

CHAPTER 1 General Introduction

1.1 Overview and Problem Statement

Water is a vital natural resource that sustains life on Earth, is called the "elixir of life," and is essential to human survival. It plays a crucial role in agriculture, aquatic ecosystems, industrial processes, global climate regulation, and economic development. Ensuring water quality, conserving water resources, and promoting sustainable water management practices are essential to safeguarding freshwater supplies. The rapid pace of industrialization has led to increased pollution of water bodies with harmful substances like pesticides, heavy metals, dyes, and more, posing significant challenges to aquatic environments [1]. The main industries that contribute most to water pollution globally are those that deal with petroleum, mining, leather, paper and pulp, pharmaceuticals, food processing, and textiles. Since the textile sector is so important to global manufacturing, enormous quantities of freshwater are needed for the many production processes such as dyeing, printing, finishing, and washing involved in this sector. A typical textile effluent usually contains a variety of synthetic dyes, suspended particulates, pH-altering substances, heavy metals, detergents, non-biodegradable materials, additives, and organic compounds [2]. Textile effluent leads to some adverse effects on the ecosystem and human health due to its intricate composition. In addition to contaminating surface and groundwater, the direct discharge of these pollutants also leaves a persistent residue in the environment, adding to the cumulative load on the environment. Also, as water quality declines and light penetration in aquatic environments reduces, aquatic plants' ability to photosynthesize is directly hindered, which affects species at various trophic levels, and disrupts the food chain. In the past, textile effluent was treated by using several techniques, these techniques were not able to completely remove the pollutants from water and not able to mineralize the wastewater because most of the textile effluent contains dyes, which are highly

soluble in water. These techniques also use some compounds (Photo-catalysts, adsorbents, coagulants and flocculants, electrochemical oxidants, and membrane filters) that have high manufacturing costs and when synthesizing them, they produce by-products, they may harm the environment. Therefore, a sustainable or green route is required for the synthesis of these compounds to minimize the cost of manufacturing and to improve the degradation of pollutants from wastewater for the betterment of wastewater removal techniques.

1.2 Synthetic Dyes: Sources and Major Consequences

A dye is a colored compound that forms a chemical bond with the material it is applied to. Dyes are commonly used to color textiles, paper, leather, and other substrates. In contrast to pigments, which are insoluble, dyes are generally water-soluble and are absorbed by the material through chemical or physical interactions. Natural dyes are organic substances derived from the colored compounds of natural sources such as plants and animals. Major plant sources include leaves, wood, lichens, bark, fungi, berries, flowers, vegetables, and roots. These dyes are commonly used for coloring fabrics (both cellulosic and protein) and fibers dyeing, staining organic and mineral materials, and in applications such as food and beverage coloring, organic pigment production, cosmetics, feathers, and pharmaceutical compounds [3]. Today's natural colors are becoming more important in our lives since they almost always have significant advantages over many synthetic colors, such as being harmless and nearly always hypoallergenic.

William Henry Perkin developed the first synthetic dye, "Mauveine," in 1856 [4,5]. Petrochemicals and coal tar are the sources of synthetic dyes, which are widely used to add vivid colors to paints, textiles, mouthwashes, shampoos, and soaps. The textile sector is one of the biggest users of synthetic dyes, using and producing a large amount of dyes mostly for printing and dyeing fabrics. In addition, they are used in food and drink, plastics, paints, printing inks, and cosmetics. They consist mostly of benzene-derived compounds that absorb light in

the ultraviolet spectrum. Additives, also referred to as "chromophores," cause the light to shift from its absorption band into the visible region, producing a range of colors, while "auxochromes" impart a deeper color [6]. A few examples of auxochromes are amino, aldehyde, hydroxyl, and methyl mercaptan groups, and for chromophores are acids, keto, nitroso, thio groups, carbonyls, azo, nitrile, ethylene, and acetylene. Modern electronic structure theory argues that the color of dyes results from the excitation of valence π -electrons by visible light, which has replaced this hypothesis [6].

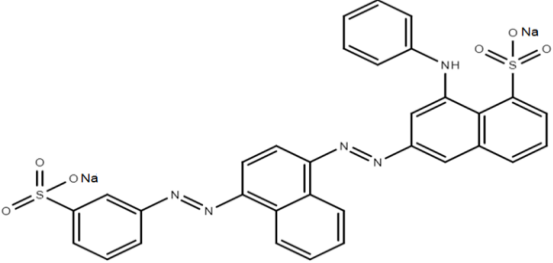
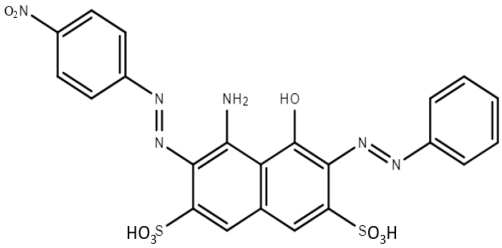
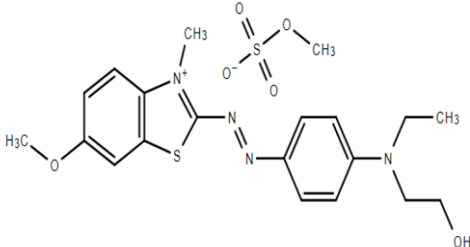
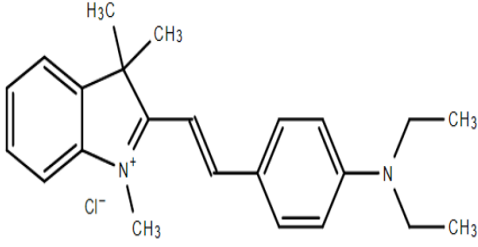
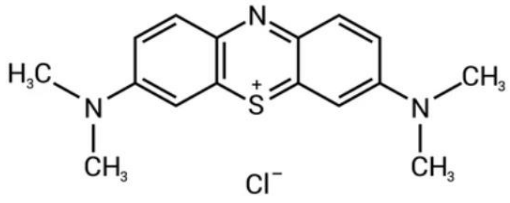
1.2.1 Classification of Synthetic Dyes

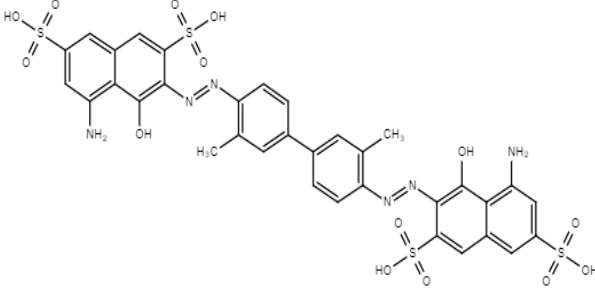
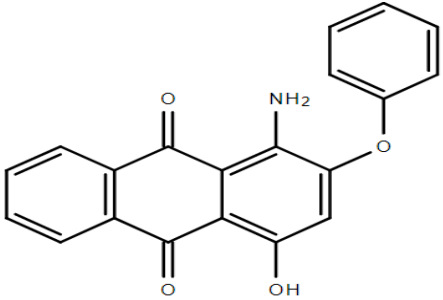
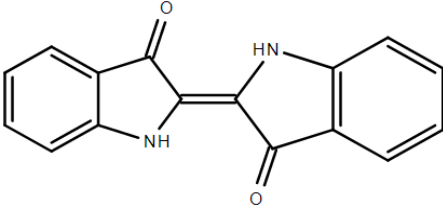
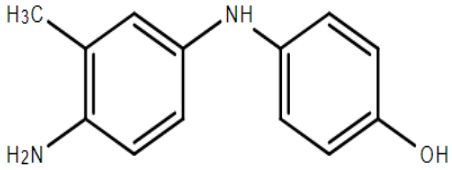
Synthetic dyes are widely used in the coloring, dyeing, and printing process in most industries because they provide a wide range of bright, vivid colors that are not easily achievable with natural dyes. They are more resistant to light, washing, and other environmental factors compared to natural dyes. The Society of Dyers and Colorists (UK), and the American Association of Textile Chemists and Colorists (USA) together publish the Colour Index (C.I.), the largest collection of dyes and pigments, and according to their chemical structure, which comprises 12,000 products grouped under 2000 C.I. generic designations [5]. Synthetic dyes can be classified based on their chemical structure, method of application, and solubility. The major classification of synthetic dyes can be carried out based on water solubility and are classified as:

- (a) Water-soluble: acid, base, direct, and reactive dyes come into this category.
- (b) Water-insoluble: disperse, pigment, vat, and sulfur dyes come into this category.

Some dyes frequently used in the industry are listed in **Table 1.1** with their structure.

Table 1. 1 Various commonly used Synthetic Dyes in the textile industry.

S. No.	Dyes	Structure
1	Acid Blue 113	 <p>The structure of Acid Blue 113 is a triphenylmethane dye. It consists of a central carbon atom bonded to three nitrogen atoms. Each nitrogen atom is part of a different aromatic ring: one is a phenyl ring, another is a 4-sulfonatephenyl ring (with a sodium counterion), and the third is a 4-sulfonate-2,6-naphthylidene ring (also with a sodium counterion).</p>
2	Acid Black 1	 <p>The structure of Acid Black 1 is a naphthalene-based dye. It features a central naphthalene ring system with several substituents: an amino group (-NH₂), a hydroxyl group (-OH), a sulfonic acid group (-SO₃H), and two azo (-N=N-) groups. One azo group connects the naphthalene ring to a 4-nitrophenyl ring, and the other connects it to a phenyl ring.</p>
3	Basic Blue 41	 <p>The structure of Basic Blue 41 is a thiazine dye. It features a central thiazine ring system with a positive charge on the nitrogen atom. The thiazine ring is substituted with a methoxy group (-OCH₃) and a methyl group (-CH₃). It is connected via an azo (-N=N-) group to a 4-(diethylamino)phenyl ring. A sulfonate group (-SO₃CH₃) is also present on the thiazine ring.</p>
4	Basic Violet 16	 <p>The structure of Basic Violet 16 is a quinoline dye. It features a central quinoline ring system with a positive charge on the nitrogen atom and a chloride counterion (-Cl⁻). The quinoline ring is substituted with two methyl groups (-CH₃) and is connected via a vinylidene group (-CH=CH-) to a 4-(diethylamino)phenyl ring.</p>
5	Methylene Blue	 <p>The structure of Methylene Blue is a phenothiazine dye. It features a central phenothiazine ring system with a positive charge on the sulfur atom and a chloride counterion (-Cl⁻). The phenothiazine ring is substituted with two dimethylamino groups (-N(CH₃)₂).</p>

6	Direct Blue 1	
7	Disperse Red 60	
8	Vat Blue 1	
9	Sulfur Blue 7	

1.2.2. The detrimental effect of textile dyes

Numerous health problems originate from the irresponsible discharge of textile effluents containing carcinogenic dyes (highly concentrated) [7]. Workers who produce or handle these dyes may experience allergic rhinitis, allergic conjunctivitis, occupational asthma, contact dermatitis, and other allergic symptoms. Among other diseases, textile dyes can cause dermatitis and problems with the central nervous system [8,9]. The inactivation of enzymes brought on by the substitution of their cofactors may be the cause of these problems. Some studies have reported that some like Methylene blue, Direct Blue 38, Malachite green, Disperse Red 1, and Crystal Violet dyes have some health issues such as an increase in heart rate, shock,

vomiting, tissue necrosis, cyanosis, the formation of Heinz bodies, jaundice, damage to the kidneys, heart, spleen, and liver, and cancer of the bladder, has cytotoxic effects including apoptosis, DNA damage, the generation of DNA adducts, chromosomal damage, and aberrant metaphase in addition to causing lesions on the skin, lungs, eyes, and bones [8,10–13].

1.3 Textile Wastewater Treatment Techniques

There are serious risks associated with textile wastewater exposure, either direct or indirect. Consequently, for the complete mineralization of textile effluents, a suitable, economically feasible, and ecologically friendly approach must be implemented. Therefore, several approaches to treating textile wastewater include physiochemical processes (such as adsorption/biosorption, membrane filtration, electrochemical oxidation, coagulation and flocculation) and Advanced oxidation processes (such as ozonation, photocatalysis, non-thermal plasma, Fenton's reagent) [14,15].

1.3.1 Physiochemical Techniques

The most common physical treatment methods are adsorption, membrane-based separation techniques, and ion exchange; chemical procedures include electrochemical, coagulation/flocculation, and electrochemical oxidation processes [15].

1.3.1.1 Adsorption

Adsorption is a surface-based phenomenon in which adsorbate molecules or ions from polluted water are attracted to the surface of a solid adsorbent, such as activated carbon, alumina, zeolite, charcoal, and silica gel. Activated carbon and other carbon-based adsorbents, including charcoal and biochar, have been used historically, even though activated carbon is important for industrial purposes [16]. This technique does not mineralize the pollutant; rather, it permits the bulk transfer of contaminants from one phase into another.

1.3.1.2 Membrane filtration and ion exchange technique

Membrane filtration, also known as the size exclusion method, is a membrane-based separation process that allows tiny molecules of solute to pass through its pores only. Reverse osmosis (RO), microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF) are widely used for salinity and COD reduction as well as dye removal from textile effluents. The ion exchange technique has been used to treat textile effluents, remove heavy metals from water, and purify water. Functional groups on ion exchange resins have a charge, while charged dyes have their distinct charge. An ionic attraction develops between the resin and charge dye molecule, which establishes the bond and deposits dye on the resin's surface, causing color degradation [17].

1.3.1.3 Chemical approach

Physical and biological procedures are comparatively less expensive than chemical approaches, except electrochemical technology. The chemical method of dye removal limits the vast range of processes it may be used for and necessitates specialized equipment, a lot of chemicals, and electrical energy. It also produces poisonous secondary waste that poses disposal issues. Two metal electrodes, in-situ generated coagulant particles, and a direct current source are part of an electrocoagulation (EC) tank. There is the metal anode and electrolytic reduction and oxidation serve as both a catalyst and a coagulant reagent. Overall, the water produced by the reactor is colorless and odorless. Additional benefits include the absence of the need for additional chemicals, the reduction of secondary waste, economic viability, and environmental friendliness. Coagulation-flocculation involves the injection of chemical coagulants, such as aluminum sulfate solution ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), under conditions of high mixing. When oppositely charged scattered particles are neutralized, flocculants contribute, causing a cluster of small particles to combine into an even larger particle. These particles are eliminated by the sedimentation process [18].

1.3.2 Advanced oxidation processes (AOPs)

AOPs, or advanced oxidation processes, are advanced techniques for treating wastewater that is used to eliminate organic pollutants and other contaminants that are hard for traditional methods to break down. AOPs entail the production of efficient oxidants, such as hydroxyl radicals ($\bullet\text{OH}$), which are extremely reactive, to decompose and convert organic molecules into less hazardous forms [19]. A wide range of contaminants, such as medications, insecticides, dyes, and emerging contaminants (ECs), can react with hydroxyl radicals due to their high oxidation potential (2.80 V). Usually, an electron is transferred from the contamination to the hydroxyl radical during these reactions, which causes the pollutant to break down into smaller, more biodegradable molecules. With sufficient oxidation potential, a typical oxidation process produces a variety of oxidizing agents, as described in **Fig. 1.1**.

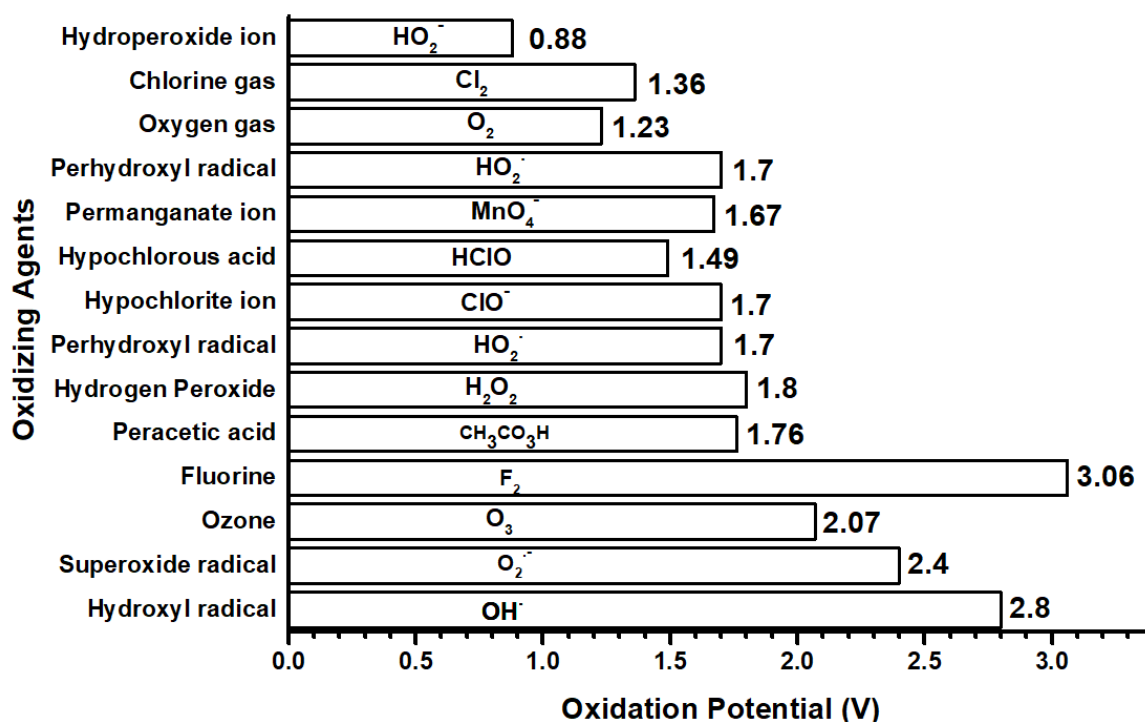
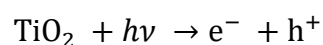


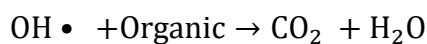
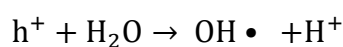
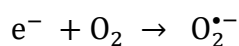
Fig. 1. 1 A description of the several oxidizing agents produced and their corresponding oxidation potential during the advanced oxidation process.

Various parameters, including the type of oxidants utilized, the circumstances of the reaction, and the presence of catalysts or energy sources, influence the efficiency and effectiveness of AOPs. Numerous AOPs, including ozonation, photocatalysis, non-thermal plasma, Fenton's reagent (a mixture of hydrogen peroxide and ferrous iron), and others, have been developed and applied in wastewater treatment [20–23]. Every method produces hydroxyl radicals or other potent oxidants through a different mechanism that makes it flexible and adaptable to various wastewater compositions and treatment needs. These procedures have garnered plenty of interest recently due to their capacity to handle new environmental issues. They are widely known for their adaptability and effectiveness in treating complicated wastewater streams. AOPs have the ability to handle a variety of wastewater compositions with greater flexibility, improve treatment efficiency, and potentially be used for on-site treatment [24]. These advanced techniques are crucial in tackling the increasing challenges of water pollution, and ensuring the provision of clean and safe water resources.

1.3.2.1 Photocatalysis

Photocatalysis is an innovative, sustainable advanced oxidation technique that utilizes light energy and a catalyst to degrade and remove organic pollutants in wastewater. In particular, photocatalysis utilizes a photocatalyst (usually a semiconductor) material like titanium (IV) oxide (TiO₂) to absorb UV light energy and produce electron-hole pairs. When these photo-induced electron-hole pairs come into contact with oxygen and water in the surrounding environment, they conduct redox reactions that produce highly reactive species including holes (h⁺), superoxide radicals (O₂^{·-}), and hydroxyl radicals (HO[·]), which can oxidize and destroy organic contaminants [21]. Many pollutants, such as colors, insecticides, medications, and organic toxins, are efficiently degraded by the photocatalytic process. The elaborated photocatalytic reactions can be expressed as follows [25]:





In addition, photocatalysis primarily works at ambient pressure and room temperature, which are mild reaction conditions. By doing this, the production of undesired byproducts or secondary pollutants is decreased as well as energy usage. Moreover, photocatalytic systems are inexpensive and simple to include in conventional wastewater treatment procedures, offering an efficient way to improve treatment efficiency. Another advantage of photocatalysis is its ability to degrade pollutants directly in aqueous solutions, eliminating the need for additional chemical reagents or the production of excessive sludge. This makes it a cleaner and more environmentally friendly approach to wastewater treatment [26].

1.4 Sustainable (Green) approach for the synthesis of nanoparticles

Nanoparticles have been manufactured using methods, including physical, and chemical synthesis processes. The physical approach requires expensive equipment, high temperature, pressure, and enough room to facilitate the reaction. Hazardous, poisonous chemicals are used in the chemical process of nanoparticle synthesis, causing adverse impacts on our environment and aquatic life. These methods also produce some harmful by-products, which are not good for the betterment of the environment and need to be replaced these methods with sustainable and eco-friendly methods. Biological (Green) synthesis is the method getting more attention nowadays because in this method plants, bacteria, fungi, yeast, algae, etc natural sources are used for the synthesis of nanoparticles, and no harmful by-products are produced in this method makes it more sustainable approach for the synthesis of nanoparticles [27].

1.4.1 Green synthesis of TiO₂ nano-photocatalyst

One of the most often utilized metal oxides on the mass market is Titanium dioxide (TiO₂) NPs, whose overall production is predicted to exceed 2 million metric tons by 2025 [28]. TiO₂ is a white metal oxide powder that is odorless, non-toxic, and hydrophobic under normal conditions. Its high band gap of more than three electron volts leads to photocatalytic activity, making it a scientifically interesting material. Green synthesis typically utilizes simple, eco-friendly, and less harmful plant extracts, microorganisms, and enzymes. As a result, the green synthesis of TiO₂ nanoparticles has gained enormous attention among researchers [29]. Because of its high stability, low cost, and safety for both humans and the environment, TiO₂ is considered a near-ideal semiconductor for photocatalysis. It has a high refractive index, high adsorption and photocatalytic capacity towards specific pollutants, high binding affinity, and oxygen vacancies in the lattice structure [30]. Plant extract contains bioactive compounds (phytochemicals) like polysaccharides, phenolic compounds, terpenoids, alkaloids, and glycosides, which act as stabilizers and reducing agents when nanoparticles have been synthesized.

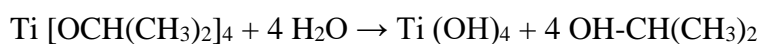
The reduction of TTIP to TiO₂ using plant extract as a reducing agent involved the following steps:

Step 1: Preparation of Ti Precursor

The Ti precursor is typically in the form of a titanium salt, such as titanium tetraisopropoxide (TTIP, Ti [OCH(CH₃)₂]₄), which contains Ti in its higher oxidation state (+4).

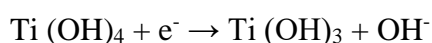
Step 2: formation of reactive species

In the presence of plant extract, which contains various bioactive reducing agents, the Ti precursor undergoes hydrolysis to form titanium hydroxide species

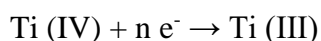


Step 3: Reduction of Ti Precursor

The reducing agents in plant extract donate electrons to the titanium hydroxide species, leading to the reduction of Ti (IV) to lower oxidation states, such as Ti (III):



The overall reduction reaction can be represented as follows:



Step 4: Nucleation and Growth

The reduced titanium species (Ti (III)) form nuclei and subsequently grow into TiO₂ nanoparticles through a series of redox reactions involving oxygen from the surrounding environment. The exact mechanism of nucleation and growth may vary depending on the specific reaction conditions.

Step 5: Stabilization and Surface Modification

During the reduction and growth process, the bioactive compounds in the plant extract, such as polyphenols and flavonoids, can adsorb onto the surface of the forming TiO₂ nanoparticles. This interaction stabilizes the nanoparticles, preventing agglomeration and providing surface modifications.

The overall reaction for the formation of TiO₂ nanoparticles using a plant extract as a reducing agent can be summarized as:



1.4.2 Green reduction of Graphene oxide (GO) nano-adsorbent

Reduction of graphene oxide using plant extract as a reducing agent is a sustainable and eco-friendly approach to produce reduced graphene oxide (rGO). This method takes advantage of natural reducing agents found in various plant extracts, which are rich in phytochemicals such as polyphenols, flavonoids, and terpenoids, to facilitate the reduction process. Plant extracts are biodegradable, non-toxic, and renewable, making the reduction process environmentally benign compared to conventional chemical reducing agents like di-methyl hydrazine [31],

hydroquinone [32], and hydrazine hydrate [33], which are hazardous and difficult to handle. This method typically operates under mild conditions (ambient temperature and pressure), reducing the energy input required for the reduction process compared to thermal or chemical methods, and also eliminates the use of harmful chemicals (reducing agents). The reduction of GO using plant extract as a reducing agent involved the following steps:

Step 1. Adsorption of Phytochemicals

When GO is mixed with plant extracts, the phytochemicals in the extract adsorb onto the surface of the GO sheets.

Step 2. Reduction Process

The functional groups in the phytochemicals, such as hydroxyl ($-OH$) and carboxyl ($-COOH$) groups, donate electrons to the oxygen-containing groups on the GO (such as epoxides, carboxyls, and hydroxyls), reducing them to form rGO. This electron transfer process reduces the oxygen functionalities and restores the conjugated graphene network.

Step 3. Formation of rGO

As the reduction proceeds, the GO loses its oxygen groups, becoming more hydrophobic and exhibiting properties closer to pristine graphene. This process not only reduces GO but can also introduce new functional groups from the plant extract, potentially enhancing the properties of the resulting rGO.

1.4.3 Antibacterial activity analysis of green synthesized nanoparticles

The antibacterial activity analysis of green synthesized nanoparticles using plant extract has garnered significant attention due to its potential environmental benefits and applications. Unlike conventional synthesis methods that often involve hazardous chemicals and high energy consumption, green synthesis employs plant extracts, which are eco-friendly and sustainable. This approach not only reduces the environmental impact but also utilizes naturally occurring phytochemicals as reducing and stabilizing agents, making the process more biocompatible

and less toxic. The importance of this method lies in its ability to produce nanoparticles with enhanced antibacterial properties, which can be used to combat antibiotic-resistant bacteria, a growing global health concern. By integrating green synthesis techniques, we can develop effective antibacterial agents that are safe for both humans and the environment [34,35]. Additionally, these green-synthesized nanoparticles can be used in multiple fields, including medicine, agriculture, and water treatment, offering a sustainable solution to environmental pollution and public health issues. This approach aligns with the principles of green chemistry and promotes the use of renewable resources, thereby contributing to a cleaner and healthier environment.

1.4.4 Sustainable production of hydrochar from waste biomass

Hydrothermal carbonization (HTC) is a fluid-based thermochemical conversion route that processes wet biomass in a sealed reactor under autogenous pressure at moderate temperatures (180- 250°C) over a few hours to convert it into hydrochar. HTC is a process in which the solid biomass undergoes multiple reactions, including dehydration, hydrolysis, aromatization, condensation polymerization, and decarboxylation [36]. which ultimately renders the carbonaceous solid (hydrochar). The raw biomass is processed into an energy-dense, more stable form to avoid pre-drying, which makes it energy-efficient. HTC is environmentally sustainable due to its utilization of waste biomass, which takes organic waste and converts it to hydrochar that can replace biochar in the soil or be sequestered as carbon, utilized as an activated carbon precursor, and also utilized for wastewater treatment. Furthermore, HTC compared to other hydrothermal processes (hydrothermal liquefaction (HTL) and hydrothermal gasification (HTG)) operates under relatively mild conditions [37,38], minimizing environmental pollutants and greenhouse gas emissions. By recycling waste biomass and producing valuable by-products, HTC supports a circular economy and contributes to sustainable waste management practices.

1.5 The broad objective of the present research

Several methods have been employed for wastewater treatment, but among them, photocatalysis and adsorption have emerged as the most effective for treating industrial effluents. In this research, the author focused on developing innovative, cost-effective, and sustainable solutions by synthesizing nano-photocatalysts, nano-adsorbents, and hydrochar. These advanced materials are designed to not only enhance the efficiency of wastewater treatment but also reduce the environmental impact, offering an eco-friendly alternative to conventional methods. Through this approach, the author aims to address the pressing need for cleaner water solutions while promoting the responsible use of resources. As mentioned above, it is clear that these nanoparticles are efficiently able to remove or minimize the concentration of dye in the textile effluents. However, the synthesis of these nanoparticles required the use of hazardous chemicals, and the synthesis process produced certain toxic byproducts, thus the production methods employed were not only cost-effective but also harmful to the environment. Therefore, in the present project, the author's broad objective is to grab attention towards the green and sustainable production of nano-photocatalyst, nano-adsorbent, and hydrochar by using naturally available plants and plant residues. The author employed a comprehensive approach, utilizing three distinct processes to rigorously validate green and sustainable synthesis methods for producing advanced materials such as adsorbents, photocatalysts, and hydrochar. These innovative materials were specifically synthesized to efficiently remove or significantly reduce dye pollutants from wastewater. Each process was meticulously designed to ensure eco-friendliness and sustainability, while maximizing the effectiveness of dye removal, providing an environmentally responsible solution for wastewater treatment. Through these methods, the research highlights a breakthrough in sustainable approaches to industrial wastewater remediation. The following objectives were set for the present work:

1. Green synthesis of nanoparticles using plant extract and its application for the removal of dye from textile effluent and also determined the antibacterial activity.
2. Green reduction of graphene oxide (GO) using plant extract and application of reduced graphene oxide (rGO) as a nano-adsorbent for removing textile dye in wastewater and examining its antibacterial activity.
3. Sustainable hydrochar production from the waste biomass using a hydrothermal carbonization process and application of hydrochar as adsorbent for dye removal in textile effluent.