

# Porphyrins and Phthalocyanines. Synthesis, properties and photocatalytic activity for wastewater treatment

## Porfirinas y Ftalocianinas. Síntesis, propiedades y actividad fotocatalítica para el tratamiento de aguas residuales

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### Abstract

Phthalocyanines are porphyrin-based dyes have plenty applications in different fields, including industrial, environmental (wastewater treatment), biomedical and chemical research. Phthalocyanine structure is able to chelate a lot of metals, which more often contribute to their huge variety of functions, including reactive oxygen species generation as photosensitizer, fluorescence and absorption spectra. All of these properties and also the synergism  $\text{TiO}_2$  – Phthalocyanine are very important to medical and environmental research, because oxygenated species generation ( $^1\text{O}_2$ ,  $^{\cdot}\text{O}_2$ ,  $^{\cdot}\text{OR}$ ) is the main topic involved in their photocatalytic processes. The presentation of this review is very important for the development of research in photocatalysts in general.

*Keywords: porphyrins, phthalocyanines, photosensitizer, photocatalysis, photo-oxidation.*

### Resumen

Las ftalocianinas son colorantes a base de porfirinas que tienen muchas aplicaciones en diferentes campos, incluyendo la investigación industrial, ambiental (tratamiento de aguas residuales), biomédica y química. La estructura de la ftalocianina es capaz de quelar una gran cantidad de metales, que contribuye a generar una gran variedad de funciones, incluyendo la generación de especies reactivas de oxígeno como fotosensibilizador, eficiente fluorescencia y espectros de absorción. Todas estas propiedades junto al sinergismo  $\text{TiO}_2$  - Ftalocianina son muy importantes para la investigación médica y ambiental, ya que la generación de especies oxigenadas ( $^1\text{O}_2$ ,  $^{\cdot}\text{O}_2$ ,  $^{\cdot}\text{OR}$ ) es el principal tema involucrado en sus procesos fotocatalíticos. La presentación de esta revisión es muy importante para el desarrollo de la investigación en fotocatalizadores en general.

*Palabras clave: porfirinas, ftalocianinas, fotosensibilizador, fotocatalisis, fotooxidación.*

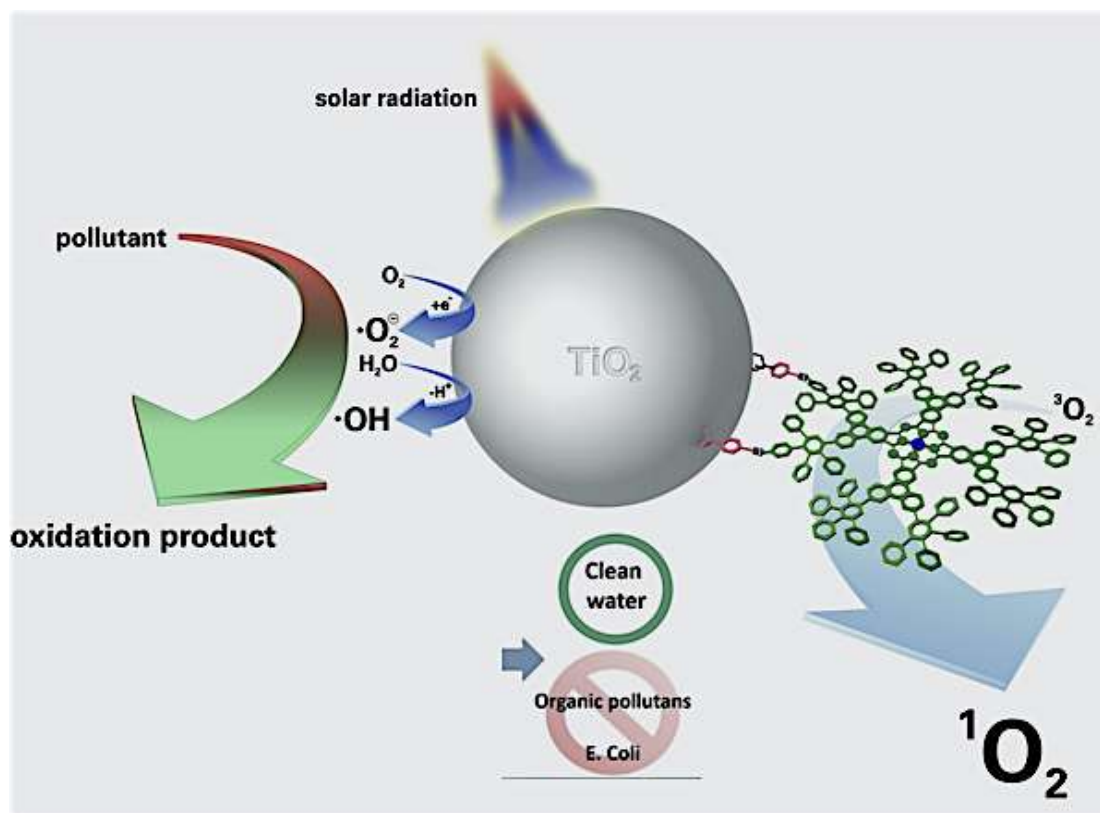
### Highlights

1. The catalytic oxidations of toxic phenols has been used in our laboratory as substrates reference for the photooxidation. Photooxidations are more efficient than in the darkness oxidations.
2. Photocatalysis and the processes of purification of water contaminated with emerging pollutants.

3. Photosensitization/Photocatalysis: synergism TiO – Phthalocyanine. Photocatalytic disinfection of water (*Gram-positive and Gram-negative Bacteria, Virus, Enterovirus, Fungi, Pesticides, Herbicides and emerging pollutants*) is gaining much interest as it involves three components that are individually harmless to the biological environment, namely, the photosensitizer, light and molecular oxygen.
4. The fast growing global population and contamination of water resources by human activities and/or industries pose a challenge in achieving clean, microbe-free water for drinking and other domestic purposes.

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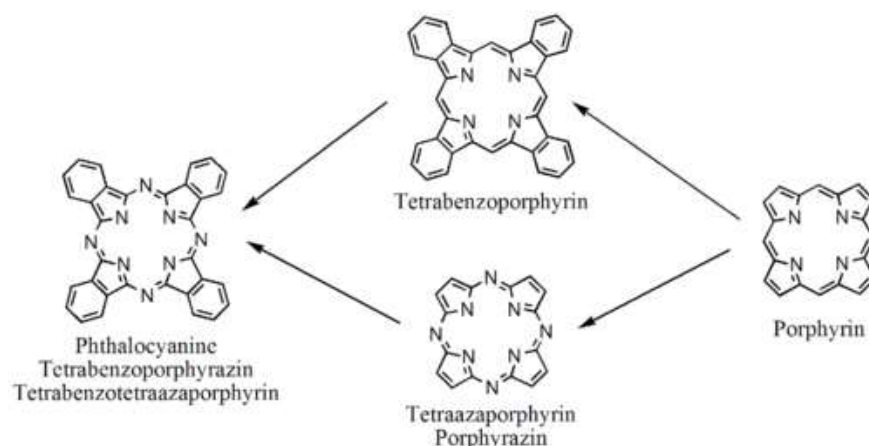
### Graphical Abstract / Resumen Gráfico



### 1. Photosensitization

Porphyrins, phthalocyanines, and other related organic dyes are well known for their use in many photocatalytic processes and also photodynamic therapy (PDT). Such molecules are also being explored for photodynamically treating microbial and viral infections, killing of unwanted pathogens in the environment. Such photosensitizers cause cell death by generating reactive oxygen species (ROS) especially singlet and superoxide oxygen in the presence of light. Hence its great importance also in the treatment of cancer through this photodynamic process. The process of photosensitization (phototreatment) can be applied for obtaining clean, microbe-free water, through oxidation processes of chemical pollutants thus taking the advantages and versatility properties that photosensitizers have. Phototreatment of water is drawing the attention of many as a promising alternative to replace methods like chlorination, ozonization, and other oxidation processes, used in current disinfection methods limiting harmful side-products and by-products that can cause damage to the flora and fauna. [1-5].

The fast growing global population and contamination of water resources by human activities and/or industries pose a challenge in achieving clean, microbe-free water for drinking and other domestic purposes. Acquiring pure water free of contaminants and pathogens is a matter of concern which calls for new, effective, and low cost water disinfection techniques. It is noteworthy that, from pigments for the textile industry and even for application in photodynamic therapy, phthalocyanines are among the most synthesized porphyrin derivatives in the laboratory due to the wide range of applications they have [6]. These compounds, although they are macrocycles coordinated with some metal, have a very reasonable structural relationship with porphyrins and porphyrazines (Figure 1). As a consequence, and also due to the particular spatial configuration of all tetra-aza, the nitrogen atoms of the pyrrole units are "found" in the center of the macrocycle. Porphyrin, porphyrazine and phthalocyanine can chelate metals and form a coordinated complex, since two of the four nitrogens involved form a coordinated bond with the metal ion in the center of the structure.



**Figure 1.** Structural relationship between porphyrin, porphyrazine and phthalocyanine.

As a reinforcement of the arduous work that had been carried out for more than a decade in the field of porphyrin compounds, E. Çelenk Kaya and coworkers investigated the synthesis and thermal stability of different kinds of Phthalocyanines (Zn, Co, Cu, among others), which are widely used in the textile industry. It was determined that the Cu-metallized Phthalocyanine has greater thermal stability, since it can only decompose at a temperature of 692.05 K. The fluorescence and absorbance values for Zn Phthalocyanine reported by research in previous years stand out, with a Q band of 672 nm and a fluorescent emission of 682 nm. The problem of the low reaction yields was solved when Dutch researchers in 2019 designed a simpler synthesis of metal-free and metalized Phthalocyanines with Zn, Cu, Mn, Fe and Co, by a direct, one-step method and an indirect two-step method. In the first case, with reaction yields of up to 70%, compounds such as phthalonitrile, n-pentanol and DBU are required, refluxed for two hours. In this way, dissolving phthalonitrile in n-pentanol produces a milky liquid, which turns orange when DBU is added. The solution, then turns a dark blue-purple color upon heating, depending on the phthalocyanine, which indicates the formation of the porphyrin ring. At the same time, since this reaction is based on the cyclization of phthalonitrile, the process must be carried out under an inert atmosphere. Because the humidity of the air can hydrolyze the nitrile groups that would form unwanted by-products. Very valuable infrared spectroscopy data were also reported [7-9].

In recent years, plenty of techniques have been developed in order to reduce inconveniences and increase reaction yields. One of these techniques has been used in the synthesis of porphyrins, phthalocyanines, and related compounds: the use of microwave irradiation. This technique is based on non-conventional thermal heating by using the microwave, which could perfectly be a substitute for conventional thermal heating that allows the use of ionic liquids instead of common solvents. This methodology is currently receiving special attention, because better reaction yields and greater purity have been achieved in the products [10, 11]. Porphyrin derivatives are very good photosensitizing compounds. They are able to produce large amounts of singlet oxygen and

other reactive oxygen species (ROS), which are very powerful oxidizing components. As a consequence, the biological, medical, or photocatalytic utility of porphyrin and phthalocyanine compounds is vast. Phthalocyanines, due to its great photosensitizing capacities, are use for the treatment of photodynamic cancer, wastewater purification, or effective purification of it through photocatalytic mechanisms, the photooxidation of toxic molecules, and the photoproduction of important intermediates for various chemical products. Phthalocyanines have the capacity to generate large concentrations of ROS with an absorption spectrum equal to or greater than 650 nm, resulting in a great advantage in all these previously named processes. Porphyrins, phthalocyanines, and other related organic dyes are well known for their use in photodynamic therapy (PDT). These photosensitizers cause cell death by generating reactive oxygen species (ROS) especially singlet oxygen in the presence of light. Such molecules are also being explored for photodynamically treating microbial infections, the killing of unwanted pathogens in the environment, and oxidation of chemical pollutants.

Heterogeneous photocatalysis, unlike most photochemical processes, is not selective and can be used to treat complex mixtures of pollutants [12]. On the other hand, the possibility of using solar radiation as a primary source of energy, gives it an important and significant environmental value [13]; the process constitutes a clear example of sustainable technology. The heterogeneous metal phthalocyanines exist either impregnated on SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, charcoal and TiO<sub>2</sub> or covalently and coordinatively bound on SiO<sub>2</sub> and organic polymers or ionically bound on an organic ion exchanger. The catalytic oxidations of toxic phenols have been used in our laboratory as substrates for the photooxidation.

## **2. Photocatalysis and the processes of purification of water contaminated with emerging pollutants**

With the definition of emerging pollutants explained, we will see below how they can be classified. Emerging pollutants often appear in wastewater, rivers, and aquifers. The sources of emissions are varied. The main ones are agriculture, livestock and poor management of toxic waste by human activity. Some of these contaminants have not yet been detected. But it has been possible to classify a large number of them:

- .- Medicines that expire are disposed of improperly through toilets, sinks or in the normal trash. These should be taken to clean medicine collection points.
- .- Pesticides or fertilizers.
- .- Pharmaceutical products with cutaneous application, such as creams, ointments and lotions. As a general rule, emerging pollutants are considered to be those remains that are not absorbed through the skin and contaminate surface waters.
- .- Personal hygiene products (PPCP): perfumes, sunscreen, makeup ...
- .- Nanoparticles of silver, gold and metallic oxides that come from industrial activities.
- .- Illegal drugs such as cocaine, heroin, or amphetamines.
- .- Endocrine or hormonal disruptors.
- .- Plasticizers and industrial additives.
- .- Microplastics are also collectively considered a type of emerging pollutant.

The first publication on this process of degradation of pollutants in both aqueous and gaseous phases was carried out by Carey and coworkers in 1976. Since then, a historical analysis of the evolution of the development of the photocatalytic process for water purification has allowed us to identify four clearly different stages. In the first stage with few publications, approximately between 1976 and 1985, only a few scientific groups work on the subject; a concrete application is not yet in sight. The second stage, from the mid-1980s to the early 1990s, coincides with growing concern and concern of the international scientific community about environmental issues; it raises the possibility of applying this process to the treatment of pollutants in water. The success of the first experiences gives rise to massive incorporation of research groups to the study of the subject. In this situation, at the end of the 1980s, as results of very optimistic extrapolations of the result obtained until then, the photocatalytic process came to be considered as a possible universal method for the degradation of organic pollutants [14, 15].

Of the known semiconductors, titanium dioxide  $\text{TiO}_2$  has been the most studied since it has been shown to be the most efficient photocatalyst in the purification and treatment of water and air in most of the cases studied [16-17]. Titania is not expensive or toxic, and it is also a biocompatible material with high photo efficiency and activity. Various attempts have been made to increase the photocatalytic activity of  $\text{TiO}_2$  both by noble metal deposition and ion doping; however, these modifications not only did not increase its activity but were also shown to be detrimental. Photo treatment of water is drawing the attention of many as a promising alternative to replace methods like chlorination, ozonization, and other oxidation processes, used in current disinfection methods limiting harmful side-products and by-products that can cause damage to the fauna and flora. The process of photosensitization (photo treatment) can be applied for obtaining clean, microbe-free water, thus exploiting the versatile properties of photosensitizers. This review collects the various attempts carried out for photo treatment of water using organic photosensitizers. Photocatalytic disinfection of water is gaining much interest as it involves three components that are individually harmless to the biological environment, namely, the photosensitizer, light, and molecular oxygen.

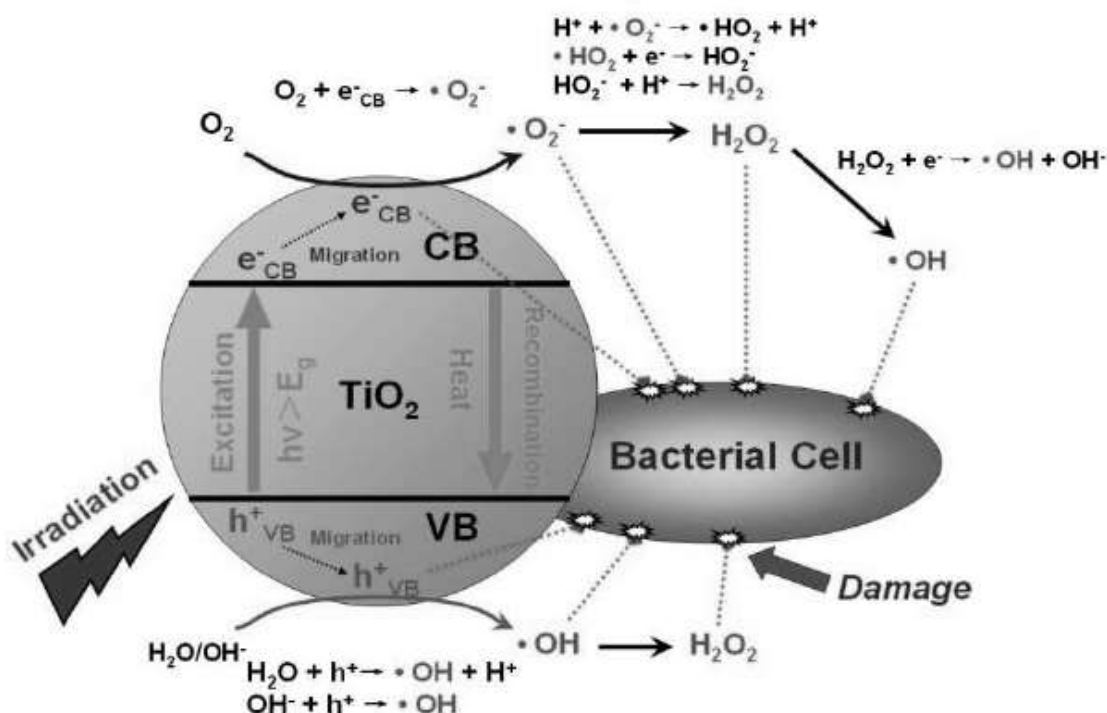
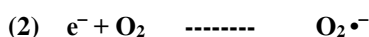


Figure 2. Photocatalytic scheme of  $\text{TiO}_2$  [2, 20].

In the photocatalytic oxidation processes, for example, pesticides are chemically transformed (degraded) to photoproducts, in the presence of semiconductor materials known as photocatalysts (e.g.,  $\text{TiO}_2$ ,  $\text{ZnO}$ ), an energetic light source in oxygenated media. As

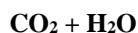
illustrated in figure 2, only photons with energies greater than the energy of the energy gap (energy band gap,  $\Delta E$ ) can give rise to the excitation of electrons of the valence band (VB) of the material, which then promote possible reactions with pollutants. The absorption of photons with energy less than  $\Delta E$  or greater than the wavelengths generally causes the dissipation of energy in the form of heat. Irradiation of the photocatalytic surface with sufficient energy leads to the formation of a positive hole ( $h^+$ ) in the valence band and an electron ( $e^-$ ) in the conduction band (CB). The positive gap either directly oxidizes the contaminant or water to produce the hydroxyl radical  $OH^\bullet$ , while the electron in the conduction band reduces the oxygen adsorbed on the photocatalyst.

The activation of  $TiO_2$ , for example, by UV light can be represented by the following steps:

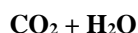


In this reaction, the  $h^+$  and  $e^-$  pair are potent oxidizing and reducing agents, respectively. The oxidative and reductive reaction steps can be expressed according to:

**Oxidative reaction:**



**Reductive reaction:**



The generation of hydroxyl radicals by the photocatalytic oxidation process is shown in the previous steps. In the degradation of organic pollutants, the hydroxyl radical  $OH^\bullet$  generated from the oxidation of adsorbed water is the primary oxidant, and the presence of oxygen can prevent the recombination of an electron-hole pair.  $OH^\bullet$  thus attacks organic compounds, for example, chlorinated aromatic compounds, aniline, nitrophenols, among others; which give rise to different reaction intermediates depending on the nature of the compounds. The resulting intermediates react with more  $OH^\bullet$  to produce degradation end products such as  $CO_2$  and  $H_2O$ . In the photocatalytic degradation of pollutants, when the oxygen reduction process and the oxidation of pollutants do not proceed simultaneously, there is an accumulation of electrons in the CB, which causes an increase in the recombination rate of  $e^-$  and  $h^+$ . In an effective photocatalytic oxidation, this is of utmost importance to avoid electron accumulation.

In photocatalysis,  $TiO_2$  (commonly known as Titania) is by far the most widely studied system due to its high activity, desirable physical and chemical properties, low cost, and high availability. Of the three common crystalline forms of  $TiO_2$ , the anatase and rutile forms have been extensively investigated as photocatalysts. Anatase has been reported as the more active phase as a photocatalyst than the rutile phase. Oxidation pathways similar to those of  $TiO_2$  are confirmed in  $ZnO$  photocatalysts, including the formation of the  $OH^\bullet$  radical and direct oxidation by photogenerated holes [18, 19].  $ZnO$  was reported to have a similar and comparable reactivity to  $TiO_2$  under sunlight. The high activity of  $ZnO$  is attributed to the fact that the energy bandgap of the material is similar to that of  $TiO_2$ , that is, 3.2 eV. Some other metal oxides including  $CeO_2$ ,  $SnO_2$ ,  $WO_3$ , and  $CdS$  have also been examined for degradation of organic pollutants [2, 20, 21].

Different sources of radiation such as UV lamps and solar radiation have been used in the photocatalytic degradation of various pesticides and herbicides in wastewater effluents [22, 24].

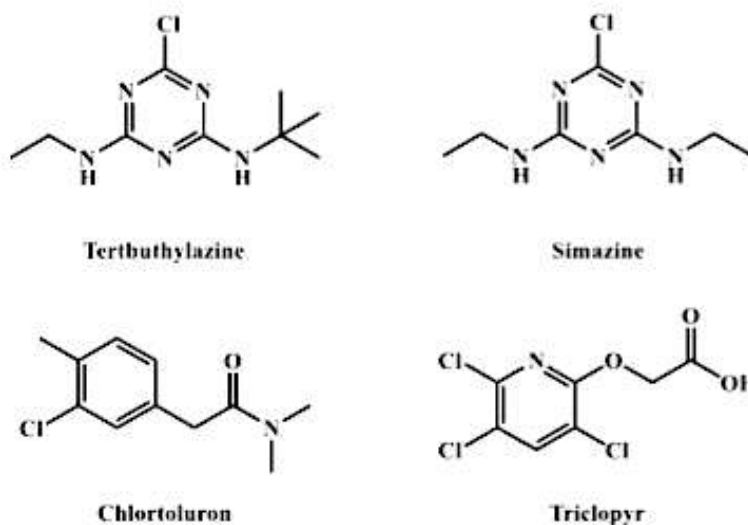
Based on these principles, a wide range of pesticides have been treated by photocatalytic degradation. In fact, there are a wide variety of semiconductor materials (ZnO, CuO, TiO<sub>2</sub>, and WO<sub>3</sub>) to be used for photocatalytic purposes [9, 20, 25]. Among them, titanium dioxide has been used most widely due to its favourable catalytic properties, the anatase phase being the most widely used due to well-studied special characteristics.

Organochlorine pesticides (POC) have been treated by the photocatalysis method. In this sense, the photocatalytic degradation of Dicofol on TiO<sub>2</sub> nanoparticles under UV light irradiation has been reported. Yu and Zeng reported that Dicofol could completely degrade into inorganic chloride ions, obtaining high mineralization efficiency [24]. Considering that titania photocatalysts are commercially available under different trade names: Degussa P25, Millennium PC 500, etc. Madani et al. [25] carried out a study to compare the activity of the two aforementioned commercial anatase products, using the pesticide Diuron as a model. The results obtained by the researchers showed that the Degussa P25 material was more efficient than Milenio PC 500.

Three zinc phthalocyanines immobilized on mesoporous aluminosilicate have been successfully employed in the degradation of pesticides fenamiphos and pentachlorophenol by Silva et al. [70]. They report 98% conversion of fenamiphos after 300 min of irradiation into fenamiphos-sulfoxide and fenamiphos-sulfone. The main photodegradation product of pentachlorophenol after 300 min of irradiation was 2,3,5,6-tetrachloro-hydroquinone. Recently, TiO<sub>2</sub> catalysts photosensitized with porphyrins are investigated for phototreatment of water [26].

Although photocatalysis is shown as an excellent methodology for the elimination of pesticides, the use of titania is limited for commercial applications due to its high activity in the UV range in relation to natural sunlight. Therefore, many researchers have investigated the possible expansion of its absorption range in the visible region (for example, through structural modifications, surface doping, among others). On the other hand, the recombination of excited electrons and the gap must be controlled and inhibited because it is another limiting factor in the photocatalysis process. In this sense, other options, such as metal / non-metal doping and other types of surface modifications, have been actively studied to improve the photocatalytic activity of semiconductor materials.

Due to their physicochemical properties, most herbicides have weak adsorption coefficients in soil. They are therefore poorly absorbed in-ground, and as a result, end into streams and groundwater. Moreover, toxicity is usually determined for native herbicides, and do not take the products of degradation into account (often much more mobile and unfortunately also dangerous) and the nature of the soil. In addition, herbicides have often extended lifetimes in the water, which increases the risk of accumulation and thus increases the contamination of water environments. As an example in 2013, in France, the General Commission for Sustainable Development (GCSD) believed that contamination of rivers “is almost universal in France, mainly by herbicides”, such as glyphosate, triazines (with atrazine des-ethyl, a decomposition product of atrazine) and substituted urea. In 2014, the latest results showed that up to 93 % of the watershed are contaminated, and sometimes with prohibited substances for 10 years. More worryingly, herbicides level higher than 0.5 µg/L was observed, which is the maximum allowed in drinking water. A major consequence of stream contamination by herbicides is the increase of some nutrients’ quantities, particularly nitrogen and phosphorus, creating an imbalance in the growth of marine plants and algae proliferation (a synergistic phenomenon with the massive use of fertilizers). It leads also to an impoverishment of oxygen content in rivers and thus excess in mortality of aquatic species.



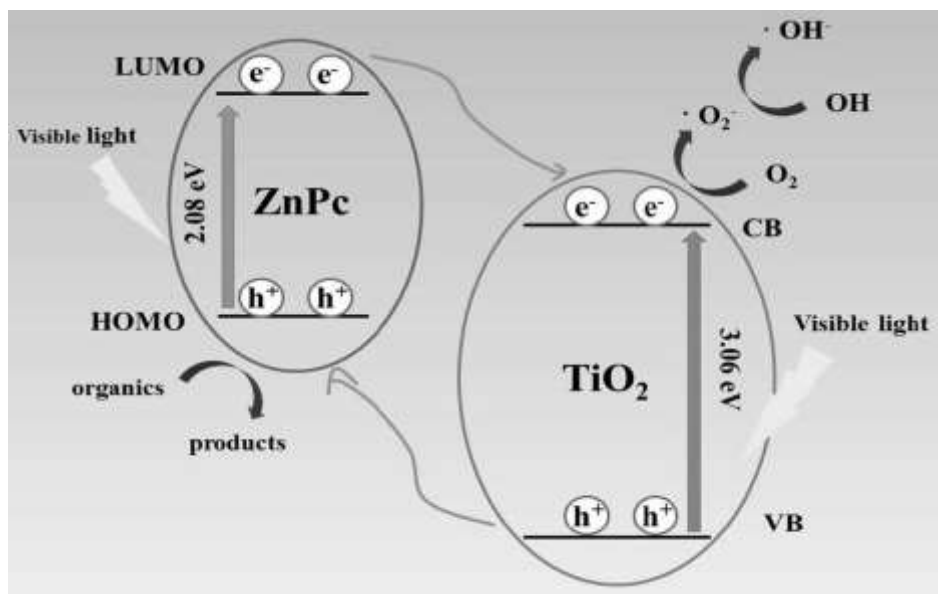
**Figure 3.** Terbutylazine, Simazine, Chlortoluron and Triclopyr.

Herbicides with high adsorption coefficients will not be affected by runoff. Nevertheless, will often have a very low penetrating power in soil and thus will deteriorate it directly at the point where they were spread. As consequence, this changes the nature and physicochemical properties of soil, creating a contamination thereof. Another source of contamination is not caused by the herbicide as such, but again by its degradation. In the case of chlorinated compounds, the mineralization and bacterial degradation emit in environmental chemicals such as hydrochloric acid (HCl). Coupling with intensive use of fertilizers, leads to an acidification of soil, being not toxic by itself. The problem is actually indirect, coming from the fact that low pH value increases the solubility of many toxic elements (such as ionic species of lead, aluminium, manganese, or copper), which are thus absorbed by plants [27-30].

### 3. Photosensitization/Photocatalysis: synergism TiO – Phthalocyanine.

As a practice, it is found in the literature that the term photosensitizer is generally used for organic catalysts whereas inorganic catalysts are termed photocatalysts. But, the term photocatalyst has been also used for organic compounds and vice versa in some instances. For simplicity, the organic catalyst will be termed photosensitizers and inorganic catalysts as photocatalysts throughout this paper. However, there is no rule stating this differentiation. The photosensitization process principally involves three components, namely, the photosensitizer, light, and oxygen. On irradiation at the appropriate wavelength, the photosensitizer transfers its energy to molecular oxygen giving rise to reactive oxygen species (ROS) [31-34]. ROS are cytotoxic in nature which enables us to employ this phenomenon in destroying unwanted microorganisms like bacteria, fungi, and viruses [3].





**Figure 4.** Synergistic photocatalytic performance of Zn-phthalocyanine/Titania (ZnPc/TiO<sub>2</sub>) [3, 32, 33].

Depending on the nature of the photosensitizer/photocatalyst, the photodynamic action proceeds through type I or type II mechanism or both. Type I mechanism involves electron transfer from excited sensitizer to substrate molecule or oxygen yielding free radicals and superoxide ion [3, 33, 34].

Photocatalysis research has been focused on the depuration of water contaminated mainly with three kinds of recalcitrant organic compounds: dyes, pesticides, and pharmaceuticals, and in this field TiO<sub>2</sub> has established itself as the benchmark material. However, the fact that it can only be activated with ultraviolet radiation due to its wide bandgap constitutes a drawback. Because of this, more recently, the scientific effort has been directed to broaden the visible light response band of TiO<sub>2</sub> using different approaches such as metal and non-metal doping, coupling with other narrower bandgap semiconductors, and dye sensitization.

Activate TiO<sub>2</sub> and several methods can be used [35]. However, due to its simplicity, impregnation of TiO<sub>2</sub> has been employed predominantly. For the latter, the solubility of the dye must be considered in order to assure that only single molecules are adsorbed onto the TiO<sub>2</sub> instead of having clusters that eventually will quench the photo-activated species during the degradation process. Another important aspect to take into consideration, in order to increase the photocatalytic activity of the hybrid photocatalytic system, is the molecular structure of the phthalocyanine sensitizer. In this regard, Sharma et al. [36] suggested that the incorporation of push-pull phthalocyanines shows great potential to improve the electron injection into the semiconductor and at the same time to avoid the back electron transfer (recombination). The incorporation of the asymmetric zinc phthalocyanine (ZnPc) to the semiconductor oxide revealed apparent changes in its optical and structural properties; particularly, a synergetic enhancement of the photocatalytic activity of the dye-sensitized materials was observed compared to the no sensitized products. It was found that the TiO<sub>2</sub>/AZnPc composite has a higher photocatalytic activity for the degradation of Rh-B (Rhodamine B) under visible light than pure TiO<sub>2</sub>. This outstanding result was rationalized in terms of the orientation of the dye (favoured by its asymmetric nature) that improves the electron injection from the photo-activated phthalocyanine to the TiO<sub>2</sub>.

Application of photodynamic action to inactivation and decontamination of water certainly seem to be a promising alternative to the conventional chemical methods of treatment. The numerous selections of photosensitizers render the possibility to explore more into this field. Many semiconductors whose bandwidths lie in the visible region are available. Also, the absorption of TiO<sub>2</sub> in the visible region has been the study of many trials by doping TiO<sub>2</sub> with other metals. Metal phthalocyanines and porphyrins and

transition metal complexes have proven to be useful in many trials of photoinactivation studies but are still limited to lab scale and pilot plant studies. However, it is desirable to avoid the use of metal centers in water disinfection purposes. Metal-free porphyrin related molecules are also gaining much attention in disinfection studies owing to their long lived triplet excited states and their presence in natural systems [37]. The rich chemistry of macrocyclic compounds allows formulating them into photosensitizers with desired absorption maximum and functional groups that are transformable to preferable attach to a support. Photocatalysis also brings about the irreversible oxidation of any unwanted and harmful pollutants in water. However, to carry this phenomenon to actual treatments of wastewater, industrial water, and drinking water treatment, it is necessary to consider the need of pre-treatments to water prior to illumination. Both inorganic and organic photosensitizers are being studied worldwide to improve water treatment processes but the scope in modelling organic sensitizers seems promising [38].

Photocatalytic disinfection of water (*Gram-positive and Gram-negative Bacteria, Virus, Enterovirus, Fungi, Pesticides, Herbicides and emerging pollutants*) is gaining much interest as it involves three components that are individually harmless to the biological environment, namely, the photosensitizer, light, and molecular oxygen. It is important to highlight the fact that there is a synergism between both types of molecules (organic and inorganic) and processes (photosensitization and photocatalysis) in favour of the wastewater treatment process.

## References

1. F. Fitzgerald, *Photodynamic Therapy (PDT): Principles, Mechanism and Applications*. Nueva York : Nova Science Publishers, 2017, pp. 1-223.
2. G. Dyrda, K. Kocot, A. Poliwoda, G. Mele, S. Pal, R. Słota, J. Photochem. Photobiol. A: Chem. 387 (2020) 112124.
3. F. Vargas, T. Zoltan, F. Pujol, H. Rangel, *Medicinal Chemistry* 4(2) (2008) 138-145.
4. F. Vargas, T. Zoltan, O. Oviedo, M. Inojosa, J. Vivas, J. Coord. Chem. 67 (2014) 1715-1730.
5. I.O. Bacellar, T.M. Tsubone, C. Pavani, M.S. Baptista, *Int. J. Mol Sci.* 16 (2015) 20523-20559.
6. N. Sergeeva, M. Senge, *Photochemical Transformations Involving Porphyrins and Phthalocyanines*. In A. Griesbeck, M. Oelgemoller, F. Ghetti, *CRC Handbook of Organic Photochemistry and Photobiology*. Nueva York: Taylor and Francis Group, 2012, pp. 831- 879.
7. E. Çelenk Kaya, M. Durmuş, E. Yanmaz, H. Kantekin, *Turkish J. Chem.* (2014) 1-17.
8. I. Denekamp, F. Veenstra, P. Jungbacker, G. Rothenberg, *Appl. Organomet. Chem.* 33(5) (2019) e4872.
9. G. Başaran Dındaş, Z. Şahin, H. Cengiz Yatmaz, Ü. İşci, J. *Porphyrins Phthalocyanines*, 23 (2019) 561-568.
10. K.S. Jung, J.H. Kwon, S.M. Shon, J.P. Ko, J.S. Shin, S.S. Park, *J. Materials Science* 39 (2004) 723-726.
11. F. Vargas, T. Zoltan, C. Izzo, *Analytical Chemistry Insights* 2 (2007) 111-118.
12. M. Bellardita, M. Addamo, A. Di Paola, G. Marcía, L. Palmisano, L. Cassar, M. Borsa, *Mater.* 174 (2010) 707-713.
13. P.A. Carneiro, R.F. Pupo Nogueira, M.V.B. Zanoni, *Dyes and Pigments* 74 (2007) 127-132.
14. S. Vilhunen, M. Sillanpa, *Reviews in Environ. Sci. Biotechnol.* 9 (2010) 323-330.
15. M.I. Litter, N. Quici, *Recent Pat. Eng.* 4 (2010) 217-241.
16. D.F. Ollis, H. Al-Ekabi (Eds) *Photocatalytic Purification and Treatment of Water and Air*. Elsevier, Amsterdam, 1992.
17. M. Keshmiri, M. Mohseni, T. Troczynski, *Appl. Catal. B: Environ.* 53 (2004) 209-219.
18. R. Krakowiak, J. Musial, R. Frankowski, M. Spychala, J. Mielcarek, B. Dobosz, R. Krzyminiewski, M. Sikorski, W. Bendzinska-Berus, E. Tykarska, R. Blazejewski, A Zgoła-Grześkowiak, B. J. Stanisz, D. T. Młynarczyk, T. Goslinski, *Catalysts*, 10(11) (2020) 1328.
19. P. Ji, J. Zhang, F. Chen, M. Anpo, *J. Phys. Chem. C.* 112(46) (2008) 17809-17813.
20. P. Ji, J. Zhang, F. Chen, M. Anpo, *Appl. Catal. B-Environ.* 85(3) (2009) 148-154.
21. C. Lin, C. Wu, Z. Onn, *J. Hazard. Mater.* 154 (2008) 1033-1039.
22. W. Bahnemann, M. Muneer, M. M. Haque, *Catal. Today* 124 (2007) 133-148.
23. H. Lachheb, A. Houas, J.M. Herrmann, *Int. J. Photoenergy* (2008). Article ID 497895. Doi: 1155/2008/497895.
24. B. Yu, J. Zeng, L. Gong, X. Yang, L. Zhang, X. Chen, *Chinese Sci. Bull.* 53(2008) 27-32.
25. M.E. Madani, C. Guillard, N. Pérol, J.M. Chovelon, M.E. Azzouzi, A. Zrineh, J.M. Herrmann, *Appl. Catal. B-Environ.* 65(1) (2006) 70-76.
26. M. Silva, M.J.F. Calvete, N.P.F. Gonçálves et al. *Journal of Hazardous Materials* 233-234 (2012) 79- 88.
27. M. Seeger, M. Hernández, V. Méndez, B. Ponce, M. Córdova, M. González, *J. Soil Sci. Plant Nutr.* 2010, 10 (3), 320-332.

28. N.E. Glozier, J. Struger, A.J. Cessna, M. Gledhill, M. Rondeau, W.R. Ernst, M.A. Sekela, S.J. Cagampan, E. Sverko, C. Murphy, J.L. Murray, D.B. Donald, *Environ. Sci. Pollut. Res.* 19(3) (2011) 821–834.
29. F. Bono-Blay, A. Guart, B. de la Fuente, M. Pedemonte, M.C. Pastor, A. Borrell, S. Lacorte, *Environ. Sci. Pollut. Res.* 19(8) (2012) 3339–3349.
30. M.C. Hermosin, M.J. Calderon, M. Real, J. Cornejo, *J. Agric. Ecosyst. Environ.* 164 (2013) 229–243.
31. M. Pelaez, N.T. Nolan, S.C. Pillai, *Appl. Catal. B: Environ.* 125 (2012) 331-349.
32. O.K. Dalrymple, E. Stefanakos, M.A. Trotz, D.Y. Goswami, *Appl. Catal. B: Environ.* 98(1-2) (2010) 27-38.
33. A.T. Gomes, M.G. Neves, J.A.S. Cavaleiro, *Annals of the Brazilian Academy of Sciences* 90(1-2) (2018) 993-1026.
34. Guifen Lu, Xudong Liua, Luyang Zhao, Peng Zhang, Yongjie Gao, *Inorganic Chemistry Communications* 113 (2020) 107795.
35. A. K. Benabbou, C. Guillard, S. Pigeot-Rémy et al., *Journal of Photochemistry and Photobiology A: Chemistry* 219 (1) (2011) 101–108
36. D. Sharma, G. Steen, J. P. Korterik et al., *J. Phy. Chem.* 117(48) (2013) 25397-25404.
37. L. Villén, F. Manjón, D. García-Fresnadillo, G. Orellana, *Applied Catalysis B: Environmental*, 69 (1-2) (2006) 1-9.
38. T. Zhang, X. Wang, X. Zhang, “*International Journal of Photoenergy*, Article ID 607954 (2014) 1-12 .