



## A Review On Application of TiO<sub>2</sub> Photocatalyst for Industrial Wastewater

Bhargavkumar Patel<sup>a)</sup>, Shivendu Saxena<sup>b)</sup>, Vishal Kumar Sandhwar<sup>c)</sup>, Diksha Saxena<sup>d)</sup>

<sup>a,b,c,d</sup>Department of Chemical Engineering, Faculty of Engineering & Technology, Parul University, Vadodara, Gujarat, India

### Abstract:

Wastewater comprises a diverse range of contaminants, including organic matter, nutrients, heavy metals, pathogens, and emerging pollutants. It originates from various sources such as domestic households, industrial processes, agricultural activities, and stormwater runoff. If left untreated, wastewater can have detrimental effects on aquatic ecosystems, contaminate drinking water sources, and propagate waterborne diseases. Industrial wastewater poses significant environmental challenges due to its complex composition and persistent nature. The application of TiO<sub>2</sub> and TiO<sub>2</sub> with metal and non-metal doped as photocatalyst offers a promising solution for the efficient degradation of various pollutants. The degradation of a wide range of organic compounds is also enhanced by the increased photocatalytic activity induced by doping techniques, which also makes it easier to purify wastewater and reduce its harmful environmental impact. Conventional treatment methods often struggle to effectively remove these compounds, leading to their persistence in water bodies. TiO<sub>2</sub> photocatalysis offers a potential solution by harnessing the power of light energy to activate TiO<sub>2</sub> nanoparticles and generate reactive oxygen species (ROS) capable of degrading organic contaminants. The wide bandgap of TiO<sub>2</sub> allows for efficient UV light absorption, enabling the generation of ROS. In addition, TiO<sub>2</sub> has a high degree of chemical stability, is inexpensive, and is non-toxic, which makes it a desirable option for different applications in various process and production industries.

**Keywords:** Nanomaterial, Photocatalyst, Wastewater Treatment, Metal and non-metal doping

### 1. Introduction

Water is disposed into waterbodies or thrown into surface waters after being used for domestic and industrial purposes. This wastewater contains dissolved organic species and hazardous contaminations which are very harmful to our environment as well as for human health, that's why wastewater must be treated and contamination present in wastewater must be removed and broken down. Wastewater treatment is an important issue for environmental protection and necessitates the deployment of advanced clean-up techniques to reduce the toxic component. Various types of wastewaters are named as municipal wastewater, pharmaceutical wastewater, wastewater from oil refineries, dye wastewater from the textile industry, and wastewater from other industries. All wastewater affects human life and pollutes the environment. Therefore, all hazardous components that harm the environment and have an impact on the abiotic ecosystem should be reduced using innovative technology to protect our ecosystem.

Wastewater treatment levels are categorized in four levels named as primary, secondary, tertiary and advance treatment which include various treatment processes as shown in figure 1. In the primary step, the heavier solid components were removed using screening and sedimentation

techniques, separated by the gravity difference. Secondary stage involves the biological treatment processes such as activated sludge process (aerobic digestion) and anaerobic digestion that remove the biodegradable organic matter and total suspended solids (TSS) through the processes. Tertiary treatment is required to remove the remaining contaminants from the wastewater. It involves processes such as coagulation-flocculation, filtration, disinfection, or chemical treatment to remove fine solids, pathogens, nutrients (like nitrogen and phosphorus), and other specific pollutants. Advanced oxidation processes such as photocatalysis, ozonation, electrochemical, and the Fenton reagent, are included in the advanced treatment and used for the degradation of bio-refractory organic compounds.

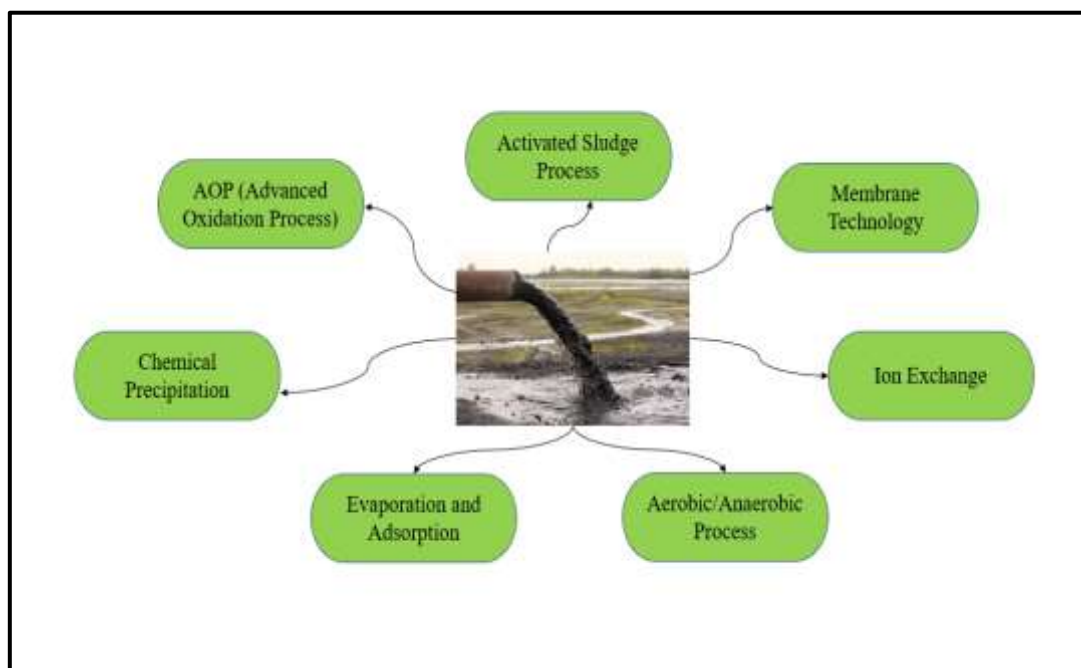


Figure 1: Various treatment technologies for Wastewater treatment

Table 1: Contrasting both the advantages and disadvantages of various treatment technologies for Wastewater treatment

Sr. no	Name of the treatment	Advantage	Disadvantage
1	Sedimentation	<ul style="list-style-type: none"> <li>• Low-cost treatment and simple water pre-treatment technology</li> <li>• To settle out suspended solids, the coagulants reduce the time required.</li> <li>• high clarification efficiency</li> </ul>	<ul style="list-style-type: none"> <li>• large area required</li> <li>• Sensitivity of the flow variation</li> </ul>
2	Biological treatment	<ul style="list-style-type: none"> <li>• High load operation can be processed</li> <li>• High reliability of the method</li> </ul>	<ul style="list-style-type: none"> <li>• High level of sludge</li> <li>• High the stability and processing effectiveness</li> </ul>



			<ul style="list-style-type: none"> <li>Operating management requires expertise</li> </ul>
3	Coagulation/precipitation	<ul style="list-style-type: none"> <li>Low sites</li> <li>high processing effectiveness</li> </ul>	<ul style="list-style-type: none"> <li>Difficult to maintain</li> <li>A lot of sludge generation</li> </ul>
4	Improved photocatalytic oxidation technology	<ul style="list-style-type: none"> <li>It is feasible to treat non-biodegradable waste water. Modifications in water quantity and quality can influence the operation of some equipment.</li> <li>Low operational and installation cost</li> <li>Easy pre-processing proceeds right to wastewater treatment.</li> <li>There are no costs associated with sludge treatment.</li> <li>There is a chance of an incompetent and unmanned operation</li> <li>The area connected to the current treatment facilities is smaller</li> </ul>	<ul style="list-style-type: none"> <li>UV lamps having a short lamp life</li> <li>When utilising powder, a photocatalyst recovery facility</li> </ul>
5	Fenton technology	<ul style="list-style-type: none"> <li>The method of treatment is easy and manageable</li> <li>Water treatment facility coloured discoloration that's effective</li> <li>Wide coverage</li> </ul>	<ul style="list-style-type: none"> <li>Exorbitant operational costs associated with the usage of Fenton's reagent</li> <li>Dump of the necessary iron salts equipment.</li> </ul>

Coagulation treatment is a process used in wastewater treatment to remove suspended particles and colloidal matter from water by causing them to clump together and settle. It involves the addition of chemicals called coagulants, which destabilize the particles, allowing them to aggregate and form larger particles called flocs. These flocs can then be more easily removed through sedimentation or filtration processes [1-3]. Biological treatment is a wastewater treatment process that utilizes microorganisms to break down organic pollutants present in wastewater. Biological treatment can occur under aerobic (with oxygen) or anaerobic (without oxygen) conditions, depending on the specific treatment objectives and the nature of the pollutants. Aerobic processes, such as activated sludge systems, involve supplying oxygen to support the growth of aerobic bacteria, which break down organic matter into carbon dioxide, water, and biomass. Anaerobic processes, like anaerobic digestion, occur in the absence of oxygen and facilitate the conversion of organic matter into biogas (methane and carbon dioxide) and stabilized sludge [4-7]. There are some drawbacks associated with biological treatment which include a high level of producing sludge, requires big land area, requires huge capital, processing effectiveness, and Operating management requires expertise. Advanced



oxidation treatment processes are used to degrade and remove persistent and refractory pollutants that are not effectively eliminated by conventional treatment methods and this process involves the generation of highly reactive hydroxyl radicals ( $\cdot\text{OH}$ ) to oxidize and break down various organic and inorganic contaminants. The advantages of this process are potential to reduce toxicity of organic compounds, rapid reaction rate, mineralization of organic compounds, and there are no costs associated with sludge treatment [8-10]. Table-1 contrasting both the advantages and disadvantages of Various treatment technologies for Wastewater treatment.

Researchers have recently investigated the different ways that nanoparticles can be used to clean up dirty areas and treat wastewater. These particles range in size from a few nanometres to about 500 nm, which is quite small. These particles are categorized into various groups based on their sizes and shapes, including polymeric, metal, and ceramic nanoparticles and these particles are composed of carbon, metal oxide, organic matter, etc. Each nanoparticle differs from its counterparts at higher scales in terms of its biological, chemical, and physical characteristics due to its nanoscale size, high surface area, and shapes [11]. In addition, due to the small in size, new structures with special features, such as nanofilms, nanocoating, and nanotubes, can be produced. Among the various groups of nanoparticles, metal oxides such as ZnO, MgO, TiO<sub>2</sub>, NiO, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> are widely used in different industrial applications [17-22].

Physical properties associated with nanoparticles are colour, radiation penetration, adsorption, and reflection capacities, as well as the ability to take in and reflect UV light within a solution or when coating with a surface. Additionally, it includes the mechanical traits that are important to their use, such as flexible, elastic, tensile, and suppleness. These particles also have properties including suspension, diffusion, settling, hydrophilicity, and hydrophobicity. The utilisation of nanoparticles is influenced by their chemical properties, such as their ability to interact with the goal, equilibrium, and resistance to elements including humidity, oxygen, heat, and light. The antibacterial, antifungal, disinfecting, and toxic capabilities of nanoparticles may be useful for biological and environmental uses. The use of the nanoparticles is determined by their corrosive, anticorrosive, oxidation, reduction, and flammability properties. Due to its low cost and photo-stability, TiO<sub>2</sub> has been used extensively, particularly in the crystalline form anatase [24]. TiO<sub>2</sub> is well known for being both physically and chemically stable due to its high refractive index, high catalytic activity, low cost, highly reactivity, facile synthesis, and high conversion of energy efficiency as presented in figure 2 [25].

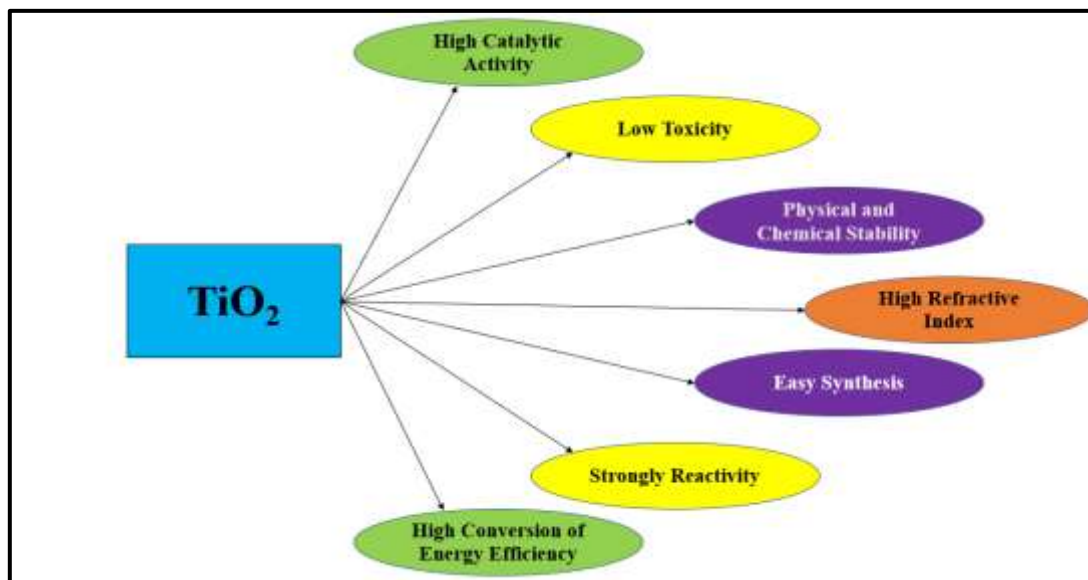


Figure 2: Properties of TiO<sub>2</sub>

## 2. Synthesis of TiO<sub>2</sub> Nanoparticle

Bottom-up or top-down procedures can be used to explain the various methods utilized to synthesize the nanoparticles. An overview of the process is shown in Figure 3.

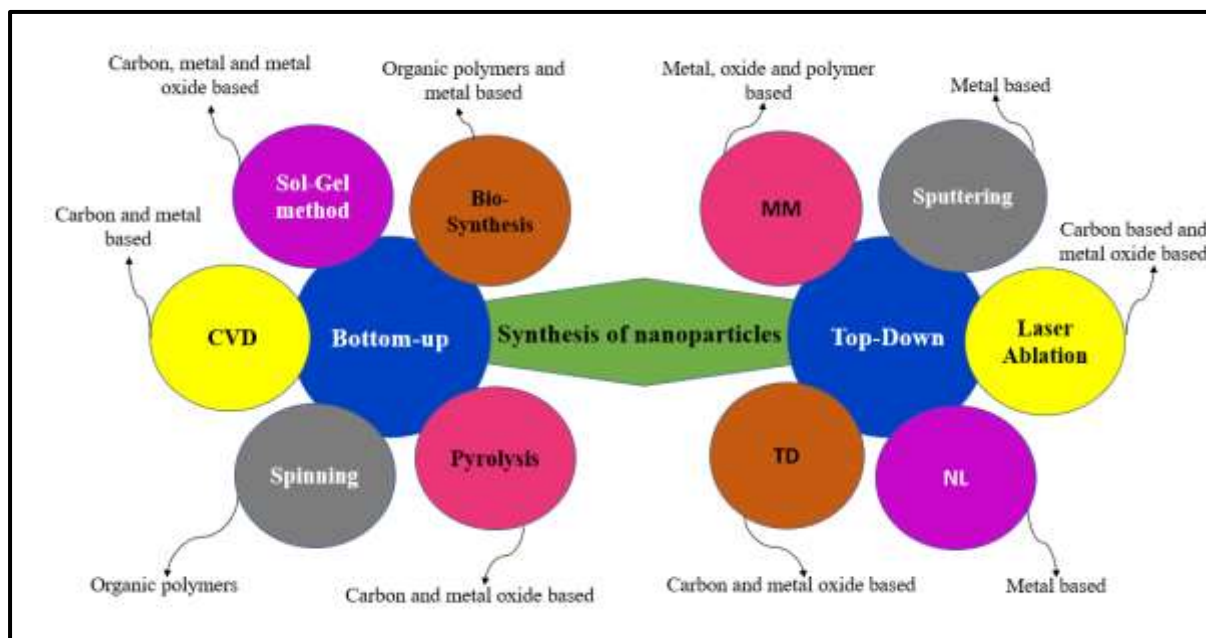


Figure 3: Classes of the nanoparticles created by various processes

### 2.1 Bottom-up Approaches:

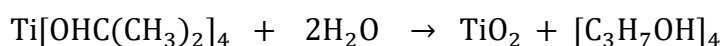
Creating the materials from particles and groups using chemical or physical processes operating at the nanoscale to assemble basic units, is known as the bottom-up approach to

prepare nanoparticles. The popular bottom-up techniques for making nanoparticles include sol-gel, Chemical Vapour Deposition (CVD), spinning, biosynthesis and pyrolysis [23].

### 2.1.1 Sol-Gel method:

A sol is a colloidal dispersion of particles in a liquid phase. The gel is a solid macromolecule that has been dissolved in a liquid. Sol-gel is the more popular bottom-up approach because to its flexibility and the ease with which most nanoparticles can be synthesised. This wet-chemical procedure makes use of a chemical combination that prepares a combined structure of separate particles. Metal oxides and chlorides are frequent precursors in the sol-gel process [26]. A system with a liquid and solid phase is produced by first sonicating, shaking, or moving the precursor with the settling liquid. After a phase separation, the nanoparticles can be recovered using a variety of procedures, such as sedimentation, filtration, and centrifugation. The moisture is then further removed by drying [27].

The various titanium salts are used in the synthesis of TiO<sub>2</sub> NPs. TTIP (Titanium Tetraisopropoxide) salt employing a sol-gel technique. The overall reaction of TiO<sub>2</sub> breakdown are as follows and presented in figure 4:



The intermediate formation of Titanyl hydroxide was obtained by the hydrolysis of titanium isopropoxide (Ti [OHC(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub>) according to the following reaction is

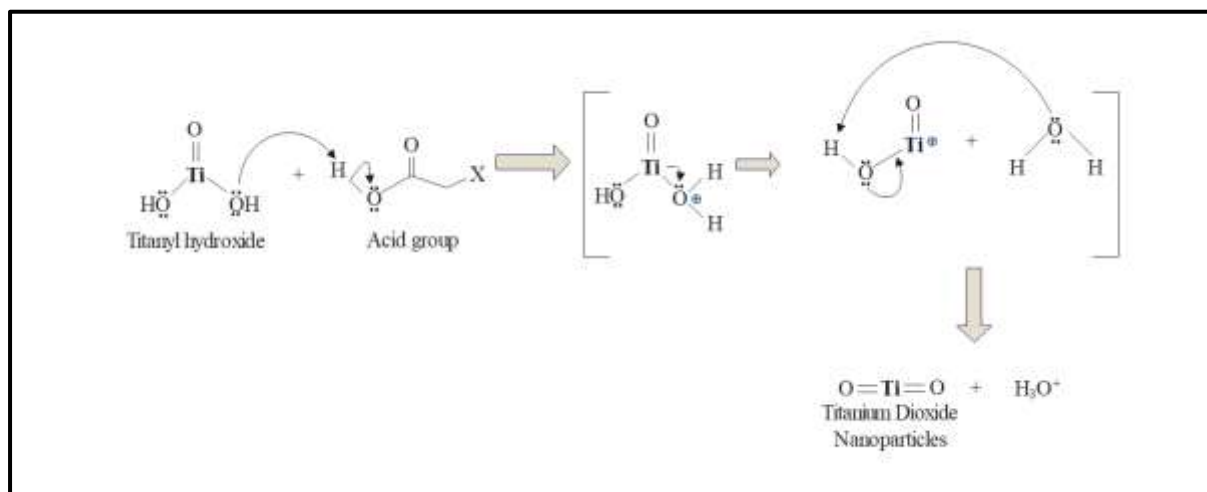
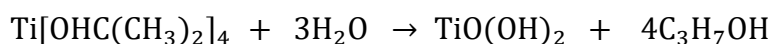


Figure 4: Mechanism of TiO<sub>2</sub> nanoparticles

### 2.1.1 Chemical Vapour Deposition (CVD):

The process of coating a material with a thin film of gaseous reactants is known as chemical vapour deposition. Through the interaction of gas molecules, the deposition takes place outside inside a reaction chamber at room temperature. When a heated substrate makes contact with the combined gas, a chemical reaction occurs [28]. A thin layer of product is created by this



reaction on the surface of the substrate, which is then removed and used. In CVD, the substrate's temperature is crucial. High purity, homogeneity, hardness, and strength are a few advantages of CVD. Special tools are needed for CVD, and the gaseous by-products are extremely dangerous [29].

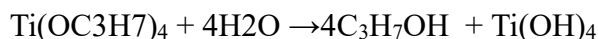
By using titanium tetraisopropoxide as a chemical vapour deposition substrate, nanoscale TiO<sub>2</sub> particles are produced. Due to the stoichiometric relationship of the formation of particles reaction, which is catalysed by the titanium dioxide deposit on the vessel wall, it occurred even at a temperature as low as 250°C.



### 2.1.2 Spinning:

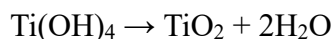
This phenomenon involves particle discharge from a surface after ion collisions, which results in the formation of nanoparticles on that surface [30]. In most cases, heating comes after sputtering a thin layer of nanoparticles onto a surface. The spinning method is a technique used to synthesize TiO<sub>2</sub> nanoparticles. It involves the controlled hydrolysis of titanium alkoxide precursors in a spinning disc reactor. The mechanism of TiO<sub>2</sub> synthesis using the spinning method can be described as follows:

**Hydrolysis and condensation:** As the precursor solution spreads over the spinning disc, it comes into contact with ambient moisture, leading to hydrolysis. The production of titanium hydroxyl species is caused by the hydrolysis of titanium alkaline compounds and water molecules. The following is a representation of this step:



The hydrolysis reaction is typically favored by the presence of an acid or base catalyst, which can be added to the precursor solution.

**Condensation and nucleation:** The hydrolysed titanium hydroxide species undergo condensation reactions, forming Ti-O-Ti linkages and leading to the nucleation of TiO<sub>2</sub> nanoparticles. The condensation reactions involve the removal of water molecules from the hydrolysed species, resulting in the formation of Ti-O-Ti bonds:



The spinning method offers advantages such as the production of uniform nanoparticles, precise control over particle size, and scalability. By adjusting parameters such as precursor concentration, spinning disc speed, and reaction conditions, the size and morphology of TiO<sub>2</sub> nanoparticles can be tailored to specific requirements. The layer's thickness, processing temperature and time, surface type, etc. all affect the shape and size of the nanoparticles [31].

### 2.1.3 Biosynthesis:

A green and eco-friendly process for creating harmless, biodegradable nanoparticles is biosynthesis [32]. Biosynthesis, which creates nanoparticles using microbes, plant extracts, fungi, and numerous other microorganisms along with the precursors, uses standard chemicals



in biological reduced and capping. Biosynthesized nanoparticles are used in biomedical applications due to their distinctive and improved characteristics [33].

#### *2.1.4 Pyrolysis:*

Pyrolysis is the process used the most commonly in industry to produce nanoparticles in large quantities. There is a predecessor that will set flame. The air is subsequently separated from the combustion products or gas-derived nanoparticles. Some furnaces maintain elevated temperatures for simple evaporation using laser and plasma instead of flame [34]. It includes setting earlier iterations on fire. The precursor enters the furnace through a tiny opening under high pressure, either as a liquid and a vapour, where it burns. The combustion by-products or gas-derived nanoparticles are then removed from the air. Some furnaces sustain high temperatures for simple evaporation without flame by using laser and plasma [35]. It benefits from being a simple, efficient, continuous process that a high output that is also effective.

## **2.2 Top-Down Approaches:**

A top-down or damaging process is disassembling a big thing into smaller parts. The most widely used methods for producing nanoparticles include thermal breakdown, mechanical milling, the sputter laser ablation, and nanolithography (NL).

#### *2.2.1 Mechanical Milling (MM):*

Different types of nanoparticles are routinely created using the top-down mechanical milling method. Throughout the manufacturing process, different elements are ground in an atmosphere of inertia while nanoparticles are mechanically milled and then post-annealed [36]. Deformation of plastic, which impacts particulate shape, fracture, which reduces the size of particles, and cold-welding, resulting in larger particle size, are the factors that effect mechanical milling.

#### *2.2.2 Laser Ablation:*

Nanoparticles can be produced from a variety of liquids using the technique that is called laser ablation synthesis in solutions (LAS). It is a "green" method since LAS enables continuous nanoparticle production in organic and water-based solvents without the need of chemicals or stabilisation agents. It is a trustworthy top-down strategy that offers an alternate way to create metal-based nanoparticles as opposed to the usual chemical reduction of metals. A plasma plume forms as a laser beam hits a metal immersed in a liquid the solution, creating nanoparticles [37].

#### *2.2.3 Thermal Decomposition (TD):*

Heat that splits molecules bonds in the substance generates thermal decomposition, an endothermic chemical breakdown [38]. The decomposition temperature is the precise temperature when an element begins to chemically break down. By carrying out a chemical reaction on the metal at the proper temperature, very small metal particles are broken down into by-products like nanoparticles. The precursor solution is subjected to a controlled heating process. As the temperature increases, the precursor undergoes thermal decomposition, leading





to the release of volatile species, such as organic ligands or chlorine atoms, and the formation of  $\text{TiO}_2$  species. The decomposition reaction can be represented as follows:



The specific by products depend on the nature of the precursor used. After the synthesis and annealing steps, the  $\text{TiO}_2$  nanoparticles are collected and purified using suitable techniques such as filtration or centrifugation. This helps remove any residual by products or impurities from the synthesized nanoparticles. The exact temperature when a substance begins to the thermal decomposition technique offers a quick and efficient way to create  $\text{TiO}_2$  nanoparticles. The technique entails carefully controlling the heating and breakdown of a precursor molecule, which produces  $\text{TiO}_2$  species, and nucleation, and the subsequent development of nanoparticles. The size, shape, and phase makeup of the synthesised  $\text{TiO}_2$  nanoparticles can be affected by the precursor compound chosen, the heating conditions, and the post-treatment procedures. It is worth noting that the specific details of the mechanism may vary depending on the choice of precursor compound, reaction conditions, and post-synthesis treatments employed.

### 3 Treatment of wastewater using Photocatalytic $\text{TiO}_2$

$\text{TiO}_2$  is indeed used as a photocatalyst in wastewater treatment processes. It is a versatile and widely studied material due to its excellent photocatalytic properties.

#### 3.1 Mechanism of Photocatalytic Treatment Technology:

$\text{TiO}_2$ , a semiconductor of the n-type, is widely used as a photocatalyst in a variety of processes, including defogging, water and air purification, decontamination, cleaning, and degradation of Organic components [39,40]. UV radiation is used in the indirect effective heterogeneous photocatalytic treatment method to degrade a variety of organic and inorganic components in wastewater [41-43]. These are steps occur in photocatalyst degradation. (1) the organic contaminant are mass transferred from the water-based phase to the  $\text{TiO}_2$  surface (2) organic contaminants get absorbed on the photon-activated  $\text{TiO}_2$  surface (3) the organic pollutants are removed from the  $\text{TiO}_2$  surface and (4) organic pollutants are mass transferred from the interface of the liquid region to the bulk fluid.

To remove hazardous/bio persistent contaminants desorption on the  $\text{TiO}_2$  surface, the total process involves the production of an extremely powerful oxidising agent  $\text{HO}^\bullet$ . In relation to other oxidising agents, the generated  $\text{HO}^\bullet$  radical has the maximum oxidation power, as shown in Table 2,

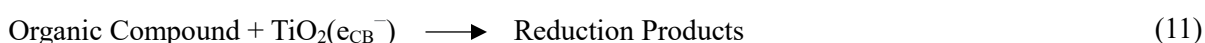
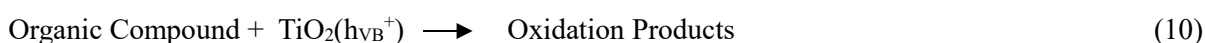
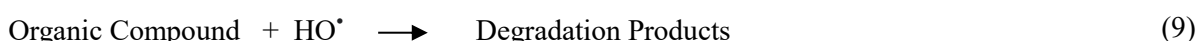
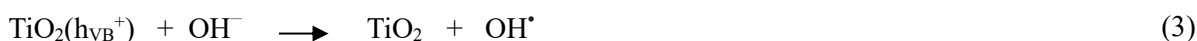
Table 2: Redox potential of the major oxidising agents [44].

Sr. No	Oxidising Agent	Oxidation Potential (V)	Relative oxidation power
1	OH radical	2.80	2.06
2	Ozone	2.07	1.52
3	Hydrogen peroxide	1.77	1.30
4	Per-hydroxyl radical	1.70	1.25
5	Permanganate	1.68	1.24
6	Chlorine dioxide	1.57	1.15



7	Chlorine	1.36	1.00
8	Oxygen	1.20	0.88

Photocatalytic reactions, which are primarily concerned with the creation, recombination, separation, and interface trapping of electron-hole pairs generated by light, are an essential part of complex physics and chemistry. Photogenerated holes develop when TiO<sub>2</sub> nanoparticles are scanned by UV/visible light (Eq.1). According to equations (2) and (3), the photogenerated holes go through an oxidation process with OH<sup>-</sup> or H<sub>2</sub>O to produce HO<sup>•</sup>. The primary component of the degradation of organic compounds is this HO<sup>•</sup> radical According to Eq. (4). To prevent the combination of electrons and photogenerated holes, effective electron stuck oxygen (O<sub>2</sub>) is utilised, other additional UV-TiO<sub>2</sub> reactions are shown in equations (5 to 8). Rapid combination of photogenerated electrons and break in TiO<sub>2</sub> decreases the efficiency of photocatalytic processes if oxygen is scarce [45]. Oxidation product and reduction product are produced when <sup>•</sup>OH, H<sup>-</sup>, e<sup>-</sup> and other oxidising agents change, degrade, deactivate, or break down various organic compounds. Other equation of the photocatalysts reaction is following as



According to Figure 5, light is emitted inside semiconductors to cause a redox reaction when combined with the absorbent material on their surfaces. This is accomplished by using a band gap of the semiconductor device with the highest energy, this term for this is the photocatalytic process. Solar energy absorption in the semiconducting material bad gap and the following photo-generated electron transference support photocatalytic processes. Therefore, photocatalysis allows the use of any semiconductor material. On the other hand, TiO<sub>2</sub> is the most commonly utilised among the few strong semiconductors for photocatalysts.

It requires activation by low-wavelength light (<400 nm) for involvement in photocatalysis due to its substantial optical energy bandgap [46]. Figure 5 shows a schematic illustration of photocatalytic degradation processes, TiO<sub>2</sub> catalyst's VB and CB form photogenerated e<sup>-</sup>/h<sup>+</sup>

pairs when UV light reaches it. In semiconductor materials, there is a valence band (VB) with electrons of constant energy and unoccupied the highest-energy conduction bands (CB). The VB of the photocatalyst determines how oxidatively the breakdown processes of contaminated materials are. As a consequence, the oxidation reaction progresses if the electrochemical voltage is higher than the potential of the standard hydrogen electrode (NHE) and the VB pores have a larger oxidant potential.

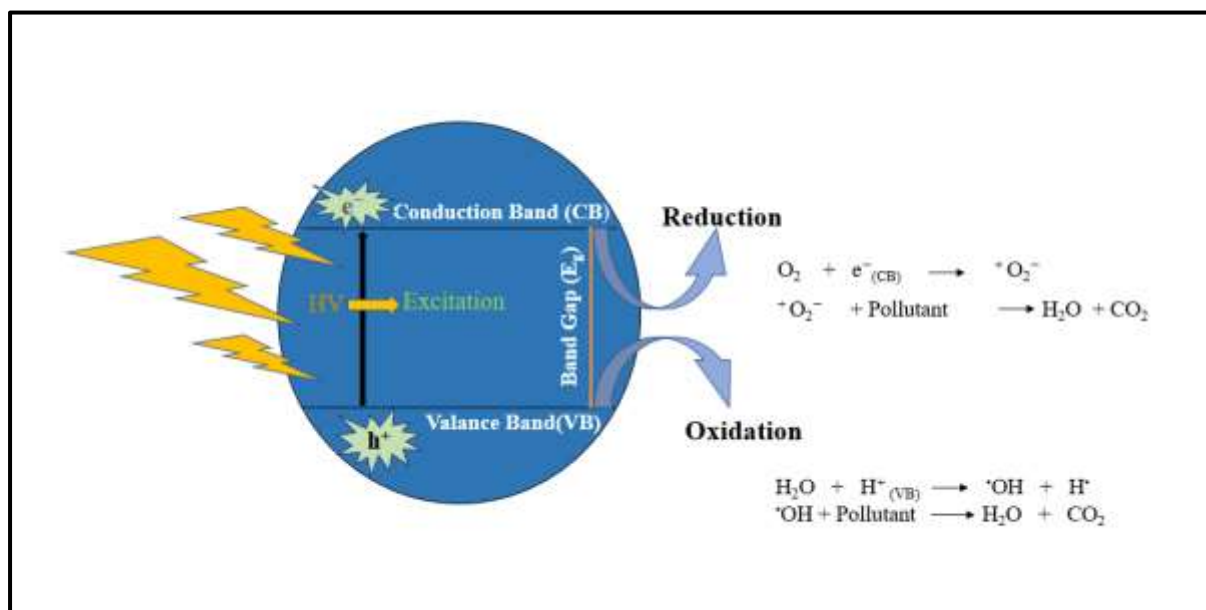


Figure 5: Diagram showing the generation of photoinduced carriers of charge ( $e^-/h^+$ ) following UV light absorption.

TiO<sub>2</sub> generally has a band gap between 3.0 and 3.2 eV, with a wavelength of approximately 400 nm. This means the start of a photo-reaction is caused by UV light radiation with wavelengths less than 400nm wavelengths [47]. One of the characteristics of TiO<sub>2</sub> is the higher oxidative power of VB holes in comparison with the reducibility of photoinduced electrons. Photocatalytic reactions need sunlight to be received in the semiconductor's bad gaps and the ensuing photo-generated electron transfer. TiO<sub>2</sub> has a powerful oxidising ability. Therefore, photocatalysis is capable of making use of any semiconductor material. On the other hand, TiO<sub>2</sub> is the most commonly utilised among the few efficient semiconductors for photocatalysts. Considering advantage of the hydrogen reference potential of around 3.0 eV and the water oxidation potential of about 1.2 eV [48]. Photons with a wavelength of 400 nm have thermal energy greater than 30,000°C. Therefore, when subjected to ultraviolet (UV) rays with wavelengths below 400 nm, TiO<sub>2</sub> surfaces is likely to attain heat exceeding 30,000°C, and this extraordinarily high temperature degrades all materials. Therefore, complete breakdown of living components into liquid and carbon dioxide occurs. [49]. Figure 6 shows graphically how impurities can be eliminated by creating photoinduced carriers of charge ( $e^-/h^+$ ) on semiconductors TiO<sub>2</sub> particle surfaces.

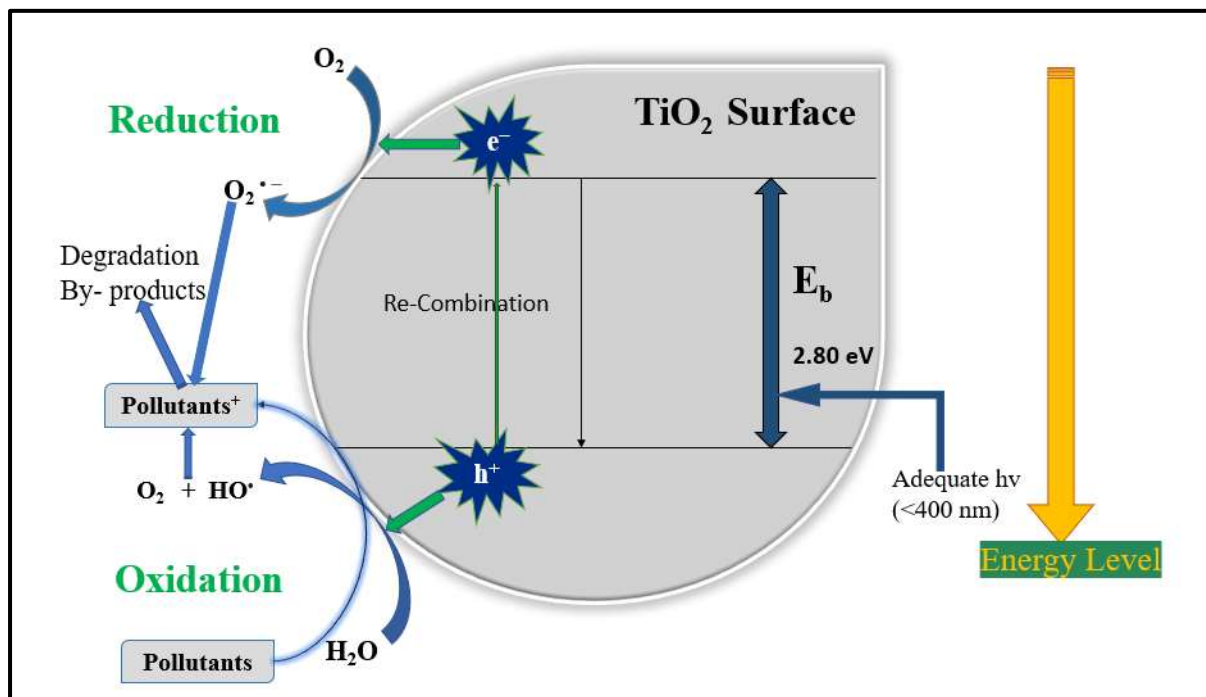


Figure 6: A diagram of the development of photoinduced carriers of charge ( $e^-/h^+$ ) on semiconductors  $TiO_2$  particle surfaces for the elimination of pollutants.

The mechanism of  $TiO_2$  photocatalysts is influenced by a number of variables, including pH, structure, and size,  $TiO_2$  loading, light intensity, and initial pollutant concentration. For azo dyes in textile wastewater, the load of  $TiO_2$  is 400–500 mg/L, and the ideal pH is hydroxyl radical dominating ( $pH > 6.8$ ); deexcitation occurs at high quantities of 2000 mg/L. The factors impacting the  $TiO_2$  photocatalysis mechanism are summarised in Table 3.

Table 3: Factors effecting on the mechanism of  $TiO_2$  photocatalysis.

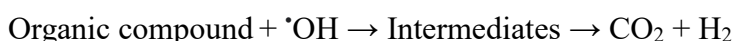
Sr. No	Name of the factor	Optimum condition	Description of the effect	References
1	pH	Hole-dominated, with a pH of 6.8 (the preferred for heavy metals), charged positively in acidic medium, negatively charged in basic fluids, and increased hydroxyl radical production ( $pH > 6.8$ )	The photo-induced reactions that takes place on the surface of $TiO_2$ is influenced by the acidity or basicity of the medium. $TiOH + H^+ \rightleftharpoons TiOH_2^+$ (acidic) $TiOH + OH^- \rightleftharpoons TiO^- + H_2O$ (basic)	[50]
2	Size and structure	-	With a larger surface area, numbers of photons will strike the $TiO_2$ surface; Degussa P25 is extremely powerful in this area.	[51], [52]

3	TiO <sub>2</sub> loading	Deexcitation was observed at high concentrations of 2000 mg/L for azo dyes, which ranged from 400 to 500 mg/L.	Depending on the size of the reactor, active sites' best capacity and accessibility must be maintained. The reaction rate first rises with increasing loading before falling.	[53-55]
4	Light intensity	-	when there is less intensity, the rate increases linearly (decolorization progresses more quickly), but when the intensity is moderate (half orders), the rate increases in proportion to the intensity's square root. High-intensity competition between separation and recombination occurs with no order.	[56]
5	Initial concentration of pollutant	-	Concentration affects degradation rate; very high concentrations will result in a drop-in rate because the dye molecules will absorb it and saturate the surface of the TiO <sub>2</sub> .	[57], [58]

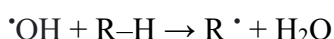
### 3.1.1 Application of photocatalytic treatment of TiO<sub>2</sub>:

#### 3.1.1.1 Removal of organic compounds utilised in cosmetics and pharmaceutical wastewater:

The hydroxyl group generated through photoexcitation of TiO<sub>2</sub> provides the ability to non-selectively oxidise virtually every organic compound with numerous of protons in water.



The similar reaction is also attained if molecules of organic matter and the electrons interact [49]. For instance, the following reaction happens when it interacts with hydrocarbons:



Aliphatic oxidation, in which radicals made up of hydroxyl remove hydrogen atoms from the molecule to create fresh radicals, and aromatic oxidation, in that the aromatic component of the molecule becomes oxidised by molecules of oxygen and superoxide radicals formed in the presence of ultraviolet (UV) radiation, are the two types of oxidations that can affect organic pollutants [60]. Additionally, it's crucial to guarantee that organic contaminants undergo substantial degradation once their Total Organic Carbon (TOC) content has decreased. This is because as the initial pollutant degrades, harmful organic compounds are generated [61].

The hydrothermal synthesis produced small quantities of TiO<sub>2</sub>, and the resulting particles were able to breakdown ibuprofen with photocatalytic efficiencies of 80–100% within 8–125 minutes [62]. TiO<sub>2</sub> has also been shown to be a potent aspirin-removing agent that functions effectively even when exposed to solar radiation. Among the organic acids created by photocatalytic degradation, acetic acid was found to be present in the highest amounts [63].

TiO<sub>2</sub> nanoparticles were used in photocatalyst treatment for the removal of the maximum amount of Amoxicillin and Metformin from the pharmaceutical wastewater in a 7.6 pH water treatment solution [64]. Degradation has primarily triggered by the generation of hydroxyl radicals. Similar to this, TiO<sub>2</sub> photo electrocatalysis was used to decrease the drugs 5-fluorouracil in wastewater to non-toxic levels [65]. It was shown that with an amount of 0.5g of antibiotics per litre of TiO<sub>2</sub> the solution, degradation peaked at a pH of 5, which is the ideal condition for using antibiotics and breaking down the drug clarithromycin to remove wastewater [66]. Other examples of Using TiO<sub>2</sub> photocatalysts to remove pharmaceuticals from water have been shown in Table 4.

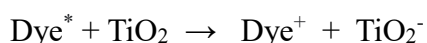
Table 4: Using TiO<sub>2</sub> photocatalysts to remove pharmaceuticals from water

Sr. no	Intended use of drug	Drug targeted	Remark	Reference
1	Antibiotic Diabetic drug	Amoxicillin Metformin	At 7.6 pH, the two drugs was maximum removed. Hydroxyl radical production was the main cause of degradation.	[64]
2	Anti-anxiety drug Antipsychotic	Buspirone Promazine	Molecules from the breakdown of TiO <sub>2</sub> by photocatalysis approximated those produced by metabolic. The capacity to control the reaction by varying the UV supply was also demonstrated.	[67]
3	Antibiotic	Clarithromycin	The rate of breakdown for 0.5g of antimicrobial per litre of TiO <sub>2</sub> solutions was discovered to be greatest at pH 5.	[66]
4	Antibiotic	Cephalexin	The optimum pH value for the drug's break down was discovered to be 7. When compared to amoxicillin, cephalexin was said to be more successfully removed under UV irradiation.	[68]
5	Antibiotic Antibiotic	Sulfamethoxazole Trimethoprim	The degradation process was slowed down by the beneficial interaction between the two drugs. It was discovered to be non-	[69]

			toxic as a result of the sulfamethoxazole's breakdown.	
6	Antidepressant	Sulfamethoxazole Trimethoprim	It was discovered that the efficiency and starting concentration of the antibiotic were inversely associated. It was demonstrated that both suspended and immobile catalysts may be used, although fixed catalysts produced the best results.	[70]
7	Antidepressant	Venlafaxine	With a maximal degradation efficiency of 96%, activity was found to be optimum at a pH of 10. This was also a significant decrease in toxicity.	[71]

### 3.1.1.2 Removal of dye from Textile wastewater

There are two possible methods for the photodegradation of dyes in water that occurs during photocatalytic degradation. The first is an indirect method in which the dye is excited by the energy it receives from visible light and enters its excited triplet state. Electrons are subsequently introduced into the titanium dioxide's conduction bands, further transforming the dye into a semi-oxidized radical [72].



The direct process is the second method by which dyes are photodegraded. In this mechanism, the molecules of dye interact with the produced hydroxyl radicals as well as with the holes and electrons that are created as a result of the energy in the conduction band, leading to the degradation and oxidation of the dyes, respectively [73]. Different organic dyes are eliminated using UV-TiO<sub>2</sub> photocatalysis therapy to overcome these restrictions because numerous colours are very water soluble and conventional wastewater treatment procedures are growing less and less effective.

Reactive orange 16, reactive orange 4, methylene blue, methyl orange, and methyl red are the colours that are most frequently employed in the textile industry. Under the use of UV lamps, TiO<sub>2</sub> as photocatalyst, and conditions like pH and dye concentration, the degradation of these colours in textile wastewaters was investigated. The ideal parameter settings for maximal Reactive Orange 16 dye breakdown in an environment of TiO<sub>2</sub> nanoparticles were explored. The decolorization and degradation were seen by measuring both the initial and final chemical oxygen demand, that matched the pseudo-first-order kinetics model. In general, the COD

continue to decrease as the irradiation period increases whereas the organic ion continues to grow. Reactive Orange 16 dye can be neutralised with an effectiveness of around 78% by using an 18 W LP Hg light at 254 nm for 80 minutes [74]. The study also looked at the effects of various operational circumstances. When the decolorization of the reactive red 198 dye in TiO<sub>2</sub> solution in water was researched, it was discovered that ethanol was commonly added to stop the process. The dye removal efficiency increased by 80-98% with a drop in the initial concentration of dye from 80 to 10 ppm [75]. The required time for reactive orange 4 deterioration is sixty minutes, the solution's pH is 4.8, and an 8 W MP Hg lamp operating at 365 nm. The efficiency removal observed is 95.1 [76].

Phenol and phenolic compounds are among the most major organic pollutants produced into aquatic ecosystems by the textiles and petrochemical industries. Using TiO<sub>2</sub> as a photocatalyst, the effectiveness and viability of phenol photodecomposition was studied. The degree of the efficiency at which phenol and its derivatives were degraded was observed to be 80 [80]. It was found that the quantity of the substrate and catalysts had an effect on the efficiency and pace of photodegradation of phenolic and its by products. Table 5 shows another example of photocatalyst dye degradation in textile water.

Table 5: TiO<sub>2</sub> photocatalyst degradation of the dye Compounds in textile water.

Sr. No	Catalyst dosages	Concentration of Dye	Volume of Dye	pH	Pollutant	Efficiency	References
1	0.4 gm/L Aqueous TiO <sub>2</sub> solution	25	2300	6.8	Reactive Orange 16	100	[74]
2	4.0 gm/L Aqueous Degussa P25 TiO <sub>2</sub>	50	300	4.8	Reactive Orange 4	95.1	[76]
3	0.1 gm/L Supported TiO <sub>2</sub> nanoparticle	4	500	6.0	Methyl Red	92	[77]
4	2.0 gm/L Aqueous TiO <sub>2</sub> nanoparticles,	50	200	3.0	Reactive Red 195	100	[78]
5	1.5 gm/L Nanocrystalline TiO <sub>2</sub>	10	250	6.4	Phenol	97	[79]
6	0.125 gm/L TiO <sub>2</sub>	20	25	10.0	Phenol	80	[80]
7	8.0 gm/L Supported TiO <sub>2</sub> Zeolites	20	10	8.0	Methyl Orange	96.6	[81]
8	0.1 gm/L Aqueous Degussa P25 TiO <sub>2</sub>	20	250	4.0	Methylene Blue	90	[82]





### 3.1.1.3 Heavy metal removal from water:

Due to its strong oxidising capabilities and stability,  $\text{TiO}_2$  is frequently utilised as a photocatalyst. It can be prepared in various forms such as nanoparticles, thin films, or immobilized on a support material. If the reduction potentials are suitable, the electrons generated by photo-excitation of  $\text{TiO}_2$  can reduce metal ions in water to their ground state [83]. The  $\text{TiO}_2$  photocatalyst is exposed to ultraviolet (UV) light, which activates its photocatalytic properties. When the photons from the UV light interact with the  $\text{TiO}_2$  surface, electron-hole pairs are generated. The excited electrons can react with water and oxygen to form hydroxyl radicals ( $\cdot\text{OH}$ ), which are highly reactive and can oxidize organic compounds and some heavy metals. The hydroxyl radicals generated during the photocatalytic reaction can react with heavy metal ions in the water, leading to their transformation or degradation. This process can convert soluble heavy metal ions into insoluble forms, making them easier to remove through sedimentation or filtration. In some cases, the heavy metals can also be directly adsorbed onto the  $\text{TiO}_2$  surface. After the photocatalytic treatment, the water may need to be filtered or subjected to additional treatment steps to separate the photocatalyst particles and any by-products formed during the reaction. This can be achieved using techniques like sedimentation, activated carbon filtration, or membrane filtration.

It has been widely shown that heavy metals are extremely hazardous to a variety of human organs, with potentially fatal results like cancer and chromosomal defects [84]. Initial research suggested that heavy metals would be reduced to lower oxidative states, then they would deposit on the catalyst, making  $\text{TiO}_2$  a time and money-effective way to remove heavy metals [85].  $\text{TiO}_2$  has been successfully employed in photocatalytic reductions of  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cu}^{2+}$  in a process that adhered to first order kinetics. The ability to remove heavy metals improved when the pH was lower, indicating that it might function in acidic settings. Studies have also shown that the method employed to remove heavy metals was absorption, that was made feasible by the nanoparticles great surface area [86]. The extensively characterised generated TNTs showed a rather high surface area ( $320 \text{ m}^2/\text{g}$ ). The high surface area revealed exceptionally good optimal removal circumstances (60 min of contact for 0.1 g TNTs dose at a pH of 5 and room temperature), with a high capacity for adsorption compared to prior studies and typical adsorbent. The binary system and separation coefficient calculation indicated that TNTs can adsorb  $\text{Co}^{2+}$  more effectively than  $\text{Ni}^{2+}$  in a binary system [87]. Highly effective adsorption was demonstrated using hierarchically porous metal oxide monoliths for Pb(II) and Cd(II). The adsorption experiments were conducted in multiple batches. Operating conditions pH carried out to 3 to 10 and time required for the 80 min, 92-98% of Pb(II) and Cd(II) were removed by  $\text{TiO}_2$  monoliths [88]. Other heavy metal removes from the water by the using  $\text{TiO}_2$  by the photocatalyst show in table 6.

Table 6:  $\text{TiO}_2$  photocatalyst removed the heavy metal from the water

Sr. No	Metal	Condition	Remark	References
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1	Cobalt ( $Co^{2+}$ ), Nickel ( $Ni^{2+}$ )	60 minutes at a steady time, 0.1g doses at pH 5, and room temperature	Because the nanotubes, catalysts, have a larger surface area than typical, it was found that the adsorption capacity is substantially higher than usual. The best outcomes were found to be achieved with a catalyst loading of 0.1 g, with pH 5 being the most effective. Nickel has a lower affinity than cobalt, it was found.	[87]
2	Lead ( $Pb^{2+}$ ), Cadmium ( $Cd^{2+}$ )	Time (0-80min), Temperature (303,313, and 323 k) pH (3 – 10)	The nanoparticles were cast to create the monolith. In this method, the issue of nano powder miscibility in water is reduced. The monolith's photocatalytic breakdown of the ions was improved by the huge surface area and adsorption capabilities.	[88]
3	Chromium ( $Cr^{6+}$ )	Low temperature and acidic medium	Because polyethylene glycol was used throughout the whole synthesis, the nanocrystals showed improved bonding abilities. The kinetics was discovered to be very advantageous for photocatalysis.	[89]
4	Chromium ( $Cr^{6+}$ )	Presence of formic acid	The addition of formic acid considerably accelerated the process. This is explained by the fact that it serves as a hole scavenger.	[90]
5	Arsenic ( $As^{3+}$ )	pH < 9	In addition to the presence of graphene oxide, hydroxyl radicals were encouraged to form, causing $As^{3+}$ to be oxidised to the transportable $As^{5+}$ form.	[91]

### 3.2 TiO<sub>2</sub> with Metal Doping and non-metal doping as photocatalyst:

#### 3.2.1 Metal Doping:

The transition metals, the noble metals, and metallic rare earths have been discovered to be used frequently for doping TiO<sub>2</sub> in the literature due to the decrease in band gap energy that they have been able to achieve. To enhance TiO<sub>2</sub>

photocatalytic activity and shift the frequency range of its spectrum reaction towards the visible spectrum, transitional metals such as V, Zn, Mn, Ni, Cr, Co, and Fe were investigated as dopants [92]. The incorporation of metal dopants into TiO<sub>2</sub> can have significant effects on its optical,



electrical, and catalytic properties. Metal doping, for instance, can change the bandgap energy, boost photocatalytic activity, increase the charge carrier movement, and change the electrical structure of the substance. Metal-doped  $\text{TiO}_2$  finds applications in various fields, including photocatalysis, solar cells, gas sensing, energy storage, and environmental remediation. For instance, doping  $\text{TiO}_2$  with noble metals can improve its photocatalytic efficiency, while doping with transition metals can enhance its visible light absorption. While transition metals function as photoinduced transporters of charge and may increase photocatalyst activity by reducing the energy required for photon production, it has been suggested that their presence in the  $\text{TiO}_2$  anatase may result in thermal instability [93]. It's important to note that the specific doping method, dopant concentration, and desired properties may vary depending on the intended application. Therefore, thorough research and experimentation are necessary to optimize the doping process and achieve the desired material properties.

### 3.2.2 Non-metal Doping:

Non-metal doping of  $\text{TiO}_2$  involves incorporating non-metal elements or compounds into the  $\text{TiO}_2$  lattice structure. Since non-metal dopants commonly substitute oxygen molecules in the  $\text{TiO}_2$  crystalline lattice, this procedure is also known as anion doping. It can be done using a variety of processes, including chemical vapour deposition, hydrothermal synthesis, sol-gel procedures, and solid-state reactions. Non-metal doping, including N, C, S, Cl, and F, is mostly used to improve  $\text{TiO}_2$  photocatalysts. Non-metal doped can be preferred to metal doping due to the  $\text{TiO}_2$  photocatalyst's enhanced stability, the simpler doping method, and its greater photocatalytic activity [94]. The preferred doping concentration, the type of non-metal dopant, and the intended application all influence the technique selection. The characteristics of  $\text{TiO}_2$ , particularly its visible, electrical, and catalytic properties, are being dramatically impacted. Bandgap energy can be changed, the separation of charges and transport is improved, photocatalytic activity is increased, and the material can be tailored for certain uses. due to the electrical features, which are better than those of regular  $\text{TiO}_2$  and include remarkable stability, low ionisation, and comparable atomic size with oxygen, non-metal nitrogen adding onto the  $\text{TiO}_2$  photovoltaic catalyst is the subject of intensive research [95,96]. Carbon doping can increase the electrical conductivity of  $\text{TiO}_2$  and improve its charge carrier mobility, making it suitable for applications like dye-sensitized solar cells and energy storage devices. Sulphur doping can improve the photocatalytic properties of  $\text{TiO}_2$  and enhance its stability under certain conditions. Fluorine doping can modify the surface energy and hydrophilicity of  $\text{TiO}_2$ , influencing its wettability and surface reactivity. Phosphorus doping can enhance the visible light absorption of  $\text{TiO}_2$  and improve its photocatalytic efficiency.

### 3.2.3. Application of Metal Doping and non-metal doping:

#### 3.2.3.1 Removal of dye from Textile wastewater of the photocatalyst by the metal doping and non-metal doping.

$\text{Co}^{2+}$  was doped into the  $\text{TiO}_2$  photocatalyst degradation of methyl orange was observed 85% efficient under the 500 W tungsten-halogen lamp at 420 nm was conducted by the for the 180 min, the operating condition of the solution pH was 7 and catalyst dosages was applied the 0.1gm/L [97]. When  $\text{Fe}^{3+}$  was doped into  $\text{TiO}_2$  using the sol-gel technique, the photocatalytic degradation of methylene blue was around 97% efficient. The photocatalytic process was



carried out for 60 minutes under an extremely high-pressure mercury (HP Hg) lamp with a wavelength of 254 nm. The inclusion of an appropriate amount of  $\text{Fe}_2\text{O}_3$  into  $\text{TiO}_2$  was linked to changing optical and physical-chemical properties of samples [98]. The photocatalytic capacity under UV light can be enhanced by coating  $\text{TiO}_2$  with noble metals including Au, Pt, Ag, and Pd. Due to the reduction in band gap energy, electron trapping, and charge transfer, doping precious metals with  $\text{TiO}_2$  may enhance performance. The doped the  $\text{Ag}^+$  with  $\text{TiO}_2$  photocatalyst degradation Direct red was observed the 97% efficiency, the presence of 8W MP Hg vapor lamp at 365 nm, the dose of the catalyst is 3gm/L and the reaction was conducted by 120 min [99]. Two widely used textile dyes, Reactive Blue 21 and Acid Red 114, each contain an azo group. Using rare earth metals such as  $\text{Pr}^{3+}$  and  $\text{Ce}^{4+}$  doped onto  $\text{TiO}_2$ , ultrasonic deterioration of those dyes was investigated. After 50 min at 3.79 weight percent dopant, both dyes were almost entirely deteriorated, and a kinetic investigation revealed the second-order mechanism was followed.  $\text{Ce}^{4+}$  doped  $\text{TiO}_2$  outperformed  $\text{Pr}^{3+}$  doped  $\text{TiO}_2$  due to the chemical compounds created by their absorption of dyes for 250 W UV light [100]. Other metal doped with  $\text{TiO}_2$  photocatalyst degradation of the dye from the textile wastewater shown in the table 7.

Nonmetal doping can be more advantageous than metal doping because titanium dioxide photocatalyst stability is higher, the doping process is easier, and there is increased photocatalytic activity. When Congo red azo dye was photocatalyzed under 8 W Osram lamps, 98% or greater of the N-doped  $\text{TiO}_2$  catalyst was removed from the solution of water in under 70 minutes. A 6-weight percent N-dopant material was considered optimum. The rutile phase of  $\text{TiO}_2$  is known to have less photocatalytic capacity than the anatase phase [101]. As the activated carbon content increased as a result of the increased surface area, the catalytic activity of a  $\text{TiO}_2$  photocatalyst with active carbon increased. The  $\text{TiO}_2$  catalyst composition, however, restricts the surface of the activated carbon, so activity declines as the amount of  $\text{TiO}_2$  rises [99]. C-doped with  $\text{TiO}_2$  photocatalyst degradation of the methene blue dye was observed 81% efficiency and the reaction time was 200 min and dye solution of the pH was 10.6 and catalyst dosage was required 2gm/L [102]. Other non-metal doped with  $\text{TiO}_2$  photocatalyst degradation of the dye from the textile wastewater shown in the table 8.

Table 7: Optimum dopant concentration and modification of the  $\text{TiO}_2$ -metal photocatalyst for enhancing photocatalytic activity.

Sr. No	Photo catalyst	Catalyst dosages (gm/L)	Pollutant	Concentration of the dye	Volume of dye	Optimum Doping	pH	Efficiency (%)	References
1	$\text{Co}^{2+}$ - $\text{TiO}_2$	0.1	Methyl orange	20	100	0.7 wt %	7	85	[97]
2	$\text{Zn}^{2+}$ - $\text{TiO}_2$ /	1	Congo red	10	250	0.06 wt%	7.8	100/78	[103]

	V <sup>5+</sup> - TiO <sub>2</sub>								
3	Fe <sup>3+</sup> - TiO <sub>2</sub>	0.1	Reactive black 5	20	150	0.5 mol%	7.2	100	[104]
4	Ag <sup>+</sup> - TiO <sub>2</sub>	0.1	Methyl orange	20	100	0.5 wt%	-	100	[105]
5	Au - TiO <sub>2</sub>	1	Rhoda mine B	10	100	5 wt%	-	99.3	[106]
6	pt -TiO <sub>2</sub>	0.1	Methyl orange	10	50	1.5 wt%	8	98	[107]
7	Yb <sup>3+</sup> - TiO <sub>2</sub>	0.3	Direct Blue	100	150	-	-	89.8	[108]
8	Gd <sup>3+</sup> - TiO <sub>2</sub>	0.3	Direct Blue	100	150	1 wt%	4	91.5	[108]
9	Ce <sup>4+</sup> - TiO <sub>2</sub>	0.1	Methyle ne Blue	100	100	5 wt%	2.5	78	[109]

Table 8: The most effective dopant concentration and modifications of the TiO<sub>2</sub> non-metal photocatalyst are used to increase the photocatalytic efficiency.

Sr. No	Photo catalyst	Catalyst dosages (gm/L)	Pollutant	Concentration of the dye	Volume of dye	Optimum Doping	pH	Efficiency (%)	References
1	N-TiO <sub>2</sub>	1.0	Methylene Blue	10	100	1 wt%	-	92	[110]
2	N-TiO <sub>2</sub>	0.3	Rhodamine B	20	100	3 wt%	7.5	98	[111]
3	C-TiO <sub>2</sub>	2	Methylene Blue	50	-	0.5 wt%	10.6	81	[102]
4	F-TiO <sub>2</sub>	0.3	Methylene Blue	10	150	6 mol%	2	98	[112]
5	I-TiO <sub>2</sub>	0.5	Orange II	5	100	0.32 wt%	8	85	[113]

## 4 Conclusion

The modifications that are made to TiO<sub>2</sub> nanoparticles, among the most desirable and useful photocatalyst with high levels of photocatalytic activity in the process of treatment of different industrial wastewater under UV radiation, are reviewed in this study. Frequent modification techniques, including metal doping and nonmetal doping, were developed for TiO<sub>2</sub> photocatalyst manufacture in order to decrease recombine losses. The impacts of ideal dopants



on UV-TiO<sub>2</sub> photocatalytic performance had been discussed in this review paper. It was observed that the photocatalytic degradation of dyes using rare earth metals (Gd, Yb, and Ce), transition metals-doped TiO<sub>2</sub>, and precious metals (Ag, Au, Pt, and Pd) is very attractive. Due to its significant photocatalytic capacity, low toxicity, and photostability, improved UV-TiO<sub>2</sub> photocatalysis is anticipated to be applied in industry in the future. The problems with water contamination can be resolved by using this approach to entirely remove organic pollutants from industrial wastewater. For the desired treatment efficiency, it is crucial to optimise the photocatalyst dosage, UV light intensity, and reaction time. To ensure environmental sustainability, it is also important to consider the used TiO<sub>2</sub> nanoparticles must be regenerated, reused or properly disposed as per regulation suggested by pollution control board.

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