

Original Article: Investigation of Photocatalytic Degradation Process in Wastewater Treatment Industry

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ABSTRACT

The photocatalytic degradation process has emerged as a promising technology for removing pollutants from the air. It is one of the most important and growing technologies in wastewater treatment. This process in ambient temperature and pressure operating conditions can remove several types of pollutants in aqueous and gaseous environments that are superior to other methods. Some of the other advantages of this new technology are: Unlike conventional treatment methods that transfer pollutants from one environment to another. The photocatalytic method usually leads to the production of harmless products. The usual methods and effluent flow should be used in this process, which is impossible with other treatment methods. In this process, the reaction conditions are balanced and gentle, the reaction time is relatively short, and the minimum additive chemicals are required. Combining this with other treatment methods is possible, especially for biological treatment. Since the goal of photocatalytic reactions is generally the oxidation of organic matter and the reduction of inorganic matter, the main applications studied for this process are decolorization and removal of pigment, reduction of effluent COD, complete removal of hazardous organic matter, elimination of hazardous inorganics such as cyanides, heavy metal treatment, fungicide decomposition, herbicides, harmful pesticides, purification and sanitation of water, elimination of foul-smelling compounds, removal of soil contaminants, removal of air pollutants, and elimination of cancer cells and viruses.

Introduction

Photocatalysts are semiconductors activated by the absorption of photons. If the energy difference of the layers is provided, the electron jumps from the

capacitance band to their conduction band, which uses light energy for this excitation. Unlike metals, semiconductors, which have an attached environment of electrons, are solids with electrical conductivity between conductive and non-conductive materials. Semiconductors

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have two separate energy bands. In each band, the distance between energy levels is minimal, and in practice, a continuous spectrum of energy is seen. The distance between the conduction energy band and the capacitance is called the gap band, which contains the energy levels at which the electron cannot stay. The reason for using semiconductors as photocatalysts is due to their suitable electronic structure, light absorption, and charge transfer properties, and their long life in the excited state. Metal oxide semiconductors are the most suitable photocatalysts with optical abrasion resistance, such as titanium oxide (TiO_2), zinc oxide (ZnO), zinc sulfide (ZnS), iron oxide III (Fe_2O_3), cadmium sulfide (CdS) and zirconium dioxide (ZnO_2) [1].

The oxidation mechanism of substances by hydroxyl radicals depends on the type of organic matter. For linear compounds such as alkanes or alcohols, the hydroxyl radical is converted to a water molecule by taking hydrogen from the organic molecule. However, in the case of aromatics and olefins, the degradation is done by adding this radical to the substance's molecular structure. In the first stage of the radical reaction of hydroxyl with aromatic pollutants, aromatic intermediates are formed. In the next step, these intermediates are broken down into aliphatic acids and finally, from the decomposition of the produced acids, water, and carbon dioxide. Very little research has been conducted on the photocatalytic degradation process, especially in treating styrene-containing effluents. In addition, all reports of styrene degradation have been investigated using the photocatalytic process in ultraviolet light. The following is a brief description of each report. This group overcame the above problems by using a new photoreactor and titanium oxide photocatalyst in the bubble/liquid heterogeneous phase. In other words, the degradation of toluene, paraxylene, styrene, and formaldehyde organic compounds in this reactor was investigated as the release of these gases in the form of micro-bubbles in the liquid phase inside the reactor. They found that by using micro-bubble gaseous organic compounds in the bubble/liquid phase, the degradation efficiency is higher than in the

pollutant degradation process, increasing in the gaseous phase. Finally, after 10 h using gl-1 0.75 titanium oxide and three 8-watt UV lamps, 75% degradation of styrene with an initial concentration of 5 ppm was reported [2].

An integrated photoreactor system followed by a three-stage biofilter has been used to investigate the photocatalytic degradation of styrene in the gas phase. C-TiO₂ photocatalyst was also synthesized by the sol/gel method, and its performance in the system was investigated by ultraviolet light. In their study, the styrene concentration was measured by gas chromatography, and the biofilter bed was filled with inorganic porous ceramic materials. The main intermediate compounds produced with the system mentioned above are cyclohexane and methyl alcohol. The results showed that the degradation efficiency of styrene after 4 hours with an initial concentration of 105 mgm-3 in the photoreactor was about 40%, which increased to 99% with the use of the integrated system.

Chen *et al.* [2019] synthesized the C-TiO₂ photocatalyst and statistically optimized the parameters affecting catalyst synthesis. Then, the performance of the mentioned catalyst was studied by examining the photocatalytic degradation of styrene in gaseous form in ultraviolet light. In the optimal synthesis conditions, by using 0.1 g of catalyst, the degradation efficiency was 74.4%. Of course, since styrene is used in this article only as a model contaminant for statistical analysis of photocatalytic synthesis parameters, so no more information about the styrene degradation process is mentioned. In another study, this group of researchers synthesized an intermediate spherical titanium oxide catalyst using the hydrothermal method. It re-examined its performance by assessing the degradation of styrene in the gas phase. The operating conditions of the demolition process are similar to the previous research mentioned above. The results demonstrated that the performance of this photocatalyst was better than TiO₂-p25. After 3 h, they achieved a degradation efficiency of 73%. They attributed this to the synthetic photocatalyst's higher specific surface area, the

anatase's excellent crystallinity, and its unique empty intermediate structure [3].

Investigated the photocatalytic degradation of low-concentration styrene in the liquid phase using TiO₂-p25 in ultraviolet light. The influence of effective parameters on photocatalytic degradation efficiency was investigated using the one-factor method at any time, and 95% of styrene degradation with an initial concentration of 15.3 ppm was reached after 90 min. Finally, the optimal photocatalyst, hydrogen peroxide, and pH values were reported as 0.55 gl-1, 5.8 and 6 mmoll-1 and 6, respectively. In addition, benzaldehyde was identified as the intermediate compound produced during the process [4].

More than 94% of COD is removed from wastewater using the integrated Fenton neutralization-evaporation process. It was reported that neutralization-evaporation can reduce COD from 40,000 mg/L and sulfide from 19,000 mg/L to 1,400 mg/L. Adding the Fenton process to the above sequence also further reduces COD to about 150 mg/L COD.

Nu eza *et al.* evaluated caustic effluent treatment using an electrochemical oxidation process. He reported a 93 % elimination of COD [5].

Study of caustic effluent treatment using a combined process of UV / H₂O₂ and UV / H₂O₂ / O₃. He reported 68% removal of COD in the UV / H₂O₂/O₃ process. Also, the UV / H₂O₂ process will have a 44% efficiency in COD removal [6].

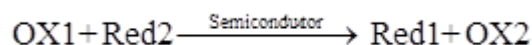
Study of caustic effluent treatment using the Electro-Fenton process. He reported the removal of 95% COD at pH 4 and 40 °C using 100 mg/L of iron [7].

An ideal photocatalyst has the following characteristics:

- ✓ Corrosion resistance.
- ✓ Non-toxicity.
- ✓ Chemical and biological neutrality in the environment.
- ✓ Availability and cheapness.
- ✓ Ability to absorb the reactant under photon activity.

Basis of the performance of photocatalysts

The basis of photocatalyst performance is based on electron transfer at the photocatalyst surface and the division of the surface into two regions of oxide and reduction. Light can excite electrons to jump from the capacitance band to the conduction band as an energy source. When an electron in the capacitance band absorbs energy through photons, its energy increases, making it move to an unoccupied energy level from the conduction band. This creates an extra electron in the conduction band and a space of electrons or holes in the capacitance band. Thus, an activated electron can react with an oxidant to form a reduction product and a positive hole reaction with a reducing agent to produce an oxidized product [8].



However, because the energy level in the capacitance band is lower than in the conduction band, the electrons in the conduction band tend to return to the capacitance band for more excellent stability. Under these conditions, energy is released in the form of heat or photons according to the energy difference between the two bands (Table 1). For this reason, semiconductors are also called optical conductors. Photons are utilized to excite the electrons of semiconductors and give them the ability to conduct.

Table 1: The energy difference between the layers of some semiconductors used as photocatalysts

Layer energy difference (eV)	Photocatalyst	Layer energy difference (eV)	Photocatalyst
2/3	Fe ₂ O ₃	2/76	WO ₃
0/286	PbS	2/42	CdS
3/87	ZrO ₂	3/6	ZnS
3/54	SnO ₂	3/03	TiO ₂
2/172	Cu ₂ O	3/44	ZnO

Figure 1 reveals the formation of an electron/hole pair at the electron levels of a semiconductor due to the collision of an optical

photon. The formation of electron/hole pairs takes place with high energy in the second phase.

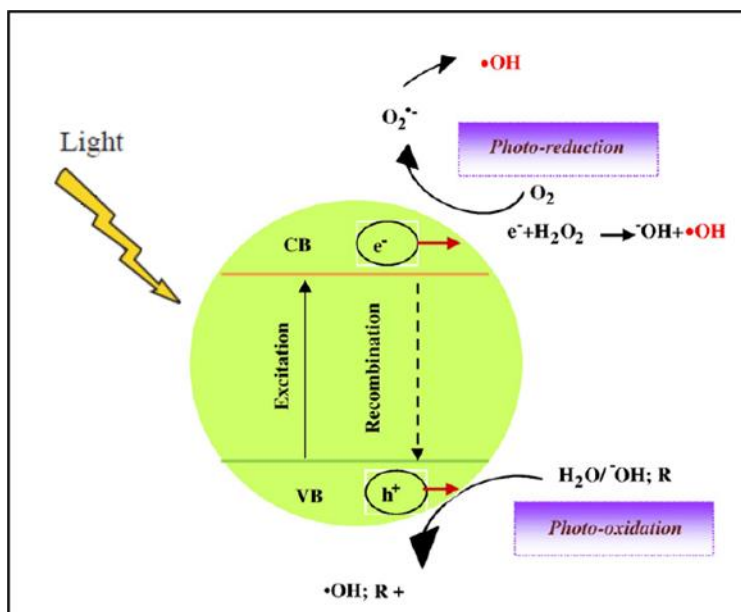


Figure 1: Diagram of electron/hole pair formation in the electron balances of a semiconductor due to the collision of a suitable optical photon

As mentioned, the electron/hole pair formed tends to return to its previous state because the electron is in an unstable state. However, the fission of the bond causes the return phase to be delayed, which gives the excited electrons and holes near the semiconductor surface the opportunity to participate in the reactions that occur near the semiconductor surface. In general, the steps of a photocatalytic degradation process can be summarized as follows:

- ✓ Transfer of reagents (contaminants) in the form of gas or liquid on the catalyst's surface.
- ✓ Adsorption of the reactants by the photocatalyst surface.
- ✓ Creating electron pairs/holes generated by light energy.
- ✓ Separation of electrons and cavities by traps on the photocatalyst surface.
- ✓ Photocatalytic light-induced reaction with reactants.
- ✓ Desorption of reaction products.

- ✓ Remove products from the reactor/photocatalyst interface.

In the photocatalytic degradation of pollutants, if the reduction reaction of oxygen and oxidation of the pollutant or water does not coincide, the electron accumulates on the conducting layer, which causes the electron to recombine with the positive cavity. Therefore, adequate electron consumption is essential for the development of photocatalytic oxidation. Therefore, the presence of oxygen is essential as a factor that absorbs electrons and plays a role in producing hydroxyl radicals [9-12].

Titanium Oxide

In 1972, while Professor Fujishima and his student Honda were experimenting, they encountered a strange phenomenon. They observed that when titanium and platinum oxide electrodes were placed in water, a circuit was formed that could decompose water into oxygen and hydrogen without applying electricity from outside and only exposed to ultraviolet light. They did not see any bubbles on the electrodes when the light was turned off. Following this phenomenon, Honda discovered

that titanium oxide (TiO_2) has solid oxidizing properties. Therefore, he focused his studies on the effect of this valuable substance on environmental phenomena such as sterilization, disinfection, and pollution removal. This material is a powder and its color varies according to its purity (from white to gray). Since titanium oxide is chemically and biologically neutral, it has high activity, high stability against light radiation, and low cost. So it has been widely used as a photocatalyst. The photocatalytic activity of titanium oxide depends on the surface properties and semiconductor structure, such as the electrical nature of the particles, the crystal composition, the specific surface area, the particle size distribution, the porosity, and the density of the surface hydroxyl groups. These factors affect the adsorption behavior of pollutants and intermediate products resulting from

degradation, longevity, and electron/hole recombination rate. The effect of particle size on photocatalytic activity is also due to the difference in specific surface area, which increases the active site per unit area and provides the ability to absorb more pollutants. In addition, the primary electron/hole recombination path will vary depending on the particle size. In the nanometer particle range, the physical and chemical properties of the semiconductors are modified, and a slight change in particle diameter leads to a significant increase in the surface-to-mass ratio, thus modifying the volume and surface area for electron/hole recombination. Titanium oxide has four crystal structures: anatase, rutile, brookite, and monoclinic. The crystalline structures of titanium oxide are revealed in Figure 2.

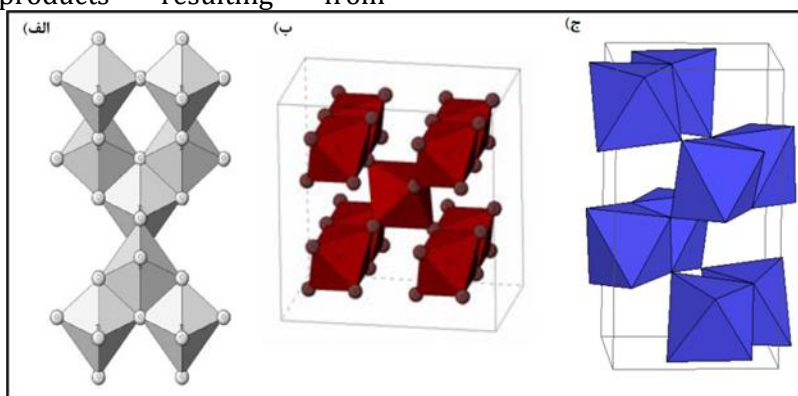


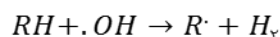
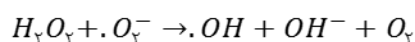
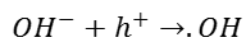
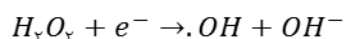
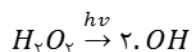
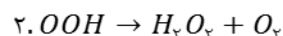
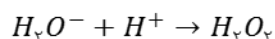
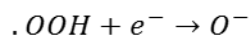
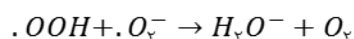
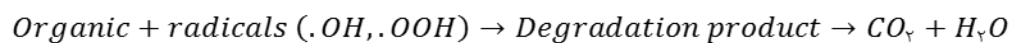
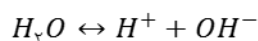
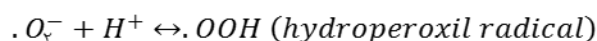
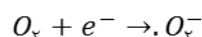
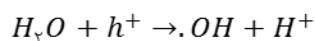
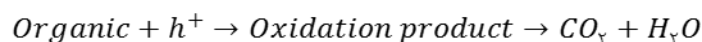
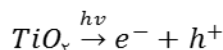
Figure 2: Titanium oxide crystal structures (a) anatase (b) rutile (c) brookite

Recent advances have made it possible to study the photocatalytic activity of titanium oxide based on its crystal structure and particle size. Due to the direct effect of specific surface area and crystal composition on photocatalytic activity, anatase and rutile crystals in the nanostructured phase have been further studied, and reports on the other two crystals are rare. Anatase type has a crystalline structure that is related to the tetragonal system. The state of the oxygen atom on the anatase crystal forms a triangular compound. It allows more organic matter to be adsorbed, but this is not the case for rutile with the tetragonal crystal structure. The position of the titanium oxide atoms provides a favorable condition for the reaction of the adsorbed organic matter. Therefore, the

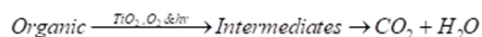
photocatalytic activity of the anatase form is higher than that of rutile.

Contrary to popular belief, the anatase form is the most active form of titanium oxide. Reports of pure anatase have not been reported to produce the best photocatalytic performance. Based on these reports, it can be inferred that a mixture of anatase and rutile phases can be the best combination to achieve the maximum photocatalytic activity. Several commercial titanium oxide samples with different particle sizes and purities have been studied to estimate photocatalytic activity. A general agreement has been reached that titanium oxide has the best efficiency compared to other samples due to its low electron/hole recombination rate. The reaction mechanism of photocatalytic degradation of pollutants using titanium oxide

can be expressed in the following steps. Electrons and cavities can react with adsorbed compounds on the catalyst's surface, thus initiating redox reactions. The positive cavity (h^+) can directly oxidize organic pollutants and convert water molecules to hydroxyl radicals.



And in general:



Modification of Titanium Oxide

Because the energy difference between titanium oxide layers is significant, it is only active in the ultraviolet range, covering less than ten percent of the intensity of sunlight. In other words, the only problem with the application of titanium oxide is its inactivity in visible light and requires ultraviolet radiation. In addition, most people are aware of the effects of UV radiation on skin problems. Therefore, modification of this

On the other hand, the conducting layer electron reduces the absorbed oxygen to a superoxide anion. Hydroperoxyl radicals are produced by the collision of superoxide radicals with existing protons. This radical is an intermediate and eventually converts to hydroxyl radical [13-15].

photocatalyst is essential, and research has focused on other generations. In recent years, attempts have been made to increase the activity range of titanium oxide and even shift it to visible light. Modifying titanium oxide with different types of metal ions or anionic components as substitutions or subsets in photocatalytic particles is a way to increase its response to the visible light region. In both types, an impurity state is created between the two conducting layers and the photocatalyst capacity layer, narrowing the energy distance between its alignments [16].

A) Modification of titanium oxide with metal ions: There are many reports in which

titanium oxide has been deposited with several metal ions such as Ca^{2+} , Sr^{2+} , Ba^{2+} , Fe^{3+} , Cr^{6+} , Co^{3+} , Mo^{5+} and rarer ions such as La^{3+} , Ce^{3+} , Pr^{3+} , Gd^{3+} , Nd^{3+} , Sm^{3+} . When homogeneous cations with charges less than Ti^{4+} , such as Al^{3+} , Cr^{3+} , Ga^{3+} , and Ln^{3+} , are placed in the titanium oxide network, they act as receptor centers and trap photoelectrons. Once negatively charged, they absorb the holes, causing the electron/hole to recombine. Other homogeneous cations with a charge higher than Ti^{4+} , such as Nb^{5+} , Ta^{5+} , Sb^{5+} , act as donors and trap positive cavities. After being positively charged, they absorb electrons and cause electron/hole recombination. In either case, the added cation helps to recombine the electron/hole, which is detrimental to the efficiency of the photocatalyst. In addition, metal ions doped in titanium oxide structure become the main factor for the partial blockade of active sites of photocatalysts. In most research, researchers believe that modifying photocatalysts with metals can lead to photocatalyst thermal instability, which is undesirable and costly.

B) Titanium oxide modification with non-metallic ions: An effective method in modifying titanium oxide photocatalyst and activating it under visible light is to replace oxygen ions with anions such as N^{3-} , C^{4-} , S^{4-} , X^- (F-, Cl-, Br-) Which leads to a narrowing of its energy layer. Since the first report by Sato *et al.* (2020), significant research has been conducted on nitrogen-doped titanium oxide's preparation, detection, and photocatalytic activity. Asahi *et al.* (2019) introduced nitrogen as the most influential element in modifying the optical properties of titanium oxide. Morikawa *et al.* (2020), also believe that nitrogen modification is more effective than other non-metals.

This is because its p-level reduces the energy difference between titanium oxide layers and the p-oxygen level. Valentin *et al.* (2020) showed that nitrogen is doped in the structure of titanium oxide in the form of substitution (Ns) and substitution (Ni). Substitution nitrogen has a local nitrogen level of about 0.14 eV, and subsurface nitrogen has a characteristic π level of about 0.74 above the titanium oxide capacity layer (Figure 3).

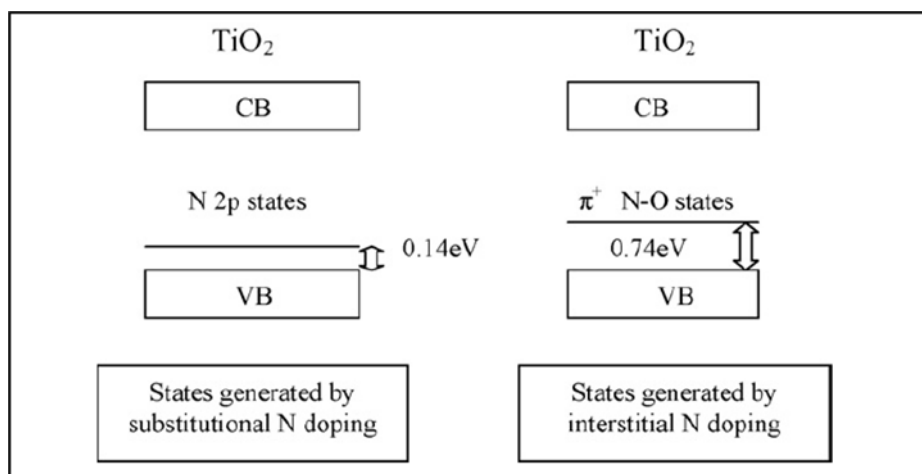


Figure 3: Structure of the modified nitrogen oxide layer of nitrogen

In general, it can be said that among these non-metals, nitrogen is essential due to its low ionization energy, similar size to oxygen, and high stability. It reduces the recombinant nature of the electron/photocatalyst hole. Other research has reported the successful use of N-TiO₂ in the photocatalytic degradation of toluene and dyes. So far, different methods have been reported for nitrogen doping in titanium oxide structures. These methods include cell gel,

hydrothermal, solothermal, sonochemical, sputtering, plasma, titanium nitride oxidation, electrochemical anodizing, and inoculation [17].

Regardless of the type of reactor used, there are usually two ways to use a photocatalyst to treat wastewater:

A) Use of photocatalyst dispersed in solution:

B) Use of photocatalyst as a stabilized layer:

A) How to use the photocatalyst in the photoreactor: In slurry photoreactors, the catalyst particles are freely dispersed in the liquid phase, and as a result, the photocatalyst is completely dispersed in the liquid phase. Mechanical or magnetic agitators are used to properly diffuse the catalyst in the liquid phase. In most studies, photocatalyst particles are dispersed in the effluent solution to create a large surface area for liquid/solid phase contact. However, this method requires catalyst separation after the purification step. This separation is usually a physical process such as filtration, centrifugation, or coagulation. To this end, attempts have been made to combine the photocatalytic and membrane processes.

*Types of slurry photoreactors are:**Slurry Cyclic Photoreactors (SAR):*

The cyclic reactor consists of two all-center tubes to which the inner tube is exposed. In this type of photoreactor, the photocatalyst suspension flows through the annular channel created by the two mentioned tubes. The radiation source (lamp) is placed inside the transparent inner tube. This design has the advantage of providing a symmetrical radiation field. Slurry ring reactors are widely used on a laboratory scale, are easy to operate, and are generally an option for industrial applications.

Open Upstream Fluorescent (OUR): This type of fluorescent consists of immersion lamps located perpendicular to the mainstream of water. This design with an asymmetric radiation field requires a complex reactor model, and more reactor volume is required to have the same performance as a slurry ring reactor.

Rotary Flow Reactor (SFR): Two circular glass plates form the SFR reactor. The water/photocatalyst suspension is injected tangentially into the outside of the reactor, creating a helical flow that causes the photocatalyst suspension to mix. The photocatalyst suspension exits the center of the reactor top plate. This device provides an entirely agitated slurry with non-uniform

radiation distribution, which leads to the creation of a complex reactor model.

Integrated Flow Membrane and Filtration System (IFR-MF):

This type of reactor consists of an annular chamber in the form of a thoroughly agitated slurry with a hollow fiber membrane modulus of the ultrafiltration type. This type of reactor allows the separation of fine photocatalyst particles from the refined solution and the return of the photocatalyst to the reactor.

Cyclic Taylor Fluorescent (TVR):

This type of reactor consists of two coaxial cylinders and free catalyst particles rotating in an annular channel. The lamps are installed in the inner cylinder. The turbulent current is created by rotating the inner cylinder, and the photocatalyst is exposed to radiation intermittently, moving circular currents of the photocatalyst particles closer to the reactor section exposed to the radiation. One of the disadvantages of TVR reactors is the added complexity due to its moving parts.

Turbulent slurry fluoride (TSR): This fluoride consists of a turbulent slurry system with a ceramic membrane for catalyst separation and recovery. The membrane is cleaned intermittently with a backward flow of air. According to the suppliers of these reactors, its main advantages are low-volume design and high efficiency.

Photo-CREC-Water-II photo-reactors: This type of photo-reactor consists of an annular container and a lamp placed in the center. At the top of the reactor, a slurry distributor ensures suspension turbulence at the reactor inlet. This type of photoreactor is equipped with quartz windows and parallel side pipes. This design allows the measurement of absorbed photons and radiation reflection and is very valuable for measuring energy efficiency and quantum [18].

Photo-CREC-Water-III Photoactors: This type of photoactor is a circular container with an external radiation source. This device is designed to simulate solar photoreactors and has standard features with Photo-CREC-Water-II photoreactors [19].

B) Use of photocatalyst as a stabilized layer:

In photocatalysts with a fixed catalyst, an attempt is made to avoid the separation step in slurry photo actors by fixing the photocatalyst on the walls of the photovoltaic or on a neutral and suitable base. Various bases are used, including glass, aluminum, ceramic, perlite, zeolite, and ceramic membranes. Some catalysts with fixed catalysts include fixed bed fluoride, fluidized bed fluoride, and rotating disk fluoride. These photoreactors hold the photocatalyst on a fixed base by surface physical forces or chemical bonds. Several methods have been used to coat and stabilize the photocatalyst on the desired surface, including immersion, chemical vapor deposition, sol-gel, spray coating, immersion coating, sputtering, etc. Researchers widely use the immersion method because it is simple and does not require more complex devices. However, the photocatalytic coating obtained from this method is not uniform and can be easily detached from the base. The photocatalyst coating is obtained homogeneously and uniformly in chemical vapor deposition and sol-gel methods. The sol-gel method for producing a photocatalyst film on the base surface has several advantages over the chemical vapor deposition method. It has been used to produce a photocatalyst thin film; however, since the reactor's active surface and volume decreased, it has led to a sharp drop in process efficiency. In addition, part of the porosity is lost during the heating process that is performed to stabilize the photocatalyst on the base. As a result, the effective level of the photocatalyst is reduced. Therefore, the efficiency of a reactor with a stabilized catalyst is still lower than that of a reactor with a dispersed catalyst. In general, the advantages of catalysts with stabilized catalysts can be summarized in the possibility of continued use of the reactor and no need for other processes such as filtration to separate the catalyst and regenerate it. On the other hand, such photoreactors may have the following defects:

- ✓ Low ratio of active level of photocatalyst to reactor volume.
- ✓ Low intrinsic efficiency due to light absorption and diffusion in the surrounding photocatalyst medium.

- ✓ Relatively high-pressure drops.
- ✓ The problem of regenerating photocatalysts stabilized all the time with the process [20-23].

Types of photocatalysts with stabilized photocatalysts are:

Fillers (FFR): This fluorescent design may provide only a limited active catalyst level per unit volume of the reactor. Film-forming photoreactors are known by the following characteristics.

- ✓ The photocatalyst is fixed on the inner wall of the column.
- ✓ The thin layer of water moves downwards.
- ✓ A lamp is located in the center of the column.

Multi-tube photoreactors (MTR): This type of photoreactor consists of a cylindrical chamber with more than fifty quartz tubes on which the photocatalyst is coated on the outer surface. Multi-tube photoreactors are like a tube and shell heat exchanger in which water flows through the shell. Radiation is emitted through an aluminum reflector in quartz tubes. This type of design provides a relatively large photocatalytic active surface per unit volume of the reactor [24].

Fluorescent bed fluorescent (PBR): This type of fluorescent is a filled column consisting of a central lamp. So far, different types have been offered:

- ✓ Photocatalyst fixed on glass meshes.
- ✓ Photocatalyst fixed on fiberglass.
- ✓ Photocatalyst fixed on glass spheres.

A possible disadvantage of this type of photoreactor is the non-uniform and partial irradiation of the catalyst surfaces. Also, the unbalanced distribution of water flow may limit the amount of water in contact with the photocatalyst exposed to radiation and negatively affect the reactor's overall performance [25].

Photocouplers with fiber optic cables (FOCR): In this type of photoreactor, radiation is transmitted by optical fibers to photocatalysts stabilized inside the reactor. This system allows radiation to the photocatalyst remotely with minimal scatter and the possibility of integrated radiation. The relatively high cost of optical fibers and the loss of energy during light concentration and photon transmission are some disadvantages that reduce the tendency to design FOCR photoreactors [26].

Alternating Radiation Controlled Rotating Fluorescent (RDR-CPI): This type of fluorescent consists of thin layers of photocatalysts fixed on a rotating disk's surface. This disk is connected to an axis that rotates at 20-100 rpm. A set of lamps is used to irradiate the surface of the disk. Rotating hydrodynamics allow for proper contact between the contaminant and the surface of the photocatalyst. RDR-CPI moving components increase the complexity of the photocatalytic system [27].

Spiral Glass Tube Photoreactor (SGTR): This photoreactor consists of a circular tube with a photocatalytic coating wrapped around a lamp. Although this design may irradiate a relatively large surface area of the photocatalyst per unit volume of the reactor, it requires complex hydrodynamics and limited contact between water and the photocatalyst [28].

Tubular optical fluorescent (TLR): A stainless steel plate at the top and an internal welded plate are the hallmarks of this type of reactor. In this type of reactor, several U-shaped lamps coated with photocatalysts are placed around the welded plate, all of which are often housed inside a rectangular stainless-steel housing. One of the advantages of LR is the high catalytic active surface per unit volume of the reactor and the ease of scale increase of this type of reactor. Disadvantages of this photoreactor include non-uniform distribution of radiation and hydrodynamic complexity of fluid motion [29].

Photo-CREC Water I Photoreactor: This photoreactor is a ring-shaped reactor whose radiation source is located in its central axis. This design allows high photocatalyst loading on

the glass lattice, good radiation on the catalyst, and the possibility of integrated photocatalyst contact with circulating water [30].

Light Sources

As mentioned, a suitable light source is required to activate the photocatalyst and produce hydroxyl free radicals in the photocatalytic process. The light sources used in the photocatalytic degradation process are classified into solar radiation and artificial radiation. Artificial radiation also includes ultraviolet radiation and visible radiation. The position of the lamp or radiation source is a distinguishing factor in photocatalytic reactors. The different positions of the radiation source in a photoreactor are as follows:

- ✓ Reactors with the immersed radiation source.
- ✓ Reactors with the external radiation source.
- ✓ Reactors with distributed radiation sources.

In reactors with an immersed radiation source, the lamp is placed inside the reactor, while in photocatalytic reactors with an external source, lamps are placed outside the reactor chamber. In distributed radiation reactors, radiation is transmitted from the source to the reactor by optical instruments such as reflectors and optical conductors [31, 32].

A) Ultraviolet Radiation:

Ultraviolet light is electromagnetic radiation with a wavelength shorter than visible light but longer than X-rays in 100 to 400 nm and energies of 3 to 24 electron volts. This light is called ultraviolet because it consists of a spectrum of electromagnetic waves with frequencies higher than what humans know as a purple light. The growth and development of mechanisms in photochemistry have led to the discovery of the benefits of this light spectrum as an oxidation technology. The ultraviolet light spectrum can be divided into three regions: UV-A (wavelength range between 315 and 400 nm), UV-B (wavelength range between 280 and 315

nm), and UV-C (wavelength range between 100 and 280 nm). The sun emits ultraviolet rays in the UV-A, UV-B, and UV-C bands. The ozone layer prevents 97 to 99% of ultraviolet radiation from penetrating the atmosphere. 98.7% of the ultraviolet radiation that reaches the earth's surface is UV-A. Some reports have suggested that UV-C has been more effective than UV-A in the photocatalytic degradation of organic matter. Because quartz only absorbs wavelengths shorter than 180 nm, UV light bulbs are produced from quartz [33-35].

B) Visible radiation: The wavelength range of visible light is between 400 to 700 nm. Visible light-generating lamps should be used to activate modified photocatalysts that are activated under visible light. Fluorescent, halogen-tungsten, halogen, and xenon lamps have been used in most studies that have examined the photocatalytic degradation of pollutants in visible light. Fluorescent lamps are a typical example that generates radiation in the visible area. In other words, it is a type of electric gas discharge lamp that stimulates mercury vapor in argon or neon gas with electricity, which results in the formation of a plasma that emits ultraviolet light. This beam is then converted into visible light by a fluorescent material [36-39].

Parameters affecting the photocatalytic degradation process

In photocatalytic degradation, after the transfer of reactants from the fluid phase to the photocatalyst surface and the adsorption of the reactants, the reaction occurs in the adsorption phase. Based on studies in the photocatalytic oxidation of pollutants and according to the principles described above, the most critical operational parameters affecting the overall degradation efficiency with photocatalytic processes are as follows.

A) Temperature effect: Since photocatalytic systems use light radiation to excite the photocatalyst, these systems do not need heat. One of their significant advantages is that they do not need to waste energy to heat water with a high heat capacity. Therefore, this process is preferably performed at ambient temperature.

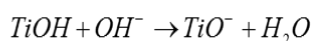
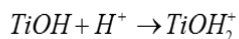
However, due to the release of energy in the decomposition process and pairing of electrons, as well as the incandescence of lamps, the temperature of the solution increases. Therefore, it is necessary to cool the solution. This process is less temperature-dependent in the temperature range of 20-80 ° C. Still, at higher temperatures, the recombination conditions and the adsorption reaction process of the adsorbed reactor are better, and the photocatalytic activity is reduced [40, 41].

B) The effect of oxygen: In photocatalytic degradation, the presence of electron receptors is recommended to prevent the recombination reaction between the created holes, which are positively charged, and the electrons. Therefore, oxygen as an oxidizer in the photocatalytic process is necessary to degrade organic matter. In other words, the oxygen molecule in the electron solution is friendly. It absorbs electrons from the photocatalyst surface, helping the photocatalyst start the activity by preventing electron/hole recombination by absorbing electrons from the photocatalyst surface. In addition to electron adsorption, the oxygen molecule plays an essential role in producing active components such as hydroxyl radicals. In addition, depending on the type of organic compound, it can also play a direct role in the degradation mechanism. Airflow is usually used to provide oxygen. In addition to providing oxygen, aeration causes uniform and dispersed mixing and suspension of catalysts in slurry photoreactors. According to Royai *et al.*, the photocatalytic degradation of phenol in the absence of oxygen (air) does not improve [42-45].

C) The effect of pH: The study of the effect of pH on the performance of the photocatalytic process is complex because pH interferes with the efficiency of the process in three ways at all times:

- ✓ With effect on the rate of hydroxyl radical formation.
- ✓ By acting on the electrostatic attraction between the surface of the photocatalyst and the pollutant molecule.

Creating a tendency for photocatalytic particles to accumulate reduces the effective surface area for the absorption of pollutants and the absorption of radiation. The acidic/alkaline properties of the solution significantly affect the photocatalytic reaction that occurs on the photocatalyst surface. Based on practical



Therefore, changes in pH can be effective by creating an electrostatic force in the adsorption of organic matter to the surface of titanium oxide, which is one of the critical stages of photocatalytic oxidation. In addition, titanium oxide particles tend to agglomerate under acidic pH conditions, which reduces the effective surface area for the absorption of pollutants and radiation. Therefore, determining the optimal pH value in the photocatalytic degradation process is essential [46-49].

Effect of Nature and Concentration of Photocatalyst

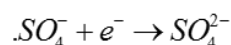
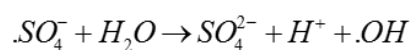
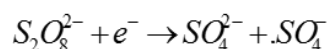
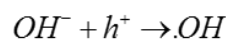
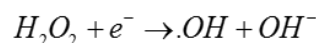
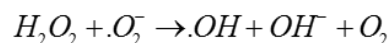
Reports indicate that the reaction occurs only in the adsorbed phase on the photocatalyst. Therefore, an essential parameter in the performance of a photocatalyst is the surface morphology, particle size, and mass size. Zhang et al. (2020) showed that the photocatalytic activity of 15 nm titanium oxide particles is much higher than that of 30 nm particles. On the other hand, the photocatalytic reaction rate is strongly dependent on the amount of photocatalyst used. In general, in any photocatalytic process, the optimum amount of photocatalyst should be estimated to avoid the use of additional catalysts and to ensure that all input photons are absorbed and effective. In addition, the presence of additional catalysts causes unwanted scattering of light and reduces light penetration into the solution.

A) Effect of Pollutant Concentration: Those organic substances that are well absorbed on the photocatalyst surface are more exposed to direct oxidation. Wu *et al.* Concluded that the removal of benzene decreases with increasing

studies, the zero-pH charge point indicates a neutral pH, reported 6.8 for the Degussa p25 photocatalyst. Therefore, the titanium oxide level at pH <pHPZC (acidic medium) has a positive charge, but at pH > pHPZC (alkaline medium), the titanium oxide level has a negative charge.

concentration, since at high concentrations of benzene, there is more competition for active photocatalytic sites. In addition, the lack of photons relative to the pollutant molecules adsorbed at high concentrations of the pollutant can slow down the reaction.

B) Auxiliary oxidizing effect: To improve performance and increase the rate of contaminant degradation, auxiliary oxidants can be used along with oxygen in the photocatalytic process. Hydrogen peroxide and sodium peroxydisulfate are common auxiliary oxidants that act as dual-acting agents. First, they prevent electron/hole recombination by absorbing electrons. Second, ultraviolet radiation generates free radicals such as hydroxyl and sulfate, which play a crucial role in the photocatalytic process. The peroxydisulfate ion also enhances the photocatalytic process by absorbing electrons from the conducting layer of the photocatalyst and preventing electron/hole recombination.



Conclusion

In the photocatalytic process, it is necessary to first activate the photocatalyst due to effective radiation. The need for a light path in the photocatalytic reactor controls the geometry and shape of the reactor. Because the maximum amount of effective radiation must be absorbed by the photocatalyst. Second, the maximum contact between the activated catalyst and the organic matter should be made, and the resulting products should be removed from the photocatalyst surface in the best way. These are just some of the goal-setting sharewares that you can use to get the most out of your reactor. Nanoparticles are incredibly effective in increasing the effective surface area relative to the reactor volume and reducing the internal resistance. In addition, in these photo actors, a stirrer is used to create a homogeneous environment, and aeration is performed due to the need for oxygen. One of the applications of this technology that has attracted many researchers today is the creation of self-cleaning surfaces and hydrogen sensors. Finally, related practical examples that can be mentioned are solar units with a capacity of 300 liters per hour in Almeria (Spain), which are operated by sunlight, and units of 60 to 6000 liters per hour, which purify commercializes

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