Biosynthesized Carbon-derived Nanomaterials as a Photocatalytic Solution for Sustainable Water Pollution Control

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Abstract: Carbon nanomaterials are one of the most widely investigated nano-materials for the degradation of organic and inorganic pollutants like dyes and insecticides in an environmentally benign and that too in sustainable manner. The problems associated with the existing catalysts are related to their high band gap values and large particle sizes. In this review, the photocatalytic degradation of pollutants from industrial wastewater by using negligible amounts of carbon nanocatalysts has been covered as a solution to such types of problems. The photocatalytic activity of the carbon nanocomposites was reported to be affected by factors like particle size, nature of crystallinity, band gap, morphology and total surface area of the nanomaterials per unit mass. Despite various required optimizations, the carbon-containing nanomaterials such as carbon nanotubes, graphene, and metal oxide nanocomposites synthesized by using different methods have shown better photocatalytic activity as compared to others. This review article may open a new avenue to control water pollution efficiently and cost-effectively.
Keywords: Carbon nanomaterials; Dye; Adsorbent; Photocatalyst; Graphene.

1. INTRODUCTION

As the global population grows, pollution rises at an alarming rate due to improvements in the pharmaceutical and cosmetics sectors, persistent economic expansion, the textile industry, rising living standards, and growing urbanization. Environmental pollution has emerged as a significant problem across the biosphere, endangering both developing and industrialized nations. The clean and natural water shortage due to industrial development, soil contaminations and toxic heavy metals in ground water pollution in developing countries has been prevailing for many years. In environmental problems, water pollution is one of the major concerns to the growing mankind and marine life. Water is the prominent resource provided by nature in the biosphere but the accessible percentage of water for human consumption is less than 3% irrespective of the fact that 70% of the planet's surface is covered by water (Madima *et al.,* 2020). According to data from the World Health Organization (WHO) in both 2001 and 2017, approximately 1.1 billion people on our planet lack access to an adequate water supply. The primary challenge in providing clean water is the prevalence of diverse pollutants in water sources, which results in water contamination. Typical contaminants are organic and inorganic substances, bacteria, micro-organisms, dyes, pesticides, viruses, and heavy metals. Nanotechnology encompasses the manipulation of things at the atomic scale. Nanomaterials are materials whose sizes range between 1-100 nm and are distinguished by exceptional chemical and physical properties such as crystallite size, particle size, shape, large surface area, specific affinity and surface reactivity. Nanomaterials play an important role in the treatment of this polluted water with the help of characteristic particle size, high surface area, nano sorbet capacity, easier regeneration, chemical modification and hence nanocomposites are developed to overcome their aggregation (Arun *et al.*, 2022; Tomar *et al.*, 2020). Some of the nanocomposites and nanomaterials apart from being adsorbents are very active photo-nanocatalysts and can easily reduce the dyes and harmful organic compounds (Rana *et al.*, 2023; Rana *et al.*, 2023 & 2024; Tripathi *et al.*, 2023). According to their physical, thermal, chemical, and electrical properties, carbon-based nanomaterials like graphene oxide, carbon nanotubes, and graphene are extensively used in applications such as waste water treatment, energy storage, drug delivery, diagnosis, adsorption, desorption, electronics and energy storage, etc. (Fig. 1). The distinctive multifunctional properties of carbon-based nanomaterials, as elaborated in the section titled "Carbon-based Nanomaterials" (Ali *et al.*, 2012; Thines *et al.*, 2017) have led to considerable interest in their application for wastewater treatment, as depicted in Fig. 2. Bio (using plants extract) based nanomaterials also plays a vital role in the field of nanotechnology. Plant extract contains biomolecules such as phenolic compounds, flavonoids, steroids, etc, which have the potential to function as reducing and stabilizing or capping agents. Plant extracts are used to control the particle size (uniform quantum size), increase surface area, crystalline size, shapes of the particles, etc. which plays a key role in environmental remediation (removal of pollutants from the industrial waste water), and biological applications (antibacterial, antioxidant, antifungal, anti-inflammatory, anticancer, etc.). Some bio-based nanomaterials (metal oxide nanocomposites) such as Copper-Nickel Oxide composite nanomaterials were synthesized and their photocatalytic reduction of volatile organic compounds and photoelectrochemical hydrogen evolution was investigated by Younas *et al.*, 2021. Cu-NiO bimetallic composite nanomaterials based on leaf extract were synthesized by Younas *et al.* and their antioxidant and photocatalytic activity were studied by Maslamani *et al.*, 2021. CMC/Cu-NiO composite nanomaterials were prepared by Maslamani *et al.*, 2021 for the exclusion of organic and inorganic contaminants.

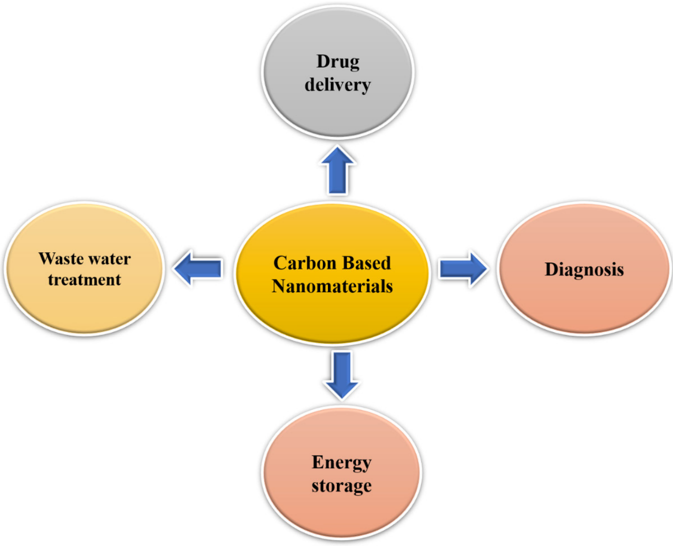

Figure 1. Role of carbon-based nanomaterials in various fields.

The literature review reveals a limited number of studies dedicated to the production of carbon-based nanomaterials derived from biological sources for addressing wastewater pollutant treatment. This review primarily emphasizes the bio-derived synthesis of carbon nanomaterials and their particular utility in removing pollutants from wastewater.

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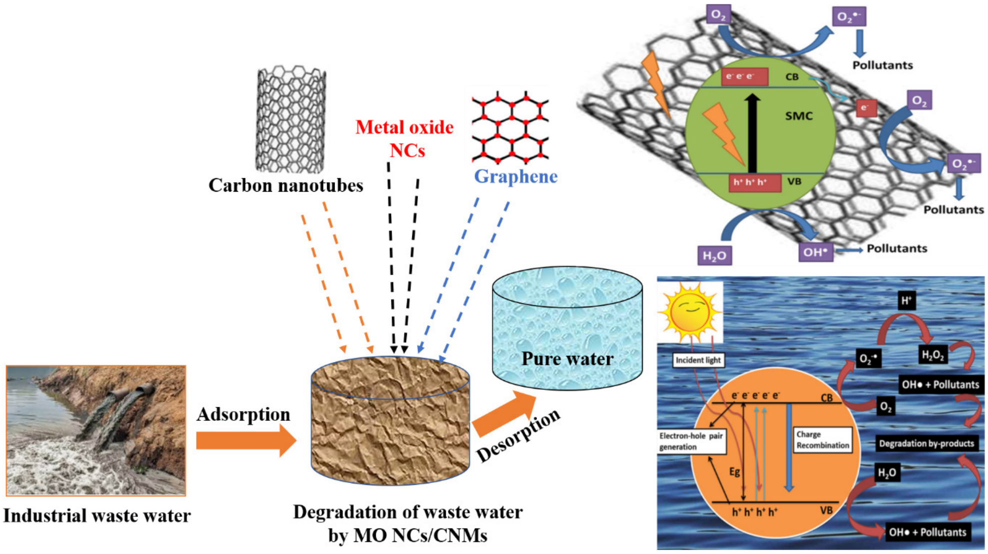

Figure 2. Photocatalytic degradation of industrial wastewater pollutants utilizes metal oxide nanocomposites and carbon-based nanomaterials, as explained by Madima *et al.* (2020) with permission granted by Springer Nature under License no. 501801066.

2. CARBON-BASED NANOMATERIALS

Among plenty of carbon-based nanomaterials, the most famous ones include carbon nanotubes, graphene, fullerenes and their derivatives, carbon quantum dots and graphene oxide. These materials possess distinctive attributes encompassing mechanical, electrical, optical, thermal, and chemical properties, making them suitable for applications in photocatalysis and biomedicine (Shan *et al.*, 2017; Patel, Singh & Kim, 2019). Researchers have shown significant interest in these nanomaterials due to their exceptional characteristics, including a substantial surface area, small particle size, remarkable thermal and chemical stability, and nanoscale catalytic potential. The substantial surface area of these materials enhances their capacity to adsorb various pollutants from industrial wastewater. Carbon nanomaterials come in various allotropic forms such as graphene, carbon nanotubes, diamond, and fullerenes, among others, as depicted in Fig. 3. Owing to their unique properties, carbon-derived nanomaterials play a crucial role in wastewater treatment and hold promise for harnessing renewable energy through processes like light-driven water splitting.

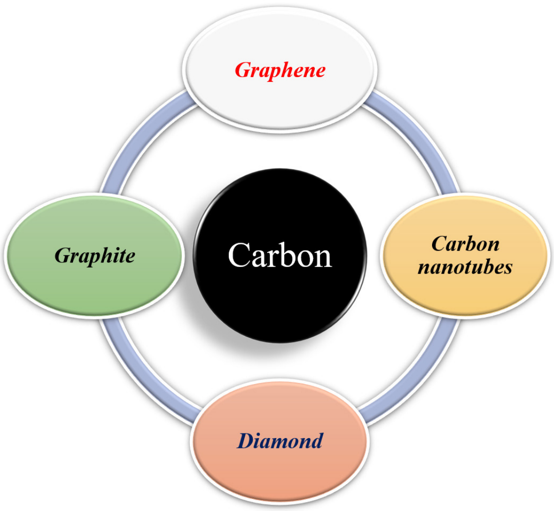

Figure 3. Allotropical forms of carbon.

2.1. Carbon nanotubes

Carbon nanotubes are cylindrical carbon structures (Cha *et al.*, 2013). They have found extensive use in the field of photocatalytic applications, functioning as adsorbents, catalysts, and sensors, as illustrated in Fig. 5. This is attributed to their remarkable characteristics, including a high surface area, hollow structure, lightweight nature, high porosity, strong chemical stability, and excellent affinity for both organic and inorganic contaminants present in industrial wastewater. A range of organic and inorganic pollutants has been successfully removed from polluted water using carbon nanotubes, benefiting from their unique properties (Cha *et al.*, 2013; Sarkar, Mandal & Tsang, 2018). Additionally, carbon nanotubes can be combined with plant phytochemicals or other carbon-based nanomaterials to enhance their efficiency in photocatalysis for wastewater treatment and other biological applications. In the context of photocatalytic activities, carbon nanotubes have been employed alongside other carbon materials to eliminate organic, inorganic, and pesticide-related chemicals from water sources in industrial, ground, and crop fields. These materials based on carbon nanotubes have proven to be excellent adsorbents for the removal of organic and inorganic contaminants from industrial wastewater. They make a valuable contribution to environmental preservation by their exceptional adsorption capabilities, as well as their capacity for effective regeneration and recovery, as demonstrated in Fig. 4. (Mubarak *et al.*, 2017).

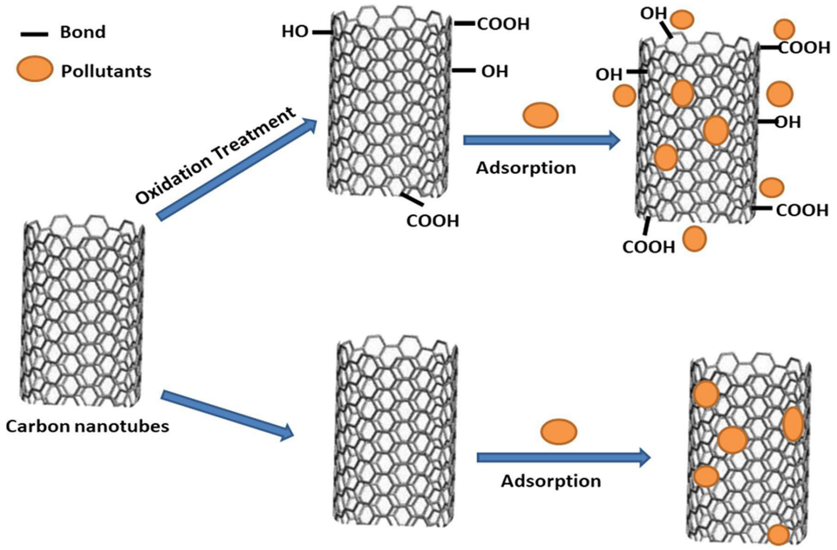

Figure 4. Reduction of organic dyes by carbon nanotubes. Reproduced with permission from Madima *et al.* (2020). This content is included here with permission from Springer Nature (License no.501801066)

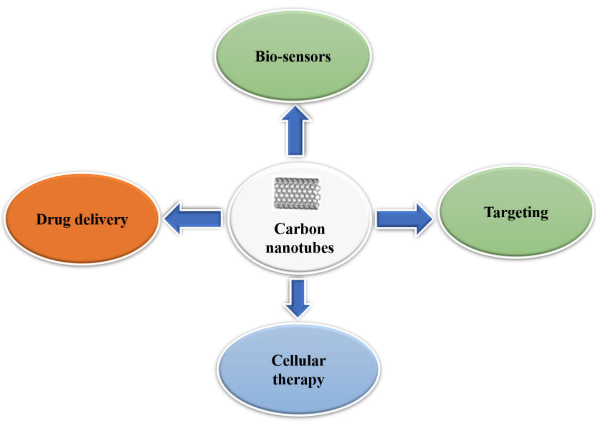

Figure 5. Role of carbon nanotubes in different fields.

For instance, Yang *et al.* (2016) successfully synthesized CuO/CNTs hierarchical chrysanthemum-like nanocomposites (nanoflowers) by a simplistic wet chemical method. These three-dimensional (3D) nanostructures typically have a diameter of approximately between 80-120 nm. CuO/CNTs nanomaterials exhibit greater ability for phenol degradation under the exposure of visible light. From this study, the CuO/CNTs chrysanthemum composite nanomaterials exhibited greater activity in the photocatalytic reduction of phenol as compared to other prepared CuO/CNTs materials. SEM micrographs of the CuO/CNTs nanocomposites attained after different heat treatments: (a) $t^{1/4}$ 5 min; (c) $t^{1/4}$ 30 min; (e) $t^{1/4}$ 60 min; (g) $t^{1/4}$ 240 min (b), (d), (f), and (h) are the magnified SEM micrographs of (a), (c), (e) and g respectively are shown in Fig. 6.

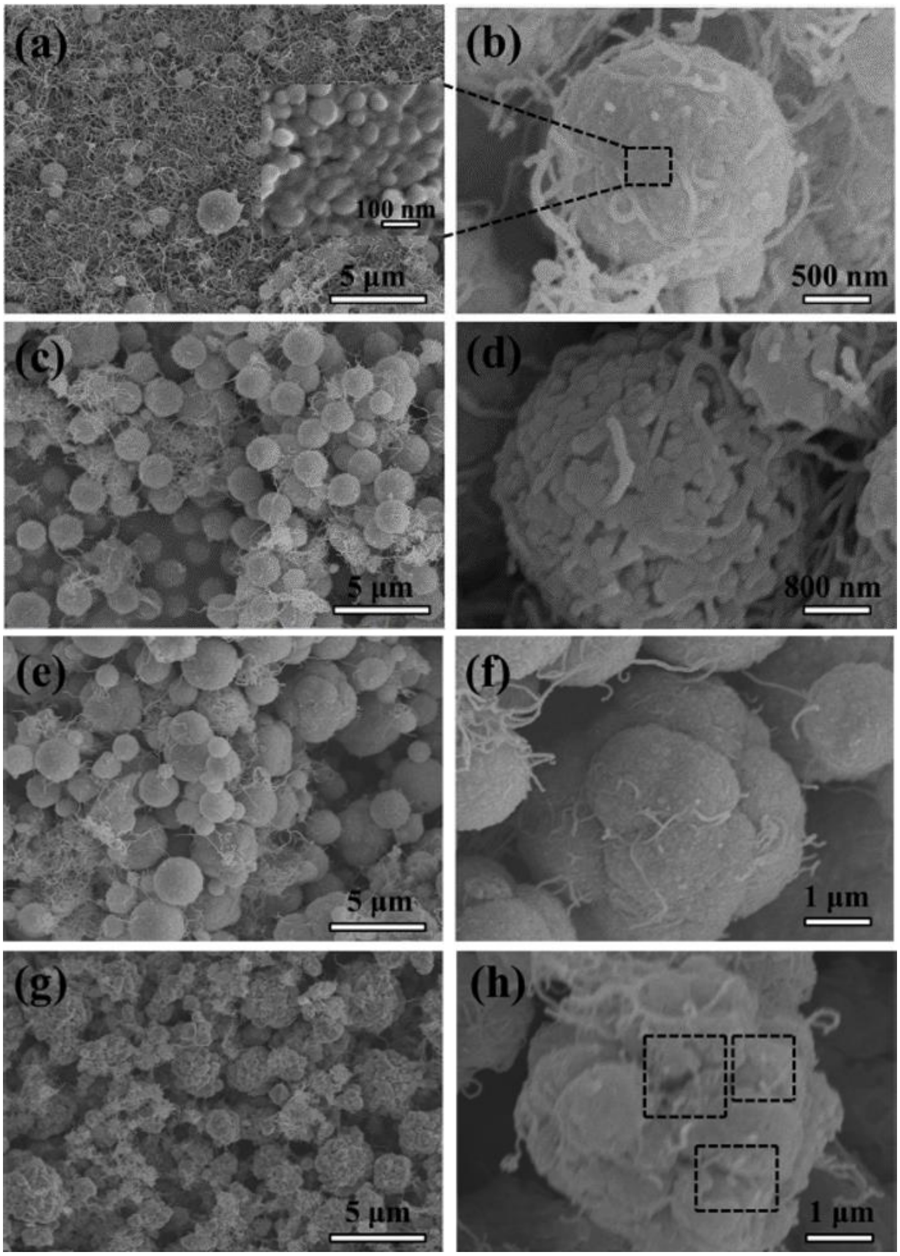

Figure 6. SEM micrographs of the CuO/CNTs nanocomposites attained after different heat treatments: (a) $t^{1/4}$ 5 min; (c) $t^{1/4}$ 30 min; (e) $t^{1/4}$ 60 min; (g) $t^{1/4}$ 240 min (b), (d), (f), and (h) are the magnified SEM micrographs of (a), (c), (e) and g respectively (License no.5524090434702).

2.2. Fullerenes

Fullerene nanomaterials, comprising closed-cage carbon molecules arranged in spherical structures, known as buckyballs or Buckminster fullerenes, possess remarkable properties that render them highly versatile for a range of applications (Arbogast *et al.*, 1991; Guldi & Prato, 2000). Their inherent stability, stemming from the delocalization of electrons within the carbon framework, ensures resistance to chemical reactions and environmental degradation. Buckminsterfullerene (C_{60}) is named as Fullerene, which was discovered in 1985. Fullerene has received significant attention due to its exclusive photo physical and chemical properties (Yin *et al.*, 2016; Accorsi & Armaroli, 2010). Fullerene lies in the category of spherical fullerenes (Sharma, Chiang & Hamblin, 2011; Lucky, Soo & Zhang, 2015; Liu *et al.*, 2012; Huang *et al.*, 2012; Chistyakov *et al.*, 2013). The special feature of fullerenes is their capacity to act as sensitizers for the photoreduction of singlet oxygen ($^1O2$), and their utilization for blood sterilization and photodynamic cancer therapy (Chistyakov *et al.*, 2013; Hu *et al.*, 2012; Ryan *et al.*, 2007; Benn, Westerhoff & Herckes, 2011). Developed fullerenes have numerous medical properties such as antibacterial, anticancer, antiviral and antioxidant properties. For the treatment of various diseases, fullerenes in the forms of fullerosomes were prepared which can act as multivalent drug delivery vehicles with the surety of successfully targeting properties (Zhang *et al.*, 2014; Wang *et al.*, 2011). Moreover, certain fullerene derivatives exhibit semiconducting behavior, making them valuable in electronic devices, sensors, and photovoltaic technologies. Their ability to absorb light across a broad spectrum enables applications in photodynamic therapy, photovoltaics, and light-related processes (Ryan *et al.*, 2007; Benn, Westerhoff & Herckes, 2011). Additionally, fullerene's antioxidant properties have implications in biomedical fields, including drug delivery systems and antioxidant therapy. Synthesis methods, such as laser ablation and chemical vapor deposition, allow for the tailored modification of fullerene derivatives to suit specific applications (Zhang *et al.*, 2014; Wang *et al.*, 2011). Challenges include the high cost of production and concerns regarding toxicity and environmental impact, necessitating further research and regulation. Despite these challenges, fullerene nanomaterials continue to hold immense promise across diverse domains, from electronics and energy to biomedicine and environmental remediation, driving ongoing exploration and innovation in their utilization and development.

2.3. Graphene

Graphene, a relatively recent addition to the family of carbon-based nanomaterials, was first discovered in 2004 as a two-dimensional single layer of carbon atoms (Mohanta *et al.*, 2024). Its unique characteristics, such as a large theoretical surface area of approximately 2630 m^2/g, rapid heterogeneous electron transfer, mechanical strength, high negative charge density, hydrophilicity, and exceptional thermal stability, have made it a subject of significant interest for environmental clean-up applications (Prabhakar *et al.*, 2024). Graphene-based nanomaterials can be categorized into graphene, graphene oxide, and reduced graphene oxide, as depicted in Fig 7. The production of graphene and reduced graphene oxide involves a straightforward exfoliation process, where single-layer materials are derived from graphite precursors. Additionally, graphene can be transformed into graphene oxide using Hummer's method, resulting in a high density of oxygen functional groups (e.g., carbonyl, hydroxyl, and epoxy) within its carbon framework (Cui & Wu, 2024; Liaqat *et al.*, 2024). This oxygen-rich graphene oxide is of particular interest for the removal of a wide range of contaminants from industrial water, crop field storage, and collected groundwater waste. Graphene oxide nanomaterials are of significant interest due to their hydrophilic nature, large surface area, and high density of hydrophilic groups. They serve as excellent adsorbents and photocatalysts for the degradation of both organic and inorganic contaminants (Fig. 8). Graphene-based nanomaterials are often combined with nanomaterials synthesized from natural sources for enhanced properties, taking advantage of their zero-band gap and susceptibility to oxidation reactions (Ruiyi, Xiaoyue & Zaijun, 2024). When used in conjunction with plant extract-based or other nanomaterials, they enhance the photocatalytic activity of these materials through redox processes, acting as electron acceptors and transporters.

Iqbal *et al.* (2023) successfully employed a biosynthesis approach to create a CeO_2-graphene oxide composite via sonication, using leaf extract from Phoenix dactylifera. This composite exhibited a remarkable photocatalytic efficiency of 93% for degrading the organic dye methyl orange. The

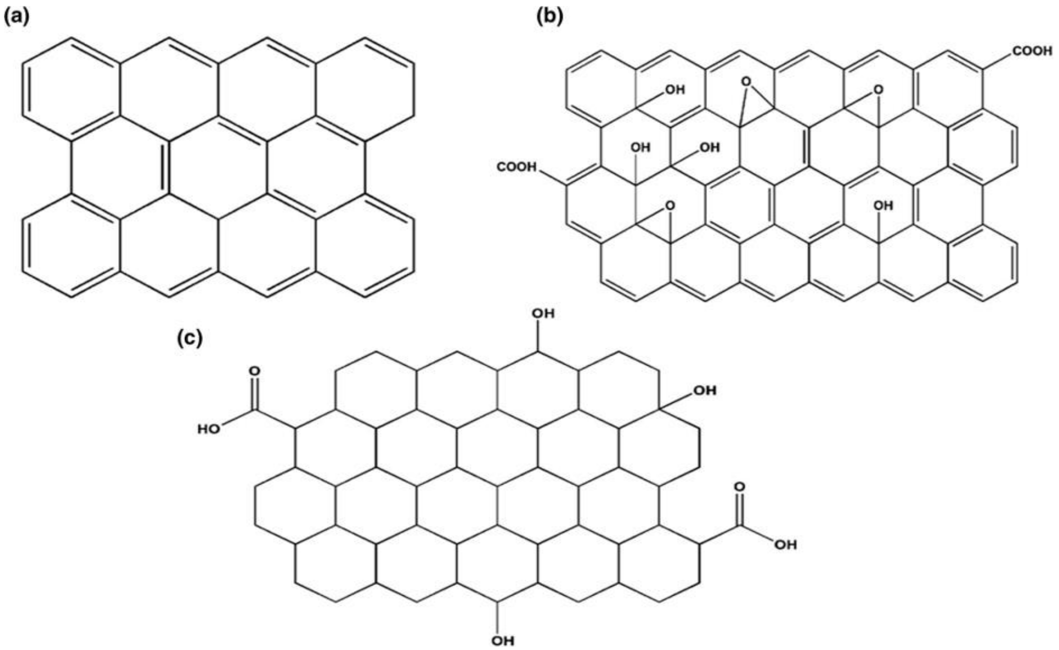

Figure 7. Graphene-based nanomaterials encompass graphene sheets (a), graphene oxide (b), and reduced graphene oxide (c). This content is shared here with permission from Springer Nature under License no. 501801066, with a copyright date of 2020.

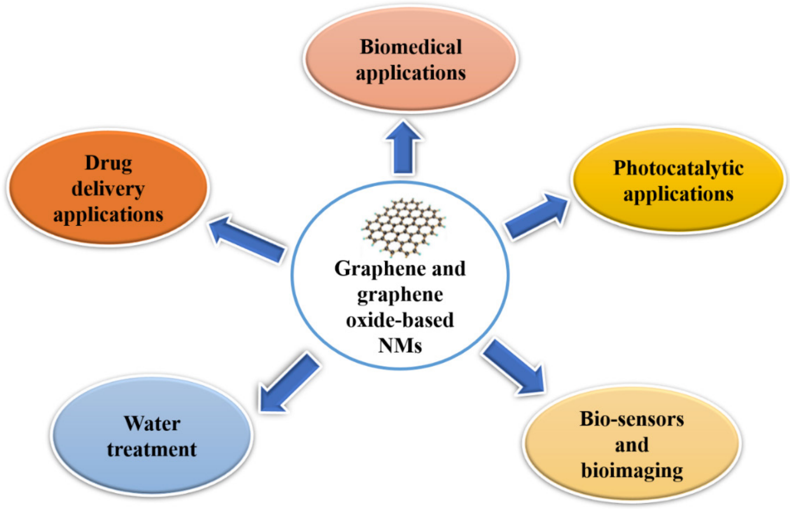

Figure 8. Applications of graphene and graphene oxide-based nanomaterials in various fields.

composite nanomaterials underwent thorough analysis through various spectroscopic and structural techniques. Ganesan *et al.* (2020) bio-derived Graphene oxide-Copper oxide (GO-CuO NCs) nanocomposites using leaf extract from Acalypha indica. These nanocomposites were highly effective, achieving an 83.20% photoreduction of methylene blue (MB). Additionally, they demonstrated significant cytotoxic activity of around 70% against HCT-116 human colon cancer cell lines.

Parvathi, Umadevi, and Raj (2015) conducted a study where they bio-synthesized graphene sand composites (GSC) based nanomaterials for the treatment of wastewater, which included textile waste (TW), domestic wastewater, and sugarcane industrial wastewater (SW) collected from a local filtration Center in Kodaikanal (KWW). These nanomaterials were exposed to UV radiation and subsequently used to degrade the mentioned wastewater. The photocatalytic activity was evaluated, and the rate constant for textile waste degradation increased from 0.0029/min under UV light to 0.0032/min under visible light. The rate of photocatalytic activity for sugarcane industrial wastewater also improved, with a rate constant of 0.0023/min under visible light compared to 0.0016/min under UV light. Similarly, in the case of KWW, an enhanced degradation rate was observed when exposed to visible light, with a rate constant of 0.0025/min. Additionally, the nanomaterials exhibited antibacterial activity against the gram-negative bacterium *Escherichia coli*, showing a 20 mm zone of inhibition (ZOI). These results suggest the effectiveness of these materials for environmental remediation.

Malik *et al.* (2022) conducted a study in which they synthesized Zinc oxide nanoparticles on reduced graphene by using an extract from *Oscimum basilicum* leaves. These nanoparticles were then decorated on reduced graphene oxide (RGO) sheets. The resulting RGO-ZnO nanocomposites had a spherical morphology with particle sizes measuring 31 nm. RGO-ZnO nanocomposites exhibited antioxidant, antibacterial, and photocatalytic activity. They demonstrated enhanced antibacterial properties against both gram-positive *(Cocci)* and gram-negative *(E. coli)* bacterial species as the concentration increased. In terms of photocatalytic activity, ZnO nanoparticles and RGO-ZnO nanocomposites were employed as effective photocatalysts, achieving the degradation of organic dyes, specifically rhodamine, with removal rates of 91.4 and 96.7 % respectively, under UV-light conditions. This study highlighted that RGO-ZnO nanocomposites outperformed pure ZnO nanoparticles in terms of photocatalytic and antibacterial activity, making them a promising material for treating organic pollutants in industrial wastewater. Selvam *et al.* (2022) focused on the biosynthesis of cost-effective, easy, and sustainable *Canthium coromandelicum* copper oxide nanoparticles (CC-CuO NPs). These nanoparticles had an average size of 33 nm and exhibited a spherical shape. Photocatalytic tests revealed that bio-derived CC-CuO NPs had the potential to decompose organic dyes, methylene blue (MB) and methyl orange (MO), by 91.32 and 89.35 %, respectively. These results indicated that bio-derived CC-CuO NPs effectively removed pollutants in an environmentally friendly manner.

Fatimah *et al.* (2023) conducted a study in which they biosynthesized environmentally friendly reduced graphene oxide/nickel oxide nanocomposites using the stem extract of Tinospora cordifolia. These nanocomposites were applied to address pharmaceutical wastewater treatment through photocatalytic activity. The results of the study demonstrated that NiO/rGO materials exhibited significant potential as photocatalysts, with a higher energy band gap (3.28 eV) compared to NiO nanoparticles (3.01 eV). Additionally, the NiO crystalline size within the nanocomposite was smaller (42 nm) than that of NiO nanoparticles. NiO/rGO nanocomposites displayed outstanding photocatalytic activity, achieving a 100 % reduction of tetracycline within 30 minutes under both UV and visible light illumination. Furthermore, the study revealed the antibacterial potential of NiO/rGO nanocomposites against bacterial species such as *Staphylococcus aureus* and *Escherichia coli*. These biosynthesized NiO/rGO nanomaterials hold promise as functional materials, serving as effective photocatalysts for pharmaceutical wastewater treatment and as antibacterial agents.

Kayalvizhi *et al.* (2021) developed copper oxide nanoparticles (CuO NPs) and graphene oxide nanocomposites (CuO NPs@GO) to assess their photocatalytic and antibacterial capabilities. The researchers applied these nanomaterials to degrade methylene blue in the presence of natural sunlight. The results indicated that CuO NPs@GO nanomaterials achieved approximately 95 % degradation within 150 minutes, surpassing the performance of pure copper oxide nanoparticles (CuO NPs). Furthermore, these nanomaterials exhibited significant antibacterial effectiveness against both *Staphylococcus aureus* and *Salmonella typhi*, demonstrating a substantial zone of inhibition (ZOI). These outcomes highlight the potential of biosynthesized CuO NPs@GO as highly promising catalysts and antibacterial agents, particularly when integrated with graphene oxide (GO).

2.4. Composite nanomaterials

The bio-derived metal oxide nanocomposites make use of eco-friendly, cost-effective and non-toxic ways of preparation. Metal oxide nanocomposites are significant and hopeful materials of nanotechnology, which have attained enormous consideration to accumulate the desired properties of different nano-scales that are not found in chemically synthesized pure metal oxide nanoparticles (Decher, 1997). Furthermore, metal oxide nanocomposites have been known as suitable options to address the drawbacks related to nanoparticle aggregation (Sultana *et al.*, 2013; Camargo, Satyanarayana & Wypyc, 2009). Researchers have developed a variety of metal oxide nanocomposites to enhance their surface area, thereby improving their performance in photocatalytic, antibacterial, antifungal, and antioxidant applications (Ahmed at al., 2016; Shanker *et al.*, 2016) as illustrated in Fig. 9. Different synthesis methods, including physical, chemical, and biological approaches, have been employed to create these metal oxide nanomaterials. However, physical and chemical methods have been found to be economically inefficient and environmentally harmful, with adverse effects on human health and the ecosystem.

Lonkar, Pillai & Abdala (2019) synthesized ZnO-graphene nanocomposites using a ball milling process, with potential applications in sensors, solar cells, energy storage, and wastewater treatment through photocatalysis. These composite nanomaterials were utilized for the degradation of methylene blue (MB) when exposed to visible light. Noman and Alkhadher (2021) bio-synthesized Zinc oxide nanoparticles (ZnO) with the assistance of orange peel extract, facilitating wastewater treatment through photocatalytic activity. The bio-derived ZnO nanoparticles effectively decolorized Congo red, a model for dye wastewater, with a maximum reduction of approximately 96 %.

Kiani *et al.* (2021) fabricated Ag NPs@Chitosan and Co_3O_4 using *salvia hispanica.* Photocatalytic experiments revealed that dye degradation occurred within 135 minutes for AgNPs@Chitosan and 105 minutes for Co_3O_4-NPs Chitosan, respectively. Preethi *et al.* (2020) prepared eco-friendly chitosan/zinc oxide (CS/ZnO) nanocomposites using leaf extract from *S. lycopersicum* through a bio-engineered method. These nanocomposite particles were spherical in shape and had an average size ranging from 21 to 47 nm. CS/ZnO nanocomposites acted as photocatalysts for the reduction of Congo red when exposed to sunlight. Additionally, they demonstrated antibacterial properties against *B. subtilis, S. aureus,* and *E. coli.* In conclusion, the as-prepared CS/ZnO nanocomposites can serve as antibacterial agents and effective photocatalysts for the removal of organic and inorganic contaminants from industrial wastewater.

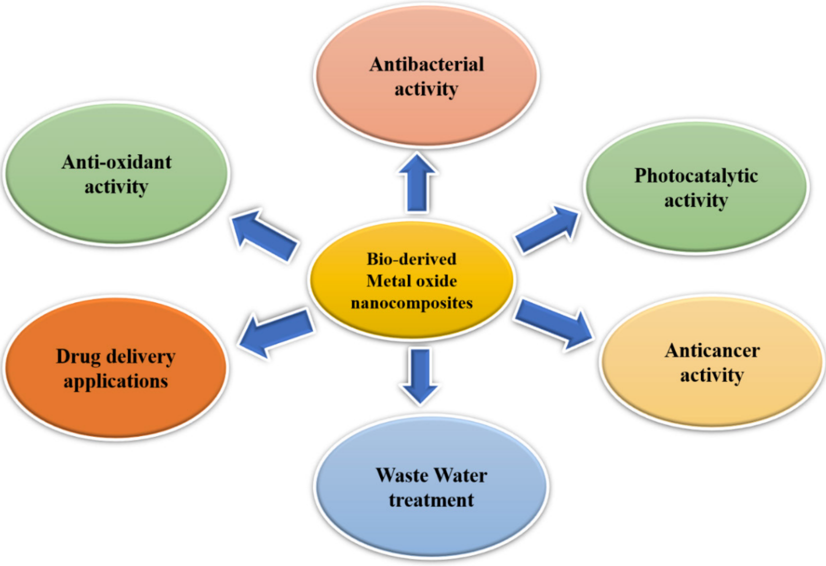

Figure 9. Applications of metal oxide nanocomposites in different fields

Bibi *et al.* (2019) employed a biosynthesis method to create iron oxide nanoparticles (Fe_2O_3) using pomegranate *(Punica granatum)* seed extract. These nanoparticles had a size range of 25-55 nm. Liquid chromatography-mass spectroscopy (LCMS/MS) was employed to identify various biomolecules present in the pomegranate seed extract, including p-hydroxy benzoic acid, gallic acid, catechin, ferulic acid, vanillic acid, magnolol, and 3-deoxyflavonoids. These nanomaterials were utilized for the decomposition of contaminants in industrial wastewater, achieving a maximum degradation of 95.08 % of reactive blue under UV light within 56 minutes.

Zinatloo-Ajabshir, Morassaei, and Salavati-Niasari, (2019) developed $Nd_2Sn_2O_7$ nanostructures through a novel, facile, and environmentally friendly approach, utilizing grapes extract as a green fuel. The resulting spherical nanoparticles were employed for the 90 % degradation of erythrosine. Furthermore, the incorporation of Nd_2O_3 into $Nd_2Sn_2O_7$ enhanced the photocatalytic degradation, achieving a 96 % reduction of erythrosine.

Saini *et al.* (2022) reported carbon dots (CD), doped-CD, and their nanocomposites, exhibit promising potential for photocatalytic applications due to their excellent light absorption capabilities. Doped-CD and CD-based composites demonstrate enhanced light absorption compared to bare CD, a crucial factor for efficient photocatalysis. Various parameters including fabrication methodologies, efficiency, and stability have been discussed, along with mechanistic insights into multiple chemical reactions such as organic dye degradation, metal ion reduction, CO_2 conversion, water splitting, organic transformation reactions, and NOx removal. Overall, these findings underscore the significant role of carbon-based nanomaterials in addressing environmental and energy-related challenges through photocatalytic processes.

Goswami *et al.* (2022) reported that metal-based nanomaterials, nanocarbons, and metal-organic frameworks have shown efficiency, they often suffer from high costs, potential toxicity, and energy-intensive synthesis processes. Nanobiochar-based catalysts present a cost-effective alternative with competitive pollutant removal capabilities, though their efficiency depends on synthetic conditions and post-synthesis treatments. Biochar, a porous biocarbon, serves as an excellent carbon source for functional nanocarbon synthesis, offering versatile catalytic properties under broad light spectra. This study underscores the synthesis techniques of nanobiochar catalysts, emphasizing their properties and recent advancements in pollutant remediation from wastewater. Specifically, the focus lies on nanobiochar's unique features like functionalization, doping, and composite fabrication, crucial for enhancing catalytic efficiency. Additionally, the mechanisms governing biochar's interaction with contaminants and subsequent degradation are briefly discussed, illuminating its potential in wastewater treatment applications.

Aggarwal *et al.* (2020) reported a simple and sustainable method for synthesizing photoactive carbon dots (CD) from Bitter Apple (BA) peels has been demonstrated, akin to biochar synthesis. These BA peel-derived photoactive-CDs exhibit potent photocatalytic properties, particularly showcased in the efficient photodegradation of the organic dye crystal violet (CV) under sunlight illumination. Through trap experiments, it was inferred that electrons and holes play a significant role in the photodegradation mechanism. Notably, BA peel-derived photoactive-CDs displayed remarkable efficacy, achieving a significant reduction in CV concentration (20 ppm in approximately 90 minutes) under sunlight exposure, surpassing performance under dark conditions.

3. PHOTOCATALYTIC ACTIVITY

Carbon nanomaterials or metal oxide nanocomposites have a great scope for the elimination of contaminants from industrial waste water. The photocatalytic degradation of pollutants (organic and inorganic) from industrial wastewater requires a small number of photocatalysts. Their method of synthesis, size, specific surface area, nature of crystallinity, band gap, and morphology as well. Researchers have used different biosynthesized nanomaterials for the elimination of pollutants (organic/inorganic) from textile and pharmaceutical industries, using different amounts of photocatalysts and observed percentage degradation. Table 1 reviewed the use of different nanomaterials for the elimination of organic and inorganic contaminants with the help of photocatalytic activity.

3.1. Mechanism

Photocatalysis is a process of accelerating light action when catalysts are present. Photocatalysis is the best and most economically viable route to use sunlight light as a renewable source of energy or UV radiations for the decontamination of contaminated water. The mechanism of photocatalysis is shown in Fig. 10. In this context, a catalyst with a specific extensive surface area is being used efficiently to decrease the concentration of dyes in the aqueous medium leading to the oxidation of water molecules to $OH^•$ free radicals on the catalyst surface. The procedure is usually executed in dark conditions where oxygen is reduced to generate $O_2^•$ (superoxide) radical. For photocatalysts, the redox potential of valence band must be sufficiently positive and conduction bands must be adequately negative. The reduction process results in the formation of the superoxide anion $O_2^{•-}$ by reacting with oxygen

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molecules, and the oxidation process involves the abstraction of electrons from water or hydroxide ions, leading to the generation of OH• free radicals (Zinatloo-Ajabshir, Morassaei, & Salavati-Niasari, 2019). Both O_2• and OH• are potent oxidants capable of breaking down a wide range of organic, inorganic, and biological molecules, including dyes, carbohydrates, proteins, lipids, nucleic acids, and more. Consequently, they can be effectively used to purify polluted water (Lin, Liao Hung, 2005; Du & Gebicki, 2004. In simpler terms, the oxygen molecule scavenges electrons from the conduction band, thereby preventing recombination and extending the lifespan of holes in the aerated aqueous medium. Furthermore, the interaction between O_2• and OH• ultimately leads to the degradation of organic pollutants. In the presence of solar or UV light, photocatalysts produce oxidizing agents (OH•, $O_2^{\bullet-}$ and H_2O_2) that can eliminate both organic and inorganic molecules, as well as microbial contaminants in water. The mechanistic perspective of photocatalysis is illustrated in Scheme 1.

$$\mathrm{CNMs}\left(\frac{\mathrm{MO}}{\mathrm{XO}}\right) + h\upsilon \rightarrow e^- + h^+ \quad (1)$$

$$O_2 + e^- \rightarrow \underset{\text{Superoxide}}{O_2^{-\bullet}} \quad (2)$$

$$h^+ + OH^- \rightarrow OH^\bullet \quad (3)$$

$$O_2^{-\bullet} + H_2O \rightarrow HO_2^\bullet + OH^\bullet \quad (4)$$

$$HO_2^\bullet + H_2O \rightarrow H_2O_2 + OH^\bullet \quad (5)$$

$$H_2O_2 \rightarrow 2\,OH^\bullet \quad (6)$$

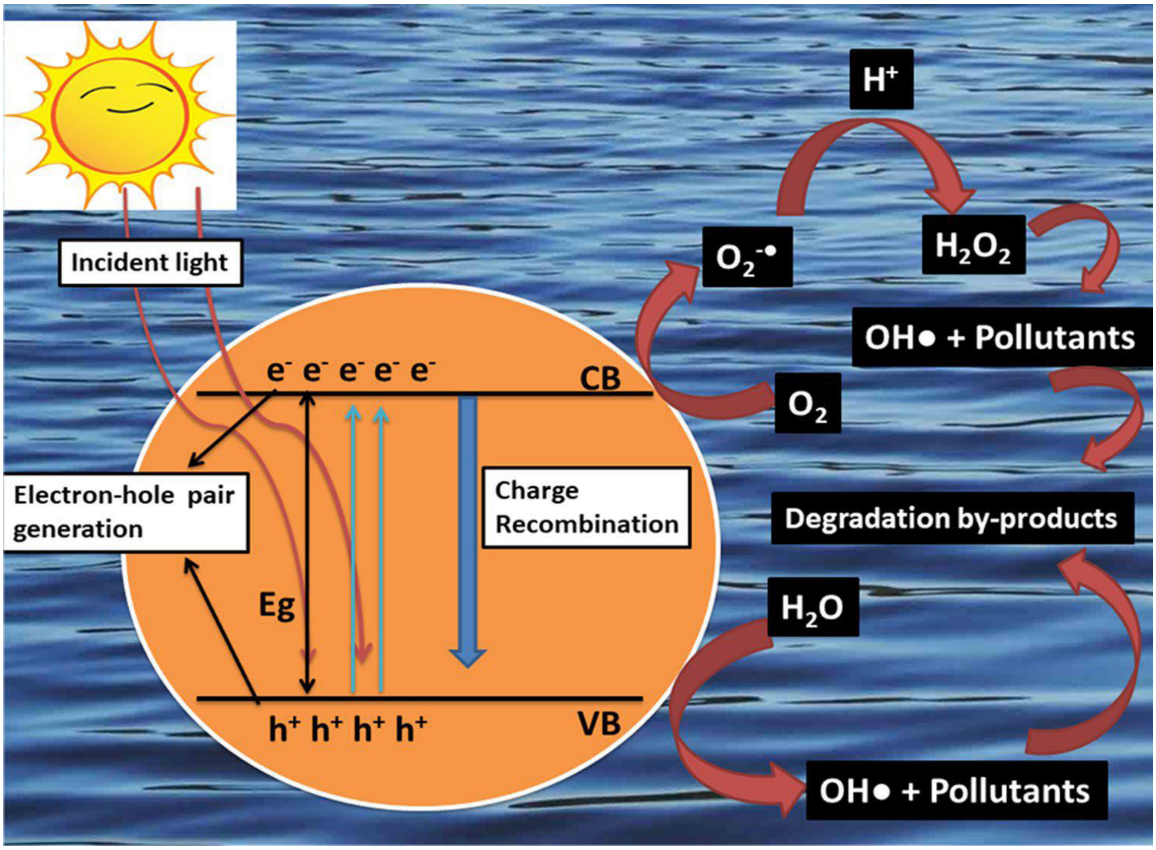
$$OH^\bullet + \mathrm{Dye} \rightarrow \underset{\text{Degradation}}{\mathrm{Dye}\bullet + H_2O} \quad (7)$$

$$H_2O \rightarrow H^+ + OH^- \quad (8)$$

$$OH^- + h^+ \rightarrow OH^\bullet \quad (9)$$

$$\mathrm{Dye} + h^+ \rightarrow \mathrm{Dye}\bullet \rightarrow \text{Final degradation product} \quad (10)$$

Scheme 1. Schematic Diagram showing photocatalytic mechanism of dyes solution



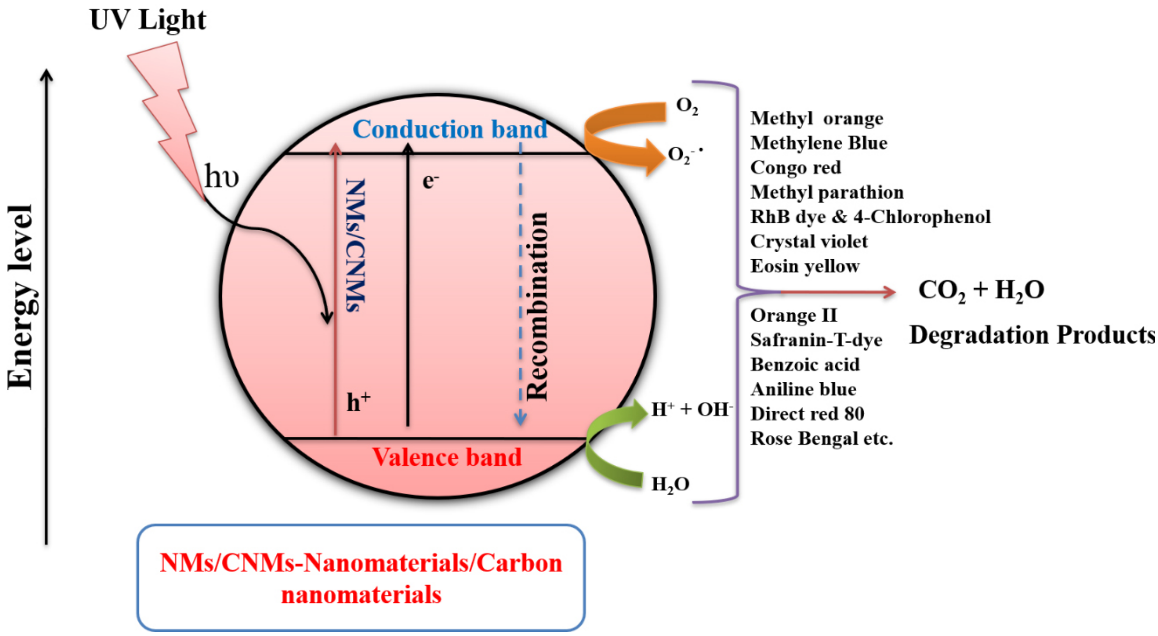


Figure 10. Photocatalytic mechanism of degradation of pollutants. Reproduced with the authorization of Madima *et al.*, 2020 under copyright held by Springer Nature (License no. 501801066).

S. No.	Materials	Synthesis Methods	Pollutants used	Percentage Degradation (%)	Light Source	Time (minutes)	References
1	N-TiO_2/rGO composite	Photoreduction method	Tetracycline hydrochloride	98	Visible light	60	Tang, Wang & Wang, 2018
2	3D CdS-rGO complex	Hydrothermal method	Rhodamine B	91.8	Visible light	–	Gao *et al.*, 2018
3	$BaTiO_3$/GO	Freeze-drying method	Methylene Blue	67	Xenon light	150	Zhao *et al.*, 2018
4	CdS-graphene	Hydrothermal method	Methyl Orange	95	Visible light	60	Ye *et al.*, 2012
5	CNT-agarose complex	Green method	Rhodamine B	96	Electro-catalytic source	20	Liu *et al.*, 2018
6	ZnO/ MWNT	Hydrothermal method	Methylene Blue	100	UV light	After 30	Liu *et al.*, 2014
7	Cu-TiO_2-CNT	Sol-gel	Methylene blue	81.5	Visible light	60	Shafei & Sheibani, 2019
8	Ag_3PO_4 @ MWCNT@ Cr: $SrTiO_3$	–	Malachite green	100	Visible light	10	Lin *et al.*, 2018
9	Ag-ZnS-MWCNTs	Ultrasonic probe	Rhodamine B	87.53	Visible light	116	Yazdani & Mehrizad 2018

S. No.	Materials	Synthesis Methods	Pollutants used	Percentage Degradation (%)	Light Source	Time (minutes)	References
10	Pd NPs @chitosan-MWCNT	–	Congo red, Methyl orange, Methylene blue & Methyl red	–	–	2 1 Instantly Instantly	Sargin, Baran & Arslan, 2020
11	N-doped ZnO/fulvic acid (FA)/ carbon quantum dot	Hydrothermal method	Methylene blue	94	Ultrasonic irradiations	50	Moalem-Banhangi, Ghaeni & Ghasemi, 2021
12	Zn-MOF@AC	Ultrasonication method	Methyl orange & Brilliant Green	85 & 77.5	UV light	90	Govindaraju *et al.*, 2022
13	Pd@ NCNS	–	Methyl orange & Rhodamine B	93 & 95	–	–	Dorraj, Sadjadi & Amani, 2021
14	Microalgae-carbon dots	Microwave method	Methylene blue	83	Visible light	–	Nu *et al.*, 2022
15	CQDs/NiO	Hydrothermal method	Malachite green	98	Visible light	60	Pebdeni *et al.*, 2021
16	RGO/Fe_3O_4 composite	–	Methylene blue	95.18	–	12	Vinothkannan *et al.*, 2015
17	NC-Ag NPs(N-doped carbon supported silver nanoparticles)	Hydrothermal method	Methylene blue & Methyl orange	99.9 &99.96%	–	15 30	Edison *et al.*, 2020
18	Co_3O_4@ Mesoporous carbon spheres	Microwave assisted method	Methyl orange & Malachite green	89.4 & 88.6	400W Xenon lamp	40 40	Akshatha *et al.*, 2021
19	PI/CNTs (Polyimide-modified carbon nanotubes)	Solvent-free method	Acid Orange 7 (AO7)	98.9	Without light	15	Wei *et al.*, 2020
20	AO-Fe-SWCNTs	Arc discharge method	Methylene blue & Methyl orange	>90 & >90	300W Xenon lamp	10 —	Ge *et al.*, 2019
21	Ag-MWCNTs	Green method	Methylene blue	89	Visible light	–	Nagajyothi *et al.*, 2021
22	MWCNTs/ $CoFe_2O_4$	Solvothermal co-precipitation method	Acid blue 113	100	UV light	40	Al-Musawi *et al.*, 2022
23	CNTs/FeS_2	Co-precipitation method	Methylene blue	99.5	–	–	Fayazi, 2021
24	Zr-N-S-CDs	Microwave-induced pyrolysis	Malachite green	99	Sunlight	90	Laddha *et al.*, 2022

S. No.	Materials	Synthesis Methods	Pollutants used	Percentage Degradation (%)	Light Source	Time (minutes)	References
25	CdS Ag NPs	Hydrothermal method	Methylene blue & Methyl orange	99.5 & 99	–	–	Perumal *et al.*, 2022
26	C_{ZnO}-dots	Microwave method	Malachite green	94.8	Visible light	60	Sekar & Yadav, 2021
27	TiO_2 NPs @C	Hydrothermal method	Methylene blue	90	UV light	40	Atchudan *et al.*, 2018
28	GQDs (Graphene quantum dots)	Pyrolysis method	Celestine Blue	80	Visible light	4	Roushani *et al.*, 2017
29	Fluorescent carbon dots	Hydrothermal method	Methylene blue	89.20	UV light	30	Jothi *et al.*, 2021
30	C-dots @ CdS	Hydrothermal method	Crystal violet	97.3	Visible light	120	Smrithi *et al.*, 2022
31	C-dots/ZnO	Hydrothermal carbonization method	Naphthol blue-black	100	UV light	45	Prasannan & Imae, 2013
32	r-Mg-N-CD	–	Methylene blue	99.1	Sunlight	120	Bhati *et al.*, 2018
33	G-CDs	Hydrothermal method	Malachite green, Methyl orange & Methyl violet	98, 97.1 & 63.6	–	40, 50, 90	Wang *et al.*, 2022
34	Carbon dots	–	Crystal violet	20ppm	Sunlight	90	Aggarwal *et al.*, 2020
35	GQD/TiO_2 nanocomposite (Graphene quantum dots)	–	Rhodamine B	88	UV light	35	Teymourinia *et al.*, 2017
36	Mn doped CDs	Hydrothermal method	Malachite green & Acid fuchsin	95 & 95	Visible light	–	Zhang, Yang & Zhou, 2022
37	TiO_2(B)/ fullerene	Ball milling-hydrothermal method	Crystal violet	77	Visible light	–	Panahian, Arsalani & Nasiri, 2018
38	F-TiO_2(B)/(MWCNT)@ Nickel ferrite ($NiFe_2O_4$) F-TiO_2(B)/Fullerene(C_{60}) @Nickel ferrite ($NiFe_2O_4$)	Hydrothermal method	Malachite green	93 & 98	Visible light	120 120	Arsalani, Panahian & Nasiri, 2019
39	C_{60}-AuNPs-TiO_2	–	Methyl orange	95	500W Tungsten halogen lamp	160	Islam *et al.*, 2018

S. No.	Materials	Synthesis Methods	Pollutants used	Percentage Degradation (%)	Light Source	Time (minutes)	References
40	Fullerene-type WS_2	Hydrothermal method	Malachite green	71.2	UV & Visible light	120	Hazarika & Mohanta, 2017
41	La_2O_3-ZnO@C_{60}	Solution method	Methylene blue	100	UV light	40	Sardar *et al.,* 2023
42	ZnCPP-Fullerol@TiO_2	–	Rhodamine B	94.7	300 W Xenon lamp	150	Wu *et al.,* 2021
43	ZnO/CNT	Ultrasonication/ hydrothermal method	Methylene blue	98	Visible light	180	Mohamed *et al.,* 2019
44	TiO_2-Pt/GO & TiO_2-Pt/rGO	Chemical-thermal method	Amaranth, Sunset yellow & Tartrazine	99.56, 99.155 & 96.23	UV & Sunlight	–	Rosu *et al.,* 2017
45	F-TiO_2 (B)/ SWCNT	Ball milling-hydrothermal method	Malachite green	91	Visible light	–	Panahian & Arsalani, 2017
46	Ag_3PO_4/ Fe_3O_4/C_{60}	Hydrothermal method	Methylene blue	95	Visible light	300	Sepahyand & Farhadi, 2018
47	N-RHC-QDs & Bi-RHCQDs	–	Methylene blue	72.16 & 68.91	300 W Xenon lamp	–	Hui, Ang & Sambudi, 2021
48	Bio-CDs	Hydrothermal method	Rhodamine B & Methylene blue	71.7 & 94.2	Visible light	–	Zhu *et al.,* 2020
49	ZnO@N-C	Hydrothermal method	Methylene blue	>95	UV-light	60	Atchudan *et al.,* 2018
50	Safe modified biochar (OBC)	Green method	oxytetracycline	91	–	–	Fan *et al.,* 2023
51	Ag NPs	Green approach	ciprofloxacin	98	Sunlight	180	Golmohammadi, Hanafi-Bojd & Shiva, 2023
52	MgO/PEG NCs	Green synthesis	Rose Bengal (RB) & Toluidine (TB)	98	Sunlight	120	Mohammed *et al.,* 2023
53	NiO NPs	Green method	Methylene blue (MB) & Acid blue (AB)	92 & 63	UV-light	–	Ravichandran, Sengodan & Radhakrishnan, 2023
54	$NiFe_2O_4$	Green approach	MB	98.5	UV-light	70	Alamier *et al.,* 2023
55	ZnO@WO_3 NCs	Green method	Bisphenol A (BPA) & Auranine O (AO) dye	91 & 96	UV-light	3h	Rani *et al.,* 2024
56	N-doped carbon/TiO_2	Camphor combustion technique	Methyl orange	86	Sunlight	25	Rajput *et al.,* 2024
57	CuO/Fe_2O_3/ ZnO	Green approach	Rhodamine B (RhB)	88.8	UV-Light	120	Jansanthea *et al.,* 2024

Table 1. The photocatalytic activity of different biosynthesized carbon nanomaterials against different organic and inorganic pollutants.

Abbreviations used: reduced graphene oxide (rGO); Carbon nanotubes (CNTs); multi-walled carbon nanotube nanocomposites (MWCNTs); CNTs/nanocomposite (Carbon nanotubes/NCs); carbon quantum dot (CQDs); reduced graphene oxide (rGO); carbon nanotubes/pyrite nanocomposite (CNTs/pNCs); Nitrogen-doped rice husk-derived carbon quantum dots (N-RHCQDs); Bismuth-doped rice husk-derived carbon quantum dots (Bi-RHCQDs); N-doped carbon nano sheet (NCNS); Safe modified biochar (OBC); MgO/PEG (Magnesium oxide nanoparticles/polyethylene glycol).

The compiled data (table 1) showcases a diverse range of photocatalytic materials and their efficiencies in degrading various pollutants under different light sources and times. Notable examples include N-TiO_2/rGO composite with 98% degradation of tetracycline hydrochloride under visible light in 60 minutes, CdS-graphene achieving 95% degradation of Methyl Orange in the same time frame, and Ag_3PO_4@MWCNT@Cr: $SrTiO_3$ exhibiting complete degradation of Malachite green within 10 minutes under visible light. Other significant findings include ZnO/MWNT achieving 100 % degradation of Methylene Blue under UV light in 30 minutes, and NC-Ag NPs showing remarkable degradation rates of Methylene blue and Methyl orange. Additionally, synergistic composites like TiO_2-Pt/GO and TiO_2-Pt/rGO displayed high degradation percentages of various dyes under both UV and sunlight. These results underline the potential of various photocatalytic materials for pollutant degradation, with significant variations in efficiency, synthesis methods, and pollutant targets, providing valuable insights for advancing wastewater treatment technologies.

The notable examples provided are all related to the field of photocatalytic materials used for pollutant degradation. Here are some advantages and disadvantages of these materials:

Advantages:

- *Efficiency:* Many of these materials demonstrate high degradation percentages of pollutants within relatively short time frames, indicating their effectiveness in wastewater treatment (Abid *et al.*, 2022; Yaqoob *et al.*, 2020).
- *Versatility:* Different materials exhibit effectiveness under various light sources (UV, visible light, sunlight), providing flexibility for application in different environmental conditions (Yaqoob *et al.*, 2020; Parveen, Banse & Ledwani, 2016).
- *Synergistic Effects:* Composite materials, such as TiO_2 nanomaterials, TiO_2-Pt/GO and TiO_2-Pt/rGO, demonstrate synergistic effects leading to enhanced degradation capabilities compared to individual components (Tang, Wang & Wang, 2018; Shafei & Sheibani, 2019; Abid *et al.*, 2022; Kumar *et al.*, 2023).
- *Selectivity:* Some materials show specificity in degrading certain pollutants, which can be advantageous in scenarios where specific contaminants need to be targeted (Abid *et al.*, 2022; Kumar, Kumar & Thakur, 2023; Kumar *et al.*, 2023).
- *Renewable Energy Source:* Utilizing sunlight as a catalyst for pollutant degradation reduces the reliance on external energy sources, making these materials more sustainable (Abid *et al.*, 2022; Yaqoob *et al.*, 2020; Kumar *et al.*, 2023; Kumar *et al.*, 2023).

Disadvantages:

- *Cost:* Some materials, particularly those incorporating noble metals like Pt or Ag, can be expensive to produce, limiting their widespread application, especially in large-scale wastewater treatment plants (Abid *et al.*, 2022; Parveen, Banse & Ledwani, 2016; Jamkhande *et al.*, 2019).
- *Synthesis Complexity:* The synthesis of certain composite materials may involve complex processes, which could hinder scalability and reproducibility (Abid *et al.*, 2022).
- *Photostability:* Some photocatalytic materials may degrade over time due to prolonged exposure to light, reducing their long-term effectiveness and necessitating regular maintenance or replacement (Kumar, Kumar & Thakur, 2023; Kumar *et al.*, 2023).
- *Toxicity Concerns:* While these materials are designed for pollutant degradation, there might be concerns about the toxicity of the photocatalytic nanoparticles themselves or their byproducts formed during the degradation process (Jamkhande *et al.*, 2019; Murthy, Effiong & Fei, 2020).
- *Specificity Limitations:* While specificity can be an advantage in some cases, it can also limit the applicability of these materials to a broader range of pollutants, requiring tailored solutions for different contaminants (Kumar, Kumar & Thakur, 2024; Kumar *et al.*, 2023).

Overall, while photocatalytic materials hold significant promise for wastewater treatment, addressing these challenges will be crucial for realizing their full potential in practical applications. Continued research and development efforts are necessary to optimize their performance, reduce costs, and address environmental and safety concerns.

3.2. Adsorption and Photocatalysis

Adsorption and photocatalysis are two distinct processes used for pollutant removal or degradation, each with its own mechanisms and applications. Adsorption involves the physical or chemical bonding of pollutants onto the surface of a solid material, known as an adsorbent (Oumar *et al.*, 2022). This process relies on the affinity between the adsorbent and the pollutant molecules, which can be influenced by factors such as surface area, pore size, and chemical properties of the adsorbent material. Adsorption is typically a passive process that does not require external energy sources and can be highly effective for removing a wide range of contaminants from water or air. On the other hand, photocatalysis involves the use of a catalyst, typically a semiconductor material, to accelerate the degradation of pollutants through the generation of reactive oxygen species (ROS) or other highly reactive intermediates upon exposure to light, usually UV or visible light (Bickley & Stone, 1973). The catalyst absorbs photons and creates electron-hole pairs, which then participate in redox reactions with adsorbed pollutant molecules, leading to their degradation into harmless by-products (Abebe, Murthy & Amare, 2018). Photocatalysis is an active process that relies on the presence of a light source to drive the catalytic reactions and can be particularly effective for breaking down organic pollutants into smaller, less harmful molecules. One key differentiation between adsorption and photocatalysis lies in their mechanisms: adsorption involves the physical or chemical interaction between pollutants and the adsorbent surface, while photocatalysis relies on the generation of reactive species through the absorption of light by the catalyst material (Tran, Nosaka & Nosaka, 2006; Lv & Xu, 2006). Additionally, adsorption is typically reversible, meaning that pollutants can be desorbed from the adsorbent surface under certain conditions, whereas photocatalysis results in the irreversible degradation of pollutants into harmless products.

In practice, distinguishing between adsorption and photocatalysis can be achieved through experimental techniques such as monitoring changes in pollutant concentrations over time, analysing reaction kinetics, and studying the effects of light intensity and catalyst concentration on pollutant degradation rates. Understanding the underlying mechanisms and characteristics of each process is essential for designing effective pollutant removal or degradation strategies tailored to specific environmental remediation challenges.

3.3. Size Dependency

The size dependency of the photocatalytic properties of nanomaterials is a well-studied phenomenon that arises due to the unique electronic and surface properties exhibited by nanoparticles at the nanoscale. As nanomaterials decrease in size, their surface area-to-volume ratio increases, leading to a higher density of surface defects, active sites, and a greater number of exposed atoms or molecules (Li & Liu, 2011; Li *et al.*, 2020; Jassby, Farner Budarz & Weisner, 2012). These factors can significantly influence the material's photocatalytic performance in several ways as listed below:

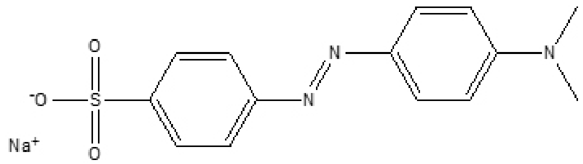
- *Enhanced Light Absorption:* Smaller nanoparticles have a larger surface area, which enhances light absorption due to the increased interaction between photons and the material's surface. This results in improved photon utilization efficiency and higher photocatalytic activity (Santhosh *et al.*, 2016).
- *Improved Charge Carrier Dynamics:* Nanoparticles with smaller sizes often exhibit higher charge carrier mobility and reduced recombination rates due to quantum confinement effects. This facilitates more efficient charge separation and transfer processes, leading to enhanced photocatalytic performance (Li *et al.*, 2020; Zhang, 1997).
- *Altered Band Structure:* Quantum size effects can alter the band structure of nanomaterials, resulting in shifts in the position of energy levels such as the conduction band and valence band. This can affect the material's ability to generate and utilize photoexcited charge carriers, influencing its photocatalytic activity (Kusiak-Neiman *et al.*, 2021).
- *Surface Reactivity:* Nanoparticles possess a higher density of surface defects and reactive sites, which can promote adsorption-desorption processes and facilitate the interaction between

photocatalysts and target pollutants, enhancing the overall photocatalytic efficiency (Khan *et al.*, 2013; Li & Liu, 2011).

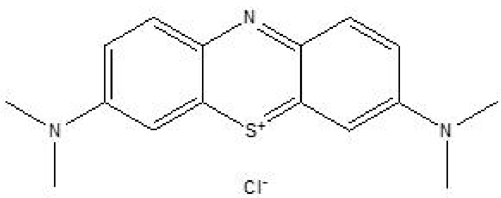
However, it is essential to note that the size dependency of photocatalytic properties can exhibit a complex interplay with other factors such as composition, morphology, crystallinity, and surface modification. Additionally, there may be optimal size ranges for specific photocatalytic applications, beyond which further size reduction might not necessarily lead to improved performance due to factors like increased aggregation, decreased stability, or altered electronic structure. Overall, understanding the size-dependent behaviour of nanomaterials in photocatalysis is crucial for the rational design and optimization of photocatalysts tailored for specific environmental remediation or energy conversion applications. Experimental and theoretical studies aimed at elucidating the underlying mechanisms governing size effects in photocatalysis continue to advance our knowledge in this field and inform the development of more efficient and sustainable photocatalytic materials.

3.4. Structures of organic dyes

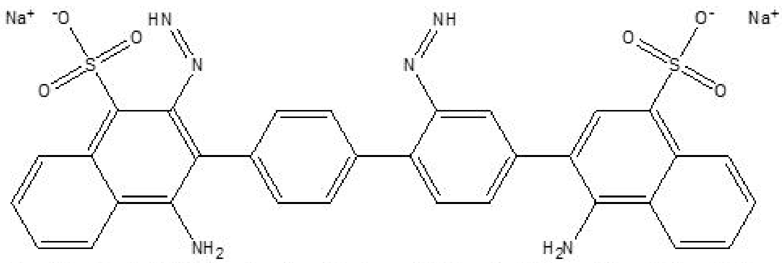
The discharge of organic pollutants from pharmaceutical and textile industries into the environment has emerged as a significant health concern for both living organisms and their surroundings. These industries release a substantial number of toxic dyes and chemicals into nearby water bodies during their dyeing and pharmaceutical manufacturing processes. Addressing this issue is crucial, and the use of eco-friendly carbon nanomaterials for the reduction of these wasted dyes and harmful chemicals through photocatalysis is a promising solution. Photocatalysis involves a chemical reaction that is initiated by light, where free radicals play a key role in starting the reaction between various organic dyes and the photons emitted by carbon nanomaterials (as illustrated in Scheme 1 and Fig. 10). These photons possess sufficiently high energy levels to trigger the reaction. In this photo-activated chemical process, the complex molecular structures of different organic dyes are broken down into simpler compounds. Here are some examples of different organic dye structures are given as follows:



Sodium 4- {[4-(diethylamino) phenyl] diazenyl} benzene-1-sulfonate (Methyl orange)

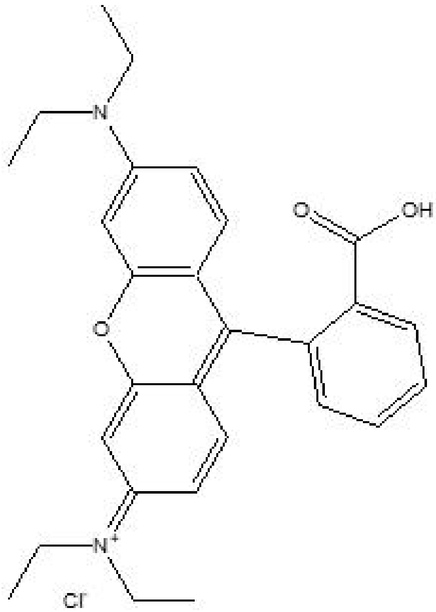


3, 7- bis (Dimethylamino)-phenothiazin-5-ium chloride (Methylene blue)

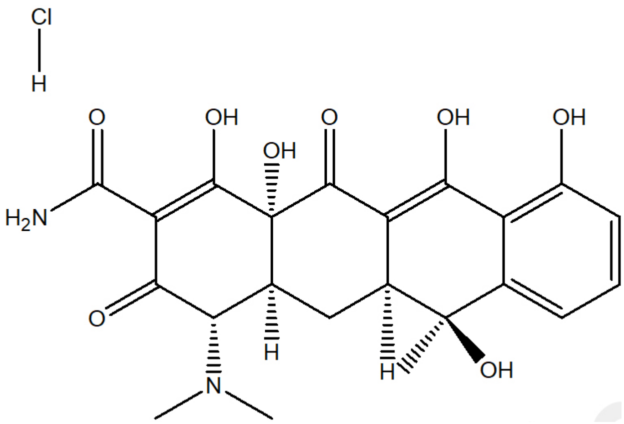


diazenylphenyl] phenyl] diazenyl-naphthalene-1-sulfonate (Congo red)

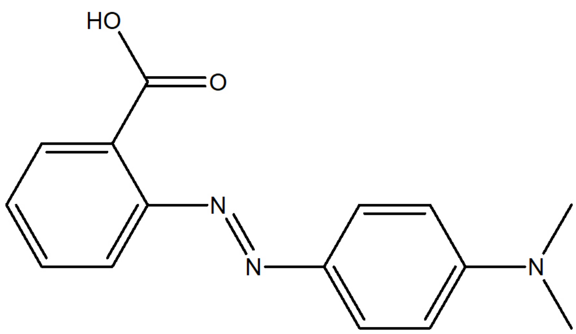
 https://doi.org/10.37819/nanofab.9.1827



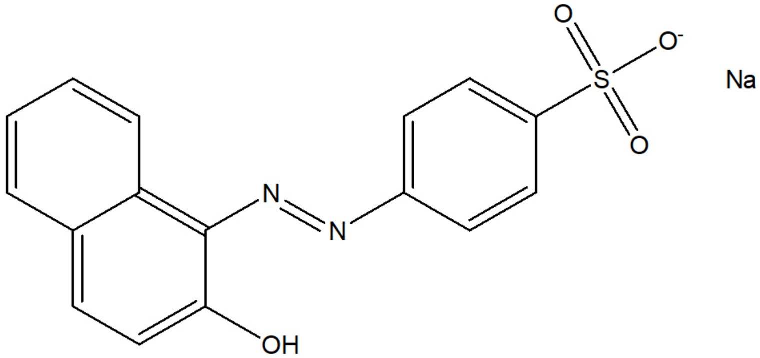
9-(2-carboxyphenyl)-6-(diethylamino)-N,
N-diethyl-3H-xanthen-3-iminium chloride (Rhodamine B)



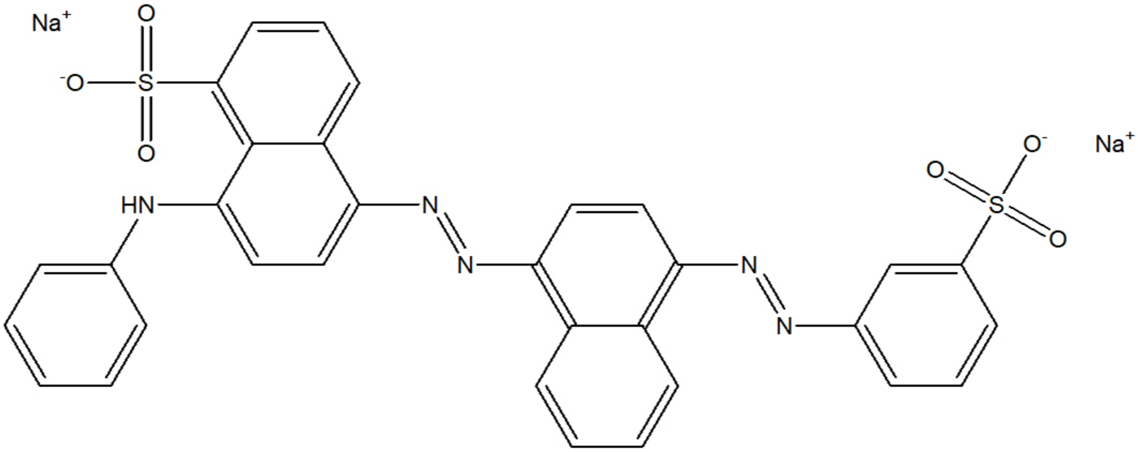
(4S,4aS,5aS,6S,12aR)-4-(dimethylamino)-1,6,10,11,
12a-pentahydroxy-6-methyl-3,12-dioxo-4, 4a,5,5a-tetrahydrotetracene-
2-carboxamide; hydrochloride (Tetracycline hydrochloride)



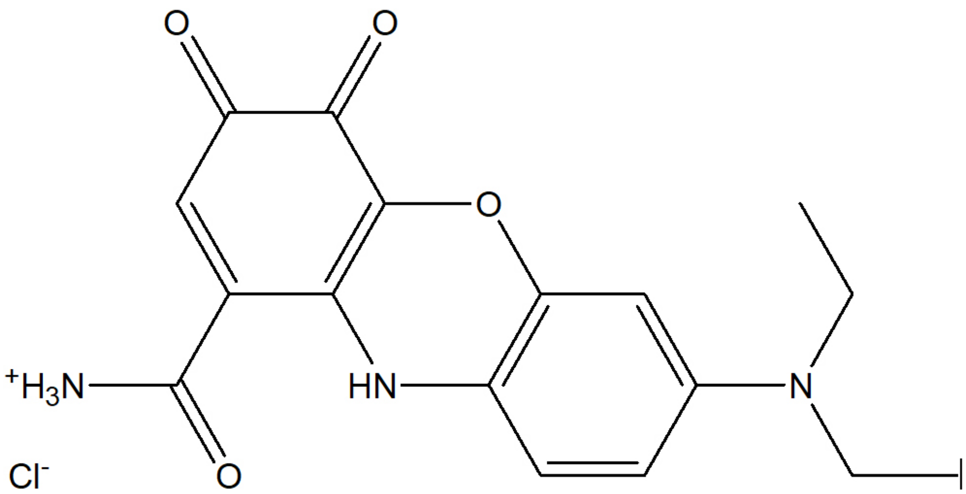
2-[[4-(dimethylamino)phenyl] diazenyl] benzoic acid (Methyl red)



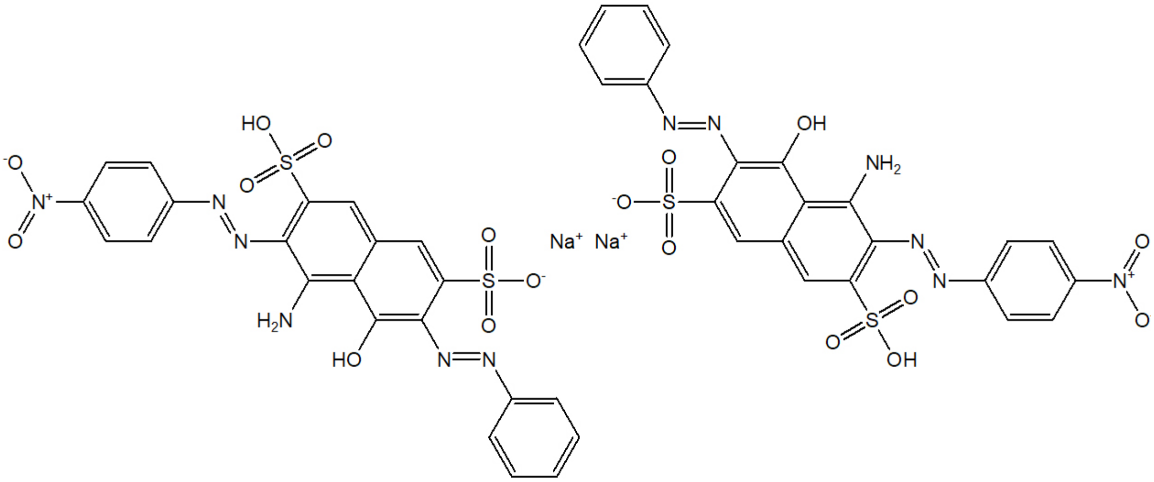
sodium;4-[(2-hydroxynaphthalen-1-yl) diazenyl] benzenesulfonate (Acid orange 7)



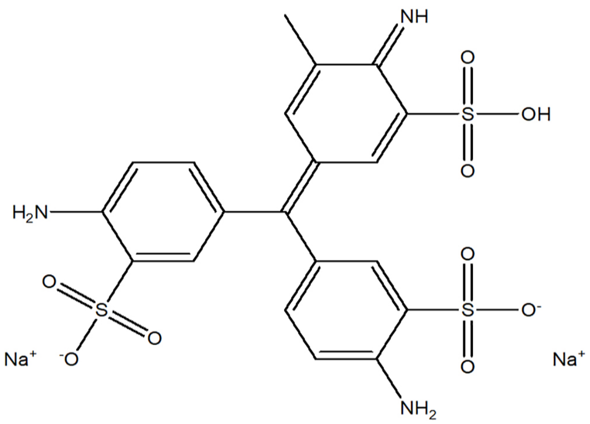
disodium;8-anilino-5-[[4-[(3-sulfonatophenyl) diazenyl] naphthalen-1-yl] diazenyl] naphthalene-1-sulfonate (Acid blue 113)



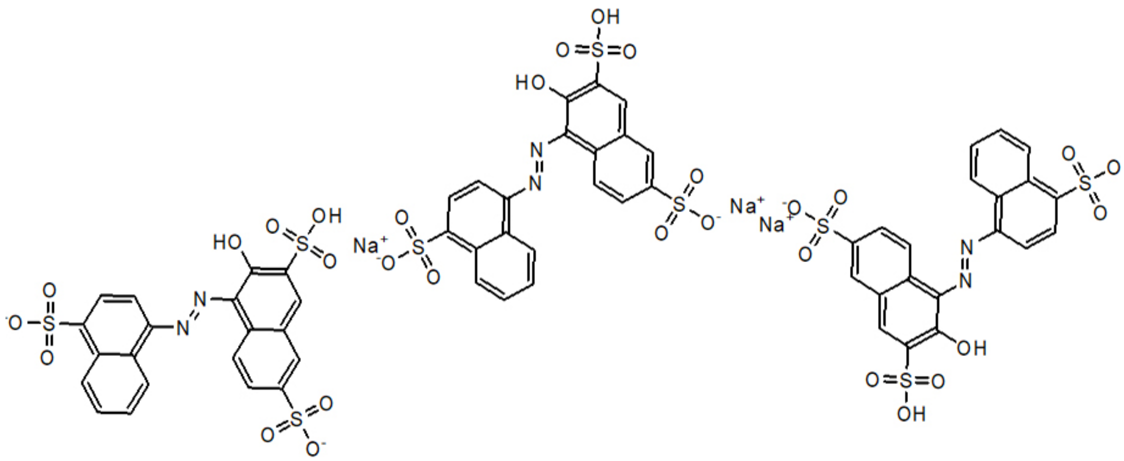
[7-(diethylamino)-3,4-dioxo-10H-phenoxazine-1-carbonyl] azanium; chloride (Celestine blue)



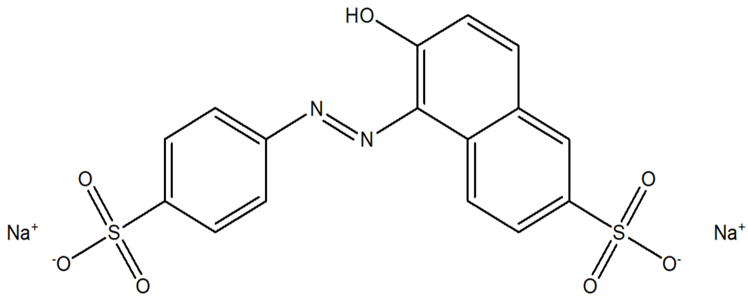
disodium;4-amino-5-hydroxy-3-[(4-nitrophenyl) diazenyl]-6-phenyldiazenylnaphthalene-2,7-disulfonate (Naphthol Blue Black)



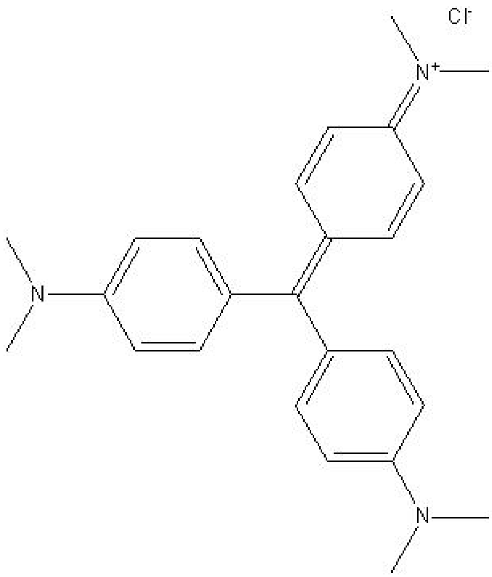
disodium;(3Z)-3-[(4-amino-3-sulfonatophenyl) -(4-amino-3-sulfophenyl) methylidene]-6-imino-5-methylcyclohexa-1,4-diene-1-sulfonate (Acid fuchsin)



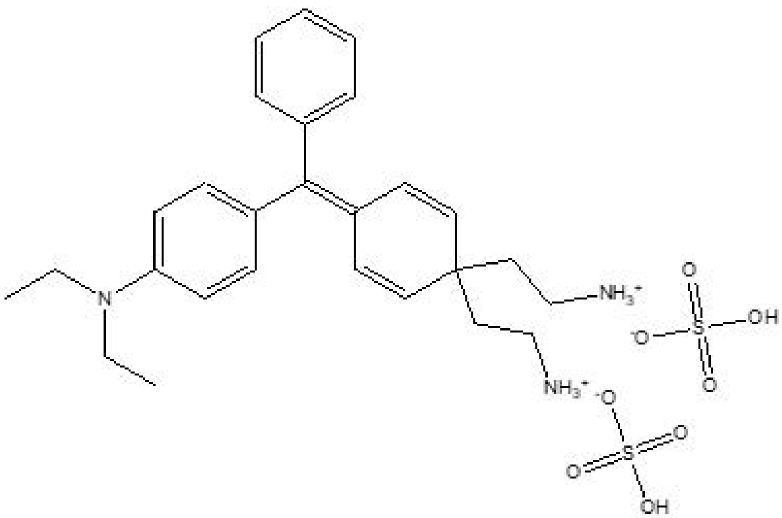
trisodium;3-hydroxy-4-[(4-sulfonatonaphthalen-1-yl) diazenyl] naphthalene-2,7-disulfonate (Amaranth)



disodium;6-hydroxy-5-[(4-sulfonatophenyl) diazenyl] naphthalene-2-sulfonate (Sunset yellow)



4-{Bis[4-(dimethylamino) phenyl] methylidene}-N, N-dimethylcyclohexa-2,5-dien-1-iminium chloride (Crystal violet)



[4-[[4-(diethylamino) phenyl]-phenyl methylidene] cyclohexa-2,5-dien-1-ylidene]-diethylazanium; hydrogen sulfate (Brilliant green) conclusions and perspective

4. SOLUBILITY AND STABILITY OF CARBON NANOMATERIALS

4.1. Water solubility

The water solubility of carbon nanomaterials varies depending on factors such as their structure, surface functionalization, and degree of dispersion (Zhang *et al.*, 2013; Al-Hamadani *et al.*, 2015). Carbon nanomaterials encompass a diverse range of structures, including fullerenes, carbon nanotubes (CNTs), graphene, and carbon dots, each with unique properties that influence their solubility in water:

- *Graphene:* Graphene sheets are generally hydrophobic due to their sp^2-hybridized carbon structure, making them insoluble in water. However, graphene oxide (GO) and reduced graphene oxide (rGO), which contain oxygen-containing functional groups like hydroxyl and carboxyl groups, exhibit improved water solubility due to increased hydrophilicity. The presence of these functional groups enhances the dispersibility of graphene-based materials in water (Neklyudov *et al.*, 2017).
- *Carbon Nanotubes:* The water solubility of carbon nanotubes (CNTs) can vary depending on their surface functionalization and degree of oxidation. Pristine CNTs are typically hydrophobic and insoluble in water, but their solubility can be enhanced through surface modification with polar functional groups such as carboxyl (-COOH) or hydroxyl (-OH) groups. Additionally, the length and diameter of CNTs can influence their dispersibility in water (Naqvi *et al.*, 2020; Kharisov *et al.*, 2009).
- *Fullerenes:* Fullerenes, such as C_{60} and C_{70}, are sparingly soluble in water due to their hydrophobic nature. However, their solubility can be improved through chemical modification with hydrophilic functional groups or encapsulation within surfactant or polymer molecules, which enhance their dispersibility in aqueous solutions (Liu *et al.*, 2010; Sayes *et al.*, 2004).
- *Carbon Dots:* Carbon dots (C-dots) are typically highly water-soluble due to their small size and surface functionalization with hydrophilic groups such as carboxyl, hydroxyl, or amino groups. These functional groups impart water solubility to C-dots and make them suitable for various biomedical and sensing applications (Zhai *et al.*, 2014; Zhao & Zhu, 2018).

Overall, while some carbon nanomaterials exhibit inherent hydrophobicity, surface functionalization techniques can be employed to enhance their water solubility and dispersibility. Understanding and controlling the factors influencing the water solubility of carbon nanomaterials is essential for their applications in areas such as biomedicine, environmental remediation, and nanotechnology.

4.2. Stability

The stability of carbon nanomaterials encompasses various aspects, including chemical, thermal, and colloidal stability, which can influence their performance and applicability in different environments and applications (Al-Hamadani *et al.*, 2015). Here is a brief overview of the stability considerations for carbon nanomaterials:

- *Chemical Stability:* Carbon nanomaterials can be susceptible to chemical degradation under certain conditions, such as exposure to strong acids, bases, or oxidizing agents. For example, graphene and carbon nanotubes may undergo oxidation or functionalization when exposed to strong acids or oxidative environments, leading to changes in their structure, properties, and performance. Enhancing chemical stability often involves surface functionalization or encapsulation strategies to protect the nanomaterials from chemical degradation (Safaee *et al.*, 2019).
- *Thermal Stability:* Carbon nanomaterials generally exhibit high thermal stability, with graphene, carbon nanotubes, and fullerenes retaining their structural integrity at elevated temperatures. However, thermal stability can vary depending on factors such as structural defects, surface functionalization, and synthesis methods. Understanding the thermal stability of carbon nanomaterials is crucial for applications involving high-temperature processes or environments (Wang *et al.*, 2020).
- *Colloidal Stability:* In aqueous or colloidal systems, the stability of carbon nanomaterials refers to their ability to maintain dispersion and prevent aggregation or precipitation over time. Factors such as surface charge, surface functionalization, and solvent composition influence colloidal stability. For instance, graphene oxide (GO) and carbon dots can form stable

colloidal suspensions in water due to their surface functional groups, while pristine carbon nanotubes may require surfactants or polymer coatings to prevent aggregation (Radovic & Bockrath, 2005).

- *Environmental Stability:* Carbon nanomaterials may also undergo degradation or transformation in environmental settings, such as exposure to ultraviolet (UV) radiation, moisture, or reactive species. Understanding the environmental stability of carbon nanomaterials is essential for assessing their long-term fate, transport, and potential environmental impacts (Radovic & Bockrath, 2005).
- *Biological Stability:* In biomedical applications, carbon nanomaterials encounter biological environments that can influence their stability and biocompatibility. Factors such as protein adsorption, cellular uptake, and enzymatic degradation can affect the stability and performance of carbon nanomaterials in biological systems (Al-Hamadani *et al.,* 2015; Wang *et al.*, 2020; Radovic & Bockrath, 2005).

Overall, ensuring the stability of carbon nanomaterials is critical for their successful integration into various applications, including electronics, energy storage, catalysis, biomedical devices, and environmental remediation. Addressing stability challenges often involves surface engineering, functionalization strategies, and rigorous characterization to optimize performance and mitigate potential degradation pathways.

5. CONCLUSION AND PERSPECTIVES

Photocatalytic activity plays a pivotal role in mitigating water contamination by efficiently eliminating pollutants. This review highlights the significance of using eco-friendly carbon nanomaterials, including carbon nanotubes, graphene, graphene oxide, and metal oxide nanocomposites, as cost-effective, environmentally friendly, and recyclable photocatalysts. Furthermore, these materials require minimal quantities for the treatment of wastewater from the textile and pharmaceutical industries. Research from literature reviews suggests that the adsorption capacity of carbon and metal oxide nanomaterials surpasses that of pure metal oxide nanoparticles. The application of carbon nanomaterials in photocatalysis presents a promising avenue for addressing environmental challenges while offering opportunities for sustainable technological advancements. Carbon nanotubes, graphene, and related materials exhibit unique properties such as high surface area, excellent electron transport capabilities, and efficient light absorption, which can significantly enhance the performance of traditional photocatalysts like TiO_2. This enhancement opens doors to versatile applications in environmental remediation, including air and water purification, with the potential to mitigate pollutants effectively and reduce harmful by-products. However, several challenges must be addressed to realize the full potential of carbon-based photocatalysts. These challenges include synthesizing materials at scale with consistent quality, ensuring long-term stability under harsh operating conditions, addressing safety concerns associated with nanomaterial handling, and deepening our understanding of fundamental photocatalytic mechanisms. Moving forward, research efforts should focus on advancing synthesis techniques, surface engineering, and integration with support materials, while embracing multidisciplinary collaboration to accelerate progress towards sustainable and efficient photocatalytic systems for environmental and energy-related applications.

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Conflict of interest

The authors declare no competing financial interests. ♦

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