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Titanium Dioxide nanoparticle: A green solution for Heavy Metal pollution and agricultural sustainability

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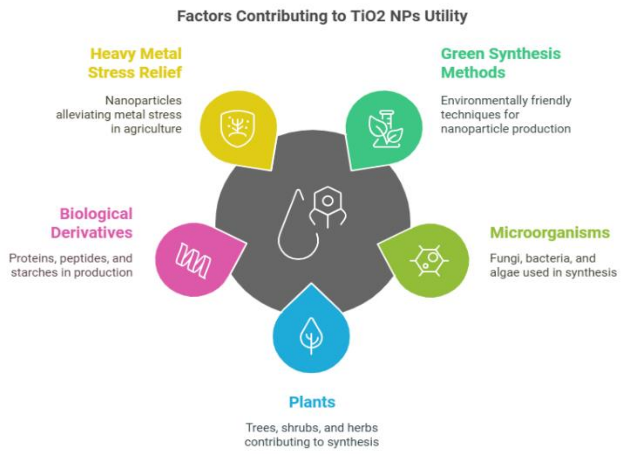
KEYWORDS

Titanium dioxide nanoparticles, Heavy metal stress, Green synthesis, Cadmium, Rice (Oryza sativa)

ABSTRACT

Applications of nanotechnology are becoming more and more well-known worldwide, especially in the manufacturing of titanium dioxide (TiO2) nanoparticles (NPs). Green synthesis is a non-toxic, economical, and safe method of creating NPs. The properties, uses, and production processes of TiO2 NPs are covered in this review. Because green synthesis methods use less energy, time, and precursors than chemical synthesis, they are more efficient. TiO2 NPs have beneficial effects on plant physiology, including purifying contaminated water. The regulating properties, prospects for the future, and quantifiable enrichment of TiO2 NPs are also covered in this paper. The utilization of nanoparticles in agricultural soil to reduce heavy metal stress is also covered, and the relationship between NPs and heavy metals is investigated. The existing research highlighted the relief mechanism to overcome the HM stress and included enough information about how NPs behave in plants when pollutants are present. This paper also outlines the kinds of microorganisms (fungi, bacteria, and algae), plants (trees, shrubs, and herbs), and biological derivatives (proteins, peptides, and starches) that used in the production of TiO2 NPs. The physiology of plants was positively impacted by TiO2 NPs, which can be utilized to clean polluted water. However, the reaction varied depending on the metal species, size, shape, dose, time of exposure, and other aspects. Additionally, this review focuses on the regulating characteristics, future perspectives, of TiO2 NPs application as well as the measurable enrichment in the product. By providing creative and practical knowledge to a wide range of environmental problems, nanotechnology is significantly contributing to their resolution. The rapidly rising concentrations of heavy metals (HM) in agricultural Soil has significant interest in recent years. Nanoparticles (NPs) is used to decrease the stress because of their *special physiochemical characteristics. A comprehensive summary of recent developments concerning Heavy Metal stress and the potential mechanism of interaction between NPs and HM in the agricultural system is also provided. Furthermore, this review paper will help advance knowledge of phytoremediation and micro-remediation of contaminated soils and will draw attention to the necessity for further research on the use of NPs in soil for sustainable agriculture.*

GRAPHICAL ABSTRACT



1. INTRODUCTION

In agricultural soils, increased metal contamination has become one of the major human-caused issues in the world. According to **(Abedi and Mojiri., 2020)**, cadmium (Cd) is a persistent, quick, and extremely harmful heavy metal among non-essential elements. According to **(Shi and Wang .,2021)**, eating plant parts with greater concentrations of Cd might lead to serious health problems such liver, kidney, and heart illnesses. Cd toxicity has been associated to low enzymatic activity, disrupted physiological processes, and reduced plant development. A major threat to food supply could arise from the growing levels of Cd pollution in arable soil, which are restricting the growth of edible crop plants **(Wang et al., 2020)**. Numerous industries make extensive use of metal oxide nanoparticles with unique physiochemical properties. **(Chaudhary et al.,2019)** claimed that metal oxide nanoparticles (NPs) have great potential in agriculture, including the production of fertilizers, insecticides, and fungicides. Additionally, metal oxide nanoparticles have shown amazing promise in soil reclamation **(Anderson et al., 2017)**. According to **(Khan et al.,2020)**, metal oxide nanoparticles also reduce metal stress in plants that are exposed to them. Through the immobilization and sorption of polluted metals and metalloids, the unique physicochemical characteristics of NPs aid in soil recovery **(Zand et al., 2020).** Heavy metal-induced food contamination has grown to be a significant global environmental, economic, and social problem that has had a profoundly adverse impact on human health. **(Munir et al., 2020); (Charvalas et al., 2021)**. The primary sources of soil contamination with metals include pesticide use in agriculture, excessive mining practices, fertilizer applications driven by the need for food production, and various natural, industrial, and human activities. Cadmium (Cd), recognized for its high bioavailability, detrimental impact on ecosystems, and potential risks to human health via the food chain, is considered one of the most dangerous heavy metals and poses a significant challenge for agricultural crops worldwide. Existing literature has demonstrated the toxicity of Cd on plant growth, along with its other physiological effects. The past few decades have witnessed a rapid advancement in science and engineering, but these advancements have also brought about adverse effects of human activity, such as pollution and the spread of bacteria resistant to antibiotics (**Ojemaye et al.,2020; Maganha de Almeida Kumlien et al.,2021**), as well as the health risks that go along with them. Even though there have been coordinated attempts the harmful effects of these pollutants on the environment's health and well-being, adsorption and oxidative mineralization have received a lot of attention. Therefore, it has been successfully shown that nanoparticles can attenuate pollutants of several types, including organic, biological, inorganic, and trace pollutants **(Villaseñor and Ríos 2017)**. Several options, such as transition oxides, are used in environmental projects. The use of photocatalysis to degrade chemical contaminants, such as medications, and clean up water has been the subject of numerous initiatives. Titanium (IV) oxide has been regarded as a possible photocatalyst because of its advantageous physicochemical characteristics, whether it is present as a mineral, dopant, or composite system. Applications of titanium oxide materials are discussed in this article. These include the degradation of developing pollutants, such as medications, using bare TiO_2 as well as its hybrid and composite materials. Growing across the world, coriander, or *Coriandrum sativum* L., is a significant herbaceous spice. Growing this therapeutic plant has become a highly valued export commodity in many parts of the world. The horticultural crop's growth and output are being significantly impacted by higher concentrations of Cd in the soil (8 mg kg1) and water (0.02–0.029 mg L−1) **(Dutta et al., 2020**). In addition, they found that the production and use of Cd-containing products, such as paints, dyes, batteries, and phosphatic fertilizers, along with the use of wastewater for irrigation, has ten times greater Cd pollution compared to nature. The growth, antioxidant defense system, physiochemical activities, and nutritional value of the coriander plant are all impacted by cadmium toxicity **(Zaouali et al., 2020; Sardar et al., 2021).** Thus, it becomes essential to identify a cost-effective and environmentally responsible method to reduce the toxicity and uptake of Cd in coriander **(Liu et al., 2016)**. Researchers typically use NPs directly in growth media. Aqueous media have been the focus of the majority of research projects investigating the application of TiO_2-NPs. But the goal of the current study was to clarify how TiO_2-NPs may be used as a seed priming agent to reduce Cd stress in *C. sativum* plants developing in soil media. **(Abedi and Mojiri et al., 2020).** The seed priming process is quite straightforward and cost-effective. This research also sought to highlight the potential advantages of TiO_2-NPs on the growth, physiological aspects, antioxidant mechanisms, and yield of coriander grown in soil tainted by Cd contamination. The expansion of urban areas and economic development is leading to greater environmental damage due to the discharge of various chemicals into soil and waterways. These substances, referred to as emerging contaminants, present a significant threat due to their harmful impact on environmental changes. Several toxicological studies have been conducted on many of these compounds, allowing for the assessment of potential risks. Various xenobiotic hazards have been identified as particularly severe, especially concerning aquatic organisms. Among industrial sectors, the fuel industry is the largest contributor to environmental pollution, alongside the energy, chemical, metallurgical, wood, and paper industries. Emerging contaminants include organic compounds, mineral acids, salts (such as phosphates, nitrates, and sulfates), heavy metals (like cadmium, lead, copper, and mercury), and other new substances that are either not well-studied for their toxicological effects or entirely unknown. However, it is important to note that pollution is not solely an industrial issue. Waste from agriculture, healthcare facilities, and animal farming can pose significant risks to human health and the environment, even in small amounts (ng × dm−3 to μg × dm−3). Among the contaminants detected in wastewater, substances found in common consumer products are easily traceable, particularly those present in cosmetics, hair care items (such as shampoos and shower gels), and cleaning products like soaps, detergents, and surfactants. **(Abedi and Mojiri et al., 2020)** This also holds true for hormonal substances, insecticides, dyes, aromatic compounds and their derivatives, phthalic esters, hydrocarbons, phenols, colors, aromatic amines, and radioactive substances. The utilization of photocatalysis for water remediation and the breakdown of chemical contaminants, including medications, has been the subject of numerous efforts. Because of its advantageous physicochemical characteristics, titanium oxide, whether it is a crystalline forms or in a composite system, has been explored as a possible photocatalyst. **(Abedi and Mojiri ., (2020)** This article describes the use of photocatalysts based on titanium (IV) oxide materials for the degradation of new pollutants, such as medications, starting with bare TiO_2 and progressing to its hybrid and composite components. *Triticum aestivum* L., or wheat, is a staple grain grown in many parts of the world and utilized as animal feed and human nourishment. Researchers have also explained the toxicity of Cd in wheat by demonstrating that it decreases the harvesting index, root length, photosynthetic rate, mineral intake from the soil, and grain **(Rizwan et al., 2016)**. The increased demand for wheat has led to its production on every available plot of land worldwide, regardless of the soil characteristics. Thus, reducing agricultural plants' absorption of Cd is essential to ensuring food security. The hypothesis was that TiO_2 NPs could reduce the buildup of Cd in wheat grains, albeit this could vary depending on how the NPs are prepared. In order to fill this information gap, the study was planned to examine the effects of TiO_2 NPs made using various techniques (chemical vs. green) on wheat growth and photosynthesis, as well as the accumulation of Cd in wheat when TiO_2 NPs are applied and health risk assessment at the field level. The study's findings may significantly advance the potential application of TiO_2 NPs in agriculture to lower plant metal uptake, which could be crucial for ensuring food security and addressing related public health issues. One of life's essential elements, water is utilized in agriculture, industry, and habitation. As a result of increased consumption, the toxicity of contaminants in water increases. Pharmaceutical chemicals and other developing contaminants have become more prevalent. Antibiotics are among the many kinds of medicinal substances that are found in the aquatic environment. Through human livestock, pharmaceutical industries, and hospital effluents, these substances enter the aquatic environment. The emergence of antibiotic-resistant bacteria can be attributed to the increasing use of antibiotics and their concentrations in water environments. Titanium dioxide (TiO_2) primarily exists in two forms: crystalline and amorphous. In its crystalline state, particles are systematically arranged in a uniform pattern. The most stable crystalline phase, known as rutile, is formed at a high temperature of 800 °C. In contrast, amorphous particles lack this organized structure, resulting in irregular shapes. Anatase, a specific type of amorphous form, is produced when thin films are deposited at elevated temperatures of 350 °C. Thanks to their excellent oxidizing capabilities, strong chemical stability, and affordability, titanium dioxide nanoparticles (TiO_2 NPs) are widely used. The presence of oxygen vacancies in the TiO_2 lattice is due to the dissociation of oxygen and emissions of electrons. TiO_2 is the most commonly utilized photocatalyst for the degradation of organic pollutants and antibiotics due to its remarkable stability, cost-effectiveness, high photocatalytic efficiency, and non-toxic nature. TiO_2 functions as an N-type semiconductor with an energy band gap of 3.2 electron volts. TiO_2 uses UV light instead of visible light because of this (**Shi and Wang.,2021)**. Not with standing the disadvantages, TiO_2 NPs are used in a variety of cosmetic products, including lotions, creams, skin ointments, UV light, papers, food coloring, paints, and inks. It has many uses in the electrical industry, including photovoltaic cells, different kinds of electrodes, and solar cells. The catalysis food business also uses TiO_2 NPs. TiO_2 NPs are also used in biomedicine, such as in drug delivery, cancer treatment. Because TiO_2 NPs have a very tiny surface area, the electrical and optical characteristics require an increase in surface area. TiO_2 NPs' crystalline phase and particle size can alter their chemical and physical characteristics. TiO_2 NPs are utilized as a catalyst to increase the pace of organic processes.

Particularly in South China, cadmium contamination of paddy soil has grown to be a significant environmental issue. The safety of agricultural goods and human health are impacted by the Cd in soil, which is readily absorbed and enriched in rice grain **(Shi and Wang., 2021)** Cd immobilization in soil was accomplished using a variety of minerals, including hydroxyapatite, lime, and charcoal **(Shi and Wang., 2021**). To evaluate how TiO_2 nanoparticles influence the phytotoxicity of cadmium on Oryza sativa L. throughout its growth stages, and to examine the role of TiO2 nanoparticles in the movement and accumulation of cadmium within the soil-rice ecosystem, different concentrations of TiO_2 nanoparticles were introduced to cadmium-contaminated paddy soils. A pot experiment was also conducted, according to **(Emamverdian et al.,(2022)**. This study could deepen our understanding of the potential risks posed by synthetic nanoparticles to human health and the environment.

A thorough investigation of the biological synthesis of TiO_2NPs by a variety of plants belonging to several taxonomic groups is covered in this review, along with a discussion of the mechanism of action for this biosynthesis. Furthermore, the review concentrates on the features of TiO_2 NPs optical and physiochemical properties. Lastly, promising uses of TiO_2 NPs across several domains are showcased. **(Emamverdian et al.,2022)**

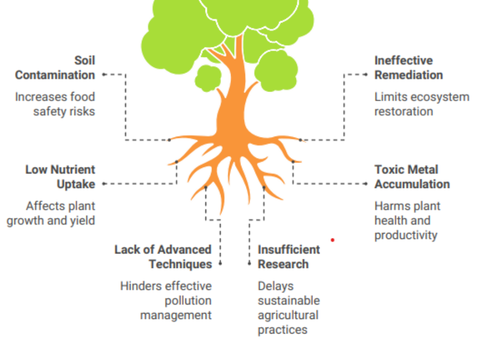


Fig 2 :- Picture Showing Heavy metal contamination in agriculture

2. Mechanism of Titanium dioxide Photocatalysis

Since titanium dioxide (TiO_2) is a semiconductor, there is a slight energy difference between the valence and conduction bands. When ultraviolet light strikes a surface, electrons in the valence band are stimulated to move into the conduction band. Both positive and negative charges are created on the semiconductor surface as a result of this event. The highest absorption wavelength of titanium dioxide is 400 nm, and its band gap is between 3 and 3.2 eV. **(Ojemaye et al.,2020; Maganha de Almeida Kumlien et al.,2021)** Shows the complete electron excitation phenomenon. When titanium dioxide is exposed to light continuously, a high temperature forms on its surface, which causes the contaminants in the water system to degrade. The breakdown of contaminants using the water's dissolved oxygen is illustrated in Equations (1–3). According to **(Yao et al.,2017)**, hydroxyl radicals produced during these reactions also aid in the photocatalytic degradation pathway, which breaks down contaminants. They protonate here and produce hydroperoxyl compounds, which aid in scavenging undesirable radicals and promoting slowness in electron and hole recombination.

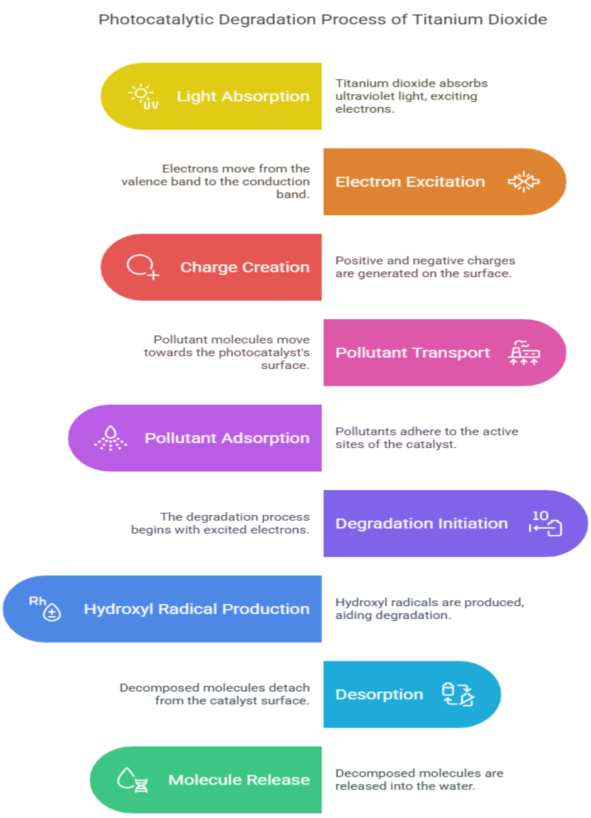


Fig 3 :- Picture Showing the five main stages of degradation

Pollutants go through five main stages of degradation Showing in **Fig 3** . Steps one and two include the transport of pollutant molecules to the photocatalyst's surface, which is followed by adsorption onto the active sites. Step 3: The photocatalytic degradation process is started when the contaminants connect to the active sites and photoexcite the electrons. Following the pollutant's degradation in steps 4 and 5, desorption takes place, and the broken-down molecules are eventually discharged to the water's surface **(Gopinath et al.,2020)**. Additionally, five distinct products may develop as a result of the degradation process. The type of pollutant and photocatalyst selected determine the photocatalytic degradation process and final products.

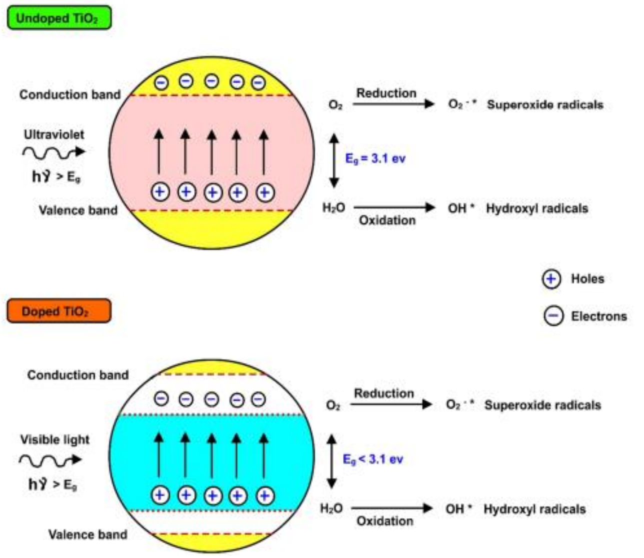


Fig 4 :- Shows a comparison of the doped and undoped (pure) titanium dioxides' energy band gap values. After being exposed to light with an energy that matches the bandgap, the electrons in titanium dioxide's valence band become excited and concurrently move to the conduction band. This behavior makes it easier for different reactive oxygen species to be produced, which degrades the contaminants in wastewater. O2: oxygen, H2O: water, For instance, h^4:-photon energy, energy gap.

3. Role of Titanium dioxide nanoparticles in enhancing Phytoremediation Processes

Titanium Dioxide (TiO_2) nanoparticles (NPs), with their special qualities of high surface area, photocatalytic activity, and biocompatibility, are important for improving phytoremediation processes. Due to their increased bioavailability to plants, these nanoparticles can enhance the uptake of toxins, especially organic pollutants and heavy metals. By encouraging plant growth and root development, TiO_2 NPs increase the surface area that can be used to absorb pollutants. Additionally, TiO_2 NPs can increase antioxidant activity in plants by producing reactive oxygen species (ROS) when exposed to UV radiation. (**Ojemaye et al.,2020); (Maganha de Almeida Kumlien et al.,2021).** This helps plants activate defense mechanisms, increasing their resistance to contaminants and environmental stress. The overall burden on the plants is lessened by their photocatalytic qualities, which are helpful in breaking down organic pollutants like dyes and pesticides into less harmful forms. In the rhizosphere, TiO_2 NPs may also encourage the development of helpful microorganisms that aid in the degradation of pollutants. Despite the potential benefits of TiO_2 NPs, issues including toxicity at higher concentrations and possible long-term environmental effects need to be taken into account. TiO_2 NPs have the potential to greatly increase the efficacy and efficiency of phytoremediation overall, especially when combined with other nanomaterials. **(Ojemaye et al.,2020); (Maganha de Almeida Kumlien et al., 2021)**

Long-term effect: To fully comprehend the sustainability of TiO_2 NP applications, long-term studies are necessary, as the majority of research focuses on short-term effects.

Mechanistic Insights: - Although the broad mechanisms are well understood, more research is required to determine the precise chemical routes by which TiO_2 NPs reduce heavy metal stress.

Field Studies: The majority of research has been carried out in controlled settings. To confirm the efficacy of TiO_2 NPs in practical settings, field research is required. Show in **fig 5**

Environmental Impact: Thorough analyses are required to determine the possible environmental effects of TiO_2 NPs, including their fate and movement in soil and water.

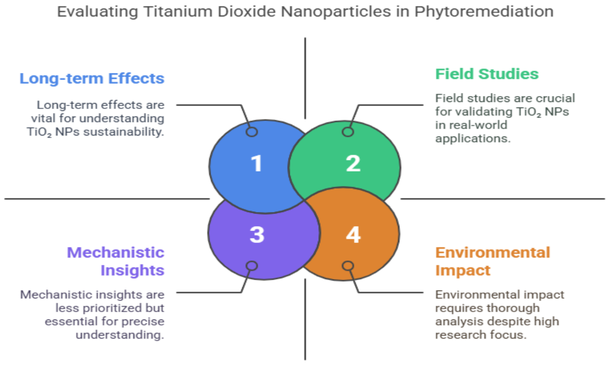


Fig 5 :- Picture showing the Long-Term Effects, Mechanistic Insights, Field Studies, and Environmental Impact of Titanium Dioxide Nanoparticles (TiO_2 NP_s) in Agricultural Systems.

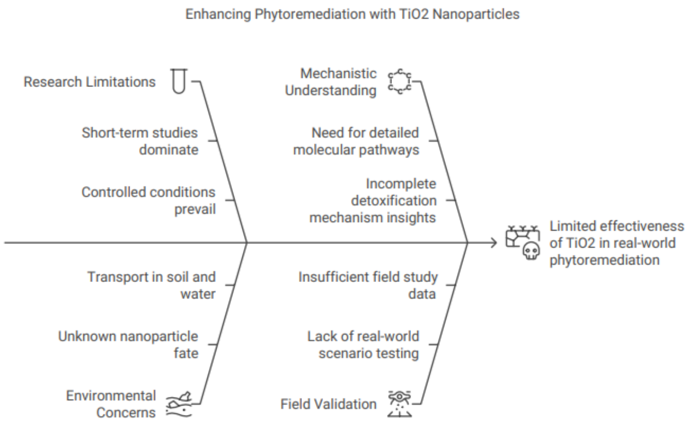


Fig 6 :- Enhancing the phytoremediation with TiO2 nanoparticles

4. Synthesis of Titanium dioxide nanoparticles

Research indicates that titanium dioxide (TiO_2) can be produced using a variety of methods, including chemical, physical, and environmentally friendly approaches **(Nabi et al.,2020)** a; (**Sharma et al.,2020; Wang et al.,2020b**). A comprehensive literature review has compared different synthesis routes for titanium dioxide-based catalysts designed for environmental uses. Recently, a diverse array of techniques has been employed to synthesize nano-titanium dioxide, such as vapor deposition **(Singh et al., 2019a)**, electrodeposition **(He et al.,2019)**, sol–gel process **(Phattepur et al.,2019**), hydrothermal process (**Wang et al., 2020b**), solvothermal process microwave synthesis and sonochemical synthesis (**Moreira et al., 2020**). Although the chemical synthesis of titanium dioxide nanoparticles allows for controlled manipulation of their size and shape, certain limitations persist, including high expenses, the requirement for elevated pressures and temperatures, and potential ecotoxic effects. These issues significantly hinder the industrial manufacturing of titanium dioxide as well as its applications in various domains (**Nadeem et al.,2018**). Consequently, the use of reducing agents derived from biological sources is adopted for synthesis through "green synthesis," an eco-friendlier alternative that has gained traction recently. The subsequent subsection of the review paper elaborates on some of the most prevalent techniques for titanium dioxide synthesis. New possibilities for environmental applications, particularly in the extraction of heavy metals from plants, have emerged due to the recent advancements in the production of titanium dioxide (TiO_2) nanotubes. Innovative techniques, such as sol-gel and hydrothermal procedures, improve the photocatalytic efficiency of TiO_2 under a variety of circumstances by providing fine control over particle size and shape. The incorporation of innovative techniques, such microwave-assisted synthesis, remarkably shortens manufacturing times while producing high-quality nanostructures. (**Ojemaye et al.,2020; Maganha de Almeida Kumlien et al.,2021)** Additionally, the investigation of titanium dioxide as a photocatalyst demonstrates its capacity to break down harmful contaminants in water and efficiently transfer heavy metals from polluted soil into a form that plants can absorb. These discoveries highlight TiO_2 nanoparticles' potential for both environmental cleanup and the advancement of sustainable farming methods, where the nanoparticles can promote the growth and resilience of plants by reducing the negative effects of heavy metal stress.

4.1Chemical synthesis methods

4.1.a. SOL GEL METHOD

Sol-gel is a dependable technique for create extremely thin metal oxides through the hydrolysis reactions and densification of alkoxide precursors . There are various ways that researchers have applied the sol-gel process. After mixing tetra n-butyl titanate with deionized water and adding hydrochloric acid or ammonia, (**Wang et al.,2021)** created a gel that, when dried, ground, and calcined at different temperatures, yielded titanium oxide (TiO_2) nanopowder. The annealed powders' spectra at various temperatures demonstrate that the anatase to rotai phase transition began about 600 °C and was finished at roughly 800 °C. The size of the nanoparticle increases from 6 nm to 36 nm when the annealing temperature rises from 350 °C to 600 °C. shows that while the growth rate of particles is modest at low annealing temperatures, the diameter of the nanoparticles increases more quickly at high temperatures. The low-temperature synthesis of nanoparticles will be especially crucial because high temperatures cannot produce catalytic compounds, electrodes, and other Titanium oxide (TiO_2) equipment on polymer substrates and other specific metals. (**Li et al.,(2022)** used the sol-gel approach to create titanium oxide nanoparticles at temperatures lower than 100 °C. Once the dry gel was prepared using the original solution of ethanol and tetrabutyl titanate, it was placed in the medium for 12 hours at 100 °C (shelf life). Persistence crystallizes the anatase phase in addition to aiding in the removal of organic contaminants.

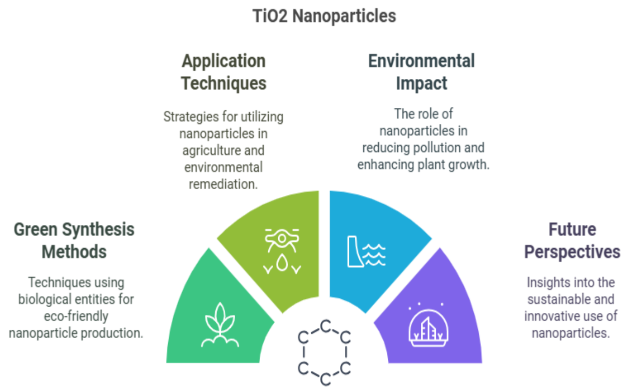


Fig 6:- Picture showing the Sol gel Method

4.1.b. CO-SEDIMENTATION METHOD

Co-precipitation is a technique for creating colloidal materials from the liquid phase that entails hydrolyzing the starting material followed by the addition of a base solution (NaOH, NH_4OH) to create the precipitate. **(Shi and Wang et al.,2021).** By sintering the precipitate that results, the required oxide is created. Due to the relatively quick deposition response, one of the method's drawbacks is the inability to manage particle size and distribution. The co-precipitation process typically uses $TiCl_4$ or $TiCl_3$ as a raw material to create titanium oxide (TiO_2) nanoparticles.

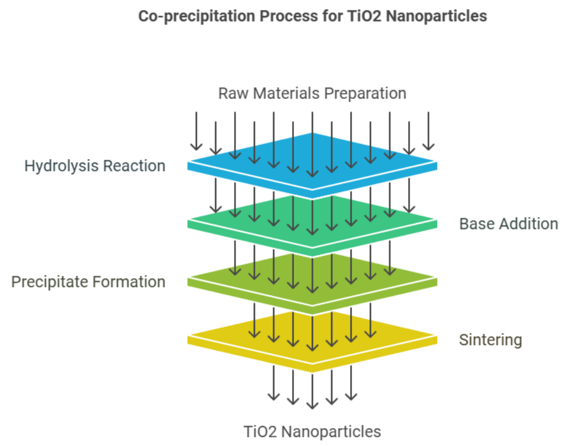


Fig 7 :- Co-sedimentation Method

4.1.c. HYDROTHERMAL METHOD

A diverse range of chemical compounds, including oxides, sulfates, carbonates, phosphates, and sulfides, can be formed as nanoparticles by hydrolyzing metal salt solutions. Hydrothermal synthesis is typically performed by reacting in aqueous solutions within steel pressure vessels, referred to as Teflon-lined autoclaves, under controlled temperature and pressure conditions, according to **(Shi and Wang et al.,2021)**. By avoiding the gel phase of the sol-gel process, the hydrothermal synthesis technique directly calcines solid Mock right after drying to room temperature following the hydrolysis of metal-alkoxides in an alcohol-water medium. By manipulating factors such as temperature, pH, reactant concentrations, and additives, nanoparticles with the desired sizes and shapes can be produced.

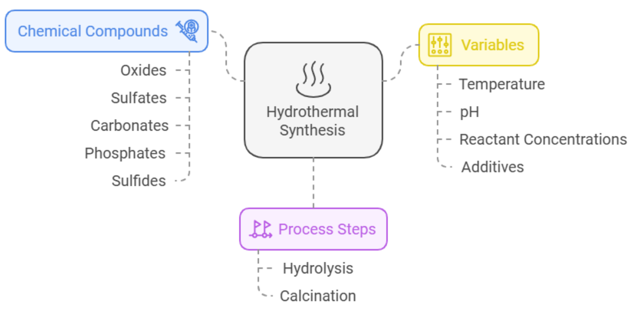


Fig 8 :- Picture showing the process of Hydrothermal synthesis

4.2 Green Synthesis

The recent popularity of titanium dioxide nanoparticles as renewable resources has led to a plethora of studies in this area. Various research has shown, for example, that betel pepper leaves, *aloe vera* paste, and hay bacillus (*Bacillus subtilis*) bacteria have been utilized to synthesize TiO_2-NPs in different sizes. Another important aspect of the green synthesis of titanium dioxide nanoparticles is the selection of initiators. Four different initiators are employed in this process. These include tetra-n-butyl orthotitanate (TBT), titanium chloride ($TiCl_4$), titanium tetraisopropoxide (TTIP), and commercially available titanium dioxide powder. These initiators can produce nanoparticles that vary in size from 1 to 100 nm. In the conventional sol-gel method, TTIP is the most frequently used initiator. **(Rueda et al.,2022)** prepared the extract by using 150 mL of distilled water and 50 g of tangerine peel as a solvent, stirring for two hours at 90 ± 3 °C with a magnetic stirrer at 400 rpm. The tangerine peel extract was then added to a 1.5 Normality TTIP solution in two different proportions. In one set of solutions at pH 5, 68 mL of TTIP was combined with 1 mL of extract to create one type of sample, while another sample type comprised 68 mL of TTIP and 55 mL of extract. Following the mixing of these samples, they were centrifuged for three hours at 700 rpm. The precipitated samples were subsequently dried for eight hours at 100 °C and calcined at 600 °C. In these two sample types, nanocrystals were observed to form, measuring between 50 and 150 nm, with significant differences in cluster sizes. A-type nanocrystals aggregated at 700 nm, while B-type nanocrystals clustered at 350 nm. **(Irshad et al.,(2020)** utilized plants such as *Trianthema portulacastrum* and *Chenopodium quinoa* to generate TiO_2 nanoparticles. After meticulously washing the leaves with deionized water, they allowed them to dry for several days. The dried leaves were ground into a powder and soaked in deionized water for 36 hours. Titanium tetra isopropoxide was the initiator used in this process. A hydrolysis reaction was achieved by balancing the solvent and initiator in a 1:2 ratio, with the resulting product being calcined at 450 °C. The sol-gel method incorporated plants as substitutes for Tween-80, isopropyl alcohol, and acetic acid, which served as solvents in another TiO_2-NP synthesis. Nanoparticles produced through the chemical sol-gel method typically measure around 10–13 nm, whereas those synthesized via the green method tend to be larger. **(Kashale et al.,2022)** used chickpeas (*Cicer arietinum L.*) to produce titanium dioxide nanoparticles. After allowing twenty grams of dry chickpea leaves to sit in 100 mL of deionized water for six hours, they were filtered. This was followed by mixing 10 mL of chickpea extract with 10 mL of $TiCl_4$ to complete the process with a total of 50 mL. Ammonia was added until the pH reached 7, and then the mixture was calcined at 500 °C to eliminate the organic components and yield nanoparticles. This method resulted in the formation of titanium dioxide nanoparticles approximately 14 nm in size. **(Madadi et al.,2020**) also used licorice to synthesize titanium dioxide nanoparticles. After being cleaned and dried, the licorice root was finely chopped and degreased using a Soxhlet apparatus with acetone and methanol. It was then air-dried before undergoing extraction with methanol in a Soxhlet device. In addition to centrifugation, the extract was dried using a flash evaporator. Titanium dioxide nanoparticles were synthesized using conventional sol-gel methods with tetra-n-butyl orthotitanate (TBT) as the initiator. The XRD analysis indicated that the particle size was 24 nm. **(Saranya et al.,2020)** utilized a titanium oxysulphate initiator to produce TiO_2-NP from *Cochlospermum gossypium*. They combined 10 mL of 0.1 M titanium oxysulphate with 50 mg of *Cochlospermum gossypium* while maintaining a temperature of 90–95 °C and stirring at 750 rpm. The extracted material underwent cleaning, drying, and centrifugation before being calcined for four hours at 500 °C to yield the final product. Through this method, titanium dioxide nanoparticles with an anatase crystal structure were achieved with sizes ranging from 8 to 13 nm.

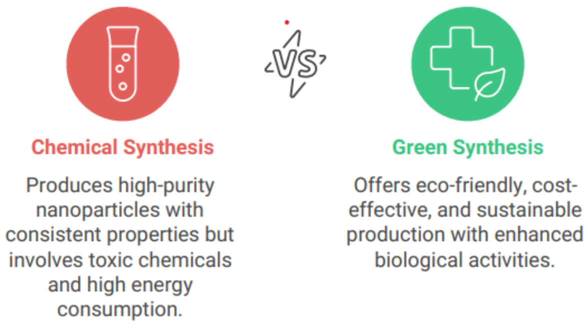


Fig 9:- Picture showing the difference between chemical synthesis and green synthesis

5. Toxicity of Titanium dioxide nanoparticles in animals

A fundamental method for doing an in vitro cytotoxicity research is the 3-(4,5-Dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide) (MTT) assay (3-[4,5-dimethylthiazol 2-yl]-2,5diphenyl tetrazolium bromide). This technique uses the MTT dye to alter the stain's color in the cells. The mitochondrial activity approach is unique in that it is easy to use, sensitive, and reliable. It can also detect the harmful effects of various cell lines, making it suitable for in vivo animal research **(Vijaya Lakshmi et al.,2020)** used osteoblast-like MG63 cell lines treated with TiO_2-NPs at several doses for 24 and 48 hours to estimate the viability assay. Both treated and untreated cells' morphological characteristics and degree of toxicity are determined by the considerable rise in MG63 cell lines' cell viability and rate of proliferation. The produced nano TiO_2 particles demonstrate biocompatibility in MG63 cell lines since they are non-toxic and do not inhibit proliferation. This is because, during the two hours of sintering at 900°C, anatase changes into rutile without affecting the other stages. Compared to the highly active, high refractive index anatase form, TiO_2-NPs are more inert. Instead of looking like fibers, titanium nanoparticles resemble clumped platelets. The more hazardous fiber-shaped particles are fullerenes and carbon nanotubes. Using green produced titanium nanoparticles, researchers have also examined the cytotoxicity assay of A549 cell lines, demonstrating increased anticancer activity efficiency. This is because cancer cells produce superoxide radicals. In order to assess the anticancer potential of the plain and bio-modified NPs, the other group also investigated MTS activity using KB oral cancer cells. Compared to pure and bio-modified samples, titanium nanoparticles modified with *Withania somnifera*, *Eclipta prostrata* shown better anticancer properties. Therefore, our findings showed that bio-modified samples are more active than pure titanium nanoparticles.

6. TiO_2 NP and application in agriculture

TiO2 nanoparticles are insoluble, semiconductive materials that have antibacterial, photocatalytic, UV absorption, and a high refractive index. The varied crystal symmetries exhibited by these ENPs, which are represented by mineral phases including rutile, brookite, and anatase, contribute to their highly tuneable features. The distinctive characteristics of each crystal structure can help with its application; typically, the appropriate mineral form is chosen based on its higher or lower photocatalytic capacity. During the synthesis process, TiO_2 nanoparticles (NPs) can be formed into both spherical and nanorod shapes, with sizes adjustable from a few nanometers to 100 nm in any dimension. To obtain nanomaterials with specific properties, various synthesis methods have been employed to produce TiO_2 NPs, including sol, sol-gel, micelle, solvothermal, hydrothermal, and vapor deposition techniques, among others. Due to their unique characteristics, TiO_2 NPs are utilized in numerous areas of human activity, including agriculture. Similar to ZnO NPs, the surface properties of TiO_2 NPs are often modified to enhance stability, amplify beneficial effects, and minimize toxicity. Their environmental applications encompass drug delivery, antimicrobial coatings, water treatment, pollutant degradation, and biosensing. TiO_2 NPs have been deployed to promote plant growth and germination, safeguard seeds, prevent crop diseases, decompose pesticides, and detect their residues. Reports indicate that these nanoparticles also improve plant health, increase seed or product yield, and encourage both root and shoot development. There have been mentions of elevated levels of carotenoids, soluble leaf proteins, and chlorophyll production, as well as enhanced absorption of several essential nutrients. Furthermore, TiO_2 NPs have proven effective in significantly alleviating environmental stressors, such as drought conditions in wheat and excessive cadmium levels in maize.

7. Alleviation of different Heavy Metals by TiO_2 Nanoparticles application

7.1. *Iron*

The development and growth of plants, animals, and humans are all reliant on iron (Fe). It plays a crucial role in physiological and biochemical processes such as respiration, photosynthesis, and cellular metabolism. For example, an iron deficiency leads to yellowing leaves and reduced photosynthetic efficiency, as it is vital for creating specific chlorophyll-protein complexes within chloroplasts. Iron is intricately linked to enzyme functionality and serves as a cofactor for numerous enzymes. The unique structure and electrical properties of iron nanoparticles (Fe NPs) make them particularly effective as adsorbents. Magnetic nanoparticles (NPs) like Fe_3O_4 and γ-Fe_2O_3 can be easily separated from the adsorbing medium using a magnetic field. Nano Fe alleviates issues primarily through the adsorption of heavy metals (HM), promoting the growth of iron coatings on root surfaces, activating oxidative defense mechanisms, and scavenging reactive oxygen species (ROS). Several studies have indicated that nano Fe holds significant potential for application in fertilizers. For instance, Fe_2O_3 NPs have been proposed as iron-containing fertilizers for peanut cultivation, yet the potential risks have not been thoroughly addressed. Additionally, it has been shown that pre-soaking seeds in low concentrations of Fe_2O_3 NPs can enhance legume root development by 88–366%.

Research suggests that nanoscale zero-valent iron (nZVI) boosts superoxide dismutase (SOD) and peroxidase (POD) activities in plant leaves, reduces heavy metal accumulation in sunflowers, and promotes plant growth. **Guha** reported that the application of nZVI (100 mg/L) to rice seedlings significantly down-regulated the gene expressions of iron transporters (IRT1, IRT2, YSL2, YSL15), which are responsible for the uptake of both iron and cadmium (Cd). Conversely, the overexpression of the OsVIT1 and $OsCAX_4$ genes led to the sequestration of cadmium in vacuoles.

(**Hussain et al**) found that applying Fe_2O_3 NPs (at concentrations of 5, 10, 15, and 20 ppm) both topically and in the soil to wheat plants under cadmium stress (with available Cd at 0.93 mg/kg) reduced electrolyte leakage from the leaves, lowered cadmium levels in the grains, and enhanced the activity of antioxidant enzymes, along with increasing the dry weight of the wheat. They also noted that foliar application of Fe NPs is more effective than soil application, as various factors such as pH and the presence of other minerals can affect the amount of iron absorbed through the soil. When used in combination, foliar application of Fe NPs further mitigated the impacts of cadmium stress in rice, with the effect being enhanced when biochar was incorporated into the soil. However, the biochar-Fe_3O_4 nanocomposites facilitated the movement of cadmium in naturally wet soil, indicating that the risks are still not fully understood. Fe_2O_3 NPs applied to wheat soil under drought and cadmium stress improved photosynthesis, yield, and cadmium concentration in grains during combined stress conditions.

7.2 Titanium dioxide Nanoparticles

Due to their minimal toxicity, beneficial optical properties, strong adhesive qualities, and great stability, titanium dioxide nanoparticles (TiO_2 NPs) rank among the most widely manufactured engineered nanoparticles globally and are commonly used in coatings, cosmetics, and pigments. In 2012, an estimated 1,175,176 tons of TiO_2 NPs were produced worldwide each year. The primary mechanisms through which TiO_2 NPs mitigate heavy metal (HM) stress are their adsorption capabilities and the activation of the oxidative defense system. Numerous studies have demonstrated that TiO_2 NPs can reduce oxidative stress in plants. For example, **Wang et al.,**found that incorporating TiO_2 NPs into the nutrient solution increased the activity of antioxidant enzymes in maize tissues.

Cai et al.,observed that rice exposed to four different types of TiO_2 NPs (at concentrations of 10 and 1000 mg/L) alongside $Pb(NO_3)_2$ (at 1.0 mg/L) showed lead accumulation. The three types of TiO_2 NPs—anatase, pure rutile, and rutile with hydrophilic characteristics—effectively decreased Pb accumulation in the roots by over 80% and in the shoots by 77% to 97%, yet they did not find any effects on rice growth. Similar results were noted by Ji et al., who indicated that TiO_2 NPs had a negligible effect on the biomass of hydroponically grown rice seedlings. However, after exposure to TiO_2 NPs, improvements were observed in plant height, hormone levels, root length, and antioxidant enzyme activity, suggesting that the addition of TiO_2 NPs alleviated serum damage caused by Cd stress in rice.

When maize was cultivated in soil contaminated with Cd, TiO_2 NPs at concentrations of 100 and 250 mg/L were mixed into the soil and applied topically. The results showed that while soil treatment facilitated Cd absorption by maize and significantly reduced biomass, foliar application of TiO_2 NPs inhibited Cd absorption and increased biomass. Additionally, foliar spraying TiO_2 NPs was found to mitigate Cd stress damage in maize by activating metabolic pathways such as galactose, alanine, and aspartate, while also enhancing SOD and GST activity. The results indicated that the effectiveness of this relief was strongly influenced by the method of application.

Dai et al.,(2020) examined the effects of both uncoated and sodium dodecylbenzene sulfonate (SDBS)-coated TiO_2 NPs on wheat seedlings subjected to Cd stress. They observed that the hydrodynamic diameter of TiO_2 NPs decreased after SDBS coating, which improved the dispersion stability of TiO_2 NPs due to spatial and electrostatic repulsion. This enhancement resulted in an increase in the number of available adsorption sites and the capacity for Cd2+ adsorption. Furthermore, they found that SDBS-coated TiO_2 NPs significantly reduced Cd toxicity more effectively than uncoated TiO_2 NPs. This indicates that the bioavailability and toxicity of heavy metals can be influenced by nanoparticles coated with surfactants or other substances.

7.3 Arsenic

Both ZnO nanoparticles and Zn2+ significantly reduced the levels of arsenic in the roots and shoots of rice. In contrast, it was only the ZnO nanoparticles that lowered the concentration of cadmium in rice shoots, while Zn2+ was found to elevate the cadmium levels in the shoots. Khan et al.,noted that both cadmium stress and normal water conditions led to a reduction in wheat biomass, yield, and photosynthesis. As indicated by **(Irshad et al.,2021)** and **(Aravind et al.,2021**), drought stress intensified the negative impacts of cadmium stress on wheat; however, ZnO nanoparticles mitigated the effects of both cadmium and drought stress. **Hussain et al.,**applied different concentrations of ZnO nanoparticles (25, 50, and 100 mg/L) through foliar spray and soil application to wheat affected by cadmium and found that both methods promoted wheat growth, enhanced photosynthesis, and increased grain yield. Additionally, foliar application proved to be more effective than soil application in improving grain yield and reducing cadmium levels in the grains.

7.4 Silicon

After oxygen, silicon (Si) ranks as the second most abundant element in the Earth's crust. Although it is not essential for the growth of higher plants, its relationship to plant development is significant, especially for members of the Gramineae family, such as rice. Research indicates that the application of Si can enhance plants' ability to withstand abiotic stresses. Currently, Si is recognized for its capacity to alleviate heavy metal (HM) stress through four primary mechanisms: 1) activation of biochemical and physiological defense mechanisms to boost reactive oxygen species (ROS) scavenging, 2) complexation and immobilization of HMs to reduce their biological activity, 3) provision of nutrient sources that support the creation of structural protective agents that chelate HMs, and 4) regulation of expression related to HM transport.

Most of the early research was performed in hydroponic environments. For example, rice cultivated in a nutrient solution containing 20 µM $CdCl_2$ and treated with 2.5 mM nano Si exhibited lower levels of malondialdehyde (MDA) and cadmium (Cd) accumulation in the shoots, indicating that nano Si alleviated Cd-related stress. When different sizes of silicon nanoparticles (Si NPs) (19, 48, and 202 nm at 1.0 mM) were incorporated into a rice cell culture assay, the viability of cells in a Cd solution (40 µM) increased by 95.4%, 78.6%, and 66.2%, respectively. This outcome may be due to the up-regulation of genes responsible for Cd transport (OsHMA3) and Si uptake (OsLsi1), along with the down-regulation of genes that facilitate Cd uptake and transport (OsLCT1 and OsNramp5). **(Hussain et al.,2020)** found that topical applications of Si NPs (10 and 20 mg/L) effectively reduced Cd accumulation in rice grains and improved yield. They also demonstrated that a combination of Se NPs (20 mg/L) and Si NPs (10 mg/L) significantly lowered Cd (by 62%) and lead (Pb) (by 52%) levels in rice grains.

By activating antioxidant defense systems, **Sousa et al.,**discovered that Si NPs (4 mg/kg) mitigated aluminum toxicity in maize, although Si NPs did not affect aluminum accumulation in the plant. The variation in results compared to earlier findings may arise from the different types or concentrations of heavy metals utilized in these studies.

7.5 Lead (Pb)

The use of TiO2 NPs for lead removal has also been thoroughly investigated. When employed for photocatalytic lead removal from industrial wastewater, green-synthesised TiO_2 NPs from *Syzygium cumini* extract have reduced lead concentrations by 82.53%. **Sethy et al., (2020).** These nanoparticles are very successful in heavy metal cleanup because of their enormous surface area and photocatalytic qualities. Although there are few particular research on the use of TiO_2-NPs to reduce lead stress, the general mechanisms of TiO_2-NPs heavy metal detoxification point to possible advantages in lowering Pb toxicity as well. The mechanism by which lead (Pb2+) ions adsorb onto TiO_2 nanoparticles includes ion exchange and surface complexation. At a maximum capacity of 65.65 mg/g at 313 K, TiO_2 nanoparticles made by microemulsion-assisted precipitation demonstrate a strong adsorption capacity for Pb2+ ions. Studies using X-ray photoelectron spectroscopy (XPS) have demonstrated that the production of hydrated Pb2+ ions on the TiO_2 surface is a characteristic of the adsorption process.

Table 1: TiO_2 Nanoparticles Application in Different Plants to Alleviate Heavy Metals stress

S.No	Plant Species	Heavy Metal(s)	TiO2 NP Concentration	Observed Effects	Method of synthesis	Citation
1	*Pleioblastus pygmaeus*	Cu, Cd	100 µM	Increased antioxidant activity, reduced heavy metal accumulation and translocation, improved photosynthetic capacity and plant tolerance.	Chemical	Emamverdian et al ., 2022
2	*Arundinaria pygmaea L.*	Cu, Pb	50, 80, 100, 150 µM	Improved photosynthetic efficiency, reduced Cd uptake, enhanced antioxidant enzyme activities	Chemical	Emamverdian et al ., 2022
3	*Coriandrum sativum L.*	Cd	40, 80, 160 mg/L	Reduced Cd content, improved agronomic traits, reduced oxidative injuries, enhanced proline biosynthesis.	Chemical	Sardar et al., 2021
4	*Oryza sativa L.*	Cd	50, 100, 200, 400	Improved photosynthet	Chemical	Iqbal et al., 2023

	(Rice)		mg/L	ic efficiency, reduced Cd uptake, enhanced antioxidant enzyme activities		
5	*Arundinaria pygmaea L.*	Cd	100, 200 µM	Enhanced antioxidant activities, reduced ROS, improved photosynthetic parameters	Chemical	Emamverdian et al ., 2022
6	*Sorghum bicolor*	Sb	40, 80, 160 mg/L	Reduced Cd content, improved agronomic traits, reduced oxidative injuries	Chemical	Zand et al., 2020
7	*Coriandrum sativum L.*	Cd	40, 80, 160 mg/L	Reduced Cd content, improved agronomic traits, reduced oxidative injuries	Chemical	Sardar et al., 2021
8	*Oryza sativa L.* (Rice)	As	10, 100, 1000 mg/L	Reduced As bioaccumulation, alleviated oxidative stress	Chemical	Zhang et al., 2020
9	*Triticum aestivum*	As	25 mg/L	Improve root development , reduce at toxicity	Green	Zhang et al., 2020
10	*Glycine max*	Cu	75 mg/L	Decreased Cu levels and increased antioxidant activity	Green	Sardar et al., 2021
11	*Arabidopsis thaliana*	Pb	50 mg/L	Growth acceleration and decreased Pb accumulation	Green	Emamverdian et al ., 2022
12	*Zea mays*	Hg	200 mg/L	Increased root and shoot length and decreased absorption of mercury	Green	Emamverdian et al ., 2022
13	*Brassica napus*	Zn	150 mg/L	Improved Zn tolerance and seed germination	Green	Zhang et al., 2020
14	*Allium cepa*	Ni	75 mg/L	Better root growth and Ni detoxifying	Green	Sardar et al., 2021
15	*Cucumis sativus*	Cd	50 mg/L	Increased growth and reduce accumulation of Cd	Chemical	Zhang et al., 2020
16	*Pisum sativum*	Pb	50 mg/L	Reduced Pb uptake and enhanced pod formation	Green	Sardar et al., 2021
17	*Solanum tuberosum*	Cd	100 mg/L	Reduced Cd concentration and improved tuber formation	Green	Zhang et al., 2020
18	*Zea mays*	Pb	75 mg/L	Greater ability to withstand Pb stress	Chemical	Emamverdian et al ., 2022
19	*Vigna radiata*	Cu	100 mg/L	Reduced Cu toxicity and increased growth	Chemical	Zhang et al., 2020
20	*Allium sativum*	Hg	50 mg/L	Decreased levels of mercury and increased antioxidant activity	Green	Emamverdian et al ., 2022
21	*Cajanus cajan*	Cd	150 mg/L	Better growth indicators and lower levels of CD	Green	Zhang et al., 2020
22	*Capsicum annuum*	As	100 mg/L	Improved fruit quality and decreased As content	Chemical	Sardar et al., 2021
23	*Nicotiana tabacum*	Pb	100 mg/L	Increased development and decreased Pb accumulatio	Green	Zhang et al., 2020

				n		
24	*Cicer arietinum*	Ni	150 mg/L	Growth acceleration and decreased Ni toxicity	Chemical	Sardar et al., 2021
25	*Vigna mungo*	As	75 mg/L	Improved growth indicators and decreased As intake	Chemical	Zhang et al., 2020

Table 2: TiO2 Nanoparticles Application to improve Plant growth and development

S.No	Plant Species	Heavy Metal(s)	TiO2 NP Dosage	Beneficial Role	Citation
1	*Arundinaria pygmaea L.* (Bamboo)	Cu, Pb	0, 50, 80, 100, 150 µM	Reduced oxidative stress, increased antioxidant capacity, chlorophyll content, and biomass, reduced heavy metal accumulation	Emamverdian et al 2021
2	Pleioblastus pygmaeus (Bamboo)	Cu, Cd	100 µM TiO2 NPs + 10^{-8} M EBL	Increased antioxidant activity, photosynthetic capacity, reduced heavy metal accumulation and translocation	Emamverdian et al ., 2022
3	*Triticum aestivum* (Wheat)	-	0, 30, 50, 100 mg/kg	Enhanced root and shoot length, increased nutrient content, improved crop yield and quality	Ullah et al., 2020
4	*Sorghum bicolor* (Sorghum)	Sb	0, 100, 250, 500 mg/kg	Increased Sb accumulation, improved chlorophyll content, enhanced plant growth	Zand et al., 2020
5	*Trifolium repens* (White clover)	Cd	0, 100, 250, 500, 1000 mg/kg	Enhanced plant growth, increased chlorophyll content, improved Cd uptake and accumulation	Zand et al., 2020
6	Tomato (*Solanum lycopersicum*)	Pb	50 mg/kg	Better photosynthetic rate, higher levels of chlorophyll, and increased activity of antioxidant enzymes	Emamverdian et al., 2021
7	Wheat (*Triticum aestivum*)	Cd	100 mg/kg	Better grain production, longer roots, and decreased uptake of Cd	Emamverdian et al., 2021
8	Rice (*Oryza sativa*)	As	50 mg/kg	Reduced Increased grain yield, improved antioxidant enzyme activity, and accumulation	Emamverdian et al., 2022
9	Soybean (*Glycine max*)	Cu	25 mg/kg	Better photosynthetic rate, higher chlorophyll concentration, and decreased Cu toxicity	Zand et al., 2020
10	Maize (*Zea mays*)	Ni	100 mg/kg soil	Diminished Ni absorption, longer roots, and higher grain yield	Ullah et al., 2020
11	Cucumber (*Cucumis sativus*)	Cr	50 mg/kg soil	Better fruit yield, higher chlorophyll content, and decreased Cr uptake	Zand et al., 2020

12	Spinach (*Spinacia oleracea*)	Hg	25 mg/kg soil	Decreased absorption of mercury, elevated activity of antioxidant enzymes, and enhanced chlorophyll content in leaves	Ullah et al., 2020
13	Lettuce (*Lactuca sativa*)	Zn	100 mg/kg soil	Greater chlorophyll content in the leaves, longer roots, and less toxicity from zinc	Emamverdian et al., 2022
14	Mung bean (*Vigna radiata*)	Fe	25 mg/kg soil	Improved seed yield, higher chlorophyll content, and enhanced Fe uptake	Zand et al., 2020
15	Pea (*Pisum sativum*)	Mn	100 mg/kg soil	Improved seed yield, higher chlorophyll content, and enhanced Mn uptake	Emamverdian et al., 2021
16	Radish (*Raphanus sativus*)	B	50 mg/kg soil	Improved root biomass, longer roots, and better B uptake	Emamverdian et al., 2022
17	Wheat (*Triticum aestivum*)	Drought stress	100 mg/kg soil	Increased grain yield, better water use efficiency, and increased activity of antioxidant enzymes	Zand et al., 2020
18	Rice (*Oryza sativa*)	Heat stress	50 mg/kg soil	Higher grain production, improved antioxidant enzyme activity, and improved thermotolerance	Ullah et al., 2020
19	Lettuce (*Lactuca sativa*)	Fungal infection	100 mg/kg soil	Improved leaf chlorophyll content, decreased fungal development, and increased plant resistance	Zand et al., 2020
20	Maize (*Zea mays*)	UV-B radiation	100 mg/kg soil	Increased grain yield, improved antioxidant enzyme activity, and decreased oxidative damage	Ullah et al., 2020

8. Effect of TiO_2 nanoparticle on plant physiology

Nanomaterials research has been increasingly popular in many scientific fields, especially in the fields of agriculture and environmental science. Similar gains in shoot length, root length, root area, and chlorophyll content were seen in mung beans (*Vigna radiata*) after foliar treatment of TiO_2-NPs. As demonstrated in Lemna minor, where growth was encouraged at low concentrations but inhibited at higher concentrations, high quantities of TiO2-NPs can, nevertheless, hinder growth. TiO2-NPs have different effects on pigment concentration and photosynthesis. TiO2-NPs caused a brief rise in stomatal conductance and net photosynthetic rate in *Raphanus sativus*, indicating a brief improvement in photosynthetic efficiency. (**Tighe-Neira et al.,2020).** In *Spirodela polyrrhiza*, on the other hand, photosynthetic pigment contents significantly decreased as TiO_2-NP concentrations increased, suggesting possible photosynthetic disruption. Plants' antioxidant defense mechanism is impacted by TiO_2-NPs. Higher concentrations of TiO_2-NP caused a considerable increase in superoxide dismutase (SOD) activity in *Spirodela polyrrhiza*, most likely as a result of scavenging reactive oxygen species (ROS). However, there was a drop in peroxidase (POD) activity, which might be attributed to either damage to the plant defense system or direct impacts on the molecular structure of the enzyme. TiO_2-NPs increased the antioxidant capacity of wheat via inducing SOD and POD activities. Likewise, in Lemna minor, SOD, POD, and catalase (CAT) activities rose to remove accumulated ROS at lower TiO_2-NP concentrations, but SOD activity fell at higher concentrations, causing damage to the cell membrane. Significant metabolic alterations in plants can result from exposure to TiO_2-NPs. TiO_2-NPs caused sugar deficiencies in wheat and changed metabolic pathways to focus on amino acid metabolism; the leaves showed more changes than the roots. **(Silva et al.,2020).** The application of TiO_2-NPs in phosphorus-deficient soil in rice (*Oryza sativa*) resulted in increased shoot length and phosphorus content in plant tissues. Additionally, metabolic changes such as increased amino acid and glycerol content in grain were observed. Research has also been done on the genotoxic effects of TiO_2-NPs. High concentrations of TiO_2-NPs (750 mg/kg) in rice had a negative impact on soil microorganisms and plant growth, increasing lipid peroxidation, H_2O_2 generation, and the leaf membrane damage index while lowering microbial biomass and soil enzymatic activity. According to this, TiO_2-NPs can promote plant growth at the right concentrations, but at greater concentrations, they may also be harmful to soil health and plant growth.

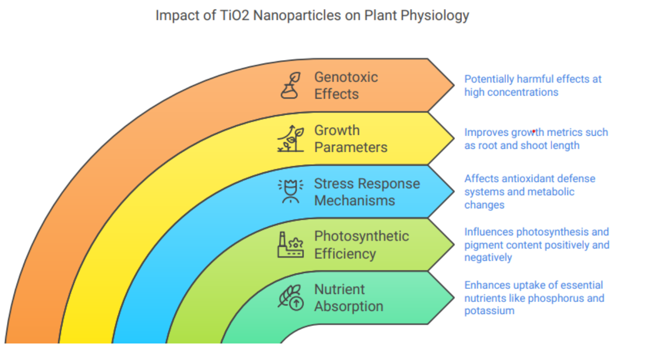


Fig 10:- Impact of TiO_2 Nanoparticles on plant Physiology

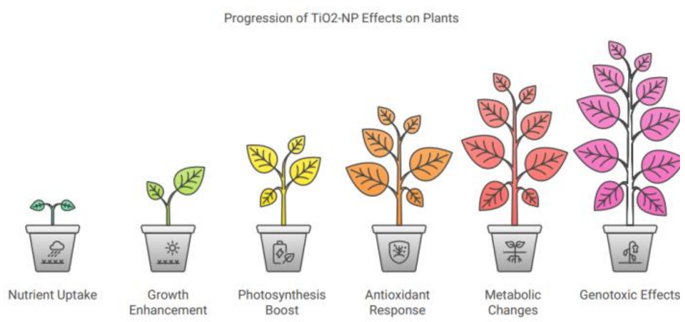


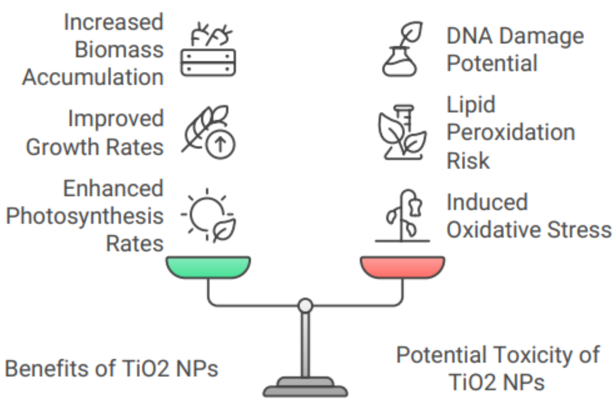
Fig 11:- Progression of TiO_2 Nanoparticles effects on Plants

9. Phytotoxicity and Genotoxicity

Since titanium dioxide nanoparticles (TiO_2 NPs) have special physicochemical characteristics, they have become a viable technique in heavy metal cleanup. Recent developments in their use demonstrate how well they can increase phytoremediation of harmful metals including arsenic (As), lead (Pb), and cadmium (Cd) and promote plant growth. The enzymatic antioxidant system in plants is strengthened by TiO_2 NPs, which lessen oxidative stress brought on by exposure to heavy metals. They also aid in the immobilization and sequestration of heavy metals in soils, which restricts the absorption and bioavailability of minerals. Their use, however, carries some risk of phytotoxicity and genotoxicity since high doses might alter plant DNA integrity, oxidatively damage cells, and disturb cellular homeostasis. Research shows that the effects of TiO_2 NPs vary with dosage, highlighting the necessity of optimizing. Moreover, sophisticated formulations such as surface-modified TiO_2 NPs have demonstrated enhanced heavy metal chelation efficacy while reducing side effects. The significance of controlled application and additional study to ensure sustainable use in agricultural systems is highlighted by the dual role of TiO_2 NPs in encouraging remediation and their possible hazards.

Recent studies have highlighted the significant interest in titanium dioxide nanoparticles (TiO_2 NPs) due to their dual role in promoting plant growth and cleaning up heavy metal contamination. These nanoparticles are effective at reducing heavy metal toxicity in plants thanks to their exceptional photocatalytic properties, extensive surface area, and chemical durability. By adsorbing and immobilizing heavy metals such as arsenic (As), lead (Pb), and cadmium (Cd) in the soil, they restrict their bioavailability and reduce metal absorption by plants, aiding in the detoxification of these environmental contaminants. In addition, TiO_2 NPs enhance photosynthesis, improve nutrient absorption, and boost antioxidant enzyme activity, which helps plants combat oxidative stress caused by heavy metals. Recent findings indicate that TiO_2 NPs can mitigate the negative impacts of heavy metals by influencing key physiological and biochemical processes. For example, they enhance cellular defense mechanisms and encourage the creation of stress-related proteins. The effectiveness of modified TiO_2 NPs, such as those doped with other elements, in heavy metal chelation and remediation is much higher. But there are several issues with using these nanoparticles. Excessive levels of TiO_2 NPs can be phytotoxic, which damages plant membranes, degrades chlorophyll, and stunts growth. Another serious problem is genotoxicity, since too much nanoparticle buildup in plant tissues can result in mutations, chromosomal abnormalities, and DNA damage.

TiO_2 NPs dose-dependent effects emphasize the need for exact adjustment to maximize their advantages and reduce their hazards. Evaluation of these nanoparticles' long-term effects on the environment, particularly their interactions with soil microbes and their bioaccumulation in food chains, is also crucial, according to research. TiO_2 NPs have enormous potential in sustainable agriculture, especially when it comes to tackling heavy metal contamination in polluted areas, despite these obstacles. Technological developments in nanoparticle design, like controlled release systems and biocompatible coatings, have the potential to enhance the safety and efficacy of these particles and open the door for their wider use in phytoremediation techniques.



Balancing TiO2 NPs Benefits and Risks in Agriculture

10. FUTURE PROSPECT

ZnO and TiO_2 nanoparticles (NPs) possess the capacity to enhance plant growth and vitality while simultaneously minimizing material usage, rendering them highly effective and economical alternatives to conventional fertilizers. To address malnutrition, engineered nanoparticles (ENPs) could serve as a beneficial approach for increasing the absorption of micronutrients into the consumable parts of plants. Given that ZnO and TiO_2 NPs are photoreactive, their application on plants, alongside their dosage and extended exposure to sunlight, may bolster the antioxidant systems in leaves; however, excessive amounts may overwhelm the plants' defenses and inflict harm. Consequently, further research and innovation regarding the application of low yet effective concentrations of ZnO and TiO_2 NPs, as well as adjuvants that facilitate absorption and ENPs that protect plants from abiotic stressors, remain essential. This review compiles studies on the administration of various NPs through seed priming, soil application, foliar spraying, and solution application aimed at enhancing plant tolerance to heavy metal (HM) stress. Heavy metal stress significantly influences the morphology, physiology, and biochemistry of plants. Key strategies for improving plant resistance to heavy metals include enhancing the capacity of the apoplastic barrier to intercept heavy metals, regulating the expression of HM transport genes, reducing the bioavailable heavy metals in the soil, and providing additional nourishment to plants. This involves increasing the production of structural protective compounds (such as organic acids, phytochelatins, and root exudates), enhancing the efficiency of plant antioxidant systems, and reinforcing organ functionality. Moreover, we summarized how various NPs impact plants under cadmium (Cd) stress. With the ongoing advancement in science and technology, numerous NPs are now available, including those that are surface-coated or combined with other substances (such as surfactants) to improve or enhance their properties. Additionally, further investigation is necessary to fully comprehend the physicochemical attributes of NPs (size and charge) that determine their interaction with heavy metals in soil while agricultural plants are present. Some NPs can penetrate plant cell walls due to their 15 nm porosity. Furthermore, negatively charged NPs exhibit a greater capacity to traverse membranes compared to neutral and positively charged ones. Although several studies have reported the toxicity of NPs to plants and animals, more extensive research on the toxicity within more complex environments is warranted. Most existing studies have focused on individual NPs.

The impact of NP exposure level and different application methods varied in studies aimed at decreasing HM stress. Low doses typically show no significant control effect, while high doses can lead to unnecessary costs or negative consequences for plants. This poses a significant concern. Additionally, uncertainties remain regarding the application of NPs in soil environments. Therefore, more research is needed to explore the mechanisms and therapeutic effects associated with various application methods. Moreover, investigating the joint application of several NP types alongside other materials represents a promising research avenue. For example, it is important to explore the combination of NPs with different alleviators, such as hydrogen peroxide, nitric oxide, auxins, biochar, and heavy metal-resistant microbial strains. The integration of big data and artificial intelligence (AI) with environmental science and other disciplines is already underway. For instance, Rossi et al.,utilized AI to predict the accumulation of CeO_2 NPs and Cd in Brassica napus based on physiological data. Collectively, it is believed that a range of plant physiological traits and the levels of heavy metals in plants can be forecasted based on soil characteristics, plant variety, and NP properties, thanks to the accumulation of experimental data and advancements in technology. It is possible to select the appropriate types and concentrations of nanoparticles (NPs) for application, which would reduce unnecessary costs and enhance their beneficial effects. Ultimately, one of the significant barriers to the broader adoption of NPs in agriculture is their cost. Therefore, a crucial factor in the future development of nanotechnology is the cost-effective, eco-friendly, and efficient production of NPs. To better understand how NPs can enhance plant resistance, it is essential for researchers to examine their impacts on the terrestrial environment more thoroughly. Moreover, integrating NPs with computational methods and other disciplines will provide a more precise approach to applying NPs and understanding their environmental effects, thereby aiding in the advancement of NP technology for mitigating heavy metal stress.

11. CONCLUSION

This review provides an overview of the synthesis of TiO_2-NPs through various biological methods, along with their properties, mechanisms of action, and different biomedical uses. TiO_2-NPs have gained significant attention due to their diverse applications, such as antibacterial, antifungal, antiviral, anticancer, antioxidant, drug delivery, and various other biomedical roles. A range of methods, including chemical, physical, and biological techniques, has been employed to produce TiO_2-NPs. The biological approach represents an eco-friendly, cost-efficient, effective, safe, low-energy-consuming, and straightforward method.

Considerable research is essential to explore the potential local and widely available natural resources to achieve sustainable NP biosynthesis and improve the stability of nanoparticles, despite the preliminary stage of this field. Utilizing local resources, instead of large-scale nanoparticle production, can reduce development costs, making them economically viable compared to traditional methods. The success of this innovative technology, which presents significant advantages for the biomedical sector, relies on a comprehensive understanding of the biomolecule binding mechanisms involved. However, the biosynthesis mechanism is not thoroughly characterized, highlighting the need for research into the phytochemistry that drives this process.

A major challenge in using natural resources such as plants for nanoparticle synthesis is our incomplete understanding of the underlying processes, chemical components, and stabilizing agents of nanoparticles. Isolating NPs from biological materials and avoiding contamination from biological cells poses significant challenges in NP biosynthesis, which could adversely affect biomedical applications. To enhance the efficacy of NPs, particularly concerning biocompatibility and bioavailability, it is vital to consider the active groups involved and how functional groups from natural sources interact with the nanoparticle surface. In conclusion, the article's exploration of green technology through biosynthesis showcases impressive results that may motivate researchers and beginners alike to further investigate nature's potential and develop new, safer techniques for creating nanomaterials with desirable traits and valuable characteristics for a wide range of applications. TiO_2, recognized as one of the leading photocatalysts for heterogeneous photocatalysis, remains a safe and cost-effective material, whether in its natural mineral state, as dopants, or within composite systems. Despite the recent application of bare TiO_2 as a photocatalyst in wastewater treatment, there continues to be significant room for advancement in this material. In order to fully unlock its potential, it is necessary to address its limitations, such as the narrow excitation gap that often renders light irradiation ineffective and the complexities involved in its separation. This study investigated the influence of TiO_2 NPs on the mobility and phytotoxicity of Cd within the soil-rice ecosystem. Based on our findings, we draw the following conclusions: the addition of TiO_2 NPs to the soil enhanced plant height, biomass, and chlorophyll content, while reducing MDA levels and antioxidant enzyme activity. Therefore, the phytotoxic effects of Cd on *Oryza sativa L*. were mitigated by the inclusion of TiO_2 NPs. Although introducing TiO_2-NPs did not reduce the concentration of Cd in the grains to below the legally allowable limit, it was therefore impractical to utilize TiO_2-NPs as a strategy to minimize the risk of Cd within the soil-rice system. Furthermore, there is a need for additional research into the environmental dynamics of nanoparticles within the soil-plant system, particularly in the rhizosphere soil environment. In recent years, the importance of environmental preservation and care has increased significantly. The rapid progress in environmental sciences has allowed us to recognize both new challenges affecting human habitats and various shortcomings in the current remediation technologies for water purification. Years of neglect have led to a sharp increase in novel pollutants in both ground and surface water. The efficacy of existing facilities designed for water purification and remediation has proven inadequate for these new contaminants, as they have not been updated to address them effectively. Consequently, considerable scientific efforts are focused on discovering innovative methods to treat surface and groundwater. In the field of heterogeneous catalysis, anatase TiO_2 can be applied in various ways. This is due to titania, whether as unmodified TiO_2 or in doped or composite forms, being effective in breaking down a wide range of chemical compounds. Emerging contaminants that may pose environmental threats include analgesics, psychiatric drugs, antiarrhythmic medications, antibiotics, anticonvulsants, β-blockers, preservatives, corticosteroids, lipid-lowering agents, NSAIDs, organic dyes, psychiatric medications, and sex hormones, which can adversely impact the environment if they are allowed to enter nearby ground and water systems unchecked. To reduce their accumulation in the environment and prevent negative effects on ecological systems, human health, and ultimately our quality of life, timely actions must be taken. Recognizing the dangers associated with emerging contaminants has spurred extensive research to identify the most effective solutions to these challenges, resulting in the formulation of various innovative treatments.

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Data availability

Not applicable.

Conflict of interest statement

Authors declare that they do not have any conflict of interest.

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