

ABSTRACT

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Name of thesis Effective photocatalytic waste water treatment system using metal oxides semiconductors A REVIEW		
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<p>Life is not possible without water. Worldwide, there is an urgent need for clean and safe water. This review presents the principles and mechanisms underlying heterogeneous photocatalysis, and its applications in wastewater treatment.</p> <p>The purpose of photocatalysis is to break down complex molecules such as viruses, bacteria, organic compounds into simple and non-hazardous substances which are then disposed by wastewater treatment. This means that no residues or sludge are left behind. The hydroxyl radical and superoxide radicals are formed by the oxidation of solar photons using semiconductor photocatalysts. TiO_2 is the principal studied photocatalyst in this thesis, its modification by doping, parameters for efficiency, and its removal at the end of the process are also reviewed. Photocatalysis is also known to be a green technology since solar energy can be used as the activation agent of the photocatalyst. Although other methods of light exposure are also mentioned in this thesis a special emphasis on solar photoreactors is made in sub-chapter 7.2, since solar energy is the preferred source for decontaminating for its environmental and low economic impact.</p>		
Key words Photocatalysis, TiO_2 , water treatment, solar energy		

ABSTRACT
CONTENTS

1 INTRODUCTION	1
2 HETEROGENEOUS PHOTOCATALYSIS	2
2.1 Metal oxide photocatalysts	3
2.2 Mechanism of photocatalysis	4
3 TiO₂ PHOTOCATALYST	7
3.1 Degussa P25	8
3.2 Modification of TiO ₂	8
3.3 Nonmetal Doping	9
3.3.1 N-doped TiO ₂	10
3.3.2 S-doped TiO ₂	11
3.3.3 C-doped TiO ₂	11
3.3.4 B-doped TiO ₂	12
4 OPERATIONAL FACTORS INFLUENCING PHOTOCATALYTIC REACTION	13
4.1 pH	13
4.2 Substrate concentration.....	14
4.3 Photocatalyst concentration	14
4.4 Temperature	14
4.5 Light wavelength	14
5 WATER POLLUTANTS	15
5.1 Phenols	15
5.2 Pesticides	17
5.3 Dyes.....	18
6 WATER DISINFECTION	19
7 PHOTOCATALYTIC REACTORS	22
7.1 Cylindrical Photoreactors	23
7.2 Solar reactors.....	24
7.2.1 Parabolic through reactor (PTR)	24
7.2.2 Thin film fixed bed reactor (TFFBR)	25
7.2.3 Compound parabolic collecting reactor (CPCR).....	26
7.2.4 Double skin sheet reactor (DSSR)	27
8 SEPARATION AND RECYCLABILITY OF CATALYSTS	28
8.1 Immobilized photocatalysts.....	28
8.2 Photocatalytic membranes	28
8.3 Magnetic photocatalysts	29
9 CONCLUSION	30
REFERENCES	31

FIGURES

FIGURE 1 Photocatalytic mechanism for TiO ₂ photocatalyst	4
FIGURE 2 TiO ₂ in rutile , anatase, and brookite phase	7
FIGURE 3 Band gap modification of TiO ₂ photocatalyst	8
FIGURE 4 Phenol photodegradation route adapted from	16
FIGURE 5 Cylindrical photoreactors components (TiO ₂ /WO ₃ heterostructure photocatalyst)	23
FIGURE 6 Schematic diagram of solar photocatalytic pilot plant reactors system (one parabolic trough reflector + tank + pump + connections).	25
FIGURE 7 TFFBR reactor schematic	25
FIGURE 8 Comound parabollic collecting reactor (CPCR) schematic.....	26
FIGURE 9 Schematic View of a DSSR reactor showing the inner structure of the transparent structured box made of PLEXIGLAS®	27

TABLES

TABLE 1 Preparation methods of Nonmetal doped Titanium Dioxide photocatalysts Adapted from ..	10
TABLE 2 Synthesis of N-doped TiO ₂ via different methods and its photocatalytic activity for the degradation of phenol compounds adapted from	16
TABLE 3 Synthesis of N-doped TiO ₂ via different methods and its photocatalytic activity for the degradation of various types of pesticides adapted from	17
TABLE 4 Synthesis of N-doped TiO ₂ via different methods and its photocatalytic activity for the degradation of various types of dyes adapted from	18
TABLE 5 Inctivation of microorganisms by TiO ₂ photocatalyst	21

1 INTRODUCTION

The fast industrialization development and the population growth are causing several environmental issues, one of which is the availability of clean and safe water. If water is contaminated, it indicates that undesirable materials have been introduced into a water body or reservoir that render it unfit for drinking or other uses. Human health depends on clean water free of toxins, carcinogens, and harmful bacteria. Nevertheless, nearly 4 billion people lack access to clean and sanitized water, while millions die each year from waterborne diseases (Malato, Fernández-Ibáñez, Maldonado, Blanco, J., & Gernjak, W 2009). The United Nations World Water Development Report 2018 reports that by 2050 the demand for clean water will rise by nearly one-third. Therefore, the development of new methods for reclaiming wastewater, whether from households or industries, is thus becoming more important in order to meet the needs of water supply. Furthermore, researchers are still examining different new technologies to develop affordable water purification systems. Advanced oxidation processes (AOPs) is among the best options for solving this issue. It has become apparent that semiconductor photocatalysis is the most promising of the AOPs, with the potential for total mineralization of both organic pollutants and metal ions. (Kalyanasundaram 2013.) Heterogeneous photocatalysts aim to decompose completely or degrade into biodegradable fragments. Most often, a combination of chemical and photochemical degradation processes is applied. In this thesis, the mechanisms, and the process of heterogeneous photocatalysis are studied, trying to find a better understanding in the structure of the photocatalyst, the photoreactors, and the pollutants to have an effective but simple photocatalytic water treatment system.

2 HETEROGENEOUS PHOTOCATALYSIS

Photocatalysis was first used by Doerffler and Hauffe in 1964 as a label to indicate that the combination of light and a solid catalyst could affect a reaction (Doerffler 1964). Fujishima & Honda published their first paper on photocatalytic water splitting in 1972, which laid the foundation for every subsequent investigation of photocatalysis (Fujishima & Honda 1972). The photocatalytic research field was flooded with papers following Fujishima and Honda's paper. As a result, a glossary of terms and definitions was needed for proper communication and understanding of photocatalytic studies. According to the Glossary of Terms Used in Photocatalysis and Radiation Catalysis (IUPAC recommendations 2011) photocatalysis definition is “change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible, or infrared radiation in the presence of a substance, the photocatalyst, that absorbs light and is involved in the chemical transformation of the reaction partners”. (Braslavsky, Braun, Casano, A., Emeline, A., Litter, M., Palmisano, L., . . . Serpone 2011.)

Photocatalysis explained simply is when Photoirradiation excites an electron in an electron-filled valence band (VB) into an empty conduction band (CB), which is separated from the VB by a bandgap, leaving a positive hole in the VB. By emitting electrons and positive holes, a photocatalyst reduces or oxidizes compounds that adhere to its surface. (Marcí & Palmisano 2019.)

Solar energy is considered to be the best source of radiation for photocatalysis, on both an economic and an environmental level (Rueda-Marquez, Levchuk, Fernández Ibañez, & Sillanpää 2020). As a result of the abundance of solar light, semiconductor-based heterogeneous photocatalysis is considered a promising technique for solving environmental pollution (Ansari, M. O., Kumar, R., Pervez Ansari, S., Abdelwahab Hassan, M. S., Alshahrie, A., & Barakat, M. A 2019). Various semiconductor materials such as TiO_2 , SrTiO_3 , CdS , BiVO_4 , Ta_3N_5 , TaON , $\text{g-C}_3\text{N}_4$, and Ag_3PO_4 have been extensively employed to directly harness solar energy for various redox reactions in the past 40 years. (Wen, Xie, Chen, & Li 2016.) Researchers have been studying heterogeneous photocatalysis using metal oxide semiconductors since the discovery of a photoactivated water splitting process using titanium dioxide (TiO_2) (Fujishima & Honda 1972). During photocatalytic oxidation, hydroxyl radicals are formed, which are among nature's most powerful oxidizing agents. Bacteria and viruses can be destructed using photocatalysis, according to a study by Mills and LeHunte in 1997. There has been much progress in the area of photocatalysis over the past few years. Many of these advances have been made possible by selective control of the

morphology of nanomaterials, the doping of elements, the design of photocatalytic reactors, and porous material support (Li, Chen, He, Wang, & Tang, 2019).

2.1 Metal oxide photocatalysts

In photocatalysis, photocatalysts are the central component. A semiconductor photocatalyst is a “substance able to produce, by absorption of ultraviolet, visible, or infrared radiation, chemical transformations of the reaction partners, repeatedly coming with them into intermediate chemical interactions and regenerating its chemical composition after each cycle of such interactions” (Marcì & Palmisano 2019). In order for this process to be successful, the use of a crystalline semiconductor is essential since only a crystal semiconductor can absorb light with an energy equal to or higher than the semiconductor bandgap and creating electron-hole pair is only possible when energy is greater than or equal to that of the semiconductor bandgap. It is only when atoms are spatially ordered, as in a crystal that radiation is absorbed with the generation of pairs, in which the radiation can be resonant that pairs can be generated. In amorphous phases, radiation can be absorbed, but electrons and holes do not develop. In order for the photocatalytic cycle to be electroneutral, the photocatalyst must be able to adsorb two reactants, one which is reduced, and the other which is oxidized. This means that the semiconductors' capabilities in transporting electron-holes to superficial species can be controlled according to the band energy position of the semiconductors as well as the redox potential of the adsorbates. The level of energy at the bottom of the CBs represents the electron reduction potential and the energy level at the top is concerned with the oxidizing capacity of the holes, they represent the capability of the system to promote reductions and oxidations, respectively. (Marcì & Palmisano 2019.)

Semiconductors like TiO_2 , ZnO , Fe_2O_3 , CdS , ZnS all serve as suitable photocatalysts. Research and studies demonstrate that the 'ideal photocatalyst' should possess the following chemical and physical factors that determine the efficiency of heterogeneous photocatalysts. The required bandgap, large surface area, biologically and chemically inert, suitability towards visible or near UV light, high conversion efficiency and high quantum yield, can be react with wide range of substrate and high adaptability to various environment ,good adsorption in solar spectrum (Chee, Abd, Ibrahim, Matheswaran, & Sarav 2012.) In addition, an effective catalyst should possess an optimal combination of properties, such as ease of regeneration, long lifetime, nontoxicity, low cost, ease of preparation, and non-polluting synthetic methods. By varying the synthesis conditions and the methods of synthesis, one is able to improve the performance of some properties in favour of others, thus favouring the properties that are desired. (Marcì & Palmisano 2019.)

2.2 Mechanism of photocatalysis

The electronic structure of a semiconductor plays a key role in this process. Semiconductors consist of a valence band and a conduction band FIGURE 1. The band gap energy (E_g) is the space between the valence band and the conduction band. Both electrons and holes starting point are in the valence band this is when they are not excited by an external source only photons with energies greater than the band gap energy can result in the excitation of electrons in the valence band to the conduction band. (Aziz, Palaniandy, Aziz, & Dahlan 2016.)

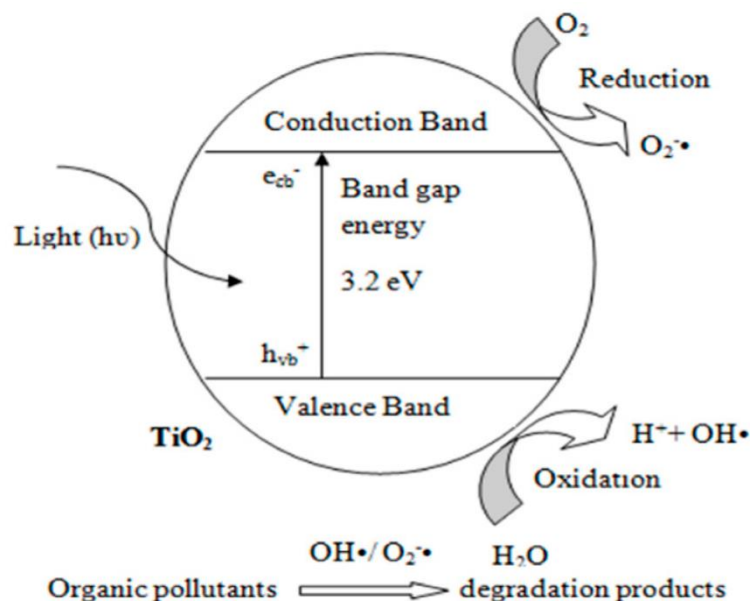
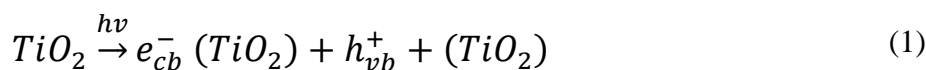


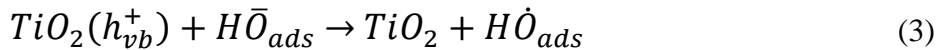
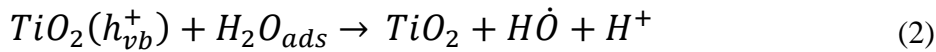
Figure 1 Photocatalytic mechanism for TiO_2 photocatalyst (Sujatha, Shanthakumar, & Chiampo, 2020)

The absorption of a photon from the energy source excites an electron (e_{CB}^-) to the conduction band creating a positive hole (h_{VB}^+) in the valence band as shown in Equation 1. for titanium dioxide



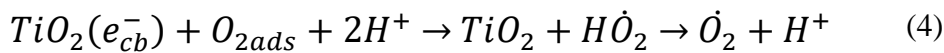
As electrons and holes recombine, the absorbed light energy is released as heat, preventing redox reactions. Scavengers or surface defects are important to trap electrons and holes throughout the entire process, to avoid recombination. (Bahnemann, 2004.)

In the valence band of the TiO_2 particle, the positive hole can react directly with the adsorbed (ads) pollutants, Water or hydroxide ions (OH^-) are oxidized by the hole to produce hydroxyl radicals ($\bullet\text{OH}$):

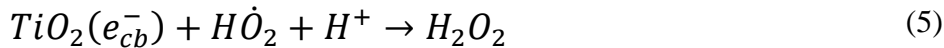


Oxygen plays a critical role in photocatalysis. Superoxide ($\bullet O_2^-$) is formed during the reduction of oxygen (O_2) in the conduction band. (Konstantinou & Albanis 2004.)

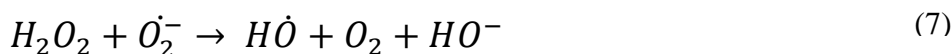
By preventing electrons from recombining with holes, this step leads to an accumulation of oxygen radicals that can contribute to destroying contaminants (Aziz, N. A., Palaniandy, P., Aziz, H. A., & Dahlan, I. 2016).



The reaction producing the superoxide ions in the conduction band can then be further protonated to produce the intermediate hydroperoxyl radical ($HO_2\bullet$), which can then react with hydrogen ions (H^+), leading to hydrogen peroxide (H_2O_2) (Chong, Jin, Chow, & Saint 2010).



When H_2O_2 is used as an oxidizing agent, it can produce more amounts of hydroxyl radicals during this photocatalytic process (Aziz, et al., 2016). The increased hydroxyl radical yield can result in an increase in degradation rates of pollutants, which results in significant cost savings and less complexity in the operation of the treatment process:



Hydrogen radicals as well as superoxide ions have the ability to rapidly attack pollutants which are residing on the surface of TiO_2 particles, as well as in solution. As such, these two substances ($\bullet OH$ and

•O₂) are the most important products formed during TiO₂ photocatalysis. During this continuous process, no residue of the original material remains, so there is no sludge left for landfill disposal, since the contaminant molecules are continuously broken down. It does not require consumable chemicals and the TiO₂ itself does not change. (Aziz, et al., 2016.)

3 TiO₂ PHOTOCATALYST

The white pigment TiO₂ has been used extensively in the industry such as textile, paint, cosmetic, and food industry for years, it is considered non-toxic at normal concentrations. The potential photocatalytic property of TiO₂ has been the subject of extensive research, including photocatalytic degradation of organic pollutants, water dissociation, solar energy conversion, and disinfection. Some of its qualities are durability, low cost, low toxicity, super-hydrophilicity, and remarkable chemical and photochemical stability. (Nosaka, Y., Matsushita, M., Nishino, J., & Nosaka, A. 2005.) TiO₂ has also been developed and used as a photocatalyst for air purification indoors and outdoors, as well as for remediating contaminated waters in the past decade. (G.Li Puma, A.Bono D.Krishnaiah and J.G Collin 2008.)

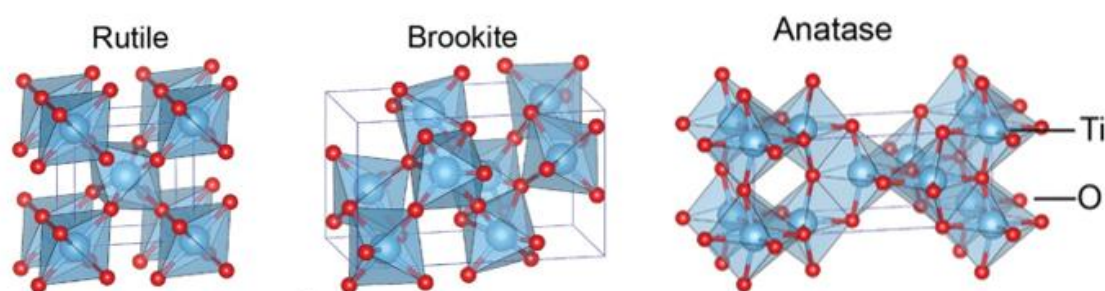


Figure 2 TiO₂ in rutile, anatase, and brookite phase (Haggerty et al., 2017)

There are many ways of making titanium dioxide and most of them require further thermal treatment to achieve the desired characteristics. Titanium dioxide is produced using a variety of techniques, and in many cases, it is at first obtained as an amorphous or poorly crystalline solid. Both the morphology and the structure of titania are affected by this treatment. The solid becomes denser and undergoes several phases, from amorphous to anatase (tetragonal), rutile (tetragonal), or brookite (orthorhombic) Figure 2. is a representation of the three crystalline structures of TiO₂. (Marci & Palmisano, 2019.)

TiO₂, in its anatase crystalline form, is one of the most researched photocatalysts due to its high quantum yield, which is primarily responsible for its high rate of photocatalysis. The bandgap energy of 3.2 eV, due to its large band gap it requires photoexcitation wavelengths less than 385 nm, corresponding to a near-UV light irradiation which uses <5% of the solar light. The high rate of electron-hole recombination also results in a low quantum yield and poor efficiency for photocatalytic reactions (Serpone, Emeline, Kuznetsov, & Ryabchuk, 2010.)

Due to these limitations, several researchers have concentrated their efforts on the development of structures of TiO_2 and their nanocomposites that help to degrade the toxic pollutants in water and wastewater (Santhosh, C., Malathi, A., Daneshvar, E., Kollu, P., & Bhatnagar, A 2018).

3.1 Degussa P25

There has been general agreement that Degussa (Evonik) P25 TiO_2 , one of the most famous and most extensively investigated benchmarks, is only composed of anatase and rutile crystallites, with their ratios typically between 70: 30 and 80: 20 (Marci & Palmisano, 2019).

Degussa P25, Aeroxide TiO_2 P25, is a titania photocatalyst that is widely applied since it exhibits relatively high levels of activity in several photocatalytic reactions. P25 has therefore become a standard titania photocatalyst for a long time for its high activity; it has been featured in over a thousand papers since 1990. (Ohtani, Prieto-Mahaney, Li, & Abe, 2010.)

3.2 Modification of TiO_2

The use of solar energy via photocatalysis has gained considerable interest in wastewater treatment as it is a sustainable method. With regards to using clean and inexhaustible energy, photocatalysis has been noticed as a "green" technology. An ideal photocatalyst should be able to utilize full-spectrum light effectively and separate photogenerated charge carriers efficiently. Due to their large bandgap and high recombination rate of electron-hole pairs, TiO_2 alone could not meet the prerequisite requirements. This results in limited photocatalytic performances. (Heng, Chong, Pang, & Koo 2021.)

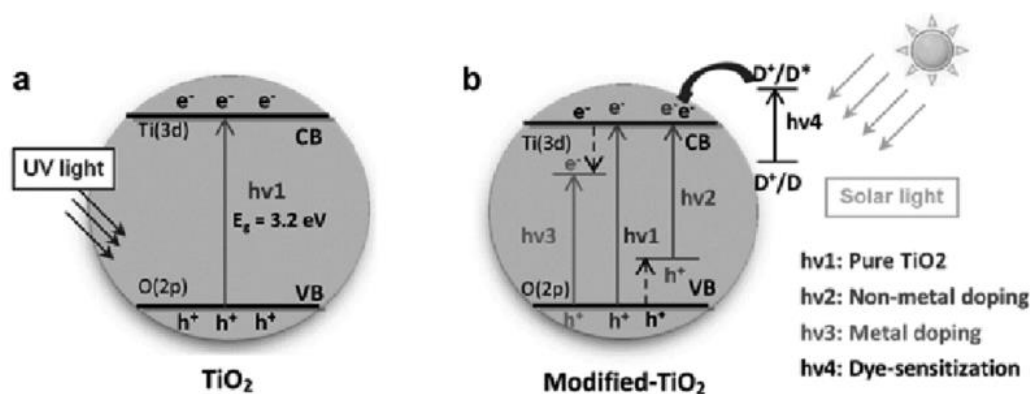


Figure 3 Band gap modification of TiO_2 photocatalyst (Huang, Zhang, & Lai 2015)

Achieving the desired bandgap in photocatalytic systems is therefore extremely important via bandgap engineering of semiconductors (Heng et al. 2021). There is a successful strategy for reducing the absorption edge of this metal oxide by doping it with appropriate dopants (e.g., metal ions and/or non-metals) to get a longer wavelength effect. Figure 3. shows a) TiO_2 without modification and b) different types of dopants in the TiO_2 photocatalyst. For metal doping the energy level is lower than the CB as shown in the line hv3 whereas for the nonmetal the energy level is higher than the VB as shown from line hv2. Various physical and chemical methods have been used for doping, resulting in materials whose absorption edges are redshifted beyond 550 nm (and sometimes beyond these wavelengths). (Serpone et al., 2010.)

3.3 Nonmetal Doping

As early as 2001, non-metallic doping was an interesting alternative strategy to red-shift the absorption edge of TiO_2 when used for photocatalytic purposes. To test the effect of doping or co-doping of non-metals with metals or metalloids, almost all non-metals have been studied up to now. Several factors affect the chemical state, the amount, and the position of the non-metal during the doping process, including the type of dopant selected, the synthesis method, and the way the non-metal is combined (Portela 2013.)

The nitrogen doping of TiO_2 by sputtering in nitrogen-containing gas mixture was first reported by Asahi et al. This enhanced the response to visible light irradiation from photoelectrochemical reactions (Asahi, Morikawa, Ohwaki, Aoki, & Taga, 2001.) There are also additional dopants such as carbon, fluorine, sulfur, and boron which have been introduced into TiO_2 using a variety of technique and these nonmetals have been shown to be beneficial to the visible absorption and photoelectric efficiency (Huang, Zhang, & Lai 2015). Table 1. Shows different experiments using N, S, C and B doping in a TiO_2 molecule, the preparation and the potential application are noted.

TABLE 1 Preparation methods of Nonmetal doped Titanium Dioxide photocatalysts Adapted from (Zaleska 2008)

Kind of Dopant	Doped element	Preparation method	Potential application	References
Nonmetal dopants	N	Titanium nitride (TiN) oxidation: Heating of TiN at 450-550° for 2 hr in air (heating and cooling temperature rate 2°C/min)	photooxidation of aromatic compounds (e.g toluene)	(Wu, Dong, Zhao, & Guo, 2008)
	S	Oxidation annealing of titanium disulfide (TiS ₂) at 300-600°C	waste water decoloring	(Takeshita et al., 2006)
	C	Sol gel method: TBOT was hydrolysed in the presence of ethanol, water and nitric coprecipitated titanium hydroxide was dried at 110°C and calcinated in air at 150-200°C Acid catalyzed solgel process. Alkoidide precursor was dissolved in corresponding alcohol ,mixed with hydrochloric acid aqueous solution. Obtained gel was aged for several days and calcinated in air (3 h at 65°C and 3 h at 250° C) and grounded	Degradation of NO _x ; wastewater decolouring photooxidation of phenol compounds in aqueous phase	(Treschev et al., 2008) (Lettmann, Hildenbrand, Kisch, Macyk, & Maier, 2001)
	B	Anatase TiO ₂ powder (ST01) was grinding with boric acid triethyl ester and calcinated in air at 450°C	photooxidation of phenol compounds in aqueous phase	(Zaleska, Sobczak, Grabowska, & Hupka, 2008)

3.3.1 N-doped TiO₂

The most commonly used non-metal dopant is nitrogen. A significant reason for this is its small ionization energy and its size, which is comparable to oxygen. (Bergamonti, L., Predieri, G., Paz, Y., Fornasini, L., Lottici, P., & Bondioli, F. 2017.)

Hydrolysis, sol-gel, solvothermal, plasma enhanced electrolysis, and solvothermal methods are typically used for synthesising. Other methods include dry methods, such as magnetron sputtering and chemical vapor deposition (CVD) (Quesada-Cabrera, R., Sotelo-Vázquez, C., Quesada-González, M., Melián, E. P., Chadwick, N., & Parkin, I. P. 2017), pulsed laser deposition (PLD), and arc melting (Zhao, Z., Kou, T., Zhang, L., Zhai, S., Wang, W., & Wang, Y 2018). According to Zhang et al. 2015 the calcination temperature influences the optical and photocatalytic properties of the photocatalysts. Their findings suggest that the temperature should not be below 200°C (Zhang, X., Zhou, J., Gu, Y., & Fan, D. 2015). Furthermore, it has been reported that calcination at very high temperatures adversely affected

the photocatalytic activity of TiO₂. At a calcination temperature of 350°C, the best visible light activity of N-TiO₂ was observed at a N/Ti molar ratio of 1. A N-doped TiO₂ photocatalyst was successfully used to enhance the removal of organic compounds from water, especially dyes and pharmaceuticals. Besides phenol, furfuryl, and parabens, there were other pollutants broken down. (Piątkowska, Janus, Szymański, & Mozia, 2021.) Note that, due to the presence of N-doped titania, efficient photocatalytic reduction of water to H₂ can be achieved in the absence of supplementary catalysts such as Pt photocatalyst. (Kalyanasundaram 2013.)

3.3.2 S-doped TiO₂

Sulfur can be doped in two different ways: either by cationic or anionic ions. The cationic process involves superposition of titanium with S₄⁺ or S₆⁺ whereas the anionic process is based on oxygen substitution with S²⁻. (Vorontsov & Valdés, 2019.)

Although doping of the TiO₂ with sulfur is less common than doping it with nitrogen, this process is still among one of the largest strategic approaches in non-metal modification of TiO₂ for improving its photoactivity during visible light exposure. Sulfur is principally obtained from thiourea, though many other sulfuric compounds have also been used in the past, including DMSO, TiOSO₄, and sulfur powder. There are a number of different synthesis methods, but the most common techniques are sol-gel and hydrothermal treatment. (Piątkowska, A., Janus, M., Szymański, K., & Mozia, S. 2021.)

3.3.3 C-doped TiO₂

TiO₂ structure can be optimized with C atoms to narrow the bandgap and improve the absorption of visible light. C-doped TiO₂ photocatalysts perform more efficiently due to changes in the crystalline structure, narrowing of the bandgap, and lowering of the point of zero charge. Various researchers have reported fabricating C-doped TiO₂ by common techniques, including sol-gel, sol-microwave, as well as solvothermal. In addition, there are other works that include electrospinning, CBD, or hydrothermal treatment of TiC powder. (Shi, J., Liu, C., He, C., Li, J., Xie, C., Yang, S., . . . Niu, C. 2015.)

A photocatalyst's crystalline structure depends on its preparation conditions, such as its calcination temperature and atmosphere. Anatase to rutile phase transitions are slowed down by carbon. C-doped TiO₂ photocatalysts have been used for removing organic compounds from aqueous matrices, e.g., dyes and pharmaceuticals producing hydrogen, and acting as bacterial inhibitors. (Piątkowska, et al., 2021.)

3.3.4 B-doped TiO₂

Boron doping inhibits grain growth and facilitates the transformation of anatase to rutile before it forms the diboron trioxide phase. Many references have confirmed that the anatase phase influences absorption and photocatalysis in the visible spectrum. (Marcì & Palmisano, 2019.)

Zhao et al. (2004) demonstrated that boron can extend the spectral response of TiO₂ into the visible range via incorporation into the crystal lattice. A Sol-Gel method was later used to prepare and characterize B-TiO₂ (boron-doped TiO₂). To optimize the activity of B-TiO₂ materials, the atomic ratio of B to Ti (from 1 to 20%) was examined. Chen et al. (2006) found that 5 % boron doped TiO₂ had the best photoactivity.

4 OPERATIONAL FACTORS INFLUENCING PHOTOCATALYTIC REACTION

Basic parameters such as the pH of the solution, the concentration of substrate, amount of photocatalyst, temperature of reaction medium, and the light wavelength are contributors for the effectiveness of a photodegradation reaction. With an adequate amount of photocatalyst, organic compounds photodegraded most readily at low organic substrate concentrations. Photodegradation of organic substrates is also affected by the pH of the solution. Photodegradation of organic substrates is largely determined by the surface area. When increasing the surface area of a photocatalyst, the rate of photodegradation amplifies. (Ahmed, et al. 2018).

4.1 pH

The pH of the solution plays a vital role in the degradation process. Depending on the nature of the materials and pollutant properties, it can either induce or inhibit the reaction during photocatalysis. (Durgalakshmi, Ajay Rakkesh, Rajendran, & Naushad, 2019.)

In the presence of a zero charge on the surface of TiO_2 , the electrostatic attraction between the photocatalyst particles and water pollutants becomes minimal. pH values below point of zero charge (PZC) result in positively charged surfaces of TiO_2 . This electrostatic force is transmitted to negatively charged compounds. However, if the pH is higher than the ZPC level, the surface of TiO_2 is negatively charged, thereby repelling the anionic compounds in the water. Besides changing the charge on catalyst particles, pH also affects positions of the conduction and valence bands. (Ahmed, S.N & Haider 2018.)

Researchers studied degradation of EDTA (Ethylenediaminetetraacetic Acid) by controlling the pH of TiO_2 . By holding the pH constant (i.e., at pH 5) during the experiment, Alkaim et al. demonstrate that the rate of photocatalytic degradation is enhanced by 50% as compared to tests carried out under "free-floating" pH conditions, i.e., after the pH is adjusted to 5 at the start of the reaction. EDTA molecules adsorb to the TiO_2 surface influenced by various pH levels. An important prerequisite for photocatalytic degradation of molecules is strong adsorption of those molecules (Alkaim, A. F., Kandiel, T. A., Hussein, F. H., Dillert, R., & Bahnemann, D. W. 2013).

4.2 Substrate concentration

A large quantity of contamination negatively affects the efficiency of the TiO₂ by saturating its surface. Furthermore, it is important to note that elevated contaminant concentrations will act as blocks between incident photons and the catalyst (Ahmed, et al. 2018). In case of high concentration of organic substrates, the photocatalyst may deactivate, since they would saturate the photocatalyst surface and reduce the photonic efficiency. Das et al studied the degradation of 4-nitrophenol (4-NP) having an initial concentration of 0.02 g/l , when the concentration was increased to 0.1g/L the photocatalytic degradation decreased from the initial 100% to 40.9%.(Das, Patra, Baliarsingh, & Parida, 2006;Aziz et al. 2016.)

4.3 Photocatalyst concentration

Photocatalyst dosage depends on the type of organic compound, as well as the geometry of the photoreactor and the operating conditions. Increasing the dosage of the photocatalyst increases the reaction rate due to more photons being absorbed by the photocatalyst, more light scattering due to dispersion and larger adsorption of organic compounds (Zhang et al., 2003.) A maximum amount of photocatalyst is optimal when all particles are illuminated to a maximum extent, i.e. all the exposed surface are illuminated (Herrmann 1999).

4.4 Temperature

The adsorption of reactants on the TiO₂ surface is disfavoured at temperatures above 80°C, whereas the recombination of charge carriers is favoured. However, temperatures as low as 0 °C increased the apparent activation energy, limiting the desorption of the final product. Hence, the optimum reaction temperature is reported to be in the range of 20 °C to 80 °C. (Ahmed, et al. 2018.)

4.5 Light wavelength

In photocatalytic reactions, both the wavelength and intensity of light are important, and they are affected by the type of photocatalyst used. The light intensity determines the degree of light absorption of the semiconductor catalyst at a given wavelength. (Aziz et al., 2016.) According to Chong, Jin, Chow, & Saint, 2010 a wavelength of light that is not longer than 380 nm is suitable for the commercial Degussa P-25 TiO₂. There are, however, means by which the required wavelength of light can be tailored by different methods with the addition of doping to P-25 TiO₂. (Ahmed, et al. 2018)

5 WATER POLLUTANTS

Increasing urbanization and rapid growth of industrial sectors result in the release of vast quantities of pollutants, which are released into the environment. Some of them are toxic and highly hazardous, such as pharmaceuticals, dioxins, phenols, pesticides, and textile dyes. A significant increase in organic pollutants in the environment is presenting a grave and dangerous threat to the health, safety, and longevity of humans and other living beings. As a result of their high (bio)chemical stability, conventional treatment methods are frequently incapable of removing these kinds of residues from the system entirely. (Marcì & Palmisano 2019.)

5.1 Phenols

Phenolic compounds are among the most significant pollutants in wastewater. They are released to water resources naturally via algal decomposition or the decomposition of organic matter. They can occur in a range of industries, such as oil refineries, petrochemicals, pharmaceuticals, resin manufacturing, paint, pulp paper, and wood products (Vaiano, V., Sacco, O., Stoller, M., Chianese, A., Ciambelli, P., & Sanino, D. 2014). It is important to remove phenols from wastewater before it is released into aquatic habitats due to their toxicity and hazardous nature (Lee, Kim, Lee, & Lee 2010). Untreated discharge of these compounds can cause serious health problems for both humans and animals. According to the World Health Organization (WHO), a concentration of phenol as part of conventional water treatment must be 2 g/L. Furthermore, a concentration of 2, 4, 6 trichlorophenol as part of drinking water must be <0.1 µg/L. (Nickheslat, Amin, Izanloo, Fatehizadeh, & Mousavi 2013.)

Fig 4 is a schematic representation of the photocatalytic degradation of phenol and the formation of intermediates.

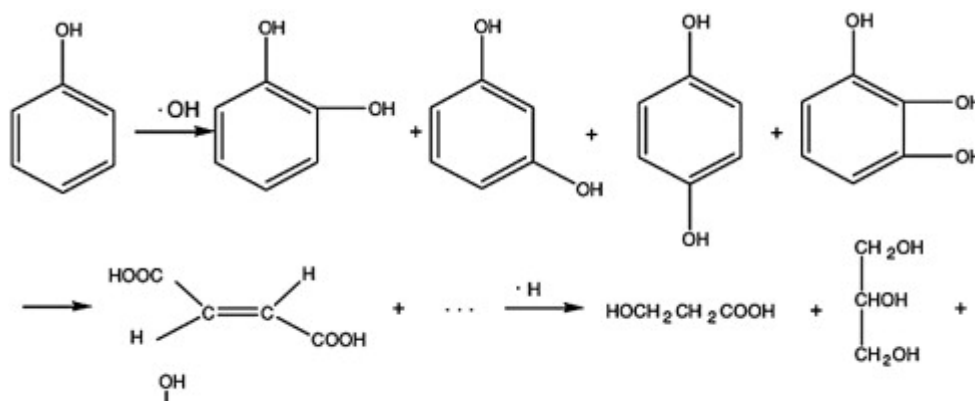


Figure 4 Phenol photodegradation route adapted from (Guo, Ma, & Li, 2006)

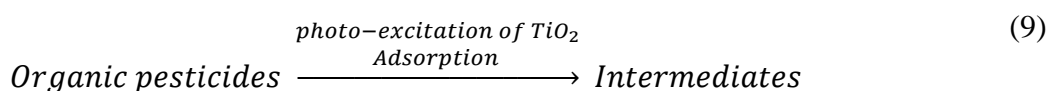
As a result of the attack of the OH radical on each phenyl ring, catechol, resorcinol, 1,2,3-benzenetriol, and hydroquinone are formed, after which the phenyl rings in these compounds break down to give malonic acid, followed by short-chain organic acids, including maleic acid, oxalic acid, acetic acid, formic acid, 3-hydroxy propyl carboxylic acid, 2-hydroxy propanal, 2-hydroxy-ethanoic acid, CO₂ and H₂O. It has been reported that H \cdot , that is produced during the attack of bonds by the radicals produced by $\cdot\text{OH}$, is one of the most active radicals in the degradation process. As a result of this process, both H \cdot and H \cdot are scavenged by oxygen to form HO₂ \cdot radicals, which then become $\cdot\text{OH}$ radicals so it stands to reason that the principal reaction leading to decomposition of organic matter will be the one with radicals $\cdot\text{OH}$. (Ahmed, Rasul, Martens, Brown & Hashib 2010.) Table 2 are lab scale degradation of phenol compounds using N-doped TiO₂.

TABLE 2 Synthesis of N-doped TiO₂ via different methods and its photocatalytic activity for the degradation of phenol compounds adapted from (Ansari, Khan, Ansari, & Cho, 2016)

Synthesis methods	Photocatalyst	Organic pollutants	Reference
Chemical vapor deposition	N-doped TiO ₂	2-Chlorophenol	(Buzby et al., 2006)
Solution based method	N-doped TiO ₂	4-Chlorophenol	(Sakthivel, Janczarek, & Kisch, 2004)
Solvothermal method	N-doped TiO ₂	4-chlorophenol	(Gai et al., 2012)

5.2 Pesticides

Pesticide pollution of environmental waters is a widespread ecological problem. Agricultural industries and pesticide plants are the major sources of pesticide pollution. Pesticides may be present in water from these sources in concentrations as high as several hundred mg/L. No matter how much pesticide is detected, it needs to be removed. (Lee 2010.) TiO₂ has proven to be highly effective at destroying pesticides, both in its pristine form as well as when doped. Upon reaction with dissolved oxygen, the radicals produced through the reaction below produce organic peroxy radicals (ROO •) that ensure pesticide mineralization. (Vela, N., Pérez-Lucas, G., Fenoll, J., & Navarro, S. 2017.)



Researchers have stated that TiO₂ nanoparticles successfully photocatalyzed chlorpyrifos, a phosphate-based pesticide, degrading almost 80% of the pesticide within a day regardless of bacterial activity. UV radiation was needed for catalysis, whereas visible light could not provide the reaction with sufficient energy. (Farner Budarz, J., Cooper, E. M., Gardner, C., Hodzic, E., Ferguson, P. L., Gunsch, C. K., & Wiesner, M. R. 2019.) Table 3 are lab scale degradation of pesticide compounds using N-doped TiO₂.

TABLE 3 Synthesis of N-doped TiO₂ via different methods and its photocatalytic activity for the degradation of various types of pesticides adapted from (Ansari, Khan, Ansari, & Cho, 2016)

Synthesis methods	Photocatalyst	Organic pollutants	Reference
Calcination process	N-doped TiO ₂	atrazine	(Dawson, Soares, & Ribeiro, 2014)
Anodic oxidation method	N-doped TiO ₂	Organophosphorus pesticide acephate	(Zhang, Zhou, Gu, & Fan, 2015)
Electrospinning method	N-doped TiO ₂	Photooxidation of arsenite(III) to arsenate(V)	(Zhang et al., 2015)
Microwave assisted method	N-doped TiO ₂	Malathion	(Kadam, Dhabbe, Kokate, Gaikwad, & Garadkar, 2014)

5.3 Dyes

Among the many uses of synthetic dyes, there are those of the textile, the leather tanning industry, paper production, food processing, in light-harvesting arrays, photoelectrochemical cells, and hair colorings. Chemical dyes are harmful to the environment and human health due to their large-scale production and widespread use. Unfortunately, the exact number of dyes produced in the world is unknown. It is estimated to be over 10,000 tons per year (Konstantinou & Albanis 2004). Table 4 are lab scale degradation of dye compounds using N-doped TiO₂.

TABLE 4 Synthesis of N-doped TiO₂ via different methods and its photocatalytic activity for the degradation of various types of dyes adapted from(Ansari, Khan, Ansari, & Cho, 2016)

Synthesis methods	Photocatalyst	Organic pollutants	Reference
Sol-gel method	N-doped TiO ₂	Methylene blue 57	(Vaiano, Sacco, Sannino, & Ciambelli, 2015)
Solvothermal method	N-doped anatase	TiO ₂ Methylene blue and methyl orange 27	(Yang, Jiang, Shi, Xiao, & Yan, 2010)
Electric field and heat treatments	N-doped TiO ₂ composite	Methylene blue 54	(Mei, Zuo, Xie, Liao, & Ding, 2014)
Solution method	N-doped TiO ₂	Rhodamine B 59	(Jiang et al., 2015)

6 WATER DISINFECTION

Traditionally, chemical disinfectants have been used for centuries in the cleaning of environmental contamination, including alcohols, aldehydes, iodine, phenols, and chlorine. This type of disinfectant is highly effective in the fight against pathogenic microbes however there are some drawbacks that must be considered. The main problem with these disinfectants is that they are volatile, and by-products of these disinfectants can be toxic to humans as well as carcinogenic. In order to control human pathogens and prevent infectious diseases, there is a necessity for creating new disinfection strategies. (Liou & Chang, 2012.)

Mills and LeHunte in 1997 reported that *Streptococcus mutans*, *Streptococcus natans*, *Streptococcus cri-cetus*, *Escherichia coli*, *Saccharomyces cerevisiae*, *Lactobacillus acidophilus*, poliovirus were destructed effectively using heterogeneous photocatalysis (Mills & LeHunte, 1997).

In terms of disinfection, TiO_2 photocatalysis could be considered as a feasible option. The use of TiO_2 photocatalysts in comparison with conventional disinfectants has been proven safe, nontoxic, and it does not produce any harmful by-products (Fujishima 2000; Gamage and Zhang 2010).

For the first time, Matsunaga et al. reported in 1985 that TiO_2 could be used to disinfect water (Matsunaga, Tomoda, Nakajima, & Wake, 1985). After 120 min of incubation with irradiated TiO_2/Pt , the authors reported inactivation of the Gram-positive bacteria *Lactobacillus acidophilus*, the Gram-negative bacteria *E. coli* the yeast *Saccharomyces cerevisiae*, and the algae *Chlorella Vulgaris* (Malato, et al., 2009).

In a paper published by Fernández, Blanco, Sichel, and Malato 2005, the authors showed that the CPC solar photoreactor is effective for the photocatalytic inactivation of *E. coli* using TiO_2 slurries and supported TiO_2 with treatment periods of 30–60 min. Furthermore, they demonstrated that *E. coli* suspensions were totally deactivated by the combined effect of sunlight and the oxidants generated in the TiO_2 . In spite of the fact that sunlight deactivated suspensions of *E. coli*, if TiO_2 was not added, bacteria regrowth could be detected. It should be noted though that our CPC (solar) photoreactor is very effective for drinking water disinfection using photocatalytic process.

As compared to other generally employed substances for water disinfection, such as chlorine (1.36 V), hydroxide radicals have the highest electrochemical reduction potential (+2.8 V vs. a normal hydrogen electrode (NHE)). In other words, TiO_2 photocatalysis does have the potential for disinfecting resistant microorganisms. Traditionally, photocatalytic studies have focused on the effects of hydroxyl radicals

(OH) as reactive oxygen species (ROS) responsible for microbes inactivation, even though other species in the body can produce ROS as well such as hydrogen peroxide (H_2O_2) and the superoxide anion radical ($O_2^{\cdot -}$). (Keane, D. A., McGuigan, K. G., Ibáñez, P. F., Polo-López, M. I., Byrne, J. A., Dunlop, P. S., Pillai, S. C. ,2014.)

As a part of the disinfection process, light intensity has an important role to play. An experiment in which the same water was subjected to the UV-A radiation of 25 W/m^2 (average irradiance) for 2 hours produced different results from one where the water was subjected to 50 W/m^2 of UV-A for 1 hour. Based on the microorganism and the reactor configuration, the minimum amount of UV energy that is required for complete inactivation varies. It was Rincon and Pulgarin 2009, on the other hand, who devised the very first method for determining the inactivation rate of bacteria in drinking water that was based on solar photocatalytic reactions. They indicated that, for an effective system, the solar UV dose needed to reach target disinfection levels alone cannot tell us if we are meeting our disinfection objectives, hence, they proposed the new concept of effective disinfection time (EDT), defined as the duration of time necessary to prevent bacterial regrowth after 24 (or 48) hours in the dark after phototreatment. (Malato,et al.,2009.) Table 5 shows examples of TiO_2 photocatalysis for different types of microorganism inactivation.

TABLE 5 Inactivation of microorganisms by TiO₂ photocatalyst (Foster, Ditta, Varghese, & Steele, 2011)

MICROORGANISMS	CATALYST	REFERENCES
Bacteria		
Escherichia coli	Degussa P25 suspension	(Benabbou, A., Derriche, Z., Felix, C., Lejeune, P., & Guillard, C ,2007).
Escherichia coli	TiO ₂ impregnated cloth filter	(Vohra, Goswami, Deshpande, & Block, 2006)
Enterobacter aerogenes	Degussa P25 suspension	(Ibáñez, Litter, & Pizarro, 2003)
Flavobacterium sp	TiO ₂ coated glass beads	(Cohen-Yaniv, Narkis, & Armon, 2008)
Fusobacterium nucleatum	Anatase TiO ₂ Thin film	Suketa N, Sawase T, Kitaura H, Naito M, Baba K, Nakayama K, Wennerberg A, Atsuta M (2005)
Bacillus cereus	TiO ₂ suspension	(CHO et al., 2007)
Fungi		
Aspergillus niger	TiO ₂ coated on wood	Chen FN, Yang XD, Wu Q (2009)
Aspergillus niger spores	Degussa P25 film on quartz discs	(Wolfrum et al., 2002)
Candida famata	TiO ₂ coated catheters	Yao Y, Ohko Y, Sekiguchi Y, Fujishima A, Kubota Y (2008)
Penicillium citrinum	TiO ₂ coated air filter	(Lin & Li, 2003)
Protozoa		
cryptosporidium parvum	Nanostructured TiO ₂ films	(Sunnotel et al., 2009)
Giardia sp	Fibrous ceramic TiO ₂ filter	(Navalon, Alvaro, Garcia, Escrig, & Costa, 2009)
Acanthamoeba castellanii	Degussa P25 suspension	(Sökmen, Değerli, & Aslan, 2008)
Algae		
Cladophora sp	TiO ₂ coated glass	(Peller et al., 2007)
Chroococcus sp	Anatase TiO ₂	(Hong, Ma, & Otaki, 2005)
Oedogonium sp	TiO ₂ coated concrete	(Linkous et al., 2000)
Melosira sp	TiO ₂ coated glass	(Kim & Lee, 2005)
Virus		
Influenza A/ H ₅ N ₂	Degussa P25/TiO ₂ Millenium PC500	(Guillard et al., 2008)
Influenza A/H ₁ N ₁	TiO ₂ suspension	(Lin et al., 2006)
Influenza A/H ₃ N ₂	TiO ₂ /Pt -TiO ₂	(Kozlova et al., 2010)
SARS coronavirus	Titanium apatite filter	(Han et al., 2004)
Toxins		
brevetoxins	Degussa P25 suspension	(Khan et al., 2010)
microcystines LR,YR and YA	Degussa P25 suspension	(Shephard et al., 1998)

7 PHOTOCATALYTIC REACTORS

Several photocatalytic reactors for water purification have been developed over two decades of development. Photocatalytic reactors may be grouped into two categories: slurry and immobilized. Slurry reactors use suspensions of catalyst, while thin film reactors use thin films of catalyst. (Chee, et al., 2012.) When compared to thin film reactors, suspensions are typically more efficient. The catalysts in suspension reactors have a larger effective surface area, so they come into contact with more substrate surface area. Thus, a larger number of photons hits the surface, which causes a large amount of adsorption to occur. In contrast to slurry-type photoreactors, immobilized thin film photocatalytic reactors use photocatalyst with a thin film coating either on the reactor walls or on glass beads. (Ahmed, et al. 2018.) In fact, Several parameters can be used to compare the photoreactors: geometrical shape, type of catalyst, fluid dynamics, or application (Enesca 2021).

To achieve the desired irradiated volume of the catalyst, there must be consideration of the features of the photoreactor as well as of the particle's intrinsic optical and geometrical features. As such, according to the type of photoreactor, the amount of irradiated catalyst can differ from the total amount of catalyst. The radiation can reach a limited number of particles in a fixed bed photoreactor, depending on the particle layer arrangement in front of the light source. On the other hand, in continuously stirred photoreactors, all particles may have equal chances of being irradiated. There are several phenomena that occur in radiation when it reaches solid particles suspended in liquids, such as reflection, refraction, absorption, and transmission. It is possible that the catalyst particles can be either porous or nonporous solids, with different ratios of surface areas at the external and internal sides. (Marci & Palmisano 2019.)

7.1 Cylindrical Photoreactors

An array of lamps placed in the centre of the reactor is used to irradiate cylindrical reactors where the light source is located within the reactor is also a significant factor because it affects how much light can reach the photocatalyst. There are several ways to install the photocatalyst, including dispersing it in the liquid volume or immobilizing it on substrates (including the lamp cover). In addition, the set-up often includes a storage tank (using aeration and a mixer), pumps, valves, flowmeters, and control systems capable of managing the system as a whole. Aeration of the storage tank is necessary to ensure oxygen saturation conditions during the formation of oxidative radicals. Cylindrical reactors benefit from radial flow, which allows the photocatalysts to diffuse uniformly. (Enesca 2021.) Figure 5. representation of the cylindrical photoreactor.

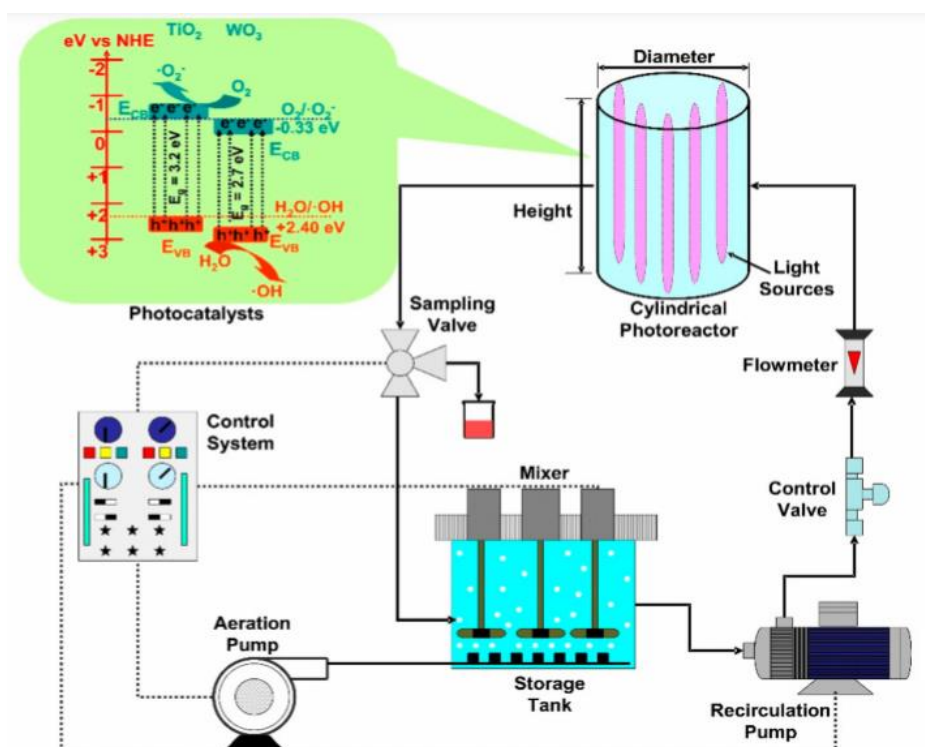


Figure 5 Cylindrical photoreactors components (TiO_2/WO_3 heterostructure photocatalyst) (Enesca, 2021.)

7.2 Solar reactors

The advantage of light-concentrating systems that use a reflecting surface to concentrate solar light in a photocatalytic reactor is that for the same light-harvesting area, a smaller reactor volume is possible. As a result, the reactor can use more expensive components without negatively affecting its cost. In addition, they can operate at higher flow rates, resulting in better mass transfer. They are strong reactors capable of withstanding high pressures, enabling the use of expensive supported catalysts in the reactor. (Alfano, Bahnemann, Cassano, Dillert, & Goslich, R. 2000.)

For non-concentrating (one sun) systems, not having a reflective surface, lowers optical losses which is an advantage to non-concentrating systems. One sun system can capture diffuse UV light as well as direct sunlight, making it possible to penetrate the system with more sunlight. Even on a clear day, diffuse light can contribute up to 50 percent of the total UV light since shorter wavelength UV photons are more readily scattered. A non-concentrating system will continue to work under cloudy conditions, since the diffuse solar light is still available, which is not available to a concentrating system. Some disadvantages of the non-concentration reactors are that they occupy more space since they operate both the solar collector and the photocatalytic reaction. The weather-resistant, chemically inert UV-transmitting glazing needs to be made from inexpensive material since the reactor has a larger surface to be covered, therefore usually certain types of plastics are used for this purpose. These plastics may have lower tensile strength and therefore a careful design of both the reactor's flow control and its hydrodynamics is required due to pressure limitations, the volume requirement, and the requirement for the photocatalyst to be suspended. (Alfano et al., 2000.)

7.2.1 Parabolic through reactor (PTR)

In a parabolic through reactor (PTR), the sun is focused on the focal point by concentrating it through a Dewar tube which is almost similar to a parabolic through solar concentrating tube. The PTR was tested by several research groups from different countries on the European continent, which installed it in the early 1990s at the Plataforma Solar de Almeria (PSA) in Spain as a means of solar wastewater treatment. (Bahnemann, 2004.) In this process, parallel (direct) rays of the ultraviolet part of the solar spectrum are refocused on the particle surfaces of the particle, which are then easily consumed via photocatalysis. Using a Borosilicate glass tube positioned with the focal line and filled with titanium dioxide (TiO₂)

suspension in a flow rate of 250–3500 liters per hour, contaminants were added. (Chee, C., Abd, A., Ibrahim, S., Matheswaran, M., & Sarav, P. 2012.)

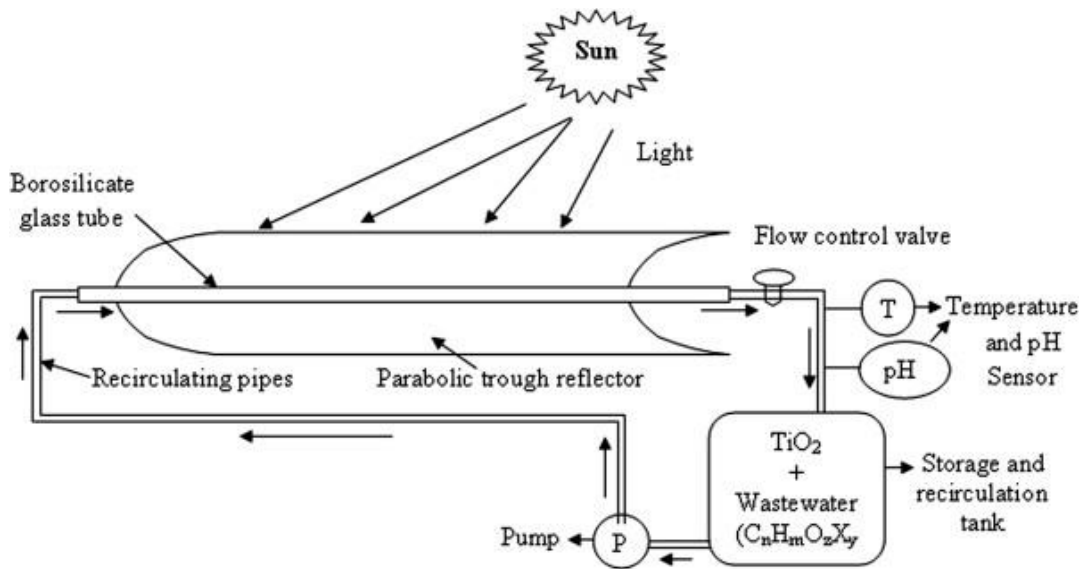


Figure 6 Schematic diagram of solar photocatalytic pilot plant reactors system (one parabolic trough reflector + tank + pump + connections). (Singh, Chaudhary, & Gandhi 2013.)

7.2.2 Thin film fixed bed reactor (TFFBR)

A thin film fixed bed reactor (TFFBR) is one of the very first solar reactors that does not require a concentrating system. As a result, the TFFBR uses both diffuse and direct parts of the solar UV-A light for photocatalysis. An important parameter in the TFFBR process is the sloping plate with photocatalyst like Degussa P25 and rinsed with contaminated water in a very thin film (*100 m). (Bockelmann 1993.) In order to test the TFFBR, it was in order to validate its operation. A comparative study involving

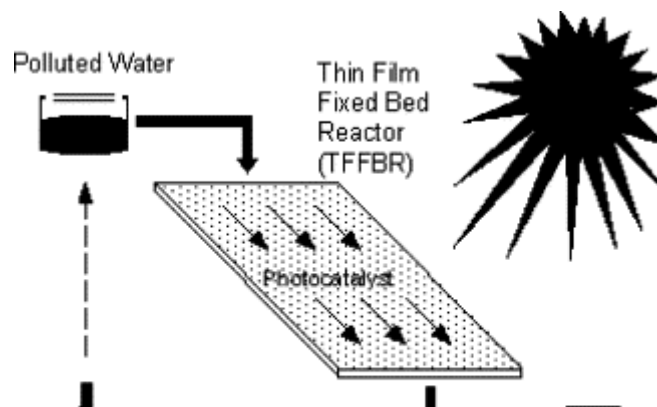


Figure 7 TFFBR reactor schematic (adopted from (Goslich et al. 1997.))

both model pollutants dissolved in pure water and real wastewater samples collected from a variety of industrial facilities revealed that the TFFBR was more effective than the PTR. (Bahnemann 2004.)

7.2.3 Compound parabolic collecting reactor (CPCR)

The compound parabolic collecting reactor (CPCR) is a through reactor without any solar concentrating properties. The major difference between the PTR and CPCR is the shape of their reflecting mirrors. The reflector of a PTR has a parabolic profile, and the pipe is positioned along the focal line. Subsequently only parallel light which enters the parabolic through can be concentrated on the pipe. The reflector of a CPCR generally made up of two half circle profiles side by side. The focal line is situated just above the connections of the two circles. (Chee et al.,2012.) Figure 8 shows the schematic view of the reflector of a CPCR.

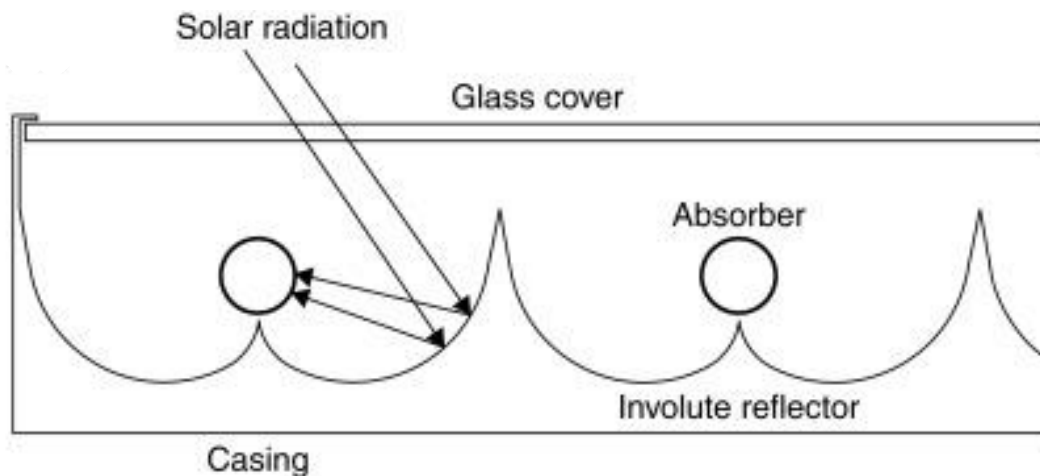


Figure 8 Compound parabolic collecting reactor (CPCR) schematic (Kalogirou 2014.)

With one or more reflections within the core, compound parabolic concentrators can be used to collect radiation of varying angles depending on the angle at which the solar rays fall upon the surface. A beam of radiation that enters the collector's aperture within its acceptance angle will be absorbed by the absorber surface located at the bottom of the collector. A low reflectivity of the concentrating surface can lead to significant optical losses. (Kalogirou 2016.)

7.2.4 Double skin sheet reactor (DSSR)

The double skin sheet reactor was developed by Röhm GmbH Chemische Fabrik, Darmstadt, Germany and the Institut fuer Solarenergieforschung GmbH, Hannover, Germany (ISFH) is a new kind of reactor which does not have a light concentrating properties. It is a flat and transparent structured box made of PLEXIGLAS® (Van Well et al., 1997). PLEXIGLAS® is a trademark of a commercialized Poly(methyl methacrylate) (PMMA) which is a transparent thermoplastic. PLEXIGLAS® transmission begins below 400 nm, which is the wavelength of the UV-A portion of the solar spectrum (Alfano et al.,2000). The inner structure of the DSSR is depicted in Figure 9. The suspension of the model pollutant and the photocatalyst is allowed to flow through these channels. The DSSR can use both the diffuse and direct portion of the sunlight (Chee,et al., 2012).

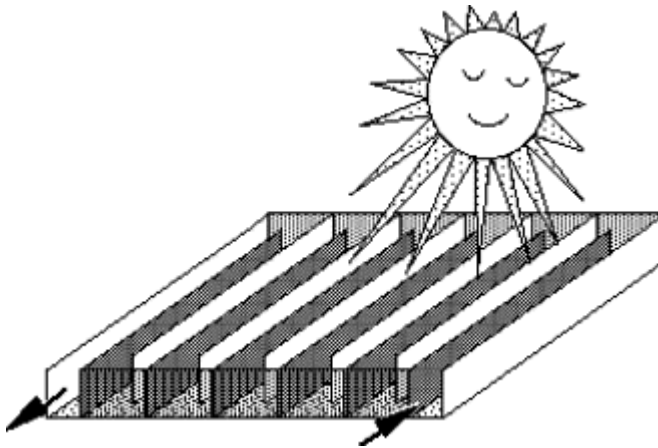


Figure 9 Figure 5 Schematic View of a DSSR reactor showing the inner structure of the transparent structured box made of PLEXIGLAS® (adapted from (van Well et al., 1997)).

8 SEPARATION AND RECYCLABILITY OF CATALYSTS

The overall cost of the process should be minimized in order to make heterogeneous photocatalysis suitable for practical applications such as water and wastewater treatment. It has been determined that one of the ways to reduce the cost of the photocatalyst is to improve its recyclability. The water currents, however, can wash some of the photocatalyst away after each cycle. In order to continue enhancing recyclability, many efforts have been made. The most common of these involves either of the following approaches: immobilizing the photocatalyst, using magnetic photocatalyst and photocatalytic membranes. (Ahmed et al. 2018.)

8.1 Immobilized photocatalysts

An important advantage of TiO_2 is that it can be immobilized easily on a variety of substrates, including quartz, glass, concrete, or fluorine-doped tin oxide in a transparent form. Immobilisation is one way to reduce the overall cost of the application process by eliminating the separation and recovery chamber, but reduces the area of contact between the photocatalyst and the reactants, which compromises efficiency. (Ahmed et al. 2018.)

8.2 Photocatalytic membranes

In terms of polymeric and ceramic membranes, one of the most important limitations is that it is extremely easy for them to become fouled. It has been found that photocatalytic membranes have displayed a greater fouling resistance, in addition to having antimicrobial properties. It is fully possible to develop such membranes by assembling nanomaterials through a variety of techniques, such as assembling nanoparticles as thin membranes, or fabricating a membrane through the assembling of nanofibers or aligned nanotubes. Graphene and other two-dimensional nanosheets have also been investigated for their uses in membrane applications. Additionally, new developments in the combination of nanowires with graphene sheets have also garnered considerable attention in recent years. An antimicrobial property and anti-fouling property are also provided by such a structure as well as hydrophilicity and aqueous stability. The use of Fe_3O_4 and TiO_2 nanoparticles as fillers in composite membranes has also been proven to be successful in some studies. It is with this background that nanomaterials give rise to a broad spectrum of recycling applications, such as applications for metal and nonmetal membranes. (Ahmed, et al. 2018.)

8.3 Magnetic photocatalysts

The incorporation of a magnetic element into photocatalytic nanocomposite is also another way to ensure the recyclability of the photocatalyst. In this way, a magnetic field can be applied to the photocatalyst after it has been treated in order to recover it magnetically. As an additional benefit, the incorporation of magnetic components means that the photocatalyst particles do not agglomerate during the recovery process. The most widely used magnetic material is Fe_3O_4 . It has been successfully used as a core-shell material in conjunction with ZnO , TiO_2 , β -cyclodextrin and Bi_2O_3 . Despite this, separating metals by magnetic separation is a time-consuming process that does not allow the photocatalytic reactor to keep flowing continuously. Therefore, magnetic separation is a better choice for batching operations compared to continuous operations. (Ahmed, et al. 2018.)

9 CONCLUSION

Photocatalysis is a very attractive green strategy that has great applications in wastewater, as it is proven to efficiently degrade the most common and toxic pollutants in wastewater. Although the modified photocatalysts show superior properties compared to the undoped TiO_2 , more investigations are still needed to develop the production methods at the industrial scale. The selective control of the nanomaterials morphology, the doping of elements, the design of photocatalytic reactors, and porous material support are areas in which efforts should be focused to produce more effective photocatalytic reactions. Obtaining stable and reusable photocatalysts using simple and economically feasible methods is of paramount importance. In the coming years, more developments resulting from recent advances are to be seen.

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