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Porphyrins and Phthalocyanines: Photosensitizers and Photocatalysts

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Additional information is available at the end of the chapter

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Abstract

The porphyrins and phthalocyanines are among the most representative macrocycles in synthetic chemistry, characterized by specific molecular structures, responsible and associated with their particular properties. They have high versatility and an adequate variability introduced either by macrocycle metallation or by different substituents at its periphery called meso-substituents. The porphyrins could find, together with the synthetic phthalocyanines, various scientific and technological applications in chemical and photochemical areas. They can serve as catalysts and photocatalysts in different reactions, or as photosensitizers in photodynamic therapy of cancer, due to their high efficiency to generate free radicals and excited state species. The aim of this chapter is to achieve a better understanding of the complex and various properties of the porphyrins and phthalocyanines in different solvents or in heterogeneous media, trying to draw the relationships between these topics with their possible applications in catalytic, photocatalytic area (photodegradation of Kraft-lignin, photooxidation of different unsaturated hydrocarbons, photodegradation of different organic aquatic pollutants, oxirans polymerization) and some preliminary results about the heterogeneous porphyrin sensitizers in the photodynamic therapy area. Their photobleaching mechanisms in different conditions are also discussed.

Keywords: porphyrins, phthalocyanines, catalysis, photocatalysis, photosensitization, photodynamic therapy

1. Introduction

Porphyrins and phthalocyanines are synthetic dyes characterized by the specific molecular structure which is associated with their particular spectral and photoelectric properties. They can serve as photosensitizers in photodynamic therapy of cancer, as catalysts and photocatalysts in different reactions, as good systems to generate free radical and excited state species [1]. Porphyrins (P) constitute a class of the molecules which contain four pyrrole rings linked by the methane carbon

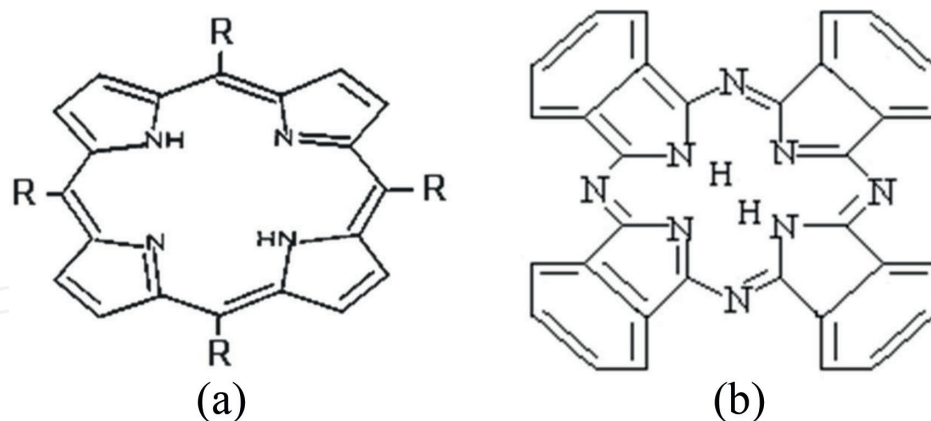


Figure 1. The general chemical structure of the (a) porphyrins and (b) phthalocyanines.

bridges, whereas the phthalocyanine molecules (Pc) are composed of four indole units—pyrrole rings linked by nitrogen atoms conjugated with benzene rings [2], (**Figures 1a** and **b**).

A large group of porphyrins could exist as free bases and metallo complexes, which can be obtained by introducing some metals in the center of the pyrrole rings. Different structures could be obtained by attaching the peripheral groups to the outer rings of the methane bridges or isoindol units, respectively. With a more symmetrical structure than the free bases, the metallo-porphyrins present a reduced structure bands in the absorption spectra, called beta and alpha, the first being at longer wavelengths than the last one. Their ratio is known as a stability indicator. When $\beta \approx \alpha$, the metal forms a stable square-planar complex with porphyrin (Ni, Pd); when $\alpha \approx \beta$, the generated complexes show a strong instability. For the porphyrins containing diamagnetic metals, the triplet lifetimes are high (Mg, Cd, Zn), while those porphyrins with paramagnetic metals (Cu, Ni), will have short triplet lifetimes [3]. By comparison with porphyrins, the phthalocyanines are more stable and their lifetimes during different reactions are longer [4].

The phthalocyanines (Pcs) hold a special position due to their interesting electronic and physicochemical characteristics, and could be organized into different condensed systems [5–7]. Pcs are planar aromatic macrocycles constituted by four isoindole units linked together through nitrogen atoms. The internal and external positions of the fused benzene ring are also commonly known as α - and β -positions, respectively. Their 42 π -electrons are distributed over 32 carbon and 8 nitrogen atoms, but the electronic delocalization mainly takes place on the inner ring, which is constituted by 16 atoms and 18 π -electrons, the outer benzene rings maintaining their electronic structure [8].

2. Porphyrins and phthalocyanines in catalytic processes

A series of metallo-porphyrins and metallo-phthalocyanines shows an increased catalytic activity in different chemical/photochemical processes:

- Photodegradation of Kraft-lignin [9, 10];
- Photooxidation of different unsaturated hydrocarbons [11];
- Photodegradation of different organic aquatic pollutants [12].

In all these processes, the porphyrins are used either in organic solutions or supported on different inorganic supports in order to increase the catalytic activity and their stability (photostability) (due to their strong interaction between the support and the complex) [13, 14].

The necessary conditions for their catalytic capacity are as follows: (i) the metallic ion from the macrocycle has to be redox active, i.e., two or higher oxidation states [15]; (ii) free coordination positions could be available to coordinate different molecules to the metallic ion [16]; (iii) the coordination sphere of the metallic ion must be labile and must have sufficiently high exchange rates for the catalyst. Many authors found that the organic radical (the substituents) and the π character, especially the dative π effect of coordination, play an important role in the catalytic activity of such compounds [17].

2.1. Degradation of Kraft-lignin

Lignins and lignosulfonates are formed as by-products in pulping processes [18], but they have not found wide-scale industrial applications. One reason could be the price and technological scheme, which are pretty complex, and the necessary catalysts for such processes are not very stable and with a modest turnover number. Under such circumstances, the efforts to find new and efficient catalysts are increasing. The photochemical degradation of lignin can be achieved in solution with porphyrins supported on metallic oxides (Al_2O_3 , SiO_2 , TiO_2 , ZnO , and WO_3) as photocatalysts, leading to some useful products, like vanillin, syringyl, and cinnamyl derivatives [9, 19]. An example is cobalt-5,10,15,20-p-tetraphenylporphyrin (Co(II) TPP) supported on the above-mentioned metallic oxides. Co(II)TPP supported on TiO_2 was the best photocatalyst used for the photodecomposition of Kraft-lignin. The metallic oxides suspended in aqueous solutions are recognized as the most widely used photocatalysts for many interesting reactions, since the photoinduced hole and electron pairs formed on the surface of the semiconductor particle can act as oxidizing and reducing agents, respectively [20]. Also, they could improve the stability and catalytic activity as metallo-porphyrins and metallo-phthalocyanines. The active species participating at such photocatalytic process are mentioned in **Table 1**.

Metallic oxide	Oxidized forms of Co(II)TPP
SiO_2	(Co(III)TPP)+
TiO_2	(CO(III)TPP+, (Co(II)TPP)
ZnO	(CO(III)TPP+, (Co(II)TPP)
WO_3	(Co(III)TPP)++

Table 1. The oxidized forms of Co(II)TPP.

In all these cases, by adsorption, Co(II)TPP suffers a strong interaction between metallic oxide and the porphyrin ring, like an isoenergetic electron transfer from porphyrin to the metallic oxide conduction band. By supporting on these metallic oxides, the new oxidized forms of Co-TPP could appear [21]. Vanillin formation from Kraft-lignin is a favorable reaction, because vanillin and its derivatives are widely used in perfumery and in pharmaceutical applications and also because Kraft-lignin is a by-product in the industrial preparation of pulp and paper.

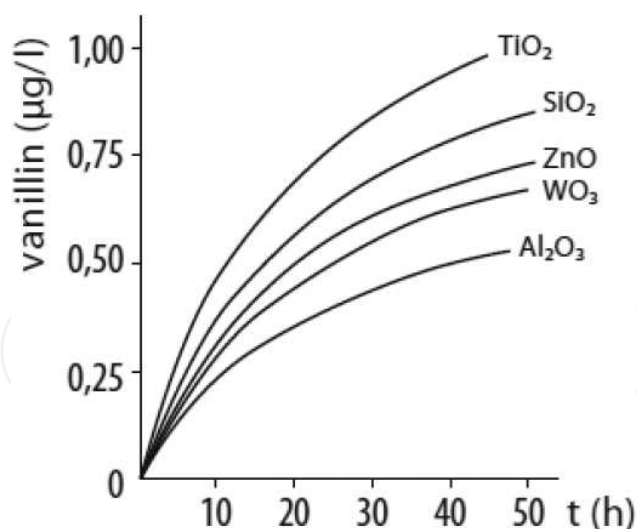
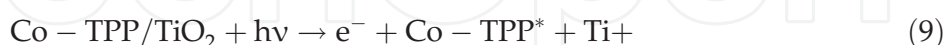
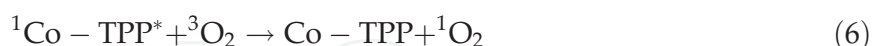
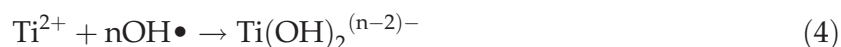
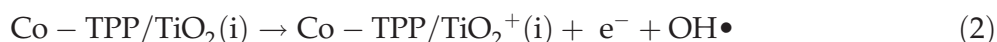
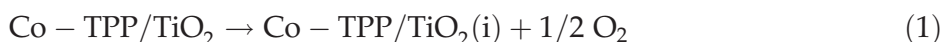


Figure 2. The kinetic diagram for vanillin generation during the photocatalytic degradation of Kraft-lignin with Co(II) TPP supported on metallic oxides as catalysts.

The photocatalytic degradation of lignin has been investigated by using TiO₂, known as one of the best photocatalysts, generating good concentrations of vanillin (**Figure 2**). These photocatalysts are acting either by energy transfer or by initial radical abstraction, after a reaction mechanism shown below, adapted after [22].



2.2. Catalytic/photocatalytic oxidation

The iron porphyrins (**Figure 3**) are efficient catalysts both in epoxidations and in hydroxylations reactions, by using either of some oxygen donors or molecular oxygen in the presence of one reductant agent.

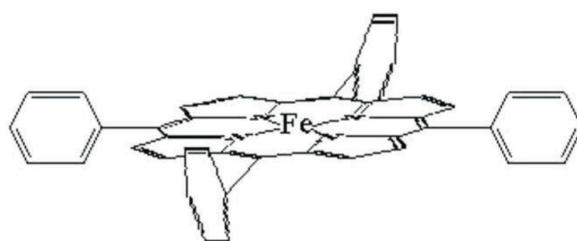


Figure 3. The structure of iron-5,10,15,20-tetra-phenyl-porphyrin (Fe(III)TPP).



The cycloalkanes are oxidated by molecular oxygen under normal conditions with good yields, without some reductant agents and by using iron(III) meso-tetra (2,6-dichloro-phenyl)-porphyrin (Cl₂Fe(III)TPP), with light irradiation $\lambda = 350-450$ nm, leading to cyclooctenes, by the reaction mechanism shown in **Figure 4**. The axial ligand of the central metal could be OH or different halogen ions.

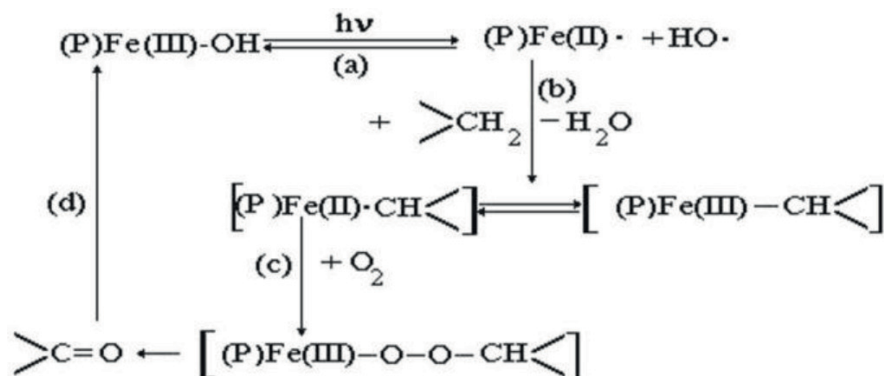


Figure 4. The oxidation cycloalkane oxidation mechanism with (OH Fe(III)P).

Fe(III)(TSPP) supported on TiO₂ is a new catalyst which, if suspended in a hydrocarbon and irradiated with $\lambda = 365$ nm, yielded selective oxidation products (for example, the cyclohexan and cyclohexene oxidation) (**Table 2**).

Cyclohexane oxidation with TiO₂ leads in principle to cyclohexene and CO₂. When TiO₂ is complexed with silan, a pronounced decreasing of catalytic activity occurs. In the presence of the system TiO₂-Sil-Fe(III)(TSPP), the cyclohexanol amount significantly increases. Iron cation could easily coordinate in the reduced form, forming an oxygen molecule and a superoxide complex [23], which is the essential form in the hydrocarbon monooxygenations (**Figure 5**).

The final oxidation products appear only due to the final decomposition of the complex hydrocarbon radical—peroxide [24, 25].

2.3. Catalytic/photocatalytic epoxidation

The porphyrin μ -oxo-dimers are recognized as the best catalysts in the olefins chemical epoxidation reactions; however, there are reported some results for few unsaturated organic substrates (styrene and dodecene) which could support both chemical and photochemical mechanism.

Catalyst	Substrate	Products	Φ_{ox}
TiO ₂	Cyclohexane	-one	0.09
		-ol	–
		CO ₂	0.024
	Cyclohexene	-one	0.57
		-ol	0.01
		-Oxide	0.01
TiO ₂ -sil-Fe(III)(TSPP)	Cyclohexane	CO ₂	0.004
		-one	0.03
		-ol	0.01
	Cyclohexene	CO ₂	–
		-one	0.79
		-ol	0.48
		-oxide	0.01
		CO ₂	0.0027

Table 2. The catalytic photooxidation of cyclohexane and cyclohexene on modified TiO₂.

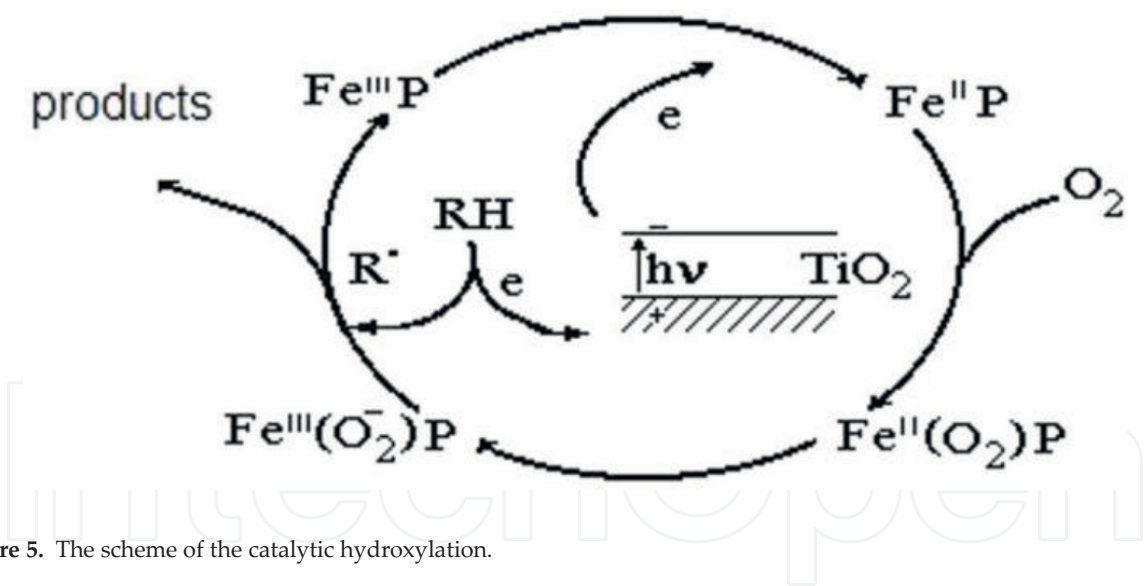


Figure 5. The scheme of the catalytic hydroxylation.

The responsible mechanisms involve the metal inside of the macrocycle and oxygen bond between the two porphyrin macrocycles. (Figure 6). Styrene supports an epoxidation reaction with higher yield than dodecene due to its own aromatic structure. For dodecene, the epoxide content of 3–8% has been obtained for Mn compounds, higher than 1.5–6.5% obtained with Fe compounds (better catalytic efficiency by the photochemical pathway than by the chemical one) [26]. The reaction mechanism is shown in Figures 7 and 8.

The high efficacy of Mn-μ-oxo-dimers could be explained by means of the high valence state of Mn (IV), which could contribute to the electron transfer and to different oxidation states of this

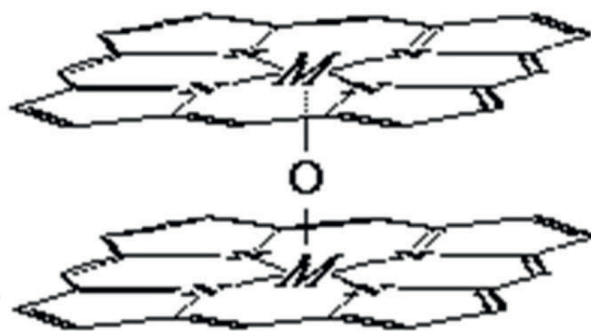


Figure 6. The structure of the porphyrinic μ -oxo-dimer.

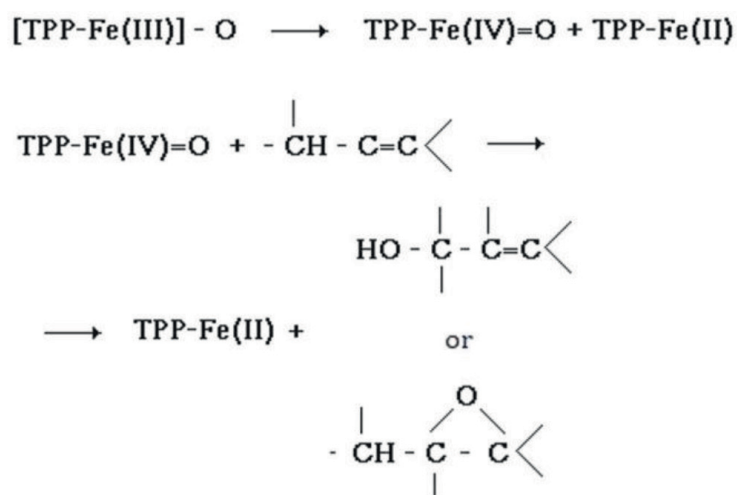


Figure 7. The general reaction mechanism of olefins photo-epoxidation.

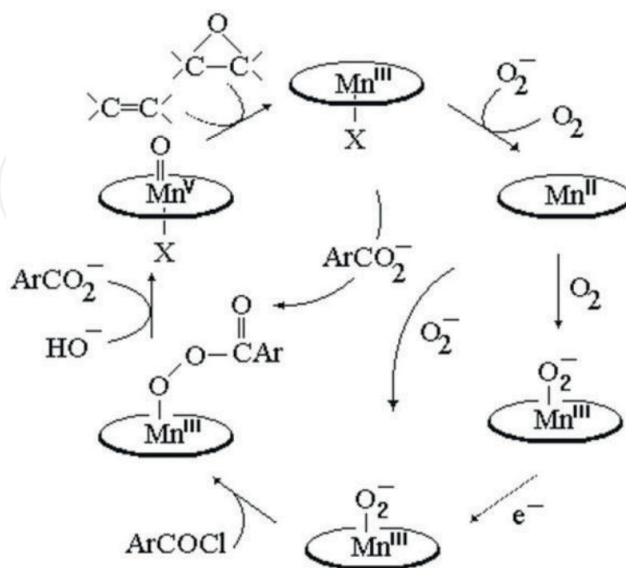


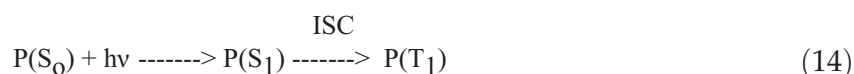
Figure 8. The catalytic mechanism of the epoxidation reaction.

metal coordinated to porphyrins (**Table 3**). The dissociation rate of the μ -oxo-bridge is bigger for 5,10,15,20-p-tetra-naphthyl-porphyrin (TNP) derivatives than for TPP derivatives, this fact contributing to a higher concentration of active species [27].

At the dodecene epoxidation, a higher catalytic efficiency of manganese oxo-dimers could be evidenced. From all the unsaturated hydrocarbons, the most efficient epoxidated is styrene compound, due to the π - π strong interactions between the phenyl ring of styrene and the large macrocycle of porphyrins [28]. The epoxide content is higher for TNP derivatives than to TPP derivatives. The greater dissociation rate of oxo-bridge is caused by some internal tensions inside of the macrocycle responsible for the subsequent catalytic activity. In photochemical epoxidations, a higher photocatalytic activity for Mn complexes could be observed due to the Mn(IV) state [29].

2.4. Photooxidation reaction with porphyrins as sensitizers

The photooxidation reactions ("ene" reaction) are characteristic reactions of singlet oxygen with different substrates (alchenes, dienes, aromatic compounds, and heterocycles) [30]. The generation of $^1\text{O}_2$ molecules occurs through the following mechanism:



Compounds with a triplet state energy lower than the excitation energy for $^1\Delta_g \text{O}_2$ (7900 cm^{-1}) are generally unable to transfer their excitation energy (the excitation energy is necessary to be

Catalyst/hydrocarbon	Epoxide concentration (%)
Dodecene	
(TPP-Fe) ₂ O	43.1
(TNP-Fe) ₂ O	3.27
(TPP-Mn) ₂ O	15.46
(TNP-Mn) ₂ O	17.45
Styrene	
(TPP-Fe) ₂ O	27.34
(TNP-Fe) ₂ O	35.56
(TPP-Mn) ₂ O	25.45
(TNP-Mn) ₂ O	21.17
Dodecene (irradiated)	
(TPP-Fe) ₂ O	82.03
(TNP-Fe) ₂ O	62.02
(TPP-Mn) ₂ O	55.74
(TNP-Mn) ₂ O	11.43

Table 3. The concentrations of epoxide obtained by chemical and photochemical conditions in the presence of different porphyrinic μ -oxo-dimeric catalysts.

approximately 13,200 cm⁻¹) to the ground state of molecular oxygen (³Σ_g⁺ O₂) and to generate ¹Δ_g O₂. The energy of the sensitizer S₁ state (with a lifetime higher than 500 ns) could be transferred to the molecular oxygen, which in fact is a triplet state, but only if the energy gap S₁ → T₁ is higher than 7900 cm⁻¹. When this energy gap is lower than 7900 cm⁻¹, the compound could be a valuable candidate for type I sensitizers, but only if the singlet and/or triplet states is higher than 500 ns, necessary for electron transfer reactions. By means of this reaction, some new hydroperoxides or peroxides could be obtained, the most efficient sensitizers being porphyrins in homogeneous or heterogeneous solutions. The porphyrins could be used as sensitizers, but only those with the triplet lifetimes >10⁻⁶ s can generate singlet oxygen. If a mixture of iso-amilenes (85% 2-methyl-2-butene and 15% 2-methyl-1-butenă) (**Figure 9** and **Table 4**) is irradiated with a mercury lamp or with sunlight, an alcoholic mixture as a precursor for isoprene is obtained [31]. The yields for such photooxidation reaction under different conditions are shown in **Tables 5** and **6**.

The same plant and processing scheme has been used for isoamilene dimers, with the following compositions: 23%, 3,4,5,5-tetramethyl-2-hexene; 6%, 2,3,4,4-tetramethyl-1-hexene; 15%, 3,5,5-trimethyl-2-heptene; 37%, 3,4,4,5-tetramethyl-2-hexene; 17%, unidentified). Their structures are shown in **Figure 10**.

By using some metallo-porphyrins supported on different metallic oxides, at different solar irradiances, it has been obtained at not very high HP concentrations, the best being observed for divalent metallo-porphyrins, but with the disadvantages of their price and limited stability (**Table 7**).

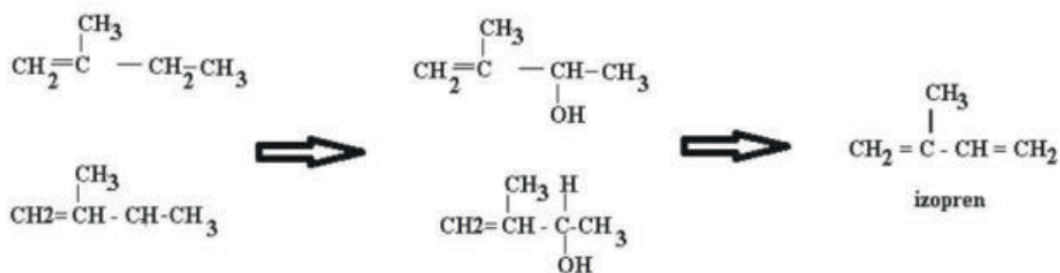


Figure 9. The scheme of isoamylene photooxidation to isoprene via hydroperoxides.

Component	Concentration (%)
Acetone	0.08
2-Methyl-2,3-epoxybutan	2.37
t-Amylic alcohol	5.57
sec-Amylenic alcohol	5.68
2-Methyl-1-buten-3-ona	3.80
2-Methyl-2-buten-1-al	1.28
HP t-amylenic	41.47
HP-s-amylenic	29.68
HP unidentified	5.93
Unidentified products	4.14

Table 4. Isoamylene HP composition.

Sensitizer	Irradiation time (h)/irradiance (W/cm ²)					
	0/860	0.5/860	1/880	2/880	4/790	6.5/750
NiTPP/SiO ₂	0.06	0.275	0.5005	0.3905	0.5	0.72
SnTPP/SiO ₂	0.83	0.94	0.5	0.72	0.83	1.05
PbTPP/SiO ₂	0.17	0.61	0.72	0.83	0.94	1.16
MgTPP/SiO ₂	0.39	0.72	0.72	1.04	1.27	1.49
ZnTPP/SiO ₂	0.17	0.39	0.39	0.39	0.83	1.16
CuTPP/SiO ₂	0.275	0.39	0.5	0.5	0.83	1.05
PdTPP/SiO ₂	0.1705	0.39	0.94	0.83	1.27	1.27

Table 7. Concentration variation of C₁₀ HP.

2.5. Photocatalytic oxidation of o-nitro-phenol on heterogeneous organic semiconductors

The most common pollutants include a wide range of aliphatic and aromatic halogenated compounds, different types of herbicides, mercaptans, and other groups unaccountable industrial organic compounds. Sulfur-based compounds such as mercaptans, alkaline sulphides, sulphites, and alkaline thysulphates constitute byproducts in industrial processes, such as reform Processing, petroleum processing, etc. [35].

The photochemical processes for destroying aquatic pollutants have been used in the last decade as a viable alternative for wastewater purification. Organic pollutants’ direct photolysis is induced by light irradiation with $\lambda = 290\text{--}400\text{ nm}$. New technologies such as enhanced oxidation processes (EOP) or advanced oxidation processes (AOP) were able to convert pollutants into useful chemicals. They are described as oxidative processes with full oxidation

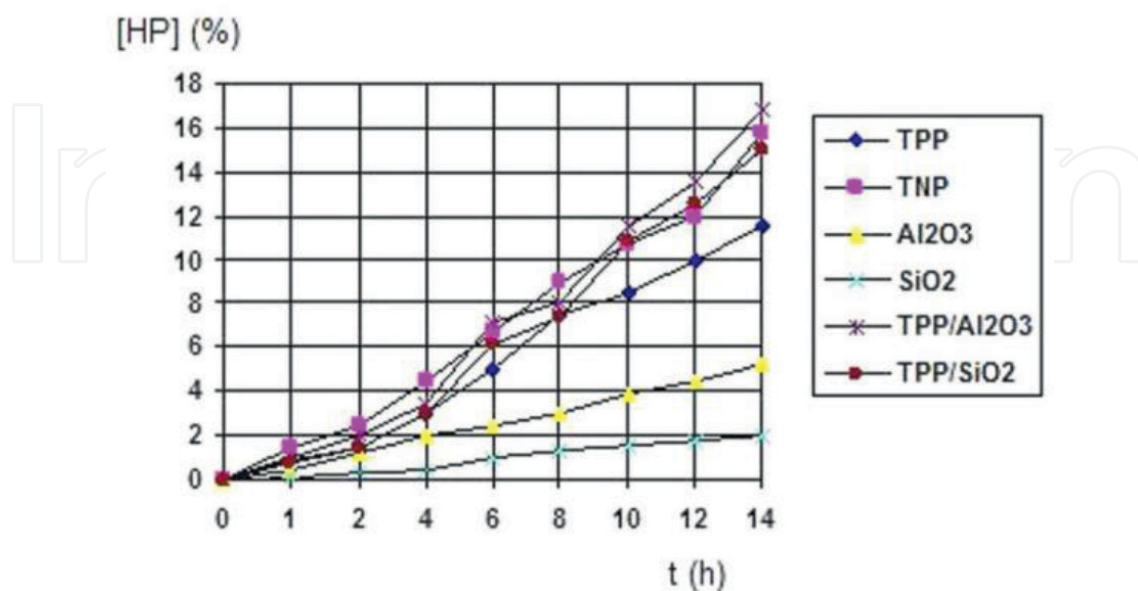


Figure 11. The kinetic for C10 fractions oxidation (lamp irradiation).

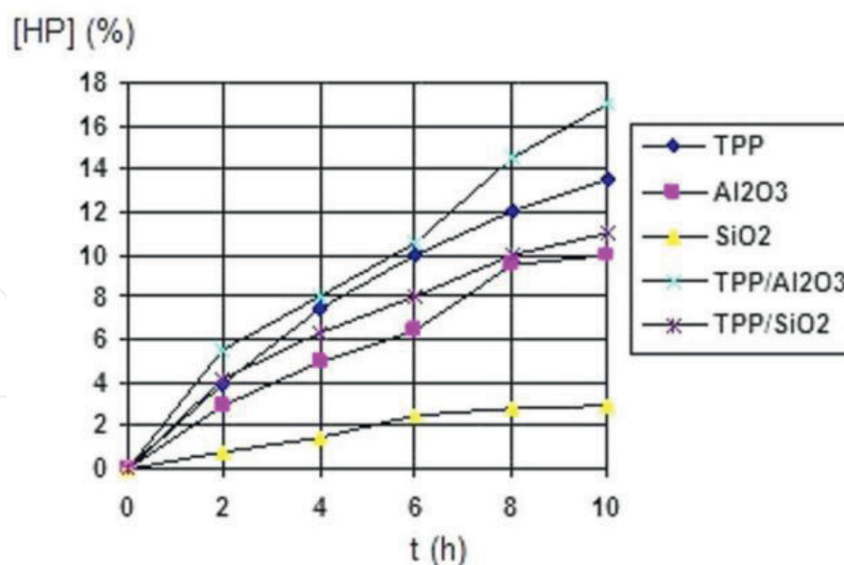


Figure 12. The kinetic for C10 fractions oxidation (sun light irradiation).

reactions (mineralization) of pollutants, to give CO_2 and a small amount of HCl , H_2SO_4 , and HNO_3 . EOP technologies are based on the generation of highly reactive free radicals, such as hydroxyl (OH), which act as initiators [36].

Although the quantum yields of photocatalytic reactions are small, the organic pollutants could be destroyed by heterogeneous photocatalysis by a pseudo zero order.

It is necessary to differentiate between the terminologies:

- Photocatalytic reaction: when the catalyst is photochemically generated, and the reactant is transformed via the thermal conversion to the final product.
- Photoassisted reaction: when the catalyst is also formed via the photochemical conversion and the reactant is interacting by thermal mechanism with the catalyst.
- Catalyzed photoreactions involving a catalytic effect, which is different from that of the photocatalytic reactions, in the sense that the catalyst is not generated via the photochemical reaction, but the active species in the presence of a catalyst lead to the product.
- Photosensitized reactions: when the system is not isolated, $\phi < 1$, the energy must enter each cycle and is transferred to the substrate.

The metal complexes of phthalocyanines are known to play important biological roles as electron mediators for different catalytic processes [37]. Heterogeneous photocatalysis with organic semiconductors is a fast-growing field of applied research, especially for the case of the oxidation processes of organic pollutants [11]. The main advantage is the complete destruction of pollutants to harmless compounds, e.g., carbon dioxide and inorganic acids.

The oxidative photochemical reaction (via hydroxyl radicals, generated through heterogeneous photocatalysts) is one of the most appropriate reaction types for the photochemical degradation

process of many aquatic refractory pollutants; even some of them (e.g., nitro-phenols) may degrade very slowly. Some photocatalysts such as zinc (II) 2,9,16,23-tetrasulphophthalocyanine (ZnTSPc) supported on SiO_2 and zinc (II) 2,9,16,23-tetracarboxyphthalocyanine (ZnTCPc) supported on hydrotalcite (HT) have been used for ONP photodegradation. Reactions are 4–10 times faster than those obtained using the same photocatalysts but in water solution (**Figure 13**).

It is well known that upon irradiation with visible light, the non-metallic phthalocyanine complexes and those containing metal ions with filled electron shells (Mg and Zn) or with empty d orbitals (Al) show long lifetimes of the first excited triplet state [2, 38, 39]. All these compounds are good sensitizers for electron or energy transfer reactions [40–43]. Oxygen in its ground triplet state interacts with the excited triplet electronic state of the complexes yielding to singlet oxygen [44–46].

Nitrophenols have been recognized as priority pollutants. The allowed concentrations from 1 to 20 ppb [47] in lakes and fresh water reservoirs justify the search for new purification methods having low cost and practical value.

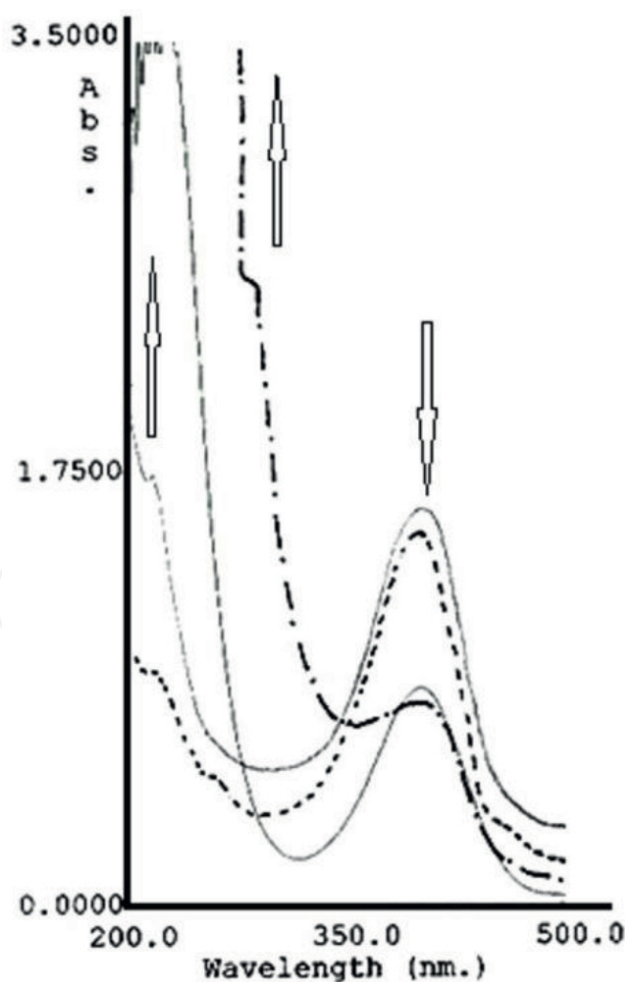


Figure 13. The changing of the ONP during the photodegradation reaction.

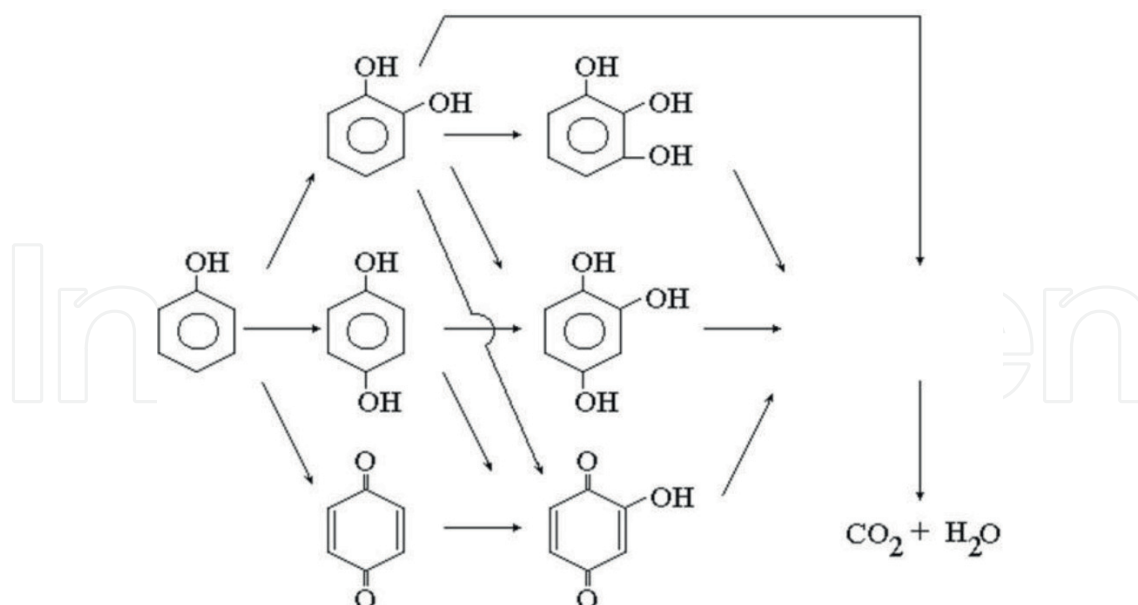


Figure 14. The reaction mechanism of ONP degradation.

The direct photodegradation of nitrophenols has not been found to be an effective method for destroying them using UV light in a homogeneous solution (**Figure 14**) [48].

Many efforts have been done in the area of porphyrins and phthalocyanines supporting them on different substrates (metallic oxides and cellulose) knowing that longer photochemical stability is essentially important for their longer activity as luminescent materials [49].

Microcrystalline cellulose (MC) can form hydrogen bonds, both within its own structure and with other molecules that may remain attached to the polymer chains by localized interactions (**Figure 15**).

In order to obtain more stable and more efficient photocatalysts for o-nitrophenol degradation, some porphyrins, such as zinc-5,10,15,20-sulphonato-phenyl-porphyrin (ZnTSPP) and zinc-4,8,18,22-tetra-sulphonato-phthalocyanine (ZnTSPc) (**Figures 16** and **17**), could be entrapped into the polymer chains of some cellulose derivatives, such as microcrystalline cellulose, their adsorption efficacy being evaluated by the state diffuse reflectance technique (GSDR).

The anionic porphyrins and phthalocyanines are rather closely packed in the submicroscopical pores of MC. It has been shown that cellulose is composed of amorphous and crystalline

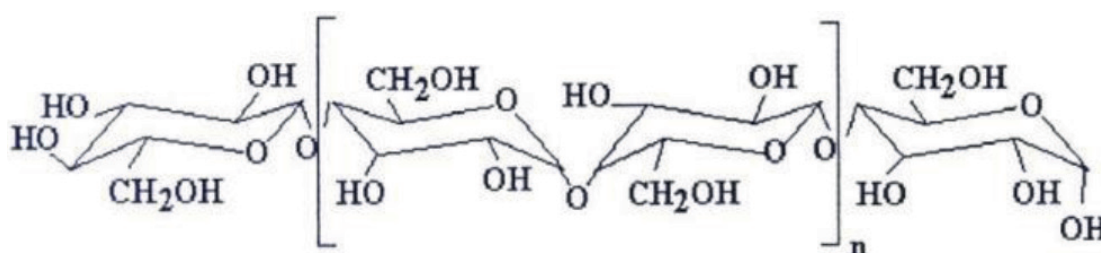


Figure 15. The microcrystalline cellulose structure.

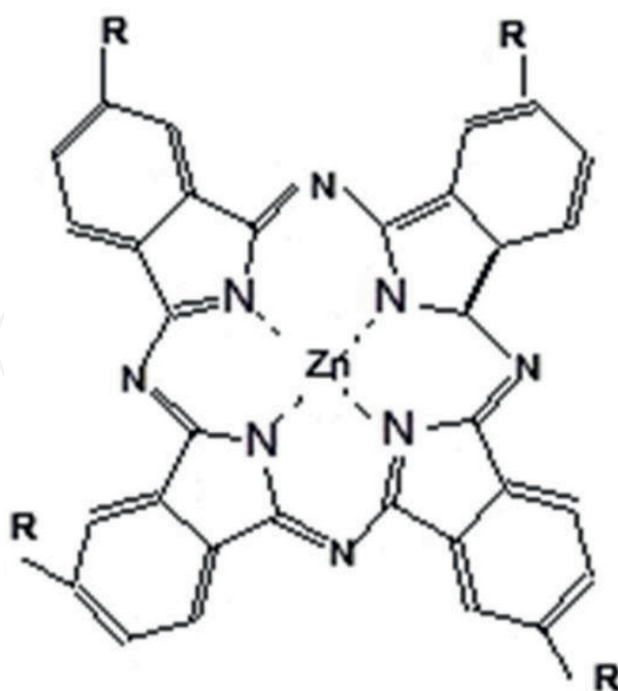


Figure 16. The structure of ZnTSPc.

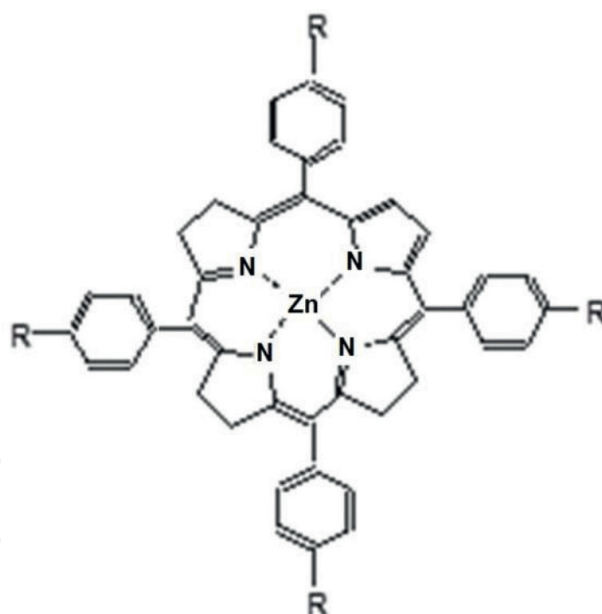


Figure 17. The structure of ZnTSPP.

domains. When MC is added to the solution, cellulose-to-cellulose hydrogen bonds are replaced by cellulose-to-solvent bonds due to the strong interactions with glycosidic chain segments, thus providing the swelling of the polymer. Tetrasulfonated porphyrin or phthalocyanine complexes could be adsorbed into microcrystalline cellulose by entrapping between the glycoside chains in the crystalline area of MC for low concentrations of complexes or by entrapping in amorphous domains for high concentrations of these complexes.

Due to the diffusion of the pollutant and O_2 toward the ZnTSPc molecules entrapped in the modified MC, due to an increase in the aggregation degree of the complexes on the solid support. The specific structure of MC prevents a larger degree of aggregation of ZnTSPP and ZnTSPc molecules because of their location in the intracrystalline voids and galleries of the supports. Also, MC being a strongly hydrophylic support coadsorbs water. This effect improves the diffusion of reactants and products. Another possible reason for this behavior is that the residual positive charge in MC interacts with the oppositely charged voluminous organic ions.

Negatively charged porphyrins and phthalocyanine complexes could form molecular associates as dimers and oligomers even in diluted solutions [50]. The well-defined structures of MC prevent the aggregation of the phthalocyanine molecules because of their location in the intracrystalline voids and galleries of the supports. Also, MC being strongly hydrophilic supports the coadsorption of water in the galleries and cavities, which improves the diffusion of reactants and products. This is the major reason for the lower catalytic activity of the phthalocyanine supported on MC. Another reason for this is residual positive charge of MC, which is able to interact with the oppositely charged voluminous organic ions [51]. The concentration-time profile for the degradation of ONP using a series of four catalysts is shown in **Figures 18 and 19**.

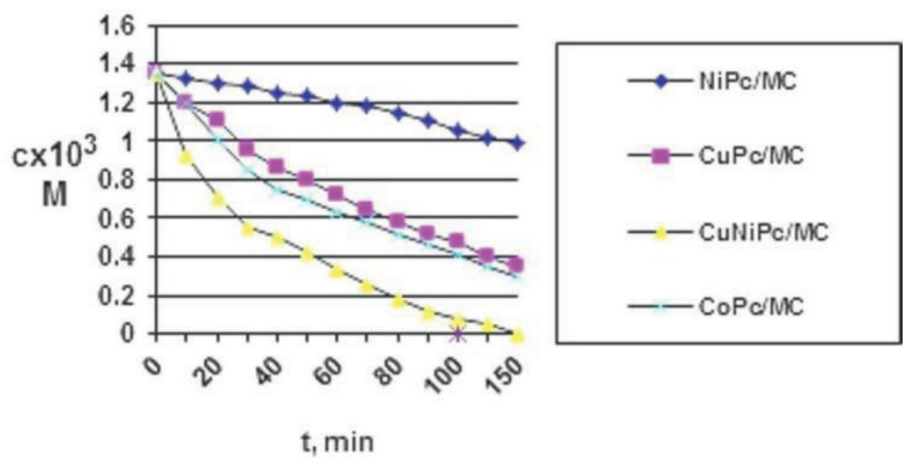


Figure 18. The kinetic graphical representation of ONP photocatalytic degradation.

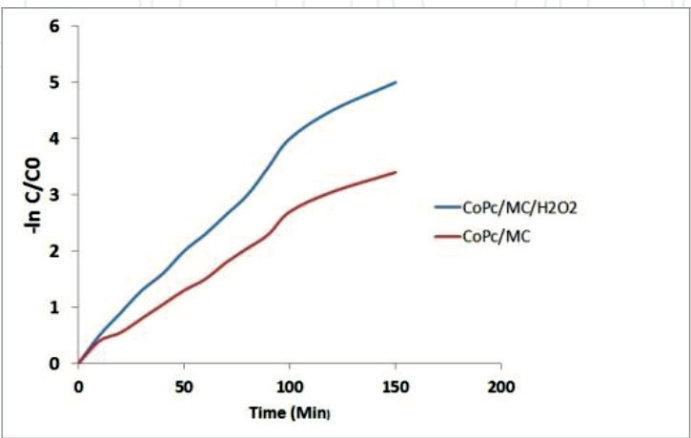


Figure 19. Graphical determination of apparent rate constant for ONP photocatalytic degradation.

It was possible to conclude that the efficacy of the studied MPc complexes as photocatalysts toward the degradation of ONP is in the order CuNiPc/MC > CoPc/MC > CuPc/MC > NiPc/MC.

The influence of hydrogen peroxide and light on the kinetic and reaction mechanism of ONP photodegradation was investigated. Reactions are 4–10 times faster in the presence of hydrogen peroxide when compared to those obtained using the same photocatalysts but in water solution (in the absence of hydrogen peroxide). The activity of heterogeneous catalysts depends on the nature of the supports and decrease from Co to the complex CuNi (Table 8).

The combined effect of light, H₂O₂, and photocatalysts is higher than the summed individual effects, due to the higher capacity of the UV/H₂O₂ system for OH radical generation.

Photocatalyst	$k_{app} \times 10^3 \text{ (min}^{-1}\text{)}$	$k_{app} \times 10^3 \text{ (s}^{-1}\text{)}$
CoPc/MC/H ₂ O ₂	40	0.666
CoPc/MC	25	0.416
CuPc/MC/H ₂ O ₂	18.33	0.305
CuPc/MC	13	0.216
NiPc/MC/H ₂ O ₂	11	0.205
NiPc/MC	9	0.189
CuNiPC/MC/H ₂ O ₂	7	0.165
CuNiPc/MC	5	0.123

Table 8. The rate constants for ONP photocatalytic degradation.

3. Porphyrins in polymerization processes

3.1. Living polymerization of oxirans

Living polymerization is important for obtaining polymers with uniform molecular weight. Aluminum porphyrins are excellent initiators for ring-opening polymerization of acrylic monomers, lactones, cyclic carbonates, and conjugated vinylic monomers, such as methacrylic esters, and have the advantage of uniform molecular weight and a thin molecular weight distribution [52]. For example, diethyl aluminum chloride (Et₂AlCl) induces the epoxides polymerization, and the $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrin (TPP)H₂ and Et₂AlCl could be considered a catalytic and very strong system, generating aluminum tetraphenylporphyrin (TPP) AlCl, with a structure or plan of a square pyramid (Figure 20).

By the coordination of one monomer molecule, aluminum becomes hexacoordinated, and the final system becomes a square bipyramide (Figure 21).

Many other catalysts for the epoxidation reaction could be used in the oxiran epoxidation, for example, aluminum tetra-carboxyphenyl porphyrin (TPP)AlO₂CR, aluminum alcoxyde-tetraphenyl porphyrin, (TPP)AlOR, or the corresponding phenoxide, (TPP)AlOPh, all of them being prepared by the reaction between (TPP)AlEt and a protic compound [53].

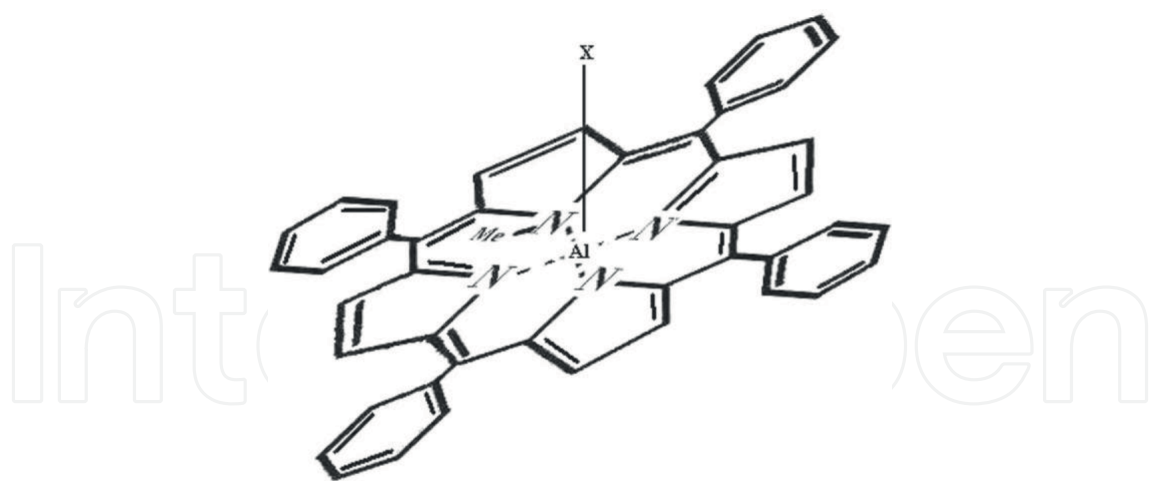


Figure 20. The structure of aluminum 5,10,15,20-tetraphenyl porphyrin.

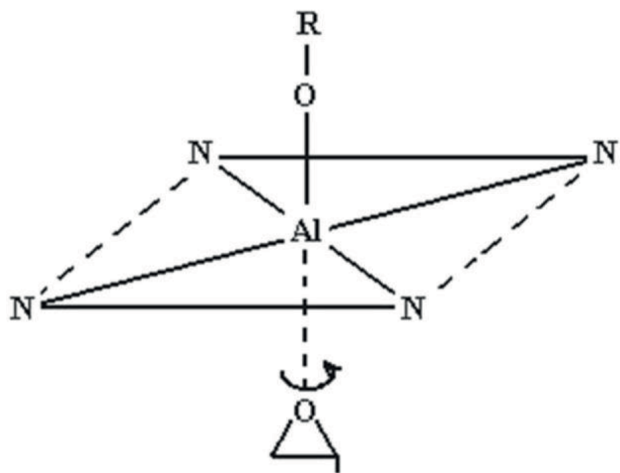


Figure 21. The spatial structure of an aluminum porphyrin.

Monomer	[M]/[Cat] ₀	Time (h)	Conversion (%)
Ethylene oxide	200	6	100
Propenoxide	200	6	100
1,2-Butenoxide	200	6	100
Epichlorohydrine	400	3	80
Cyclohexenoxide	200	6	85
Cyclopentoxide	200	6	70
Styreneoxide	200	8	13
Izo-butenoxide	200	8	15

Table 9. The epoxides polymerization with (TPP)AlCl [54].



(TPP)AlCl immediately reacts with the epoxide in order to initiate the polymerization.



The results obtained from alkylene oxide with the catalytic system (TPP) AlCl are shown in Table 9.

4. Applications of porphyrins in photodynamic therapy of cancer

Photodynamic therapy (PDT) consists of three essential components: **photosensitizer** (PS), light and oxygen, is an interesting concept that destroys diseased tissue via light-driven reaction. After administration of a photosensitizer, which is selectively retained by tumor cells, the subsequent irradiation with visible light in the presence of oxygen specifically inactivates neoplastic cells. Antitumor effects of PDT derive from three mechanisms: direct cytotoxic effects on tumor cells, damage to the tumor vasculature, and induction of a robust inflammatory reaction that can lead to development of systemic immunity [55, 56].

For a good correlation between preclinical phase and the possible outcomes from clinical trials, some 3D systems have been created, which have been tested during the preparation of a liposomal suspension of different drugs: folinic acid, oxaliplatin, and 5-fluorouracil loaded with meso-tetra (4-sulphonato phenyl) porphyrin [57].

Cancer treatment is one of the most important topics that are associated with photocatalysis [58]. In PDT, the porphyrins are recognized as ideal sensitizers, because these have good absorption in the NIR region, low toxicity, are better incorporated into different cells, show selective solubility and, in monomeric forms, have good penetration rate through cell membranes [58]. To be efficient, a photosensitizer should be selectively incorporated into a tissue. Following the Jablonski diagram, the first primary photochemical process is represented by the sensitizer excitation from the ground state to the first excited state in a very short time (10^{-15} s), in which the spins of the excited and unexcited electrons are still paired. The excited electron can lose its energy by falling back down to the electronic ground state, giving up most of the energy it has absorbed in a burst of fluorescence. This is a highly probable process, so that the lifetime of the singlet excited state is usually not more than a few nanoseconds ($\sim 10^{-9}$ s). However, it is possible for either one of the electrons to undergo the forbidden process of flipping their spins so that both electrons have parallel spins, giving a triplet excited state of the sensitizer, $^3\text{S}^*$.

The generated singlet oxygen and free radicals are very reactive species and can damage proteins, lipids, nucleic acids, and other cellular targets, as important membrane components, responsible for cell damage and death [59, 60].

Three consecutive processes occur during the PDT treatment: initial consumption of oxygen through the photodynamic process, pathophysiological alterations in regional blood supply (hypoxia), and total vascular occlusion (ischemia).

The following could be used as laser sources: He-Ne laser ($\lambda = 6328 \text{ \AA}$, power 180 J/cm^2), Ar ion laser ($\lambda = 514.5 \text{ nm}$ and fluence rate less 100 J/cm^2), Ar ion laser ($\lambda = 488 \text{ nm}$, 100 J/cm^2).

Some porphyrins were studied, and 5,10,15,20-tetra-phenyl-p-sulfonato-porphyrin (TSPP) has been filed in concentration of 10^{-4} M on nanostructured compounds: covalently bound to titanium oxide—TSPP-Sil-TiO₂. As an alternative to homogeneous solutions, using a suspension of TiO₂ nanopowder may create premises; this compound is used in studies of cell functionality. The effect of a new drug such as TSPP-Sil-TiO₂ was also studied (**Figure 22**). By coupling with TiO₂, TSPP is losing the proper absorption bands, due to the chemical bonds SO₂-NH, present in the new synthesized system. The particle size and the morphology of TSPP-Sil-TiO₂ nanoparticles in acrylate matrix visible in AFM showed sizes around 30–50 nm. The images of TSPP-Sil-TiO₂ nanoparticles in polymer matrix have been compared with TiO₂ nanoparticles alone. Injected into a mouse tumor (about 0.5 cm), after 2 or 3 days, a further marked antineoplastic effect was obtained [61, 62].

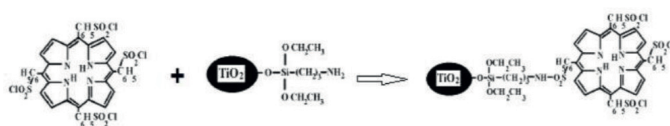


Figure 22. TSPP-sil-TiO₂ structure.

5. Photodegradation reactions of porphyrins

Porphyrins and metallo-porphyrins, due to their electronic spectra in the visible region, and their excited states with relatively long life, are considered to be good photosensitizer agents almost ideal, generating singlet oxygen in the presence of light radiation and atmospheric molecular oxygen [63, 64]. However, as singlet oxygen generator, porphyrins and their complexes metal can be oxidative degraded, generating the tetrapyrrole linear (phlorine) species with distorted photophysical and photochemical properties [65].

Structure and product names for photolysis of porphyrins differ from one porphyrin to another: from biliverdin, the bilivioline, or benzoilbilitriene (**Figure 23**).

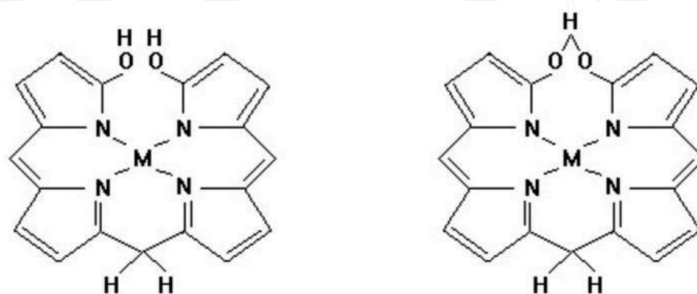


Figure 23. Structure of photolysis products of porphyrins.

The mechanisms underlying the photolysis products could be:

- mononuclear, where photodegradation products were obtained via singlet oxygen atom which is attached;
- bimolecular, where the product of photodegradation is attached to two oxygen atoms;
- mechanism called hydrolytical, where the product of photodegradation is attached to the oxygen atom derived from molecular oxygen and the other coming from a water molecule [66] (see **Figure 24**).

The photodegradation reaction mechanism can be:

- mechanism type I (or mechanism singlet), in which the reactive singlet oxygen species is formed by energy transfer processes:



- mechanism type II (or free radical mechanism) in which the species are the reactive superoxide anion formed by electron transfer processes:



The main factors influencing the photolysis reaction of porphyrins are meso-substituent, central metal, axial ligand, solvent, and binary mixture of solvents, and so on.

Among the complex range of disruptive factors, the meso-substituents attached to the porphyrin ring produce one of the weakest effects on photophysical and photochemical properties of porphyrins (**Table 10**). Meso-substituents are generally of aromatic character and inductive load and have an effect on electron system π porphyrin macrocycle. At the same time, a phenomenon of mixing the meso-substituents of the porphyrin macrocycle with the meso-carbon (hereinafter referred to as phenomenon hyperconjugation) leads to reducing the electron-electron repulsion configuration and interaction between them. In order to evaluate

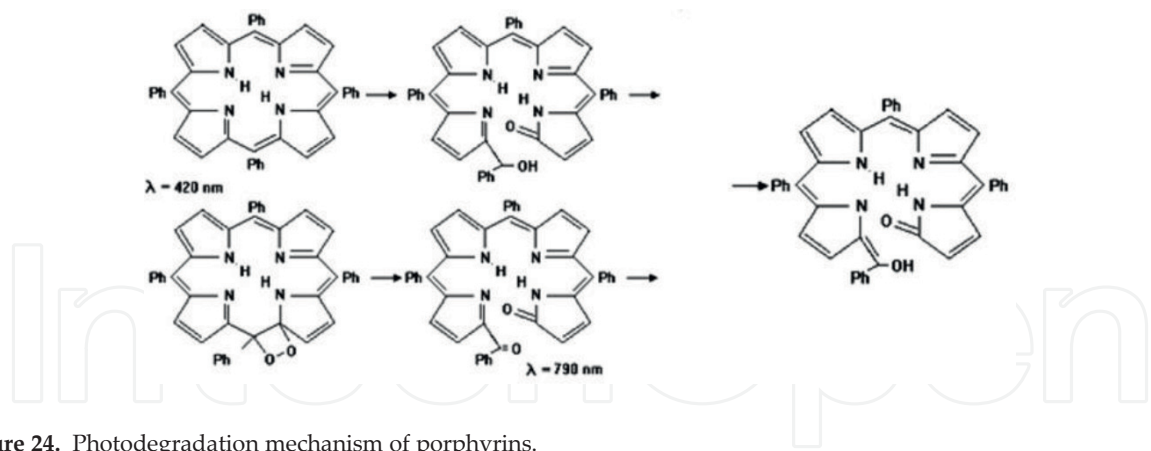


Figure 24. Photodegradation mechanism of porphyrins.

No	R	Porphyrin name	Abbreviation
1.	C ₆ H ₅ -H	5,10,15,20-Tetra(p-sulfonato)phenyl porphyrin	TPP
2.	C ₆ H ₅ -NH ₂	5,10,15,20-Tetra(4-amino-phenyl)porphyrin	TAPP
3.	C ₆ H ₅ -NO ₂	5,10,15,20-Tetra(4-nitro-phenyl)porphyrin	TNPP
4.	C ₆ H ₅ -SO ₃ H	5,10,15,20-Tetra(4-sulfonato-phenyl)porphyrin	TSPP
5.	C ₆ H ₅ -OH	5,10,15,20-Tetra(4-hydroxy-phenyl)porphyrin	THPP
6.	C ₆ H ₅ -CH ₃	5,10,15,20-Tetra(4-methyl-phenyl)porphyrin	TMPP
7.	C ₆ H ₅ -OCH ₃	5,10,15,20-Tetra(4-methoxy-phenyl)porphyrin	TMOPP
8.	C ₁₀ H ₇ -H	5,10,15,20-Tetra(1-naphthyl)porphyrin	TNP
9.	C ₁₀ H ₇ -SO ₃ H	5,10,15,20-Tetra(4-sulfonato-naphthyl)porphyrin	TSNP
10.	C ₁₀ H ₇ -OH	5,10,15,20-Tetra(4-hydroxy-naphthyl)porphyrin	THNP

Table 10. The structure of the meso-substituents and the name of the porphyrins.

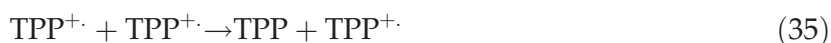
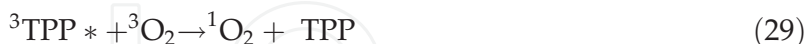
the effect of meso-substituent on the spectral properties of porphyrins is important the assessment of donor/acceptor of the substituents (assessed by constant values Hammett (constant substitute) which is a measure of the ability of donor/acceptor substitutes) [67].

For the meso-substituted porphyrins, a rigorous correlation between the Hammett substituent constant and the rate of photodegradation has been noted (Figure 25).

For a photostable meso-substituted porphyrin is needed a meso-substituent with small capacity of electron acceptor ($\sigma < 0$), which involves:

- inductive load small effect (from meso-substituent on the porphyrin macrocycle);
- conjugation effect of meso-substituent macrocycle to be large;
- a small hyperconjugation macrocycle-meso-carbon.

- the photodegradation reaction mechanism of meso-substituted porphyrins involving active oxygen species (singlet oxygen, superoxide anion species dioxetane via hydroperoxide).



They have been identified by UV-vis (**Figure 26**), IR (**Figure 27**), and mass spectrometry (**Figure 28**).

The optimal parameters that must be taken into account in the photolysis reaction of metalloporphyrins are a high electronegativity of the central metal, a high oxidation potential, the

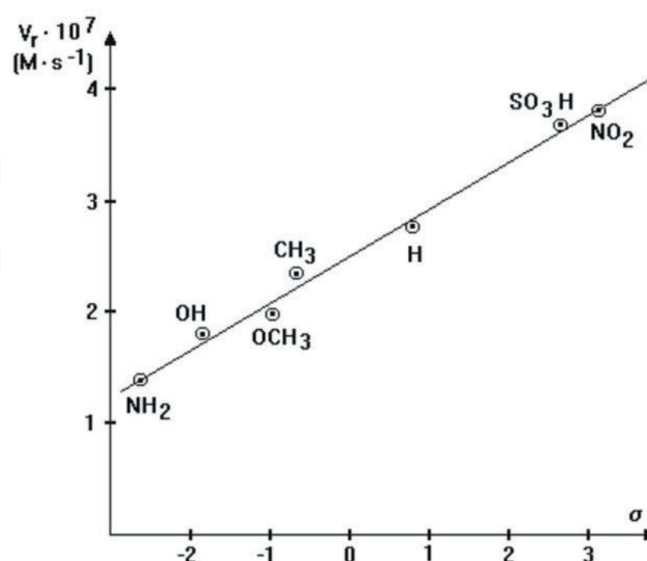


Figure 25. Correlation between the photodegradation rate and Hammett constant.

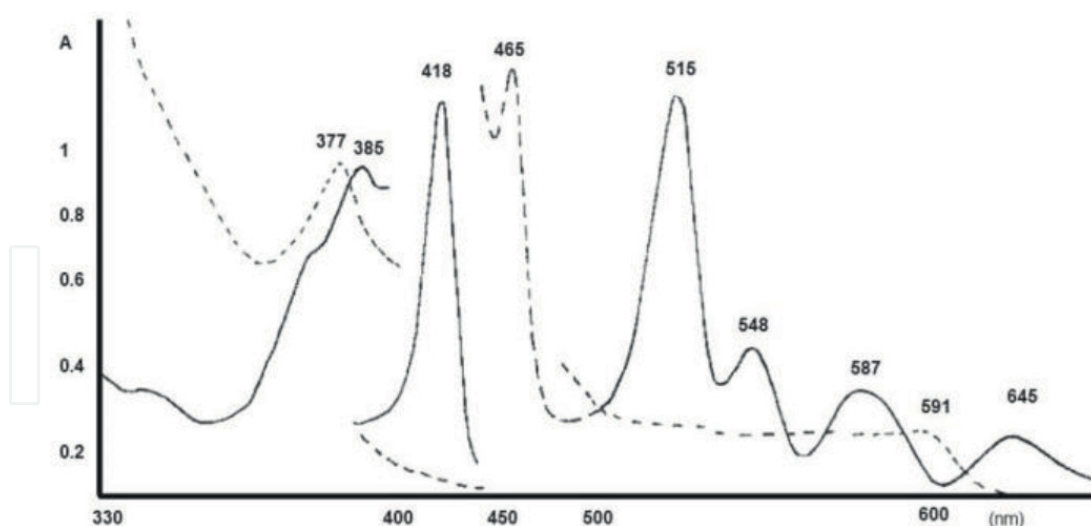


Figure 26. UV-vis spectra of TPP (—) and its photodegradation product (....).

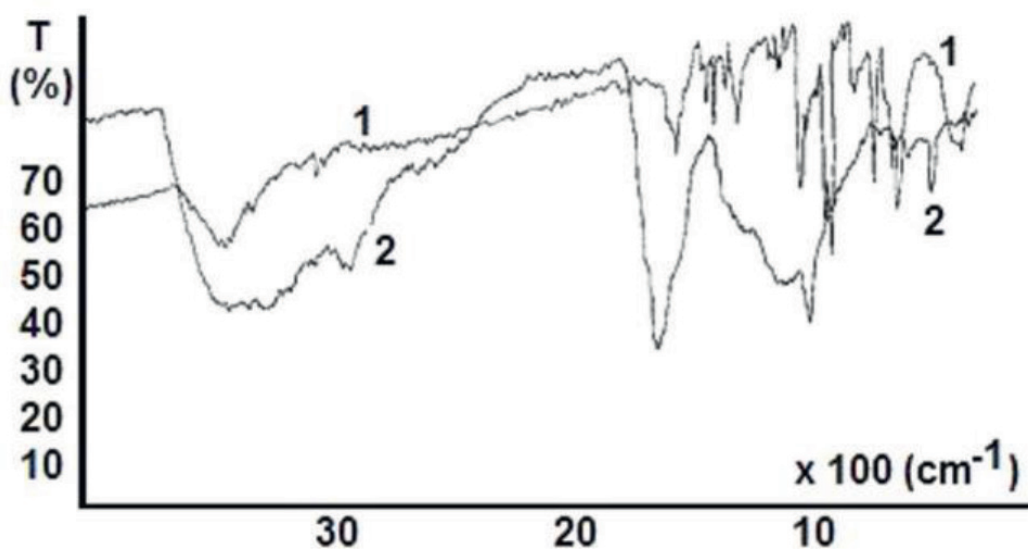


Figure 27. IR spectra of TPP (1) and its photodegradation product (2).

occupancy of d orbitals low, β and α band intensities ratio to be as low as possible (assuming that a smaller energy band β) [67, 68].

In the context of finding parameters that reflect the order of photodegradation rate variation, the following are taken into consideration: the lifetime of the first excited singlet states, lower metallo-porphyrins that easily photodegraded the metallo-complexes exhibiting strong fluorescence, and the photodegradation mechanism that could involve the dioxetane species that decomposition leads to ketones and peroxides (Figure 29).

In the case of metallo-porphyrins with trivalent metal and axial ligand Cl, regardless of the meso-substituent attached to the macrocycle, the photodegradation mechanism involves the following:

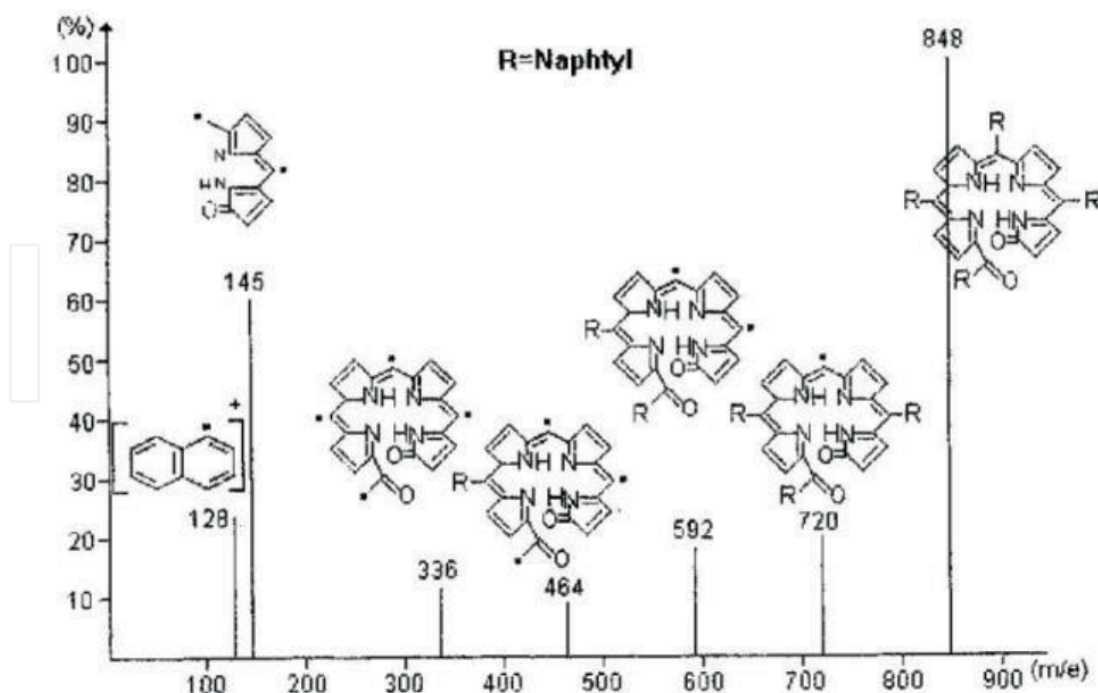
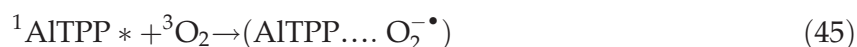
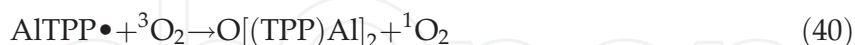
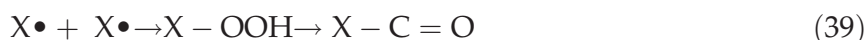


Figure 28. Mass fragments of TNP and its photodegradation product.

A homolytic break of the Cl-metal bond followed by irreversible degradation of the porphyrin macrocycle [69]. If instead of the axial Cl ligand, there are different other ligands (methyl, ethyl, octyl, and dodecyl), the trivalent metal ion is transformed from pentacoordinated into tetracoordinated by forming μ -oxo-dimers (identified by ^{27}Al -NMR spectrometry) (Figure 30) and by formation of peroxides and ketones, as shown in the following diagram:





The photostability of aluminum porphyrins increases up to axial ligands with eight carbon atoms and declines thereafter [70]. Obviously, one of the most difficulties in using porphyrins is the solvent used for solubilizing them, through its physical and chemical characteristics [71]. To have an optimal photostability, the solvents used to dissolve the porphyrins should fulfill the following criteria: a high polarity (solvents with nitrogen), an aromatic character, and an alcoholic structure by forming hydrogen bonds between the alcoholic OH group and the N (NH) group from the porphyrin (**Figure 30**) [72].

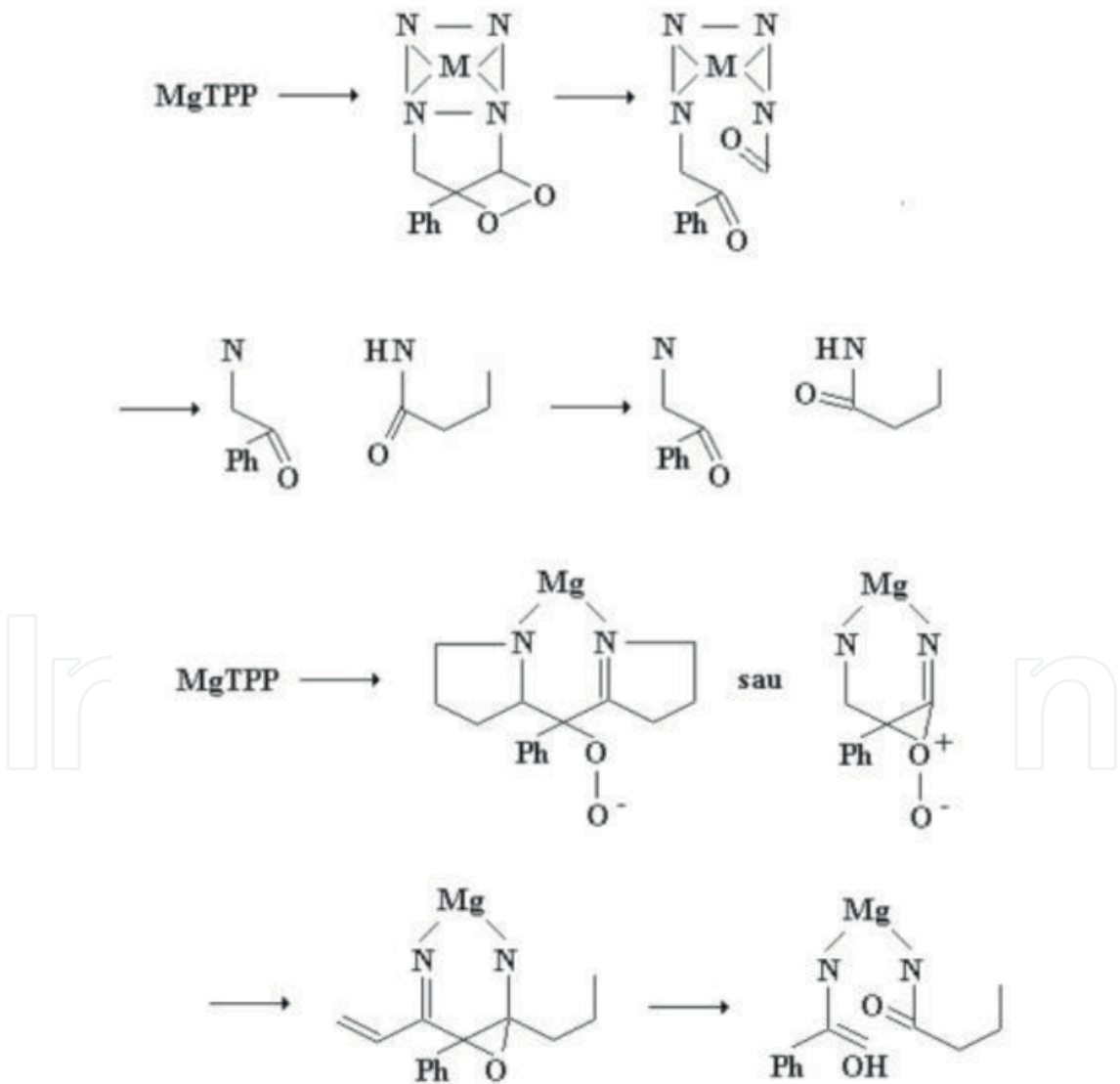


Figure 29. The scheme of the photodegradation process.

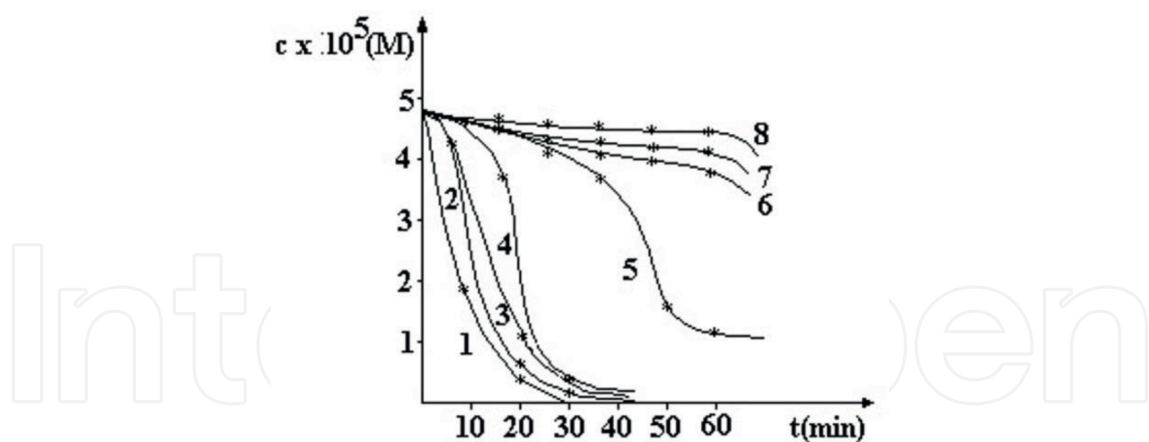


Figure 30. The photodegradation rate variation of porphyrins in various solvents: 1, benzene; 2, nitromethane; 3, piperidine; 4, pyridine; 5, nitrobenzene; 6, pentanol; 7, hexanol; 8, dodecanol.

The use of chlorinated solvents, which causes the formation of free-base porphyrin in diacid form and metallo-porphyrins, causes demetalation generated by the action of HCl. The demetalation constant varies with increasing their ability to be more easily photodegradable. The photodegradation rate is higher for the metallo-porphyrins with the d orbitals being full or completely free. The use of binary mixtures of solvents (e.g., DMSO:water (0.05%:99.95%)) is essential for the porphyrins solubilization and application (**Table 11**).

In conclusion, for a more stable porphyrin, the necessary criteria are porphyrins with meso-substituent having positive Hammett constant, metallo-porphyrins d0 or d10, regardless of the valence central, most unstable being the porphyrin with Mg, Zn, Cd, Pb, Al, aromatic solvents, and with OH groups or NO₂ [73, 74].

DMSO:water (%)	Non-sulfonated porphyrins	Sulfonated porphyrins
100:0–80:20	Neutral forms	Neutral + anions
80:20–50:50	Dimers	Dimers
50:50–25:75	Cations + aggregates	Neutral
50:50–37:73	–	Monocations
25:75–0.5:99.5	Aggregates (J) + monomers	Dications + aggregates

Table 11. Porphyrin forms in DMSO:water mixture.

6. Conclusions

Porphyrins and metallo-porphyrins are very versatile and efficient sensitizers and chemo-responsive materials, with a very extensive list of applications. The structures, chemical characteristics, optical properties, and photo-physical/photochemical properties have been detailed

in this chapter. Specific applications of porphyrins and phthalocyanine, either as free base or metallic complexes, are exemplified.

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