**MULTIFERROIC-BASED PHOTOCATALYSIS FOR THE TREATMENT OF WASTEWATER**

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**Abstract**

Multiferroic-based photocatalysis presents a promising avenue for wastewater treatment, leveraging materials with coupled ferroelectric and magnetic properties. This innovative approach combines the benefits of traditional photocatalysis with the unique attributes of multiferroic materials, enhancing the efficiency of pollutant degradation. By harnessing the multifunctional characteristics of these materials, we can create photocatalysts that respond to both light and external magnetic fields, allowing for precise control over catalytic processes. This not only accelerates the degradation of contaminants but also enables the treatment of wastewater in challenging conditions. Multiferroic-based photocatalysis holds great potential for sustainable and efficient wastewater remediation, contributing to environmental preservation and clean water availability.

**Introduction**

Our earth is known as ‘BLUE PLANET’ for the amount of water present on it. But 97% of water present on it is saline and only 3% of its water is fresh water. Now, out of that 3%, only about 1% water is available for drinking and human use, rest of it is present in the form of ice glaciers and ice caps [1]. Water is much needed but scarce natural resource which should be used sustainably. Excessive use of water for agricultural and industrial activities is leading in water scarcity problem. Water conservation is an essential for long-term development and reusing used water is the most effective way to conserve it. Recently, industrial waste effluents are directly dumped into the fresh water [2]. The most effective way to reuse the water and for treatment of waste water is advanced oxidation process (AOP). In this procedure, the oxidation process and specific chemical reactions can eliminate organic contaminants from water [3]. Some AOP’s include radiation, photolysis, photocatalysis, electrochemical oxidation reactions, fenton-based reactions, ozone-based reactions [4]. Among AOP’s, photocatalysis is most beneficial and effective method for detoxification of waste water, which has several benefits, including no secondary pollution, total pollution degradation, and environmental protection [5]. In Photocatalysis, organic waste from water gets degraded into water or CO2 or some other molecules [6].

**The following are the primary characteristics of photocatalytic reactions:**

1. The reactions take place under the influence of light with different wavelength spectrum which has been absorbed by the reactants, and the catalyst acts as a sensitizer [7].
2. The fundamental step is the phototransfer of an electron within a catalyst molecule or its complex with an oxidant [8].
3. Free radicals are the major products of the photocatalytic reaction [9].
4. Redox changes are always taking place in the catalyst, which is regularly updated due to the influence of oxygen and other substances.

As a result, the catalyst with these characteristics is appropriately referred to as a photocatalyst [10].

A **photocatalyst** is a material that absorbs light to increase its energy level and then transfers that energy to a reacting substance to cause a chemical reaction [11].

**Types of Photocatalysis:**

1. **Homogeneous Photocatalysis**
2. **Heterogeneous Photocatalysis [12]**

**(a) Homogeneous Photocatalysis:**

The existence of reactants and photocatalysts in the same phase is known as homogeneous photocatalysis. However, for this process, both the reactant and the photocatalyst is required to be in the gaseous state [13]. Ozone is a well-known example of a homogeneous photocatalyst. The reactive species in this case is the hydroxyl radical (•OH), which is used for a variety of purposes and objectives [14]. This mechanism of hydroxyl radical (•OH) production by ozone can take either of the two paths listed below:

**O3 + hν → O2 + O(1D)**

**O(1D) + H2O → •OH + •OH**

**O(1D) + H2O → H2O2**

**H2O2 + hν → •OH + •OH [15]**

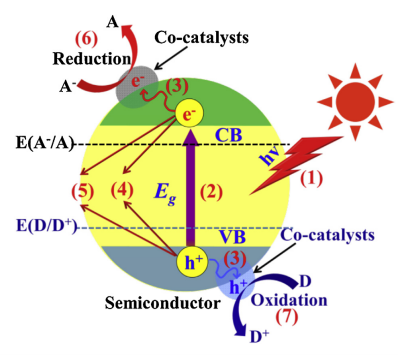
In this method, light sensitivity of up to 450 nanometers is utilized during the photosynthesis process, which spares it from utilising expensive UV lamps [16]. The homogeneous photocatalysis reactions are more practical and cost-effective [17]. It is important to note, however, that this process has a major disadvantage in terms of pH values being low [18]. Ozone and photo-Fenton systems (Fe+ and Fe+/H2O2) are the most commonly used homogeneous photocatalysts [19].

**(B)** **Heterogeneous Photocatalysis:**

**It is another type of photocatalysis in which the reactants and photocatalyst are present in different phase [20].** **A relatively wide range of reactions are involved in heterogeneous photocatalysis, including mild or total oxidation reactions, hydrogen transfer reactions (O2)18-(O2)16 , deuterium-alkane isotopic exchange reactions, metal deposition, water detoxification and gaseous pollutant removal process [21].**

**The following are the steps involved in heterogeneous photocatalysis:**

(i) Light harvesting. (ii) Charge excitation, (iii) Charge separation and transfer (iv) Bulk charge recombination, (v) Surface charge recombination, (vi) Surface reduction reactions and (vii) Surface oxidation reactions [22]. **Figure 1 shows the various process of heterogeneous photocatalysis [23].**

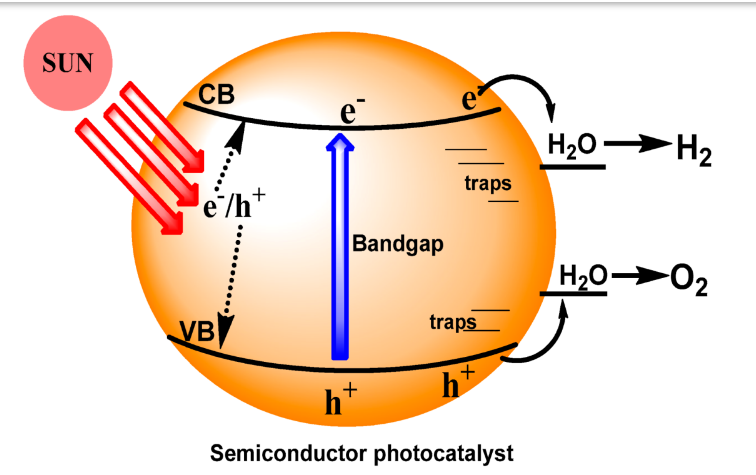


**Fig. 1 The core process of heterogeneous photocatalysis [23]**

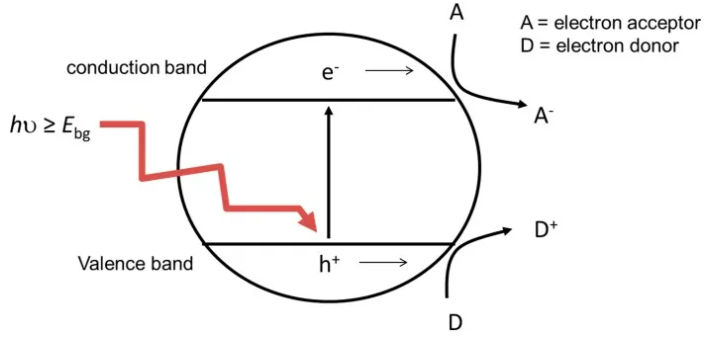
**Importance of Heterogeneous photocatalyst and their basic mechanism:**

The heterogeneous catalysts are crucial in the production of industrial chemicals which were preferred over homogenous catalysts due to their cost effective, robustness and it is easier recovery/separation from the products, which allows chemical processes to be streamlined [24].

During heterogeneous photocatalysis, semiconductor materials absorb the incoming photons. As a result of which, a solid phase gets distributed in contact with a fluid medium and it absorbs a photon to form an electron-hole pair that reduces and oxidises into two corresponding species in the fluid [25]. There are numerous substances that are used as photocatalysts. **The transition metal oxides and semiconductors based photocatalysts are generally utilised by heterogeneous photocatalysis [26]. In contrast to metals, semiconductors generally have ineffective energy zones where these energy levels are not present to develop the re-joining of an electron and a hole produced by light activation in the solid. The band gap is empty and it extends from the top of the filled valence band to the bottom of the empty conduction band [27].**



**A photon with energy equal to or greater than the band gap of the material is absorbed by the semiconductor used in this process, and an electron excites from the valence band to the conduction band, generating a positive (+ve) hole in the valence band [28]. The exciton is a photo-generated electron-hole pair phenomenon.** **The excited electron and hole can recombine and the energy gained when the electron was excited is released as heat [29]. Increased amounts of this undesired exciton and recombination make the process ineffective as a photocatalyst [30].** **Oxidized products are produced by reactions between the holes generated by the reductants. Redox reactions occur at the surface of semiconductors which results in the generation of positive (+) holes and electrons [31].**



**The oxidative reaction mechanism depicts positive holes that react with moisture on the material's (metal oxide) surface to produce a hydroxyl radical (•OH) [32]. This reaction starts with photo-induced exciton generation on the surface of a metal oxide (MO stands for metal oxide, as shown below):**

**MO + hν → MO (h+ + e−)**

Oxidative reactions due to photocatalytic effect are:

**h+ + H2O → H+ + •OH**

**2 h+ + 2 H2O → 2 H+ + H2O2**

**H2O2→ 2 •OH**

Reductive reactions due to photocatalytic effect are:

**e− + O2 → •O2−**

**O2−+ H2O + H+→ H2O2 + O2**

**H2O2 → 2 •OH [33]**

Finally, both of the aforementioned reactions generate hydroxyl radicals (•OH). These hydroxyl radicals (•OH) are extremely oxidative and non-selective, with a redox potential of (E0 = +3.06 V) [34].

Photocatalysts used in waste water treatment include ZnO, ZnS, CdS, SrO2, WO3, and Fe-TiO2 [35]. Due to its stability, low-energy band gap, excellent optical and electronic properties, high photocatalytic activity, high chemical stability, low cost, non-toxicity, and environmental friendliness, Semiconductors has become a promising material that has been widely used in photocatalytic processes [36].

When an ultraviolet light with wavelengths ranging from 200 nm to 400 nm strikes on semiconductor materials, an electron within semiconductor atoms are photoexcited and transferred to the conduction band [37]. Many electron hole (e-h) pairs were formed during this process, which results in a complex   
oxidative-reduction chain [38]. Contrary, an ultraviolet A radiation is only about 5% that of sunlight, implying that sunlight's photon efficiency which is quite low [39].

Hence, as a result, its application on a commercial scale are limited and an ultraviolet lamp is required for semiconductoractivation; sunlight can be added to artificial light sources [40].

**MULTIFERROICS:**

Multiferroics, which concurrently exhibit magnetic and ferroelectric ordering, are a subject of intense research because of their intriguing physics and significant potential for utilization. Multiferroic materials are those that display more than one of the essential ferroic characteristics in the same phase which suggests that multiferroic materials exhibit (anti)ferroelectricity, (anti)ferromagnetism, and/or ferro-elasticity [41].

**Multiferroics of type I and type II:**

D. Khomskii presented a useful classification approach for multiferroics into type-I and type-II multiferroics in 2009 [42].

**TYPE-I:** type-I Multiferroic refers to substances in which ferroelectricity and magnetism emerge at various temperatures with various methods. The magnetic ordering, which is often antiferromagnetic, takes hold at lower temperatures while the structural deformation that gives birth to ferroelectricity typically happens at high temperatures. At the magnetic phase transition, the majority of type-I multiferroics exhibit changes in dielectric susceptibility as well as a linear magnetoelectric response [43].

**TYPE-II:** Materials known as type-II multiferroics are those in which the magnetic ordering directly results in the ferroelectricity and breaks the inversion symmetry. The ordering temperatures for the two events in this type are the same [44].

**MULTIFERROIC MATERIALS USED IN PHOTOCATALYSIS**

The various multiferroic materials used for photocatalysis applications are discussed as under:

1. g-C3N4
2. TbMnO3CeO2
3. TiO2
4. ZnO
5. BiFeO3 [45]
6. **g-C3N4 BASED PHOTOCATALYSIS:**

Heterogeneous photocatalysis, as one of the most appealing and appealing technologies, has been used to directly harvest, transform, and store renewable solar energy for the production of sustainable and green solar fuels as well as a wide range of environmental applications [46]. A wide range of g-C3N4-based photocatalysts have been created to drive various reduction and oxidation reactions under suitable light irradiation due to their unique physicochemical, optical, and electrical features. As a metal-free polymer n-type semiconductor, graphite-like carbon nitride (g-C3N4) has many promising properties, including unique electric, optical, structural, and physiochemical properties, which make g-C3N4-based materials a new class of multifunctional nanoplatforms for electronic, catalytic, and energy applications [47].

g-C3N4 has a moderate band gap of 2.7 eV, equivalent to an optical wavelength of 460 nm, making it visible light active. Taking into account thermodynamic losses and over potentials in the photocatalytic process, the band gap of 2.7 eV accidentally lies between 2 eV and 3.1 eV, achieving both water splitting with sufficient endothermic driving forces (much larger than 1.23 eV) and visible light absorption (much smaller than 3.1 eV). The photo-generated electrons in   
g-C3N4 have a strong thermodynamic driving force that allows them to decrease various small molecules such as H2O, CO2, and O2. As a result, the proper electrical band structures of g-C3N4 make it suitable for a wide range of applications, including photocatalytic water splitting, CO2 reduction, pollutant degradation, organic synthesis, and disinfection.

Apart from the obvious advantage of having a suitable optical band gap and position, it is widely accepted that this metal-free g-C3N4 material also has a stacked 2-D layered structure, in which the single-layer nitrogen hetero-atom substituted graphite nanosheets formed by sp2 hybridization of C and N atoms are bound by van der waals forces [48].

**PHOTOCATALIC DEGRADATION OF POLLUTANTS BY C3N4:**

Serious environmental contamination impedes the human race's long-term growth. Because of its great efficiency and low cost, photocatalysis has proven to be a promising technique for environmental decontamination. When exposed to light, the excited semiconductor can create a significant number of electrons in the Conduction Band and holes in the Valence Band. The photogenerated holes (h+) have a somewhat high oxidation ability due to the band location of g-C3N4. Furthermore, photogenerated electrons can reduce O2 to form •O2-, whereas photogenerated h+ can oxidise OH- to make •OH in some g-C3N4-based heterojunctions. Certain contaminants can be oxidised by these active species (h+, •O2-, and •OH). Photocatalysis has been shown to be effective in the destruction of organic and inorganic air pollutants, poisonous dyes, phenol, and persistent organic micropollutants in water. Yu et al. reported photocatalytic degradation of gas phase formaldehyde using g-C3N4/TiO2. Yan et al. studied the photocatalytic degradation of RhB and MO by B-doped g-C3N4. The active species in photocatalytic degradation reactions vary according to the contaminants. The major active species in photodegradation of RhB was h+, whereas the main active species in photodegradation of MO was •O2-.B-doping can improve dye adsorption and light absorption in g-C3N4, contributing to its strong photocatalytic activity. Because of the high pollutant adsorption and light absorption capabilities of carbon materials, g-C3N4/carbon composite materials are projected to be advantageous for pollutant degradation. Under visible light irradiation, g-C3N4/graphene, g-C3N4/C60, and g-C3N4/carbon spheres have been observed to degrade contaminants.

Furthermore, greater separation of photogenerated charge carriers remains a key feature in photocatalytic pollution degradation. Because of the higher separation efficiency of photogenerated charge carriers, g-C3N4-based type II and Z-scheme heterostructures can significantly improve photocatalytic degradation performance [49].

**DRAWBACKS OF C3N4 BASED PHOTOCATALYSIS:**

However, pristine g-C3N4 has numerous drawbacks, including a narrow visible-light response range, small surface areas, and a low electron-hole pair separation rate. All of these negative conditions limit photocatalytic efficiency greatly (Tan et al. 2021) [50].

**IMPROVEMENT CAN BE DONE BY:**

Various methods have been developed to improve g-C3N4's abilities for light adsorption and electron-hole pair transfer, including morphology control, the introduction of defects, doping with other atoms, and coupling with metal, semiconductor, and carbonaceous materials [51].

**(ii) TbMnO3 AND CeO2 BASED PHOTOCATALYSIS:**

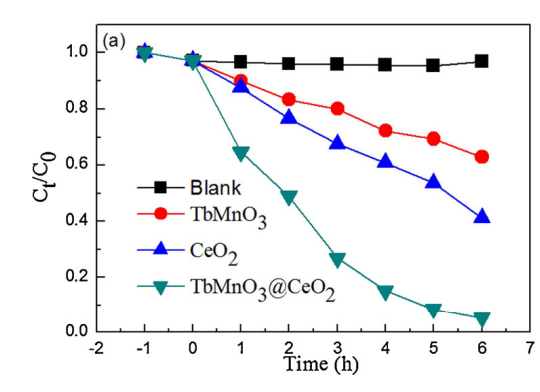
TbMnO3 is a well-known multiferroic material that has numerous applications in data storage and other sectors [52]. Kumar et al. used a hydrothermal technique to create TbMnO3 nanoparticles with strong photocatalytic activity for the breakdown of methyl orange (MO) [53]. According to Jin et al., microwave-assisted TbMnO3 has a strong photocatalytic activity for the degradation of MO [54]. TbMnO3 has a high electron hole pair recombination rate and a poor photon utilization rate as a photocatalyst, hence its photocatalytic activity is relatively modest. As a result, employing another semiconductor oxide to build a heterojunction photocatalyst has significant scientific implications [55].

Cerium oxide (CeO2) is a type of high efficiency photocatalyst that has been widely employed in organic dye degradation. When CeO2 was utilised to form a heterojunction with other metal oxides and noble metal particles, the overall photocatalytic activity of the system was significantly increased. The creation of type I and type II energy band arrangements is advantageous for semiconductor photocatalysts in order to boost the photocatalytic activity of the system. At the moment, microwave sintering of two types of semiconductor oxides is a simple way for creating heterojunctions [56].

As a result, it is of considerable interest to build TbMnO3CeO2 heterojunction composites using microwave aided sintering and investigate their physical and chemical properties [57].

**PHOTOCATALYTIC ACTIVITY:**

Methyl orange (MO) is a common azo dye that has numerous applications in the culinary, textile, and other industries. However, when it is directly dumped into the environment, it is difficult to decompose, resulting in substantial environmental damage [58]. MO was chosen as the target degradation dye in this experiment, with a concentration of 0.1 g/L, while the catalyst concentration of 0.5 g/L [59]. The photocatalytic degradation curve of the blank experiment is presented below to indicate that methyl orange does not decay when exposed to light [60].

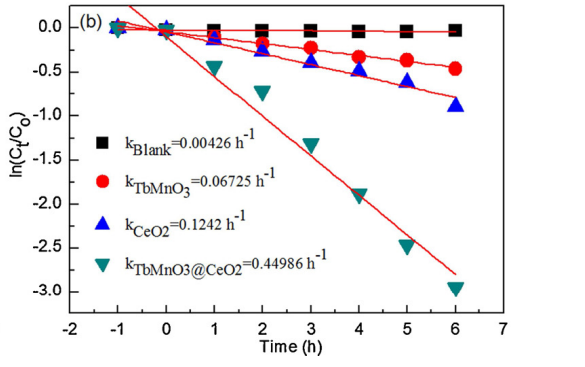


**Ct/C0 of MO as the function of irradiation time [61]**

Only around 5% had degraded after six hours. The findings indicate that MO is a stable and nondegradable organic dye. The degradation rate of MO increased with increasing irradiation time with the presence of photocatalyst. TbMnO3, CeO2, and TbMnO3CeO2 composites degrade at around 30%, 62%, and 97%, respectively. The first order kinetics rate of TbMnO3, CeO2, and TbMnO3CeO2 composites for the degradation of MO is studied to further define the photocatalytic degradation capacity of photocatalysts. The first order kinetics rate is easily stated by the equation below:

1n (Ct/C0) = (-kt)

Where Ct is the dye concentration at different light irradiation time (t), C0 is the initial dye concentration, k is the rate constant.



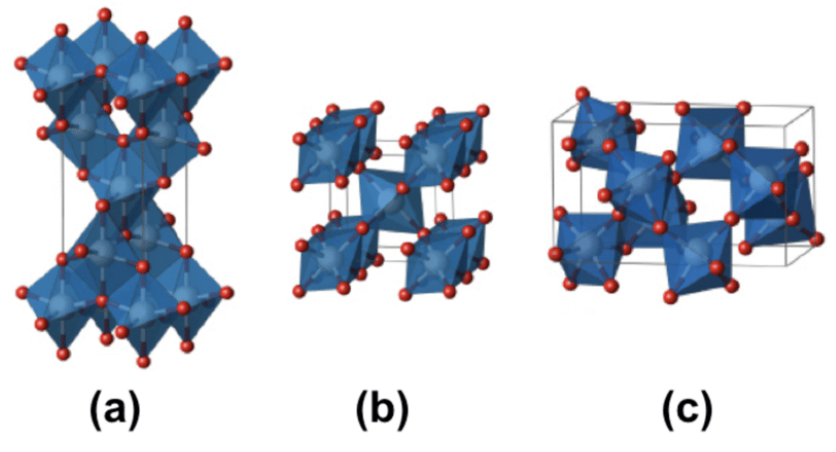
**During the photodegradation process, plots of ln(C/C0) vs. irradiation duration were made in the presence of TbMnO3, CeO2, and TbMnO3@CeO2 composites.**

The graphs of ln(C/C0) vs. irradiation time in the presence of TbMnO3, CeO2, and TbMnO3CeO2 composites during photodegradation are shown above. TbMnO3, CeO2, and TbMnO3CeO2 composites have k values of 0.06725, 0.1242, and 0.44986 h1 for MO degradation, respectively. The photocatalytic degradation rate of TbMnO3CeO2 composites is approximately 6.69 times that of TbMnO3.

The strong photocatalytic activity of TbMnO3CeO2 composites was mostly due to the synergistic effect of light absorption capacity, electron hole pair recombination rate, and hydroxyl radicals. The photo absorption capacity, magnetic characteristics, and photocatalytic activity of the monophase oxide were improved when CeO2 nanoparticles were added to the TbMnO3 precursor. TbMnO3CeO2 composites have a lower ultraviolet emission peak and a weaker blue emission when compared to CeO2. TbMnO3CeO2 composites have a photocatalytic breakdown rate of MO under visible light irradiation that is approximately 6.69 times that of TbMnO3 alone [62].

**(iii) PHOTOCATALYSIS USING TiO2:**

Anatase, rutile, and brookite are the three polymorphs of natural TiO2. Rutile and anatase are the most common modifications utilized in photocatalysis. Anatase and rutile both have crystalline tetragonal structures made up of TiO6 octahedra. TiO6 octahedra share common edges in the planes (001) and (100) in anatase. Each octahedron has four shared edges that form zigzag chains with their neighbors. TiO2 octahedra in rutile are joined by ribs on the (001) plane with two adjacent octahedra, forming lengthy ribbons in the crystal lattice. The structural lattice differences between anatase and rutile determine their density and electric band structure. As a result, anatase and rutile absorb light at wavelengths of 388 and 413 nm, respectively.



**Titanium dioxide comes in three distinct polymorphs. Anatase (a), rutile (b), and brookite (c).** **The small red spheres indicate oxygen atoms, the large grey spheres represent titanium atoms, and the blue polyhedral forms depict the TiO6 octahedra's orientation in space.**

Rutile has stronger photocatalytic activity than anatase, which is likely due to its narrower band gap. The band gap width is a critical characteristic in photocatalysis because it governs the rate of electron transmission and thus the rate of charge recombination [63].

Photoactive surface formation the absorption of photon energy causes the appearance of holes in the valence zone (h+) and electrons in the conduction zone (e-) in TiO2. The last must be greater than or equal to the width of the TiO2 band gap (3.2 eV for rutile, 3.0 eV for anatase). Holes contribute to the creation of hydroxyl radicals and the oxidation of organic compounds, while electrons contribute to the development of peroxide radicals and the decomposition/oxidation of organic molecules.

Following are the reactions that lead to the formation of hydroxyl and peroxide radicals:

TiO2 + h → TiO2 (e- CB + h+ VB);

TiO2 (h+ VB +e- CB) → TiO2 (recombination);

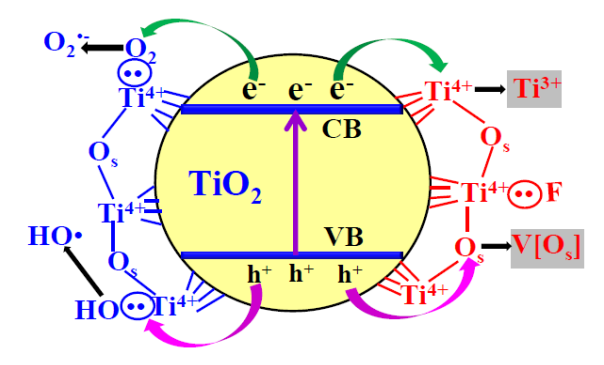
TiO2 (h+ VB) + OH- → TiO2 + ОН•

TiO2 (e- CB) + О2 → TiO2 + О2 • Where VB stands for valence band and CB represents the conduction band.

The features of TiO2 (crystallinity, surface area, particle size, defect position, surface charge), as well as the substrate-surface interaction, all have a significant role in the photocatalytic activity of this material. In particular, TiO2 should have a high specific surface area and tiny particle sizes for the photocatalytic process to be effectively conducted. Because of this, understanding photocatalytic activity necessitates a thorough examination of numerous factors [64].

**The effect of TiO2 surface chemical state on photocatalytic activity:**

The chemical condition of the TiO2 surface influences photocatalytic activity significantly. Figure below depicts the complex of surface physicochemical properties of TiO2 photocatalysts.



**Surface chemical state of TiO2-based modified photocatalysts**

Surface charge is critical in determining photocatalytic activity, particularly in the kinetics of photooxidation of organic dyes. The properties of surface charge TiO2 in water at various pH values are determined by the point of zero charge pHZpc.

Theacid-base equilibrium reactions for titanol groups TiO2 are as follows:

> Ti‒OH2 + ↔ > Ti‒OH + H+ (pKa1);

> Ti‒OH ↔ > Ti‒O- + H+ (pKa2);.

The pH of the zero-charge point corresponds to the average value of pK (pKa1+pKa2) / 2. The PhZpc is determined experimentally by measuring the electrokinetic potential (zeta potential) of suspended particles at various pH levels. The pHzpc of titanium dioxide P25 from Degussa, for example, is 6.2 (pKa1 =4,5 and pKa2 = 8). The surface of TiO2 particles is positively charged at pH 6.2, and negatively charged at pH > 6.2. Increased efficiency in the production of hydroxyl radicals Because of the ideal concentration of OH-, TiO2 is reached by a weak alkaline media, which leads to the photocatalytic destruction of organic molecules in aqueous solution [65].

**The influence of chemical modification on TiO2 photocatalytic activity:**

Free of impurities (chemically pure) TiO2 typically has unfavorable charge transfer kinetics and band gap width. To increase photocatalytic activity, the chemical state of the TiO2 surface must be changed. The following basic surface modification strategies for the production of highly active photocatalysts based on TiO2 can be recognized based on the photocatalysis mechanism:

1. Doping can be used to narrow the band gap;
2. adding visible light photosensitizers on top of TiO2 to expand the range of the solar spectrum that is available;
3. surface heterojunction formation to optimize charge carrier dynamics
4. Nanosized cocatalysts are loaded to prevent surface charge recombination processes.
5. improving photocatalytic activity by increasing accessible surface area
6. introduction of surface F-effects in TiO2 to enhance the concentration of free radicals OH, hence enhancing photodegradation efficiency;
7. exposing highly reactive faces to light in order to improve surface-active regions and redox capacity

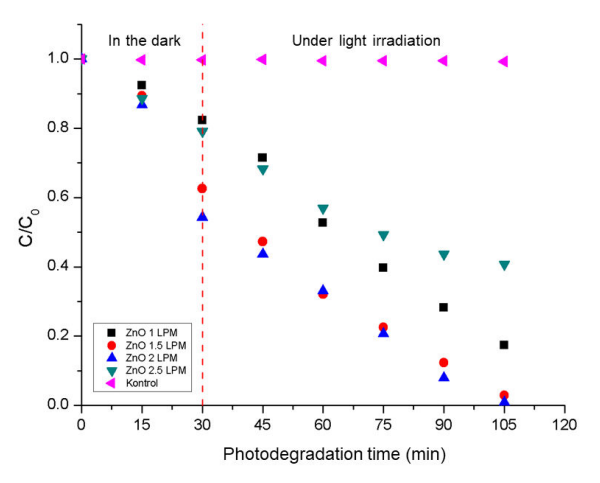
Many investigations have been undertaken in order to create a TiO2-based photocatalyst that absorbs photons in the visible light spectrum while having a low electron-hole recombination coefficient [66].

**ZnO BASED PHOTOCATALYSIS:**

AOP based on photocatalysis and employing semiconductor materials has emerged as a viable approach for pollutant degradation. ZnO occurs naturally in the mineral zincite, although the majority of industrial ZnO is produced through the high-temperature oxidation of metallic zinc or zinc ores [67]. ZnO is one of the semiconductor substances that can be utilized as a photocatalyst. Many researchers were drawn to ZnO particles because of their UV absorption applications [68]. Gancheva also stated that zinc oxide has received a lot of attention due to its high photosensitivity, which causes the breakdown of numerous contaminants [69]. Because of its broad band gap, ZnO has has potential as a photocatalyst material. Shakti discovered that zinc oxide is an N-type semiconductor with a significant exciton binding energy of 60 meV and a broad band gap of 3.37 eV [70]. ZnO has been synthesised using a variety of techniques, including hydrothermal synthesis, thermal decomposition, precipitation, and flame spray pyrolysis (FSP). The benefits of FSP include the fact that it is a one-step method that uses an aqueous-base salt solution as a precursor. The product has a generally consistent size and shape, is single and multicomponent, and can be doped with other materials [71].

**PHOTOCATALYTIC PROPERTIES OF ZnO:**

The rate of decline in amaranth concentration was measured using an ultraviolet-visible spectrophotometer. The drop in amaranth concentration implies that ZnO has photocatalytic capabilities. The ZnO absorbance value was acquired as a result of the measurement. According to Lambert-Beer's rule, the absorbance value of a solution is proportional to its concentration, hence the ZnO absorbance value is proportional to the amaranth solution's concentration. Based on Spectrophotometer Uv-Vis measurements, an amaranth photodegradation chart was created utilizing ZnO photocatalyst synthesised at various rates of oxygen gas flow rates. The figure below shows that in the dark, the concentration of amaranth reduced due to the process of ZnO absorption. In contrast, the photodecomposition mechanism is involved in the decrease in amaranth concentration under direct irradiation circumstances.



**Photocatalytic activity of FSP-prepared ZnO at various O2 flow rates: a) 1, b) 1.5, c) 2, and d) 2.5 L/min**

The amaranth concentration decreases with time under direct irradiation conditions, as seen in the above two figures (XRD and SEM figures). At 105 minutes, ZnO with oxygen gas flow rates of 1.5 and 2 L/min. degraded the amaranth solution to close to a C/C0 value of 0. Whereas ZnO with an oxygen gas flow rate of 1 L/min. can degrade amaranth solution to a C/C0 value of less than 0.2, ZnO with a flow rate of 2.5 can degrade amaranth solution to a C/C0 value of 0.4.

Increased oxygen gas flow rates result in greater photocatalytic capabilities, but on Zno with 2.5 L/min. oxygen gas flow rate, the particle floats, making direct contact less effective than in the other samples. At 105 minutes, the oxygen flow rate was able to destroy amaranth dye up to 95.3% [72].

**Bismuth ferrite** **(BiFeO3)** **as a newly discovered visible light active nanostructured photocatalyst:**

Because there is a scarcity of fresh water for drinking, it is necessary to recycle dirty water. The problem of water contamination is a big challenge, and many researchers are working to find better ways to deal with it [73]. Nowadays, an improved approach called as "advanced oxidation process" is establishing a name for itself in the remediation of dirty water. This approach involves the oxidation of effluents (pollutants) with hydroxyl ions (OH) [74].

The primary phases are as follows: (a) production of hydroxyl ions OH-, (b) hydroxyl radicals assault pollution target molecules and promote their breakdown into smaller compounds until complete mineralization occurs [75]. As a result, it attracted attention due to its ability to eliminate dangerous organic pollutants while avoiding the conversion of pollutants into harmful products [76]. Advanced oxidation processes include ozonation, Sonolysis, fenton process, photo-Fenton process, photocatalysis, bio-degradation and UV-photocatalysis [77].

Photocatalysis is an efficient technology among them since it employs solar energy to remove organic contaminants [78].

Some photocatalysts that have still to be researched include ferrites (LaFeO3, BiFeO3, GdFeO3), tantalates (AgTaO3, NaTaO3, KTaO3), titanates (SrTiO3, CdTiO3, NiTiO3, CoTiO3, CaTiO3, FeTiO3, BaTiO3), and others (LaCaO3 and LaNiO3) [79].

The following qualities of BiFeO3 materials have attracted attention:

1. Band-gap exists in visible-light area
2. Multiferroic existence at room temperature (25 C), which aids in efficient separation of cations and anions
3. Strong chemical stability. [80]

**STEPS TO IMPROVE BiFeO3 PHOTOCATALYTIC EFFICIENCY:**

1. **THE IMPACT OF DOPING:**

Many scholars have investigated the use of BFO in heterogeneous photocatalysis [81]. Unfortunately, the reported BFO's photocatalytic reaction rate and efficiency were not met due to the rapid recombination of photogenerated electrons and holes. Thus, it is investigated if metal doping could be an effective technique for improving photocatalytic effectiveness by substituting an iron element in pure BFO, resulting in a longer response in the visible light area [82]. For the cause of aqueous pollutant degradation, several organic contaminants, such as Rhodamine B (RhB), 4-nitrophenol, methyl orange (MO), methylene blue (MB), and 4-chlorophenol, have been utilized as model contaminants for photocatalyst testing [83]. Whereas, the photocatalytic efficiency of a photocatalyst is primarily determined by numerous aspects such as surface area, nano-structuring, photocatalyst loading, initial pollutant concentration, type of organic pollutant, and light source [84].

The doping approach is the most effective way to add impurities into photocatalysts. Typically, a tiny amount of dopant can limit the recombination rate of photo-generated charge carriers, hence increasing the photocatalytic activity of the photocatalyst [85]. The essential factor, however, is the selection of an appropriate dopant. If the amount of dopant surpasses a threshold value, it may act as recombination centres for photo-generated charge carriers, lowering photocatalytic performance [86].

Sarkar et al. used electrospinning to create nanofibers of Dy-doped BiFeO3 [87]. Methylene blue photocatalytic degradation demonstrated that DY-doped BiFeO3 nanofiber had improved photocatalytic efficiency under visible light. It could be because Dy reduced the band-gap, which assisted in moving charge carriers to the photocatalytic surface, lowering the rate of charge carrier recombination. Another study discovered that doping Sc onto BiFeO3 can be effective for methylene blue breakdown using sunlight. It was discovered that Sc-doped BiFeO3 totally decomposed methylene blue after 3 hours of UV irradiation, but pure BiFeO3 only degraded 69% of Methylene blue. The deformation in the structure of BiFeO3 caused by Sc doping improved its ferroelectric characteristics. Following that, researchers began investigating co-doping onto BiFeO3 with various elements on Bi3+ and Fe3+ -sites [88].

Vanga et al. chose Nd and Ni as co-dopants for Bi3+ and Fe3+ sites on BiFeO3. They discovered that co-doping Nd and Ni facilitated charge transfer and reduced the recombination rate of photo-generated charge carriers, which improved photocatalytic activity under visible light. According to Irfan et al., increasing the charge carriers capturing centres can also enhance and speed up the photocatalytic activity of BiFeO3 under different wavelengths of light, because these charge carriers capturing centres increased the recombination time of the carriers, which produced more radicals and thus increased the activity [89]. They discovered that the Congo red was degraded in 50 minutes by the La and Se co-doped BiFeO3 sample (Bi0.92 La0.08 Fe0.925 Se0.075 O3). It could be owing to the increased surface area (3.3-10) m2.g1, decreased recombination time, and decreased band-gap (2.06-1.97) eV after co-doping of La and Se onto BiFeO3. The high crystallinity of pure and co-doped BiFeO3 was confirmed [90].

As reported by previous researchers, the cobalt (Co) element was thought to be one promising element that may be doped into BFO. Because cobalt element doping materials shown outstanding electrochemical characteristics, the light absorption zone of BFO could be enlarged and strong photocatalytic activity might be expected [91].

**Conclusion**

In conclusion, the integration of multiferroic materials in photocatalysis for wastewater treatment presents a compelling solution to contemporary environmental challenges. Multiferroic-based photocatalysis offers unparalleled advantages through its ability to respond to both light and external magnetic fields, accelerating pollutant degradation in a controlled and efficient manner. This innovative approach not only enhances treatment efficiency but also enables wastewater remediation in challenging conditions. As we strive for sustainable and clean water resources, multiferroic-based photocatalysis stands as a promising avenue, merging the unique properties of multiferroic materials with the urgency of wastewater treatment, promising a greener and more effective solution for safeguarding our environment and public health.

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