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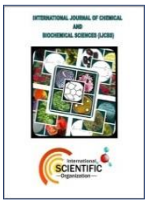

Wastewater Treatment by Photocatalysis: Approaches, Mechanisms, Applications, and Challenges

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Abstract

Concerns about chemical and biological contamination of water have emerged as major issues for society, government, and industry. Wastewater has adverse effects on the fauna and flora. Effluents in wastewater require effective treatments which are eco-friendly and cost-effective in order to prevent hazardous effects on the environment and aquatic life. A significant amount of research has been conducted in the development of appropriate water treatment techniques capable of improving water quality. Biological, chemical, and physical techniques can be applied to treat wastewater. Biological treatment systems have several drawbacks, including unequal removal effectiveness and being uneconomical. The physical method is not appropriate for the treatment of wastewater because it is time-consuming. Chemical methods like electrochemical treatments, ozonation, and oxidation process for the treatment of wastewater are eco-friendly. Photocatalysis using different catalysts is an advanced oxidation process for the treatment of different effluents in industrial and domestic wastewater. Photocatalysis is a viable approach for removing aquatic viruses, harmful metal ions, and industrial wastes. Photocatalysis is an adaptable, cost-effective, versatile, and environmentally safe treatment method for a wide range of contaminants. The photocatalysis technique uses catalysts that convert photon energy into chemical energy. These catalysts may be semiconductors, polymers, clays, metal oxides, and doped metal oxides.

Keywords: Wastewater, Treatment, Photocatalysis, catalyst, Effluents

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1. Introduction

Environmental pollution is a widespread issue with significant implications for human health. Pollution reaches its peak in the more developed countries in densely populated urban-industrial areas. More than 80% of polluted water is used for irrigation in poor countries around the world [1-2]. These days, between 300 and 400 million tons of untreated organic pollutants are created annually, which causes water pollution issues, particularly close to industrial locations. According to the World Health Organization (WHO), prolonged exposure to water pollution causes approximately one-quarter of the diseases that plague humanity today. The majority of these water pollution-related diseases, however, are difficult to detect and may be acquired during childhood and manifest later in life [3-4]. Chemical, nutritional products, fabric and textiles, herbicides and pesticides, coloring, and publishing industries all contribute to water pollution. Water pollution harms animals, plant life, and humans.Water pollution is primarily caused by dye-based industries, where wastewater is colored due to dye components. This polluted water is not used for irrigation or household purposes [5-6]. Dyes are used in the textile industry for coloring fabric. These dyes originate from intermediates of the petroleum industry and coal tar and these synthetic dyes have chromophore and axochromes groups which are responsible for color. Organic, heavy metals, surfactants, and salts are added for better color adsoption and these are key contaminants in wastewater [7-8].

At the moment, different methods are used to remove these compounds from wastewater, including chemical, biological, and physical methods [9-10]. In the chemical methods; electrocoagulation, ozonation, and advanced oxidation are included. This method is not favorable due to its high cost [11]. In biological methods; bacterial degradation is common. Because biological treatment has drawbacks such as waste production, the need for energy, and continuous maintenance, it is not a very good option on its own [12-13]. However, photocatalytic methods that consume cheap photons from the UV visible region are the most promising for treating such complex systems. It recovers both organic and metal pollutant from wastewater [14]. Many publications on the use of photocatalysts and photocatalysis in the treatment of water were published between 1981 and 2023. In these 42 years, there has been a consistent upward trend in the number of publications [15-16]. Using photocatalysts is one of the appealing ways to decompose organic, inorganic, and many other contaminants. This is due to its effective, efficient, and promising degradation of contaminants, which happens by allowing both spontaneous and non-spontaneous responses to optimize the entire process. The procedure is described as a series of advanced oxidation processes (AOPs) that overcome the shortcomings of conventional methods, such as high cost, insufficient mineralization, and high hydroxyl radical need. This is intriguing because the reaction is controlled using light or photon sources, which is necessary for the photocatalysis process to activate the photocatalyst [17-18].

Titanium dioxide is now the most researched photocatalyst. Titanium dioxide photocatalyst has been utilized to clean textile effluent for the past ten years, and its diverse applications have aroused the interest of researchers. Because of its low operating temperature, biological inertness, low use of energy, water insolubility, easy accessibility, and photoactivity, as well as its non-toxic nature, high chemical stability, narrow band gap, and ecological friendliness, it has been used in a wide range of photocatalytic applications. The photocatalyst's quality, the type of pollutants, and the light source are all important factors that must be in close contact for photocatalysis to work effectively and successfully. Titanium dioxide photocatalyst has been utilized to clean textile effluent for the past ten years, and its diverse applications have aroused the interest of academics. In the presence of ultraviolet (UV) radiation, textile wastewater is treated using the TiO_2 photocatalyst. TiO_2 is used as thin films or as a suspension in the photocatalytic degradation process. UV-TiO_2 treatment is very effective at removing color and other organic components from the combined effluent of municipal and textile colors [19-20].

Photocatalysis is thought to be suitable for decomposing long-lasting contaminants with high chemical stability that are not recyclable or have a low rate of biodegradability[21-22]. Photocatalysis is a flexible, affordable, and ecologically safe treatment method for a variety of contaminants. These procedures represent one of the most promising green chemical technologies and an environmentally beneficial choice. Now it is successfully used to eliminate low concentrations of microbes and persistent organic contaminants from water [23]. The fundamental advantage of photocatalysis is its ability to utilize solar energy, specifically solar photons, giving the degrading process a huge boost in environmental value. Photodegradation of wastewater contaminants using sunlight is an economically feasible technique, particularly for large-scale aqueous-phase applications [18-24]. The primary benefit of photocatalytic treatment is its capacity to convert pollutants into mineral end products without transmitting contaminants from one phase to the next, as is the normal method for traditional treatment technologies [25-26].

2. Approaches to Photocatalysis

Different approaches can be used alone or in combined form to treat a wide range of pollutants in wastewater effectively. Different types of photocatalysis approaches are used to degrade the effluents in wastewater. Photocatalytic approaches are classified based on the light source and catalyst used. The wavelength of the light source may be in the range of visible or ultraviolet regions. In the photocatalytic technique, the form of the catalyst is either suspended or fixed. Suspended reactors are well renowned for their straightforward design and high efficiency. Catalysts are also categorized on the basis of size i.e. micron or nanometer size. The type and size of photocatalysts have a significant impact on photocatalysis [27].

2.1. Approaches Based on Catalyst

2.1.1. TiO_2 Based photocatalysis

TiO_2 is one of the most promising photocatalysts in heterogeneous photocatalysis among several metal oxide semiconductors due to its high ability to react, chemical resistance, inexpensiveness, and low toxicity [28]. Several semiconductors are used as photocatalysts in heterogeneous photocatalysis. An energy gap or bandgap separates the valence and conduction bands in semiconductor materials. When a semiconductor molecule absorbs photons with energy equal to or greater than its band gap, electrons in the valance band become excited and move up into the conduction band, resulting in the generation of charge carriers. Photocatalysis technique particularly using semiconductors such as TiO_2, ZnO, WO_3, Fe_2O_3, CuO, ZrO_2, CdS, In_2O_3, SnO_2, etc. Because of its ability to destroy and transform a wide range of harmful dyes at ambient temperature to the simplest form of non-toxic products, CO_2 and water [29]. TiO_2 is a most promising photocatalyst but its large band gap limits its photocatalytic activity. Which is approximately 3.2 eV. Adsorption to visible light can be shifted by lowering the band gap energy below 3.2 e V. Energy-doped catalysts are commonly used to lower the band gap [30].

2.1.2. Metal Doped Photocatalysis

Doping and sensitization are used to shift the semiconductor response of light absorption towards visible light. This extends the lifetime of electrons and holes. Different methods can be used to boost TiO_2 photocatalytic activity. Metal ion doping or co-doping of metals and nonmetals, as well as metal oxide modification with capping agents, are both promising methods for reducing charge carrier recombination [31]. The sol-gel process was used to create photocatalysts based on TiO_2-SiO_2. Doped TiO_2-SiO_2 has a high adsorption capacity and serves as both a photocatalyst and an adsorbent in hybrid photocatalysis and adsorption [32]. Bismuth trioxide (Bi_2O_3) is the simplest and most significant bismuth compound. It has also been used as a photocatalyst in both water splitting and organic pollutant decomposition [33]. Bi2O3 as a semiconductor has a band gap that varies from 2.1 eV to 2.8 eV [34].

ZnO is an n-type semiconductor inorganic material with three different crystal structures: wurtzite, zinc blende, and rock-salt. ZnO is a semiconductor material with a direct wide band gap of approximately 3.3 eV having a large free exciton binding energy of 60 meV [35]. Pure ZnO is not used as an effective catalyst because of its large band gap, low utilization of photons of light, and quick charge carrier recombination induced by photocatalysis. ZnO is modified using various strategies such as interfacing with narrow band gap semiconductors, accumulation of noble metal, the sensitivity of surface by organic dyes, and elemental doping to catalyze pollutant degradation [36].

2.1.3. Homogeneous Photo Fenton photocatalysis

The photo-Fenton process is an emerging technique for the removal of several contaminants such as dyes, pesticides, inorganic and organic. Furthermore, the use of solar energy in photo-Fenton processes improves their economic and environmental sustainability [37-38]. In the photo-Fenton process oxidation reaction take place between H_2O_2 and Fe^{+2} in an acidic medium to produce hydroxyl radicals which are highly oxidant species responsible for the degradation of pollutant [39]. However, photo-Fenton reactions involving inorganic Fe (II) salts and H_2O_2 have several drawbacks that keep them from being widely used in wastewater treatment. The main issue is the limited pH range for attaining the greatest rate [40]. The narrow pH range for operating the photo Fenton process is 2.8-3.5. To avoid the precipitation of inactive iron oxyhydroxides and maximize the concentration of photoactive species, strict pH control is required. The procedure should be altered for this purpose [41].

2.1.4. Carbon-based photocatalysis

Carbon-based nanomaterials have attained great attention in the water and wastewater remediation fields. In carbon based Photocatalysts different forms of carbon nanocomposites used as catalysts for the elimination of pollutants from wastewater [42]. Carbon quantum dots and C-60 are both good electron acceptors and donors, increasing the functionality of carbon materials in photocatalytic applications. Carbon fibers, activated carbon, and carbon black are also nanocarbon family members that have played important roles in the design and preparation of high-performance photocatalytic materials [43]. Carbon-based materials have a high specific surface area, which improves photocatalytic activity [44].

2.2. Approaches Based on Configuration

2.2.1. Suspended photocatalytic reactor

In a suspended photocatalyst reactor, the photocatalyst in suspended form is used for the treatment of wastewater then photons of light fall on the catalyst, and after some time pollutants break down. It gives a large surface area for the interaction of light as compared to all other photocatalytic reactors. However, the cost of separating the catalyst particles is very high so it is not an effective reactor for wastewater treatment [45]. It was also reported that it is very difficult to irradiate all the photocatalyst particles in a suspended photocatalytic reactor due to the presence of particles of suspended catalyst form closer to the reactor walls. Therefore, the depth of light penetration into the suspended reactor was restricted [45].

2.2.2. Photocatalytic membrane reactors

Wastewater treatment using a membrane is an effective technique. Inorganic and polymeric membranes are used to remove contaminants from wastewater. The inorganic membrane is more efficient as compared to polymeric because of the excellent chemical and thermal stability of the material used [46]. Membrane technology for the separation of organic pollutants from wastewater is extensively used. In photocatalytic membrane reactors, the catalyst is used in two different forms, immobilized form, and slurry form. A polymeric or inorganic membrane is submerged in a photocatalytic reactor in an immobilized catalysis system, and a light source is located above the membrane. In a slurry photocatalysis (SPCS) system membrane filtration units are used. In SPCS the radiation apply in three different ways such as radiations fall on the membrane module, radiations fall on the feed tank, and irradiation of photoreactors, which is a separate reservoir situated between the feed tank and the membrane module as in Figure 1,2 and 3 [47].

3. Mechanism of photocatalysis

The mechanism of photocatalytic oxidation includes a number of intermediary processes. When semiconductor catalyst absorb photon energy, it may be equal to or greater than the energy of its band gap. After absorbing photon energy electrons (e^-) in the valance band become energized and go to the conduction band. The photoexcited electron's migration leaves photogenerated holes (h^+) in the valence band. After that the photogenerated holes combine with adsorbed water to generate strong oxidizing $OH^\bullet$ radicals while the photoexcited electrons react with adsorbed oxygen to generate $O_2^{\bullet-}$ radicals [3-48]. For instance, if a reaction occurs with molecular oxygen adsorbed on the catalyst surface (from dissolved oxygen), superoxide radicals will be produced, whereas if a reaction occurs between water molecules, OH radicals will be produced. Pollutant breakdown is predominantly brought on by superoxide and OH radicals A detailed insight into this mechanism (using TiO_2) is as follows[49].

$$pollutant + hv \rightarrow pollutant^\bullet$$

$$pollutant^\bullet + TiO_2 \rightarrow pollutant^+ + TiO_2\,(e)$$

$$TiO_2\,(e) + O_2 \rightarrow O_2^{-\bullet}$$

$$H^+ + O_2^{-\bullet} \rightarrow H_2O_2$$

$$2HO_2^\bullet \rightarrow O_2 + H_2O_2$$

$$H_2O_2 + e^- \rightarrow OH^\bullet + OH^-$$

$$pollutant^+ + O_2\,(O_2^{-\bullet}\ or\ OH^\bullet \rightarrow Degradation\ products$$

Overall, there are five main steps in the photocatalysis process: (1) moving the reactants from the fluid phase to the surface; (2) adsorbing the reactants; (3) reacting in the adsorbed phase; (4) desorbing the products; and (5) removing the products from the interface region[50]. Quantum yield is used to assess the efficiency of the reaction in photocatalysis. It depends on how many molecules are broken down and how many photons the solution has absorbed. In circumstances where the number of photons absorbed is uncertain, the photonic efficiency is employed as an alternative measurement. Quantum efficiency is the number of molecules of a specific pollutant degraded per photon of light absorbed. The number of molecules transformed per photon striking the system is known as photonic efficiency. Therefore, the ratio of the photocatalytic response to the photonic flux incident on the system can be used to determine photonic efficiency [51].

4. Applications

4.1. Removing trace metals

The health risks associated with trace metals like mercury (Hg), chromium (Cr), lead (Pb), and other metals are high. Therefore, eliminating these harmful metals is crucial for both human health and water purity. The removal of heavy metals like (Hg), chromium (Cr), lead (Pb), cadmium (Cd), lead (Pb), arsenic (As), nickel (Ni), and copper (Cu) is one of the environmental applications of heterogeneous photocatalysis. Gold, platinum, and silver have all been recovered from industrial effluent using photocatalysis's photo reducing ability [52].

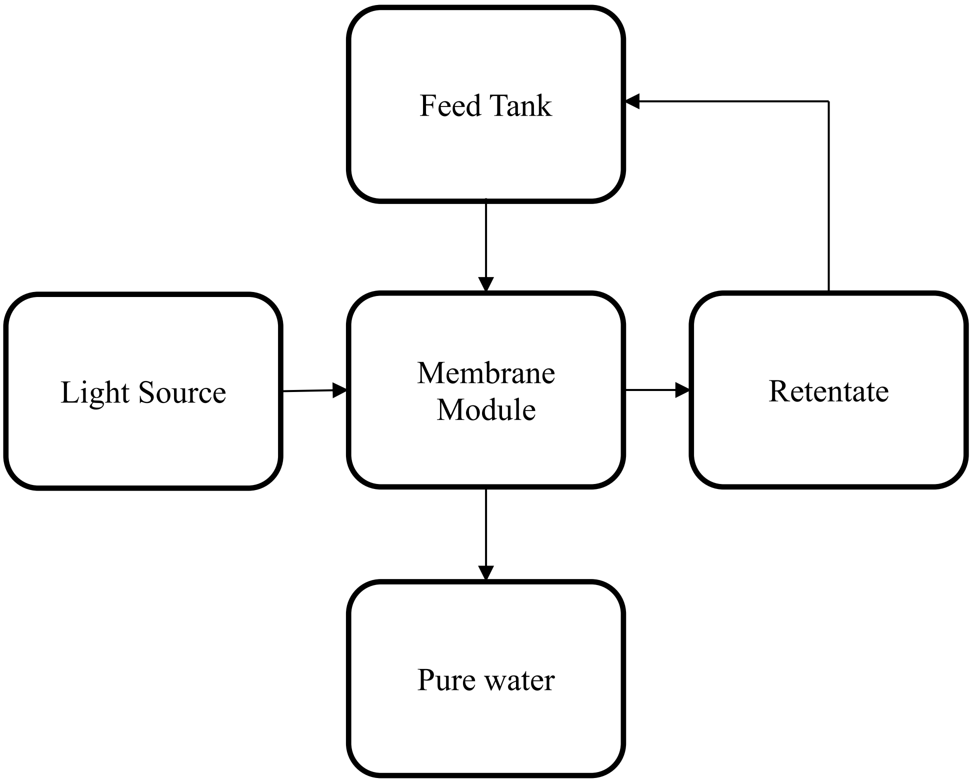

Fig. 1. Irradiation to the membrane

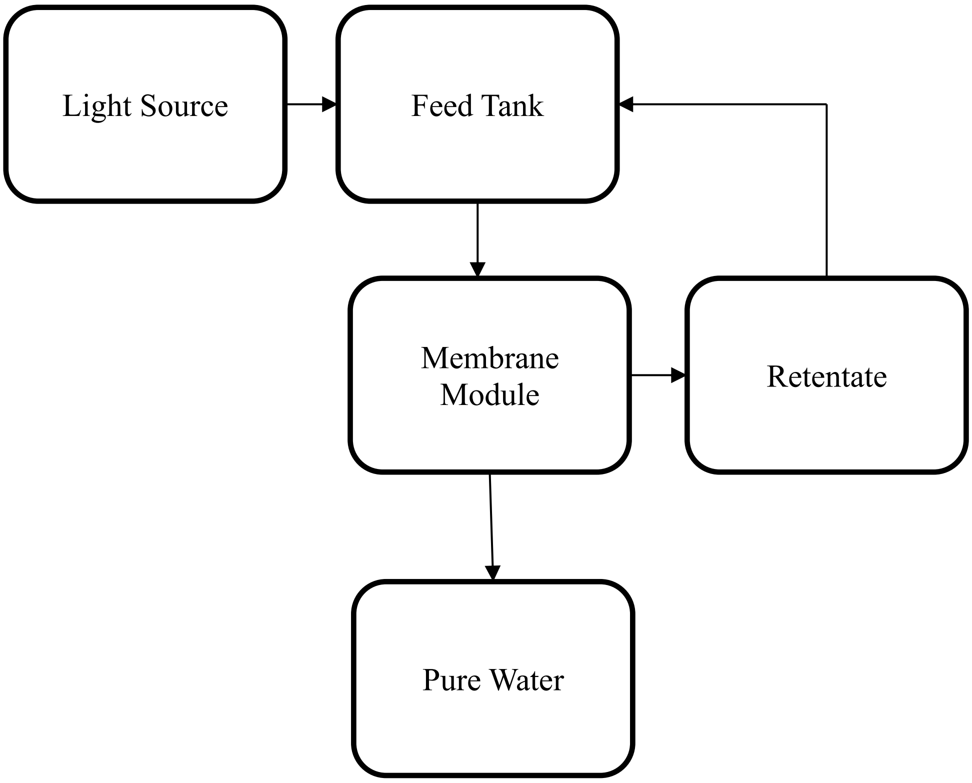

Fig. 2. Irradiation to feed tank

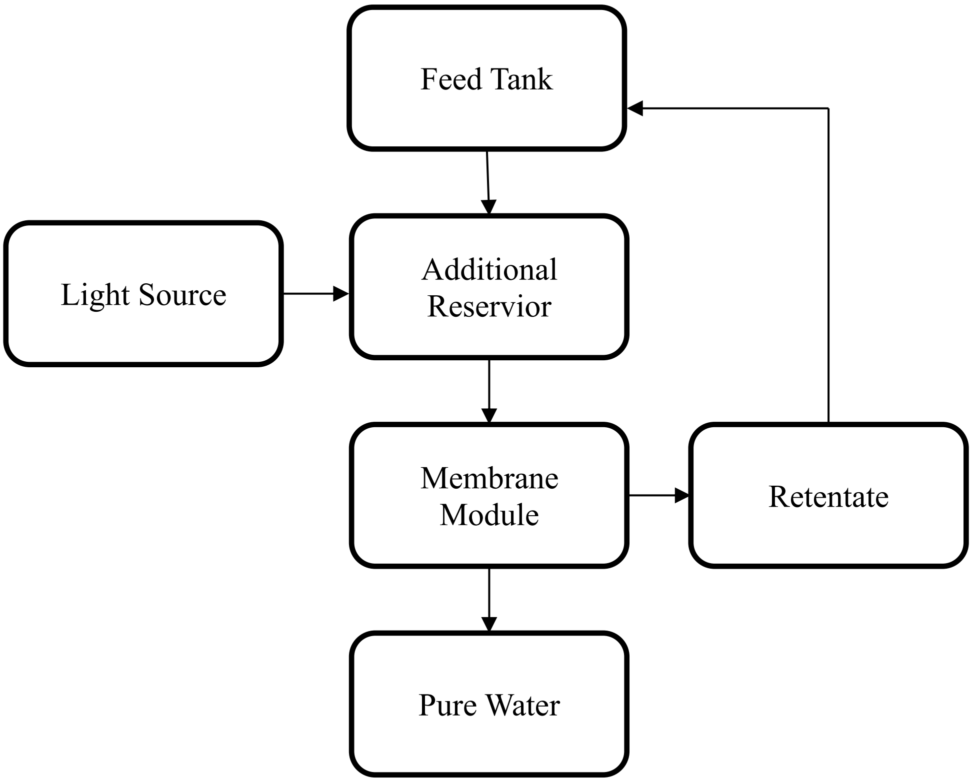

Fig. 3. Irradiation to additional reservoir

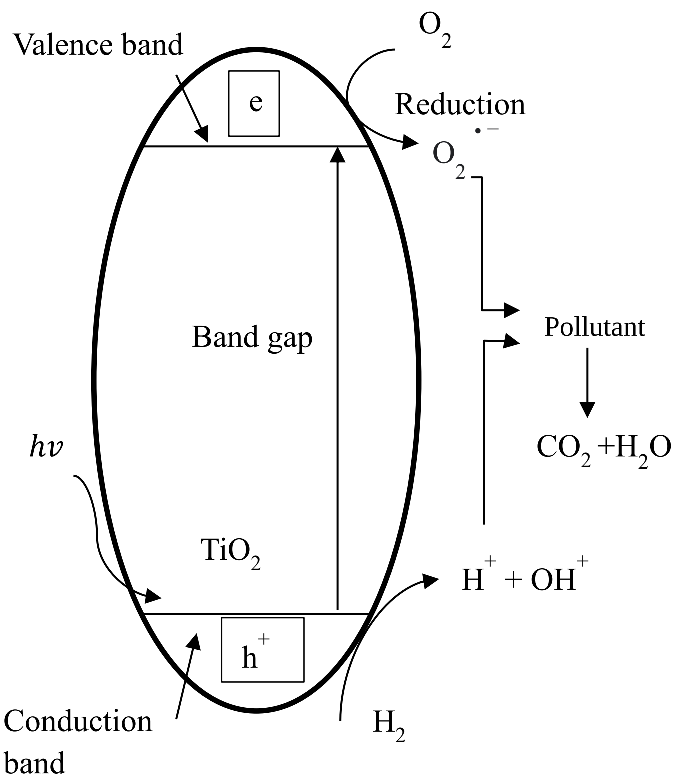

Fig.4. Mechanism of degradation of pollutants

However, because TiO_2 alone is not usually a good adsorbent for the contaminants, photocatalysis using bare TiO_2 is never effective for the treatment of trace pollutants [53]. As a result, metal-organic frameworks (MOFs) can effectively reduce heavy metal ions in aqueous solutions when used as photocatalysts. MOFs and MOF-based composites have been used as photocatalysts to reduce heavy metals in recent years, with the main focus being on chromium photocatalysis in aqueous solutions [54].

4.2. Photocatalytic removal of inorganic pollutants

Inorganic pollutants, cyanide-containing waste, and NO^{2-} containing waste are the main cause of water pollution. These contaminations are poisonous and have a long half-life, so their degradation is also a challenge. The inorganic pollutants are mostly produced by the wastewater discharged by the leather, metallurgical, and electroplate industries. So the removal of these pollutants is essential for the safety of aquatic life. There are typically two types of photocatalytic mechanisms used to remove inorganic pollutants: photocatalytic reduction and photocatalytic oxidation. The elimination of inorganic contaminants via the photocatalytic mechanism is as

$$Mn^{+} + e^{-} \rightarrow M$$

(Mn+ represents inorganic metal oxide, and M represents the photocatalysis product) [55].

Cyanide (particularly free cyanogen root) is also extremely poisonous, originating primarily in the metallurgy industry, particularly gold mines, the electroplating industry, and other corresponding chemical industries. Cyanide emissions have recently increased in those fields. TiO_2 photocatalysis can effectively convert toxic CN^- to CO_2 or nontoxic N^2. NO^{2-} is a hazardous environmental pollutant that can cause cancer; especially at low concentrations, NO^{2-} is more stable and difficult to decompose. The photocatalytic treatment of NO^{2-} in water is very common now and researchers still work on it. In the photocatalytic reactions NO^{2-} is adsorbed in the surface of the catalyst [56].

4.3. Eutrophic Water Treatment

Treatment of eutrophic water is another use for photocatalytic technique. Eutrophic water has cyanobacterial blooms which have negative effects on human health, so controlling blooms of algae in eutrophic water is crucial [57]. These blooms can be controlled with copper-based algaecides, however doing so causes additional environmental issues [58]. Using TiO_2-coated glass beads and UV-light irradiation, researchers investigated the photocatalytic inactivation of three algae species: Anabaena, Microcystis, and Melosira. Anabaena, microcystic, and Melosira were completely photo-catalytically inactivated in around 30 minutes, however, Melosira's inactivation efficiency was somewhat lower because of the inorganic siliceous wall encircling the cells [59].

4.4. Degradation of reactive dyes

Reactive dyes and the byproducts of their breakdown in wastewater can be directly hazardous to aquatic life and interfere with photosynthesis by blocking sunlight[60].The discharge of wastewater with high quantities of reactive dyes is a well-known concern associated with dyestuff operations. Due to the relatively low fixation rates and limited effectiveness of the biological processes commonly used for wastewater cleanup, around 20% of the unfixed dyes are discharged into the environment. The need to research novel options for the effective treatment of this type of waste is obvious given the carcinogenic or mutagenic nature of some reactive dyes, the negative impact of color on receiving waters, and the effluents' typical resistance to biological breakdown. The ability of semiconductor-assisted photocatalysis to degrade a large number of chemically resistant compounds in recent years has led to extensive research into the process [61].

5. Challenges

5.1. Low photocatalytic activity

Photocatalytic activity is a key challenge in photocatalysis to purifying wastewater. Photocatalyst efficiency depends on the surface area of the catalyst and the intensity of light. Photocatalytic activity decreases by increasing the amount of photocatalyst above the optimum level this is because of the shadowing effect and the penetration depth of light exposure by the high turbulence suspension [62]. Photocatalytic activity enhances by dopping the catalyst by using metal and non-metal [63]. When the intensity of light is low the degradation of water effluents will be high because the electron-hole formation reaction will be faster than the electron-hole recombination [64].

5.2. Reactor Design

Photocatalytic reactors inherit some design issues from traditional catalytic reactors, including the requirement for a large specific surface area and rapid mass transfer rates. As a result, several reactor layouts employed in traditional catalytic applications for photocatalytic applications have been examined [65]. The reactor design and how light approaches the photocatalyst affect the efficiency of photocatalysis. The main problem in photocatalytic reactors is the uniform distribution of light to the catalyst [66]. Photocatalytic reactor development is important for the photocatalytic wastewater treatment process as innovative reactor designs can improve the performance of photocatalysts [67].

5.3. Presence of Interfering Species

While treating domestic, river, and commercial water natural, organic matter produced, inhibits the photocatalytic activity. It blocks the active sites and reduces the illuminated area. The accumulation of NOM decreases the production of reactive oxygen species even when the catalyst is well illuminated. Mostly NOM-generated aromatic products are more likely to be hydrophobic and have more adsorption power at the photocatalyst surface. This aromatic content quenches the holes in the valance band of the photocatalyst. These not only reduce the degradation of pollutants but also reduce the production of hydroxyl radicals [68].

6. Conclusions

The photocatalytic technique is a versatile and effective disinfection technology that can inactivate a wide range of harmful microorganisms in a variety of media. It is a versatile disinfection method that is risk-free, non-toxic, and inexpensive, and it may be used in a range of scenarios. Photocatalytic disinfection is the subject of substantial research with numerous applications. The photocatalysis method has applications in every field of life. Instead of its versatility, this method has some challenges. With time, researchers cope with these challenges. Now photocatalysis become more advance because of its approaches which may be used in single and may be in combined forms. The unique property of this method is that it does not produce contaminant waste or volatile organic compounds which were produced by conventional methods.

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