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Review

Adsorption and Photocatalytic Degradation of Methylene Blue in Carbon Nanotubes: A Review with Bibliometric Analysis

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Abstract: Wastewater-containing dyes are an environmental problem. The prime source of dye pollutants is the textile industry, such as paper manufacturing, food processing, leather, pigments, etc. Dye removal from wastewater using nanotechnology has received attention in recent decades thanks to efficient nanomaterials improving traditional technologies. In recent years, multiple research reports on carbon nanotubes for dye removal and photocatalytic dye degradation provided substantial insight into the comprehension of nanotechnology and remediation. This work presents a review and bibliometric analysis of carbon nanotubes for dye removal and photocatalytic dye degradation, which have an environmental impact today. The bibliometric study showed that the current research tendency on carbon nanotubes applied in dye removal and photocatalysis is still growing. According to research, this work observed that carbon nanotubes for dye removal exhibit high removal and efficient photocatalysis activity, indicating the functionality of nanotechnology for environmental remediation. The analysis of the parameters involved in the removal studies, such as temperature and pH, showed adsorption behavior. The photodegradation of methylene blue demonstrated the photocatalytic activity of carbon nanotubes attributed to the sp^2 lattice of graphitic configuration.

Keywords: adsorption; carbon nanotubes; methylene blue; photocatalysis; photodegradation of methylene blue

1. Introduction

Water pollution has become an environmental problem, particularly pollution caused by organic dyes. Even in low concentrations, they are toxic, mutagenic, carcinogenic, and decrease the amount of dissolved oxygen [1]. Dyes also prevent light penetration, reducing the photosynthetic activities in waterbodies and disturbing the aquatic balance [2]. Dyes are of great use in several industries, such as textiles, and are highly resistant and difficult to eliminate in conventional treatment plants [3]. Methylene blue (MB) is an organic dye widely studied and used in various industrial sectors, including textiles, pharmaceuticals, and healthcare. Its industrial use means that significant quantities are released into wastewater systems, becoming a contaminant that needs attention [4].

This feature highlights the need for innovative and effective treatment approaches, such as adsorption and photocatalysis. Adsorption is a dye removal technique for retention of dye molecules on the surface of the adsorbent. The interaction between the dye and the adsorbent, the specific surface area, the size of the dye molecule, temperature, pH, and contact time are the parameters that determine the efficiency of the adsorption process [5]. Some of the most used materials for adsorption are carbon nanotubes. They have exceptional characteristics, such as large surface area, high microporosity, and high aspect ratio. Carbon nanotubes are widely used for the adsorption of toxic materials due to their hollow and large-surface-area nanostructures (~150–1500 $m^2 \cdot g^{-1}$) [6].

After dye adsorption, it remains stored in the adsorbent; the proposed photocatalysis process is one of the ways to remedy this complication because it allows for the degradation of the molecule. Adsorption and photocatalytic degradation of MB on carbon nanotubes have been the subject of extensive research due to their relevance in the removal and degradation of organic pollutants in wastewater and the purification of the environment [7]. Surface adsorption is the first step to guarantee adhesion to the catalyst to ensure accelerated chemical reactions under light for photocatalysis. The dual functionality of carbon nanotubes, adsorbents, and photocatalysts is due to their high surface area, outstanding conductivity, and electronic properties. These characteristics are relevant for research and environmental remediation strategies [8]. Previous reports present carbon nanostructures, resulting in such dual synergistic processes for carbon nanotubes and carbon dots; however, they do not focus on the degradation of MB occurring over a carbon surface [9,10].

Combining adsorption and photocatalysis for MB management becomes a suitable model pollutant to study the effectiveness of carbon nanotubes in environmental remediation. This review seeks to examine the current and future state of the art for research on carbon nanotubes, their electronic properties, and their application in adsorption and photo-degradation of MB as a model through bibliometric analysis. In addition, the adsorption and photocatalytic process is planned for carbon nanotubes, MB degradation is investigated, and a photocatalytic mechanism proposed.

2. Carbon Nanotubes

Carbon nanotubes (CNTs), resulting from the folding of a single graphene sheet, were first observed by Japanese scientist Sumio Iijima in 1991 using an electron microscope [11]. Earlier in 1952, Russian scientists Radushkevich and Lukyanovich provided initial evidence of nanotubes, demonstrating their tubular structure and internal cavity [12]. They are one-dimensional carbon allotropes and have received attention in nanostructured materials research at both academic and industrial levels due to their remarkable characteristics and potential use in different areas. CNTs exhibit high tensile strength compared to steel due to sp^2 carbon bonds. These bonds are more robust than the sp^3 bonds that make up the diamond structure. They can bind and exchange sp^2 and sp^3 bonds for hybridization states at high pressure. CNTs exhibit fascinating thermal and electronic characteristics, making them a material capable of being used in water treatment [13].

Nanotubes have unusual properties which are valuable for nanotechnology. Depending on the degree of winding and the conformation of the original sheet, the result can lead to nanotubes of different diameters and internal geometry. CNTs roll as if on the ends of a sheet joined by their edges closing the tube; those are monolayer or single-walled carbon nanotubes (SWCNTs). There are also nanotubes whose structure resembles that of a series of concentric tubes, including one inside the other or multi-walled carbon nanotubes (MWCNTs) [14].

2.1. Synthesis Methods

The main synthesis methods of CNTs are arc discharge, laser ablation, and chemical vapor deposition [15]. The arc discharge is a continuous electric discharge that generates intense light and heat and uses high temperatures to grow CNTs with fewer structural defects. The potential difference between 20 and 40 V and a current between 50 and 100 A produces the arc discharge between the cathode and anode graphite bars. The consequence of arc discharge is the acceleration of many electrons toward the anode. The intense current evaporates carbon atoms, generating plasma around the electrodes. The advantage of this method is that in addition to obtaining structures with few defects, SWCNTs and MWCNTs are formed. The disadvantage of this methodology is the short length that the nanotubes obtained tend to have [14]. Another method is laser ablation. In the synthesis of CNTs by laser ablation, a pulsed laser vaporizes a graphite target in a high-temperature reactor, approximately 1200 °C, while an inert gas circulates in the chamber. CNTs are developed on the cold surfaces of the equipment as the vaporized carbon condenses. One of the advantages that this method offers is the high-quality production of SWCNTs and diameter control [16]. Chemical vapor deposition (CVD) is a chemical process for carbon nanotube synthesis using Fe, Co, or Ni as catalysts forming a thin film 1 to 50 nm thick in a furnace, and methane, acetylene, or benzene gas is gradually released, releasing carbon atoms in sp^2 honeycomb arrays. The advantage of this technique is the scalation at an industrial level and the facility of synthesizing long nanotubes; the principal disadvantage is that only MWCNTs are manufactured, and they tend to have a relatively high level of defects. This technique is one of the preferred techniques for the synthesis of nanotubes [17].

2.2. Electrical and Optical Properties of CNTs

Due to their arrangement of carbon atoms and unique one-dimensional and tubular structure, CNTs present remarkable electrical and optical properties modified by chirality, diameter, and length. The electrical and optical properties are tuned to improve photocatalytic activity in the photodegradation of organic pollutants, such as MB.

2.2.1. Chirality, Diameter, and Length Variations and Their Impact on Photocatalytic Performance

The prediction of the electronic properties of CNTs, specifically SWCNTs, carried out by theoretical calculations, determined that they could be either metallic or semiconducting. For example, depending on their chiral indices (n, m), nanotubes could be metallic, semiconducting, or chiral; the p-tight binding calculations within the zone-folding scheme showed that one-third of a CNT is metallic, and the other two-thirds are semiconducting. The curvature of sp^2 folded graphene produces the combination of s and p bands, inducing semiconducting nanotubes to have a narrow gap; the tight-binding calculations using p and n bands allowed us to determine this result. The overlapping of MWCNTs or bundles of SWCNTs generates the appearance or disappearance of the band gap due to lower symmetry exhibited by these arrangements concerning the individual SWCNTs [18].

Metallic carbon nanotubes are good conductors because they have a small or zero bandgap; in this case, electrons move freely due to the Fermi level intersecting with the electronic band structure, presenting high electrical conductivity. Semiconductors have a narrow band gap (meV to eV) and could depend on the CNTs' chirality [19]. The characteristics and dimensions of carbon nanotubes (CNTs) significantly influence their photocatalytic performance. Chirality affects photocatalysis by influencing semiconducting behavior and the movement of electron–hole pairs along CNTs. Efficient photocatalysis depends on the separation and migration of these photogenerated charge carriers. The length and diameter of CNTs play a crucial role, with longer CNTs providing more pathways for charge carrier movement. Small diameters increase gaps, enhancing adsorption capacity, while large diameters reduce gaps. Additionally, the synthesis conditions impact the band gap of CNTs, with chemical vapor deposition resulting in a band gap of approximately ~100 meV [20]. Alwash et al. proposed a photocatalytic activity enhancement in CNTs due to their outstanding electron storage capacity [21].

2.2.2. Band Structure and Light Absorption

The band gap is the most relevant property of semiconductors for determining the performance of materials applied to sensitivity, conductivity, photocatalysis, etc. The lattice and atomic structure determine the band gap of semiconducting materials. The band gap of MWCNTs may be tuned thanks to their exceptional mechanical and electrical properties like chemical robustness, surface reactivity, one-dimensional transport, and strong C-C covalent bond. In CNTs, even multi-walled CNTs, the band gap depends on the chirality and the CNT's diameter; if the diameter increases, the semiconducting band gap decreases due to the circumferential direction appearing as more allowed wave vectors. Ando proposed a periodic boundary condition with a simulated Aharonov–Bohm flux that determined the energy bands in CNTs, which decide whether a nanotube is metallic or semiconducting [19]. However, carbon nanotube diameters have a wide distribution despite the fact that they are produced in the same production batch and independently of the synthesis methods. In addition, they mixed and self-aggregated in black powder, making it impossible to select any carbon nanotube with a desirable band gap [22]. Light absorption in CNTs depends on various parameters such as the dielectric function, dimensions, band structure, type of light, absorption coefficient, etc. The absorption coefficient is the ability of CNTs to absorb light at a particular wavelength. And the dielectric function describes the response of a material to an external electric field. Some of these parameters, such as the band structure, absorption coefficient, and the dielectric function, depend on the geometry and dimensions of CNTs [23].

2.2.3. Absorption Properties in the UV-Visible Light Ranges

The absorption properties of CNTs in the ultraviolet (UV) and visible light ranges depend on diverse factors but mainly on the electronic structure. SWCNTs have second-order hyperpolarizabilities, and the helical structure of metallic and chiral nanotubes determines their optical characteristics. Because of the helical structure of SWCNTs, they present discrete dispersions dependent on diameter. MWCNTs behave like graphite when studying their optical properties, and their helical structure is not a problem; the radii of the MWCNTs modify their optical properties. In thin films of carbon nanotube bundles, the light polarized differently along and perpendicular to the structure, being birefringent [24]. Considering the presence of Aharonov–Bohm flux, the optical absorption spectra of CNTs exhibit a shift in absorption peaks, and the band gap presents drastic modifications [25].

The interaction between UV light and CNTs reveals characteristic absorption bands between 200 and 300 nm of the UV-visible regions. The concentration of a solution with CNTs is proportional to the plasmon resonance peak intensity. The Lambert–Beer law describes the light absorption by CNTs. The UV absorption in CNTs occurs because of the transitions of electrons between energy levels attributed to π and π^* orbitals, which are influenced by the band gap that depends on the dimensions and chirality of CNTs. The transitions between higher-energy π and σ^* orbitals are involved in the absorption in the visible region [26].

2.2.4. Strategies for Tuning the Band Structure for Enhanced Photocatalysis

As mentioned above, the light absorption in the UV-visible region and photocatalysis in CNTs depend on their band gap and semiconductor nature. These properties vary with the dimensions and chirality of CNTs. The strategies to tune the band structure of CNTs for enhanced photocatalysis correlate with the band gap modification or reduction. The main objective of these strategies is to enhance the light absorption and the charge carrier's generation to improve photocatalysis. The first method to tune the band structure is to modify the energy levels to enhance UV and visible light absorption by doping with atoms other than carbon, such as N, P, or Cl [27,28]. Functionalization is another route to improve photocatalytic activity by altering the band structure with the new energy state introduction without altering the carbon nanotube structure [29]. For example, the oxygen group's introduction alters the position of the valence band, and they become electron acceptors [30]. Additionally, functionalization allows better sonication and reduces the self-aggregation of CNTs. The absorption spectrum and the efficiency of light absorption are affected by the electronic states induced by defects in CNTs. The light absorption of CNTs in the visible spectrum was enhanced by wide-band gap oligomer functionalization [31].

Combined hybridization of materials resulted in a successful strategy to take advantage of the synergistic effect of CNTs with other materials. Beneficial effects are produced when incorporating CNTs into hybrid structures with other semiconducting or catalytic materials. The effectiveness of the photocatalytic reaction increases when it combines with materials with complimentary band structures because charge separation and migration are improved. Phin et al. mixed zinc oxide/CNTs, improving the behavior of zinc oxide because it has problems with agglomeration and photocorrosion, and the fast photo-induced charge carrier recombination reduces its performance in photocatalytic degradation. In this work, CNTs served as nucleation sites of zinc oxide, avoiding aggregation and generating the formation of a zinc carboxylate group. Better photocatalytic activity than pure zinc oxide was seen in the degradation of MB when exposed to sunlight, and the photocatalytic activity of the zinc oxide/CNT photocatalyst increased with increasing CNT loading [32]. The absorption spectrum extension is possible when combining CNTs with semiconductor nanoparticles (NPs) with complementary absorption properties. CNT–metal oxide composites are one type of hybrid structure to accomplish this issue. Manda and coworkers reported advanced nanocomposites obtained by the laser ablation of bismuth on CNT-α-Fe_2O_3 nanoparticles, highlighting their improved efficiency in the photocatalytic degradation of MB. The presence of bismuth acted as a co-catalyst, improving the generation of electron–hole pairs and enhancing photocatalytic activity [33].

3. Methylene Blue

MB, also called methylthionine chloride, is an aromatic and basic organic dye with the molecular formula $C_{16}H_{18}ClN_3S$ [34]. Figure 1 presents the structure of this dye, and Table 1 lists the respective properties [35]. This dye is classified as a direct dye because it is applied by direct immersion of the sample in the dye solution, which saturates the organic group or material with great affinity, allowing the observation of visible colors in the sample, and it is also a thiazine dye. MB shows a deep blue color in an oxidized state while being colorless in its reduced form, called leukomethylene blue. Both exist as a redox pair in equilibrium and together form a reversible system of oxidation and reduction [36].

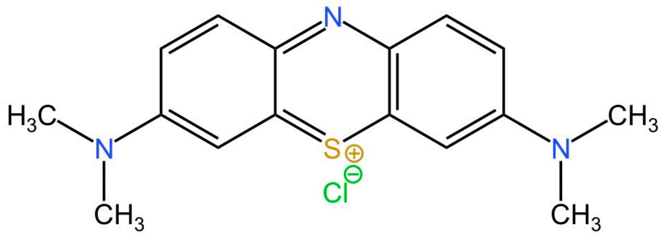


Figure 1. Structure of methylene blue.

Table 1. Properties of methylene blue at room temperature [35].

Formula	**$C_{16}H_{18}ClN_3S$**
Molecular weight	319.859 uma
Average solubility	Water between 3.5 and 9.5%, alcohol between 1.48 and 63%, and glycol 10%
Absorbance	If pure, 663–667 nm

MB is crystal-shaped or presents as a crystalline powder and has a dark green color with a tanned luster. It is odorless and air-stable. Its solutions in water or alcohol are intensely blue. It is easily soluble in water and chloroform, and moderately soluble in ethanol. Table 2 presents the dose-related toxicity from MB exposure [37–39].

Table 2. Dose-relative toxicity of MB for different studies in animals and humans.

Studies	Toxic Doses (mg/kg)	Manifestation/Symptoms
Rats	1180–1250	Hypotension, neuronal apoptosis, a drop in systemic vascular resistance (SVR), decreased renal perfusion, and confusion
Mice	3500	
Sheep	40	
Dogs	10–20	
Humans	2–5	Hemolytic anemia, fever, methemoglobinemia, nausea, vomiting, chest pain, dyspnea, and hypertension
	>5	Fatal serotonin toxicity
	20–80	Refractory hypotension, reduced renal blood flow, fainting, and dermal discoloration

Dyes cause harmful effects on the environment, even at low concentrations. The textile industry is the second most polluting industry and is also responsible for 20% of global wastewater. Colored wastewater from the textile industry, which may contain dyes that are not always detectable by the naked eye (<1 ppm), have high levels of chemical oxygen demand and biological oxygen demand, which is vital to the existence of most aquatic organisms and is an important indicator of water quality; variations in this parameter can increase the amount of algae present, which can even lead to the suffocation and death of fish and other aquatic organisms [37].

The color associated with dyes in textiles causes aesthetic pollution and damage to water bodies as it prevents the penetration of light through water, which results in a decrease in the photosynthetic rate and affects all aquatic biota [37]. In the wastewater from the textile industry, we also find an increase in the values of physicochemical and biological parameters such as total dissolved solids (TDS), total nitrogen (TN), total phosphorus (PTF), and non-biodegradable organic compounds [40].

The recalcitrant nature of MB makes it difficult to remove from wastewater by conventional treatment processes [41]. It is constituted by atoms of functional groups containing nitrogen, aromatic rings, and conjugated double bonds (responsible for the intense blue color), which gives it a complex, very resistant, and chemically stable conformation that hinders its decomposition into less harmful or innocuous simple compounds when exposed to photolysis or conventional water treatment under typical environmental conditions. This type of dye reduces light penetration into the water, alters photosynthesis activity, and promotes the growth of various microbes harmful to aquatic life and human health [42]. To efficiently remove MB from water systems, novel and specialized treatment strategies are frequently needed, such as photocatalysis and sophisticated oxidation techniques.

4. Adsorption

When analyzing the chemistry of dyes, four types of technologies can be defined for their removal, which are grouped within the categories of physical, chemical, biological, and combined treatment [43]. One of the most effective physical methods for the removal of toxic pollutants, such as dyes, is the adsorption process, because it is inexpensive, highly efficient, and easy to perform [6,44]. Adsorption is the phenomenon of accumulation on a surface. Adsorption occurs through a physical force (London dispersion forces, electrostatic type, interactions of type π-π and van der Waals). This process does not involve electron exchange, which makes it reversible [45]. Like surface tension, adsorption is the result of surface energy. In bulk materials, all bonding requirements (ionic, covalent, or metallic) of the constituent atoms of the material are consistent with those of the other atoms present in the material. However, the constituent on the adsorbent surface is not surrounded by other adsorbent atoms and can attract the adsorbate [46].

4.1. Steps of Adsorption

The general adsorption process consists of a series of steps. When fluid passes around the particle in a fixed bed, the solute first diffuses from the fluid volume to the entire outer surface of the particle. The solute then diffuses inside the pore, forming a porous material that acts as an adsorbate. Finally, the solute adsorbs on the surface. Accumulation per unit area is small; therefore, highly porous solids with large internal area per unit volume are preferred. Generally, the surfaces are irregular, and the binding energies are basically due to van der Waals forces. According to the characteristics and mechanism, adsorption could be physical or chemical. The main difference between physical and chemical adsorption is the forces operating in the process. In physical adsorption or physisorption, the interaction is through van der Waals forces, hydrogen bonding, or hydrophobic interactions. In chemical adsorption or chemisorption, a covalent or ionic bond occurs between the adsorbent surface and adsorbate. The substance concentration in water, the temperature, and the polarity of the substance determine the level of adsorption activity [46].

4.2. Kinetics of Adsorption

In adsorption processes, two aspects must be considered: the effect of adsorption on the interfacial energy of the system in equilibrium (thermodynamics) and the speed of the adsorption process (kinetics). An adsorption isotherm is a general relationship between the amount of gas adsorbed by a solid at a constant temperature as a function of gas pressure. The adsorption isotherm is the relationship in the equilibrium between the amount of gas adsorbed and the pressure of the gas at a constant temperature [47]. The adsorption equilibrium is the ratio of the amount adsorbed to the rest in the solution. It is established when a phase containing the adsorbate has been in contact with the adsorbent for enough time. And the concentration of adsorbate in the bulk solution is in dynamic equilibrium with the interface concentration [48]. Analyzing this relationship allows us to study the adsorption process and the particle–surface interactions, the characteristics of the surface, as well as whether the surface is smooth, porous, or microporous [49].

A variety of adsorption isotherm models have been proposed, such as the Langmuir, Freundlich, Flory–Huggins, Brunauer–Emmett–Teller, and others. The models of adsorption isotherms are formulated based on three approximations fundamentally. In the first kinetic approximation, the adsorption equilibrium is defined as a dynamic equilibrium, where the adsorption and desorption velocities are equal. Thermodynamics is the basis of the second approach, avoiding a framework for deriving many models of adsorption isotherms and even potential theories. And the third approach usually conveys the main idea of a curve or graph characteristic of isotherms. A trend in isotherm modelling is the derivation in more than one approach [50].

The contaminant removal rate prediction depends on adsorption kinetics and helps us to understand the velocity of removal from water interacting with the adsorbent. The critical factors influencing the kinetics of MB adsorption onto the CNTs are temperature and pH. The temperature affects the equilibrium capacity of the adsorbent and the diffusion rate of adsorbate molecules due to the accessibility of vacant surface sites for adsorption and the changes in solution viscosity [51–53]. In a previous research study, the temperature effect on MB adsorption with an increment from 272 to 333 K increased the adsorption capacity from 26.14 mg/g to 41.63 mg/g. The early rapid adsorption may be due to the availability of vacant surface sites. Repulsive forces between dye molecules and the CNTs cause reduced adsorption in later phases, making it difficult for the dye molecules to occupy the remaining unoccupied sites [52].

The influence of pH depends on chemical interactions that involve electron sharing or exchange between MWCNTs and MB, characterized by valency forces. Song and colleagues conducted research for the study of pH using a composite with iron magnetic nanoparticles and MWCNTs. They found that in weakly alkaline conditions, the process works optimally, influencing the adsorption of the dye by pH. The results of the kinetic analysis showed that the adsorption process followed the pseudo-second-order kinetic model and matched the Dubinin–Radushkevich model well, suggesting a mix of chemical and physical interactions [54]. The functional groups on the surface of MWCNTs may be protonated or deprotonated depending on pH, which will alter the ionization levels and, in turn, the adsorption capacity. Significantly, the CNTs' surface charge increased in the alkaline solution, encouraging electrostatic interactions with the cationic dye [54].

4.3. Adsorption and Active Sites in Carbon Nanotubes

The adsorption of organic molecules on CNTs is based on non-covalent interactions, such as van der Waals forces, π-π bonds, hydrogen bonds, electrostatic forces, and hydrophobic interactions; this allows an efficient capture of molecules on the nanotube surface. In addition, functional groups on the surface of CNTs can further enhance the adsorption capacity through specific chemical interactions [6,55]. Adsorption of contaminants occurs on the walls of the CNTs and the interstitial spaces between the nanotubes [6]. Li et al. evaluated the adsorption capacity of MB on activated carbon, graphene oxide, and CNTs. The BET surface area-normalized adsorption capacity is 7.50, 1.23, and 0.16 mg/m^2, respectively. This led them to conclude that the adsorption of MB was due not only to the surface area of the materials, but also to the π-π electron–donor–acceptor interactions and electrostatic attraction between positively charged dye ions and negatively charged adsorbents [55].

5. Photocatalysis for the Degradation of Contaminants

Photocatalysis consists of the direct or indirect absorption by a semiconductor solid of light, visible, or UV photons to destroy contaminants using ultraviolet solar radiation and catalysts to form hydroxyl radicals, which will subsequently have an oxidizing effect on chemical pollutants, as seen in Figure 2. Photocatalysis is an advanced oxidation process that consists of the acceleration of a photoreaction through the presence of a catalyst. It is activated by the absorption of light, accelerating the process. The catalyst interacts with the pollutant through its excited state (C^*) or by the appearance of electron–hole pairs, as described by Equation (1) [56].

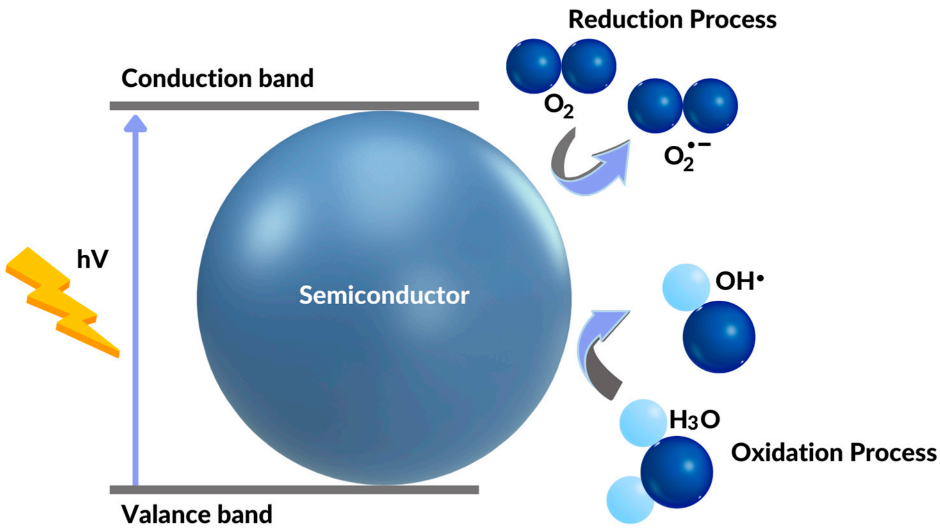


Figure 2. Photocatalysis process.

Subsequently, the excited electrons transfer to the reducible species. Next the catalyst accepts electrons from the oxidizable species occupying the gaps. The consequence is a zero flow of electrons, and the catalyst is not altered. Photocatalytic activity is also the property of a solid material induced by the irradiation of photons with an energy equal to or greater than the energy of the material's bandgap on its surface, which causes electrons in the valence band to be excited into the conduction band, leaving holes in the valence band. In this way, electron–hole pairs called excitons are generated, and they are used to carry out redox reactions. C is the catalyst, R is the reducible species, P is the products, and * is an oxidated state [56,57].

$$C\ hv \rightarrow\ C^* \quad (1)$$

$$C^* + R \rightarrow\ R^* + C \quad (2)$$

$$R^* \rightarrow P \quad (3)$$

$$C\ hv \rightarrow\ C\left(e^- + h^+\right) \quad (4)$$

$$h^+ + Red_2 \rightarrow Ox_2 \quad (5)$$

$$e^- + Ox_1 \rightarrow Red_1 \quad (6)$$

5.1. Electron–Hole Pair Formation in Carbon Nanotubes

The formation and dynamics of a charge pair is a fundamental key piece that determines the photocatalytic process efficiency. In the context of CNTs, this phenomenon depends on the adsorption of photons on their surface for the generation of electron–hole pairs. Once the pairs are separated and excited, they participate in redox reaction for further pollutant degradation. This study focuses on the photocatalytic properties of CNTs in the context of dye degradation; however, the understanding of charge pair formation is foundational. This concept should be addressed in a recent study by Xue et al., highlighting the significance of charge pair dynamics in photoresponsive systems [58].

5.2. Photodegradation of Methylene Blue in Carbon Nanotubes

CNTs are known for their large specific surface area, high-quality active sites, and their high electrical conductivity. Due to their conductivity, CNTs are acceptors of photogenerated electrons and can act as an effective electron transfer unit. Therefore, when the organic contaminant, dye, is adsorbed on the surface of the CNTs and irradiated with (ultraviolet/visible) light, the photodegradation of the organic contaminant (dye) found on the CNT surface begins. The oxygen molecules adsorbed on the CNTs react with the electrons, forming a very reactive superoxide radical ion ($O_2^{\bullet-}$) [59] that oxidizes the dye, and the holes (h^+) are responsible for oxidizing the hydroxyl groups to form a hydroxyl radical ($OH^\bullet$) [60] which can decompose the organic contaminant, such as MB.

Due to their graphitic structure, CNTs, which contribute to the existence of π and dipole–dipole interactions, SWCNTs, and MWCNTs may have photocatalytic properties. These properties will help to promote the formation of active species that will eventually result in the photocatalytic degradation of the organic dye [27]. Figure 3 presents a schematic for MB photodegradation, based on previous works [27,61]. Figure 3a exhibits the sp^2 surface structure of SWCNTs or MWCNTs. Figure 3b represents the dye adsorption by $\pi - \pi$ interactions. After that, if the catalyst surface ($CS - sp^2$ surface structure of SWCNTs or MWCNTs) irradiates with UV light, it absorbs the photons (Figure 3b). The photon absorption produces electron–hole pairs described by the next equation, where CS is the catalyst surface, hv is the light energy, h^+ is the positive hole, and e^- is the electron:

$$CS + hv \rightarrow h^+ + e^-. \quad (7)$$

The hydroxyl radical ($OH^\bullet$) forms due to positive holes reacting with water molecules (H_2O) adsorbed on the surface catalyst, which is followed by the reaction in the next equation, resulting in H^+ protons after the reaction:

$$CS\left(h^+\right) + H_2O \rightarrow CS + H^+ + OH^\bullet. \quad (8)$$

The superoxide radical anions ($O_2^{\bullet -}$) form because of the reaction of electrons with the molecular oxygen dissolved in the MB solution:

$$CS(e^-) + O_2 \rightarrow \text{MWCNT(SWCNT)} + O_2^{\bullet -}. \quad (9)$$

And the hydroperoxyl radical ($HO_2^{\bullet}$) forms when the superoxide radical anion reacts with a H^+ proton, as follows:

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^{\bullet}. \quad (10)$$

Those formed radicals, $OH^{\bullet}$, $O_2^{\bullet -}$, and $HO_2^{\bullet}$, react with MB molecule adsorbed on the sp^2 lattice of CNTs, causing the decomposition of the dye.

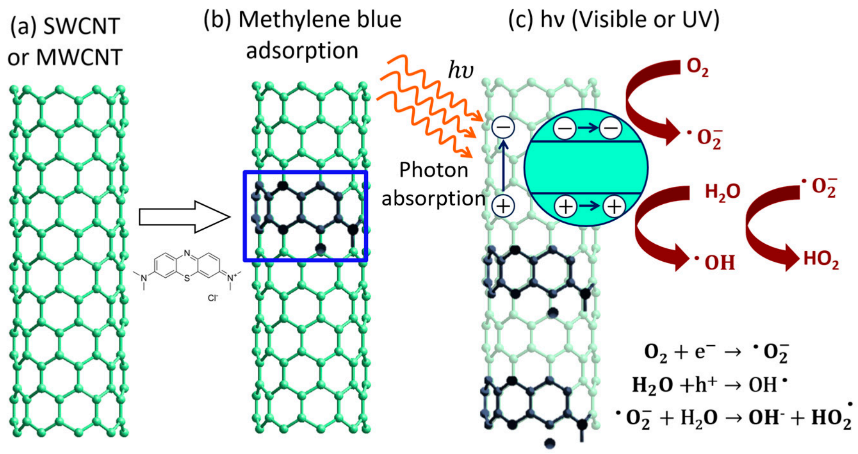


Figure 3. (**a**) Schematics for the surface of carbon nanotube (SWCNT or MWCNT). (**b**) Adsorption of MB on the surface of CNTs. (**c**) Photocatalytic degradation process of MB by the reaction with hydroxyl radicals ($OH^{\bullet}$), superoxide radical anions ($O_2^{\bullet -}$), and hydroperoxyl radicals ($HO_2^{\bullet}$).

Simple and less complex compounds result after the photodegradation of MB; such compounds depend on the photocatalyst and the employed conditions. The route for degradation ends in small molecular fragments by the breaking down of the aromatic structure of the dye. Depending on the level of degradation, different intermediate compounds like aliphatic compounds, aromatic fragments, and possibly carbon dioxide could be the final products. To understand the degradation of MB, Huas et al. explained the photodegradation and transformation into toxic subproducts [62]. The intermediate products in Figure 4, generated during the degradation process and analyzed by gas chromatography-mass spectrometry and liquid chromatography-mass spectrometry, are toxic. The main disadvantage of photocatalysis is that the intermediate and final products are toxic.

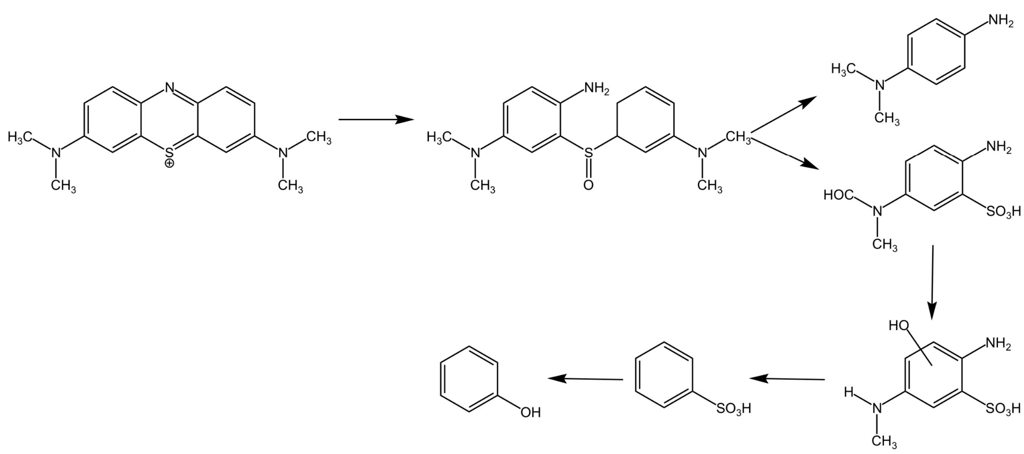


Figure 4. Proposed methylene blue degradation mechanism.

Figure 5 presents an example of the disappearance kinetics of MB, with an adsorption period in the dark of 90 minutes [62]. Kinetics follows an apparent first order, like the Langmuir–Hinshelwood mechanism [63], with a rate (r) proportional to the fraction of the adsorbent surface covered by adsorbate (θ), which becomes proportional to C at low concentrations:

$$r = k\theta = \frac{kKC}{1+KC} \approx kKC = k_{app}C \quad (11)$$

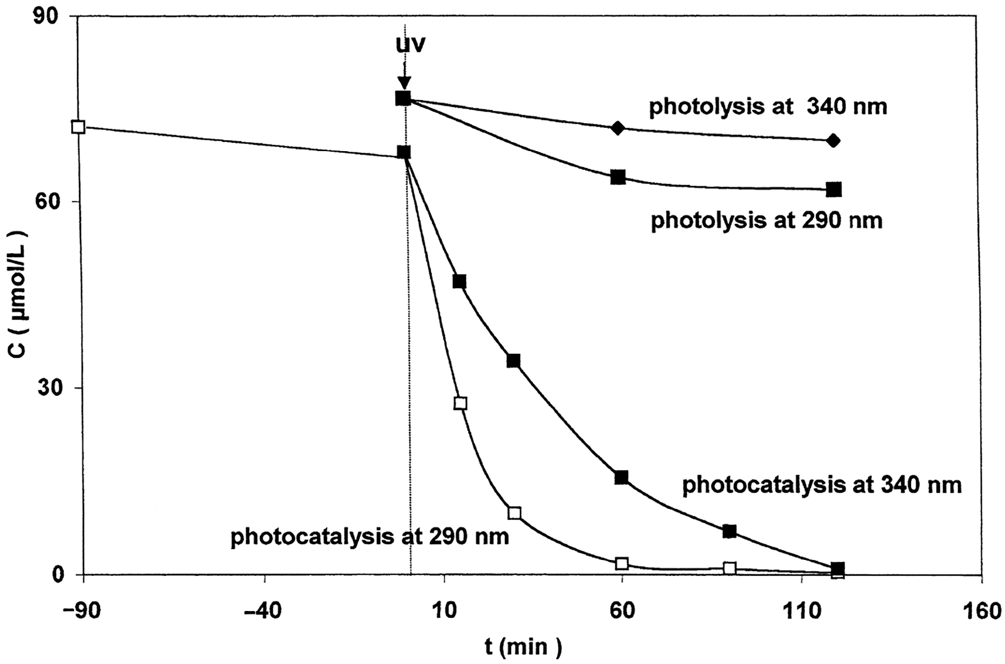


Figure 5. Disappearance of MB by photochemical irradiation and photocatalysis under UV radiation at λ = 290 nm and λ = 340 nm. (Reproduced with permission from Houas A. et al., Appl Catal B, Elsevier, 2001 [62]).

The total disappearance of MB in this example required 60 to 120 minutes for $\lambda \geq 290$ and $\lambda \geq 340$ nm, respectively.

5.3. Synergistic Effects in Combined Systems

Different hybrid structures with nanoparticles and nanocomposites based on CNTs have been obtained by various synthesis techniques and for several applications. One-dimensional nanostructures such as CNTs disperse easily by mechanical stretching, electrical fields, magnetic fields, and spinning techniques. Due to their excellent electrical, mechanical, thermal, and optical properties and high chemical resistance, CNTs and graphene are ideal candidates to support materials such as nanoparticles of Pt, Au, Ag, etc., metal oxide semiconductor materials, etc. [64]. Feng et al. reported that the SnO_2-CNT composite improves the catalytic activity of pure SnO_2 and CNTs due to the synergistic effect between these materials. The CNTs provide a three-dimensional structure and high electrical conductivity, while SnO_2 contributes to the catalytic active sites, thus improving catalyst efficiency [65]. David et al. reported the production of hybrid materials based on MWCNTs and different types of NP, such as ZnO, Ag, etc., with antimicrobial properties to improve antimicrobial activity. This research showed that the NP attached and aggregated to the surface of MWCNTs was indicative of their supporting role as a center for cluster deposition [66]. Warsi et al. investigated the synthesis of photocatalytic materials using a simple wet redox method. The resulting materials were the MnO_2/CNTs hybrid structure and the Al-doped MnO_2/CNTs hybrid structure used for the photodegradation of MB. Their results showed that their doped hybrid architecture enhanced the photocatalytic efficiency compared to MnO_2 and Al-doped MnO_2; this behavior is due to a larger surface area and better contact between CNTs and MnO_2 nanomaterials. However, they also found that the photodegradation efficiency of the hybrid structure of doped MnO_2/CNTs nanomaterials decreased when various scavengers (ethylenediaminetetraacetic, ascorbic acid, silver nitrate, etc.) of different intermediates were applied [67].

6. Bibliometric Study and Review

Bibliometrics is a tool for evaluating and analyzing scientific production or the number of publications. The principal indicators are the productivity of authors, publishing institutions and places of publication, topics of interest, and citation analysis and impact indices [68]. Bibliometrix by RStudio was used for the bibliometric study. Bibliometrix is a package for the statistical programming language R for quantitative research in scientometrics and bibliometrics. For this research, we import bibliographic data from PubMed. The file (.txt) was downloaded for analysis in Rstudio. This bibliometric study has allowed us to obtain and analyze scientific maps and bibliometric parameters that allow us to determine the evolution of the topics over time, and the related words of major relevance led to refining the study. From the information obtained from the Connected Papers tool, we produced a graph that relates the articles [69]. Finally, an analysis of the data obtained was carried out to find the relationships with current relevant issues, such as the application of nanotechnology for environmental remediation.

6.1. Methodology

A systematic review was carried out, with a search period that includes from 2001 to August 2023, of documents of scientific studies focused on the science of bibliometrics, in addition to a systemic review of the topic to be studied. The search in PubMed included Books and Documents, Review, and Systematic Review for the search “Photocatalysis” and “Photocatalysis and visible light”. And for the subsequent searches, “(carbon nanotubes or CNT) and (methylene blue)”, “(carbon nanotubes or CNT) and photocatalysis”, we considered all documents.

6.1.1. Search Strategy

First, a PubMed search was conducted for documents within the established topics with the established date limits, and without restriction of language or country of publication. Subsequently, a similar search was carried out in Google Scholar, complying with the same characteristics. Regarding the inclusion and exclusion criteria used in this analysis, the relationship of the document to organic inks, methylene blue, and their removal for the search for environmental remediation was raised as a requirement, in addition to the use of CNTs for the purpose of measuring their capacity as an adsorbent. From the reading and analysis of the downloaded documents, articles that presented some relationship with the established search topics and words were selected, in addition to meeting the criteria. The bibliographic references of the selected articles were also analyzed to compile other documents that were presented as derivatives.

6.1.2. Data Extraction and Analysis

The initial search for “Photocatalysis” and “Photocatalysis and visible light” indicated the trend of the subject over the last year. After that, search of the words “(carbon nanotubes or CNT) and (methylene blue)” yielded 219 results related to the topics. To evaluate the historical and current trends of searches on biodegradation and photocatalytic degradation of organic pollutants, bibliometric analysis with RStudio allowed us to obtain the bibliometric indicators. Bibliometric methods primarily involved various statistical literature counting techniques to evaluate and enumerate the development of the literature in the context of a particular topic [68]. Here we explored the development time of the published literature on the photocatalytic degradation of organic pollutants. Also, we determined the distribution by country of research on the subject and studied its relationship with social and economic factors. We identified the most relevant journals or journals that were dedicated to a considerable portion of the literature on the topic of interest. The combined keywords for the search using Boolean operators were "(carbon nanotubes or CNT) and (methylene blue)" and "(carbon nanotubes or CNT) and (photocatalysis)". The specific keywords were "chemistry of carbon nanotubes", "adsorption", "chemistry of methylene blue", "electrodes", and "humans". From these keywords, the articles were obtained from which we derived the specific information on the topic proposed in this work.

6.2. Results of the Bibliometric Study

6.2.1. Search "Photocatalysis" and "Photocatalysis and Visible Light"

Figure 6 shows the growth of research by the increase in the number of research documents about "Photocatalysis" and "Photocatalysis and visible light" during the last 20 years. The interest in photocatalysis became noticeable in 1972 due to the discovery of photo-assisted electrochemical hydrolysis of water with a monocrystal of TiO_2 as a working electrode and a platinum counter electrode under the application of a chemical or electrochemical potential [70]. Studies of carbon nanomaterials such as photocatalysts exhibited CNTs with high photocatalytic activity in the degradation of organic dyes due to their semiconducting nature and the formation of electron–hole pairs, so they are a viable option for this analysis [2,27,71]. Among these carbon nanomaterials are the three-dimensional carbon nanostructures of interest reported, such as graphene oxide and reduced graphene oxide platelets pillared with CNTs [72]. CNTs/catalyst nanocomposites have received a lot of interest due to the inherent properties thanks to the incorporation of CNTs into the composite, such as the enhancement of the photocatalytic activity of metal oxides [73,74].

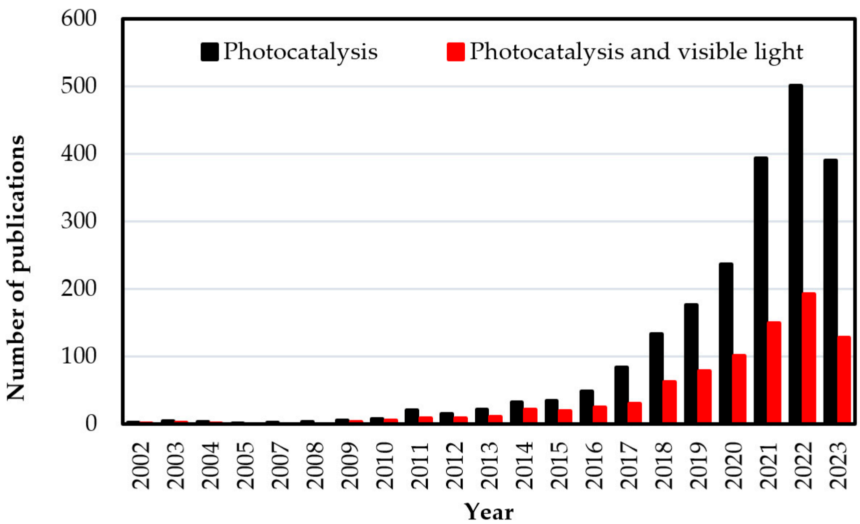


Figure 6. Number of publications on the topics "Photocatalysis" and "Photocatalysis and visible light" on PubMed.

6.2.2. Search "(Carbon Nanotubes or CNT) and (Methylene Blue)"

The first PubMed search of the words "(carbon nanotubes or CNT) and (methylene blue)" yielded 227 results related to the topics. Figure 7a shows the number of publications focused on the adsorption or degradation of MB in the last twenty years. This graph presents an increasing tendency of the number of articles over time. Most of these articles come from five countries, and a relationship between parameters and social situations is observed. The countries presented in Figure 7b that have a high scientific production concerning CNTs and MB are China (60%), Iran (9%), India (6%), South Korea (6%), the USA (5%), and Malaysia (7%). Another parameter that helps us to describe the publications and group them is the journals published in these 219 results. Figure 7c presents the ten most frequent sources with three principals: Biosensors & Bioelectronics with 21 articles, Journal of Hazardous Materials with 12 documents, and Talanta with 11 publications.

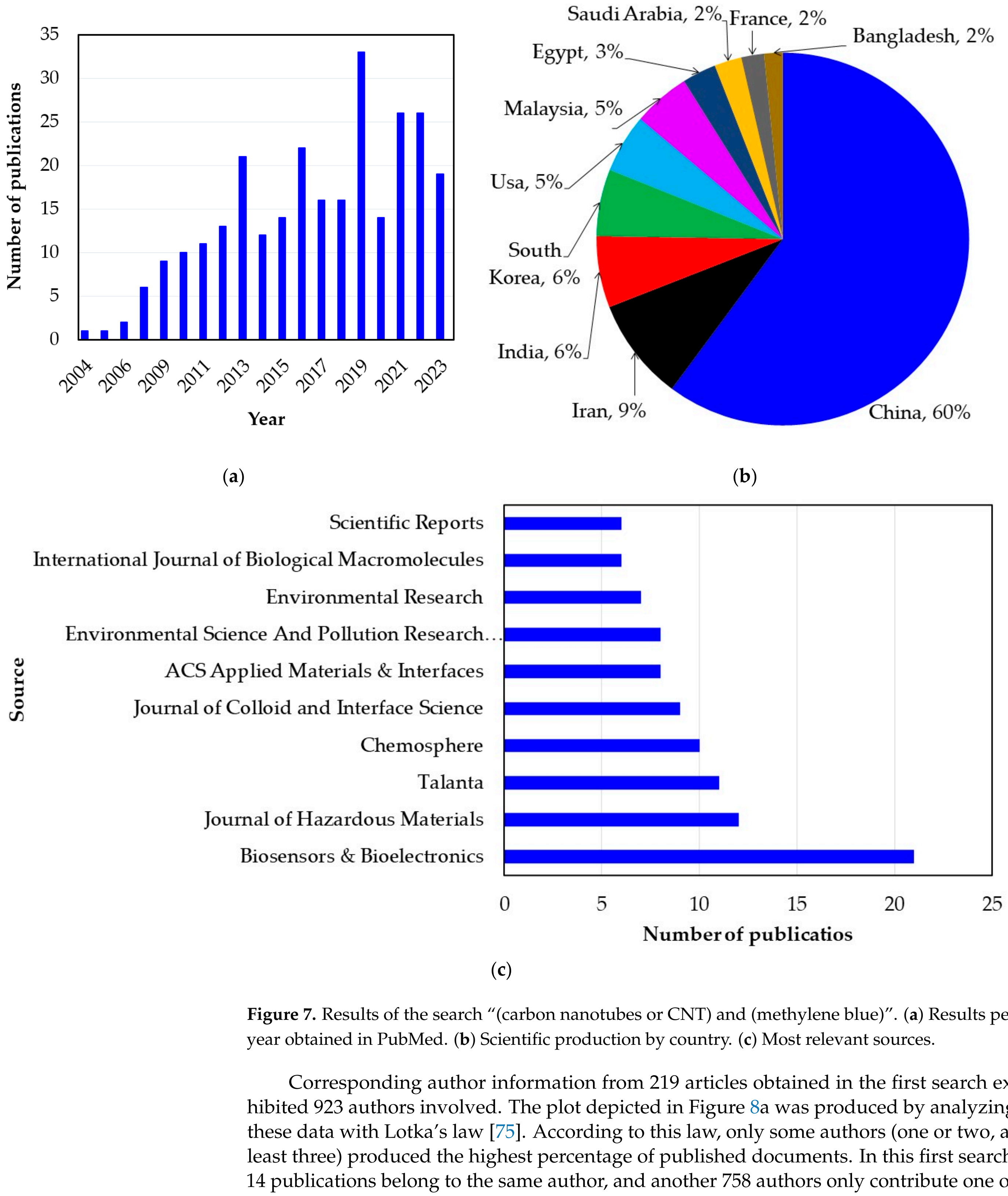
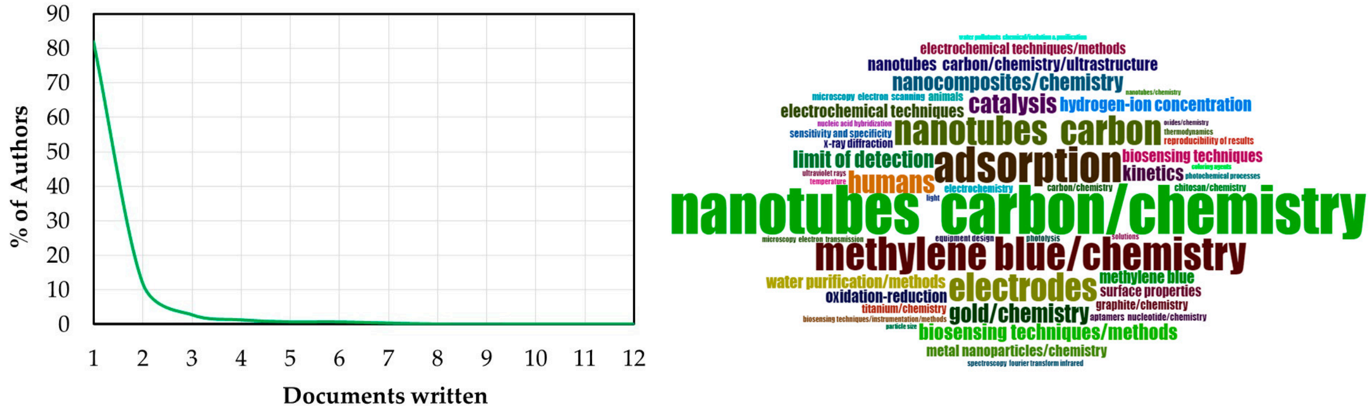


Figure 7. Results of the search "(carbon nanotubes or CNT) and (methylene blue)". (**a**) Results per year obtained in PubMed. (**b**) Scientific production by country. (**c**) Most relevant sources.

Corresponding author information from 219 articles obtained in the first search exhibited 923 authors involved. The plot depicted in Figure 8a was produced by analyzing these data with Lotka's law [75]. According to this law, only some authors (one or two, at least three) produced the highest percentage of published documents. In this first search, 14 publications belong to the same author, and another 758 authors only contribute one of them. The relationship between articles from this first search gave the documents the maximum relation with the established words and the selected topic. The analysis performed with the Connected Papers tool helped to establish the inclusion and exclusion criteria. The information selection was carried out after reading the articles with the help of the information obtained in the first analysis and the inclusion and exclusion criteria. This tool revealed many publications related to the first search and organized them according to their similarity. That means that even articles that do not directly cite each other are connected and positioned very closely. In addition, it allows us to follow up on relevant documents. Co-citation and bibliographic coupling principles are the foundation for the similarity metrics employed by the criteria. By this measure, two articles with highly overlapping citations and references have a higher chance of dealing with a related topic. From these criteria, we obtain more documents than with the same established strategy, which leads to the second selection of articles.



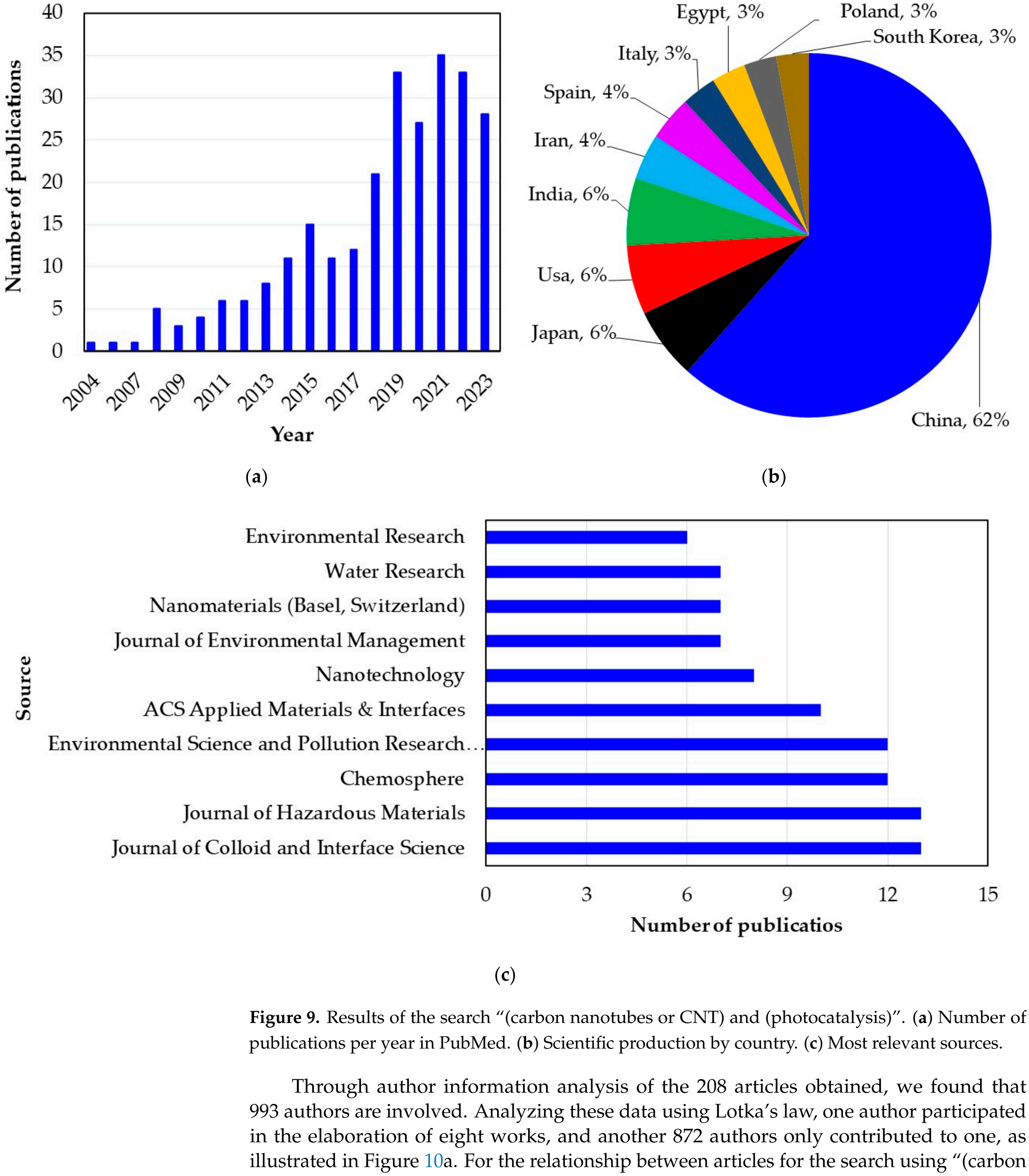
(**a**) (**b**)

Figure 8. (**a**) Lotka's law applied to the search "(carbon nanotubes or CNT) and (methylene blue)". (**b**) Word cloud originated from the same search through the tools RStudio and Biblioshiny.

The analysis in Bibliometrix returned the most frequent keywords in the documents and generated maps or word clouds, detecting trending research topics. The words presented in Figure 8b were derived from the first search and the first proposed keywords to specialize the search. In addition, bibliometric keyword analysis can answer several interesting questions, such as search-related research topics, most frequent or popular ones, and relevance over time. In this first search, the five most relevant words are the highest and bolded in the word cloud of Figure 8b. They are nanotubes carbon/chemistry, adsorption, methylene blue/chemistry, electrodes, carbon, nanotubes, and humans. These searches and words allowed future findings and requirements for the selection of relevant articles.

6.2.3. Search "(Carbon Nanotubes or CNT) and (Photocatalysis)"

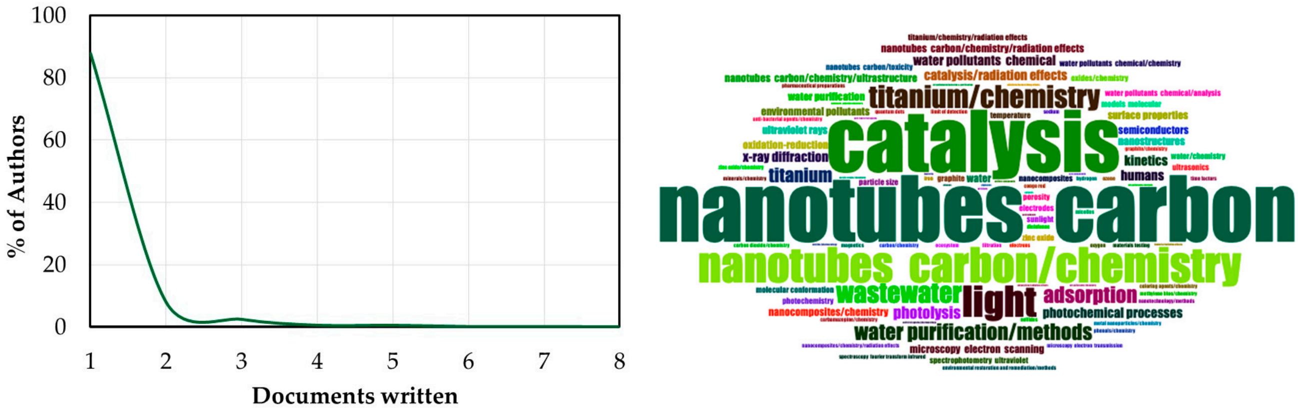
The second search using "(carbon nanotubes or CNT) and (photocatalysis)" yielded 208 results related to the topic, considering articles from October 2001 to August 2023. Figure 9a presents the number of articles over time; the number of documents increases with the passage of time. The keywords for this search determined the posterior analysis and are independent of those obtained in the previous search. Most of these articles come from six countries, allowing a relationship with parameters and social situations later. The countries in Figure 9b with the highest scientific output in this search are China (62%), Japan (6%), the USA (6%), India (6%), Iran (4%), and Spain (4%). Figure 9c presents the ten fundamental sources, showing that the five principals were the Journal of Colloid and Interface Science with 13 articles, Journal of Hazardous Materials with 13 documents, Chemosphere with 12 publications, Environmental Science and Pollution Research International with 12, and ACS Applied Materials & Interfaces with 10 publications.



(**a**) (**b**) (**c**)

Figure 9. Results of the search "(carbon nanotubes or CNT) and (photocatalysis)". (**a**) Number of publications per year in PubMed. (**b**) Scientific production by country. (**c**) Most relevant sources.

Through author information analysis of the 208 articles obtained, we found that 993 authors are involved. Analyzing these data using Lotka's law, one author participated in the elaboration of eight works, and another 872 authors only contributed to one, as illustrated in Figure 10a. For the relationship between articles for the search using "(carbon nanotubes or CNT) and (photocatalysis)", the texts with more relevance were selected. This selection occurred after reading the documents following the inclusion and exclusion criteria, elaborating on the correlation between articles. The inclusion and exclusion criteria allowed us to collect more information and start seeing an association with other areas. The outstanding word analysis functioned by applying bibliometrics to keywords presented in Figure 10b, detecting the trend of research topics related to carbon nanotubes and photocatalysis. From these words, the connection between the principal theme and social issues of current relevance, such as the importance of environmental remediation and water purification methods, could be determined. Among these words, the most relevant are catalysis, nanotubes, carbon, carbon nanotubes/chemistry, and light.



(**a**) (**b**)

Figure 10. (**a**) Lotka's law applied to the search for "(carbon nanotubes or CNT) and (photocatalysis)". (**b**) Word cloud obtained in the same search.

6.2.4. Analysis of the Data

Analyzing the data established in the previous searches showed relevant characteristics and changes in the results. The search carried out in 2020 with the words "(carbon nanotubes or CNT) and (methylene blue)" provided 163 articles, while in 2023, the search gave 219, showing an increasing trend line. By the year 2023, we find an increase in the scientific production of the topics of carbon nanotubes and organic inks, as well as environmental remediation and water remediation, illustrated in Figure 11. Through the Connected Papers tool, the link between the words "environmental remediation", "water remediation", and "methylene blue" showed that this dye and others with a similar organic nature are useful for other environmental strategies. Therefore, the expected trend should be an even more noticeable increase in scientific production about environmental remediation and the removal of these inks. Another interesting parameter is the scientific production by country. When establishing the correlation with the principal textile-producing countries, it was found that the main ones in both areas coincide with China.

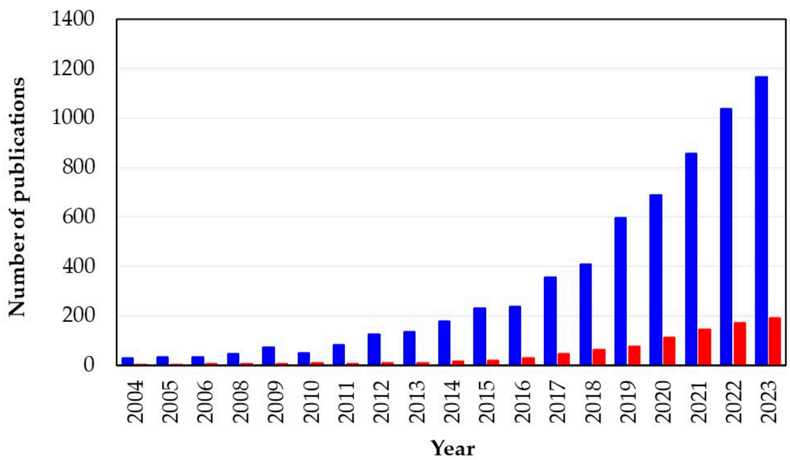


Figure 11. Results by year of the search: "water remediation" (in blue) and "environmental remediation" (in red). In both cases, we see an increase for the year 2023.

6.3. Advances in Adsorption and Carbon Nanotubes

Based on the information obtained in the bibliometric study, Table 3 summarizes the selection of the articles that presented the most cited research and the most relevant current research in the removal and adsorption of dyes with CNTs, some of them functionalized or forming a composite. The table is organized by the adsorbent material, the surface area (S_{BET} m^2/g), the Pore-Volume (cm^3/g), adsorption capacity (mg/g), dye concentration (mg/L), catalyst dosage (mg/L), removal efficiency (%), reference, and year. The composite Fe_3O_4-MWCNT-bentonite [8] and MWCNTs [54] exhibited superior surface area, with values of 204.1 m^2/g and 177 m^2/g, respectively. However, the highest adsorption capacity proved to be 603 mg/g for MWCNT with β-Cyclodextrin and chitosan composite due to the strong π-π interaction between MB and sp^2 lattice, and because of the enhanced adsorption capacity attributed to the functionalization [76]. The increased surface area and 100% removal efficiency of Fe_3O_4-MWCNT-bentonite composite revealed the importance of the synergistic effect of combined systems with CNTs [8].

Table 3. Resume of relevant applications to adsorption of MB between different CNTs compared with graphene oxide, activated carbon, and carbon nanospheres.

Adsorbent Material	Surface Area (S_{BET} m^2/g)	Pore-Volume (cm^3/g)	Adsorption Capacity (mg/g)	Reaction Conditions		Removal Efficiency (%)	Ref. Year
				Dye concentration (mg/L)	Catalyst Dosage (mg/L)		
Fe_3O_4-MWCNTs-bentonite	204.01	0.367	48.2	10	0.3	100.0	[8] 2009
Purified CNTs	160.00	0.67	35.4–64.7	5–40	0.3	---	[52] 2010
MWCNTs	177.00	0.54	188.68	40–120	0.5	82.70	[54] 2012
β-Cyclodextrin/ MWCNTs/Chitosan	98.23	---	603	23.00	---	96.75	[76] 2020
Functionalized MWCNTs	---	---	440	10–300	0.5	99.10	[77] 2020
PET-MWCNTs	---	---	7.047	34–37	34–37	71.01	[73] 2022
Gel MWCNTs composite	19.00	~0.3	106	100	0.5	81.00	[74] 2022
Nitric acid /MWCNTs	65.77	0.321	288.65	50	1000	95.18	[78] 2022
Acrylic acid/MWCNTs	---	---	329.8	50	16.66	---	[79] 2023

6.4. Advances in Photocatalysis and Carbon Nanotubes

The advances in photocatalysis-integrated CNTs for sustainable and efficient environmental remediation are due to their electronic properties and tunable surface functionality. As mentioned above, CNTs exhibit distinct band structures attributed to chirality control, influencing light absorption and enhancing the absorption spectra. Many reports presented enhanced photocatalysis by modifying the band structure of CNTs by heteroatom doping, by forming composites or anchoring nanoparticles, producing a synergistic effect between CNTs and additional elements [64,65].

The precision of catalytic site localization and dynamic control strategies are topics raised by the advancements in photocatalysis. Dynamic photocatalytic systems respond to external stimuli such as light intensity or electric fields, marking a paradigm shift in the adaptation of catalytic activity on demand. This responsive behavior allows for greater efficiency during specific operating conditions. The design of efficient photocatalysts is facilitated by understanding the interaction of electronic structures and charge transfer processes. As research advances in the improvement of band structure, the introduction of defects, and the dynamics of charge carriers, a new generation of photocatalytic materials with extraordinary capabilities will be generated. Table 4 provides an overview of antecedents and their contributions to these advances in photocatalysis. This table shows some results by year, from 2012 to 2023, showing different CNTs combined with semiconductors to remove MB from water. When combining CNTs with semiconductor, the contaminant removal is superior, independent of the time. In our previous work on nitrogen-doped and undoped CNTs, we showed discolorations of 100% for doped MWCNTs. This result suggests the potential for the use of individual CNTs [27]. However, their combination with semiconductors augments the synergistic effect of the system formed under photocatalysis.

Because we can control whether the CNT is metallic or semiconducting during fabrication, doping the CNTs with electron-rich oxygen functional groups or nitrogen alters the gap of sp^2, promoting electron–hole recombination [27]. CNTs are great catalyst support materials because of their characteristics, such as a wide surface area, and because they help to prevent charge recombination. For example, Liu et al. synthesized a non-metal photocatalyst nitrogen-doped CNT for photocatalytic degradation of organic dye [80].

Table 4. Relevant investigation of MB and photocatalysis on different CNTs.

CNTs/Semiconductor	% Removal Contaminant				Ref. Year
	Semiconductor (%)	Conditions/ Time (min)	CNTs/Semiconductor (%)	Light/ Time (min)	
MWCNTs/ZnO	68.0	UV light/ 30	98	UV light/ 30	[81] 2012
Carbon xerogel/CNTs/Ti	90 (CX/CNT)	Visible light/ 60	99	Visible light/ 60	[82] 2019
Magnetic MWCNTs/cerium dioxide (MWCNTs-CeO_2)	82.2	Visible light/ 120	97.5	Visible light/ 120	[83] 2019
SWCNTs/HgS	73	Sunlight/ 180	99.08	Sunlight/ 180	[84] 2019
Al doped MnO_2/CNTs	24	Solar light/ 75	88	Solar light/ 75	[67] 2020
CNTs-CuO	~60.0	In dark/ 60	92.0	Visible light/ 60	[85] 2021
Undoped-MWCNTs N doped MWCNTs	99.0 (Undoped)	UV light/ 60	100.0 (N-doped)	UV light/ 60	[27] 2021
Polystyrene-NiO-CNTs	81	UV light/ 250	96	UV light/ 250	[86] 2022
CNTs@$CuBi_2O_4$/$AgBiO_3$	-	-	97.94	Visible light/ 60	[87] 2022
Ag/TiO_2/CNTs	89.8 (TiO_2/CNT)	UV light/ 50	96	UV light/ 50	[88] 2022
MWCNTs/ Zeolite	65.0	In dark/ 210	98.0	Sunlight/ 210	[89] 2023
nS-SnS/Poly(CC-co-BP)-CNTs	95	UV light (254 nm)/ 120	100	UV light (254 nm)/ 60	[90] 2023

7. Discussion

Employing cutting-edge carbon-based materials as catalysts is fundamental in chemical and materials engineering research for efficient visible-light-induced catalytic applications. CNTs are capable of being used in water treatment because of their unique thermal and electronic characteristics [13]. The engineering aspects play a fundamental role in considering the exceptional properties of CNTs for practical applications in photocatalysis. The engineering considerations we consider to be relevant for exploiting CNTs in photocatalytic applications would be as follows. (i) The synthesis of CNTs, considering them as photocatalysts, requires structural control of morphology, chirality, and dimensions to optimize their electronic structure and enhance photocatalytic activity. Doping may improve the reactivity and selectivity of target pollutants. Composite design with other semiconductors or catalysts may create synergistic effects. (ii) It is crucial to tune the optical properties of CNTs to maximize light absorption in the UV and visible spectrum. (iii) It is important to separate and transport photogenerated electrons and holes, reduce recombination rates, and facilitate charge transfer by inducing interfaces in composites of CNTs with other semiconductors. (iv) Under light and reactive environments, it is crucial to ensure the stability of CNT-based photocatalysts; for this aspect, coatings or modifications may be an alternative to prevent degradation and enhance durability. (v) For application in realistic conditions, there are some aspects to consider, such as upscaling, environmental impact of CNTs, cost–benefit analysis to evaluate the economic viability of CNT-based photocatalysis, and compliance with safety standards and regulations in handling and CNT applications.

7.1. Safety and Environmental Impact of Byproducts

This section addresses environmental and safety considerations associated with byproducts resulting from adsorption and photocatalytic degradation of MB using CNTs. The review of these byproducts serves to understand the risks and ecological impact of photocatalysis to examine the safety implications and environmental consequences. This section reviews the byproducts concerning their toxicity, persistence, and further implications for environmental sustainability.

The main objective of photocatalysis is the formation of less toxic byproducts than the original molecule; however, byproducts are not always innocuous [91–94]. The formation of toxic byproducts during photocatalytic degradation can be a problem, which is why the implementation of strategies is required to identify the reaction mechanisms and intermediates generated during the degradation process and avoid the formation of toxic substances. Given the diverse characteristics of environmental matrices, each system optimization requires pilot-scale studies.

7.2. Future Directions

The adsorption and photocatalysis of contaminants on CNTs are subjects with significant advances in recent years, offering sustainable and efficient approaches for environmental remediation. In particular, the interaction between CNTs and MB, a representative organic dye used as a contaminant model, has become of research interest due to its relevance in water treatment and water management.

The adsorption and photocatalytic degradation of dyes on carbon nanotubes, particularly MB, still faces several challenges. In addition to the adsorption capabilities and removal efficiency of CNTs, it is necessary to improve their photocatalytic activity. Among the different factors that influence the photocatalytic performance of CNTs, doping with rare earth cations, changes in the synthesis conditions, and new nanocomposites can be promising alternatives. In addition to dyes, heterogeneous photocatalysis must extend to the absorption and degradation of emergent organic compounds and other harmful pollutants in environmental compartments. Accordingly, the efforts must focus on the chemical structure elucidation of degradation subproducts. Its risk and toxicity need assessment and consideration as quality control during the development of the method to avoid their disposal to the environment because several of them could be dangerous to biota and human health.

8. Conclusions

This work mainly provides an overview and a bibliometric evaluation of the adsorption and photodegradation of organic dyes, using MB as a model, to trace historical and current trends in research on the effect that these dyes have on the environment, their removal, and degradation using nanomaterials to meet this objective.

The study of MB in this work represented a case study for presenting the degradation process by the reaction pathway and the resulting byproducts generated during the photocatalysis reaction considering the existing research literature. The interest of studying this dye focuses on the comprehensive analysis of a recalcitrant model pollutant with real-world relevance.

This study observed that, although the research results on the photodegradation of dyes in carbon nanomaterials show an increasing trend, we find that most of this research mainly concentrates on three countries, with China being the main one, demonstrating that although research on this topic is relevant today, there is a large gap between these countries and the rest, which should lead us as a scientific community to a greater interest in the subject, since the pollution caused by these dyes represents a health problem.

On the other hand, when analyzing the information collected, we find encouraging results that allow us to see that MB and organic inks, in general, can be removed and degraded with the mechanism proposed with high effectiveness, using CNTs as photocatalysts, and that these have advantages over other materials.

This work discussed the interaction between MB and CNTs in the adsorption and photodegradation processes. We examined the environmental and safety considerations from the generation of byproducts during these treatments. The findings reveal the importance of assessing the toxicity and persistence of these byproducts, emphasizing the need for comprehensive risk assessments. Safety concerns associated with CNT inhalation risks, skin contact, and potential environmental impact require safety measures during synthesis, handling, and application.

This study continues research to resolve the effects and long-term behavior of methylene byproducts, contributing to the development of sustainable and safe nanomaterial application. In summary, while CNTs show efficient removal of MB, it is necessary to ensure worker safety, prevent environmental contamination, and find a way for the responsible application of these nanomaterials in environmental remediation. This work leaves an open perspective, integrating safety, regulations, and environmental impact assessments to continue developing nanotechnology for water treatment.

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