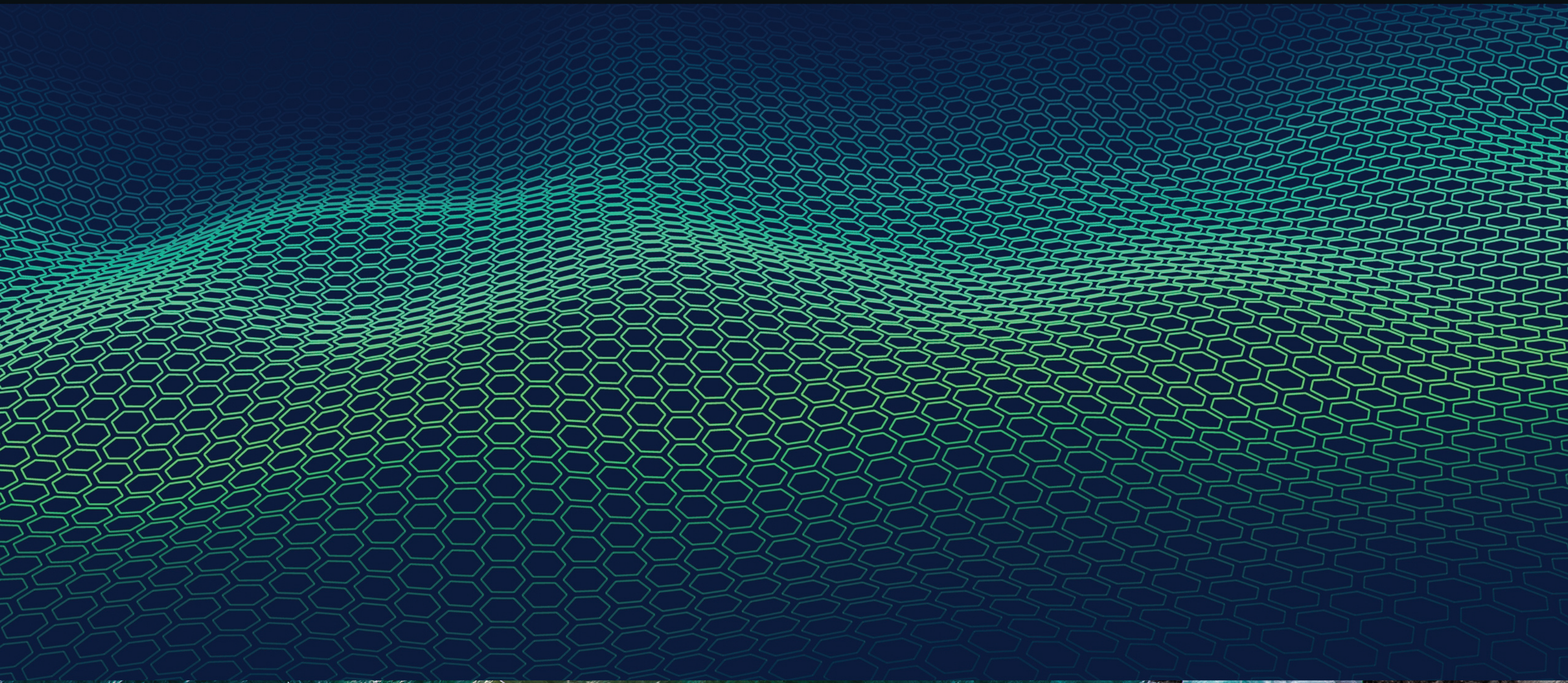
Nano Materials Induced Removal of Textile Dyes from Waste Water



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PREFACE

It has been a long time since Feynman's pioneering lecture unlocked the world of Nanomaterials. A large number of extensive research works have already enlightened the properties and key applications of Nanoscience. Nano-science has been strongly correlated with quantum physics and chemistry. Most of the basic features of Nanoscience are basically extended from those two classic subjects. Thus, proper expertise in basic Nano-science is still not independent; it often requires a strong basic understanding of traditional subjects like advanced physics and chemistry. On the other hand, Nanoscience has already been applied from the smallest electronic chip to the large displays of modern smartphones. To extend the applications of Nanoscience in a further variety of sectors, the correlation between Nanoscience and Nanotechnology must be opened up in front of the general engineering community in addition to classic science scholars.

Another key aspect of nano-science is its mimicking nature. Different nanostructures have strong similarities with the natural pattern, and spontaneously open up their possible applications in different fields. One of such fields which is a matter of most acute concern nowadays is the environment. Actually, in science and technology, whatever be the fields of research, ultimately has a connection with either energy or the environment. It is an irony that from the very advent of scientific and technological development, we always harnessed energy issues with the cost of the environment. Now it is nature’s turn to repay the debt. As we know that today we are standing beneath a tremendous environmental crisis in terms of air, soil, water, noise and radioactive pollution, thus, a potential field of science and technology such as nanotechnology should be used to address the problem.

Keeping this in mind, this book brings a small effort of the authors to give the reader an idea of how nanomaterials may be used to address the environmental issue. As the entire topic is too vast, we have taken only a single part, *i.e.*, water pollution, and even after that, we have only concentrated the textile dye-induced water pollution and their negative impact and have shown how nanomaterial, can help us in getting rid of this problem through various processes.

This book is properly designed to solve basic queries of common academicians and technologists about the fundamentals of Nanoscience and nanomaterial-induced removal of textile dyes. Its basic concepts, chronological development and applications have been thoroughly discussed with appropriate examples and comparisons. We strongly believe that this effort shall be very important and useful for the budding engineers and scientists who are interested in the environmental aspect of Nanoscience.

The efforts have been made so that the style of the writing can be kept simple and easy to understand, and the essence of the subject can be fed even to a school student. Also, we have tried to keep the volume of the book reasonable so that the journey into this subject from the introduction to the advanced application can be finished within a couple of hours, say within a certain four-hour journey from Kolkata to Mumbai. In our previous book (by DB and NSD), "Nano Science - Concepts and Fundamentals" published by NOLEGEIN (an imprint of Consortium e-Learning ISBN: 978-93-87376-77-9), we put our effort into making the beginner interested in the subject for further study and offer deep learning about a specific topic. Now in this venture, we have taken advancement one step forward to deal with a particular topic likenanomaterial-induced removal of textile dyes from water.

The entire book has been divided into eight chapters, of which the first two chapters are mainly related to history and basic science behind the technology and resemblances between nature and nano-science. Chapter 3 has been dedicated to discussing the ways and means of seeing nanomaterials, *i.e.*, the basic principle of microscopies, mainly electron and scanning probe microscopes. Chapter 4 is all about the basics of textile dyes and their impact on the environment. In Chapter 5, we have given ideas about the basic structures and properties of a few nanomaterials having potential as dye remover. The next two chapters have detailed theories and experiments regarding ways and means of removing dyes through photocatalysis and adsorption. The last chapter is basically a concluding Chapter 5 discussing the efficiencies of different nanomaterials as dye remover.

We really enjoyed a lot writing this book and sincerely hope that readers will enjoy reading the book as well.

Last, it is a humble request of the author to the reader to kindly provide feedback, suggestions and unbiased, critical comment for further improvement of the book. Though we have tried our best to make the content of the book error-free still, if some mistakes are found, kindly let us know and thus help us to make the project perfect and error-free.

CONSENT FOR PUBLICATION

None.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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The authors want to thank all the **publishers** who have kindly provided permission to reuse different content already published in their different journals.

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CHAPTER 1

Introduction to Nanomaterials: Interaction with Water

Abstract: The first chapter helps the reader to get acquainted with the basic features of the nanomaterials. Here, the basic properties of nanomaterials, basic synthesis processes, and different applications of nanomaterials are discussed. The novel features of the material are also mentioned. How the suppression of degrees of freedom of electrons that affects the electrical, optical, and other properties, has been discussed in detail. Special emphasis has been given to the resemblance of nano-systems in mother nature, and as a result, few examples have been mentioned. As the objective of the book is to discuss the nanomaterial-induced removal of dye materials from water, thus the interaction between water and the nanomaterials plays one of the major roles. Keeping this in mind, we have discussed the concept of surface tension, surface energy, surface energy components, hydrophobicity, and lotus effect in much depth with their consequences to different particular applications. The discussion has also been done on the concept of contact angle, hysteresis, porosity, and related topic. Thus, this chapter familiarizes the reader acquainted with the basic characteristics, properties, and applications of nanomaterials and provide useful information regarding the interaction of nanomaterials with water, which is the central theme of this book.

Keywords: Contact Angle, Density of the State, Hydrophobicity, Hysteresis, Lotus Effect, Nanomaterial, Quantum Confinement.

INTRODUCTION TO NANOMATERIALS

The term "nano" does not refer to a substance, science, or technology. It is simply a dimension of 10^{-9} meters. Thus, any material having this dimension along any direction is called a nanomaterial. The science that deals with the dynamics of the material in nanoregime is called nanoscience, and the technology established manipulating nanomaterials is called nanotechnology. Nanotechnology is an interdisciplinary science in which material scientists, mechanical and electronic engineers, biologists, chemists & physicists work together to extend the nanoscale boundaries. Nano is a Greek word which means micro or small. Every particle whose size is 100 nm or smaller is considered a nanoparticle. Nanoscience is the study of the fundamental principles of a molecule and structure with at least one dimension, roughly between 1 & 100 nm.

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In 1959, Richard Feynman, an American physicist at the California Institute of Technology, said in one of his lectures, "*There's plenty of room at the bottom*." These lines laid the foundation for nanotechnology, which is why Richard Feynman is known as the "Father of Nanotechnology." To indicate how small an object is, we compare it to human hair. We know that the average diameter of human hair is about fifty thousand nanometres. In comparison, the smallest features etched on a commercial microchip are typically less than 100 nm. The human eye can resolve objects with a diameter up to 10,000 nm. Fig. **(1.1)** shows the size dependence of different objects in the universe.

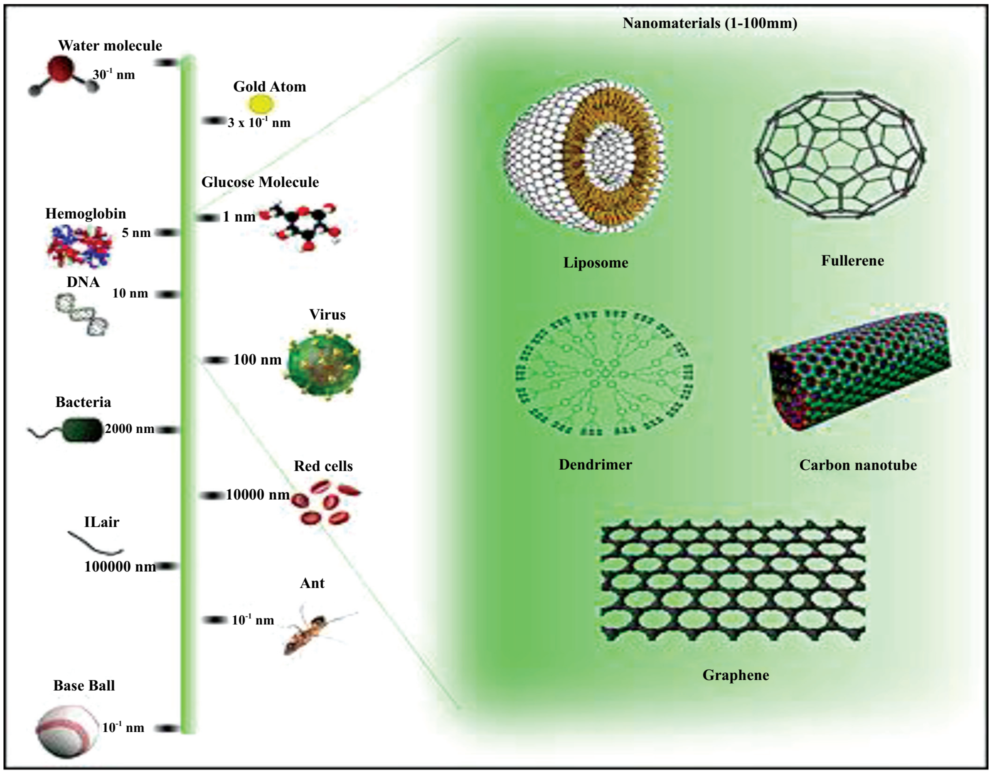

Fig. (1.1). Size dependence of different objects in the universe.

Nanoscience is a study that deals with small things and the use of nanotechnology in various places. The chemical and physical characteristics of nanoparticles change due to their extremely small sizes. For example, the cubes of sugar are less sweet than the castor sugar because the surface area of the castor sugar is larger than the cubes of sugar. With the help of nanotechnology, we have the ability to control atoms and molecules. The materials which we use in nanotechnology are called nanomaterials.

Following are the reasons for unique properties seen in nanomaterials compared to their bulk form:

The Higher Ratio between Surface and Volume

The very high surface-to-volume ratio gives rise to higher numbers of dangling bonds, which, in turn, develop very high chemical activities within the nanomaterial, making them different from its bulk form (detailed mathematical treatment has been given in the next chapters).

Quantum Effect

From the very basic particle in a box problem one faces in quantum mechanics, it is seen that the energy gap between the two successive energy levels or rather any two energy levels, depends inversely on the square of the box dimension, thus enhancing the optical gap of the material. This optical gap governs the optical properties of the nanomaterial (detailed mathematical treatment has been given in the next chapters).

Density of the States

Density of the state, *i.e.*, the numbers of states per unit energy interval per unit volume, are highly dimension dependent and thus shows marked differences for 0, 1, 2, and 3-dimensional structure of the same material (detailed mathematical treatment has been given in the next chapters).

It is to be noted that there are number of quality books related to the basic properties of nano, even by the authors themselves. Thus, here the same particular topics are not being focussed in much depth. However, the reader may focus on the following reference [1-4].

Synthesis of Nanomaterial

In order to explore the unique physical properties & phenomena and also to realize the useful applications of nanostructures and nanomaterial, the ability to fabricate and process nanomaterial and nanostructures is the first hurdle in nanotechnology.

CHAPTER 2

Uniqueness of Nanomaterials and Associated Science

Abstract: This chapter deals with the concept of nanomaterials, especially basic quantum mechanics and solid-state physics. It is now a well-established fact that the dynamics of materials in nano-regime cannot be described by simple Newtonian mechanics, and, therefore, one should opt for quantum mechanics. Thus, the focus of this chapter will be on basic quantum mechanics and solid-state physics in order to gain an understanding of the system's transport properties. A few characteristic phenomena of nanomaterials like the density of state, quantum confinement, excitonic radius, *etc.*, will also be discussed in detail. To acquaint the reader with the Fermi energy and related properties, efforts will be made to provide a fundamental concept of statistical physics, specifically the Fermi-Dirac statistics. The authors have focused their efforts exclusively on dealing with different length scales, namely Ballistic transport and the associated Landauer-Buttiker formula of quantum transport in nanomaterials. Also, the relationship between exciton radius and quantum confinement and optical properties of nanomaterial has also been explained in detail. The concept of tunnelling, which is the foundation of quantum transport, has been explained, and an effort has been made to acquaint the reader with quantum conductance and Coulomb blockade.

Keywords: Ballistic transport, Crystallography, Density of state, Exciton, Quantum confinement.

A BRIEF REVIEW OF CRYSTAL STRUCTURES

Depending upon the extent of periodicity of atoms in a solid (mainly), the material has been classified into amorphous material and crystalline material. It is a well-known fact, as described in Fig. **(2.1),** that when a material has periodicity over a substantial distance, it is called crystalline material, and when there exists no periodicity or periodicity over a very short range, it is called amorphous material. Both materials have distinct properties that differ greatly from one another, and the properties of the same material in amorphous form differ significantly from those of the crystalline form. As a result, it is to be mentioned that in a crystalline material, when the same periodicity exists throughout the material, it is called a single crystal, and when periodicity changes from one crystal grain to another separated by a region called grain boundary, it is called a poly-crystalline material.

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Table **2.1** summarizes the basic differences in the properties of amorphous and crystalline material.

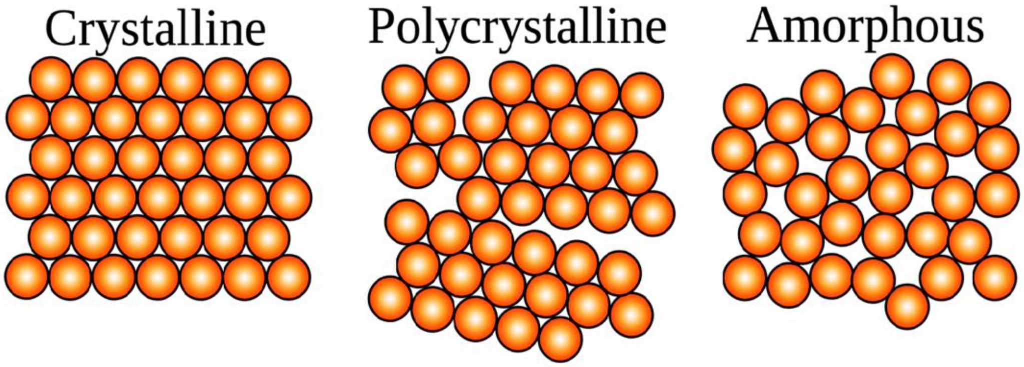

Fig. (2.1). Basic schematic representation of crystalline and amorphous structures.

Table 2.1. Differences in the properties of crystalline and amorphous material [1].

Crystalline Material	Amorphous Material
Atoms are arranged in regular 3 dimensions	They do not have a regular arrangement
Sharp melting point	No particular melting point
Anisotropic	Isotropic
True solid	Pseudo solid
Symmetrical	Unsymmetrical
More rigid	Less rigid
Long-range order	Short-range order
Example: Potassium nitrate, copper	Example: Cellophane, polyvinyl chloride

A crystalline material has two units, depending on which the entire structure of a crystal gets developed, *i.e.*, which determines the periodicity of the crystal. The first part is a set of imaginary points arranged in proper periodic ways within the crystal that determines the periodicity of the material. These are called lattice points. The second component, called basis, is the presence of an actual atom or collection of atoms at each lattice site. Thus, one can say, as shown in Fig. (**2.2**), that a unit cell of a crystal is nothing but the building block of the crystal system whose repetitive arrangement along all three directions develops the entire crystalline material. If a unit cell effectively contains only one single atom, it is called a primitive unit cell as in the case of a simple cubic system, or on the contrary, if the effective numbers of atoms in the unit cell are more than one, it is called a non-primitive unit cell as in the case of body-centered or face-centered cubic system. Both systems are shown in Fig. (**2.3**).

Lattice + Basis = Crystal,

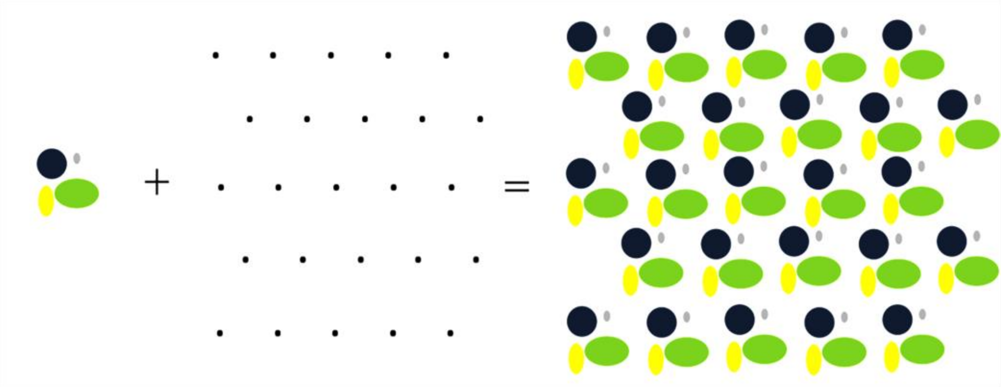

Fig. (2.2). Basic schematic of lattice and basis.

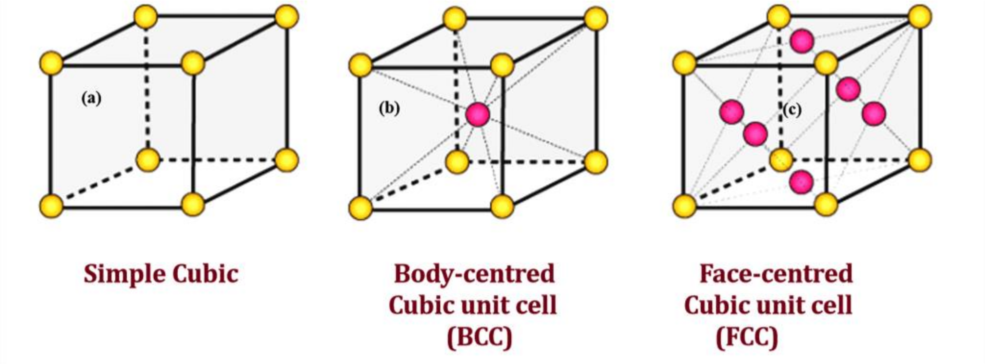

Fig. (2.3). Type of unit cells: Primitive (**a**) non-primitive (**b, c**) unit cell.

CHAPTER 3

Basic Microscopic Techniques to Characterize Nano Materials

Abstract: It is not surprising that materials with nanoscale dimensions have existed since the creation of the universe. The reason is simple since all the materials are composed of different atoms or molecules, so an assembly of a few molecules can give rise to what one calls “nanomaterials”. The concept of nano, or more specifically, nanoscience and technology, is relatively new, as it requires a long journey of technological advancement to develop distinct optical devices that can see materials with dimensions of 10-9 metres and thus manipulate them for greater purposes. These special devices are commonly known as microscopes; however, they are not the same as traditional microscopes, which have a maximum resolution of 10-6 (micro) meters. In this chapter, the basic constructions and working principles of the more commonly used microscopes, rather than nanoscopes, will be discussed. Discussions on field emission scanning electron microscope (FESEM), high-resolution transmission electron microscopes (HRTEM), and scanning tunnelling microscope (STM) will also be done. Besides, the name and the main working principle of some other microscopic techniques will be mentioned. Apart from imaging, some other uses (if any) of these devices would also be mentioned.

Keywords: AFM, FESEM, Microscopy, Resolving power, Resolution, SPM, STM, TEM.

WAVE NATURE OF LIGHT

According to the ancient corpuscular theory of light, a source of light emits light in all directions in terms of a stream of small particles. These particles are assumed to be so small that when two such streams of particles overlap or are superposed, any collisions between these particles are really hard to occur. These assumptions give rise to a separate and rather an earlier branch of optics called geometrical optics. This theory can satisfactorily explain the basic optical phenomenon like reflection, refraction, *etc.*, but fail to explain some other practical phenomenon like the light entering into the geometrical shadow region of a sharp object (diffraction) or production of dark fringe by superposition of two light sources (interference). All these phenomena can be well understood only if one assumes that light has some wave character. The corresponding branch of optics is called physical optics. Based on this, Huygen was first able to give a satisfactory explanation for the propagation

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of light. According to him, every point on a wavefront may be considered a source of secondary spherical wavelets which spread out in the forward direction at the speed of light. The new wavefront is the tangential surface to all of these secondary wavelets. According to Huygens' principle, a plane light wave propagates through free space at the speed of light, c. The light rays associated with this wavefront propagate in straight lines, as shown in Fig. **(3.1)**. It is also fairly straightforward to account for the laws of reflection and refraction using Huygens' Principle. Though according to the principle, there would be a backward propagation of light, which has to be neglected.

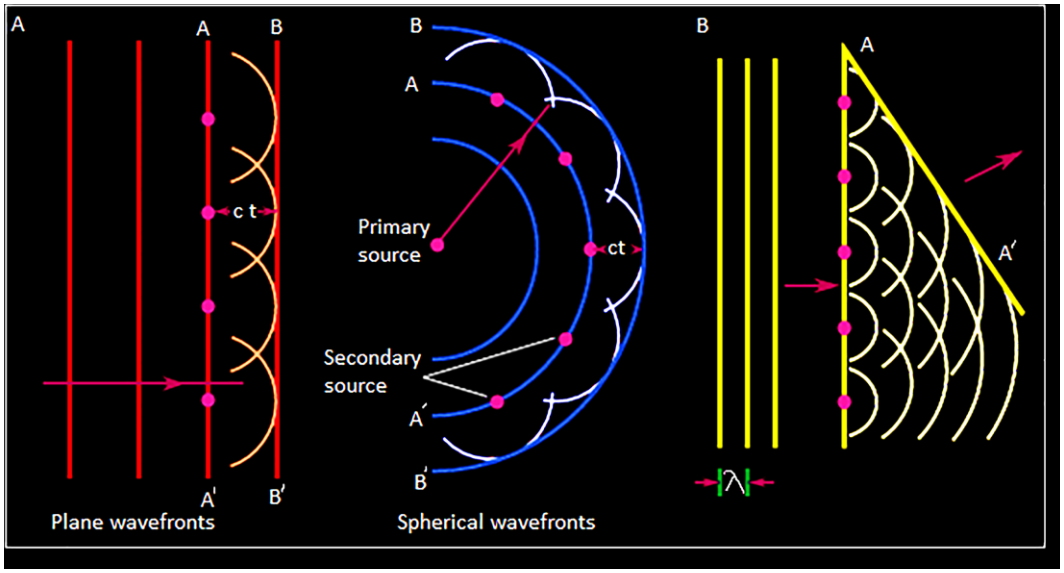

Fig. (3.1). Propagation of light according to Huygens' Principle.

This theory can successfully explain the previously mentioned phenomena like interference diffraction, *etc.*, all of which originate from the basic principle of superposition of light waves.

Superposition Principle

The principle of superposition states that when two waves interact, the resulting wave function is the sum of the two individual wave functions. The superposition may be constructive or destructive, as shown in the side by Fig. (**3.2**). When the crests overlap, the superposition wave reaches a maximum height. This height is the sum of their amplitudes (or twice their amplitude, in the case where the initial waves have equal amplitude). The same happens when the troughs overlap, creating a resultant trough that is the sum of the negative amplitudes. This sort of interference is called constructive interference because it increases the overall amplitude.

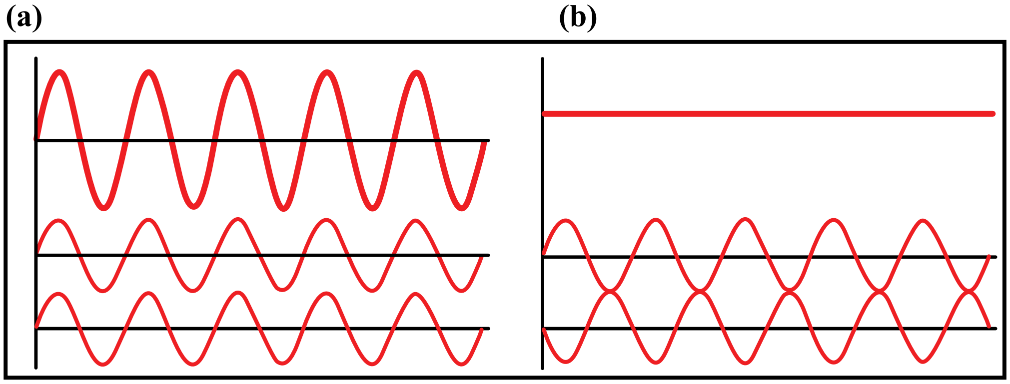

Fig. (3.2). Superposition of light (**a**) constructive (**b**) destructive interference.

Alternately, when the crest of a wave overlaps with the trough of another wave, the waves cancel each other out to some degree. If the waves are symmetrical (*i.e.*, The same wave function, but shifted by a phase or half-wavelength), they will cancel each other completely. This sort of interference is called destructive interference. Thus, interference can be considered broadly to be the modification of resultant lights due to the superposition of primary light waves coming from two different coherent sources (*i.e.*, the waves emitted from them have the same frequency and are 'phase-linked'; that is, they have a zero or constant phase difference).

The phenomenon of diffraction (which can be considered a special kind of interference), on the contrary, is nothing but the interaction of light coming from the different points, *i.e.*, secondary wavelets of the exposed part of the same wave fronts. Due to this kind of interaction, light gets bent around the sharp corners of an obstacle or slit (having a size comparable to the wavelength of light) and spreads into the regions of the geometrical shadow. The whole state of affairs is shown in Fig. (**3.3**).

It is to be noted that the phenomenon of diffraction is more closely related to the basic working principle of an optical microscope since the image of a point object is basically always a circular patch of light with centre illuminated as bright

CHAPTER 4

Structures and Basic Properties of Textile Dyes and their Impact on the Environment

Abstract: In today's world, the textile industry is one of the most important sectors, both economically and in everyday life. The textile industry is one of the most important commercial sectors that require a significant amount of water and chemical ingredients for several types of processing needed during the conversion of fibres to final textile products ready for sale. Textile dyes are an important topic to discuss from both a positive and negative perspective, as dyes are an unavoidable part of colouring clothes or papers, but when they end up in the environment as a waste product from the industries mentioned above, they have a significant negative impact on the environment and the water ecosystem. Thus, it becomes necessary to handle the dyes properly and develop ways and means to remove/reuse them. However, in order to do so, one must have an in-depth understanding of the structures and properties of various dyes, as well as the treatment that should be applied. Keeping this in mind, we have discussed the basics of textile dyes in this chapter. The classifications of textile dyes, as well as their chemical structures and qualities, were also covered in this chapter. The in-depth discussion on the fundamental of textile dyes may help the workers handle dyes in a controlled way to protect the environment from the associated toxicity.

Keywords: Dyes, Toxicity, Water pollution, Ecosystem, Chromophores, Environment.

INTRODUCTION

The textile dye industry has a history of more than 4000 years, but it was only around 150 years ago that people got capable of synthesizing dyes artificially [1]. This boom was a result of the work of William Henry, who discovered Mauveine accidentally, while working on Quinine synthesis [2].

This accidental discovery led to a community of a new generation of dyes, and subsequent research into the synthesis and applications of dyes and pigments began. It is noteworthy that there exists firm demarcation between dyes and pigments, mainly in terms of stability as well as molecular size. Dye molecules are soluble either in water or oil, lesser in molecular size, and thus more vulnerable to external perturbation compared to pigments [3]. Dyes basically are unsaturated organic

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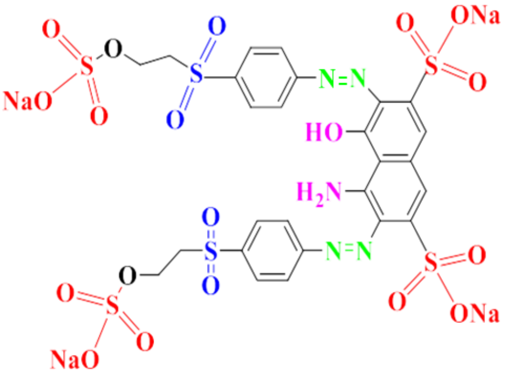
molecules with complex structures capable of absorbing light and subsequently giving colors in the visible region [4]. There are a variety of dyes with varying formulas, structures, and properties. As mentioned before, dyes are capable of absorbing part of the visible spectrum (chromophore) and thus, the color is associated with the part that is not absorbed. Dyes may be distinguished from one-another, from the point of view of their ability to absorb a specific part of the entire visible spectrum, *i.e.*, wavelength between 380 to 750 nm. In the process, a selective portion of white light gets absorbed by a group of atoms during reflection, transmission, diffusion, or other processes. The very group of atoms responsible for the absorption of colour is called chromophoric groups. This clearly suggests it is the chemical composition as well as the molecular structures that are responsible for the intensity of coloration. It basically takes certain luminous radiation in turn, giving their complementary colours [5]. As mentioned before, the use of natural dyes was rather common in ancient days when different natural materials like beetroot, other plants, insects, and animal minerals were used as natural dyes. The concept was environmentally friendly as all these natural dyes are low or null toxic, and the corresponding wastewater can be degraded by different biological means [6].

Nowaday, natural dyes are almost totally replaced by synthetic dyes due to the constantly growing demand for color in textile, paper and associated other industries. A recent survey says that now a day, around 10 % of the stuff is coming out as waste material from almost 10^8 tons of synthetic dyes produced every year [7]. It is also an alarming fact that almost 50 % of the dyes actually have nothing to do with textile but exist in the liquid phase with all its toxicity.

In a dye, the most important part is the chromophore which is actually nothing but the spatial arrangements of atoms responsible for absorbing colors. The absorption takes place due to the photo-induced excitation of electrons that exists in these chromophores. It is very clear that depending on the nature of dye; chromophores are representatives of different functional groups that include azo, Nitro, nitroso, carbonyl, thiocarbonyl, and alkenes or others [8]. The molecules containing chromophores are called chromogenic. However, they are not effective unless the remaining part of the molecule called auxochrome comes and joins together to modify the color of the dye and thus to open the dye possibilities. The auxochromes may be of both the types, *i.e.* acidic and basic. The remaining part of the molecule is the third part only. It is the existence of a stable functional group only that makes it difficult to handle them by conventional treatment [9].

If we discuss more the basic structures of dyes and their connection in the entire procedure, we have to remember that there are three parts consisting of chromophoric, auxochromic group and the basic skeleton aromatic rings (like benzene or anthracene or other). Depending upon the relative abundance of all the groups mentioned above, the conjugation of the unsaturated bonds increases, which in turn affects the activity of the electrons giving different colors [10]. Presently, we can hear around 40000 trade names that have been given to 8000 different synthetic dyes, having specific color index (CI) specifying color, class and order numbers [11]. Just for a better understanding of the reader, we have taken Reactive Black 5 dye as an example, which happens to be a diazo dye. The structure is shown in Fig. (**4.1**).



Molecular formula : $C_{26}H_{21}N_5Na_4O_{19}S_6$

Molar mass (g/mol) : 991.82

Molecular Structure : Double azo class

C.I. number : 20505

CAS Registry Number : 12225-25-1/17095-24-8

Application class : Reactive

Commercial names : Reactive Black 5 ; Remazol black B Diamira Black B.

Fig. (4.1). Reactive Black 5 as an example of how to classify and uniquely recognize a dye uniquely representative example for the color index classification.

CLASSIFICATION OF DYES

As mentioned before, there are very few numbers of natural dyes that are available for use, thus, a simple nomenclature was enough to remember their detailed properties, structures and applications of them. With the advent of different industries like textile, papers and other demand for dyes found new exponential growth, which basically initiated the need for systematic classifications of dyes. The classifications have been done based on a number of parameters, mainly chromophore structures or color index and Industrial application.

CHAPTER 5

Basic Structures and Properties of Few Potential Nanomaterials

Abstract: After the discussion of all the preceding sections/chapters, now we are in a position to review some typical nanomaterial systems that have established themselves as materials of immense potential in the field of water purification by successfully removing different textile dyes through different processes like catalysis adsorption or others. In this chapter, we will discuss a few such particular materials from different domains. The material will mainly include metal oxide nanostructures and related derivatives like zinc oxide, *etc.*, and also carbon nanostructures like carbon nanotube, graphene, *etc.*, and their hybrids. A detailed discussion regarding the dye removal ability of graphitic carbon nitride is also included here. In this regard, the results of other researchers will be accompanied by a few of our own findings, which will help the reader in better understanding the topic. Apart from these well-known materials that have higher dye removal effectiveness, a few other less studied and newly evolved systems, such as silicon nanowire and p-type conducting oxides like copper borate, have also been discussed with a few established results.

Keywords: Carbon, Carbon Nanotubes Zinc Oxide, Graphene, Nanostructures, Silicon nanowire.

CARBON NANOSTRUCTURES: BRIEF HISTORY AND PROPERTIES

Among all the materials, carbon nanostructures have attracted the attention of researchers as well as technologists from the last few decades due to their versatile applications in various fields of complete difference. Fullerene, carbon nanotube, nano fibers, nanocoils, *etc.*, have already established their importance in different fields, but still, day after day, new novel carbon nanostructures are being discovered and being used for different applications. The element carbon is unique in the sense that it has a wide variety of allotropes with a fascinating range of mechanical, optical and electrical properties. Among all other fields mentioned above, carbon fibers, tube, coil, diamond-like carbon, diamond, graphene, and even amorphous carbons have established themselves as field emitters as well as efficient coating elements and are used in different applications.

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Carbon and its Different Hybridized States

Carbon is the chemical element with the symbol **C** and atomic number 6. As a member of group 14 on the periodic table, generally it is nonmetallic and tetravalent, making four electrons available to form covalent chemical bonds. There are three naturally occurring isotopes, of which ^{12}C and ^{13}C are stable, while ^{14}C is radioactive, decaying with a half-life of about 5730 years. There are several allotropes of carbon, of which the best known are graphite, diamond, and amorphous carbon. The physical properties of carbon vary widely with the allotropic form. For example, diamond is highly transparent, while graphite is opaque and black. Diamond is among the hardest materials known, while graphite is soft enough to form a streak on paper. Diamond has a very low electrical conductivity, while graphite is a very good conductor. Under normal conditions, diamond has the highest thermal conductivity of all known materials. All the allotropic forms are solids under normal conditions, but graphite is the most thermodynamically stable. A general list of different properties of carbon has been given in Table **5.1**.

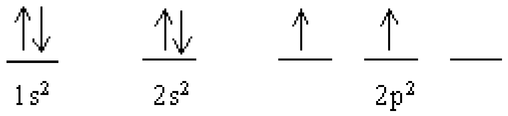
Table 5.1. Some properties of carbon.

General Properties	
Name, symbol, atomic number	Carbon, C, 6
Group, period, block	14, 2, p
Standard atomic weight	12.0101gmol^{-1}
Electron configuration	$1s^2\ 2s^2\ 2p^2$
Physical Properties	
Phase	Solid
Density (at room temperature)	1.8–2.1 (amorphous carbon), 2.267 (graphite) 3.515 (diamond) g·cm^{-3}
Sublimation point	3915 K
Triple point	4600 K

(Table 5.1) cont.....

Specific heat capacity (at room temperature)	8.517 (graphite), 6.155 (diamond) J·mol^{-1}·K^{-1}
Atomic Properties	
Oxidation states	4, 3, 2, 1, 0, -1, -2, -3, -4
Electronegativity	2.55 (Pauli scale)
Ionization energies	1st: 1086.5 kJ·mol^{-1} 2nd: 2352.6 kJ·mol^{-1} 3rd: 4620.5 kJ·mol^{-1}
Covalent radius	77(sp^3), 73(sp^2), 69(sp) pm
Vander Waals radius	170 pm

The element carbon is one of the most versatile elements on the periodic Table in terms of the number of compounds as it may form an infinite number of compounds virtually. This is largely due to the types of bonds it can form and the number of different elements it can bond. Carbon may form single, double, and triple bonds by means of different hybridization with the ground state configuration, as shown in below Schematic **1**.



From the ground state electron configuration, it can be seen that carbon has four valence electrons, two in the 2s subshell and two in the 2p subshell. The 1s electrons being the core electrons do not contribute in any kind of bonding. There are two unpaired electrons in the 2p subshell, so if carbon were to hybridize from this ground state, it would be able to form at most two bonds. It is known that any bond formation corresponds to the release of energy, so it would be to carbon's benefit to try to maximize the number of bonds it can form. For this reason, carbon will form an excited state by promoting one of its 2s electrons into its empty 2p orbital and hybridize from the excited state. By forming this excited state, carbon will be able to form four bonds. The excited state configuration is shown below in Schematic **2**:

CHAPTER 6

Introduction to Photo-Catalysis

Abstract: The matter-energy reaction is the basis of a variety of fundamental scientific phenomena we have witnessed in nature. Photoreaction is related to the interaction of photons and the molecules of a substance. When the necessary photon in the ultra-violet or visible range of the electromagnetic spectrum is absorbed by the materials in concern, it may convert different poisonous elements into harmless substances, such as water and carbon dioxide. The study of photon physics and chemistry is fundamental for our understanding of the world we live in. The basic physiological processes through which the living species maintain their life cycles are also somehow related to the different photochemical reactions. Photo-catalysis happens to be a low-cost, versatile, and environment-friendly method that deals with a variety of harmful pollutants. Pollutants can be inorganic, organic, or even biological, and they can be found in both air and water. Photo-catalysis is a process in which the catalyst, light source, and contaminants must be in close proximity or contact. There have been numerous studies on the oxidation-induced removal of different organic pollutants as well as microorganisms, especially those found in water. In this chapter, we have covered the basics of photo-catalysis, the characteristics of various catalysts, their types, and photochemical laws, as well as the conditions and limitations of quantum yield.

Keywords: Photolysis, Photocatalysis reactions, Photochemical laws, Quantum Yield.

INTRODUCTION

The term photocatalysis may fundamentally be defined as the acceleration of a chemical reaction in the presence of light with different energy ranges, which may be visible or UV.

This method being one of the simplest, has gathered world-wide attention in the last couple of decades. The main reason behind this rapid spreading lies in the fact that this particular mechanism has two very important applications like hydrogen evolution through the splitting of water under solar power and the water purification by removing pollutants contained in small concentration. There is another practical reason also, and that is because of the fact as the mechanism, as well as application related to the phenomena, has multidirectional aspects; this has brought physicists, chemists, material scientists, pharmacists and researchers of other domains into a

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single platform [1]. In the context of history and research, interest in heterogeneous photocatalysis can be traced back to many decades when Fujishima and Honda discovered in 1972 the photochemical splitting of water into hydrogen and oxygen in the presence of TiO_2. From this time, extensive research, much of it published, has been carried out to produce hydrogen from water in oxidation-reduction reactions using a variety of catalyst materials.

It is mentioned worthy that catalyst is a topic of prime interest that one might come across while studying physical chemistry, especially while learning about photochemical or chemical reactions. Some of the catalyst reactions occur rapidly or take a long time, depending upon the catalyst material and environmental media. Catalysis is of great importance as it changes our physical life. The major regions where the world economy depends upon the technology in the developing fields of nanosensors, water purification, polymer production, petroleum and energy production, chemicals, food industry and pollution control, all routes involve catalytic processes. Heterogeneous photocatalysis is explained as the acceleration of a photoreaction in the existence of a catalyst.

Generally, photocatalysis is a significant use for our environment, especially in industrial effluents and cleaning the wastewater. They help us to reduce pollution in water and air by developing such technology. This removal mode of existence would advantage everyone around the world. Today's, high-quality photocatalysts should be photoactive, competent to employ in visible or near UV light or both, photostable, inexpensive, and nontoxic for the living nature. A photocatalyst (*i.e.* semiconductor) should have positive redox potential so that the photo-generated valence band (VB) hole is photo-chemically active and can generate $^{\bullet}OH$ radicals for oxidizing the organic pollutants. For this, the conductance band (CB) electron must be suitably negative so that they become capable to decrease absorbed oxygen to superoxide. The main benefit of photocatalysis is the reality that there is no further requisite for any secondary removal methods as the organic contaminants are changed to inorganic ions, carbon dioxide and water. Other processes, such as adsorption by activated carbon and air stripping simply concentrate the pollutants and transfer them in the adsorbent or air so that they will not transfer them into nontoxic wastes as happens in photocatalysis. Photo-catalysis is an important means of advanced oxidation processes (AOPs) and are widely used for the removal of recalcitrant organic elements from industrial and wastewater. Further, the photocatalytic systems are classified into two categories, firstly, a homogenous photocatalytic system is a promising method for wastewater treatment, but the ions remain in the solution at the end of the process. For this reason, the removal of waste in wastewater treatment becomes essential, and it will increase the cost. This drawback of homogeneous catalytic systems can be prevailing by heterogeneous photocatalysis. The current examples of semiconductor photo-catalysts are TiO_2, ZnO, CdS, ZnS, SnO_2, WO_3, WSe_2, Fe_2O_3, and so on that can be used as potential photo-catalysts in cleaning the wastewater to solve the problem of environmental pollution, globally.

The photodegradation or removal of toxic elements from environmental sources has increased remarkably using nanometer-sized semiconductor materials over the last couple of decades due to their unique characteristics like quantum efficiency effects as well as their high potential in chemical or bio-chemical reactions. The term "quantum confinement effect", was introduced to explain a wide range of electrical and optical properties of nano-sized materials in connection to the removal of toxic materials from environments**.** The nano-sized detection methodology, referred to as "*quantum confinement effect*", is of significant interest from both fundamental and technological points of view for higher sensitivity, cost-effectiveness, or simple detection of environmental threats. This accounts for the removal of pesticides in the water using nanotechnology, UV source and kinetic study. Fig. (**6.1)** illustrates a fraction of the complex sequence of events that may take place in a semiconductor photocatalyst. The heterogeneous photocatalysis describes a process whereby illumination of a semiconductor particulate (TiO_2 and ZnO) with UV-visible light suitable to its bandgap energy ($\geq E_g$) ultimately generates conduction band electrons (e^-) and valence band holes (h^+) pair. Subsequent to their separation, other proposed photochemical and photophysical decay channels are poised at the particulate/solution interfaces (Fig. **6.1)**.

Initially, the irradiation of the semiconductor particle generates a bound electron/hole pair (the exciton). It either recombines or dissociates to give a conduction band electron and a valence band hole. These separated charge carriers may also recombine; migrate to the surface while scanning several shallow traps (anion vacancies and Zn^{2+} for the electrons and oxygen vacancies or other defect sites for the hole). On the surface, both charge carriers scan the surface visiting several sites to reduce adsorbed electron acceptors and to oxidize adsorbed electron donors in competition with surface recombination of the surface trapped electrons and holes to produce light emission or photon emission. Oxygen is omnipresent on the particle surface and acts as an electron acceptor, whereas OH^- groups and H_2O molecules are available as electron donors to yield the strongly oxidizing $^*OH$

CHAPTER 7

Removal of Dyes by the Process of Adsorption

Abstract: Adsorption is one of the simplest ways and means to remove dyes from water. The process of adsorption simply involves the removal of water contaminants that come in contact with adsorbents, *i.e.*, the materials of interest. The material should only have sufficient surface area, porosity, and adequate numbers of adsorption sites. Besides being one of the simplest means of dye removal, the process has further advantages in that the same material may be used many times, *i.e.*, regarding the recyclability of the material. Keeping all these in mind in this chapter, a detailed discussion regarding the adsorption process has been included. The discussion not only covers the basic principle of the process but also unfolds the analysis technique regarding the performance of certain material as an efficient absorber. The quantification of removal efficiency will also be a topic of discussion. The setup for such a kind of measurement will be unveiled, and most importantly, different theoretical models for such a process will also be a topic of interest in this chapter. The different models include the Langmuir model, Freundlich model, Temkin model, and others. An effort has also been made to enlighten the readers with the different reaction kinetics like pseudo-first-order, or second-order reaction kinetics. In every subsection, a few experimental data will be shown and discussed.

Keywords: Adsorption, Absorption, Isotherm, Reaction kinetics, Regression coefficients, UV-Visible spectroscopy.

ADSORPTION: DEFINITION

Adsorption basically means adherence of a molecule or ions or functional group onto the surface of an adsorbent. It is to be noted that there is another term which is almost similar to the former, and that is absorption" [1]. The latter simply means fluid molecules get dissolved within the absorbents, and thus it becomes a bulk phenomenon. So it follows that when in absorption fluid can enter well within the inner part of the absorbers, it only loosely adheres to the surface of adsorbents in case of adsorption and thus may be considered to be a surface phenomenon.

WHAT IS ABSORPTION?

The phenomenon like the soaking of certain fluids by solid materials without any external force being applied is called adsorption. It is a bulk phenomenon, and here, external molecules to be adsorbed, which are technically called adsorbents actually

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enter within the inner portion of the adsorbents. The adsorbents may get adsorbed both physically as well as chemically.

WHAT IS ADSORPTION?

Like the previous process, adsorption can also be divided into physisorption and chemisorption. In these phenomena, molecules that are supposed to be adsorbed (we call it adsorbate) get loosely adhered onto the surfaces or rather interface of particular liquids or solids (one calls it adsorbent). Table **7.1** and Fig. (**7.1**) summarizes the difference between adsorption and absorption.

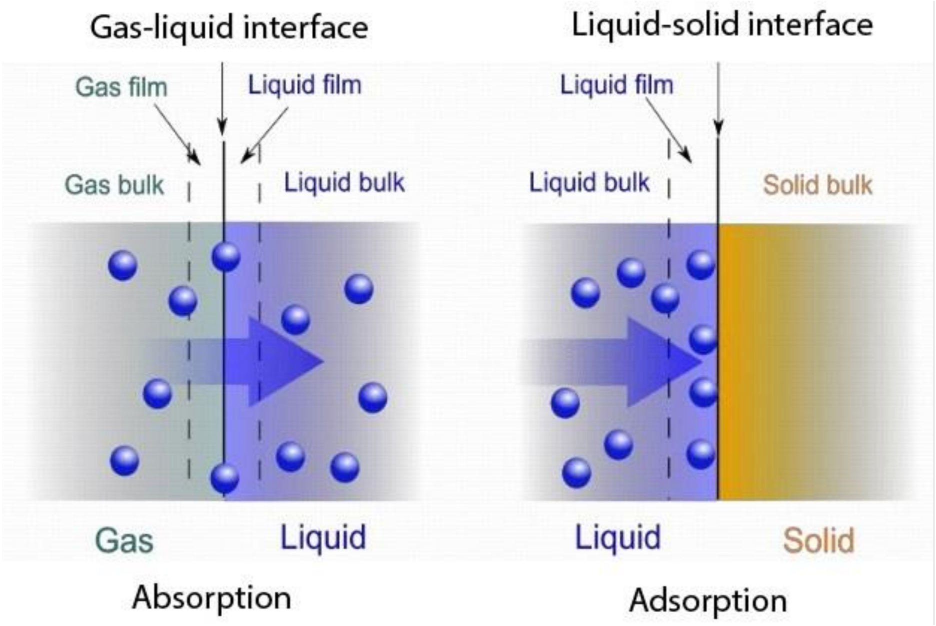

Fig. **(7.1).** Schematics for understanding of the processes of Adsorption and absorption.

Table 7.1. Absorption and Adsorption a comparison.

Absorption	Adsorption
Here substances, *i.e.*, Molecules or atoms or ions, get inserted within the inner part of the absorbents, which are likely to be solids or liquids.	Here substances, *i.e.*, molecules or atoms or ions, get loosely adhered to the surfaces of the adsorbents, which are likely to be solids or liquids.

(Table 7.1) cont.....

It is considered to be a bulk phenomenon.	It is no doubt a surface phenomenon.
In this process, heat gets absorbed (endothermic)	In this process, heat gets released (exothermic)
It takes place with a uniform rate	Here reaction rate first shows a slow increase before ultimately attaining an equilibrium
In the medium, concentration remains the same	In the medium, concentration varies as it goes from bulk to the bottom
It is temperature-independent.	It is efficient at a lower temperature.
Few practical uses are cold storage or ice production or refrigerants, *etc.*	Few common examples are air conditioning or water purification, *etc.*

TYPES OF ABSORPTION

1. Chemical absorption- As the name suggests, in this process, which is also called as a reactive absorption, a chemical reaction occurs between absorbent absorbents. Sometimes this process may also accompany physical absorption.

2. Physical absorption- In the process of physical absorption, the electronic configuration, bonding *etc.*, all get unperturbed. This process is non-reactive in nature.

TYPES OF ADSORPTION

Chemisorption: Here the adsorbates get adhered to the surface of the adsorbent by a chemical reaction forming a different chemical bond when the gas molecules are bound to the surface by a chemical bond.

Physisorption: Here no chemical reaction takes place, and adsorbate-adsorbents interactions are mainly weak attractive/repulsive forces or electrostatic forces.

BASIC OF ADSORPTION PROCESS

Adsorption study is one of the easiest processes to test the dye removal of a certain material by the process under interest. It simply requires uniform contact between the remover and the water with contaminations for a certain time. During this

CHAPTER 8

The Efficiency of a Few Potential Nanosystems as Dye Removers

Abstract: In the preceding section, we have discussed the basic characteristics of nanomaterials, their properties, as well as the basic science behind the fact that nanomaterials behave differently from their bulk form. The discussion has also been done regarding the basic features of different microscopes and their working principle. We now have an idea regarding the features of different textile dyes, their toxicity, classifications, and properties. Not only that, the two main ways, like catalysis and adsorption, that help remove dyes from water have also been discussed. We are also now familiar with the basic structures and properties of a few effective dye removers like carbon nanostructure, oxides, and others. As a continuation of all the previous discussions, this chapter deals with the efficiencies/performances of a few potential materials in removing different textile dyes from water. This chapter considers mainly the performance of materials in removing dyes through catalysis and adsorption. We have taken only those materials whose structures and properties we have discussed in the preceding section. The results related to the performance of materials in removing different dyes from water have been taken from outside literature as well as from our own experimental results. It has been shown that the dye removing efficiency of the materials depends upon the material itself, its structure, surface area, porosity as well as numbers of effective adsorption sites.

Keywords: Adsorption, Carbon, Carbon Nitride, Nanostructures, Photo-catalysis, Zinc Oxide.

GRAPHITIC CARBON NITRIDE (NITRIDE SYSTEM)

The introduction to the materials has been given in Chapter 5, along with its basic crystal structures, synthesis processes, and optical and other basic properties. This chapter will deal with the use of pure and doped GCN as the remover of dyes from wastewater.

Application of GCN as a Catalyst Material for Dye Degradation

The presence of the amine group in the GCN structure plays an important role in determining its property [1, 2]. As has been shown by Zhu *et al.*, amine-induced defects help delocalization and re-localization of electrons, introducing interesting

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surface properties like Lewis base functionalities as well as electron-rich features. All these, together with the good thermal and chemical stability of GCN, have made them efficient catalysts.

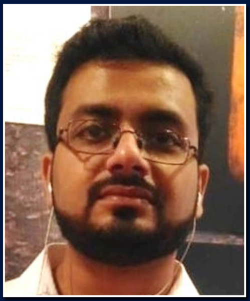
Photocatalysis

Due to different properties mentioned before, like suitable optical gap (that can make the material suitable to utilize solar energy in the visible range), or perfect VB and CB redox edge potential GCN may be considered to be a good photo-catalyst. However, the bulk form of this material suffers the shortcomings like rapid electron-hole recombination, less surface area and lesser quantum efficiency, all collectively affect the catalytic activity of the material in a negative way [3]. This discrepancy has been overcome by structural and morphological modifications as reported by many researchers. However, here the focus has been given mainly on the pristine GCN, which has not been modified by any other foreign material.

Among the numbers of reports available, only a few have been taken in order to make the reader aware of the efficiency of pure GCN as a photo-catalyst. In this regard, the work done by Paul *et al.* is worth mentioning. In separate work, they have shown how GCN can effectively remove both the cationic (RhB and MB) and as well as anionic (MO) dyes [4, 5] with a rate constant value of 0.0029, 0.0076 and 0.008 min^{-1}, respectively. Porous GCN with a surface area of 109.3 m^2/g synthesized from melamine also efficiently removes MO with a rate constant, as has been reported by Gu *et al.* [6]. Mesoporous GCN developed from guanidine hydrochloride by a template-assisted method, as reported by Erdogan *et al.*, has shown excellent UV and visible light-induced photo-degradation of the RhB, MO and MB [7].

There are other separate reports also, for example, those that came from Cui *et al.* or Shi *et al.* All showing GCN with different morphology may be used to remove dye like RhB or MO or MB rapidly with better efficiency as well as with good recyclability [8, 9]. In separate work, Gao developed mesoporous GCN with cashew morphology, which when used to remove MO under the visible Xenon lamp with 500 W power. He observed a 100 % degradation of the dye with a rate constant value of 0.0935 min^{-1}. He concluded, as stated above that the increased surface area, number of effective sites, and favourable transport from bulk to surface make the recombination phenomenon so easily happen, giving good photo-catalytic activity to the sample [10]. Wang *et al.* have shown that porous nanosheet of GCN synthesized from melamine can give rate constant 8 times greater than that of the bulk GCN in case of the removal of RhB [11]. Liu *et al.* reported an interesting phenomenon. In their urea-modified GCN, it was surprisingly seen that over 63 % of MB got removed in simple dark conditions (*i.e.*, the process may be considered as adsorption) before switching on the photon source. After that, 100 % removal of dye took place within 100 minutes [12]. Apart from them, Chang *et al.*, Ibad *et al.*, and Li *et al.* separately reported the efficient catalytic activity of the different GCN nanostructures synthesized from melamine or urea [13-15]. They all have reported a different rate constant in their respective studies. The noteworthy conclusion was taken by Chang *et al.*, who inferred that the main species that take part in photocatalysis are the superoxide anion and the photon-induced generated hole. They supported their conclusion from data obtained from the ESR study [13]. Though different workers have synthesized different structures of GCN and used them to degrade different dyes under photo irradiation with different energy ranges, the reasons they have given are almost the same, like enhanced surface area and a number of active sites reduce recombination rate. The work reported by Pwaer *et al.* for their porous GCN micro rods is not an exception [16]. Reports from Zhang *et al.*, Dong *et al.*, Cui *et al.* or Huang *et al.* followed the same trend [17-20]. Of all these, Huang *et al.* observed a 100 % removal of dyes within just 1 hour and calculated a rate constant 0.051 min^{-1}, which is much better compared to the bulk GCN [20]. Relatively inferior performance was achieved by Yan *et al.* for their ultrathin GCN sheets for the removal of RhB, where the degradation time is near about 100 minutes [21]. In this discussion, the work done by Sundaram and co-workers is mentioned as worthy [22]. They developed GCN isotype hetero-junction by separately taking the combination of melamine, urea, melamine, thiourea, thiourea and urea, all with a 1:1 ratio. They have shown that in-spite of having the greatest surface area in case GCN synthesized out of melamine-thiourea combination that synthesized from melamine, urea combination gives the best catalytic activity. If we go beyond the pristine GCN, there are efforts of doping of GCN by both metals as well as non-metals. In this regard, it should be mentioned that Liu and co-workers incorporated an oxygen functional group into GCN to get an enhanced removal activity for MB [23]. Photo-catalytic activity of doped GCN as well as $CsPbBrCl_2/g\text{-}C_3N_4$ type II hetero-junction system has been reported by author’s group also where the prolonged separation of –electron-hole pairs were considered to be the key reason for enhanced photo-catalytic activity [24, 25]. The phenomenon has been schematically shown in Fig. (**8.1**).

SUBJECT INDEX



Diptonil Banerjee

Diptonil Banerjee is currently working as an associate professor in the department of physics, faculty of engineering, Teerthanker Mahaveer University from 2020. Dr. Banerjee, completed both his graduation and Masters in Physics from University of Calcutta in the year 2005 and 2007, respectively.

He did his PhD from Jadavpur University on Materials Science and Nanotechnology in the year of 2012. Presently, Dr. Banerjee is working mainly on carbon based nanotechnology and related applications. He has also started working on some oxide based nanostructures as well. He is entrusted by the Department of Science and Technology (Gov't of India) with few projects of considerable budget.

Besides, he is an editorial board member and a reviewer of good numbers of quality journals. Currently, he is having an h index 21 and i10 index 41 with cumulative citation over 1270. Apart from this book he has authored another book in the same field of nanoscience and technology entitled "Nano Science - Concepts and Fundamentals" jointly with Dr. Nirmalya Shankar Das (co-author of the present book as well) which has been published from NOLEGEIN (an imprint of Consortium e-Learning ISBN: 978-93-87376-77-9).

Amit Kumar Sharma

Amit Kumar Sharma did his graduation (BSc) in 2000 and post-graduation (MSc) in Electronics & Computational Physics in 2002 from Dr. B.R.A. University (Agra University), Agra. He did Ph.D. in Applied Science (Physics) from Gautam Buddh University (Formerly U.P. Technical University), Lucknow in 2012. He is currently working as Assoc. Prof. in the Dept. of Physics, Faculty of Engineering, Teerthanker Mahaveer University, Moradabad since 2019. Earlier, he worked as CSIR-postdoctoral fellow (Post-Doc) in Biophysics Division, Saha Institute of Nuclear Physics, Department of Atomic Energy, Kolkata. His areas of research are Molecular Physics, Biophysics, Toxin and flavonoids, Sensors and Computational Physics. He has published 18 research papers in the International Journal of repute and more than 21 papers in proceedings of conferences. He has also received an award in the national conference (NSNTBT) in 2009 for the development of colorimetric sensors from Biosensor society of India. He has successfully completed different national and international collaboration projects. Dr Sharma has also worked at different administrative positions and in several committees of the serving institutes.

Nirmalya Shankar Das

Nirmalya Shankar Das is presently working as assistant professor in the Department of Physics in Techno International - Batanagar (formerly known as Techno India – Batanagar), Kolkata, India. He is also the teacher –in- charge of the department. He pursued his graduation with physics honors as well as masters from Jadavpur University, Kolkata. After completing his Masters, he did his PhD from the same University in the field of Nanoscience and Technology under the supervision of Prof. Kalyan Kumar Chattopadhyay.

During his PhD, he was involved in making different oxide and sulphide thin films like pure and doped NiO, ZnO, CdS films synthesized by RF magnetron sputtering technique. Also he has extensively studied the optical and electrical properties of all those thin films. Presently his research interest focuses on the optical, electrical and electronic properties of different semi-conductor oxide, sulphide and nitride nanostructures. Apart from academics Dr. Das has also engaged in different administrative activities as well. Apart from those academic aspects, he is a very good artist. His creations, both in the scientific and creative art section, have always been highly appreciated.