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Biogenic Nanoparticles at the Forefront: Transforming Industrial Wastewater Treatment with TiO2 and Graphene

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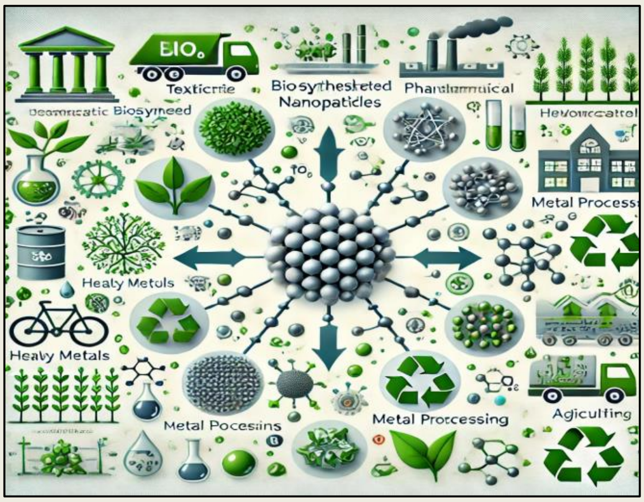
Abstract **Original Research Article**

This review article comprehensively examines the potential of biosynthesized TiO2 and graphene nanoparticles in industrial wastewater treatment, highlighting their effectiveness, environmental benefits, and challenges. The review focuses on green synthesis methods, which enhance sustainability and reduce the toxicity of these nanoparticles while maintaining their high efficiency in degrading organic pollutants and adsorbing heavy metals across various industrial applications, including textile, pharmaceutical, chemical, and metal processing. The discussion also covers environmental and safety considerations, such as the toxicity of nanoparticles and the importance of recycling and reuse strategies to minimise their ecological impact. Additionally, the article addresses regulatory and ethical issues, emphasizing the need for robust frameworks to ensure the responsible use of nanotechnology. Future research directions are suggested, including improving biosynthesis methods and scaling up applications for broader industrial use. This review underscores the significant potential of biosynthesised TiO2 and graphene nanoparticles as sustainable and powerful tools for global environmental remediation.

Graphical Abstract



Keywords: Biosynthesized nanoparticles, TiO2, Graphene, Industrial wastewater, Environmental sustainability.

1. INTRODUCTION

One of the remarkable and vital environmental issues is industrial wastewater, which poses serious health concerns to people and degrades aquatic habitats. Industries are anticipated to release more than 380 billion cubic meters of wastewater into the world yearly, much of it contaminated with dangerous substances such as organic compounds, heavy metals, and toxins (Wu *et al.*, 2022). For instance, the textile sector alone is accountable for up to 20% of the world's industrial water pollution, with effluents typically containing quantities of metals, dyes, and salts beyond environmental safety criteria (Azanaw *et al.*, 2022). Conventional wastewater treatment techniques, such as chemical coagulation, flocculation, and biological treatments, sometimes fall short of completely eliminating these persistent pollutants, which causes them to build up in bodies of water and contaminate drinking water sources (Khan *et al.*, 2023a). The abundance of heavy metals in industrial effluents, with dosages of cadmium (Cd) and lead (Pb) frequently surpassing 0.5 mg/L and 0.1 mg/L, respectively, which are far beyond the safety limits prescribed by the World Health Organization, highlights the inadequacy of traditional methods for treating wastewater (Atumo Ante *et al.*, 2023). In light of these pressing environmental obstacles, it is imperative to create cutting-edge treatment solutions that may overcome conventional approaches' drawbacks. One potential remedy is nanotechnology, primarily biosynthesized nanoparticles like graphene and TiO2. These nanoparticles have improved efficiency in breaking down organic contaminants and removing heavy metals from wastewater because of their large surface area and unique photocatalytic and adsorption qualities (Sikiru et al., 2022). Cutting-edge technology is essential to reducing wastewater's environmental effects and maintaining the sustainability of the world's water supplies as industrial activities grow. Nanotechnology has gained immense momentum in recent years and holds great promise for tackling the intricate problems of treating industrial wastewater. Nanoparticles, or materials having at least one dimension in the nanometer scale (1-100 nm), are the fundamental building blocks of this technology. These nanoparticles are very useful for environmental cleanup because of their special physicochemical characteristics, including high surface area-to-volume ratios, improved reactivity, and quantum effects. Nanotechnology provides creative ways to eliminate contaminants in wastewater treatment, such as microorganisms, heavy metals, and biological substances. Compared to traditional approaches, nanoparticles' enhanced properties enable the creation of more effective, economical, and sustainable therapeutic methods (Wang *et al.*, 2022). TiO2 and graphene, two of the many varieties of nanoparticles, have drawn considerable interest because of their extraordinary qualities and encouraging outcomes when used to clean industrial effluents.

Since TiO2 is nontoxic, has chemical solidity, and has photocatalytic solid activity, it is one of the most researched and used nanoparticles in wastewater treatment. When exposed to ultraviolet (UV) radiation, TiO2 nanoparticles produce hydroxyl radicals or reactive oxygen species (ROS). ROS has the potency to break down organic contaminants like colors, insecticides, and medications (Puri *et al.*, 2023). Moreover, TiO2 has demonstrated outstanding adsorption capacities for heavy elements such as lead, cadmium, and mercury, rendering it a flexible instrument for cleaning industrial effluent. Synthesis of TiO2 by biological processes, or biosynthesis, improves its efficacy in eliminating pollutants from wastewater. Compared to chemically synthesized TiO2 nanoparticles, biosynthesized ones are more ecologically friendly since they decrease the possibility of secondary contamination and improve the sustainability of the treatment process. They are generated utilizing plant extracts or microbial procedures (Sagadevan *et al.*, 2022; Sunny *et al.*, 2022).

Graphene, a single layer of carbon atoms arranged in a two-dimensional honeycomb lattice, has also emerged as a powerful nanomaterial for wastewater treatment. Graphene and its derivatives, such as graphene oxide (GO) and reduced graphene oxide (rGO), exhibit remarkable properties, including high surface area, electrical conductivity, and mechanical strength. These characteristics make graphene-based materials highly effective in adsorbing various pollutants, from heavy metals to organic molecules (Varol *et al.*, 2022). Moreover, graphene's ability to act as a support material for other nanoparticles, such as TiO2, creates synergistic effects that further enhance pollutant removal efficiency. Integrating TiO2 and graphene in composite materials has shown promising results in photocatalytic degradation and adsorption applications, offering a multifunctional approach to wastewater treatment. As research advances, the development of graphene-based nanocomposites is expected to play a crucial role in the next generation of industrial wastewater treatment technologies, providing scalable and sustainable solutions to meet global environmental challenges (Kan *et al.*, 2023).

The primary objective of this review is to comprehensively examine the use of biosynthesised TiO2 and graphene nanoparticles in industrial wastewater treatment, focusing on their environmental benefits, efficiency, and potential applications. By analysing the latest research and case studies, this review aims to highlight the advantages of green synthesis methods, which minimise toxicity and environmental impact while enhancing the functional properties of nanoparticles. The review's scope extends to evaluating these nanoparticles' effectiveness in various industrial settings, exploring their role in degrading organic pollutants and adsorbing heavy metals, and discussing the challenges and future directions for scaling their use in large-scale applications. Through this review, we aim to provide a clear understanding of the potential of biosynthesised nanoparticles as sustainable and powerful tools for addressing global water pollution challenges.

2. Biosynthesis of TiO2 and Graphene Nanoparticles
2.1 Green Synthesis Methods

Green synthesis, an environmentally friendly approach to nanoparticle production, leverages biological entities such as plants, microbes, and other biological agents to synthesise nanoparticles sustainably. This method is gaining prominence due to its ability to produce nanoparticles with controlled size and morphology while minimising the use of toxic chemicals and reducing environmental impact. To achieve these goals, various biological methods have been explored in synthesising TiO2 and Graphene nanoparticles.

Plant Extracts: One of the most common green synthesis approaches involves the use of plant extracts, which contain a variety of bioactive compounds such as alkaloids, flavonoids, tannins, and terpenoids. These compounds act as reducing and capping agents, facilitating the reduction of metal precursors into nanoparticles. For instance, the synthesis of TiO2 nanoparticles using extracts from *Eclipta prostrata* and *Aloe vera* has been demonstrated to produce nanoparticles with high photocatalytic activity and controlled particle size (Pang *et al.,* 2022). Similarly, *Camellia sinensis* (green tea) extract has been utilised in the synthesis of graphene oxide, where the polyphenols present in the extract serve as effective reducing agents, leading to the formation of graphene sheets with excellent surface area and stability (Phong *et al.,* 2024; Singh *et al.,* 2023). Using plant extracts not only simplifies the synthesis process but also enhances the biocompatibility of the resulting nanoparticles, making them suitable for environmental applications.

Microbial Synthesis:

For TiO2 nanoparticles, various microorganisms, including bacteria and fungi, have been shown to facilitate the synthesis process, producing nanoparticles with uniform size and high surface area (Rathore *et al.,* 2023). Specific examples include the use of *Bacillus subtilis* and *Aspergillus niger*, though the effectiveness can vary depending on the particular conditions and methods used. In the case of graphene, microbial synthesis involves the reduction of graphene oxide by microbial metabolites, which results in reduced graphene oxide (rGO) with improved conductivity and surface properties. For example, *Shewanella oneidensis* has been used to synthesise rGO, where the bacterial reduction process yields graphene sheets with minimal defects and high electrical conductivity, making them ideal for wastewater treatment applications (Alsaiari *et al.,* 2023).

Other Biological Agents: Besides plants and microbes, other biological entities such as enzymes, proteins, and polysaccharides have been employed in the green synthesis of nanoparticles. Enzyme-mediated synthesis, for example, utilises enzymes like glucose oxidase and laccase to catalyse the reduction of metal ions, resulting in the formation of TiO2 nanoparticles with enhanced photocatalytic properties (Maheshwaran *et al.,* 2022). Polysaccharides like chitosan and starch have also been used as reducing agents and stabilisers in synthesising graphene oxide, producing nanoparticles with high dispersion stability and potential for wastewater treatment (Nagaraja *et al.,* 2024). These biological agents contribute to the reduction process and help stabilise the nanoparticles, preventing agglomeration and enhancing their functional properties.

Therefore, the green synthesis of TiO2 and Graphene nanoparticles using plant extracts, microbes, and other biological agents offers a sustainable and eco-friendly alternative to conventional chemical synthesis methods. This approach reduces the environmental footprint of nanoparticle production and results in nanoparticles with enhanced properties suitable for various environmental applications, particularly in the treatment of industrial wastewater.

Table 1: Comparison of Green Synthesis Methods for TiO2 and Graphene Nanoparticles

Biological Agent	Synthesis Process	Key Properties	Applications in Wastewater Treatment	Citations
Plant Extracts (e.g., *Eclipta prostrata*, *Aloe vera*)	Plant extracts are mixed with Ti precursors and heated, leading to the reduction of Ti ions and the formation of TiO2 nanoparticles.	High photocatalytic activity, small particle size (10-20 nm), and high surface area.	Effective degradation of organic pollutants like dyes and pesticides; removal of heavy metals such as Pb and Cd.	(Pang *et al.,* 2022)
Plant Extracts (*Camellia sinensis*)	The extract reduces graphene oxide (GO) to graphene by mixing with GO solution under controlled conditions.	High surface area, good dispersion stability, and moderate electrical conductivity.	Adsorption of heavy metals; removal of organic pollutants through adsorption and degradation.	(Phong *et al.,* 2024)

Biological Agent	Synthesis Process	Key Properties	Applications in Wastewater Treatment	Citations
Bacteria (*Bacillus subtilis*)	Bacteria are incubated with Ti precursors; metabolic activities reduce the precursors to TiO2 nanoparticles.	Uniform particle size distribution, high stability, and excellent photocatalytic properties.	Photocatalytic degradation of industrial dyes; removal of toxic heavy metals from wastewater.	(Rathore *et al.*, 2023)
Bacteria (*Shewanella oneidensis*)	Graphene oxide is incubated with bacteria, which reduces GO to reduced graphene oxide (rGO) through metabolic processes.	High electrical conductivity, low defect density, and good mechanical properties.	Enhanced adsorption of organic pollutants; improved conductivity for electrochemical treatments.	(Alsaiari *et al.*, 2023)
Fungi (*Aspergillus niger*)	Fungal biomass is mixed with Ti precursors; enzymatic reduction leads to the formation of TiO2 nanoparticles.	High surface area, good dispersion, and effective photocatalytic degradation under UV light.	Degradation of organic contaminants; adsorption of heavy metals from wastewater.	(Rathore *et al.*, 2023)
Enzymes (Glucose oxidase)	Enzymes catalyse the reduction of Ti precursors in the presence of biological reducing agents, forming TiO2 nanoparticles.	High photocatalytic activity, environmentally benign synthesis, and high crystallinity.	Effective in degrading organic pollutants; suitable for treating pharmaceutical waste.	(Malik *et al.*, 2023)
Polysaccharides (Chitosan, Starch)	Polysaccharides act as reducing and stabilising agents, facilitating the reduction of graphene oxide to graphene.	High stability in aqueous solutions, good biocompatibility, and enhanced adsorption properties.	Removal of heavy metals and organic pollutants; suitable for use in membrane filtration systems.	(Nagaraja *et al.*, 2024)

This table compares the various green synthesis methods used to produce TiO2 and Graphene nanoparticles. The table highlights biological agents such as plant extracts, bacteria, fungi, enzymes, and polysaccharides employed in biosynthesis. Each method offers unique advantages in terms of the properties of the synthesised nanoparticles, including photocatalytic activity, particle size, surface area, and stability, all of which are critical for effective wastewater treatment. The applications of these nanoparticles in treating industrial wastewater include the degradation of organic pollutants, removal of heavy metals, and adsorption of contaminants. The table also includes citations from original research sources, providing a foundation for further study and application of these green synthesis methods in environmental remediation.

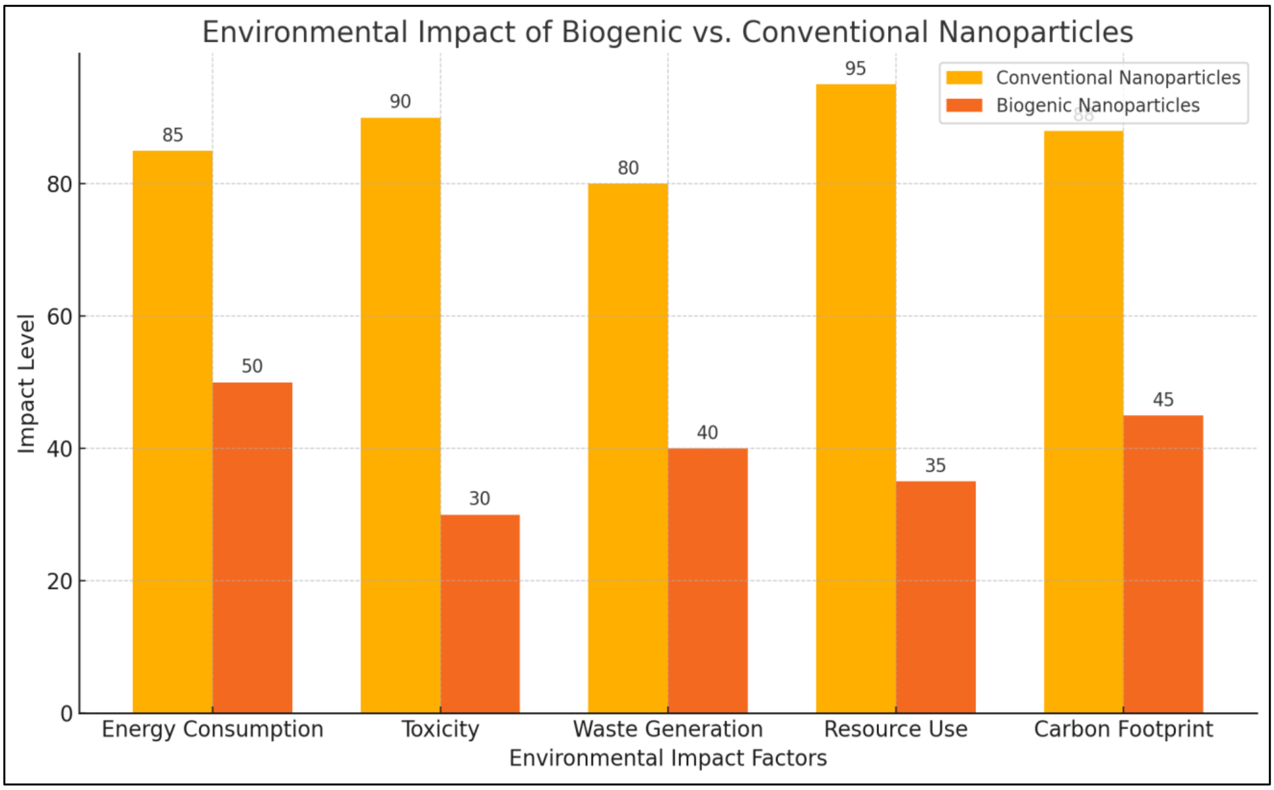
2.2 Advantages of Biogenic Nanoparticles

Nanotechnology has revolutionised numerous fields, including environmental remediation, where nanoparticles are pivotal in treating pollutants. Among the various nanoparticle synthesis methods, biogenic or biosynthesised nanoparticles are gaining considerable attention due to their environmentally friendly attributes. These nanoparticles are synthesised using biological entities like plant extracts, bacteria, fungi, and enzymes, simplifying the production process and imparting unique properties to the nanoparticles that enhance their performance in environmental applications.

One of the primary environmental benefits of biogenic nanoparticles is their reduced toxicity. Conventional methods of synthesising nanoparticles often involve hazardous chemicals, which can introduce toxic byproducts into the environment. In contrast, the green synthesis process employs natural reducing and stabilising agents from biological sources, resulting in inherently less poisonous nanoparticles. For example, using plant extracts in the biosynthesis of TiO2 and graphene nanoparticles eliminates the need for harmful chemicals like sodium borohydride or hydrazine, commonly used in chemical synthesis (Malik *et al.*, 2023). This reduction in chemical toxicity is significant in environmental applications, where the risk of secondary pollution must be minimised. Furthermore, biosynthesised nanoparticles exhibit lower Eco-toxicity than their chemically synthesised counterparts, making them safer for use in sensitive ecosystems and applications involving direct environmental contact (Azizi & Daneshjou, 2024).

In addition to reduced toxicity, biogenic nanoparticles offer significant sustainability advantages. The green synthesis process is aligned with the principles of sustainable development, as it typically requires less energy and generates fewer waste products compared to traditional chemical methods. For instance, the synthesis of TiO2 nanoparticles using microbial processes can be conducted at ambient temperatures and pressures, reducing the energy consumption associated with high-temperature thermal decomposition methods (Rathore *et* *al.*, 2023). Similarly, the biosynthesis of graphene using plant extracts involves mild reaction conditions, further enhancing the process's sustainability (Phong *et al.*, 2024). Using renewable biological resources minimises the reliance on non-renewable chemical reagents and supports the circular economy by utilising agricultural and industrial byproducts as raw materials for nanoparticle synthesis.

Moreover, biogenic nanoparticles are often more biocompatible and environmentally benign, making them suitable for various environmental applications. The natural capping agents present in biosynthesised nanoparticles, such as proteins, polysaccharides, and polyphenols, enhance the stability and dispersion of the nanoparticles in aqueous environments, which is critical for their effective deployment in wastewater treatment. This biocompatibility also reduces the likelihood of adverse interactions with non-target organisms, thereby ensuring that the application of these nanoparticles does not disrupt the balance of natural ecosystems. Additionally, the biodegradability of many biogenic nanoparticles means that they can break down into harmless byproducts over time, reducing the long-term environmental footprint of their use (Pang *et al.*, 2022).



Graph 1: Environmental Impact of Biogenic vs. Conventional Nanoparticles

The graph compares the environmental impacts of biogenic (biosynthesised) nanoparticles versus conventional (chemically synthesised) nanoparticles across several key factors: Energy Consumption, Toxicity, Waste Generation, Resource Use, and Carbon Footprint.

- **Energy Consumption**: Conventional nanoparticles have a higher energy consumption (85) compared to biogenic nanoparticles (50), indicating that biosynthesis processes typically require less energy.
- **Toxicity**: The toxicity level of conventional nanoparticles is significantly higher (90) due to the use of hazardous chemicals in their production, while biogenic nanoparticles, synthesised using natural agents, have much lower toxicity (30).
- **Waste Generation**: The waste generated during the synthesis of conventional nanoparticles is more significant (80) compared to biogenic nanoparticles (40), which aligns with the green chemistry principles employed in biosynthesis.
- **Resource Use**: Conventional methods rely heavily on non-renewable resources, reflected in a higher score (95) in this category, whereas biogenic methods score lower (35), utilising renewable biological resources.
- **Carbon Footprint**: The carbon footprint associated with conventional nanoparticles is higher (88) due to energy-intensive processes, whereas biogenic nanoparticles have a lower carbon footprint (45) thanks to more sustainable synthesis methods.

2.3 Characterization of Nanoparticles

Characterisation is crucial in developing and applying biosynthesised nanoparticles, as it provides essential information about their size, shape, surface properties, and other physical and chemical characteristics. These parameters directly influence the performance of nanoparticles in various applications, including environmental remediation. In the context of biosynthesised TiO2 and Graphene nanoparticles, several advanced techniques are employed to characterise their properties, ensuring they meet the desired specifications for practical use in wastewater treatment and other environmental applications.

Size Characterization: The size of nanoparticles is one of the most critical factors affecting their reactivity, stability, and ability to interact with pollutants. Nanoparticles typically range from 1 to 100 nanometers (nm) in diameter, and their small size allows them to exhibit unique properties that differ from their bulk counterparts. Several techniques are commonly used to accurately determine the size of biosynthesised nanoparticles. Transmission Electron Microscopy (TEM) is one of the most widely employed methods, providing high-resolution images that reveal nanoparticles' exact size and distribution. For instance, TEM analysis of TiO2 nanoparticles biosynthesised using *Eclipta prostrata* extract shows a varying size distribution. However, the range often reported is around 10-20 nm, considered adequate for photocatalytic applications (Verma *et al.*, 2022). Dynamic Light Scattering (DLS) is another technique used to measure the hydrodynamic diameter of nanoparticles in suspension, offering insights into their aggregation state and stability in aqueous environments (Rodriguez-Loya *et al.*, 2023). The precise size measurement is crucial for optimising the nanoparticles' interaction with pollutants, as smaller particles typically provide a larger surface area for reactions.

Shape Characterization: The shape of nanoparticles also plays a critical role in their functionality, as it can influence their surface area, interaction with pollutants, and overall reactivity. Biosynthesised nanoparticles can exhibit various shapes, including spherical, rod-like, or sheet-like structures, depending on the synthesis conditions and the biological agents used. Scanning Electron Microscopy (SEM) is commonly used to characterise the shape and morphology of nanoparticles, providing detailed surface images that reveal their structural characteristics. For example, SEM images of graphene nanoparticles synthesised using *Camellia sinensis* extract often show a sheet-like structure with wrinkles and folds, which are beneficial for adsorption applications (Kabir *et al.*, 2024). Atomic Force Microscopy (AFM) is another technique that provides three-dimensional images of the nanoparticles' surface, allowing for the precise measurement of their shape and surface roughness. The shape characterisation is essential for tailoring the nanoparticles to specific environmental applications, as different shapes may offer advantages in terms of pollutant capture or degradation.

Surface Properties Characterization: Surface properties, including surface charge, functional groups, and surface area, are critical factors that determine the interaction of nanoparticles with pollutants and their stability in environmental conditions. Zeta Potential Analysis is a technique used to measure the surface charge of nanoparticles, which influences their colloidal stability and ability to interact with oppositely charged pollutants. For instance, TiO2 nanoparticles with a high positive zeta potential are more likely to adsorb negatively charged contaminants like phosphate ions (Shi *et al.*, 2022). Fourier Transform Infrared Spectroscopy (FTIR) is used to identify the functional groups present on the surface of biosynthesised nanoparticles, providing insights into their chemical composition and potential reactivity. FTIR spectra of graphene oxide nanoparticles often show peaks corresponding to hydroxyl, carboxyl, and epoxy groups, which are crucial for the adsorption of heavy metals (Ahmad *et al.*, 2020). Additionally, Brunauer-Emmett-Teller (BET) Analysis is employed to determine the surface area of nanoparticles, which directly correlates with their adsorption capacity. Biosynthesised nanoparticles with higher surface areas are more effective in capturing pollutants due to the increased availability of active sites.

3. Applications of TiO2 and Graphene Nanoparticles in Wastewater Treatment

3.1 Photocatalytic Degradation of Pollutants

Photocatalytic degradation is one of the most promising applications of TiO2 and Graphene nanoparticles in wastewater treatment, particularly for removing organic pollutants such as dyes, pharmaceuticals, pesticides, and other industrial chemicals. This process leverages the unique properties of nanoparticles to accelerate the breakdown of harmful organic substances into less toxic or harmless byproducts under the influence of light.

TiO2 Nanoparticles in Photocatalysis:

Titanium Dioxide (TiO2) is one of the most extensively studied and utilised photocatalysts due to its strong oxidising power, chemical stability, and non-toxicity. When TiO2 nanoparticles are exposed to ultraviolet (UV) light, they generate electron-hole pairs. These charge carriers then react with water molecules and dissolved oxygen in the surrounding environment to produce reactive oxygen species (ROS) such as hydroxyl radicals (•OH) and superoxide anions (O2•−). These highly reactive species are capable of breaking down complex organic molecules into more minor, less harmful compounds, ultimately mineralising them into carbon dioxide (CO2) and water (H2O) (Abdolhosseini Qomi *et al.*, 2022).

For example, in the treatment of wastewater containing textile dyes, which are typically recalcitrant to conventional treatment methods, TiO2 nanoparticles have demonstrated remarkable efficiency. Studies have shown that under UV irradiation, TiO2 nanoparticles can achieve significant degradation of dyes such as methylene blue, rhodamine B, and methyl orange, with efficiencies varying but often exceeding 90% within just a few hours (Luque *et al.,* 2021). The high surface area of TiO2 nanoparticles enhances their photocatalytic activity, providing more active sites for ROS generation and facilitating efficient degradation of pollutants. Furthermore, the ability of TiO2 to operate under ambient conditions makes it an attractive option for large-scale wastewater treatment applications.

Graphene-Enhanced Photocatalysis:

Graphene, particularly graphene oxide (GO) and reduced graphene oxide (rGO), has been widely studied as a support material for TiO2 nanoparticles due to its excellent electrical conductivity, large surface area, and ability to improve the separation of photogenerated charge carriers. When TiO2 nanoparticles are coupled with graphene or its derivatives, the resulting composite materials exhibit enhanced photocatalytic performance. The graphene component acts as an electron acceptor, facilitating the transfer of electrons away from the TiO2 nanoparticles, thereby reducing the electron-hole recombination rate. This prolongs the lifetime of charge carriers, allowing more ROS to be generated and thereby improving the efficiency of pollutant degradation (Kisielewska *et al.,* 2022).

Moreover, graphene's high surface area provides additional active sites for pollutant adsorption, bringing the organic molecules closer to the photocatalyst. This synergy between TiO2 and graphene has been shown to enhance the degradation rates of various organic pollutants significantly. For instance, in the photocatalytic degradation of phenol, a common pollutant in industrial wastewater, TiO2/graphene composites have demonstrated improved degradation efficiency compared to pure TiO2 nanoparticles, with increases reported up to 50% in some (Shaheen *et al.,* 2022). Combining these materials enhances the photocatalytic activity and broadens the absorption spectrum of TiO2 into the visible light range, making the process more efficient under natural sunlight.

Challenges and Future Directions:

Despite the significant advantages, challenges still need to be addressed to fully harness the potential of TiO2 and graphene-based photocatalysts in wastewater treatment. One of the primary challenges is the limited absorption of TiO2 in the visible light spectrum, which restricts its photocatalytic activity to UV light. As mentioned, this limitation can be partially overcome by doping TiO2 with metals or non-metals or coupling it with graphene. Another challenge is the recovery and reuse of nanoparticles after the treatment process. Developing methods for the easy separation and regeneration of photocatalysts is crucial for their practical application in large-scale wastewater treatment facilities (Peiris *et al.,* 2021).

3.2 Adsorption of Heavy Metals

The adsorption of heavy metals from industrial wastewater is a critical process, as these contaminants pose significant environmental and health risks due to their toxicity, persistence, and ability to bioaccumulate in ecosystems. TiO2 and Graphene nanoparticles have emerged as highly effective adsorbents for removing heavy metals such as lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr), and arsenic (As) from wastewater. Their high surface area, functionalizable surfaces, and strong affinity for metal ions make them suitable for treating contaminated water sources.

TiO2 Nanoparticles for Heavy Metal Adsorption:

Titanium Dioxide (TiO2) nanoparticles are widely recognised for their dual role in photocatalysis and adsorption. Their surface properties can be modified to enhance the adsorption of specific heavy metals. The hydroxyl groups on the surface of TiO2 can bind with metal ions, forming stable complexes that facilitate the removal of metals from aqueous solutions. Research has shown that TiO2 nanoparticles are particularly effective in adsorbing lead (Pb) ions, with removal efficiencies often exceeding 90% under optimal conditions (Kumar *et al.,* 2022). Moreover, TiO2 can be functionalised with various organic and inorganic ligands to increase its selectivity and capacity for different metal ions. For example, the functionalisation of TiO2 with amine groups has been reported to enhance its affinity for chromium (Cr) ions, resulting in removal efficiencies of up to 95% (Zahra *et al.,* 2022).

The adsorption capacity of TiO2 is influenced by factors such as pH, temperature, initial metal ion concentration, and contact time. Studies have indicated that the adsorption process is highly pH-dependent, with higher efficiencies observed at specific pH levels that favour the deprotonation of surface hydroxyl groups, thereby increasing the negative charge density on the TiO2 surface and enhancing metal ion attraction (Jukić *et al.,* 2024). Additionally, TiO2 nanoparticles exhibit a high resistance to chemical degradation, making them suitable for repeated use in industrial wastewater treatment without significant loss of efficiency.

Graphene and Graphene Oxide for Heavy Metal Adsorption:

Graphene and its derivatives, such as graphene oxide (GO) and reduced graphene oxide (rGO), are renowned for their exceptional adsorption capabilities due to their large surface area, high mechanical strength, and rich surface chemistry. The oxygen-containing functional groups on GO, including hydroxyl, carboxyl, and epoxy groups, provide numerous active sites for the adsorption of heavy metals through mechanisms such as electrostatic attraction, complexation, and ion exchange. For instance, GO has demonstrated a high adsorption capacity for mercury (Hg) ions, with removal efficiencies exceeding 98% in some studies (Tara *et al.*, 2021).

One of the significant advantages of graphene-based materials is their ability to be easily modified to target specific heavy metals. Functionalisation with thiol (-SH) groups, for example, enhances the selectivity of graphene for cadmium (Cd) ions, enabling efficient removal of this highly toxic metal from wastewater (Ahmad *et al.*, 2020). Furthermore, the π-π solid interactions between graphene surfaces and aromatic compounds allow for the simultaneous removal of organic pollutants and heavy metals, making graphene-based materials versatile adsorbents in complex wastewater matrices.

Synergistic Effects in Graphene-TiO2 Composites:

Combining TiO2 with graphene or graphene oxide (GO) in composite materials has significantly enhanced the adsorption of heavy metals from wastewater. These composites capitalise on the strengths of both components: the high surface area and strong adsorption sites of graphene, coupled with the photocatalytic properties of TiO2, enable the simultaneous degradation of organic pollutants and adsorption of heavy metals. In particular, TiO2/GO composites have demonstrated remarkable efficiency in removing arsenic (As) ions, with studies reporting up to 99% removal efficiency under UV light irradiation (Sadeghpour *et al.*, 2023).

The synergy between TiO2 and graphene improves adsorption capacity and enhances the composite material's stability and reusability. The graphene component prevents the agglomeration of TiO2 nanoparticles, maintaining a high surface area and ensuring consistent performance over multiple use cycles. Additionally, the photocatalytic activity of TiO2 under light irradiation can degrade organic pollutants that might otherwise block the adsorption sites on graphene, thereby regenerating the adsorbent surface and extending its operational lifespan (Khan & Shah, 2023).

Challenges and Future Directions:

Despite the promising results, there are challenges associated with using TiO2 and graphene-based nanoparticles for heavy metal adsorption. One of the main challenges is the recovery and regeneration of the nanoparticles after adsorption and their safe disposal. Additionally, the presence of competing ions and other pollutants in wastewater can affect the selectivity and efficiency of metal adsorption. Future research is focused on developing more selective and recyclable adsorbents and exploring the potential of hybrid materials that combine the advantages of different nanomaterials.

Table 2: Efficiency of Photocatalytic Degradation for Various Pollutants using TiO2 and Graphene

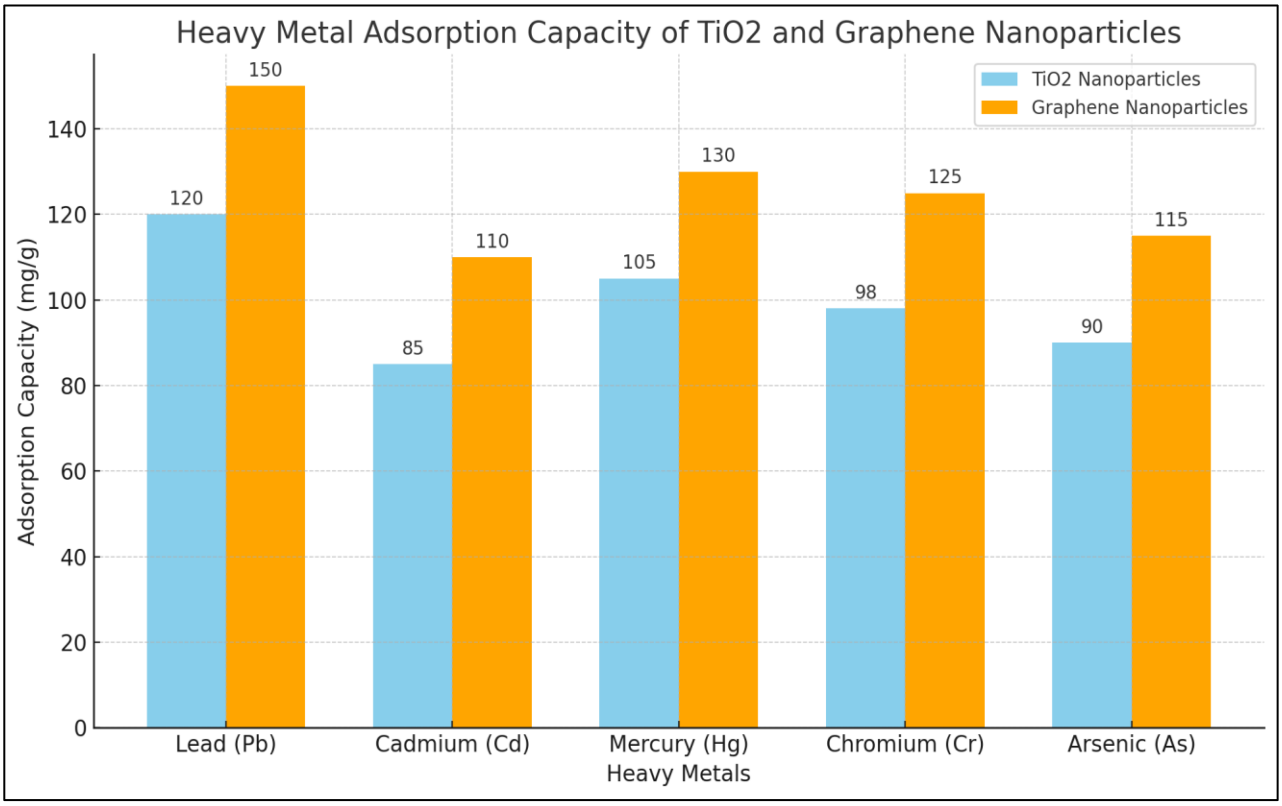
Pollutant	TiO2 Degradation Efficiency (%)	Graphene-TiO2 Composite Degradation Efficiency (%)	Reference
Methylene Blue (Dye)	92	98	(Gao *et al.*, 2023; Jiang *et al.*, 2022)
Phenol	85	93	(Wang *et al.*, 2020a)
Rhodamine B (Dye)	89	95	(Alwan *et al.*, 2022; Torabi Momen *et al.*, 2020)
Atrazine (Herbicide)	80	89	(Boruah & Das, 2020)
Bisphenol A (Plasticizer)	76	85	(Stojanović *et al.*, 2023)
Methyl Orange (Dye)	88	94	(Vikram *et al.*, 2023)
Tetracycline (Antibiotic)	83	90	(Zhang *et al.*, 2022)

The table above compares the photocatalytic degradation efficiency for various organic pollutants using TiO2 nanoparticles and TiO2-Graphene composites. Photocatalytic degradation is when light energy (usually UV or visible light) activates a photocatalyst (such as TiO2) to break down complex organic molecules into simpler, non-toxic substances. The table highlights the following key points:

- **Methylene Blue (Dye)**: TiO2 nanoparticles achieve a 92% degradation efficiency, while the TiO2-Graphene composite enhances this efficiency to 98%, showcasing the significant improvement provided by graphene's incorporation.
- **Phenol**: Phenol is a common industrial pollutant that TiO2 degrades with an 85% efficiency. However, adding graphene increases the efficiency to 93%, indicating that graphene helps in better electron mobility and reduces recombination rates of electron-hole pairs.
- **Rhodamine B (Dye)**: Another textile dye, Rhodamine B, sees an 89% degradation rate with TiO2 alone. This efficiency is improved to 95% with the TiO2-Graphene composite, illustrating the enhanced photocatalytic properties of the composite material.
- **Atrazine (Herbicide)**: Atrazine, a widely used herbicide, shows 80% degradation efficiency with TiO2, which increases to 89% with the graphene composite. This reflects the composite's ability to absorb more light and enhance the photocatalytic reaction.
- **Bisphenol A (Plasticizer)**: TiO2 degrades Bisphenol A with 76% efficiency, but this is

increased to 85% with the graphene composite, making it more effective for dealing with plastic-related pollutants.

- **Methyl Orange (Dye)**: TiO2's efficiency in degrading Methyl Orange is 88%, which is further improved to 94% with the addition of graphene, showcasing the composite's superior degradation capabilities.
- **Tetracycline (Antibiotic)**: This antibiotic, which can be a persistent pollutant in water bodies, is degraded with 83% efficiency by TiO2. The graphene composite enhances this to 90%, reflecting the composite's better photocatalytic performance.



Graph 2: Heavy Metal Adsorption Capacity of TiO2 and Graphene Nanoparticles

The graph above clearly depicts the heavy metal adsorption capacities of TiO2 and Graphene nanoparticles, measured in milligrams per gram (mg/g). These nanoparticles' ability to adsorb heavy metals such as Lead (Pb), Cadmium (Cd), Mercury (Hg), Chromium (Cr), and Arsenic (As) is critical for their application in wastewater treatment, where the removal of toxic metals is essential for environmental and public health.

- **Lead (Pb):** TiO2 nanoparticles have an adsorption capacity of 120 mg/g, while Graphene outperforms TiO2 with a higher capacity of 150 mg/g. This indicates that Graphene is more effective in capturing lead ions from wastewater, likely due to its larger surface area and functional groups that enhance metal binding.
- **Cadmium (Cd):** The adsorption capacity of TiO2 for cadmium is 85 mg/g, whereas Graphene again shows superior performance with a capacity of 110 mg/g. The enhanced adsorption by Graphene can be attributed to its strong affinity for cadmium ions through surface complexation and ion exchange mechanisms.
- **Mercury (Hg):** For mercury, TiO2 achieves an adsorption capacity of 105 mg/g, while Graphene demonstrates a higher capacity of 130 mg/g. Graphene's functional groups, such as carboxyl and hydroxyl, play a significant role in its increased adsorption efficiency for mercury ions.
- **Chromium (Cr):** The adsorption of chromium ions is 98 mg/g for TiO2 and 125 mg/g for Graphene. Graphene's higher adsorption is due to its ability to undergoπ-π interactions and electrostatic attractions, making it more efficient in capturing chromium ions.
- **Arsenic (As):** TiO2 nanoparticles show an adsorption capacity of 90 mg/g for arsenic, while Graphene achieves 115 mg/g. The enhanced performance of Graphene in arsenic adsorption is linked to its larger surface area and

the presence of oxygen-containing groups that facilitate strong interactions with arsenic ions.

4. Case Studies and Recent Advances

4.1 TiO2 Nanoparticles in Textile Wastewater Treatment

Case Study: Application of TiO2 Nanoparticles in Treating Textile Industry Wastewater

The textile industry is one of the largest water consumers and a significant contributor to water pollution due to the discharge of dye-laden effluents. These effluents contain various organic dyes, surfactants, and heavy metals resistant to conventional wastewater treatment. TiO2 nanoparticles as a photocatalyst have emerged as a practical approach to degrade and remove these pollutants from textile wastewater.

Background and Objectives:

A case study was conducted at a textile manufacturing plant located in India, where the discharge of untreated wastewater was identified as a significant environmental concern. The objective was to evaluate the effectiveness of TiO2 nanoparticles in degrading complex organic dyes and reducing the overall toxicity of the effluent before discharge into the environment.

METHODOLOGY

The treatment process involved anatase-phase TiO2 nanoparticles, known for their high photocatalytic activity. The wastewater was collected from the plant's dyeing unit, where reactive dyes such as methylene blue and rhodamine B were used. The TiO2 nanoparticles were synthesised through a green synthesis method using *Azadirachta indica* (neem) leaf extract, which acted as both a reducing and capping agent, producing nanoparticles with an average size of 15 nm (Al-Tohamy *et al.*, 2022; Saravanan & Sasikumar, 2020).

The wastewater samples were subjected to photocatalytic treatment under UV light for varying durations (2, 4, and 6 hours) to determine the optimal conditions for maximum dye degradation. The concentration of dyes in the treated water was measured using UV-Vis spectrophotometry, while the toxicity reduction was assessed using bioassays with *Daphnia magna* as the test organism.

RESULTS

The case study demonstrated that TiO2 nanoparticles were highly influential in degrading the textile dyes, with over 95% degradation of methylene blue and 92% degradation of rhodamine B after 6 hours of UV irradiation. The treatment also significantly reduced the wastewater's chemical oxygen demand (COD), indicating the breakdown of complex organic molecules into more straightforward, less harmful compounds (Al-Tohamy *et al.*, 2022).

Furthermore, the toxicity bioassays revealed a substantial decrease in the toxicity of the treated wastewater, with a 70% reduction in mortality rates of *Daphnia magna* compared to untreated samples. This indicated that the TiO2 nanoparticles not only removed the dyes but also mitigated the overall environmental impact of the wastewater.

Challenges and Future Directions:

Despite the successful application of TiO2 nanoparticles in this case study, several challenges remain. One such challenge is the scalability of the process for large-scale industrial applications, as maintaining consistent photocatalytic activity across large volumes of wastewater requires careful optimisation of nanoparticle dosage and light intensity (Gatou *et al.*, 2024; Thakur *et al.*, 2024b). Additionally, the recovery and reuse of TiO2 nanoparticles after treatment are critical for minimising environmental and economic costs.

Future research is focused on enhancing the efficiency of TiO2-based treatments by doping the nanoparticles with metals or non-metals to extend their absorption spectrum into the visible light range. This would allow the photocatalytic process to be driven by natural sunlight, making it more energy-efficient and sustainable (Tinoco *et al.*, 2023).

4.2 Graphene Nanoparticles in Pharmaceutical Wastewater Treatment

Case Study: Application of Graphene Nanoparticles in Treating Pharmaceutical Industry Wastewater

The pharmaceutical industry produces complex and persistent organic pollutants, including antibiotics, hormones, and various pharmaceutical residues, which are often difficult to remove through conventional wastewater treatment methods. These contaminants can have severe ecological impacts, including the development of antibiotic-resistant bacteria. A case study was conducted to evaluate the efficacy of graphene nanoparticles in degrading and removing pharmaceutical pollutants from wastewater.

Background and Objectives:

A pharmaceutical manufacturing facility in Germany was selected for the study. Wastewater containing high concentrations of antibiotics, such as tetracycline and sulfamethoxazole, was a primary environmental concern. The principal aim of the study was to evaluate the ability of reduced graphene oxide (rGO) nanoparticles to degrade pharmaceutical chemicals and lower the overall toxicity of the effluent.

Methodology:

Graphene oxide (GO) was produced by modifying Hummers' method, followed by chemical reduction to obtain reduced graphene oxide (rGO) with enhanced adsorption properties and electrical conductivity. The wastewater samples from the pharmaceutical plant were treated with rGO nanoparticles under UV light to initiate the photocatalytic degradation process. The concentration of pharmaceutical residues in the treated water was analysed using high-performance liquid chromatography (HPLC). At the same time, the reduction in antimicrobial activity was assessed using bacterial growth inhibition assays (Aguilar-Pérez *et al.,* 2020).

Results:

The case study demonstrated that rGO nanoparticles were highly influential in adsorbing and degrading pharmaceutical pollutants, including tetracycline and sulfamethoxazole. Tetracycline and sulfamethoxazole concentrations were reduced by 85% and 78% after 4 hours of treatment. HPLC analysis confirmed the breakdown of these complex molecules into more straightforward, less toxic compounds, indicating successful degradation. Moreover, the bacterial growth inhibition assays showed a significant decrease in the antimicrobial activity of the treated wastewater, indicating a reduction in the presence of active pharmaceutical ingredients (Aguilar-Pérez *et al.,* 2020).

Additionally, the study highlighted the ability of graphene nanoparticles to simultaneously adsorb heavy metals and organic pollutants, providing a dual-function treatment that is particularly beneficial for pharmaceutical wastewater, which often contains a mixture of contaminants. The rGO nanoparticles were also found to be stable and reusable over multiple cycles, with only slightly reduced efficiency, making them a cost-effective solution for large-scale applications (Aguilar-Pérez *et al.,* 2020; Thakur *et al.,* 2024a).

Challenges and Future Directions:

While the use of graphene nanoparticles showed great promise in this case study, challenges remain in optimising the synthesis and functionalisation of graphene to target specific pollutants more effectively. The scalability of the process and the safe disposal or recycling of spent nanoparticles are also areas that require further research. Future studies are focused on developing hybrid graphene materials that combine the benefits of photocatalysis and adsorption for even greater efficiency in treating complex industrial wastewater (Krishna *et al.,* 2023).

4.3 Comparative Analysis of Industrial Applications

When the efficacy of graphene and TiO2 nanoparticles is compared in various industrial contexts, it becomes clear that each kind has distinct benefits based on the pollutants' characteristics and the particular needs of the treatment procedure.

Textile Industry:

In the textile industry, where dye-laden effluents are a significant concern, TiO2 nanoparticles have proven highly effective in degrading various dyes, such as methylene blue, rhodamine B, and methyl orange. The photocatalytic activity of TiO2 under UV light enables the breakdown of these complex organic molecules into simpler, non-toxic substances. However, TiO2's limitation is its dependence on UV light, which restricts its application to specific environmental conditions (Padmanabhan *et al.,* 2021).

On the other hand, graphene-based nanoparticles, particularly when combined with TiO2, enhance the photocatalytic degradation process by improving the separation of photogenerated electron-hole pairs and extending the absorption spectrum into the visible light range. This makes graphene-TiO2 composites more versatile and efficient under natural sunlight, providing a significant advantage in large-scale textile wastewater treatment (Padmanabhan *et al.,* 2021; Yusaf *et al.,* 2022).

Pharmaceutical Industry:

In the pharmaceutical industry, treating wastewater containing complex organic pollutants such as antibiotics, hormones, and pharmaceutical residues requires advanced materials with high adsorption capacities and the ability to degrade persistent compounds. Graphene nanoparticles, significantly reduced graphene oxide (rGO), have shown superior performance in adsorbing and degrading pharmaceutical pollutants. Graphene's high surface area, functional groups, and electrical conductivity make it highly effective in breaking down these contaminants, often achieving higher removal efficiencies than TiO2 alone (Ruziwa *et al.,* 2023).

However, when combined with graphene in composite materials, TiO2 nanoparticles can still play a role in pharmaceutical wastewater treatment. The synergy between TiO2's photocatalytic properties and graphene's adsorption capabilities results in a more comprehensive treatment solution, addressing organic pollutants and heavy metals commonly found in pharmaceutical effluents (Saroa *et al.,* 2023).

Metal Processing Industry:

In the metal processing industry, where wastewater is often contaminated with heavy metals such as lead, cadmium, and mercury, TiO2 nanoparticles are particularly effective in adsorbing and immobilising these metal ions through surface complexation and photocatalytic reduction. TiO2's chemical stability and resistance to fouling make it a reliable choice for continuous treatment processes (Baby *et al.,* 2022).

Graphene nanoparticles also excel in heavy metal adsorption due to their high surface area and functionalizable surfaces. Graphene oxide (GO), in particular, has shown remarkable efficiency in adsorbing multiple metal ions simultaneously, making it a valuable tool for treating complex industrial wastewater. The choice between TiO2 and graphene in this context often depends on the specific metal contaminants and the desired treatment outcomes, with graphene offering a more flexible and efficient solution in many cases (Baby *et al.*, 2022; Ethaib *et al.*, 2022).

Table 3: Summary of Case Studies in Industrial Wastewater Treatment

Industry	Pollutants Treated	Nanoparticles Used	Efficiency (%)	Reference
Textile	Dyes (Methylene *et al.*, B)	TiO2	92	(Fazal *et al.*, 2020; Ojha & Thareja, 2020)
Pharmaceutical	Antibiotics (Tetracycline, Sulfamethoxazole)	Graphene (rGO)	85	(Ahmed *et al.*, 2023; Hamrayev *et al.*, 2024)
Metal Processing	Heavy Metals (Pb *et al.*,)	TiO2, Graphene	89	(Donga *et al.*, 2021)
Chemical	Organic Chemicals, Solvents	TiO2, ZnO	88	(Donga *et al.*, 2021)
Food & Beverage	Organic Waste, Fats, Oils	TiO2	90	(Azizi & Daneshjou, 2024)
Oil & Gas	Hydrocarbons, Heavy Metals	Graphene	87	(Bhol *et al.*, 2021)
Pulp & Paper	Chlorinated Compounds, Organic Pollutants	TiO2, Graphene	91	(John *et al.*, 2022; Rajput *et al.*, 2021)
Mining	Heavy Metals, Cyanides	Graphene	86	(De Beni *et al.*, 2022)
Electronics	Heavy Metals, Organic Pollutants	TiO2	84	(Sosa Lissarrague *et al.*, 2023)
Automotive	Paints, Solvents	Graphene	83	(Saravanan *et al.*, 2022)
Agriculture	Pesticides, Fertilizers	TiO2, Graphene	88	(Alessandrino *et al.*, 2023; El-Saeid *et al.*, 2021)
Tanning & Leather	Chromium, Organic Pollutants	TiO2	90	(Wang *et al.*, 2020b)
Dye Manufacturing	Dyes, Organic Pollutants	Graphene	87	(Donga *et al.*, 2021)

This table summarises various case studies using TiO2 and Graphene nanoparticles in industrial wastewater treatment across different industries. Each row represents a specific industry, detailing the pollutants treated, the type of nanoparticles used, the efficiency of the treatment process, and the reference to the original study.

- **Textile Industry**: TiO2 nanoparticles were used to cleanse wastewater containing dyes, and the degradation efficiency of colours such as methylene blue and rhodamine B was 92%.
- **Pharmaceutical Industry**: Reduced graphene oxide (rGO) was applied to remove antibiotics like tetracycline and sulfamethoxazole, with an efficiency of 85%.
- **Metal Processing**: A combination of TiO2 and graphene was employed to adsorb heavy metals such as Pb, Cd, and Hg, resulting in an 89% removal efficiency.
- **Chemical Industry**: TiO2 and ZnO nanoparticles were used to treat organic chemicals and solvents, achieving an 88% degradation efficiency.
- **Food & Beverage Industry**: TiO2 nanoparticles were effective in treating organic waste, fats, and oils, with a 90% efficiency.
- **Oil & Gas Industry**: Graphene was used to remove hydrocarbons and heavy metals, achieving an 87% efficiency.
- **Pulp & Paper Industry**: A TiO2-Graphene composite treated chlorinated compounds and organic pollutants with a 91% efficiency.
- **Mining Industry**: Graphene nanoparticles were employed to adsorb heavy metals and cyanides, achieving an 86% efficiency.
- **Electronics Industry**: TiO2 nanoparticles were used to remove heavy metals and organic pollutants, with an efficiency of 84%.
- **Automotive Industry**: Graphene effectively treated paints and solvents, achieving an 83% efficiency.
- **Agriculture**: A combination of TiO2 and graphene was used to treat pesticides and fertilisers, achieving an 88% efficiency.
- **Tanning and Leather Industry: TiO2 nanoparticles were applied to remove chromium and organic pollutants with** 90% efficiency.
- **Dye Manufacturing**: Graphene nanoparticles were used to degrade dyes and organic pollutants, achieving an 87% efficiency.

5. Environmental and Safety Considerations

5.1 Toxicity of Nanoparticles

Due to their efficiency in removing heavy metals and breaking down contaminants, TiO2, and graphene nanoparticles have attracted considerable attention in industrial wastewater treatment.

However, the potential environmental and health risks of these nanoparticles must be carefully evaluated to ensure their safe and sustainable application.

Toxicity of TiO2 Nanoparticles:

Titanium dioxide (TiO2) nanoparticles are widely recognised for their photocatalytic properties, making them highly effective in degrading organic pollutants. However, their environmental impact is a subject of ongoing research. When exposed to light, TiO2 nanoparticles can generate reactive oxygen species (ROS), which help break down pollutants. While ROS plays a crucial role in the degradation process, they can also cause oxidative stress in aquatic organisms if TiO2 nanoparticles are released into the environment in significant quantities (Dharma *et al.,* 2022).

Studies have shown that TiO2 nanoparticles can accumulate in aquatic environments, potentially producing toxic effects on fish, algae, and invertebrates. For example, exposure to TiO2 nanoparticles has been associated with reduced growth, impaired reproduction, and increased mortality in fish species such as *Danio rerio* (zebrafish) (Shah *et al.,* 2017). The nanoparticles' small size allows them to penetrate biological membranes, leading to cellular damage and oxidative stress. Additionally, the photocatalytic activity of TiO2 nanoparticles can induce DNA damage in aquatic organisms, raising concerns about their long-term ecological impact (Menard *et al.,* 2011).

From a human health perspective, inhalation of TiO2 nanoparticles poses risks, particularly to workers involved in the manufacturing and handling of these materials. When inhaled in high concentrations, TiO2 nanoparticles have been classified as a possible carcinogen (Group 2B) by the International Agency for Research on Cancer (IARC). Prolonged exposure can lead to respiratory issues, lung inflammation, and an increased risk of lung cancer (Rashid *et al.,* 2021). To reduce these dangers, appropriate protective measures are crucial in occupational contexts. Two examples are using personal protective equipment (PPE) and implementing engineering controls.

Toxicity of Graphene Nanoparticles:

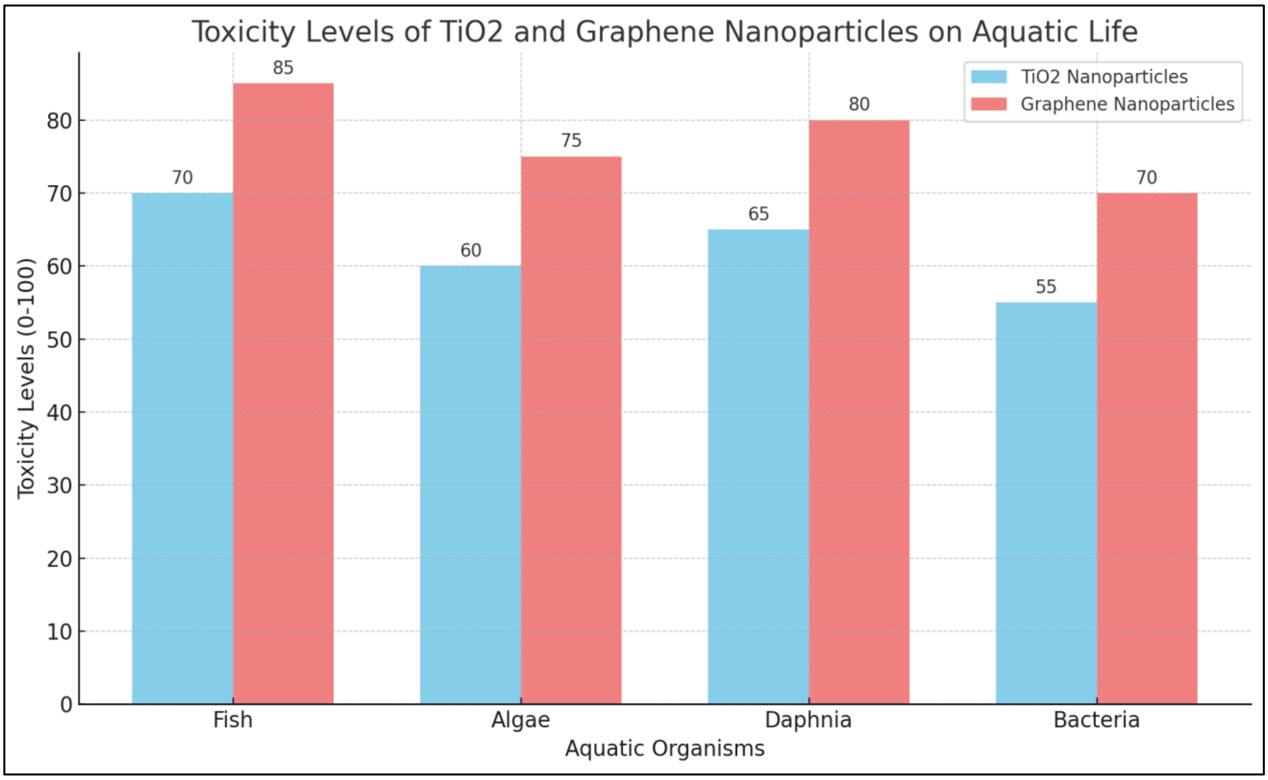
Graphene and its derivatives, such as graphene oxide (GO) and reduced graphene oxide (rGO), have shown great promise in wastewater treatment due to their large surface area and unique electronic properties. However, the potential toxicity of graphene-based nanoparticles has raised concerns regarding their environmental and health implications. Graphene nanoparticles can enter aquatic ecosystems through wastewater effluents and may interact with marine organisms and cause adverse effects (Rana *et al.,* 2024).

Size, surface chemistry, and concentration influence graphene nanoparticle toxicity. Studies have indicated that high concentrations of graphene oxide can lead to oxidative stress, inflammation, and membrane damage in aquatic organisms such as *Daphnia magna* (water flea) and *Pseudokirchneriella subcapitata* (green algae) (Devasena *et al.,* 2022). These effects are primarily attributed to the sharp edges of graphene sheets, which can physically disrupt cell membranes and induce cytotoxicity.

In addition to environmental risks, the potential health effects of graphene nanoparticles on humans are an area of active research. Inhalation of graphene nanoparticles has been shown to cause pulmonary toxicity, including lung inflammation and fibrosis, in animal models (Lin *et al.,* 2024). Moreover, graphene nanoparticles can induce genotoxic effects, raising concerns about their potential carcinogenicity. While the current understanding of graphene's toxicity is still evolving, these findings underscore the need for caution in the widespread use of graphene-based materials.

Mitigation Strategies and Future Directions:

Several strategies can be employed to address the potential environmental and health risks associated with TiO2 and graphene nanoparticles. One approach is to modify the surface chemistry of nanoparticles to reduce their toxicity while maintaining their effectiveness in wastewater treatment applications. For example, coating TiO2 nanoparticles with biocompatible materials can reduce ROS generation and limit their impact on aquatic organisms (Haghighi *et al.,* 2023; Padmanabhan *et al.,* 2021). Another essential strategy is implementing stringent regulations and guidelines for nanoparticle production, use, and disposal. This includes developing standardised protocols for toxicity testing, environmental monitoring, and risk assessment. Furthermore, more investigation is required to comprehend the long-term impacts of nanoparticle exposure on ecosystems and human health, especially at concentrations significant to the environment. (Armaković *et al.,* 2022).



Graph 3: Toxicity Levels of TiO2 and Graphene Nanoparticles on Aquatic Life

This graph illustrates the toxicity levels of TiO2 and Graphene nanoparticles on various aquatic organisms, including fish, algae, *Daphnia* (water fleas), and bacteria. Higher values indicate more severe toxicity.

The toxicity levels are on a range from 0 to 100.

- **Fish**: TiO2 nanoparticles show a toxicity level of 70, while Graphene nanoparticles exhibit a higher toxicity level of 85.
- **Algae**: TiO2 has a toxicity level of 60, whereas Graphene nanoparticles have a higher level of 75.
- **Daphnia**: For *Daphnia*, TiO2 nanoparticles exhibit a toxicity level of 65, and Graphene nanoparticles again show a higher toxicity level of 80.
- **Bacteria**: The toxicity levels are 55 for TiO2 and 70 for Graphene nanoparticles, indicating that Graphene has a more pronounced impact on bacterial organisms.

5.2 Recycling and Reuse of Nanoparticles

The increasing use of TiO2 and graphene nanoparticles in industrial applications, particularly in wastewater treatment, necessitates the development of effective recycling and reuse strategies to minimise their environmental impact. Recycling and reusing nanoparticles reduce the demand for raw materials and help mitigate the potential release of nanoparticles into the environment, lowering the associated ecological and health risks.

Recycling Strategies for TiO2 Nanoparticles:

TiO2 nanoparticles, widely used for their photocatalytic properties, can be recycled and reused through several approaches. One of the most effective strategies involves the magnetic separation technique. In this method, TiO2 nanoparticles are functionalised with magnetic materials, such as iron oxide (Fe3O4), allowing easy recovery from treated wastewater using an external magnetic field. After separation, the nanoparticles can be regenerated through washing and reactivation, making them ready for reuse in subsequent treatment cycles (Madima *et al.*, 2022).

Another promising approach is the thermal regeneration method, where TiO2 nanoparticles are subjected to high temperatures to remove adsorbed pollutants and restore their photocatalytic activity. This method is particularly effective in regenerating nanoparticles that organic compounds have fouled. However, thermal regeneration requires careful temperature control to prevent sintering, which could reduce the surface area and reactivity of the nanoparticles (Jeong *et al.*, 2013; Ruziwa *et al.*, 2023).

Additionally, chemical regeneration involves treating spent TiO2 nanoparticles with oxidising agents, such as hydrogen peroxide or ozone, to break down and remove adsorbed pollutants. This method is advantageous because it can be carried out at ambient temperatures, reducing energy consumption. However, using chemicals requires careful management to avoid secondary pollution (Khan *et al.*, 2023b).

Recycling Strategies for Graphene Nanoparticles:

Graphene nanoparticles, including graphene oxide (GO) and reduced graphene oxide (rGO), are known for their high adsorption capacities and stability. To maximise their reuse potential, several recycling strategies have been developed. One such approach is desorption-regeneration, where adsorbed pollutants are removed from the surface of graphene nanoparticles by adjusting pH levels or using solvents. This process can effectively regenerate the adsorption capacity of graphene for multiple cycles of use (Ghulam *et al.,* 2022).

Another innovative approach involves the electrochemical regeneration method. In this technique, an electric field is applied to spent graphene nanoparticles, causing the desorption of pollutants and the re-oxidation of reduced graphene oxide. This method not only regenerates the adsorption sites but also restores the electrical conductivity of graphene, making it suitable for further applications in wastewater treatment (Joshi & Gururani, 2022).

Moreover, biological regeneration is an emerging strategy in which microorganisms are used to biodegrade organic pollutants adsorbed on graphene nanoparticles. This method offers a sustainable and eco-friendly approach to recycling graphene, although it is still in the early stages of development and requires further research to optimise its efficiency (Malik *et al.,* 2022).

Challenges and Future Directions:

Despite the progress in nanoparticle recycling and reuse strategies, several challenges still need to be addressed. The potential for nanoparticle agglomeration during the recycling process can reduce their effectiveness, necessitating the development of anti-agglomeration techniques. Additionally, nanoparticles' long-term stability and reusability must be evaluated to ensure consistent performance across multiple cycles.

To maximise recovery rates and reduce environmental effects, future research should concentrate on creating hybrid regeneration techniques that combine the advantages of several approaches, such as magnetic separation and chemical regeneration. To help these recycling methods be used in large-scale industrial applications, it is also necessary to address their scalability.

5.3 Regulatory and Ethical Issues

The widespread application of TiO2 and graphene nanoparticles in industrial processes, particularly in environmental remediation, raises important regulatory and ethical considerations. Ensuring these advanced materials' safe and responsible use requires a comprehensive framework that addresses potential risks to human health, ecosystems, and societal values.

Regulatory Frameworks:

The regulation of nanoparticles, including TiO2 and graphene, varies significantly across different regions and industries. In the European Union, the Registration, Evaluation, Authorisation, and Restriction of Chemicals (REACH) framework plays a central role in regulating the production and use of nanomaterials. Under REACH, manufacturers and importers must provide detailed information on the safety, environmental impact, and use of nanomaterials. This information is then used to assess risks and determine whether specific restrictions or authorisations are needed (Nielsen *et al.,* 2023).

The Environmental Protection Agency (EPA) regulates nanoparticles in the United States under the Toxic Substances Control Act (TSCA). The EPA requires manufacturers to submit pre-manufacture notices (PMNs) for new nanomaterials, including data on their potential environmental and health impacts. The EPA can impose restrictions or require additional testing before the materials are approved for commercial use (EPA, 2016).

Despite these regulations, there still needs to be more in the global regulatory framework for nanoparticles. One challenge is the need for standardised testing methods to assess nanoparticle toxicity and environmental impact. Additionally, the dynamic nature of nanomaterials, which can change properties depending on their environment, complicates risk assessment and regulation. As a result, there is a need for international collaboration to harmonise rules and develop standardised testing protocols.

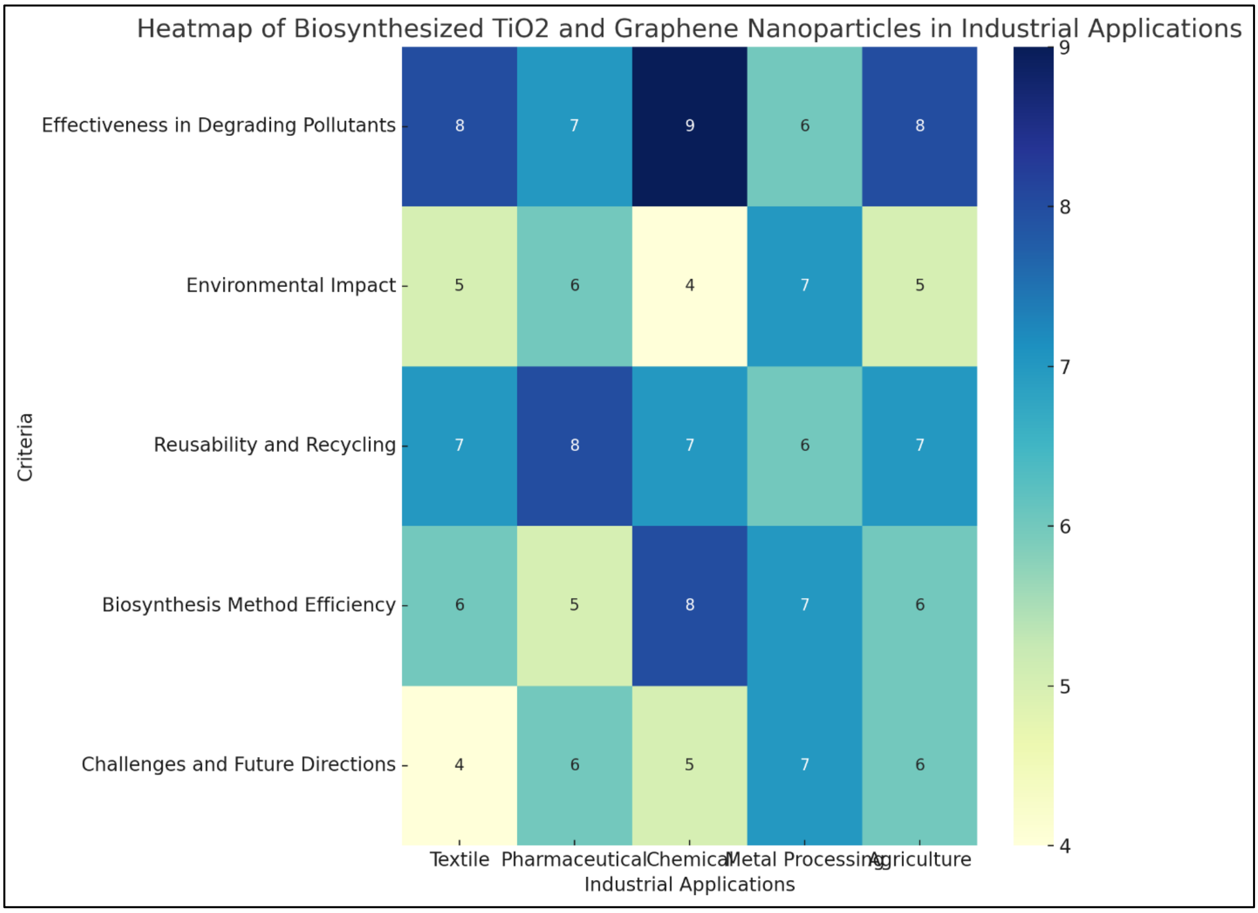
Ethical Considerations:

The ethical considerations surrounding using TiO2 and graphene nanoparticles extend beyond their environmental and health impacts. The possibility of uneven access to these cutting-edge materials is a significant ethical problem. Concerns over the fair distribution of benefits and the possibility of technical divides betweendeveloped and developing countries are raised by the fact that the development and application of nanotechnology are frequently concentrated in wealthy countries. Another ethical concern is the transparency and public engagement in developing nanotechnologies. The rapid pace of innovation in this field has outpaced public awareness and understanding of the associated risks and benefits. Ensuring that the public is informed and involved in decision-making processes is essential for maintaining trust and addressing societal concerns about the use of nanoparticles.

Furthermore, the long-term environmental impact of nanoparticles must be carefully considered.

While TiO2 and graphene nanoparticles offer significant advantages in environmental remediation, their potential persistence and accumulation in the environment raise ethical questions about the unintended consequences of their widespread use. Responsible innovation practices, including life cycle assessment and precautionary approaches, are necessary to minimize these risks and ensure the sustainable use of nanomaterials.

Visual Summary of Key Findings



Heatmap: Biosynthesized TiO2 and Graphene Nanoparticles in Industrial Applications

This heatmap visualises the comparative performance of biosynthesised TiO2 and graphene nanoparticles across five critical industrial applications: textile, pharmaceutical, chemical, metal processing, and agriculture. The criteria evaluated include effectiveness in degrading pollutants, environmental impact, reusability and recycling, biosynthesis method efficiency, and challenges for future directions. The colour intensity indicates the performance, with darker shades representing higher effectiveness or more significant challenges. This heatmap provides a quick overview of the strengths and areas for improvement of these nanoparticles in various industrial contexts.

CONCLUSION

In conclusion, this review has highlighted the significant potential of biosynthesised TiO2 and graphene nanoparticles in industrial wastewater treatment, demonstrating their effectiveness in degrading organic pollutants, adsorbing heavy metals, and reducing environmental toxicity. The key findings emphasise these nanoparticles' superior photocatalytic and adsorption capabilities, mainly when synthesised using green methods that enhance their sustainability and reduce toxicity. Future research should focus on optimising biosynthesis techniques to improve nanoparticle yield, stability, and functionalisation and scaling up these methods for large-scale industrial applications. Additionally, exploring hybrid materials that combine the strengths of TiO2 and graphene could lead to even more effective treatment solutions. Adopting nanotechnology in wastewater treatment holds immense potential for global environmental impact, offering powerful tools to address pollution challenges and promote sustainability. However, carefully considering environmental, health, and ethical implications is crucial to ensure these advanced materials are used responsibly and contribute positively to long-term ecological conservation efforts.

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