NANOMATERIALS: AN APPROACH TOWARDS ENVIRONMENTAL REMEDIATION

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Nanomaterials: An Approach Towards Environmental Remediation

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ISBN (Online): 978-981-5223-61-3

ISBN (Print): 978-981-5223-62-0

ISBN (Paperback): 978-981-5223-63-7

First published in 2024.

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PREFACE

In the present era, environmental degradation has emerged as a major threat due to widespread urbanization and industrialization all over the world. Air, water, soil and all other natural resources are getting polluted by one or the other ways. The majority of industries use various inorganic and organic toxic chemicals and discharge them into nearby water streams as effluents without treatment. These pollutants severely influence the aquatic world as well as indirectly the human life. Global crisis due to depletion of natural resources that are not replenishable as well as degrade the environment leads to harmful consequences. Thus, environmental remediation has emerged as a significant field of research towards this direction. In recent times, nanomaterials have exhibited multifunctional properties in the fundamental arena of scientific activities because of their enormous applications especially their roles in environmental monitoring and remediation. The beauty of nanomaterials lies in their small size leading to real perfection, potency and wide range of applications. The inimitable properties of nanomaterials make them suitable for energy harvesting and removal of pollutants from the environment and ultimately cleaning up of the environment. They can be readily tailored for application in different environments and these properties make them unique for developing a new generation of efficient, cost-effective and environmentally friendly functional materials for energy harvesting and water treatment processes.

This book is an attempt to spread scientific awareness among the readers and discuss various methods needed to overcome the challenges faced during environmental remediation as well. The book comprises ten chapters. In this era of digitalization, the use of electronic devices has become an integral part of our everyday life. These devices used for sensing, analysing, and transmitting signals require a very small amount of energy. An alternative source to power these devices could be through harvesting the tiny mechanical motion associated with different motions. **Chapter 1** presents a brief introduction to the need for nanomaterials for environmental remediation. Different nanoremediation pathways have been broadly catergorized into four categories: Adsorption, Photocatalysis, Nano-membrane, Nanosensors for different classes of nanomaterials. Nanomaterials for energy harvesting and storage applications have also been discussed in brief. **Chapter 2** deals with the methods of preparation of spinel ferrites and their structural and magnetic characteristics. The importance of spinel ferrite in pollutant degradation for wastewater along with its recovery and reuse has been explored. The chapter also discusses the efficacy of adsorption and photocatalysis processes in conventional wastewater treatment techniques. **Chapter 3** explains the significance of carbonaceous quantum dots in environmental remediation. In addition, the advantages of carbonaceous quantum dots over conventional quantum dots, methods for synthesizing carbonaceous quantum dots (top down and bottom up) their functionalization or doping to improve their selectivity and sensitivity, their applications in various fields such as sensing, photocatalysis, and bio-sensing have also been discussed. **Chapter 4** explores the carbonaceous materials such as activated carbon, biochar, hydrochar, *etc*. for wastewater remediation. This chapter summarizes the role of carbonaceous materials, their importance and fabrication for their multidisciplinary applications. **Chapter 5** deals with a systematic discussion of the role of pure and modified ferrites in the removal of various toxins and pollutants from the environment and their potential applications for environmental remediation. **Chapter 6** deals with another material for wastewater remediation- Carbon Nanotubes. This chapter discusses functionalization or modification procedures, depending on the intended application and the chemical makeup of the target pollutants. Designer CNTs can significantly increase the effectiveness of contaminant removal and help with nanomaterial regeneration and recovery. **Chapter 7** deals with cellulose-based nanomaterials in water remediation processes. In this chapter designing of various cellulose-based nano-materials has been depicted for the extraction of valuable metals from wastewater. Adsorption by various chemical transformations such as reduction, chelation and electrostatic interaction are discussed for the extraction of various metals. Lastly, composite systems consisting of cellulose and metal oxide nanoparticles have also been discussed for the extraction of rare earth metals from the mining industry. **Chapter 8** discusses potential sources of energy harvesting by converting waste mechanical energies into useful electrical energy by nanogenerators. This chapter reviews the basic workings of different nanogenerators based on piezoelectricity, triboelectricity, pyroelectric, and flexoelectricity. This chapter attempts to present the energy management landscape of the country by developing cost-effective materials and devices that can harness both sunlight and vibrational energy and convert them into electricity is the need of the present day for a green and circular economy-driven future. Lead-free piezoelectric energy harvesting technology has been discussed in **Chapter 9**. The fundamental piezoelectric concept and several piezoelectric materials specifically KNN, BT, and BNT-based ceramics and their applications for energy harvesting are described and assessed in this chapter. Finally, based on their current developments, different challenges and future perspectives have also been encompassed. **Chapter 10** aims to offer an overview of cold spray additive manufacturing including their advantages for sustainable manufacturing in terms of environmental concerns. Challenges associated with cold spray additive manufacturing have also been discussed. **Chapter 11** aims to assess the ecotoxicity and risk associated with nanomaterials in environmental remediation. Overall, this chapter highlights the importance of careful consideration of the ecological impacts and risks of nanomaterials before implementing them in environmental remediation programs.

We believe this book has successfully targeted the fundamental issues and challenges regarding environmental remediation. Easy to read and pictorial illustrations have focussed on the theme and have justified its purpose. We anticipate that this book will be beneficial for students and academicians in broadening their horizons.

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Prof. Prianka Sharma, an alumnus of Himachal Pradesh University has obtained her Ph.D. in theoretical nuclear physics in 2008. She is a physicist by training and has expertise in theoretical nuclear physics, experimental condensed matter physics and material science. She has published more than 15 research papers in SCI and Web of Science and 01 book and has guided 03 research scholars successfully. Her passion for understanding new phenomena's and technologies drives her interest in improving the properties of materials for environment-friendly green technology for water treatment and energy harvesting. An experimental physicist with strong analytical and logical skills makes her an expert trouble-shooter. With skills of high order interpersonal understanding, teamwork and communication, she envisions her commitment to the highest standards of professional endeavour.

Prof. Virat Khanna works as an associate professor at the UCRD, Chandigarh University, Punjab, India. He has more than 14 years of experience in academics and research. He has authored more than 30 national and international publications in SCI, Scopus, and Web of Science indexed journals. He is the editor of several books and conference proceedings with various international publishers like Springer, CRC Press, IGI Global and Bentham Science Books. He has delivered several invited seminars and keynote talks on international platforms and has been awarded with best research paper awards. He is also the academic editor of the "Journal of Nanotechnology", Wiley and "Advanced Materials Science and Engineering, Wiley and is also the book series editor entitled 'Recent Advances in Materials for Nanotechnology of CRC Press, Taylor & Francis-Publisher. He is also the guest editor of various special issues with various international journal publishers like Springer, De Gruyter *etc*. He is also a reviewer board member of several international journals.

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CHAPTER 1

Nanomaterials for Environmental Remediation

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Abstract: Environmental pollution has become biggest threat to mankind due to its adverse effects on human health and the ecosystem. Rapid industrialization, expansion of urbanization and adoption of latest technologies lead to the release of hazardous by-products and effluents that contaminate the environment. Nanotechnology has proved to be a potential technique for environmental remediation. It involves the most advanced processes that can be successfully utilized in overcoming the issues of environmental contamination due to their unique properties. Multifunctional characteristics of nanomaterials offer unparalleled opportunities in the elimination of pollutants in the nanoscale like volatile compounds, heavy metals, inorganic and organic ions, drugs, pesticides, aromatic heterocycles, biological toxins, pathogens, *etc*. Nanomaterials with smaller size, higher surface area, quantum confinement and low reduction potential bring versatility in their functionality. These nanomaterials can be utilized as chemical oxidants, catalysts, adsorbents, nanosensors, *etc*. Surface engineering of nanomaterials can be utilized to enhance their surface area and maximize their reactivity for adsorption of pollutants and promote catalytic reactions by oxidation or reduction of pollutants from contaminated medium. Besides surface area, the selectivity of specific nanoparticles also affects the remediation process. In this chapter, we have given a brief introduction to the nanoremediation pathways broadly categorized into four categories: adsorption, photocatalysis, nano-membrane, nanosensors for different classes of nanomaterials like carbon-based, metal and metal oxides, magnetic, two dimensional, *etc*. Nanomaterials can prove to be efficient in energy harvesting and storage applications due to the interplay between surface and interface. Hence, there has been continuous demand for nanomaterials with new architectures and physically controlled properties for the purpose of energy harvesting.

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Keywords: Adsorption, Adverse effects of pollutants, Carbon-based nanomaterials, Energy harvesting, Environmental crisis, Metal and metal oxide based, Magnetic nanoparticles, Multifunctional characteristics, Nanoremediation techniques, Nanotechnology, Nanomaterials, Nanomembranes, Nanosensors, Photocatalysis, Types of pollution, Two-dimensional nanomaterials.

INTRODUCTION

In present times, the world is facing major environmental crisis that is not only costing our present but will definitely affect our future also. The year 2022-2023 has seen record-breaking environmental calamities like unprecedented heatwaves, rising pollution, devastating floods, extreme weather events, energy shortages and many more. The mean global temperature in 2022 has risen 1.15°C above the earlier times as stated in the annual report of the WMO's State of Global Climate. This increase in temperatures has been followed by a series of natural disasters. In some regions, river levels have gone down affecting crops leading to, extreme drought conditions, affecting the international trade, while in other areas heavy rainfall and cloud bursts resulted in devastating floods. Unexpected heatwaves led to wildfires in Australia and Amazon forests. About 592,000 square kilometres of the ice sheet melted in the Arctic region in the middle of summer. The melting of the Greenland ice sheets has raised the sea level by one centimetre. Thus, rise in sea level by several metres has been caused due to extreme carbon emissions leading to global warming. Glaciers in the Alps and the Himalayas have lost one-third of their ice. This extensive melting of the ice sheets has affected the weather patterns and Amazon rainforests. Recently, the United Kingdom has recorded the hottest day in July 2022 alongwith Oklahoma and Texas. With these high temperatures and drought-like conditions, rivers Rhine in Germany and Po in Italy dried up, with severe consequences on hydropower and agriculture. In recent years, the air quality index (AQI) of New Delhi, the capital of India has deteriorated extremely with AQI levels between 350-400 leading to severe impacts on the environment and human health. Dr. Kshitiz Murdia stated *"Pollution is not solely an environmental concern; it constitutes a severe threat to human health, including fertility and healthy reproduction also".* Though water is an abundantly available natural resource and covers 71% of the earth's surface, only 1% of fresh water is available for drinking [1 - 3]. About 50% of the global population will face water scarcity and inadequacy in freshwater availability by 2025 and this figure will rise to 75% by 2075 [4]. Ever since industrialization, mishandling of industrial wastes has led to serious impact on mankind. In 1912, a painful disease called Itai-itai affecting bone and skin conditions outbroke in Japan as a result of the negligent dumping of toxic metal cadmium in the Jinzu River. In 1956 and 1965, Minamata disease caused by mercury was found in local water bodies. This disease leads to paralysis and sudden death. Pharmaceutical wastes released as effluents in water bodies or soil pose an extreme global threat to the environment and human health. Thirty-four different pharmaceutical drugs have been detected at a single site in the Kai Tak River of Hongkong. Hundred million barrels of toxic oil waste released into water bodies of the Amazon rainforest for many years have caused widespread health issues.

All these incidents and many more not quoted here have taken place due to the rise in global population and changes in human lifestyle. Rapid industrialization, expansion of urbanization and adoption of the latest technologies in agriculture led to the release of hazardous by-products and effluents that contaminates the environment and pose serious threats [5 - 7]. Moreover, fast-paced advancements in technology, and newer pollutants released have deteriorated the self-remediation capability of the environment [8]. These pollutants not only exhibit negative impact on the environment but have shown severe influence on human health and also on the entire ecosystem [9].

TYPES AND CAUSES OF ENVIRONMENTAL POLLUTION

The major causes of environmental contamination are related to air pollution, water pollution and land pollution due to different types of pollutants as shown in Fig. (**1**). Industries are the major contributors to environmental contamination. The effluents or by-products like plasticizers, aromatic hydrocarbons, and various xenobiotic compounds are dumped unauthorizedly putting severe warning to the terrestrial ecosystem [10]. These by-products and effluents hold carcinogenic and mutagenic properties that affect seed dormancy and decrease the efficiency of land for agricultural production. Sewage wastes from households and extensive use of fertilizers for crop production lead to the leaching of chemicals from fertilizers and pesticides, heavy metals like (cadmium, zinc, lead) and other micro-pollutants into the ground [11]. This affects the vulnerability of groundwater. Air pollution poses a major threat to the whole of mankind and is the leading cause of fatal deaths all over the world. Aerial pollutants such as carbon dioxide, methane, nitrous oxides, hydrocarbons, fuel soot particles, and ozone, *etc*. are contributing to global warming and pose a major environmental challenge [12]. Pollutants like sulfur and nitrogenous oxides lead to the deposition of acids and result in acid rain, smog, *etc*. Higher concentrations of particulates can bring about chemical and physical atmospheric changes. Volatile organic compounds emission can alter secondary organic aerosols [13]. Carbon monoxide a harmful compound present in the atmosphere when inhaled decreases the delivery of oxygen to organs in the body organs, affects vision, and excess levels are fatal. Similarly, exposure to sulfur oxides for longer time duration can cause carcinogenic effects [14]. Reactive species of oxygen are generated by a mixture of various air pollutants which create an imbalance in the concentration of free

CHAPTER 2

Spinel Nanoferrites: Adsorption and Photocatalysis of Emerging Pollutants

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Abstract: In recent years, scientists have been interested in spinel ferrite-based nanomaterials because of their exceptional characteristics, such as their high saturation magnetisation (M_s), excellent chemical stabilities, and huge surface-to-volume ratios. Spinel nanoferrites for wastewater clean-up are the subject of this chapter, which goes into great depth. Spinel ferrite has been discussed in detail, along with some of its key features. Moreover, the synthesis method and structural and magnetic characteristics of spinel ferrites are also reviewed in this chapter. There has also been a discussion of conventional wastewater treatment methods and their limitations in handling different organic and inorganic pollutants. It is possible to remove inorganic and organic pollutants from wastewater using adsorption and photocatalysis therefore, in view of this, these methods are addressed in detail. The importance of spinel ferrite nanoparticles in pollutant degradation of wastewater and its recovery has been explored. Additionally, it has been discussed how adsorption and photocatalysis can improve the efficacy of currently used conventional wastewater treatment techniques. Towards the end, the future scope of spinel nanoferrites for wastewater treatment is discussed.

Keywords: Adsorption, Co-precipitation, Dyes, Hydrothermal, Heavy metals, Industrial waste, Inorganic pollutants, Organic pollutants, Photocatalysis, Pollution, Primary water treatment, Rietveld analysis, Saturation magnetisation, Secondary water treatment, Solid state, Sol-gel, Spinel Ferrites, Synthesis, Tertiary water treatment, Wastewater treatment, X-ray diffraction.

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INTRODUCTION

Water pollution is mainly caused by two types of pollutants: organic and inorganic pollutants. Organic pollutants present in the freshwater system are mainly because of various human activities such as the use of dyes, antibiotics, pesticides, and other industrial-based organic chemicals [1, 2]. These organic pollutants are very stable and cause harm to aquatic and other life forms. Besides this, inorganic pollutants such as heavy metals, non-metal salts and some other acidic and basic industrial wastes are also very harmful to the environment [3, 4]. Inorganic pollutants can enter the water system because of mining, industries, human activities and some other natural ways (volcanic eruptions). Both of these pollutants have hazardous impacts on human health and can cause various diseases when present in drinking water [5]. That is why various techniques have been developed to get rid of these pollutants from water. Conventional methods of water treatment are mostly useful for the degradation of only inorganic pollutants [6]. There are some newly developed methods such as adsorption and photocatalysis which have gained a lot of attention from various researchers because of their different advantages [7 - 9]. These two methods are novel and can show great future potential because of their green nature and low-waste nature. There are different chemical compounds that can be utilized for both of these methods. Among various materials, spinel ferrite has come on top because of its various advantages over others [10 - 13]. Spinel ferrite is a type of magnetic material that shows good adsorption and photocatalytic activity. In the nano range, spinel ferrite shows good magnetic properties making them more useful for wastewater treatment [14 - 16]. Spinel nano ferrites, in particular, are exceedingly stable, easily regenerable and reusable a number of times without losing their characteristics, making them cost-efficient and useful for wastewater treatment techniques. Many scientists have used various spinel nano ferrites for the purpose of adsorption as well as photocatalysis. For example. Kumari *et al*. (2022) prepared $Mg_{0.4}Zn_{(0.6-x)}Ca_xFe_2O_4$ (x = 0-0.6) spinel nano ferrite by utilizing citrate precursor route. The prepared samples were utilized for the photocatalytic degradation of Rhodamine B in the presence of ultraviolet rays. The prepared samples showed photocatalytic degradation of 99.5% in only 80 minutes of reaction time [17]. Dojcinovic *et al*. (2020) prepared $Co_xMg_{1-x}Fe_2O_4$ (where x varied from 0.0 to 1.0) using sol-gel combustion route. The prepared samples were in nano range having crystallite sizes varying from 34 to 48 nm. The prepared samples also showed great magnetic characteristics having maximum saturation magnetisation of 75.7 emu/g. The prepared samples were used for photocatalytic removal of methylene blue with the presence of natural sunlight and visible light. In the presence of sunlight, maximum degradation achieved was 82% in the span of 4 hours whereas, in the presence of visible light, maximum degradation observed was 79% in 4 hours [18]. Wu *et al*. (2019) utilized hydrothermal approach for preparing $Zn_xFe_{3-x}O_4$ spinel ferrite. The prepared spinel ferrites were in the nano range having crystallite size in the range of 22.3-30.3 nm. The prepared samples were utilized for removing Arsenic As(V) from water by using adsorption. In their study, they found that the samples prepared showed an excellent adsorption towards As(V). The maximum adsorption observed was 7.86 mg/g [19]. All these examples showed that the spinel ferrites can be utilized for the degradation of organic as well as inorganic pollutants by means of adsorption and photocatalysis.

In the current book chapter, we have discussed the basics of spinel ferrites and their structural traits and also, why are they so important as magnetic ceramic material. We have also discussed various synthesis routes for preparing different types of spinel ferrites. We have also explained in detail the adsorption and photocatalytic degradation mechanism using spinel nano ferrites. In conclusion, this chapter discusses the benefits of spinel ferrites for the adsorption and photocatalysis-based wastewater treatment.

SPINEL FERRITE

Spinel ferrite belongs to the category of magnetic ceramic-like material which is currently trending because of its various useful virtues. Due to their powerful magnetic properties as well as other useful characteristics including catalytic activity, adsorption capacity and sensing ability, they are utilised all over the world. Spinel nanoferrite can be employed in a variety of disciplines, such as sensors, biomedicine, magnetic storage devices, batteries, high frequency and microwave devices, wastewater treatment, *etc.* due to its numerous properties [20 - 22]. However, by changing several variables, such as synthesis techniques, heat treatment, doping, *etc.*, different properties of spinel ferrites, such as magnetic and electrical properties, can be significantly altered. Spinel ferrites have a chemical composition of AB_2O_4 where “B” is replaced by trivalent cations like Fe and “A” by divalent metal cations like Co^{2+}, Ni^{2+}, and Zn^{2+}. Spinel ferrites are sometimes also referred to as soft ferrites because most spinel ferrites have low coercivity and high saturation magnetisation. But there are some exceptions to this, for example, cobalt ferrite which is a type of spinel ferrite shows semi-hard magnetic nature, meaning that it has moderate values of coercivity [23 - 26]. But generally speaking, most of the spinel ferrite follows the soft magnetic trend. Spinel ferrite’s structure is also very distinct separating it from the rest of the magnetic ceramic materials. Its unit cell is made by the combination of several sub-unit cells. These sub-unit cells are fcc in nature and are arranged alternatively throughout the unit cell. One unit cell is made up of 8 of such sub-fcc unit cells. Since each of the fcc sub-unit cells can have 4 octahedral and 8 tetrahedral sites. Thus, the overall unit cells have 32 octahedral and 64 tetrahedral sites. The

CHAPTER 3

Carbonaceous Quantum Dots and Their Application in Environmental Remediation

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Abstract: Carbon quantum dots are sp^2/sp^3-hybridized carbon atoms with sizes ranging from 2-10nm. They are zero-dimensional florescent nanomaterials that are less toxic, more biocompatible and highly stable in nature. Carbon quantum dots have attracted the attention of many research groups due to their novel characteristics and have found several applications in industries. They are used in various scientific fields which include synthesis and design of inexpensive biological and chemical sensors. Carbon quantum dots have several uses in optical sensing, bio imaging, bio-sensing, optoelectronics photovoltaic and photocatalysis because of their superior electronic, optical, photocatalytic, up-conversion, photoluminescence and light harvesting properties. Using CQD, a cost-effective and environmentally friendly method of cleaning up environmental pollutants is introduced. They have lately been employed in remediation experiments in place of or together with metal semiconductors due to their optoelectronic features. Recently, the world has been facing serious threats due to environmental contamination of various kinds, which has become more serious due to lesser affordable means for treating it. Industrial waste, pesticides, heavy metal ions, pharmaceutical waste and sewage are some of the commonly observed water contaminants. Compared to the earlier studied forms of quantum dots, carbonaceous quantum dots are the most prevalent ones and can be a better option. The goal of this chapter is to explain the significance of carbonaceous quantum dots in environmental remediation. In addition, the advantages of carbonaceous quantum dots over conventional quantum dots, methods for synthesizing carbonaceous quantum dots (top down and bottom up), their functionalization or doping to improve their selectivity and sensitivity, their applications in various fields such as sensing, photocatalysis and bio-sensing have also been reviewed. By adding surface defects or interstitial states between electron holes, these alterations have a major impact on the optical characteristics of carbonaceous quantum dots. Additionally, the methods of removal of pollutants have also been explored by physical, chemical conventional and biological methods. Lastly, future perspectives and conclusion speculations have been considered.

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Keywords: Adsorption, Carbonaceous quantum dots, Inorganic pollutants, Optical sensing.

INTRODUCTION

It has been a severe problem in recent years that harmful chemicals and pollutants enter the human body directly through food, water or skin absorption. Although the contaminant's toxicity may vary depending on factors like size, dosage, and exposure time [1], their increasing contact with the human body has resulted in negative effects on both public and individual health. Heavy metal ions, including Aluminum(III), Cobalt (II), Arsenic(III), Lead(II), Chromium(VI), Silver(I), Copper(II), Mercury(II) and Iron(III) are among the numerous harmful nano-molecular level pollutants. Considering their widespread occurrence in aqueous form in waste from pharmaceutical, textile, agricultural industries and organic contaminants, they are all regarded as dangerous to human health [2]. The Environmental Protection Agency (EPA) and the World Health Organization (WHO) both have a number of internationally recognized standard hazardous levels that can be used to assess the safety of the contaminants [1]. The use of highly selective and sustainable probe techniques and their evaluation with respect to the standard permitted limits, can be advantageous for toxicity testing because it is necessary to identify the contaminant(s) concentration at extremely low levels. Recently, a number of nanotechnology-based detection devices have been proposed for this situation [3]. For these current environmental problems, several nanomaterials, such as carbon-based and metallic nanoparticles, may offer a solution [4, 5].

The term "Carbonaceous Quantum Dots" refers to a variety of nanoscale carbon compounds. Carbon nanomaterials with diameters smaller than 10 nm are known as carbonaceous quantum dots (CQDs). They were first discovered in 2004 by X. Xu *et al*. while purifying single-walled carbon nanotubes using preparative electrophoresis [6]. About two years later, in 2006, Y.P. Sun and his team used laser ablation of cement and graphite powder to discover carbon nanoparticles that would later come to be known as carbon dots or carbon nanodots [7]. Due to their composition and biocompatibility, they are a viable replacement for metal-based quantum dots [8]. Due to their enormous potential for a wide range of technical applications, such as chemiluminescence, electrochemical luminescence, bioimaging, chemical sensor, biomolecule/drug delivery, photocatalysis, bioanalysis, photodynamic therapy, optoelectronic, electrocatalysis, and more, carbonaceous quantum dots have progressively attracted significant research interest (Fig. **1**) [9]. Carbon dots, graphitic carbon nitrides, and graphene quantum dots are the three types of carbonaceous quantum dots. Due to their numerous key advantages, including their excellent biocompatibility, photostability, highly tunable photoluminescence property, small size, exceptional multiphoton excitation property, electro chemical luminescence, ease of biomolecule functionalization and chemical inertness, graphene and carbon quantum dots have recently emerged as improved fluorophore [9]. Such luminous carbon nanocrystals have the potential for optical sensing and bioimaging [10]. CQDs were divided into three categories: graphitic carbon nitride quantum dots, graphene quantum dots (GQDs), and carbon quantum dots (g-CNQDs). Because of their exceptional features, such as their small size, tunable PL characteristics, chemical inertness, photostability, and simplicity of functionalization, C-dots and GQDs stand out as the only fluorophores. These properties offer CQDs the potential for optical sensing and bioimaging. The main structural difference between C-dots and GQDs is that C-dots have a quasi-spherical structure, are typically smaller than 10nm in size, and contain sp^2 hybridized carbon [11]. C-dots can have an amorphous or nanocrystalline structure [12]. Despite C-dots, Pan *et al*. created the first GQDs, which have a structure similar to that of a few layers of graphene [13]. GQDs exist in typical elliptical or circular shapes, though occasionally triangular, hexagonal and elliptical. GQDs have also been fabricated using synthetic methods [10]. In a similar way, two-dimensional, nitrogen-rich materials with graphitic structures are known as g-CNQDs. Another novel family of metal-free catalysts that is emerging is G-CNQDs [14, 15].

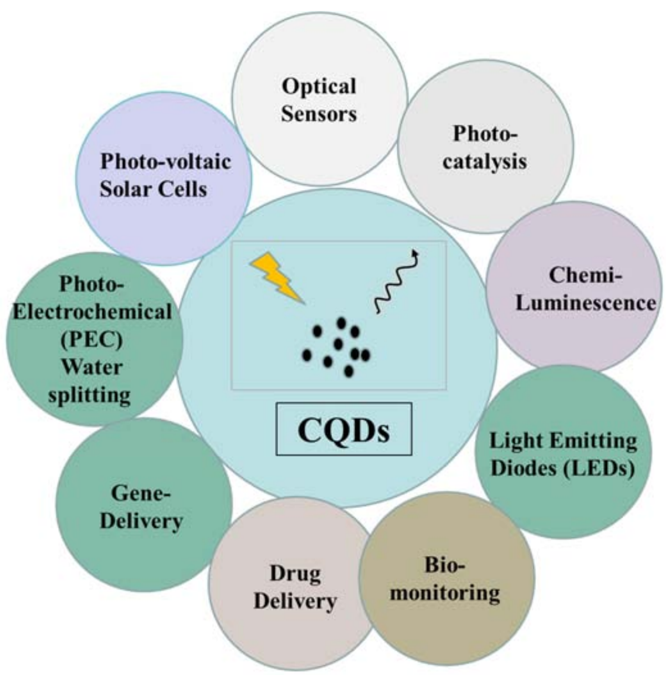

Fig. (1). Applications of carbonaceous quantum dots.

CHAPTER 4

Boosting Water Remediation Processes by Exploring the Role of Carbonaceous Material in Advance Oxidation and Adsorption Processes

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Abstract: In recent decades, considerable attention has been directed toward wastewater remediation through various processes, including adsorption, advanced photo-reduction/oxidation processes, ion exchange, and more. The linchpin of these processes lies in the judicious selection of appropriate materials, capable of not only meeting the primary requirements but also exhibiting suitable availability. The exploration of carbonaceous materials such as activated carbon, biochar, hydrochar, *etc*., emerges as a cost-effective strategy for wastewater remediation. The surface area, a well-established pivotal factor, assumes a critically influential role in the wastewater remediation process. Therefore, it is paramount, during the fabrication of such materials, to adopt appropriate strategies to ensure the fulfillment of the targeted material requirements. Due to their extensive surface area, carbonaceous materials hold immense potential in wastewater treatment through advanced oxidation processes (AOPs). The efficacy of these AOPs, encompassing photo-catalysis and photo-reduction/oxidation, hinges upon the materials employed, including nanoparticles and hetero-structures. In turn, all AOPs are orchestrated by reactive oxidation species (ROS) generated at the active sites of catalysts, such as nanoparticles and hetero-structures. This study comprehensively summarizes the pivotal role of carbonaceous materials, underscores their significance, and elucidates the fabrication techniques essential for their multidisciplinary application in wastewater treatment processes.

Keywords: Activated carbon, Agro-industries, Advanced oxidation processes, Biochar, Hydrochar, Organic pollutants, Pesticides, Photo-catalysis, Wastewater.

INTRODUCTION

Contamination of drinking water by organic pollutants stems from diverse sectors, including pharmaceuticals, petrochemicals, textiles, food processing, and coal ga-

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sification. These industries discharge substantial quantities of deleterious effluents into water sources. Classic organic pollutants encompass a spectrum of substances, ranging from pharmaceuticals such as antibiotics, anti-hypertensives, and analgesics to hazardous chemicals like polycyclic aromatic hydrocarbons and pesticides, exemplified by polychlorinated di-benzo-furans (PCDF), polychlorinated dibenzo-p-dioxins (PCDD), hexa-chloro-benzene (HCB), polychlorinated biphenyls, and polycyclic aromatic hydrocarbons [1, 2]. Consequently, environmental pollution precipitates a myriad of diseases, including but not limited to rheumatoid arthritis, cancer, respiratory tract disorders, brain hemorrhage, skin ulcers, and endocrine disruption [3]. The agro-industry exacerbates water pollution by deploying toxic herbicides, pesticides, insecticides, and fungicides, which constitute major components of agrochemicals and significantly contribute to the contamination of drinking water worldwide [4]. Pesticides, such as atrazine, metalochlor, chlorpyrifos, and carbendazim, exert adverse effects not only on target organisms but also on various facets of the ecosystem [5, 6].

Furthermore, effluents from food processing industries pose a substantial threat to the environment due to elevated levels of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) [7]. Wastewater from these industries typically contains a diverse array of inorganic and organic contaminants, including oil, salt, sugar, and various additives [8, 9]. Conversely, wastewater from dairy and livestock processing plants harbors a spectrum of harmful bacteria, including Salmonella, *Staphylococcus aureus*, and *Escherichia coli*, posing a severe threat to both aquatic ecology and public health [10].

Hence, the pressing concern revolves around the quest for eco-friendly, cost-effective, and user-friendly techniques to eliminate such harmful microorganisms from wastewater used in various industries, a task of considerable complexity. Photocatalysis has emerged as a pivotal and efficient purification technique, distinguished by its absence of secondary pollution, exceptional recyclability, and potent oxidative capacity against pollutants, surpassing conventional treatments such as biodegradation, physical methods like adsorption, and chemical methods like chlorination [11, 12] (Fig. **1**).

Cleary *et al*. (2019) reported adverse effects of Atrazine on aquatic life and subsequent animal generations. Their findings indicated an increase in atrazine exposure in the first generation of Oryzias latipes fish, a decrease in the second generation, and complete absence in the third generation. Sun *et al*. (2019) and Jin *et al*. (2011) highlighted that metalochlor herbicides, employed in crops such as maize, soybean, potato, cotton, and others, can induce thyroid issues in Oryzias latipes families at a concentration of 1,000 mg/L. Suke *et al*. (2018) documented that Wistar rats exposed to the organophosphorus insecticide chlorpyrifos exhibited oxidative stress, liver damage, and a compromised immune system.

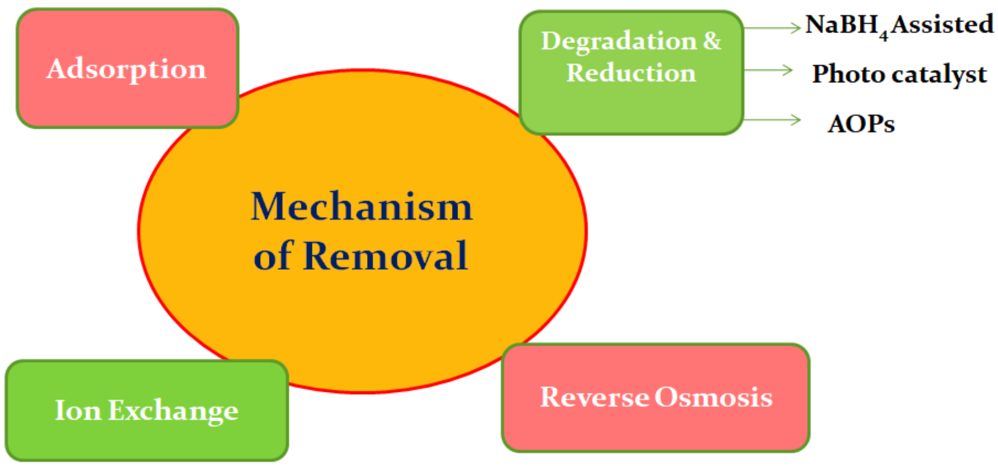

Fig. (1). Different method for pollutant removal.

Carazo-Rojas *et al*. (2018) and Jiang *et al*. (2015) suggested, among other substances, that carbendazim may have unfavorable effects on the aquatic environment. Zebrafish exposed to carbendazim during larval and fetal developmental stages, particularly at concentrations exceeding 4,000 nm, experienced immune system problems, endocrine abnormalities, and oxidative stress. The consumption of contaminated food and the persistent accumulation of hazardous trace metal ions in water, such as cadmium (Cd), lead (Pb), arsenic (As), and fluoride (F), can give rise to severe health issues affecting the skin, lungs, kidneys, brain, and other vital organs [13, 14]. To address water remediation, advanced processes such as coagulation, ion exchange, chemical precipitation, membrane separation, reverse osmosis, flocculation, adsorption, filtering, sedimentation, *etc*., must be developed with a focus on cost-effectiveness, reduced hazards, and eco-friendly practices [15].

Adsorption procedures, due to their exceptional effectiveness and lower cost compared to conventional methods, stand out as the preferred technique for heavy metal removal from wastewater. Adsorbents for removing heavy metal ions from wastewater are readily accessible [16]. Among various techniques for treating contaminated water, advanced oxidation processes (AOPs) are considered the cleanest technology. The fundamental concept behind AOPs relies on the *in-situ* production of highly reactive hydroxyl radicals, which oxidize a wide variety of organic pollutants indiscriminately [17]. This results in the complete

CHAPTER 5

Emerging Role of Ferrite Nanostructures for the Remediation of Environmental Pollution

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Abstract: An enormous growth in the concentration of various poisons and pollutants in the environment has resulted from the ongoing expansion of industrial, agricultural, and urban activities. So, environmental remediation should be given equal attention to scientific efforts in the fields of industrial and technological developments. When it comes to the adsorption and desorption of several environmental contaminants, magnetic nanoparticles have proven to be superior to other contenders. Ferrites, among other magnetic nanoparticles, have gained attention as viable options for environmental cleanup because of their tiny size, high surface to volume ratios, superior catalytic capabilities, strong magnetic properties, and favourable optical characteristics. Additionally, ferrites have demonstrated the ease with which their structural, morphological, magnetic, and optical properties may be tailored, and these changes have further improved the effectiveness of pollution removal. Additionally, formation of composites of ferrites with different materials such as CNTs, graphene, rGO, cellulose, TiO_2, ZnO *etc*. has also led to enhancement in the catalytic properties. The role of pure and modified ferrites in eliminating different poisons and pollutants from the environment, as well as their possible uses in environmental remediation, are thoroughly discussed in this chapter.

Keywords: Advanced oxidation processes, Catalytic performance, Composites, Core-shell nanostructures, Degradation, Electron-hole pair, Ferrite nanostructure, Inorganic matrices, Magnetically recoverable, Nanocatalysis, Organic pollutants, Recombination, Semiconductors, Visible light irradiation.

INTRODUCTION

The industrialization and globalisation processes have accelerated more than at any other time in the twenty-first century, resulting in an alarming level of environmental contamination. Hazardous contaminants have been dumped into

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the environment unprocessed by many sectors, leading to this worrying level of contamination. Waterbody pollution is one of the many environmental issues that is becoming a major worldwide concern [1]. Water is the most valuable gift of nature and its requirement in each and every aspect of life makes it indispensable. It is well known that without water no life would have been possible on Earth, hence the importance of water cannot be disregarded. Additionally, with the growing human population, there is an ever-increasing demand for freshwater. Water bodies are relentlessly being polluted owing to the direct discharge of dangerous effluents from industries [2]. Sharma *et al*. reported a case study of the toxins present in wastewater produced from the paper industry and the study showed the presence of a high amount of pollution parameters along with heavy metals above the permissible limit [3]. Zharikova *et al*. have suggested an artificial intelligence methodology for the detection of water pollution and compared traditional approaches based upon the application of spectral characteristics and machine learning methods towards the analysis of the situation of water bodies [4]. All these studies suggest that a grave threat is looming large on the biosphere and sincere efforts to mitigate this threat are the need of the hour.

Treatment of Industrial Waste Waters: Advance Oxidation Processes (AOPs)

Unfettered release of substituted aromatics, organic dyes, pesticides, insecticides, pharmaceutical compounds and many other industrial effluents into the water bodies has not just led to an increase in toxins in water rather it has created serious and adverse effects on the aquatic life and human health as well [5]. Thus, it has become an absolute necessity to treat these discharges rich in chemicals, prior to release, in such a way that it does not create any hostile impact on the natural environment. Different methods have been adopted to minimize the concentration of pollutants before their disposal into the natural water bodies. Generally, the treatment of waste water has been classified into four levels-primary, secondary, tertiary and quaternary with each aiming at the removal of a particular type of pollutants [6]. The primary treatment involves the employment of simple physical processes for the removal of only suspended solids from wastewater. In secondary treatment, dissolved materials are removed whereas in the other two higher treatment levels, various techniques are investigated for the removal of specific contaminants that could not be treated in the previous stages. Major techniques for the treatment of effluent water can be broadly classified as chemical, physical, biological processes, advanced oxidation (AOPs) and electrochemical processes. AOPs have appeared as an effective alternative that is robust and clean for treating degraded water [7]. Most AOPs undergo chemical oxidation processes which involve free radical pathways that successfully treat the harmful toxic pollutants and then convert them into non-toxic mineralized products. Fundamentally, hydroxyl radicals (·OH) are generated using various oxidants *viz*. O_3, H_2O_2, O_2, *etc*. at appropriate pressure and temperature. ·OH radical is highly reactive and acts as a driving force for many other oxidation processes for different organic pollutants. The efficacy of these AOPs is based upon the creation of these indiscriminating and reactive hydroxyl radicals which act as robust oxidants (E°-2.8 V) in comparison to various other commonly available oxidizing agents (H_2O_2 (E°-1.8 V) and O_3 (E°-2.0 V)). Remarkable benefits of AOPs lie in the areas of rate of reaction, hydroxyl radical's oxidation potential and unselective oxidation of different organic pollutants. A schematic representation of AOPs is presented in Fig. (**1**). AOPs can be further categorized into homogeneous and heterogeneous catalytic systems [8].

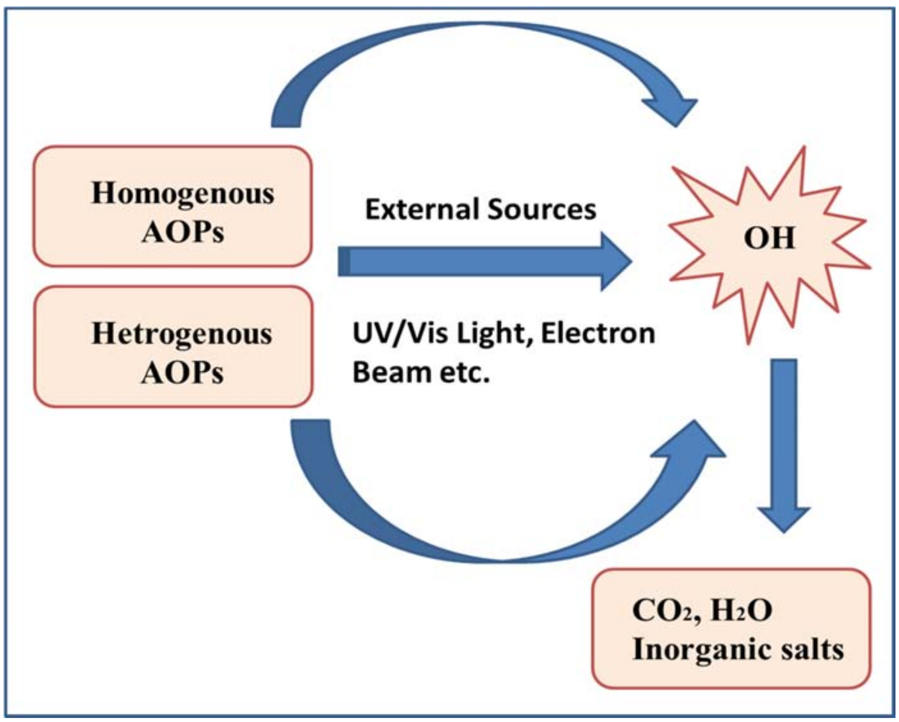

Fig. (1). Schematic representation of AOPs.

Homogeneous and Heterogeneous Systems

Two different scientific communities- molecular chemists and solid-state chemists are guarding two different spheres *i.e*. homogeneous and heterogeneous systems and have been making efforts for a collective objective *i.e.* the search for an outstanding performance. A new catalytic system has emerged out of the shared efforts of both scientific communities called nanocatalysis, which owns advantages of both systems *i.e.* selectivity and performance of homogeneous

CHAPTER 6

Carbon Nanotubes: Measure for Environmental Remediation

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Abstract: Wastewater and other environmental concerns have an impact on every area of our life. Combining novel functional carbon nanomaterials (such as carbon nanotubes, graphene oxide and graphene) with established remediation techniques will provide fresh perspective on environmental problems, their causes and potential solutions for coexisting peacefully with nature. All around the world, water contamination has grown to be a major, enduring and increasing issue. It has detrimental effects on population health, aquatic flora and wildlife and the sustainability of water resources. Because there aren't enough efficient facilities for treating pollutants, the overall amount of water that is available is drastically reduced. Current methods of water filtration take long time, cost lot of money and are ineffective in removing newly discovered micropollutants. Carbon Nanotubes (CNTs) are a class of materials with special physicochemical, electrical and mechanical characteristics that can be used as environmental adsorbents, sensors, membranes and catalysts. CNTs can be created using particular functionalization or modification procedures, depending on the intended application and the chemical make-up of the target pollutants. Designer CNTs can significantly increase the effectiveness of contaminant removal and help with nanomaterial regeneration and recovery. Different chemical, inorganic, and biological pollutants have been treated using an expanding number of CNT-based products. These success stories show how they have lot of potential for real-world uses like desalination and wastewater treatment. In this chapter, the existing research on the interactions between different pollutants and CNTs in soil and water settings has been critically reviewed. The chapter will also assist in identifying the research voids that need to be filled in order to increase CNTs' economic via bility in the environmental remediation sector. Additionally, this makes an effort to present a broad overview of the prospective low-dimensional carbon nano-materials and their composites as

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adsorbents, catalysts, or catalytic support for the social sustainable environmental remediation solutions to the various difficulties arising.

Keywords: Adsorption, Biopolymer, Carbon nanotubes, Ceramic membranes, Chemical vapour deposition, Carbon nanomaterials, Chemisorption, Catalysis, Desalination, Detoxification, Electrocatalysis, Environmental remediation, Environmental remediation, Environmental pollution, Fullerenes, Graphene, Graphene oxides, Hydrophobic surface, Hydrolysis, Hydrophobicity, Hydrophilicity, Inorganic contaminants, Mwcnt, Microwave irradiations, Methylene blue, Organic dyes, Oil spil sponge, Pharmaceutical waste, Photocatalytic sensing application, Pollutant absorption, Swcnt.

INTRODUCTION

In recent decades, with rapid growth in population and increasing industrialization, environmental degradation has become a ubiquitous menace due to the release of various pollutants like organic dyes, aromatic and aliphatic hydrocarbons, heavy metals, arsenic, iron, nitrates, antibiotics and many other compounds [1 - 3]. Contaminated industrial effluent and improper use of fertilizers and pesticides are the major cause of water and soil pollution. These chemicals released into the environment without proper assessment of any health impacts and environmental risks have worsened the daily situation, leading to increasing cancer and other life-risking diseases. Modern-day researchers are responsible for developing effective technologies for dealing with this situation. Numerous methods for treating water, including reverse osmosis, ion exchange on synthetic adsorbent resins, coagulation using chemical agents and ultrafiltration [3 - 7] are non-destructive. These conventional processes fail to completely remove multifunctional pollutants from water due to *(i)* the origination of harmful by-products released during hydrolysis, oxidation or other chemical reactions *(ii)* factors like pH, temperature, turbidity of effluent water affect the capacity of pathogen removal *(iii)* release of toxic chemicals by bacteria, for example, microcystins and nodularin toxins released by cyanobacteria during decontamination process [8]. Thus, biologically non-degradable toxins and hazardous chemical pollutants contaminate the natural water resources endangering aquatic life as well as posing severe health issues to terrestrial life also [9 - 12]. Due to high energy waste, high cost and lower efficiency, these conventional techniques are very ineffective for practical applications. These processes transfer organic compounds present in water to another phase, causing secondary pollution. Additionally, post-treatment of solid wastes, regeneration of the adsorbent materials and instability of secondary pollutants make these conventional techniques even less effective [13 - 20]. Thus, due to specific needs for the degradation of multiple pollutants, researchers have taken a keen interest in the progress of efficient wastewater treatment techniques for the complete removal of non-degradable contaminants from the ecosystem with significant efficiency that proves to be lesser time-consuming but more economical [7, 21].

Recently, many materials like ferrites, ceramic membranes [22,23], semiconductor metal oxides (TiO_2, ZnO, SnO_2, CdS), graphene, and transition metal dichalcogenides (MoS_2, WS_2) have been widely used in various water remediation processes. Graphene Oxide (GO), analogous to graphite, has well-known properties and can also be a good alternative for environmental remediation. However, its applications are limited due to its organized structure and difficulties faced in its large-scale production [24]. Carbon Nanotubes (CNTs) have attracted stimulating interest due to their distinct physical and chemical properties in this field of low-dimensional novel carbon nanomaterials [25, 26]. CNTs are technologically suitable for electronics, thermal devices, sensors, lightweight and high-strength polymer composites, nanoprobes in high-resolution imaging, hydrogen reservoirs, and many other technological applications due to their exceptional mechanical, thermal, and electrical properties [26 - 30]. CNTs are tiny active crystalline carbon forms, a new class of material that holds enormous potential to be useful for environmental applications [31 - 37]. CNTs have emerged as promising remediation options due to their large specific surface area, cylindrical hollow structure, high porosity, high length-to-radius ratio, and lightweight and flexible hydrophobic surface [38 - 41]. Their excellent ability to self-assembling *via* chemical vapour deposition and immobilization ability in membranes and filters make them more suitable for water remediation than other activated carbons [42 - 44].

CNT Structure and Types

Graphene sheets (single-layer graphite) roll up cylindrically to form CNTs (Fig. **1**). sp^2hybridization of carbon atoms of graphene is observed at the corners of the hexagon [45]. The diameter of CNTs lies in nanometer dimensions, but its length lies in micro-meter dimensions [46, 47]. According to the structural classification of CNTs, they are available in two forms- single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT) (Fig. **2**) [48 - 50]. SWCNT arises from the rolling up of a single-layered graphene sheet into a cylindrical shape with an outer diameter ranging from 1 to 30 nm. However, MWCNTs are made from the rolling up of many concentric SWCNTs into a single tubular shape with an interlayer distance between the concentric cylinders of approximately 0.33 nm, similar to the interlayer distance in graphite between graphene layers [51]. Other CNT structures also exist like fullerene combined CNT as nanobud, fullerene trapped CNT as peapod, graphenated CNT, stacked microstructure of graphene layers as cup-stacked CNT, and doughnut-shaped

CHAPTER 7

Cellulose-Based Nanomaterials (Nanobioadsorbents) for Recovery of Valuable Metals from Wastewater: A Review

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Abstract: In recent times, water pollution has become an issue of major concern. Various materials and techniques have been adopted for the purification of water. Among many, cellulose-based nanomaterials have gained valuable use in water remediation processes. These cellulose-based materials are highly biocompatible, abundantly available natural biopolymers and enjoy the advantage of containing many functional groups. The functional groups attached to cellulose biopolymers ensure their capability of modification with various nanoparticles like silver (Ag), graphene oxide (GO), and zinc oxide (ZnO) nanoparticles. These can then be easily applied for the remediation of wastewater by removing pollutants like organic dyes, microbial species, various drugs and heavy metal ions as well. In this chapter designing of various cellulose-based nano-materials has been discussed for the extraction of valuable metals from various wastewater. Mainly static and dynamic absorption processes through cellulose-based nano-materials have been also explained. Adsorption by various chemical transformations such as reduction, chelation and electrostatic interaction are discussed for the extraction of various metals from different wastewater sources. Lastly, composite systems consisting of cellulose and metal oxide nanoparticles have been reviewed for the extraction of rare earth metals from the mining industry. Metals from the recycling of battery and semiconductor devices that mostly constitute noble metals and rare earth elements are also discussed in this chapter.

Keywords: Adsorbent, Aerogel, Absorption, Composite, Chelation, Ceramic, Cellulose, Circular economy, Crystalline, Coagulation, Colloidal dispersion, Extraction, Effluent, Filtration, Flocculation, Fibrils, Hydrogen bonds, Metal organic framework, Mining, Membrane, Nanomaterials, Porous, Precious metals, Polymer, Photocatalyst, Rare earth elements, Reverse osmosis, Recycling, Semiconductor.

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INTRODUCTION

Currently, the extraction of precious metals from the wastewater of the mining industry and recovery of rare earth metals from industrial wastewater are among the hot topics [1]. With the increasing demand for electronic energy storage systems that utilize rare earth elements, recovery of these metals such as La, Nd, Gd, Nb, Pr *etc.* is a crucial task for moving towards a circular economy [2]. Currently, recovery of these metals is not being thought of on the industrial scale. However, due to limited mining resources of these rare earth metals and the reduction of greenhouse gas emissions prompted every nation to seriously consider the recovery of these metals from used products. In laboratory scale, recovery of these metals is done with the utilization of chelating and polymeric ligands such as synthetic ion-exchange resins which are carcinogenic, utilize a lot of solvents and the process is environmentally hazardous as well as energy-intensive [3]. Precious metals such as Au, Ag and Pt recovery from the mining wastewater is another area that needs immediate attention. Recovery of precious metals is done mainly by polymeric or ceramic-based membranes that can withstand acidic environments, and have various pore diameters [4]. However, there is a need for external energy input in terms of pressure because most of the membranes work under reverse osmotic pressure. Membrane fouling is another problem for commercial-scale use [4]. Although biomass carbon and cellulose nanocrystal (CNC) aerogel has been used as an adsorbent for waste-water purification [3, 4], a comprehensive review is need of the hour to address the issue of selective extraction of metal ions from industrial wastewater (Fig. **1**).

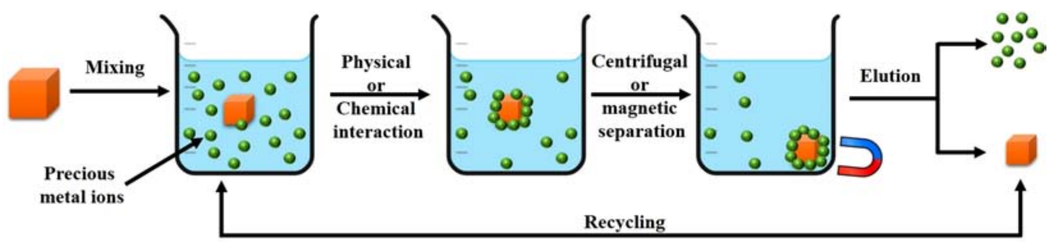

Fig. (1). Extraction of valuable metals from various leaching liquor by adsorption [3].

During the biosynthesis process, cellulose formation takes place by initiating the assembly of 36 linear chains consisting of thousands of β(1→4)-linked D-glucose rings into bundles. The bundles thus formed aggregates sidewise to form para-crystalline arrays of nanofibrilated cellulose. When these nanofibrilated cellulose self-assemble, they form cellulose microfibrils. Each of these microfibrils consists of an alternate amorphous region consisting of lignin and hemicellulose moieties and a crystalline region consisting of cellulose moieties. There are three types of cellulose-based materials that are used as coagulant and flocculant. They are cellulose nanocrystals (CNC) or nanocrystalline cellulose (NC), cellulose nanofiber (CNF) and lastly hairy nanocrystalline cellulose (HNC) [5]. These materials have a hydrophobic core consisting of glucose units joined by glycosidic bonds with polar functional groups such as -OH on the surface. These polar functional groups make these molecules create dispersion in aqueous medium. CNC, CNF and HNC have been modified in several ways to create an effective coagulant/flocculant (Fig. **2**). Modifications include making the charged CNC or CNF cationic or anionic. Also, mono-component or dual component-based flocculants are synthesized and showed good activity during flocculation. Different aggregation mechanisms were proposed for the nano-cellulose (NC) coagulation/flocculation process. Coagulation by charge neutralization, patch flocculation, hetero coagulation, bridging flocculation and complex flocculation are the common mechanisms. Anionic CNC has been prepared by H_2SO_4 hydrolysis or TEMPO oxidation of several biomass materials. During acid hydrolysis and oxidation, the reaction takes place on the surface of the cellulose and the para-crystalline region of the fibrils [6].

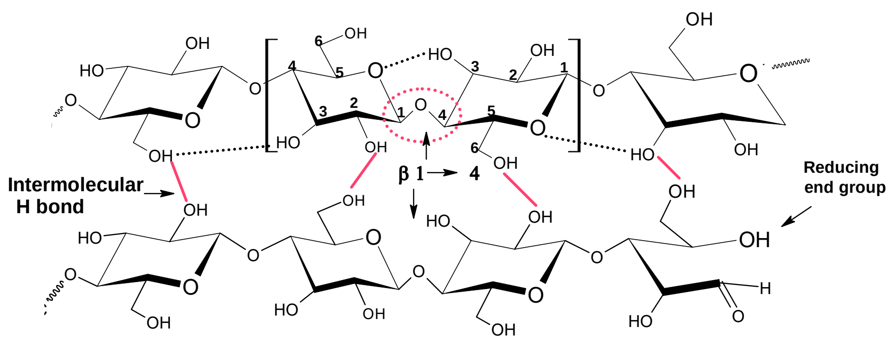

Fig. (2). Cellulose structure with inter- and intra- molecular hydrogen bonds. Adapted from Ref [6].

EXTRACTION OF METALS WITH CELLULOSE NANOMATERIALS

Noble metals are non-renewable resources that are very important in our daily life. They are an integral part of various semiconductor-based devices [7]. However, at the end of the cycle, the aqueous waste containing these noble metals when enters the environment, causes adverse effects on the ecology and human health. Hence, recovery of noble metals is not only important as they are non-renewable and in high demand but also from the health point of view as well. There are several analytical techniques for the recovery of noble metals such as solvent extraction, membrane separation electrolysis, adsorption by synthetic resins and electrochemical processes [8]. Cellulose-based nanomaterials are efficient in recovering noble metals via static adsorption, dynamic filtration and chemical reduction [9].

CHAPTER 8

Nanogenerators for Energy Harvesting

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Abstract: The use of electronic devices is an integral part of our everyday life and a major part of our activities with these devices is related to receiving, sending, and storing information. Some of these devices used for sensing, analysing, and transmitting signals require a very small amount of energy. An alternative source to power these devices could be through harvesting tiny mechanical motions associated with different types of motions. Nanogenerators (NG) are potential sources of energy harvesting by converting waste mechanical energies into useful electrical energy. NGs have already been commercialized in the health and automobile industry as pacemakers and tyre pressure monitoring systems, respectively. However, there is a wide scope of using them for common household and environment remediation applications, which is currently restricted due to the high cost of fabrication and low energy conversion efficiency. Vibrational energy associated with wind, flow of fluid, body movements, roads, train tracks, *etc.* can be converted to power devices locally and reduce the carbon footprint due to the energy produced by fossil fuels. This book chapter reviews the basic working of different nanogenerators based on piezoelectricity, triboelectricity pyroelectric, and flexoelectricity. Many non-lead-containing piezoelectric materials are promising candidates for piezoelectric nanogenerators (PENG) that can also be used for various self-powered electronic and biomedical devices. Many metal-oxides such as zinc-oxides and hafnium-oxides could be of special interest to this. Triboelectric-nanogenerators (TENG) could be the most preferred device for harvesting water-wave blue-energy and integration with conventional electromagnetic-induction (generators) that can be deployed at a large-scale.

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Keywords: Contact-Separation (CS), Compressive-Mode, Energy harvesting, Electron-affinity, Electrical energy, Flexo Electric-NanoGenerator (FENG), Freestanding (FS), Ferroelectricity, Inorganic-organic hybrid materials, Lateral-Sliding (LS), Mechanical energy, Nano Generators (NG), Nanogenerator-circuit, Nanomaterials, Olsen-Cycle, Piezo Electric-NanoGenerator (PENG), Polarization, Peltier-effect, Polymers, Pyro Electric-NanoGenerator (PyENG), Pyroelectricity, Piezoelectricity, Seeback-effect, Sliding-Mode, Single-Electrode (SE), Tribo Electric-NanoGenerator (TENG), Triboelectricity, Thermoelectricity, Thermo Electric-NanoGenerator (ThENG), Thomson-effect, ZnO Nanowires.

INTRODUCTION

An average human being currently uses energy more than 10 times required for their own survival. A significant amount of this energy is distributed in small amounts in portable electronic gadgets such as mobile phones, laptops, smart watch, music players and sensors which consume less energy (Fig. **1**) compared to large electronic equipment like fridge, television, fans, air-conditioners, heaters, washing machines, *etc.* Energy is mainly used for receiving, sending and storing information of components. Conventional electromagnetic induction-based generators are efficient for harvesting energy from wind, water gravity, coal and other fossil fuel cells. Solar and wind energy are also proposed to be alternative green routes for energy harvesting. However, there are still open questions about the overall carbon footprint they leave on the environment for manufacturing photovoltaic panels and windmills. Nanogenerators, on the other hand, can be manufactured using environment-friendly green processes [1] that utilize the tiny energy from mechanical motions locally for the applications of environmental remediation [2 - 6].

Fig. (1). Range of different sensors and electronic gadgets that can be powered using nanogenerators.

NanoGenerator (NG) is a small energy-harvesting or self-powered nanodevice that can be used for converting small-scale mechanical energy into electricity [7 - 10]. NG, which converts mechanical energy into electrical energy has found direct applications in various fields ranging from environmental, and infrastructural monitoring, transportation, homeland security, healthcare and medical science. Especially, the mechanical energy associated with motions in the human body such as breathing, walking, motions in different limbs and organs and other vibrations around us in bridges, roads, tunnels, water, ocean waves, pumps, compressors, train tracks, automobile and other engines, noises, *etc.*, can be efficiently harvested using nanogenerators. Although, in such cases, the magnitude of force or energy is not sufficient to drive a conventional energy harvesting device such as an electromagnetic generator, this energy is sufficient to locally power small electronic gadgets and sensors (examples shown in Fig. **1**). Especially, if enormous, small electronic devices such as sensors, actuators, and wireless transmitters are to be installed on a large surface area, then it would be complex to power them individually. Therefore, any nano-battery or a self-powered nanodevice would be an ideal solution to meet such a requirement.

The piezoelectric-nanogenerators (PENG) and triboelectric-nanogenerators (TENG) are two important members of the NGs family [11 - 41]. PENG is one of the first NGs that utilize piezoelectric materials [11 - 21]. On the other hand, TENG is based on the triboelectric effect which has attracted significant attention from researchers due to the large possibilities of integration with conventional electrostatic induction generators [22 - 41]. Indeed, in terms of the magnitude of energy density discovery of a triboelectricity-based nanogenerator has proved to be a major milestone. TENG harvests mechanical energy with four modes of operations hence it has become a promising mechanical energy harvester in the nanogenerators area. TENGs are capable of harvesting all types of mechanical energies which include water waves, human motions, wind, vibrations, *etc.* Low-frequency mechanical energy harvesting has become a special advantage of TENG. Researchers have also Flexoelectric-nanogenerators (FENG) are similar to PENG except that the mechanical strain has a local gradient inside the material [42]. NGs used for harvesting thermal energy harvesting are two types *viz.* Pyroelectric-NG (PyENG) and Termoelectric NG (ThENG) are based on their underlying mechanisms [43 - 46]. Apparently these structures can also be integrated into a single NG device, where multiple properties can be leveraged to enhance the performance and applicability [47 - 52].

Therefore, developing the nanogenerators gives immense opportunity to provide sustainable, energy-efficient Internet-of-Things (IoT) smart devices. Fig. (**2**) illustrates the four basic properties responsible for the working of four NGs, as summarized below:

CHAPTER 9

Development of Piezoelectric Energy Harvesting Devices from Lead-Free Piezoelectric Materials

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Abstract: Piezoelectric energy harvesting has attracted wide attention to fulfill day-by-day increasing energy demand. Owing to its benefits, which include scalability, high power density, and simple architecture, piezoelectric ceramics have become the first choice of researchers over their counterparts such as electromagnetic and electrostatic energy harvesters. Despite extensive research and widespread use of lead-based piezoelectric ceramics, removing lead from these applications for environmental concerns is still difficult. Modern lead-free piezoelectric energy harvesting technology is reviewed in this chapter. Fundamental piezoelectric concepts and several piezoelectric material qualities are presented in a succinct theory part. A literature review on the advancement of lead-free piezoelectric ceramics, specifically KNN, BT, and BNT-based ceramics, since 2010 is presented. Applications for energy harvesting have also been described and assessed. Finally, based on their current developments, different challenges and future perspectives are also encompassed.

Keywords: BT, BNT, Ceramics, Energy harvesting, KNN, Lead-free, Piezoelectric.

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Prianka Sharma & Virat Khanna (Eds.)

INTRODUCTION

Energy scavenging and storing are the two main and crucial demands of today's world. In its simplest form, energy harvesting is basically converting unused environmental energy into electrical energy. Energy harvesting, also known as power scavenging, is the act of storing a tiny amount of energy that would otherwise be wasted as heat, light, sound, vibrations, or movement for small, wireless autonomous devices. Many energy harvesting strategies, including solar, thermal, electromagnetic, capacitive and piezoelectric, have been suggested recently. Of these, piezoelectric energy harvesters (PEH) are motion-based energy harvesters as shown in Fig. (**1**) [1 - 3]. These energy harvesters can eliminate the use of chemical batteries for different applications and could overcome the energy problems of today's world.

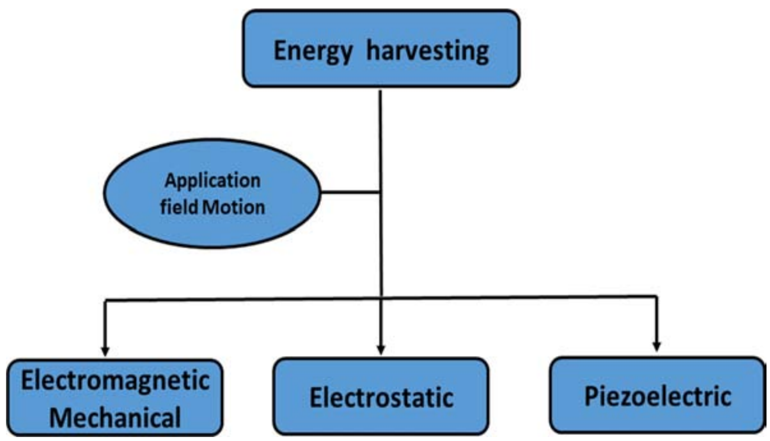

Fig. (1). Schematic flow chart of piezoelectric energy harvesting technique.

Significance of Piezoelectric Energy Harvesting Techniques

Piezoelectric energy harvesters play a pivotal role in the realm of sustainable energy, harnessing mechanical vibrations and converting them into electrical energy. This technology holds immense significance across various domains, from powering small electronic devices to contributing to larger-scale energy harvesting initiatives.

Renewable Energy Source

Piezoelectric energy harvesters provide a renewable energy source by tapping into ambient vibrations and mechanical movements. Unlike traditional energy sources that deplete finite resources, piezoelectric technology offers a sustainable solution for generating electricity [4, 5].

Ubiquitous Vibrations Utilization

One of the key advantages of piezoelectric energy harvesters lies in their ability to harness ubiquitous vibrations present in the environment. From footsteps on a busy street to vibrations in industrial machinery, these harvesters can tap into diverse sources, making them versatile and adaptable [6].

Self-Powered Electronics

The miniaturization of electronic devices has led to increased demand for self-powered systems. Piezoelectric energy harvesters can be integrated into small electronic devices, such as wearable technology or IoT devices, providing a self-sustaining power source and eliminating the need for conventional batteries.

Remote and Harsh Environments

In applications where accessing traditional power sources is challenging, such as remote locations or harsh environments, piezoelectric energy harvesters offer a reliable alternative. They can generate power in areas where other sources may be impractical or expensive to implement.

Wireless Sensor Networks

Wireless sensor networks are critical for monitoring and collecting data in various fields, including environmental monitoring, healthcare, and infrastructure. Piezoelectric energy harvesters contribute to the autonomy of these networks by providing a continuous and sustainable power source [7].

Energy Harvesting from Human Activities

The integration of piezoelectric devices into clothing or footwear allows for the harvesting of energy from human activities, such as walking or body movements. This concept has promising implications for the development of wearable technology that operates without relying on external power sources [8].

Reducing Environmental Impact

By utilizing ambient vibrations for power generation, piezoelectric energy harvesters contribute to reducing the overall environmental impact associated with conventional energy sources. This aligns with global efforts to transition towards greener and more sustainable energy solutions.

CHAPTER 10

Role of Thermal Spray Additive Manufacturing in Combating Climate Changes

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Abstract: Thermal spray coating processes are commonly employed to manufacture surfaces for distinct harsh industrial applications including power generation and aerospace. Application of various thermal spray techniques is significant for diverse applications, which can affect the mining of critical raw materials (titanium, nickel, cobalt, tungsten, yttrium *etc*.). As a result, thermal spraying alone has contributed to reducing mining through reuse, reduction and recycling of coated base materials. Thermal spraying also prevents the need to discard costly superalloys by enabling selective repair of gas turbine and aero engine parts, which would otherwise donate to increased greenhouse gas emissions from casting, remelting and additional downstream operations like machining. Recently, cold spray additive manufacturing (CSAM) has played a significant role in manufacturing industries owing to many benefits such as high process flexibility, less production time, high accuracy and quality reduced power consumption, and powder and gas requirement than traditional manufacturing processes. This advanced manufacturing process can build 3D parts and has the potential to alter the future of the manufacturing world with significant sustainable merits. Thus, the aim of this chapter is to offer an overview of CSAM including their advantages for sustainable manufacturing in terms of environmental concerns. Thereafter, the share of various processes and industries to greenhouse gas emissions has been studied. Finally, the challenges associated with cold spray additive manufacturing have been discussed.

Keywords: Additive manufacturing, Boilers, Climate change, Coatings material, Component restoration, Cold spray, Cold spray additive manufacturing, Challenges, Environmental concerns, Emissions reduction, Greenhouse gas emissions, Industrial applications, Nuclear plant, Preventive measure, Renewable energy, Sustainable coatings, Sustainable manufacturing, Superalloys, Turbine, Thermal spray.

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Prianka Sharma & Virat Khanna (Eds.)

INTRODUCTION

The UK, which had hosted the UN's COP26 summit in Glasgow (Nov. 2021), had been optimistic about this COP26 initiative to address the concerns raised about climate change in the G7 summits and many other forums. Industrial and academic communities have worked towards net-zero manufacturing and initiatives are under way to embrace digital technologies to create better recycling methods. Surfaces are created using a coating technique known as thermal spraying for a variety of challenging industrial applications. The severity of the surroundings is already evident in the fact that 55% of coatings by thermal spray are employed in aerospace and power-generating industries [1, 2]. Mining of crucial raw materials (CRMs) including Ti, Y, Ni, Co, and W can be impacted by the use of the thermal spray in a variety of applications. As a result, thermal spraying alone has helped to reduce mining by reusing, reducing and recycling the coated base materials [3, 4]. However, changes in production scale and distribution are being brought about by the development of manufacturing technologies in conjunction with consumer demand for increasingly customized items. The fundamental idea behind using additive manufacturing to create a product has been around for years. These three significant long-term advantages are provided by:

Improved Resource Efficiency

Improvements can be seen throughout the design and manufacturing phases since both the product and the manufacturing method can be changed.

Product Life Extended

Broader-reaching technological advantages, particularly for prolonging the usable service life of expensive equipment through repair and restoration operations [5].

Re-configuring the Value Chains

New distribution techniques, collaborative, shorter, localized value chains and astounding sustainability advantages [5, 6].

The market for thermal spraying is anticipated to rise from its current projected size of USD 10 billion to USD 25.82 billion by 2027 [7]. A quick scan of the market finds that flame/plasma spray combined account for between 50 and 60 percent of this industry. It should be emphasised that these two methods deposit coatings using either hydrocarbons or electricity. Consequently, as seen in Fig. (**1**), there is a substantial possibility to lower the carbon foot-print in this industry [7].

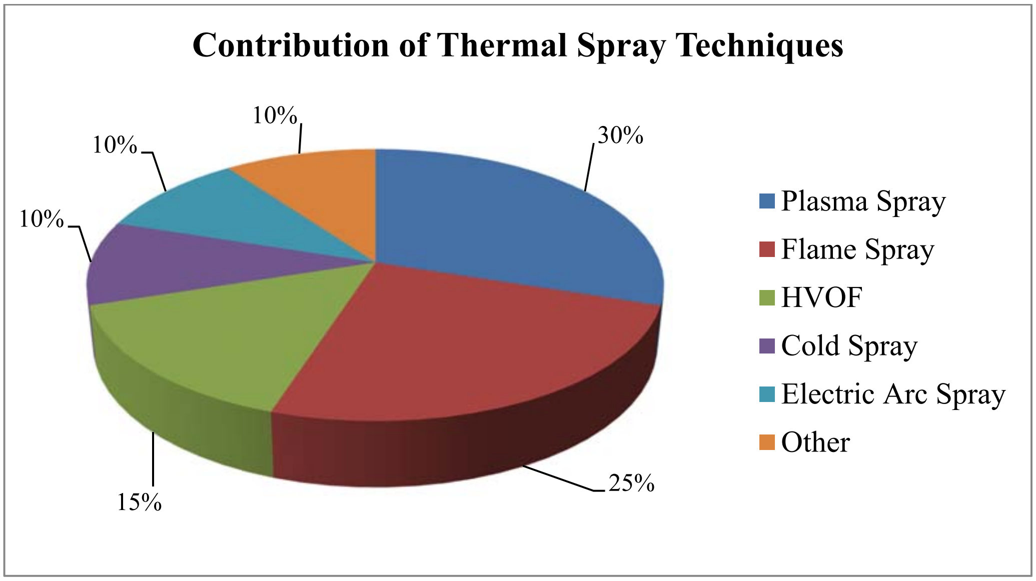

Fig. (1). US market share for various thermal spray techniques. The most prevalent options include plasma and combustion spray.

The US contribution of each subgroup of the thermal spray method is shown in Fig. (**1**). Since they all serve the same clientele, the CS method has also been incorporated into this depiction [7]. Market share of USD 5–6 billion, or between 50–60% of the thermal spray market, is held by the aviation and the power generating industries. On products like castings and manufactured parts like mating parts, paper and food processing rollers, overlay coatings are applied using thermal spray. This industry will allow businesses to reuse basic materials for a subsequent life cycle after reapplying the coating, allowing them to avoid throwing them away after a set amount of time. The pandemic is expected to cause thermal spray's market value to decline, as shown in Fig. (**2**), but it is expected to rebound due to ongoing increases in demand for energy use that require parts like turbine blades to be coated by thermal spray [7, 8].

Role of Thermal Spray in Climate Change

Catastrophic repercussions are already being caused by global warming's negative impacts on climate change [9 - 15]. The power generation sector, which contributes significantly to global warming (25 percent of all greenhouse gas emissions; see Fig. (**3a**), has been moving quickly in the direction of using more environmentally friendly fuels in order to reduce the use of fossil fuels and, as a result, lower CO_2 emissions, which are the primary cause of global warming; see Fig. (**3b**) [16, 17].

CHAPTER 11

Nanomaterials in Environmental Remediation: An Ecotoxicity and Risk Analysis

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Abstract: Nanomaterials have shown promising environmental remediation solutions owing to their unique chemical and physical properties. However, their probable impacts on human health and the environment must be evaluated before widespread implementation. This chapter aims to assess the ecotoxicity and risk associated with nanomaterials in environmental remediation. A comprehensive literature review has been conducted to evaluate the available data on ecotoxicity of nanomaterials, including their effects on aquatic and terrestrial organisms and mechanisms of toxicity. In addition, a risk assessment framework has been developed to assess the risks associated with nanomaterials in environmental remediation, taking into account the hazards, exposure, and vulnerability of different environmental receptors. Investigation of this study proposes that though nanomaterials have the potential to be effective in environmental remediation, there are significant concerns about their potential toxicity and risks. Further, research is needed to better understand the ecotoxicity and risk of nanomaterials, as well as to develop effective risk management strategies for their use in environmental remediation. Overall, this chapter highlights the importance of careful consideration of the ecological impacts and risks of nanomaterials before implementing them in environmental remediation programs.

Keywords: Assessment, Characterization, Contamination, Ecotoxicity, Environment, Green technology, Hazard, Health, Impacts, Management, Mitigation, Nanomaterials, Nonunique methodology, Physicochemical properties, Pollution, Remediation, Regulation, Risk analysis, Sustainability, Toxicity.

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INTRODUCTION

Nanomaterials are material s with unique properties that result from their small size, typically in the nanometer range [1 - 3]. These materials have acquired the attention of many research groups recently owing to their significant applications in various fields of electronics, medicine, energy and environmental remediation. The small size of nanomaterials results in unique chemical and physical properties, like enhanced reactivity due to large surface area, increase in mechanical strength, *etc*. which can be further utilized for environmental remediation purposes [4, 5]. Nanomaterials (NMs) possess unique characteristics that can lead to improved outcomes in various industries, such as electronics, pharmaceuticals and paint, *etc*. However, the small size of NMs also poses potential health risks that are distinct from bulk materials, requiring the usage of specialized assessment methods for hazards, exposure and risk evaluation. The toxicity of NMs is determined by various physical and chemical properties, including size, shape, chemistry, surface properties, charges and dissolution rate. Despite their potential benefits, limited data is available on human exposure routes of NMs, their behavior in the body and their potential to cause adverse biological effects such as oxidative stress [6 - 8]. There is limited data available through *in vitro*, animal and individual studies on breathing in NMs. So far, no long-term negative health impacts on humans have been reported, though this may be due to the novelty of NMs and ethical considerations surrounding human studies. As the use of nanotechnology continues to increase, toxicologists are increasingly concerned about the lack of information on NM's safety [9 - 12]. These days environment is increasingly exposed to NMs due to widespread production and use, presenting a risk to the well-being of humans, animals, plants and ecosystems. Research suggests that NMs have a significant impact on the environment and are harmful to aquatic and terrestrial life [13 - 22]. Health recommendations for NMs need to be guided by data from *in vitro*, animal, and associated investigations in sectors like ecological contamination while more clinical trials are accessible. Workers worldwide are more likely to be subjected to NMs on every workday due to the expanding manufacturing of NMs and their inclusion in a variety of goods, which raises the possibility of negative health effects. In an article, Watjanatepin *et al*. [23] deliberated that nanomaterials offer a growing number of commercial applications that directly affect the economy as a whole. As a consequence, there will probably be an increase in individual and ecological usage of nanomaterials. Owing to the financial importance and broad application of the field of nanotechnology, it is essential to foster a broad discourse about identified risks to fully realize the interest of nanotechnology and get rid of overly careful approaches that serve as a roadblock to their integration into products and systems. The conference identified a few pressing issues and out-of-date knowledge that might hamper this goal, including the dearth of reliable data regarding the hazardous effects of nanoforms. This inadvertent void adds to legislative uncertainty, and it is critical to ascertain the extent to which uncertainty may be tolerated given the actual effects of economics on the environment and health in general. Additionally, methods for assessing the hazards of nanoparticles are currently in their early years, which makes it challenging to use them in commerce. Boros *et al*. [5] investigated hybrid nanoparticles and eco-toxicology, as seen by the growing number of academic papers available via the Web of Science Core Library from 2010 to 2019. See Figs. (**1a** and **b**). It is crucial to look into the eco-toxicological effects of nanoparticles due to their wide range of uses, increasing importance in protecting the environment, and ability to determine the eco-toxicity of potential pollutants. An increasing amount of scholarly publications on the environmental toxicity of nanoparticles on the WOS Data Set between 2010 and 2019 provided evidence for this as seen in Fig. (**1c**). The need for evaluating the environmental toxicity of nanoparticles has arisen, making the use of conventional ecological toxicity evaluation methods for nanomaterial evaluation necessary. The assessment of risk is significantly hampered by the wide range of distinctive material formulations for identical chemical constituents that have distinct physical features, even though toxicology properties may react to modifications in their physical characteristics, such as shape and structure. The use of nanoparticles is spreading across several industries and categories of goods. While the number of employees exposed to NMs is unresolved it is rising in line with the production and use of NMs in industry [24 - 26]. If NMs are swallowed, breathed in, or acquired via the pores of the body, they may result in illness at the workplace. The lungs of humans are an ideal entry point for NMs because of a number of characteristics, including increased particular surface area, thin epithelium obstacles, and extensive vascular. Although gastrointestinal and cutaneous exposure to NMs may occur, inhaling is far more likely to occur with larger population doses of NMs. As of right moment, breathing in bio-persistent filaments and nanoparticles that resemble mesothelioma poses the biggest risk to health since they can result in malignancies and inflammation locally.

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Prianka Sharma

Prof. Prianka Sharma, an alumnus of Himachal Pradesh University has obtained her Ph.D. in theoretical nuclear physics in 2008. She is a physicist by training and has expertise in theoretical nuclear physics, experimental condensed matter physics and material science. She has published more than 15 research papers in SCI and Web of Science and 01 book and has guided 03 research scholars successfully. Her passion for understanding new phenomena's and technologies drives her interest in improving the properties of materials for environment-friendly green technology for water treatment and energy harvesting. An experimental physicist with strong analytical and logical skills makes her an expert trouble-shooter. With skills of high order interpersonal understanding, teamwork and communication, she envisions her commitment to the highest standards of professional endeavour.

Virat Khanna

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