

Photocatalysis in Wastewater Treatment

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Abstract

Large businesses like biotechnology, petrochemical, pharmaceutical, and agriculture have emerged because of urbanization and technical improvements. These sectors use a lot of water, which creates problems for wastewater treatment. A promising new field of study for managing a variety of wastes is photo catalysis, especially hazardous and refractory organics that are difficult to handle with traditional techniques. This study examines earlier studies, current research, and potential applications of nano-photocatalysis for wastewater treatment. It draws attention to the dearth of established criteria for evaluating the performance of different photo catalysts in wastewater treatment and the necessity of conducting additional pilot and field-scale studies to ascertain financial advantages. One ecologically safe, economically viable, and sustainable method for enhancing wastewater quality and addressing the shortage of clean water is photo catalysis. The development of semiconductor nanoparticles has garnered attention. The degradation of organic and inorganic pollutants by photo catalysts, such as TiO_2 , ZnO , MoS_2 , $\text{g-C}_3\text{N}_4$, CuO , Fe_2O_3 , CdS , SnO_2 , ZnS , SrTiO_3 , and their nanohybrids, has garnered interest in wastewater treatment due to advancements in semiconductor nanomaterials. It primarily focuses on operational parameter optimization and how it affects the photo catalytic breakdown of water contaminants. Metal oxide-based semiconductors have been explored as excellent photo catalysts to degrade organic pollutants in wastewater. Photo catalytic degradation allows spontaneous and non-spontaneous reactions using light energy.

Keywords: Wastewater, sustainable environment, photo catalyst, degradation

Review article

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1. Introduction

The growing demand for clean water sources due to industrialization, population growth, and long-term droughts has led to various strategies and solutions to yield more viable water resources. A major worldwide worry these days is environmental degradation, since water is essential to a sustainable way of life. With only 3% of the water accessible for consumption in the 21st century, water scarcity is a serious environmental concern [1]. However, arid areas with abundant sunlight, less rainfall, and long-term droughts face challenges in obtaining clean water, with around 4 billion people worldwide lacking access and millions dying of severe waterborne diseases annually. Water pollution is caused by untreated contaminated water effluents from domestic homes, businesses, and agricultural. This can have a negative impact on public health and increase the risk of serious illnesses like typhoid, cancer, cholera, and hepatitis. To suppress the worsening of clean water shortage, advanced low-cost and high efficiency water treatment technologies are desirable. One attractive option is the reuse of onsite rural wastewater or treated municipal wastewater from treatment plants for agricultural and industrial activities. Aquatic ecosystems are harmed by water pollution, which results in eutrophication and disturbance of the water quality. The sources of pollution include drinking water, dye, pharmaceutical waste, pesticides and heavy metals that seep

into water bodies. Numerous techniques for treating wastewater have been devised, but they are ineffectual because they require vast systems, infrastructure, engineering expertise, and chemical and operating requirements [2].

Conventional water treatment methods, such as sedimentation, filtration, chemical, and membrane technologies, involve high operating costs and can generate toxic secondary pollutants. Chlorination is the most common disinfection process, but its by-products are mutagenic and carcinogenic to human health. Because new nano-photocatalysts are being developed at a rapid pace, photocatalysis has become a viable option for treating wastewater. With the use of this technique, a variety of contaminants can be eliminated and complex contaminants, such as landfill leachate, can be broken down into simpler substances, such as water, carbon dioxide, and inorganic ions [3]. Substances including colors, antibiotics, analgesics, herbicides, pesticides, and stimulants are important sources of water pollution. Many solutions have been devised and put through experimental testing, but the primary problems with them are that they use a lot of energy, don't treat pollutants well, foul, and only work on specific pollutants [4]. Because photocatalytic degradation is a highly exciting and promising mechanism that can completely degrade a wide range of contaminants into simpler chemicals, researchers are currently interested in this enhanced way of degradation [5].

In several solar spectrum bands, photocatalysis, the act of harvesting sunlight—has shown an efficient way to address energy issues and environmental pollutants. Heterogeneous photocatalysis employing semiconductor catalysts has demonstrated its efficiency in degrading a wide range of contaminants into biodegradable compounds and mineralizing them to innocuous carbon dioxide and water [6].

2. Methodology

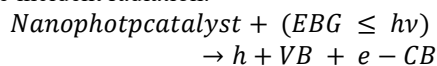
2.1. Photocatalytical Process

Technique of employing photo catalysts to transform photonic energy into chemical energy is known as photo catalysis [7-8]. Three types of light are photonic: UV, visible, and sunlight. Photons with energy greater than or equal to band gap (BG) of photocatalyst produce holes and electron pairs. In order to decrease and oxidize impurities on surface of photocatalyst, e^- from the valence band (VB) into the conduction band (CB) forms e^- – h^+ couples. Concurrent oxidation and reduction reactions are necessary for photo catalyst to function efficiently. Using a sophisticated oxidation method called heterogeneous photocatalysis, hazardous materials in wastewater can be photo degraded without creating more waste. Photocatalysts: TiO_2 , ZnO , SnO_2 , CuO , $SrTiO_3$, Bi_2WO_6 , WO_3 , CdS , MoS_2 , Ag/Ag_2Te , and $g-C_3N_4$ utilized in photocatalytic treatment of wastewater [9]. Because of their abundance, non-toxic behavior, economic viability, chemical and thermal stability, environmental friendliness, optical and electrical properties, titanium (TiO_2) and zinc oxide (ZnO) are most researched and used photo catalysts [10]. In addition to semiconductor material, photocatalysis performance is highly influenced by operational factors like pH, photocatalyst quantity, hazardous substances, light intensity, doping agents, and oxidants [11].

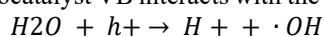
2.2. Photocatalysis Mechanism

The electrical structure of semiconductors, which consists of an occupied VB and an empty CB, makes them useful as photo-catalysts for boosting the rate of redox reactions. If the BG of the nano-photocatalyst is less than or equal to the energy of incident radiation, photons are absorbed by the electrons in VB and they reach the CB [12]. The oxidation of donor molecules and the production of hydroxyl during the reaction between them and H_2O depend on holes. An ion known as superoxide is created when water absorbs the electron present in CB. The pairs of free electrons and holes present in any pollutant that comes into contact with the photocatalyst can undergo a redox reaction, producing carbon dioxide (CO_2) and water (H_2O) [13]. Diffusion and adsorption of reactant species, photon absorption, photochemical reaction by charge carrier production, and desorption and diffusion of the product are the primary stages of the nano-photocatalysis process [14].

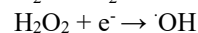
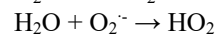
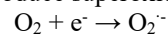
- Photocatalysts form e^- – h^+ couples when exposed to a photon with a wavelength larger than or equal to BG width. Electrons in VB absorb the photon if the BG of the nano-photocatalyst is less than or equal to the energy of the incident radiation.



- During photooxidation, OH radicals are created when the h^+ in photocatalyst VB interacts with the H_2O molecules.

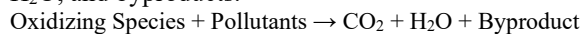


- The e^- , which starts photoreduction reactions on photocatalyst surfaces, combines with dissolved O_2 in the CB to produce superoxide ions.



Water absorbs the electron in CB, forming the reducing agent superoxide ion as a result.

- Photoreduction and photooxidation processes occur on the surface of the photocatalyst, producing e^- – h^+ pairs that result in superoxide radicals. These radicals then react with impurities, breaking them down into CO_2 , H_2O , and byproducts.



Any impurity is transformed into carbon dioxide and water by the photocatalyst via a redox reaction with free electrons and h^+ .

2.3. Factor affecting photo catalyst activities

2.3.1. Catalyst Dose

When the dose of the catalyst is increased, the amount of photo mineralization of the water pollutant also increases because the photocatalyst's more active sites absorb more photons and generate more $OH\cdot$ radicals and positive holes when exposed to radiation. As a result, the pollutants' rate of degradation accelerates. The majority of the solar energy that is irradiated is directly transmitted from the solution at lower dosages, whereas photo-degradation rate is slowed down at higher dosages [15]. Increased turbidity in the solution, which blocks UV/Vis light and improves light scattering, and high concentration of nanoparticle agglomeration, which lowers the amount of active surface sites accessible for exposure, are two potential causes. It is simple to see how photocatalytic activity and catalyst dose are related: as the catalyst dose rises, so does the number of radicals require for degradation and the rate of reaction. Raising the catalyst dose won't aid the reaction once it has reached its peak efficiency, though, as most of the catalyst surfaces will become inactive due to the inability of light to flow through [16].

2.3.2. Catalyst morphology

A catalyst's shape has an immediate effect on its photocatalytic activity. Because they have a larger surface area than bulk particles and can react with many pollutants at once, nanophotocatalysts are more effective than bulk particles. The catalyst's size, shape, and morphology all affect how quickly pollutants in wastewater degrade. Pollutant breakdown is improved by smaller nanoparticles because they have more active sites and a bigger surface area. Compared to TiO_2 (Rutile), TiO_2 (Anatase) has higher photocatalytic activity [17]. A range of ZnO morphologies, including nano-spindle, nanoflower, and nano-rod, were employed in the degradation of methylene orange dye [18].

2.3.3. Effect of pH

The pH of a reaction medium significantly impacts the efficiency of photocatalysts in reducing pollutants. Three main factors affect this efficiency: hydroxyl radical assault, reduction of pollutants by conduction band electrons, and oxidation of pollutants due to high oxidation potential of positive holes. A negative charge is produced on the photocatalyst surface when the pH rises, while lower pH

levels cause the photocatalyst's functional groups to become protonated, attracting cationic contaminants [19]. Adsorption is the first stage in effective photocatalytic destruction, with photodegradation at lower pH primarily caused by positive holes with high oxidation potential. To maximize a photocatalyst's effectiveness, the pH of the solution must be optimized. Photocatalytic performance is most effective at neutral pH, but poor at acidic or alkaline pH. Ideal working conditions must be determined as the pH of an aqueous solution affects the substance's surface charge [20].

2.3.4. Effect of light intensity

In photocatalytic processes, semiconductor materials function as catalysts by absorbing light to start the reaction. In order for electrons to be excited and produce free radicals, which break down contaminants, light energy must be at least as high as the bandgap. Light intensity affects the rate of photo degradation reaction; higher light intensities increase the likelihood of electron excitation. Charge carrier recombination, on other hand, competes with light intensity, decreasing the generation of free radicals and influencing the rate of degradation of organic pollutants. With increasing light intensity, photocatalysis becomes more efficient [21].

2.3.5. Effect of temperature

The majority of photocatalytic reactions take place at room temperature, but as a result of energy released during electron and hole pair recombination and degradation, the rate of photocatalytic degradation also rises [22]. Usually, the reaction has a limit at or above 80°C because higher temperatures cause the capacity for degradation and the lifespan of charge carriers to decrease. Since organic contaminants have a limited apparent activation energy and a weak influence on degradation rate, the ideal temperature range for them is between 20 and 80°C. As recombination rises, raising the temperature beyond the optimal point has no beneficial effect on the reaction [23].

2.3.6. Band Gap BG

At particular wavelengths, the BG of a nano-photocatalyst is essential for producing e⁻-h⁺ couples and reducing recombination rates. Photons in the VB are absorbed and go to the CB if the BG is less than or equal to the energy of the incident radiation. More energy is needed for electron or hole excitation at higher BG. Lowering the BG is intended to enable sun irradiation for wastewater treatment and visible light energization of the photocatalyst [24].

2.3.7. Effect of Doping

Dopants are contaminants added to photocatalysts in order to increase their effectiveness. By changing the photocatalyst's band gap, adding impurity energy levels, trapping electrons, producing oxygen-deficient sites, and increasing the number of active sites for pollutant adsorption, they aid in photocatalytic reactions [25]. Doping can be added at the substitution or interstitial levels; the latter requires a dopant radius smaller than the lattice spacing. A critical factor in photocatalytic efficiency reduction is dopant concentration optimization. Exceeding the optimal limit of dopant concentration decreases active surface area and increases photo-induced charge carrier recombination. In order to maximize the amount of vanadium and nitrogen dopants in the titania catalyst for photocatalytic antibiotic degradation,

Eswar et al. discovered that increasing the concentration of dopants increased effectiveness of the degradation process by lowering band gap and serving as charge trapping [26].

2.3.8. Effect of inorganic ions

Wastewater containing inorganic ions has the potential to greatly impact photocatalysts' ability to degrade organic pollutants. These ions could compete with pollutants to adsorb onto the surface of the photocatalyst and obstruct active sites. Research has demonstrated that when employing photocatalysts in a fixed-bed or slurry arrangement to treat water in the presence of inorganic ions, the photocatalysis reaction is inhibited. While Ca²⁺, Zn²⁺, and Mg²⁺ have minimal impacts, inorganic cations such as Cu²⁺, Al³⁺, and Fe²⁺ lessen the photo-mineralization of pollutants under photocatalytic reaction. Whereas BrO³⁻, SO₄²⁻, HCO³⁻ and PO₄³⁻ function as holes and radical scavengers, lowering the rate of photocatalysis, inorganic anions such as NO³⁻, Cl⁻, and ClO⁴⁻ exhibit a decrease in photocatalytic activity. One of the best methods to prevent the negative effects.

3. Discussion

3.1. Personal Care and Pharmaceutical Waste

By employing nanoparticles and nanocomposite, photocatalysis is a successful method for eliminating harmful pollutants from wastewater. However, conventional techniques for treating wastewater, such as landfilling and incineration, frequently fail. Photocatalysis solves issues such as the production of secondary pollutants, the formation of sludge, the ineffective breakdown of organic pollutants, and exorbitant expenses. Photocatalysis requires a lot of time to reuse or recycle; nevertheless, magnetic nano-photocatalysts have demonstrated promising regeneration [29]. Because of its broad-spectrum activity, chemical stability, and reusability, the doped nano-TiO₂ orientated photocatalysis technique is a promising option. An effective method for non-toxic discharge is solar-photocatalytic degradation with TiO₂. The production of e⁻-h⁺ pairs and photocatalytic performance during the photocatalytic degradation of personal care and pharmaceutical waste are greatly influenced by variables such as light source, light intensity, catalyst morphology, catalyst dose, initial pollutant concentration, irradiation time, band gap, pH, temperature, and doping type [30].

3.2. Dyes

Most commercial dyes, including Methylene Orange, Rhodamine B, Congo red, and Methyl Blue, are water soluble, non-biodegradable, and may be hazardous to human health and the environment. To solve these problems, it is essential to use different nanoparticles and nanocomposite materials for the photocatalytic degradation of dyes found in wastewater. The primary cause of the environmental issue is dyes' ability to absorb and reflect sunlight when it enters water, which lowers algae's capacity for photosynthetic activity and affects the food chain. Due to their superior photo and thermal stability, dyes have a long shelf life. Many dyes can have short- or long-term effects on exposed species and are dangerous, carcinogenic, or mutagenic [31]. Kind of oxidizing agent utilized determines the photocatalytic degradation of dye, and the species redox potential should be taken into consideration while selecting the oxidizing agent. Cationic or anionic dye's absorption and surface breakdown determined by pH of solution.

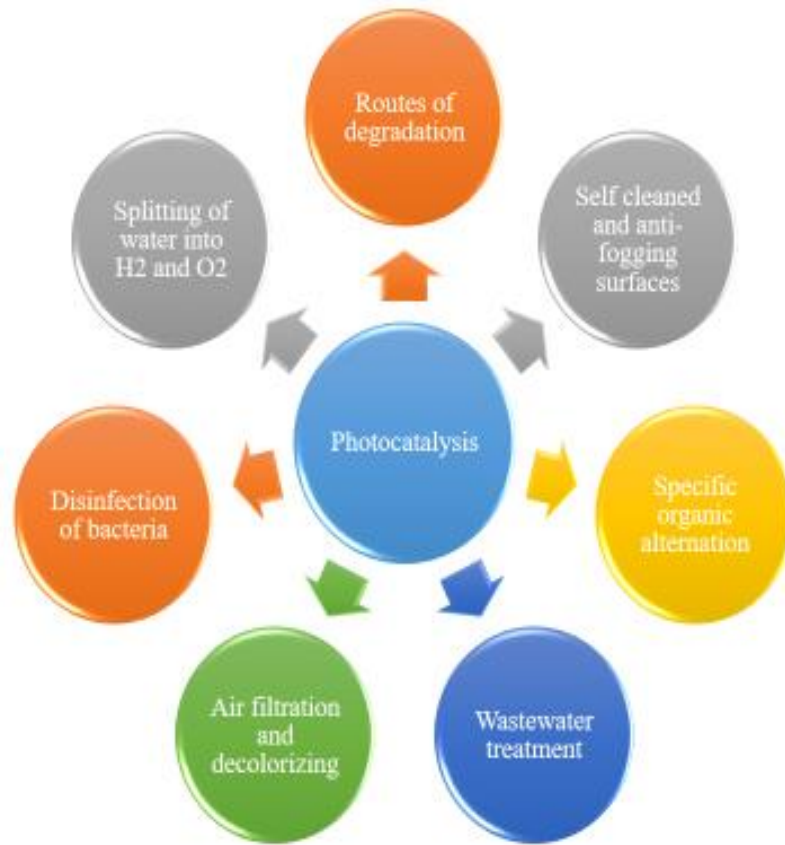


Figure 1: Photocatalysis process

Photocatalysis Mechanism

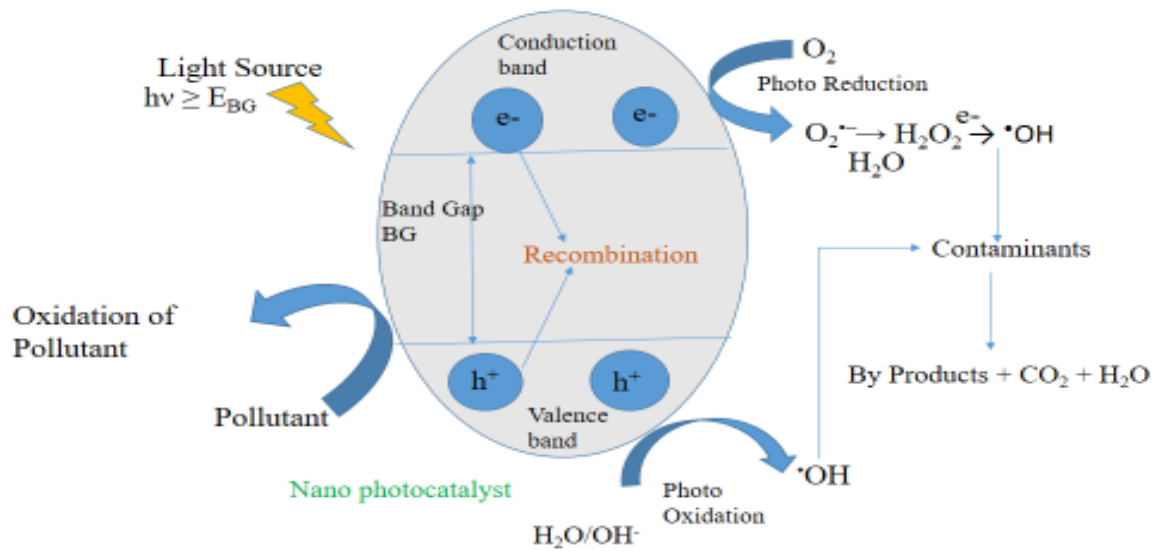


Figure 2. Photocatalysis Mechanism

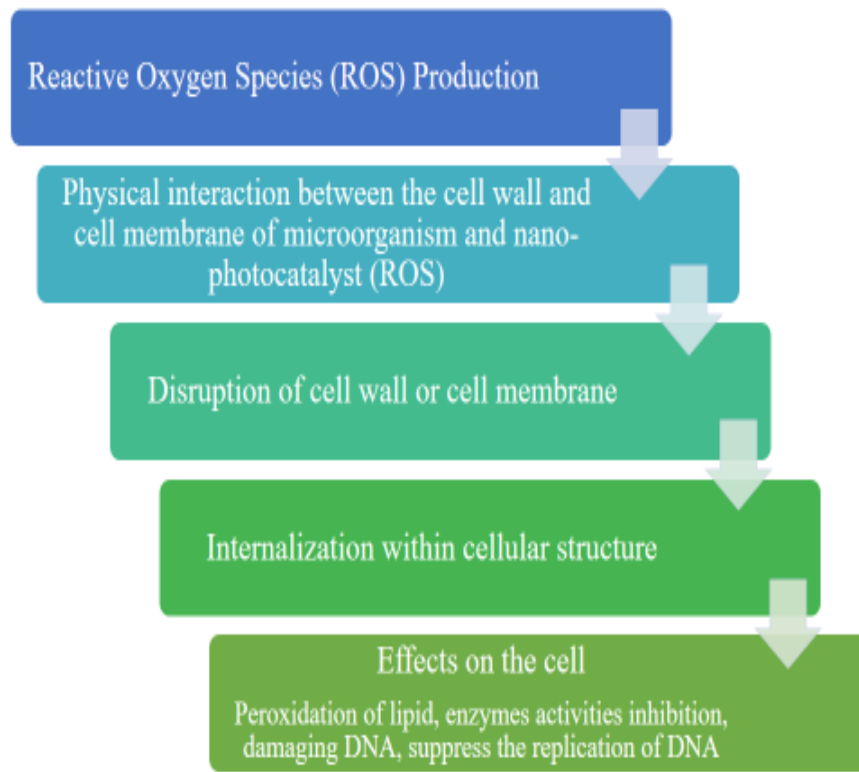


Figure 3. Impacts of Photocatalytic Disinfection on Microbes

Table 1. Advantages and Disadvantages of photocatalysts [28]

Advantages of Photocatalysts	Disadvantages of Photocatalysts
Photocatalysis works better than advanced oxidation processes (AOPs) when it comes to mineralizing contaminants in wastewater. While photocatalysis may fully breakdown organic, inorganic, and heavy metals without the use of costly external oxidizing agents, AOPs are normally employed to break down organic and inorganic pollutants	The high interfacial e-transfer rate, recombination lifetime, and electron and hole recombination rate of photo-generated e⁻ and h⁺ all affect the overall quantum efficiency of photocatalysis. The most popular method for increasing quantum efficiency is to postpone recombination.
Photocatalysts are economically viable for treating wastewater because they may be recycled and reused again without losing their effectiveness. The applicability of nanoparticles is greatly influenced by how easy they are to regenerate. A magnetic field is used in a straightforward regeneration process that makes magnetic nano-photocatalysts especially efficient.	Semiconductor nanoparticles require continuous UV light to be active since they are ineffective or underperform as photocatalysts in visible light. This requires a lot of upkeep and is not financially feasible. On the other hand, doped photocatalysts are easier to implement on a broad scale since they can operate in visible light and be activated by sunshine.
Under contrast to traditional wastewater treatment methods that require mineralization to completely break down complex contaminants, photocatalysis reactions take place under ambient settings and don't require any post-treatment processes.	The optical properties of nanoparticles are changed by aggregation and agglomeration, which impacts the particles' capacity to scatter and absorb light and, ultimately, their photocatalytic efficacy.

Table 2: Elimination of Pesticides from wastewater using nano-photocatalysts

Photocatalyst	Light Source	Technique of Synthesis	Functional Specifications	Contaminants	Removal effectiveness
TiO ₂	Solar	Readily Available in stores (Degussa P-25)	Particle size: 19-29nm pH: 7.59 Catalyst dosage: 1.42g/L Time for irradiance: 419mins Initial CBF: 54.9mg/L	Carbofuran (CBF)	100%
Ag/Ag ₂ O-TiO ₂	Visible	Sol-gel method	Intensity of light: 1mW/cm ² Irradiance time: approx. Three hrs. Quantity of Imazapyr : 0.07mmol/L Catalyst loading: 1.49wt%	Imazapyr Herbicide	100%
Ag/LaTiO ₃	Visible	Sol-gel method	Light intensity: 299W Time of Irradiance: 39mins Amount of Atrazine: 1199mg/L Catalyst loading: 2.49mg/L	Atrazine	100%

Factors including the catalyst-to-dye ratio, temperature, light source, intensity, pH, and the existence of interfering compounds all affect how well photocatalytic dye degradation works. During the photocatalytic degradation process, dyes break down into smaller pieces; occasionally, the intermediates produced during this process are more hazardous than original dye [32].

3.3. Pesticides

Pesticides are used in transportation and agriculture to preserve freshness, however they are carcinogenic and lead to water contamination. To counteract the damaging effects of pesticides on the environment and living things, nano-photocatalysts have been developed. Pesticides, including water and biodegradable chemicals, can be broken down by photocatalysis into less poisonous or hazardous parts. Scavengers present a problem for photocatalysis in wastewaters, though. Various methods have investigated, such as semiconductor-based photocatalysis, photo-Fenton, photolysis, and photo electrocatalysis. The degradation process is greatly affected by variables such as temperature, pH, band gap, shape, and intensity of light source [33].

3.4. Heavy Metals

Heavy metal ions, which are necessary for metabolic processes, represent a major hazard to water sources, because they cannot be broken down by the body. They have the ability to attach themselves to proteins, nucleic acids, and micro metabolites in living things, resulting in harm and medical problems. By converting high-valence metal ions into zero- or low-valence metal ions, photocatalytic elimination can be used to remove these harmful metal ions from wastewater. Some metal ions may only be indirectly reduced by donor-mediated reduction; they cannot be directly

reduced or elevated to a higher oxidation state. Heavy metals can be photocatalytically removed from wastewater using ZnO nanoparticles, which use physical adsorption and a redox reaction by photo-generated electron-hole pairs [34].

3.5. Disinfection of Water

Researchers are looking into photocatalysis as a potential replacement for conventional disinfection methods like chlorination, which can result in dangerous byproducts. Ozonation, chlorination, and UV disinfection are examples of traditional disinfection techniques that can be detrimental to aquatic environments while having minimal effect on viruses, *Giardia lamblia*, or *cryptosporidium*. With photocatalytic disinfection, no external chemicals are needed and it is efficient against all kinds of germs [35]. On the other hand, ROS production, negative effects on the components of microorganisms' cells, metal ion release during photocatalysis, direct interaction between the nanophotocatalyst and the microbe, cytotoxicity, and cell wall rupture can all result in photocatalytic water disinfection. ROS can cause damage to RNA and DNA, rupture cell membranes, disrupt respiratory metabolism due to suppression of CoA enzyme, and enhance ion permeability of cell membrane, among other ways that they can injure or kill microorganisms. Water containing bicarbonate and carbonate ions reduces efficiency of photocatalytic disinfection by scavenging OH radicals. Because different bacteria react differently to visible and UV light as well as nano-photocatalyst material, susceptibility of microorganisms to the photocatalytic process will depend on their nature [36].

3.6. Leachate and Industrial Wastewater Treatment

Landfill leachate, a hazardous liquid produced, is a serious environmental problem. In addition to photocatalytic treatment employing metal, metal oxide nanoparticles, and

nano-composites, leachate treatment is essential for controlling this liquid. Additionally, dangerous substances found in industrial effluents cannot be dumped straight into waterways. The literature review draws attention to the strength, diversity, and complicated composition of landfill leachate, which can be harmful to the environment and biotic components. Prioritizing reuse and recycling over disposal of waste is a good idea [37]. It is imperative that international legislation address the usage of nanophotocatalysts and the risks involved. It is advised that TiO₂ be used as a strong and affordable photocatalyst in leachate to break down organic materials that are resistant to degradation, heavy metals, and dangerous contaminants. The production of e⁻-h⁺ couples and photocatalytic efficacy during leachate degradation are greatly influenced by variables such as light source, intensity, catalyst shape, dose, initial pollutant concentration, irradiation time, band gap, pH, temperature, and doping type. Leachate pre- and post-treatment can increase the proportion of contaminants eliminated [38].

4. Future Scope

Although photocatalysis offers great potential for treating wastewater and pretreating drinking water, there are many obstacles in the way of its widespread implementation. For wastewater treatment to be effective, advances in photocatalyst efficiency, design, operating conditions, and reactor design are required. For efficient treatment, determining the extent to which contaminants have mineralized and developing reactors with low energy consumption are essential [39]. Although studies on toxicity of photocatalysts are still lacking, photocatalytic wastewater treatment is a feasible and economical solution. While long-term forecasts for photocatalytic systems are unrealistic due to technological barriers including system setup, toxicity, and regulations, stricter water treatment requirements are necessary for widespread implementation [40].

5. Conclusions

The treatment of water and wastewater is essential to the wellbeing of ecosystems and people. Conventional techniques including sophisticated oxidation processes, membrane filtering, physio-chemical, & biological processes are not enough to remove all types of contaminants and need constant upkeep. On the other hand, without need for additional chemicals, photocatalytic treatment completely breaks down contaminants into simpler components and can be recycled for additional processing. Degrading dyes, hydrocarbons, pesticides, bacteria, and microbes, as well as lowering hazardous metal ions in wastewater, are among potential uses of photocatalysis. Catalytic morphology, pH, temperature, light intensity, and e⁻-h⁺ pair formation are some of factors that affect performance. Increasing these characteristics can lead to better outcomes. Technological developments in synthesis of nanomaterials, including green nano-photocatalysts, have decreased need for chemicals and raised efficacy and efficiency of photocatalysts. All things considered, photocatalytic technology is becoming more and more popular as an effective and green wastewater treatment technique.

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