores the potential antitumor activity of greenly synthesized SNPs on cancer cells [12]. The wide world of green nanotechnology, the futuristic vision of cancer biology and the deep academic and scientific rigor will all lead to a long and visionary way towards the true emancipation of nanoscience today [12]. With immense foresight and clarity, Hutchison [13] discussed greener nanoscience as a proactive approach for advancing applications and reducing the implications of nanotechnology. Scientific cognizance, scientific sagacity and deep scientific understanding are the forerunners of research pursuit today [13]. A wide futuristic vision and overcoming the challenges of science and engineering will lead to the true realization and application of green nanotechnology. Nanotechnology continues to offer new materials and applications that will highly benefit human society, yet there is an evergrowing concern about the potential health and environmental impacts of the production and widespread use of nanoproducts [13]. The focus of this treatise is on the nanomaterial complexities through coordinated research on the applications and implications of new materials. Greener nanoscience is a revolutionary area of nanoscience today. Technological profundity and the scientific vision of the domain of green nanotechnology are veritably changing the face of scientific research pursuit today. Hutchison's treatise pointedly focuses on the research agenda in minimizing global nanomaterials and green technology issues [13]. Albrecht et al. [14] lucidly described green chemistry and the health implications of nanoparticles. Spectacular developments in nanotechnology have taken place in nanotechnology with disregard towards the veritable health issues involved in it. There are practically no specific regulations on nanoparticles except for existing regulations covering the same material in bulk form [14]. Technology and engineering science are today faced with

immense scientific obstacles and barriers. This review focuses on potential health effects of nanoparticles along with medical applications of nanoparticles, including imaging, drug delivery, disinfection, and tissue repair. Validation of science and technology are slowly gearing up today towards a newer visionary scientific future in green chemistry and green nanotechnology [14]. Fagan et al. [15] discussed green nanotechnology with deep and cogent insight, along with the development of nanomaterials for environmental and energy applications. The technology and engineering science of green nanotechnology are highly advanced today and cross visionary boundaries. Fagan et al. discuss the synthesis of various nanomaterials for green nanotechnology applications in incisive detail. Special attention is focused on the development of emerging areas such as environmental and energy areas [15]. The challenge and vision of the technology and science of green nanotechnology are reaching immense scientific heights as human civilization enters a newer scientific era. In this treatise, various approaches for preparing nanostructured photocatalysts, such as titanium dioxide, zinc oxide, iron oxide, and metal sulfides, and different conventional methods and novel methods, including sol-gel, hydrothermal, microwave-assisted and sonochemical methods, are discussed in deep detail [15]. The futuristic vision of nanotechnology, targets of scientific rigor and scientific passion and cognizance will all lead to a long and visionary way towards the true realization of nanotechnology science today [15].

#### 1.8 Opportunities and Challenges for Green Nanotechnology

Today the challenges and opportunities in the field of green nanotechnology are surpassing vast and versatile scientific frontiers. The wide futuristic vision of nanotechnology, the technological challenges, and the vision to move forward will all lead to a long and visionary way towards the true emancipation of nanoscience today. Human scientific endeavors in green nanotechnology and sustainable chemistry are transforming the visionary world of nanoscience and nanoengineering. In this chapter, the authors pinpoint the scientific success, immense scientific potential, and future research trends in the field of green nanotechnology. Humankind's immense vision and scientific prowess and the girth of scientific endeavor are forerunners of newer scientific research pursuits and innovations. Today, science and engineering are colossal with a definite vision and willpower of their own. Science, engineering, and technology are transforming the scientific genre of nanotechnology today.

#### 1.9 Sustainability of the environment, human progress, and the scientific outlook

Environmental sustainability and humankind's progress are in a state of immense scientific contemplation and deep scientific introspection today. Today, the progress of human beings is stalled and re-envisioned as regards sustainable development and environmental sustainability. The vision of the science of nanotechnology needs to be reframed and restructured regarding

application and scientific potential. Green nanotechnology is in a state of immense scientific restructuring and scientific revamping today. Environmental sustainability and human scientific research pursuit are two opposite sides of the visionary coin today. Dr. Gro Harlem Brundtland, the former Prime Minister of Norway, defined and envisioned the science of sustainability. While the modern concept of sustainable development is derived mostly from the 1987 Brundtland report, it is also rooted in earlier ideas about sustainable forest management and twentieth century environmental concerns. Technological vision, deep introspection and scientific candor will all lead to a long and visionary way towards the true emancipation of green nanotechnology and green engineering today. Environmental sustainability today stands amid immense scientific revamping and, in a similar vein, deep crisis due to frequent environmental disasters and wide environmental hiatus periods. The question of sustainability today stands widely challenged and is deeply entwined with past scientific history and vision and the passage of time.

#### 1.10 The value of research, scientific knowledge, and green nanotechnology

Scientific awareness is highly challenged today, with green nanotechnology standing amid immense scientific comprehension and deep introspection. Environmental and energy sustainability are in a state of deep crisis today due to untold environmental catastrophes. The greatness of scientific research pursuits needs to be veritably overhauled as science and technology enters a new visionary age. Green nanotechnology and sustainable development are the two opposite sides of the visionary scientific coin today.

#### 1.11 Global Water Crisis: The Science's Vision and Challenge

The global water crisis and the visionary world of water research and development initiatives today stand during deep scientific introspection and wide scientific girth. The vision and the challenge of science are the pillars of scientific endeavor today. Global water shortage, drinking water contamination and industrial wastewater treatment will all lead to a long and visionary way towards the true emancipation of global sustainability science and the true realization of environmental sustainability. The success and vision of science today are immense and groundbreaking. Technological validation and scientific candor are the pathway to scientific regeneration and scientific regarding groundwater contamination and a drinking water crisis. Science and engineering has no answers to the immense questions and vexing issues of arsenic and heavy metal groundwater contamination. The success of scientific endeavors is in a state of

deeply entrenched global water crisis. The immense scientific prowess of human beings and their civilization's scientific achievement along with the scientific girth and determination are the veritable forerunners of a newer scientific and technological age.

# 1.12 The Future of Heavy Metal and Arsenic Groundwater Contamination

Heavy metal and arsenic groundwater contamination is a primordial issue, which has continued to pose a vexing problem over the course of scientific history and in the pursuit of scientific research in today's day-to-day civilization. Technological profundity today stands during deep catastrophe with the rising issues of global water shortage and contamination of drinking water. Developing and developed economies are in a veritable quagmire of arsenic groundwater contamination. Green nanotechnology and green chemistry are in the throes of a vicious scientific struggle to control their destiny. Yet environmental engineering science has a wide range of answers to this grave global water concern. The vision for the future needs to be reframed and redefined following the course of scientific history, scientific vision, and time. Developing countries like India or Bangladesh are in a veritable quagmire because of the scientific disaster brought about by the global water crisis. In this chapter the authors bring to the forefront the success of new technologies and innovations such as membrane science, advanced oxidation processes and the wide domain of nanoscience and nanotechnology. The crisis of drinking water contamination goes beyond scientific imagination and scientific adjudication. This chapter gives a veritable glimpse into the success of scientific endeavors in the field of green nanotechnology, green chemistry and sustainable chemistry. Hashim et al. [16] discussed with immense lucidity remediation technologies for heavy metal contaminated groundwater. The contamination of groundwater by heavy metal is of grave concern for the progress of science and the vast progress of human civilization. Remediation of contaminated water is of highest priority since billions of people throughout the world use it for survival. Today, engineering science and technology are revamping the broad scientific panorama and vast scientific vision. Humankind's immense scientific prowess, scientific stature and futuristic vision are forerunners to the true realization of groundwater remediation technologies. In their paper, many approaches for groundwater treatment have been classified under categories: mainly three reviewed. which are large chemical, biochemical/biological/biosorption, and physical-chemical absorption processes.

# **1.13** Technologies for water purification and groundwater remediation

Groundwater remediation and removal of arsenic or heavy metal from drinking water stands as a major imperative to the furtherance of environmental engineering science today. Despite scientific progress, the questions concerning arsenic groundwater contamination have remained unanswered

up till now. Technological profundity and scientific success are the pillars of environmental engineering science and nanotechnology today. Water purification technologies are in the throes of a deep crisis and an unimaginable scientific catastrophe. The scientific and academic rigor of groundwater remediation are being challenged today due to the intricacies of the pursuit of wide scientific research. Humankind today stands on the threshold of deep scientific vision and scientific introspection. Today, water technologies and environmental engineering science are replete with scientific forbearance and technological profundity. Drinking water contamination is in a state of immense scientific contemplation. Science and the vision of humankind need to be readdressed and re-envisioned as scientific forbearance and profundity progresses.

#### 1.14 Treatment of Industrial Wastewater Using Nanotechnology

Nanotechnology applications are changing the face of human scientific endeavor. The crisis of environmental engineering science is highly inevitable, as the loss of ecological biodiversity and frequent environmental catastrophes are changing the face of human civilization. Industrial wastewater treatment, drinking water treatment and groundwater remediation are of utmost importance in today's world of scientific and academic rigor. Nanotechnology is a veritable answer to the numerous questions of industrial wastewater treatment. Environmental catastrophes and stringent environmental restrictions are challenging the scientific landscape and the deep technological vision. Scientific candor, scientific forbearance and deep scientific understanding are the forerunners to a newer scientific genre and scientific vision. Nanoscience and nanoengineering are changing the face of scientific endeavors today. The global water shortage and global water catastrophe are the primordial scientific issues of today. Nanotechnology has been called the Second Industrial Revolution. Its seemingly limitless potential will continue to inspire innovations and discoveries in a wide array of beneficial applications and briskly transform human society. Despite the hope and definite promise nanotechnology brings, engineered nanomaterials, the tiny engines driving this new transformative technology, also generate a widely held apprehension due to their largely unknown implications on human health and the environment. Thus ushers in green nanotechnology, an approach to managing the potential environmental, health, and safety (EHS) risks associated with the manufacture and use of nanoenabled products while veritably fostering their responsible development and application. Karn et al. [6] delineated with great lucidity the widely held promise and uncertainty in green nanotechnology. Their article describes green nanotechnology and discusses the reasons why traditional chemical-assessment and management approaches may not be adequate in all cases when applied to nanomaterials. Technological vision, the wonders of science and the futuristic vision of green nanotechnology will all lead to a long and visionary way towards the true transformation of nanovision today. Nanotechnology encompasses the science of nanomaterials,

forms of matter in a particular size range, roughly between 1 and 100 nanometers (nm). Nanomaterials are bigger than most molecules and smaller than bacteria cells. They can consist of groups of single elements such as metals, groups of compounds such as metal oxides, tubes or wires of elements, soccer ball structures, branching structures, and infinite combinations of these. Science and technology are highly advanced today as green nanotechnology surpasses visionary frontiers. This chapter widely researches the scientific success, the deep scientific potential, and the wide scientific vision in the field of application of green nanotechnology and green engineering. Sustainable chemistry, environmental sustainability and sustainability engineering are in the path of immense scientific regeneration and scientific rejuvenation today. Humankind today is on the path to deep scientific vision and rejuvenation as nanotechnology enters a new phase of scientific achievement and determination. While nanomaterials are intentionally designed to be unique, what is common to all is their super small size, which imparts properties that are surprising and special. The science and engineering of nanomaterials are entering a new phase of technological challenges and scientific profundity. This chapter widely observes the immense scientific potential, the scientific understanding, and the scientific contemplation behind nanomaterials, engineered nanomaterials and the wide domain of nanotechnology. Electric properties also can change at the nanoscale. The rolled-up carbon chicken-wire structure of carbon nanotubes (CNTs) is a conductor when the chicken wire falls in a straight line. According to Karn et al. [6], there are two aspects to green nanotechnology. The first involves nanoproducts that provide solutions to environmental challenges. These green nanoproducts are used to prevent harm from known pollutants and are incorporated into environmental technologies to remediate hazardous waste sites, clean up polluted streams, and desalinate water, among other applications. Technology needs to be revamped and restructured with the progress of scientific history, scientific vision, and time.

#### 1.15 The Goals of Technologies for Renewable Energy

Renewable energy technologies are the visionary technologies of today and tomorrow. Energy sustainability and renewable energy technology are the two opposite sides of the visionary coin. Humankind today stands amid deep scientific hope and optimism. Technological challenges and scientific vision need to be re-envisioned with the passage of scientific history and time. Renewable energies are the next generation technologies. The path of science and the vision of scientific endeavor are immensely far-reaching today in the domain of renewable energy technologies. Today, green nanotechnology and sustainable engineering are linked with wide vision and this section treads a visionary path in the direction of newer and futuristic trends in the field of renewable energy technologies such as solar energy, wind energy and wave energy. Technology is highly advanced today. The progress of humankind, the immense scientific and

academic rigor and the future path of alternate energy sources will all lead to a long and visionary way towards the true emancipation of renewable energy technology today. Human civilization and scientific research pursuits are in a state of immense distress and unimaginable catastrophe, as environmental disasters, industrial pollution, and loss of ecological biodiversity is destroying the deep scientific fabric [17]. Science and its pursuit and deep vision needs to be readdressed and re-envisioned with the passage of human history and time. Green nanotechnology and the wider domain of nanoscience and nanotechnology are rewriting scientific history today. This chapter explores the wider vision and vast challenges facing technology in order to have proper and true emancipation of nanotechnology today [18].

#### **1.16 Future Research Trends and the Circulation of Ideas**

Future research trends are veritably opening new avenues of scientific thought and scientific vision. Nanoscience and nanotechnology are ushering in a new era in the field of scientific vision and forbearance. The scientific and technological truth needs to be re-envisioned as regards application of nanotechnology and green nanotechnology. The future of human civilization and human research pursuit lies in the hands of scientists and engineers. The science of green nanotechnology is witnessing a new beginning with the advent of sustainable chemistry and the wide domain of sustainable engineering. The question of energy and environmental sustainability is creating immense scientific obstacles and barriers. Future scientific endeavors lie in unfolding the unknown areas of the science and technology of green nanotechnology. Green engineering and green chemistry are ushering in a new era in the field of nanotechnology today. Global water research and development initiatives also encompass green chemistry and sustainable engineering. This chapter gives a wide glimpse of the scientific success and scientific potential of application of green nanotechnology. Today green nanotechnology is surpassing wide scientific frontiers. The immense visionary scientific and academic rigor of nanoscience and nanotechnology are the forerunners to a greater emancipation of green engineering and green nanotechnology today. Humankind's immense scientific prowess and the progress of science will be opening new windows of scientific innovation and scientific instinct for decades to come. The future perspectives of science are immensely bright and far-reaching [19].

# 1.17 Conclusion and Looking Ahead

The science and engineering of green nanotechnology are moving towards newer knowledge dimensions and are crossing visionary boundaries. Environmental engineering science and environmental sustainability are veritably changing the scientific landscape [17–19]. The future progress of science and academic rigor lies in nanotechnology or green nanotechnology. Technological vision, scientific splendor and futuristic vision are all forerunners to a newer

visionary era in the field of sustainable development and green nanotechnology. Green chemistry, sustainable chemistry and green nanotechnology are challenging the wide scientific panorama today. This chapter gives a wider glimpse of the science of green nanotechnology with a greater emphasis on sustainable development and green engineering. Scientific success, scientific vision and scientific forbearance are changing the face of the pursuit of scientific research today. Chemical process engineering and environmental engineering science veritably need to be reenvisioned and re-envisioned with the progression of scientific history, scientific vision, and time. Scientific fortitude and grandeur are on the path to scientific regeneration today, as this century moves towards a new era of space technology and nuclear science. Today science is a colossus with a wide and definite vision and stature of its own. Technological validation and scientific profundity need to be restructured with the definite vision of nanotechnology, green engineering, and environmental engineering science today. The scientific success and scientific splendor of nanotechnology will surely bear new and definite fruits with the progress of scientific and academic rigor. The challenge of green nanotechnology is just as immense and far-reaching. The targets of science and the immense success of nanotechnology applications will surely open windows of innovation for the furtherance of science in years to come.

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# The second part Green Synthesis of Metal-Based Nanoparticles and Their Applications

#### **2.1 Introduction**

The field of nanotechnology is one of the notable active analysis areas in modern materials science [1, 2]. Nanoparticles reveal new or amended properties that are supported with characteristics like size, distribution, and morphology. There have been enormous advancements in the arena of nanotechnology within recent years related to the synthesis of nanoparticles with specific size and morphology that are reckoned for specific needs [3]. The extensive practical application of nanoparticles (NPs) (particles having single or more lengths less than 100 nm) is attributed to their numerous rare, exceptional, and fascinating characteristics which are appreciated over their bulk correspondents [4-6]. The main task is to improve specific approaches to synthesize noble NPs of definite size, specific shape, desired composition, and well-ordered dispersity that influence their physical, chemical, catalytic, optical, magnetic, electronic, and electrical properties making them ideal candidates for environmental, biomedical, and biotechnological applications [7–9]. The synthesis of biofunctional nanoparticles is extremely vital, and it has recently caught the attention of diverse analysis teams, creating a perpetually evolving space [10–13]. To address the growing demand for eco-friendly nanoparticles, researchers have utilized inexperienced strategies for the synthesis of varied metal oxide nanoparticles for pharmaceutical applications [14, 15]. There is an enormous number of physical, chemical, biological and hybrid procedures which are now usually used to fabricate different types of NPs with the preferred characteristics [14–18]. The synthetic procedures for NPs are listed in Figure 2.1. Usually, the physical and chemical techniques are applied extensively but the physical techniques to synthesize NPs are highly expensive; however, the chemical techniques are detrimental to the environment and living organisms [19-21]. Development of these synthesis techniques for large-scale production is restricted due to the high production costs resulting from unexpected energy consumption, use of noxious organic solvents, fabrication of precarious intermediates and creation of harmful waste products, resulting in environmental contamination and numerous biological hazards. Mostly aqua chemical synthesis of nanoparticles is prevalent amongst several fabrication procedures. Agglomeration or aggregation generally come about during synthesis due to the occurrence of attractive forces among the nanoparticles. Therefore, it is necessary to add some capping agent to avoid aggregation and to achieve the desired morphology of product. Figure 2.1 shows the classification of different NP synthesis techniques. Besides being contaminants of nature, various other problems also accompany these techniques for instance, slow production rate, inadequate growth, and distorted structure of synthesized NPs. Size reduction may also lead to increased reactivity and toxicity of synthesized material. Hence, prior to the wide-scale implementation of these reactions, it is essential to predict the prospective hazards to the eco-system by making an allowance for the entire chemical process relating to all the species involved during the reaction mechanism.



Figure 2.1 Classification of different NP synthesis methods.

The advancement, development, and application of nanocolloids in medicine can present a whole new opportunity for the diagnosis and treatment of different diseases [22]. Furthermore, the utilization of poisonous, harmful chemicals, along with other biological consequences, has considerably restricted biomedical applications of nanomaterials, particularly in clinical fields [23]. These conditions have elevated an increasing ultimatum to inaugurate alternative reliable, nonhazardous, and eco-friendly technologies to produce NPs to expand their applications [24–26]. The restricted use of toxic precursors subsequently decreases the quantity of impurities and byproducts, ensuing in cost effectiveness and the fabrication of desired products in high yields with no biological danger [7, 27]. There are several options to attain the goals presented in Figure 2.2. Previous reports cite the usage of microorganism, such as bacteria [28], algae [29], yeast [30] and fungi [31], for the biosynthesis of NPs. Lately, numerous plant extracts [7, 11, 32–48, 49–114], diatoms [115, 116] and human cells [117] have been shown to be innovative resources for their capability to produce safe and nontoxic nanoparticles, including iron, cobalt, gold, silver, platinum, iron oxide, zinc oxide alloys, sulfides, quantum dots, etc. During the green synthesis of NPs, products from nature or those imitative of natural products have been used as reducing and capping agents. The methods involved are typically simple, environmentally friendly, and naturally compatible one-pot processes. It has been proved by various studies that the reductive abilities of the proteins and metabolites that are present in these biological systems can change inorganic metal ions into metal NPs [118–121]. Figure 2.3 shows a basic schematic diagram of the mechanism of green synthesis by using plant extracts. This chapter highlights the recent research activities that focus on the green synthesis of inorganic NPs that have benefits over conventional methods containing chemical agents that are associated with poisoning the environment. In this chapter, we examine the conventional synthetic techniques with an emphasis on recent advancements of greener routes in order to fabricate metal, metal oxides and other important NPs; followed by a discussion of formation mechanisms and the conditions used to control the surface morphology,



Figure 2.2 Various natural resources used to synthesize green NPs.



Figure 2.3 Green synthesis mechanism.

dispersity and other properties of these biosynthesized NPs. These green synthesized NPs are employed in various areas of nanomedicine, chemistry, and related fields for use in drug carriers for targeted delivery, antimicrobial agents, DNA investigations, biosensors, catalysts, separation science, cancer treatment, gene treatment and magnetic resonance imaging. This chapter concludes by focusing on the existing margins and future projections relating to nanoparticle fabrication through different green routes.

# 2.2 Green Synthesis Was Mediated by a Botanical Extract

Green plants have shown competency to soak up, hyperaccumulate and reduce inorganic metallic ions from their surroundings [122, 123]. It is now acknowledged that numerous organic entities existent in plant tissues can perform as efficient biological factories to considerably lessen environmental contamination. Moreover, amalgamations of molecules found in plant extracts can behave as both reducing and stabilizing (capping) agents, all within nanoparticle synthesis [120, 121, 124]. Some of the essential and abundant phytochemicals of plants are listed in Figure 2.4. Nanoparticles attained from plant extracts are prepared from living plant extracts. Plant parts like leaf, root, latex, seed, and stem are widely being used for metal- and metal oxide-based NP synthesis. Figure 2.4. shows important bioreductants found in plant extracts are bioactive polyphenols, proteins, phenolic acids, alkaloids, sugars, terpenoids, etc., which are primarily composed to play a major role in relegating the metallic ions and then alleviating them [125, 126]. The discrepancy in concentration and conformation of these active biomolecules among different plants and their consequential association with aqueous metal ions are assumed to be the main supporting factor in the various sizes and shapes of fabricated nanoparticle [127].



Figure 2.4 Important bioreductants found in plant extracts.

The synthesis of NPs by metal salt reduction through plant extracts is a moderately facile ambient atmosphere action. The working process is incredibly simple. At room temperature, the plant extract and the solution of metal salt are mixed well [128]. The reaction is fulfilled within a few

minutes. When the solutions of precursor combine, biochemical reduction of the salt instantly starts and the production of nanoparticles is typically shown by a transformation in color of the reaction solution. A flow chart showing the green synthesis procedure is shown in Figure 2.5. The synthesis of plant-mediated green NPs can be divided into three stages: activation phase, growth phase and termination phase [129, 25, 130]. The activation phase is the primary stage in which the metal ions are recuperated from their salt precursors through the action of plant metabolites; biomolecules which have reduction abilities. The metal ions are altered from their mono- or divalent oxidation states to zero-valent states, then nucleation of the condensed metal atoms takes place [131]. This is followed by the growth period in which the seceded metal atoms coalesce to form metal NPs though more biological reduction of metal ions taking place. Laterally with the growth progression, nanoparticles collect to form a variety of morphologies like cubes, spheres, triangles, rods, hexagons, pentagons, and wires [132]. The growth stage rises in enhanced thermodynamic stability of NPs whereas the extensive nucleation may result in aggregation of synthesized NPs, altering their morphologies. The last step in green NP synthesis is the termination phase. The NPs ultimately get their most keenly promising and stable morphology when capped by plant metabolites. The working mechanism of greener biosynthesis by plants is displayed in Figure 2.6. Numerous properties of the solution mixture like metal salt concentration, concentration of plant extract, reaction solution pH, etc., and other reaction conditions like reaction time and temperature have extensive impacts on the size, morphology, and quality of the synthesized nanoparticles [43, 133–136]. The pH approximation of reaction mixture has a great effect on the composition of NPs [137–139]. The pH amendment leads to the charge alteration in the plant metabolism and even affects its capacity to chelate and reduce metal ions during the process, which alters the dimensions, morphology, and yield of synthesized NPs. Several plant metabolites vary in their nature and decrease capabilities from one another. This may also influence the NP synthesis process; for example, tryptophan and amino acids like tyrosine, arginine, and lysine are the most influential reducing agents amongst all the phytochemicals and therefore can decrease a huge amount of metal ions in less time. Temperature is also an essential parameter to influence properties of NP during synthesis [140, 42, 141–143]. High temperature improves certain crystallinity of synthesized NPs using improved rates of nucleation. The NP synthesis also



Figure 2.5 Flow chart of green biosynthesis.

ensures metal ion potential. Metal ions which have higher electrochemical potentials are likely to be further condensed by plant phytochemicals [144]. For example, Ag<sup>+</sup> has better ionizing potential than Au<sup>+</sup> because of its lesser size and therefore will be condensed sooner. Greener synthesis is economical, eco-friendly, sustainable, simple, and relatively reproducible. Regarding these intriguing properties, plants have been ascertained to be an eco-friendlier alternative as biologically synthesizing metallic nanoparticles and for detoxification applications [122, 145]. The biosynthetic method is uncertain and offers high-yield nano-sized materials having good crystalline conformation and appropriate properties. However, high calcination temperature is required to eradicate the precursor to form crystalline materials.



Figure 2.6 Green synthesis mechanism.

## 2.2.1 Botanical Extract and Green Metal Nanoparticles

Many scientists have synthesized metallic NPs by using broth of different parts of many plants, for instance the leaf extract of Aerva lanata [56], Hibiscus rosa sinensis [87], Chenopodium album leaf extract [43], Jasminum sambac Leaves [112], Murraya koenigii [89], Krishna tulsi [86], Mentha piperita [75], Lansium domesticum fruit peel [99], mushroom extract [85], seed aqueous extract of Pistacia atlantica [96], tea leaf extract [103], Sacha inchi (Plukenetia volubilis) leaf extracts [64], Eucommia ulmoides bark aqueous extract [48], Tephrosia purpurea leaf extract [32], Ziziphus jujuba leaf extract as a stabilizing and minimalizing agent at room temperature [45], seed extract of Curcuma pseudomontana [76], Abelmoschus esculentus [53], Cinnamomum zeylanicum leaf broth [100], Geranium [95], grape waste [61], fruit extract of Hovenia dukis [40], maple leaf pine needle [60], Magnolia kobus [101], Mangifera indica [90], Phoenix dactylifera [114], Pistacia integerrima [50], Pogostemon benghalensis (B) O. Ktz. leaf [84], Morinda citrifolia [102], Solanum nigrum [79], Stachys lavandulifolia Vahl [38], Terminalia arjuna [46], Zingiber officinale extracts [66], Vitex negundo [172], ethanolic extract of petals of Rosa indica [173] and from Prosopis juliflora leaf extract [174]. Among these NPs, gold and silver NPs are cited extensively due to their potential applications in diverse fields. Other important green metallic NPs include iron, copper, palladium, and lead. Green metal NPs prepared by various plant extracts are summarized in Table 2.1. Pure crystalline and spherical green AgNPs fabricated by using seed aqueous extract of Pistacia atlantica confirmed high surface area with 27 nm average size. The growth of NPs stopped after 35 minutes and the reaction was accomplished [96].

S. no.				Size	
	Microbial culture	NP's	Morphology	(nm)	Ref.
1.	Aspergillus flavus	Ag	Spherical	8.92	[197]
2.	Aspergillus fumigatus	Ag	Spherical	5–25	[198]
3.	Aspergillus terreus	Ag	Spherical	1–20	[199]
4.	Bacillus cereus	Ag	Spherical	4–5	[200]
5.	Bacillus licheniformis	Ag	Irregular	50	[201]
6.	Brevibacterium casei	Ag	Spherical	10–50	[202]
7.	Cladosporium cladosporioides	Ag	Spherical	10–100	[203]

8.	Coriolus versicolor	Ag	Spherical	25–75	[204]
9.	Corynebacterium glutamicum	Ag	Irregular	5–50	[205]
10.	Escherichia coli	Ag	Irregular	50	[206]
11.	Fusarium oxysporum	Ag	Spherical	5–50	[207]
12.	Fusarium oxysporum	Ag	Irregular	5–15	[208]
13.	Fusarium oxysporum	Ag	Spherical	20–50	[209]
14.	Fusarium semitectum	Ag	Spherical	10–60	[210]
15.	Macrophomina phaseolina	Ag	Spherical	5-40	[211]
16.	Penicillium fellutanum	Ag	Spherical	5–25	[212]
17.	Penicillium nalgiovense	Ag	Spherical	25 ± 2.8	[213]
18.	Pediococcuspentosaceus	Ag	Irregular	< 100	[214]
19.	Phaenerochaete chrysosporium	Ag	Pyramidal	50-200	[215]
20.	Phoma glomerata	Ag	Spherical	60–80	[216]
S. no.	Microbial culture	NP's	Morphology	Size (nm)	Ref.
21.	Pleurotus sajor-caju	Ag	Spherical	30.5	[217]
22.	Trichoderma reesei	Ag	Spherical	5-50	[218]
23.	Trichodermaviride	Ag	Spherical	5–40	[219]
24.	Trichodermaasperellum	Ag	Spherical	13–18	[220]
25.	Trichodermaviride	Ag	Spherical	5–40	[219]
26.	Trichodermaviride	Ag	Irregular	2–4	[221]
27.	<i>Verticillium</i> sp.	Ag	Spherical	5-50	[207]
28.	Yeast	Ag	Irregular, Polygonal	9–25	[38]
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29.	Aspergillus oryzae var. viridis	Au	Mostly Spherical	10–60	[222]
30.	Aspergillus niger	Au	Spherical	12.8± 5.6	[223]
31.	Aspergillus niger	Au	Polydispersed	10–20	[224]
32.	Aspergillus sydowii	Au	Spherical	8.7– 15.6	[225]
33.	Alternaria alternata	Au	Spherical, Triangular	$12 \pm 5$	[226]
34.	Aspergillus clavatus	Au	Triangular, Spherical	24.4± 11	[227]
35.	Aureobasidium pullulans	Au	Spherical	$29 \pm 6$	[228]
36.	Brevibacterium casei	Au	Spherical	10–50	[202]
37.	Candida albicans	Au	Monodispersed, Spherical	5	[12]
38.	Candida albicans	Au	Spherical	20–40	[229]
39.	Candida utilis	Au	Irregular	< 100	[230]
40.	Colletotrichum sp.	Au	Spherical	8–40	[231]
41.	Coriolus versicolor	Au	Spherical	20–100	[232]
42.	Cylindrocladium floridanum	Au	Spherical	19.05	[233]
43.	Cylindrocladium floridanum	Au	Spherical	5–35	[234]
44.	Epicoccum nigrum	Au		5–50	[235]

The silver NPs with distorted cubic shape and a mean size of 60 nm, prepared using a Sachainchi (SI) oil, showed high stability and crystalline morphology [63]. It is suggested that carbonyl groups present in SI oil were responsible for AgNPs production by reducing the AgNO3 precursor. The

synthesized AgNPs showed enhanced photodegradation capabilities for MB degradation in the absence of any other reducing agent. Spherical AgNPs possessing diameter ranging between 4 to 25 nm synthesized by using Sacha inchi leaf extract, a nontoxic reducing agent, showed radical scavenging activity when DPPH was added into the reaction solution [64]. Carbonyl groups of SI played a significant reduction role during the synthesis process. Synthesized NPs showed significant antioxidant efficacy in comparison with SI leaf extracts against 1,1-diphenyl-2picrylhydrazyl. Spherical AgNPs with size ranging from 20 to 90 nm were prepared using leaf extract of tea [103]. The FTIR spectroscopy of tea extract confirmed the presence of poly phenols, amides, carboxyl, and amino groups, which were surely responsible for AgNO3 reduction and AgNPs stabilization through surface bonding. Silver ion released from the synthesized AgNPs showed a good stability in terms of time-dependent release of silver ions. Tephrosia purpurea leaf extract is used to synthesize highly crystalline silver NPs with approximate size of 20 nm [32]. The biomolecules, flavonoids, proteins, amino acids, tannins, alkaloids and rotenoids present in the leaf extract were found to play a dual role of both reducing as well as capping agents for the formation of AgNPs. FTIR analysis showed asymmetric and symmetric stretching peaks of COO-(carboxylate group), indicating that AgNPs were bound to proteins through carboxylate groups. It is suggested that flavonoids were responsible for the metal salt reduction while the carboxylate group acted as surfactant to stabilize the synthesized AgNPs. The obtained NPs were found to have good inhibitory activity towards Pseudomonas and Penicillium spp. compared to other test pathogens using standard Kirby-Bauer disc diffusion assay. Biogenic crystalline AgNPs with facecentered cubic (fcc) structure were produced using Ziziphus jujuba leaf extract as a stabilizing and reducing agent at room temperature [45]. Nanoparticles obtained were of different shapes with diameter ranging between 20-30 nm. The hydrodynamic size of 28 nm is found from dynamic light scattering (DLS) data having high stability in a colloidal state. The FTIR analysis of Z. jujuba leaf extract confirmed the presence of bands corresponding to carboxyl groups, intermediate form of phenolic groups, proteins, and carbohydrates, which were shifted after the completion of reaction, showing the involvement of bioreductants in AgNPs preparation. UV analysis of AgNPs showed that the intensity of absorption band in visible range (434 nm) increases with an increase in the quantity of extract, with the optimized quantity of extract being 1.5 mL for 100 mL of AgNO3 (0.001 M). Moreover, the study of the effect of medium pH on synthesized particles indicated wider bands displaying red shift at acidic pH due to an increase in particle size, while at basic pH a decrease in particle size was demonstrated by band narrowing and blue shift. Ionization of phenolic groups in neutral and basic pH ensured rapid formation of AgNPs and the rather slow formation of aggregated particles in acidic medium is attributed to electrostatic repulsion of anions, concluding that optimum condition for synthesis of AgNPs is neutral pH because AgOH precipitation may occur at basic pH. Synthesized AgNPs showed high catalytic activity towards

the reduction of anthropogenic pollutant 4-nitrophenol (4-NP) to 4-AP and MB within shorter reaction time and exhibited good antimicrobial activity against Escherichia coli. Well-dispersed fcc-centered AgNPs having a diameter less than 20 nm were obtained through a biosynthetic route from aqueous silver nitrate using water extract of Vitex negundo leaves as a stabilizer and reducing agent [172]. FTIR peaks of V. negundo extract confirmed the presence of bioreductants, such as flavonoids, phenolic hydroxyl groups (friedelin, lupeol, and β-sitosterol groups) and C-H in the aromatic stretching, associated with the phenolic ring. AgNPs synthesized with the use of ethanolic extract of rose (Rosa indica) petals exhibited effectual antibacterial activity against Gram-negative (Klebsiella pneumoniae, Escherichia coli) as compared to Gram-positive (Enterococcus faecalis, Streptococcus mutans) bacteria [175]. Analysis of nuclear morphology, MTT assay, protein expression of caspase 3 as well as 9, Bax and mRNA expression of Bcl-2 showed potential anticancer activity. These AgNPs also reduced nuclear morphology, cytotoxicity, and free radical generation (NO and O-2) in rat peritoneal macrophages in vitro. Synthesis of AgNPs with size range from 11 to 19 nm using an aqueous extract of fresh leaves of Prosopis juliflora was reported by Raja et al. [176]. The synthesized silver nanoparticles were triangular, tetragonal, pentagonal, and hexagonal in structure. Phytochemical analysis of P. juliflora leaf broth showed the involvement of some proteins and metabolites, such as terpenoids or flavonoids, in the reduction and capping of AgNPs. A simple microwave-assisted method reported for the green synthesis of gold NPs by the reduction of aqueous metal salt solutions using leaf extract of the medicinal plant Aerva lanata produced particles of crystalline nature, having different morphologies with an average diameter of 17.97 nm, with most particles being in the 10–30 nm range [56]. Soon after the leaf extract addition, metal ions were reduced into atoms of nano-sized range. This reduction was believed to be carried out by various phytochemicals present in plant extract, which further capped them from agglomeration as well. The synthesized NPs were used as nanocatalysts in the reduction of 4-nitrophenol to 4-aminophenol by NaBH4. The reported microwave-assisted process was found to be rapid and thus reduced the aggregation of synthesized NPs, eliminating the major problem in NPs synthesized by greener strategies. Dwivedi and Gopal biosynthesized quasispherical AuNPs retaining a size range of 10–30 nm using the noxious weed Chenopodium album as a natural reagent [43]. The surface plasmon resonance (SPR) for gold NPs was found at 540 nm. Chemical constituents of C. album leaf extract include high concentrations of oxalic acid, (COOH)2. Its dianion, i.e., oxalate, acted as biological reductant. The aldehyde group present in oxalate ion also makes it a good ligand, reducing the particle agglomeration. FTIR analysis confirmed the presence of carbonyl group, which surely performed as reducing agent, while carboxylate ions shielded the nanoparticles, imparting them with stability for several months. The leaf extract of Hibiscus rosa sinensis produced crystalline AuNPs in the fcc structure [87]. It is observed that the AuNPs were bound to amine groups, which are responsible for bioreduction and

stabilization. Gold NPs, both individual and agglomerated, formed by seed aqueous extract of Abelmoschus esculentus showed crystalline nature having spherical morphology with a narrow size range of 45–75 nm [53]. The maximum zone of inhibition in the gold NPs was against Puccinia graminis (17 mm) and Candida albicans (18 mm), while synthesized gold NPs acted as an effective antifungal agent. Cinnamomum zeylanicum leaf broth has been espoused as reducing agent for the fabrication of crystalline gold NPs with diameter of 25 nm [100]. As-synthesized AuNPs have mixed morphologies of spheres and nanoprisms with face-centered cubic crystal structure FCC (111) of gold. The prism-shaped gold nanoparticles were predominant at the lower concentration of the plant extract whereas spherical particles were more likely expected to be found at the higher concentrations. Chemical analysis of C. zeylanicum leaf broth showed the occurrence of several metabolites, such as sucrose, tannin and terpenoids comparable to eugenol and cinnamaldehyde, which are proficient at bioreduction. It has been demonstrated that terpenoids are responsible for metal ion reduction by oxidation of aldehyde group to carboxylic acid, although starch molecules preserved the alienated particles, imparting stability. The grown gold NPs were photoluminescent and the intensity of photoemission was set up to rise with the upsurge in leaf broth concentration. Biologically active spherical AuNPs with an average diameter of 20 nm were formed by using Curcuma pseudomontana extracts [76]. Spherical AuNPs of 18.2 nm average size with FCC structure manufactured by using water extract of Eucommia ulmoides bark showed excellent photocatalytic activity for decolorization of model compounds of azo dyes, Congo Red and Reactive Yellow 179 [48]. The DLS measurements showed greater size due to the presence of the biomolecule envelope around the AuNPs' core. Geranium extracts were used to produce AuNPs having different morphologies with an average homogeneous size of  $12 \pm 3$  nm following Gaussian distribution between 6 and 35 nm [95]. The particles were mostly spherical, while a few were nanorods, pentagonal and triangular (in projection). Gold NPs possessing 15-20 nm average size and having biomedical applications photosynthesized with the help of fruit extract of Hovenia dulcis have also been reported [40]. Molecules present in the fruit extracts reduced the gold metal ions into GNPs due to a change in the color ofwater extracts within 30 min. An immobilization of copper NPs was studied on perlite [81]. The behavior of CuNPs/perlite were very encouraging in the catalytic reduction of 4-nitrophenol. It can also be recycled many times without any reduction in the catalytic activity. The pseudo-first-order reaction equation was used to find the reaction rate constant. Green FeNPs were synthesized using Eucalyptus leaf extracts having some polyphenols, which are responsible for stabilizing and capping iron nanoparticles on the surfaces of Eucalyptus leaf (EL-FeNPs) [111]. The reactivity of EL-FeNPs was calculated for the treatment of swine wastewater. As a result, removal of 84.5% of COD and 71.7% of total N were successfully obtained. Lithium NPs fabricated via green route exhibited a size of nearly 5 nm [35]. The absorption bands were set up at 315 and 415 nm in samples after the formation of NPs. Distinguished Raman band attributed to the vibrational modes in small lithium NPs can be given specifically to RBM in small lithium metallic NPs. A greener method for the synthesis of gelatin/pectin stabilized palladium nanoparticles as an efficient heterogeneous catalyst was carried out in the presence of aryl halide, alkene, n-Pr3N [177]. The products were obtained in highly short reaction times with excellent yields.

#### 2.2.2 Botanical extract and Green Oxide Nanoparticles

Many researchers have reported green synthesis routes for the preparation of metal oxide NPs using distinctive plant broth. The facts are concisely shown in Table 2.2. Monodispersed ceria NPs having 20-40 nm size was synthesized by green method via Gum tragacanth [161]. The NPs displayed strong absorption peak appearing in the UV region and have direct band gap of 3.6 eV. In-vitro feasibility studies with CeNPs on neuro 2A cells exhibited a dose-dependent toxicity, with a nontoxic effect in concentrations lower than 30 m g/mL. The CeNPs synthesized by Gum tragacanth were discovered to be like those gotten by conventional reduction method using perilous polymers or surfactants. Tinospora cordifolia was used to synthesizd cupric oxide NPs having phot-catalytic, antibacterial and antioxidant properties [152]. The particles possess a sponge-like structure and have a large surface area with the average crystallite sizes attained being 6-8 nm. CuO NPs are espoused as good catalyst intended for the efficient degradation of methylene blue (MB) in sunlight and UV. The degradation of MB was brought into pHdependence. The NPs were found to efficiently impede the activity of 1,1-Diphenyl-2picrylhydrazyl (DPPH) free radicaly. CuO NPs showed important bactericidal activity contrary to aerogenes, Escherichia coli, Staphylococcus aureus and Pseudomonas aeruginosa. The magnesium oxide nano-flowers were fabricated by the green method using acacia gum which is further used for the exclusion of divalent metallic species from synthetic waste water [155]. The particle size of acacia gum treated MgO NPs was greater in comparison to untreated n-MgO particles which confirm crust of acacia gum on simple n-MgO.NPs green synthesized by microbes.S. no.Microbial culture NP'sMorphology Size (nm).

S. no.	Microbial culture	NP's	Morphology	Size (nm)	Ref.
1.	Aspergillus flavus	Ag	Spherical	8.92	[197]

2.	Aspergillus fumigatus	Ag	Spherical	5-25	[198]
3.	Aspergillus terreus	Ag	Spherical	1–20	[199]
4.	Bacillus cereus	Ag	Spherical	4–5	[200]
5.	Bacillus licheniformis	Ag	Irregular	50	[201]
6.	Brevibacterium casei	Ag	Spherical	10–50	[202]
7.	Cladosporium cladosporioides	Ag	Spherical	10–100	[203]
8.	Coriolus versicolor	Ag	Spherical	25–75	[204]
9.	Corynebacterium glutamicum	Ag	Irregular	5–50	[205]
10.	Escherichia coli	Ag	Irregular	50	[206]
11.	Fusarium oxysporum	Ag	Spherical	5-50	[207]
12.	Fusarium oxysporum	Ag	Irregular	5–15	[208]
13.	Fusarium oxysporum	Ag	Spherical	20–50	[209]
14.	Fusarium semitectum	Ag	Spherical	10–60	[210]
15.	Macrophomina phaseolina	Ag	Spherical	5-40	[211]
16.	Penicillium fellutanum	Ag	Spherical	5–25	[212]
17.	Penicillium nalgiovense	Ag	Spherical	25 ± 2.8	[213]

18.	Pediococcus pentosaceus	Ag	Irregular	< 100	[214]
19.	Phaenerochaete chrysosporium	Ag	Pyramidal	50–200	[215]
20.	Phoma glomerata	Ag	Spherical	60-80	[216]

(*Continued*)

S.				Size	
no.	Microbial culture	NP's	Morphology	(nm)	Ref.
21.	Pleurotus sajor-caju	Ag	Spherical	30.5	[217]
22.	Trichoderma reesei	Ag	Spherical	5-50	[218]
23.	Trichoderma viride	Ag	Spherical	5-40	[219]
24.	Trichoderma asperellum	Ag	Spherical	13–18	[220]
25.	Trichoderma viride	Ag	Spherical	5-40	[219]
26.	Trichoderma viride	Ag	Irregular	2–4	[221]
27.	Verticillium sp.	Ag	Spherical	5-50	[207]
28.	Yeast	Ag	Irregular, Polygonal	9–25	[38]

29.	Aspergillus oryzae var. viridis	Au	Mostly Spherical	10–60	[222]
30.	Aspergillus niger	Au	Spherical	12.8 ± 5.6	[223]
31.	Aspergillus niger	Au	Polydispersed	10–20	[224]
32.	Aspergillus sydowii	Au	Spherical	8.7–15.6	[225]
33.	Alternaria alternata	Au	Spherical, Triangular	12 ± 5	[226]
34.	Aspergillus clavatus	Au	Triangular, Spherical	24.4 ± 11	[227]
35.	Aureobasidium pullulans	Au	Spherical	29 ± 6	[228]
36.	Brevibacterium casei	Au	Spherical	10–50	[202]
37.	Candida albicans	Au	Monodispersed, Spherical	5	[12]
38.	Candida albicans	Au	Spherical	20–40	[229]
39.	Candida utilis	Au	Irregular	< 100	[230]
40.	Colletotrichum sp.	Au	Spherical	8–40	[231]
41.	Coriolus versicolor	Au	Spherical	20–100	[232]
42.	Cylindrocladium floridanum	Au	Spherical	19.05	[233]

43.	Cylindrocladium floridanum	Au	Spherical	5–35	[234]
44.	Epicoccum nigrum	Au	_	5–50	[235]

S.				Size	
no.	Microbial culture	NP's	Morphology	(nm)	Ref.
45.	Escherichia coli	Au	Triangular, Hexagons	20–30	[236]
46.	Fusarium semitectum	Au	Spherical	10-80	[237]
47.	Fusarium oxysporum	Au	Spherical	2–50	[13]
48.	Fusarium oxysporum	Au	Spherical, Triangular	8–40	[238]
49.	Hansenula anomala	Au	Irregular	14	[239]
50.	Helminthosporium solani	Au	Variable	2–70	[240]
51.	Hormoconis resinae	Au	Spherical	3–20	[241]
52.	Neurospora crassa	Au	Spherical	32	[242]
53.	Penicillium rugulosum	Au	Spherical	20-40	[243]
54.	Pediococcus pentosaceus	Au	Spherical	< 100	[244]

55.	Penicillium brevicompactum	Au	Various	10–60	[245]
56.	Penicillium sp.	Au	Spherical	30–50	[246]
57.	Phanerochaete chrysosporium	Au	Spherical	10–100	[247]
58.	Plectonema boryanum	Au	Octahedral	10–6000	[248]
59.	Plectonema boryanum	Au	Cubic	10–25	[249]
60.	Pseudomonas aeruginosa	Au	Irregular	15–30	[250]
61.	Rhizopus oryzae	Au	Spherical	16–25	[251]
62.	Rhodococcus sp.	Au	Spherical	5–15	[10]
63.	Rhodopseudomonas capsulata	Au	Spherical	10–20	[252]
64.	Saccharomyces cerevisiae	Au	Spherical	15–20	[253]

S.				Size	
no.	Microbial culture	NP's	Morphology	(nm)	Ref.
65.	Sargassum wightii	Au	Planar	8–12	[254]
66.	Sclerotium rolfsii	Au	Spherical	25.2 ± 6.8	[255]
67.	Shewanella algae	Au	Irregular	10–20	[256]

68.	Shewanella oneidensis	Au	Spherical	< 100	[257]
69.	Trichoderma koningii	Au	Spherical	30–40	[258]
70.	Trichoderma koningii	Au	Spherical	10–14	[259]
71.	Ureibacillus thermosphaericus	Au	Irregular	50–70	[260]
72.	Verticillum luteoalbum	Au	Irregular	< 100	[230]
73.	Volvariella volvacea	Au	Triangular, Spherical	20–150	[261]
74.	Verticillium sp.	Au	Irregular	< 100	[262]
75.	<i>Verticillium</i> sp.	Au	Spherical	20 ± 8	[263]
76.	Yarrowia lipolytica	Au	Various	< 100	[264]
77.	Yarrowia lipolytica	Au	Triangles	15	[265]
78.	Yeast	Au	Irregular, Polygonal	9–25	[266]
79.	Neurospora crassa	Au,	Spherical	32	[242]
80.	Escherichia coli	Cd	Spherical	2.0–3.2	[267]
81.	Escherichia coli	Те	Spherical	2.0–3.2	[267]
82.	Enterobacter sp.	Hg	Spherical	2–5	[268]
83.	Desulfovibrio desulfuricans	Pd	Spherical	50	[269]

84.	Fusarium oxysporum	Pt	Variable	70–180	[270]
85.	Shewanella algae	Pt	Irregular	5	[271]
86.	Shewanella sp.	Se	Spherical	< 100	[272]
87.	Pyrobaculum islandicum	U, Tc, Cr, Co, Mn	Spherical	< 100	[273]

S. no.	Microbial culture	NP's	Morphology	Size (nm)	Ref.
88.	Fusarium oxysporum	BaTiO <sub>3</sub>	Spherical	4–5	[274]
89.	Lactobacillus sp.	BaTiO <sub>3</sub>	Tetragonal	20-80	[275]
90.	Shewanella oneidensis MR-1	Fe2O3	Irregular, Rhombohedral	30–43	[276]
91.	HSMV-1	Fe3O4	Bullet-shaped	< 100	[277]
92.	QH-2	Fe3O4	Rectangular	< 100	[278]
93.	Recombinant AMB-1	Fe3O4	Cubo- octahedral	20	[279]
94.	Shewanella oneidensis	Fe3O4	Rectangular, Rhombic, Hexagonal	40–50	[280]
95.	WM-1	Fe3O4	Cuboidal	< 100	[281]
96.	Yeast	Fe3O4	Wormhole- like	< 100	[282]
97.	Yeast	FePO <sub>4</sub>	Nanopowder	< 100	[283]
98.	Bacillus sp.	MnO <sub>2</sub>	Orthorhombic	4.62	[2]
99.	Saccharomyces cerevisiae	Sb2O3	Spherical	2–10	[270]

100.	Fusarium oxysporum	TiO <sub>2</sub>	Spherical	6–13	[284]
101.	Lactobacillus sp.	TiO <sub>2</sub>	Spherical	8–35	[285]
102.	Eukaryotes	Various			[286]
103.	Aspergillus fumigatus	ZnO	Spherical	1.2–6.8	[287]
104.	Aeromonas hydrophila	ZnO	Spherical	57.72	[288]
105.	Fusarium oxysporum	ZrO <sub>2</sub>	Spherical	3–11	[24]
106.	Neurospora crassa	Au/Ag Alloy	Spherical	20–50	[242]
107.	Fusarium oxysporum	Au/Ag Alloy	Spherical	8–14	[289]
108.	Aspergillus tubingensis	Ca3P2O8	Spherical	28.2	[290]

S. no.	Microbial culture	NP's	Morphology	Size (nm)	Ref.
109.	Fusarium oxysporum	CdCO <sub>3</sub>	Spherical	120– 200	[291]
110.	Candida glabrata	CdS	Irregular	< 100	[292]
111.	Coriolus versicolor	CdS	Spherical	100– 200	[293]
112.	Escherichia coli	CdS	Wurtzite	2–5	[294]
113.	Fusarium oxysporum	CdS	Spherical	5–20	[295]
114.	Fusarium oxysporum	CdS	Irregular	< 100	[296]
115.	Lactobacillus	CdS	Spherical	4.9	[297]
116.	Rhodobacter sphaeroides	CdS	Hexagonal	8	[298]

117	Dhadansaudamanas	CdS	Cubic	8	[299]
11/.	Rhodopseudomonas palustris	Cus	Cubic	0	[299]
118.	Schizosaccharomyces pombe	CdS	Irregular	< 100	[292]
119.	Schizosaccharomyces pombe	CdS	Spherical	1.8– 2.9	[300]
120.	Schizosaccharomyces pombe, Candida glabrata	CdS	Hexagonal	2	[300]
121	Schizosaccharomyces pombe	CdS	Hexagonal	1– 1.5	[301]
122.	Yeast	CdS	Spherical	3.6	[297]
123.	Fusarium oxysporum	CdSe	Spherical	9–15	[208]
124.	Aspergillus oryzae TFR9	FeCl <sub>3</sub>	Spherical	10– 24.6	[302]
125.	Prokaryotes	Fe3S4	Irregular	< 100	[303]
126.	Bacteria	FeS	Spherical	2	[304]
127.	Fusarium oxysporum	PbCO <sub>3</sub> ,	Spherical	120– 200	[291]
128.	Magnetotactic bacterium	Polyphosphate	Rectangular	< 100	[305]

Adsorption studies showed that nanoflowers are accomplished at efficiently eliminating Co (II), Cd (II), Zn (II), Cu (II), Mn (II), Pb (II) and Ni (II) from synthetic wastewater. Spherical magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles (SMNPs) having inverse spinel cubic structure were fabricated using *Syzygium cumini* seed extract, which is a safe and eco-friendly fruit waste material [170]. The hysteresis loop of Fe<sub>3</sub>O<sub>4</sub> NPs showed an exceptional ferromagnetic behavior with a saturation magnetization value of 13.6 emu/g.

## 2.3 Green Synthesis Through Microbial Extracts

Microorganisms, both unicellular and multicellular, have been widely reported as remarkable candidates for biological synthesis [178]. Studies include formation of nanoparticles by using

algae, viruses, bacteria, yeast, and fungi, as presented in Table 2.2. In fact, the microbes reduce metal ions to form water-insoluble complexes in order to defend themselves from their toxicity. Hence, microorganisms possess the ability to produce organic/inorganic composites of varying size and shape with ordered structures through detoxification of target ions by using several biopolymers generated in them, due to various cell activities [179, 181]. Various reducing agents excreted by microbes are given in Figure 2.7. As different microbes follow different routes for nanoparticle formation, the definite reaction mechanism is not yet fully understood [182, 184]. Generally, the biopolymer, excreted by microbes, capture the metal ions from metal salts and convert them to their elemental form [24, 185, 186]. The microbial reduction can be attained either extracellularly or intracellularly through bioaccumulation, precipitation, biomineralization or biosorption [187, 190]. In extracellular synthesis reduction occurs on the surface of the microbial cell. The electrostatic interaction causes metal



Figure 2.7 Reducing agents involved in microbial synthesis

cations to attach with negatively charged enzymatic groups present at the cell wall where reduction takes place [191]. On the other hand, the intracellular mechanism involves the trapping of metal ion on the microbial cell and then reducing it in the presence of enzymes [192, 193]. The synthesis process consists of making microbial extract, mixing it with a metal salt solution of definite concentration, and providing the optimal temperature and pH to the reaction mixture; the completion of the reaction is indicated by a change in color of the reaction mixture. The microbial extract preparation involves development of the desired test strain in suitable media. Liquid or solid media may be chosen according to the microorganism. Typically, the test strain is taken from microbial suspension and poured into a sterilized test tube or Petri dish. Either the molten media

is spread over the test strain or the test strain is spread over solidified media. It is then incubated in an orbital shaker at optimum temperature and centrifuged. In the case of a unicellular organism, supernatant is used as microbial source. But in the case of various multicellular organisms, supernatant is discarded and the developed biomass is washed thoroughly with distilled water several times and wet biomass is then treated as microbial culture. The prepared microbial culture is exposed to metal salt solution and incubated on an orbital shaker at required temperature until a visible color change is recorded, which ensures the formation of nanoparticles. The formation of silver, gold, manganese and zinc nanoparticles isspecified by the generation of a brownish, pinkish and whitish yellow to yellow color in the solution mixture respectively. Usually the nanoparticle synthesis is influenced by microbes in two distinctive ways. Firstly, the existence of microbes along with secreted enzymes alters the composition of the reaction mixture, making it more saturated. Secondly, the enzymes secreted by microbes either favor or inhibit nucleation of the initial particles formed [194, 195]. Both factors greatly affect the biosynthesis yield [196]

## 2.3.1 Microbes using Green Metal NPs

of metal Up till now, various studies have been reported demonstrating the production However, studies focusing on the nanoparticles using fungi, algae bacteria and other microbes. greater in number due to their vast applications in various formation of silver and gold NPs are fields.

# 2.3.1.1 Silver NPs

A fungus, *Aspergillus flavus*, was found to contain several peptides which can reduce Ag<sup>+</sup> ions to Ag<sup>0</sup> by extracellular process [197]. NPs were formed over the cell wall of fungal biomass. Fluorescence spectrum confirmed the presence of NADH-dependent reductase and similar peptides in the colloidal solution covering as-prepared AgNPs [309]. These proteins excreted by fungus acted as stabilizing and reducing agents for the Ag NP synthesis. *Aspergillus niger* was found to follow an extracellular route to form highly stable silver NPs. Elemental spectroscopic analysis revealed that quinone and nitrate-dependent reductase excreted by *A. niger* played the role of capping and chelating agents to produce silver NPs [310]. Silver NPs were fabricated using the fungal proteins of *Coriolus versicolor*. FTIR analysis revealed that the AgNPs were entirely capped by amino groups during the synthesis, hence enhancing the stability of the product. Glucose also plays an important role in the synthesis process. By tailoring the synthesis parameters, growth time could be lowered to 1 h. Moreover, an intracellular synthesis route could also be developed for AgNP synthesis by altering the reaction mixture pH [311]. *Fusarium oxysporum* is found to have the ability to grow AgNPs by hydrolyzing AgNO3 solution [284]. It is reported that *F. oxysporum* can establish highly stable hydrosol of AgNPs [208]. Kumar *et al.* 

prepared silver NPs having dimensions of 10–25 nm by incubating AgNO3 with F. oxysporum [312]. In-vitro analysis confirmed that nitrate reductase along with phytochelatin was responsible for silver ions reduction and stabilization. In another study it is suggested that anthraquinones and nitrate dependent reductase enzymes present in F. oxysporum reduced Ag ions to form silver NPs [209]. The UV-Vis spectrum of silver NPs synthesized extracellularly by Fusarium semitectum showed clear enhancement in the intensity of plasmon resonance peak (centered at 420 nm) with the passage of time [210]. The NPs in suspension were found to be capped by amino groups and other peptides, which are believed to be accountable for the accumulation of NPs. Fusarium solani is reported to produce sphere-shaped AgNPs having average size of 16.23 nm. FTIR studies indicated the presence of peptides bound to the surface of NPs which surely acted as stabilizing and reducing agents to form poly-dispersed AgNPs [313]. Rhizopus stolonifera, upon exposure to AgNO3, manufactured uniform AgNPs of 25-30 nm size [222]. Silver NPs were harvested intracellularly by incubation of Verticillium sp. with AgNO3 solution [263]. Pseudomonas stutzeri AG259 bacteria is found to precipitate 35 to 46 nm sized AgNPs intracellularly [314]. By increasing the concentration of metalion solution, particle size of AgNPs reaches 200 nm [25]. The increase in particle size is surely due to the change in growth mechanism. Morganella sp. RP-42 bacterium, separated from an arthropod, extracellularly produced 20 nm sized Ag NP crystals when reacted with AgNO3solution [315]. A silver reductant protein was found responsible for the formation of AgNPs. The study enlightens the mechanism of AgNP synthesis, as the found protein displayed an almost exactly similar structure with formerly reported protein silE. A rapid synthesis of AgNPs is reported using the microbial extract of Enterobacteriaceae (Klebsiella pneumonia, Escherichia coli and Enterobactercloacae) [316]. The study demonstrated a decrease in reduction process when piperitone is added, indicating that nitroreductase protein is responsible for silver ion accumulation. Dehydrated eatable blue green alga Spirulina platensis produced spherical AgNPs with size ranging from 6–10 nm [317]. The synthesis processfollowed extracellular route. The nucleotides secreted by alga capped andreduced Agions to AgNPs. Sphere-shaped AgNPs with mean diameter of about 13 nm werereported by using an aquatic red alga Porphyra vietnamensis [318]. A carbohydrate secreted by alga was incubated with AgNO3 solution to formAgNPs. FTIR analysis demonstrated the loss of sulphate groups present on carbohydrate, confirming that sulphate groups are responsible for the reduction and stabilization of AgNPs. Chlorella vulgaris was used to synthesize nanosilver platelets [319]. The chemicals secreted by alga acted as capping and reducing agents for the synthesis of Ag nanoplatelets. It is reported that a nucleotide Asp–Asp– Tyr–OMe was involved in the biological reduction of Ag ions.

2.3.1.2 Gold NPs

Uniform and spherical gold NPs were reported using extract of filamentous fungus Rhizopus stolonifera (KCCM 35486). AuNPs with 1-5 nm size was verified by transmission electron microscopy (TEM) and X-ray diffraction (XRD) spectra. Another study showed the synthesis of AuNPs by subjecting gold thiosulphate solution to sulphate-reducing bacteria [320]. Verticillium luteoalbum was found capable of forming AuNPs when subjected to Au cations. Gold NPs were formed as a purple black ppt, which is centrifuged to get purified NPs. The analysis confirmed the formation of AuNPs. AuNPs of desired size, shape and yield could be obtained by controlling the pH of reaction mixture [180]. AuNPs were successfully prepared by incubating Fusarium oxysporum extract with gold chloride solution. The in-vitro synthesis study showed the existence of reductase and peptides in the colloidal suspension as well as bound to the surface of AuNPs, which accounted for the formation and stabilization of gold NPs [238]. Intracellular gold NPs were formed when Verticillium sp. extract was incubated with gold ion solution. Purple ppt formed in the mycelium was thoroughly washed and characterized. The UV-Vis spectra displayed absorption peak at 550 nm, confirming the production of AuNPs [263]. Octahedral platelets of AuNPs were prepared by subjecting cyanobacteria (Plectonema boryanum UTEX 485) to gold chloride solution. The study showed that the reaction was completed in two steps. Gold sulfide NPs were first developed near the cell walls of bacteria, which were then converted to AuNPs. Chloride ions present in the reaction mixture seem to enhance the bioaccumulation of AuNPs [248]. Plectonema boryanum UTEX 485 produced intracellular AuNPs when challenged with gold thiosulphate complex. AuS NPs were also found along with AuNPs. Cubical AuNPs showed a size ranging between 10-25 nm in suspension and 10 nm inside bacterium. With the addition of gold chloride, octahedral platelets of AuNPs were obtained having size ranging from 1-10 µm [316]. Sargassum wightii Greville, an aquatic alga, transformed AuCl4 anions into gold NPs [254]. The formation of AuNPs was possible due to the extracellular carbohydrate secreted by alga. The reaction almost completed in 12 h, which is much faster than other synthesis routes involving microbes. TEM images revealed monodispersed planar AuNPs having a diameter of about 8-12 nm. A dehydrated green alga named Chlorella vulgaris is reported to form AuNPs [321]. Both intracellular and extracellular proteins created by single- celled alga performed as capping and reducing agents for the synthesis of AuNPs. The process showed high yield. TEM analysis indicated tetrahedral, decahedral, and icosahedral morphologies of synthesized AuNPs. Another study demonstrated that 28-kDa protein secreted by C. vulgaris is responsible for various morphologies of gold NPs [224]. Triangular, hexagonal, and platelike AuNPs were accumulated by varying the concentration of 28kDa protein. Micro-sized AuNPs were precipitated in the biomass of a brown alga called Fucus vesiculosus [322]. Reaction was accomplished at intense pH values. The hydroxyl groups contained by various carbohydrates and nucleotides secreted by F. vesiculosus were responsible for the whole reduction process. Brown alga shows promising results for NP formation in

comparison with other algae [323, 324]. Extracellular proteins secreted by *Spirulina platensis*, blue green alga, are found capable of reducing gold ions present in solution. Dehydrated *S. platensis* formed stable sphere-shaped AuNPs with size ranging from 7 16 nm [317].

# 2.3.1.3 Additional Metallic NPs

A fungus, *Aspergillus terreus*, is reported to extracellularly harvest spherical Se NPs having average diameter of about 47 nm in about 1 h [325]. It is a relatively fast process as compared to other biological synthesis protocols. Spherical crystalline Pt NPs, having size ranging from 3–4 nm, were obtained by consuming the extract and biomass of a fungus, *Neurospora crassa* [326]. The comparative study demonstrated that Pt NPs formed extracellularly, i.e., obtained from *N. crassa* biomass, showed more agglomeration than intracellularly produced Pt NPs. Also, the product yield of both the routes varies intensely. *Fusarium oxysporum* has been reported to produce Vanadium (V)[327]. *Fusarium moniliforme* has the ability to transform ferric ion Fe(III) to ferrous ion Fe(II) [328]. An alga, *Chlorella* sp., was explored for its ability to reduce and stabilize numerous metals like copper, cadmium, nickel, and uranium [329, 330]. An aquatic alga, *Sargassum wightii*, was reported to form palladium and platinum NPs when incubated with their corresponding metal chlorides [254].

# 2.3.2 Microbes through Green Oxide NPs

Silica, titania, zinc oxide, manganese dioxide, magnetite and other metal oxides have been synthesized using various microbes, including fungi, bacteria, algae, viruses, etc. Some of those reported are discussed below. Barium titanate NPs having tetragonal morphology and average size of 10 nm were reported by using Fusarium oxysporum extracts [274]. Another similar approach displayed the formation of nanocrystalline silica and titania NPs upon subjecting Fusarium oxysporum to corresponding ions in aqueous solutions. F. oxysporum is found to excrete various cationic proteins which can hydrolyze ZrF4- ions [331]. Zirconia NPs were formed extracellularly at ambient temperature in aqueous medium. Excreted proteins having a molar mass of 21-24 kDa were capable of hydrolyzing precursor halides in acidic medium [284]. F. oxysporumand *Verticillium* sp. are used to produce magnetite Fe3O4 NPs [332]. Magnetite NPs were fabricated by incubation of *Verticillium* sp. Extract with iron cyanide complex solution. An extracellular cationic protein secreted by fungus capped and reduced iron cyanide ions into iron oxide NPs. The reducing protein was found to have a molar mass of 55 kDa [332]. A bacterium, Saccharomyces cerevisiae, was used to form Sb2O3 NPs at ambient temperature [333]. TEM micrographs demonstrated agglomerated sphere-like Sb2O3 NPs with 2-10 nm diameter. Manganese dioxide NPs were reported by using Bacillus sp. [2]. TEM micrographs revealed monodispersed NPs with 4.62 nm diameter and orthorhombic morphology. The metal-resistant bacterium possesses several proteins capable of reducing and stabilizing the synthesized product.

# **2.4 Conclusions**

The advent and execution of innovative technologies and development of scientific cognizance has cleared the way towards a newly revolutionized nano-age. In this nano-age, biological entities are employed for the synthesis of stable NPs, with significant consideration explicitly being given to economically integrated, effortlessly scaled-up and ecologically considerate biocompatible NPs. Rapid biological reducing agents present in *bio*resources, such as global and marine microbes and plants, possess huge potential for biogenic synthesis of NPs. Among the above-mentioned entities, plants have emerged as the best candidates, due to their being abundant and easy to handle character. Green strategies utilize inexpensive harmless chemicals, eco-friendly solvents and renewable materials and occur at neutral pH close to ambient temperature and pressures. Green principles provide cleaner, safer, simpler, and controllable alternatives for the synthesis of NPs with desired characteristics, imparting greater importance to them for more effective utilization in diverse fields. Accelerating the investigations of green routes using living beings, natural resources or conditions will oustordinary traditional methods by overcoming their limitations. Hence, the present chapter envisions the importance of green metals, and metal oxide, NP fabrication schemes by referring to several reports stated so far. With the enormous variety of natural resources available, many additional species are in line to be explored for prospective use.

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