








Article

Homogeneous Photosensitized Oxidation for Water Reuse in Cellars: A Study of Different Photosensitizers

Andreia D. Santos ^{1,2,*} , Diana Gonçalves ¹ , Rui C. Martins ¹ , Marta Gmurek ³ , Anabela Nogueira ⁴ , Sérgio Castro-Silva ⁴ , Luis M. Castro ^{1,2,5}  and Rosa Quinta-Ferreira ¹

¹ CIEPQPF—Chemical Engineering Processes and Forest Products Research Center, Department of Chemical Engineering, Faculty of Sciences and Technology, University of Coimbra, Rua Sílvio Lima—Polo II, 3030-790 Coimbra, Portugal

² Polytechnic Institute of Coimbra, Coimbra Institute of Engineering, Department of Chemical and Biological Engineering, Rua Pedro Nunes—Quinta da Nora, 3030-199 Coimbra, Portugal

³ Department of Molecular Engineering, Faculty of Process and Environmental Engineering, Lodz University of Technology, Wolczanska 213, 90-924 Lodz, Poland

⁴ Adventech, Lda, Rua de Fundões, 151, 3700-121 São João da Madeira, Portugal

⁵ SISus—Laboratory of Sustainable Industrial Systems, Coimbra Institute of Engineering, Department of Chemical and Biological Engineering, Rua Pedro Nunes—Quinta da Nora, 3030-199 Coimbra, Portugal

* Correspondence: duartasantos@uc.pt



Citation: Santos, A.D.; Gonçalves, D.; Martins, R.C.; Gmurek, M.; Nogueira, A.; Castro-Silva, S.; Castro, L.M.; Quinta-Ferreira, R. Homogeneous Photosensitized Oxidation for Water Reuse in Cellars: A Study of Different Photosensitizers. *Sustainability* **2023**, *15*, 6861. <https://doi.org/10.3390/su15086861>

Academic Editors: Belisa Alcantara Marinho, Maria Alice Prado Cechinel and Bianca Miguel de Souza Chaves

Received: 15 March 2023

Revised: 11 April 2023

Accepted: 17 April 2023

Published: 19 April 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Abstract: The demand for fresh water is increasing daily, requiring industries to take action to reduce the need for fresh water. Winemaking industries represent a massive hydric impact by combining the water consumed and the high volume of wastewater produced. The sun-driven photooxidation process has been widely employed in removing wastewater pollutants. This work employed four photosensitizers, Rose Bengal, AlPcS₄, ZnPcS₄, and TPP, for water reuse in cellars. A secondary effluent has been investigated as a water matrix. Of all the photosensitizers (PS) employed, ZnPcS₄ showed better chemical oxygen demand (COD) (23%) and phenolic (TPh) (81%) removal. The effect of pH and concentration was also assessed for ZnPcS₄. The phenolic content removal was found to be highly dependent on the solution's pH, as alkaline solutions improve the singlet oxygen quantum yield where the use of a pH = 11 reached 42% and 81% of COD and TPH removal. However, a pH higher than 7 showed higher PS bleaching than pH = 7. Three different PS concentrations were evaluated: 3×10^{-6} , 5×10^{-6} , and 1×10^{-5} mol/L. The optimal PS concentration was found to be 5×10^{-6} mol/L.

Keywords: AOP; photooxidation; photosensitization; wastewater treatment; water reuse; winemaking

1. Introduction

The wine industry has a significant environmental impact, particularly in water use, energy consumption, greenhouse gas emissions, and waste generation, which must be reduced [1,2]. During the production process, many steps are involved, as presented in Figure 1, from which residues and wastewater are produced with different compositions and quantities.

Water is a critical resource in wine production, and its availability is often limited in dry areas. In these regions, the reuse of wastewater can be an attractive option to reduce the demand for freshwater. However, the quality and quantity of wastewater produced during wine production can vary significantly, making it challenging to plan and design wastewater treatment systems [3]. The characteristics of the wine produced, the industrial facilities, the country, and the technological resources available influence water consumption [2,4,5]. For instance, red wine production increases by 50–60% of the water consumption compared to the production of white wine. Small- or medium-sized wineries producing a small amount of wine have a very high water consumption ratio [3].

In addition, the volume of water consumed is proportional to the harvest time, and larger wineries can better manage the consumption of this resource.

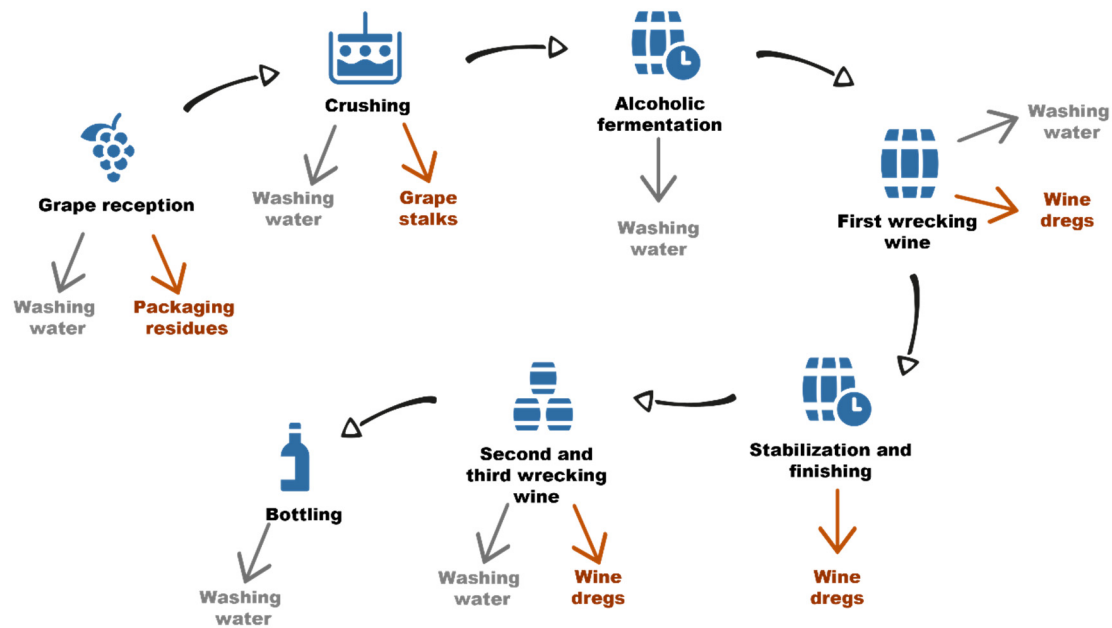


Figure 1. Wine production diagram with waste generation streams.

During the transformation process, the volume of wastewater produced is calculated between 0.5 to 14 L per liter of wine produced, with an estimated water consumption of 1 to 4 L per liter of wine [6,7].

According to the International Organization of Vine and Wine, in 2022, wine production of 260 million hectoliters was estimated, with a prevision for Portugal of 6.7 million hectoliters [8], allowing us to predict that during the 2022 harvest season, between 6.7 to 26.8 million hectoliters of water were consumed, and between 3.35–93.8 million hectoliters of an acidic, phytotoxic and with high organic matter wastewater, however biodegradable, were produced [9,10]. If the produced wastewater were reused, it would be possible to reduce the water footprint of the winemaking industries.

Due to the enormous amount of wastewater generated and its seasonality, the wine sector needs low-cost alternative treatments to treat wastewater from wineries and promote reuse. If the biological effluent is reused, there will be a greater possibility of coming into direct contact with humans and the production process. Thus, it is necessary to be more careful with the composition of the effluent that will be reused, decreasing the emission limits and including new parameters, namely microorganisms that may negatively affect the human organism [6].

Over the last few years, winery wastewater treatment has been deeply investigated, aimed at implementing cost-effective wastewater treatments and waste valorization following the circular economy guidelines [11,12]. It was found that it is possible to obtain platform chemicals, biofuels, heat and energy, and antioxidants [7,13,14]. Due to the biodegradability of this wastewater, biological treatments have been employed, such as anaerobic and aerobic, where the removal efficiency of chemical oxygen demand (COD) was higher than 80% [15]. Using physicochemical techniques, such as precipitation, sedimentation, coagulation, electrocoagulation, advanced oxidation processes (AOPs) and membrane, was also reported. However, process combinations are necessary to increase the efficiency of removal of both recalcitrant organic compounds and ecotoxicity, with a simultaneous reduction of investment and operational costs [4,5,10,15].

The Ioannou et al. [10] study shows that physicochemical treatments are effective for the pretreatment of winery wastewater, reducing total suspended solids (TSS), turbidity,

and a part of the organic content. It also reported that biological treatments are effective in reducing the high organic load; nevertheless, they are not enough to reach the limits stated in the European Directive 91/271/EEC [16]. It is concluded that combining advanced oxidation processes (AOPs) and biological treatment can lead to a higher level of COD reduction than any single-stage treatment under the same operating conditions. AOPs as post-treatment of biological processes were found to be the most effective combination for winery effluent treatment, permitting almost complete purification compared to AOPs used as a pretreatment. That combination presents advantages, as chemical pretreatment can protect microorganisms used in biological processes of different toxic and inhibitory compounds. In addition, the use of biological pretreatment can reduce the cost of chemical treatments while providing flexibility in the residence time necessary to increase the mineralization of organic compounds pretreatment [4,17]. Besides energy and value-added products, wastewater reuse is a key factor in “closing the loop” of the circular economy in industries [18,19], proving to be a sustainable resource and able to improve the production of the culture and reduce the need for inorganic/synthetic fertilizers [18,20,21]. However, industrial applications can also be an alternative, as the obtained wastewater follows the directives established by the European Union [22]. Typically, effluent from the wine industry undergoes physical pretreatment, followed by biological treatment. However, it may undergo a tertiary treatment depending on its contamination. To meet water reuse quality standards, it is essential to implement a sequence of treatments that can efficiently eliminate chemical/organic contaminants and microorganisms [23].

AOPs use one or a combination of chemical oxidants, such as hydrogen peroxide (H_2O_2) or ozone (O_3), to oxidize complex organic molecules. The oxidation of these organic molecules occurs through an attack by free radicals, which may vary depending on the type of oxidant used. Reactive oxygen species (ROS) generation relies on the increase of catalysts or energy sources such as solar or artificial energy (ultraviolet radiation) that are used. Sunlight-induced photochemical reactions involving ferric ions or carboxylate complexes in the environment result in the formation of hydrogen peroxide and its subsequent catalytic decomposition into a hydroxyl radical ($\bullet\text{OH}$), leading to the oxidation of organic substances in aquatic environments [24].

Traditionally, harsh chemicals or physiochemical techniques have achieved water disinfection for reuse. However, an alternative method called Photosensitized Oxidation (PO) has been proposed for wastewater disinfection and removal of pollutants. This technique utilizes solar light to trigger a reaction that disinfects the water and eliminates contaminants. PO represents a promising alternative to conventional methods, as it offers a more environmentally friendly and sustainable approach to water treatment [25].

Singlet oxygen ($^1\text{O}_2$) is primarily generated through the irradiation of molecular oxygen in the presence of photosensitizer pigments, such as Rose Bengal or methylene blue, during the photosensitized oxidation processes (POPs) [26]. Both $\bullet\text{OH}$ and $^1\text{O}_2$ play a crucial role in the degradation of pollutants in surface waters. In addressing the global water scarcity problem, harnessing solar energy for water treatment presents a promising sustainable solution. Over the past few years, considerable endeavors have been undertaken to create and experiment with innovative water treatment technologies that operate on solar power [27,28].

Tai et al. [29] investigate the solar-induced generation of singlet oxygen and hydroxyl radicals in sewage wastewaters. The authors used various methods, including spectrophotometry and electron spin resonance spectroscopy, to measure the production of these reactive species under different solar radiation conditions. The authors suggest that these reactive species may play an important role in the degradation of organic pollutants in wastewater treatment systems.

POPs are conducted in aqueous solutions with the direct action of visible radiation and with the participation of a photosensitizer, a compound quickly energetically excited by solar radiation. However, it is central to identify the appropriate photosensitizer for each wastewater to achieve greater efficiency [30,31].

In the POP, the photosensitizer (PS) is usually activated when a photon with a key energy level is elevated, producing a short-lived molecule known as a singlet excited photosensitizer (PS_1^*). With the energy photon moving back to lower energy states, an excited photosensitizer occurs in the triplet state (PS_3^*), which has a longer lifetime, allowing different types of reaction mechanisms to occur: type I (radical photooxidation) or type II (photooxidation by oxygen singlet (1O_2)), as presented in Figure 2.

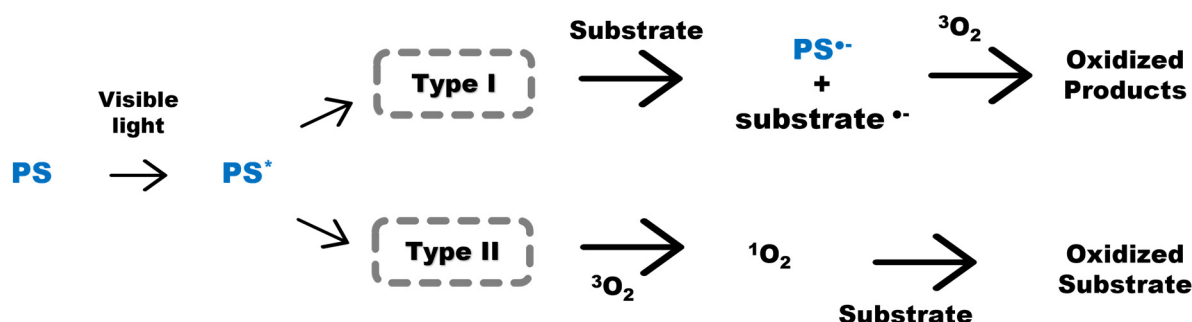


Figure 2. Type I vs. Type II photosensitization mechanisms.

With the type I mechanism, the photosensitizer molecule absorbs a photon of light and becomes excited. The excited photosensitizer then interacts with a molecule in the solution, transferring an electron and creating a radical cation. This radical cation can then react with other molecules in the solution, creating a chain reaction that ultimately leads to the oxidation of pollutants. In the type II mechanism, the photosensitizer molecule absorbs a photon of light and becomes excited. The excited photosensitizer then interacts with oxygen molecules in the solution, transferring energy and creating singlet oxygen. This singlet oxygen can then react with organic compounds in the solution, breaking them down and oxidizing them [32].

In both procedures, once the energy transfer has occurred, the PS returns to its ground state and can reabsorb photons from the radiation again. However, after a certain number of absorption and energy emission cycles, the photosensitizer undergoes photobleaching: it loses the ability to absorb energy, and consequently, the formation of oxygen singlets and oxidation of organic compounds are no longer available [30,33].

The use of POP for wastewater treatment, e.g., phenol and organic matter oxidation or water disinfection associated with bacteria inactivation, has been reported in the literature. Due to its potential, it can be utilized as a treatment method against pathogens and toxic organic pollutants in wastewater [26,34,35].

The POP can occur in a homogeneous or heterogeneous reaction. The homogeneous reaction takes place when the photosensitizer is dissolved in the substrate. This process promotes efficient energy transfer leading to faster reaction rates. As both are present in the same phase, there is more chance that the energy will transfer from the photosensitizer to the substrate. The process becomes easier to control since the concentration of PS can be adjusted. Heterogeneous POP can also occur when the PS is immobilized in a solid matrix, such as polymers or silica. The main advantage of the heterogeneous POP is the facility to recover the PS, as it is in a different phase [36].

This study aims to identify the most effective photosensitizer (PS) for removing residual COD and TPh from winery wastewater while optimizing the operational conditions. In addition, it is planned to conduct further research to assess the performance of both homogeneous and heterogeneous photosensitization. The photosensitive oxidation process aims to treat effluents by degrading organic matter and disinfecting them to ensure their safety for reuse. The disinfection capacity of this process was discovered in 1993. Tratnyek et al. [37] found that effluents from textile industries exposed to sunlight for 200 min inhibited *E-coli* colonies' growth. Faust et al. [38] studied the production speeds of 1O_2 when chromophore PS with a simple structure called Rose Bengal (RB) and methylene blue (MB) aided by sunlight were employed. Comparing the two photosensitizers, RB led to a

higher production speed of $^1\text{O}_2$ due to higher quantum yield, presenting a higher capacity to oxidize organic compounds than MB. Despite the favorable results, RB and MB showed high photobleaching, making their reuse almost impossible.

The growing evolution of chemical synthesis has brought new and more complex PS, namely phthalocyanine and porphyrin derivatives. Thus, Ozoemena et al. [39] used and synthesized phthalocyanines associated with sulfonates or carboxyl groups, such as zinc tetra-phthalocyanines (ZnPcS_4) and aluminum tetra-sulphthalocyanines (AlPcS_4) or zinc octacarboxyl-phthalocyanines (ZnOCPC) and aluminum octacarboxyl-phthalocyanines (AlOCPc), respectively. The most efficient photosensitizer to decompose 4-chlorophenol was AlPcS_4 , whose degradation reached 65% [39]. In addition, AlPcS_4 did not suffer any bleaching during the assay and can be reused in a heterogeneous phase. Zhang et al. [40] studied the $^1\text{O}_2$ generation rate when using titanium phthalocyanines. These PS presented values of quantum yields between 76% and 85%. Many photons in the radiation were used to excite oxygen and, thus, form oxygen singlets. Therefore, it is concluded that this species of a low lifetime may have a greater capacity to oxidize organic compounds.

The destruction of persistent pollutants, such as parabens, was investigated by Gryglik and Gmurek [41] using tetra-replaced photosensitizers such as AlPcS_4 and tetra-sulphatophytoporphyrin (TPPS_4) with the variation of the type of radiation, i.e., wavelength. Initially, the tests were performed with simulated radiation through Xenon lamps, as the glass and water made for the cooling jacket worked as UV. The results showed that the photosensitized oxidation process effectively degraded the parabens mixture, with more than 90% degradation achieved within 120 min of irradiation. The authors also investigated the effects of various parameters on degradation efficiencies, such as initial pH, hydrogen peroxide concentration, and irradiation time. Overall, the study provides insights into a potential method for removing parabens from wastewater using photosensitized oxidation, which could have important implications for environmental and human health.

The immobilized photosensitizer has been evaluated more recently as a heterogeneous POP, allowing for PS reuse. Foszpańczyk et al. [31] used AlPcS_4 , supported in chitosan, to remove phenolic compounds. The authors then tested the effectiveness of immobilized PS in the degradation of various phenolic compounds under visible light irradiation. The results showed that the catalysts were effective in promoting the degradation of the phenolic compounds (50%), with the extent of degradation depending on the type of catalyst used and the specific phenolic compound. The study highlights the potential of using photosensitizing catalysts incorporated into chitosan for the heterogeneous oxidation of phenolic compounds, which has important implications for the development of sustainable wastewater treatment technologies. The article provides valuable insights into the mechanisms underlying the degradation process and offers a new approach to addressing the challenges associated with phenolic compound removal in wastewater treatment systems.

Porphyrins have been studied for the degradation of micropollutants. Neves et al. [42] used $\text{H}_2\text{TF}_5\text{PP}$ as a photosensitizer to remove metoprolol from wastewater treated with a biological process. Using simulated solar radiation, the authors evaluated the effect of homogeneous and heterogeneous conditions. The author reached 90% metoprolol degradation after 12 h. During the heterogeneous reaction, with the porphyrins immobilized in silica, the source light was evaluated as well, both simulated and real sunlight. Authors reached similar results in both assays, showing that the removal efficiency of metoprolol is unaffected by the immobilization or the light source.

Also, the phenol removal after the reaction was only 50%. Aimeur et al. [43] studied phenol photodegradation using free phenalenone (PN) and immobilized it on halloysite nanotubes using ultraviolet or visible radiation. The author evaluated the effect of pH, initial phenol, and PN concentration, as well as the light intensity and source (UV or visible). Their study concluded that pH values highly affect phenol degradation. Under pH 12, it is possible to achieve a complete transformation of phenol within 120 min under UV irradiation, while visible irradiation would require 300 min for the same transformation. The degradation rate through photolysis was greater when using free PN than using

a supported photosensitizer. The primary pathway for phenol photodegradation was through a type II mechanism, with a potential contribution from a type I mechanism.

Therefore, this work will study a wine effluent that has undergone biological treatment (secondary effluent) and will undergo advanced oxidation treatment to improve the water quality for future reuse. Four different PS will be evaluated, as well as the pH effect and PS concentration on phenolic (TPh) and organic matter (COD) removal.

2. Materials and Methods

2.1. Analytical Methods

Chemical Oxygen Demand (COD) was determined by employing the standard Closed Reflux Colorimetric Method 5220 D as established in the Standard Method; Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS) were calculated using the 2540 B, D, and E also defined in the Standard Method [44]. To determine the total phenolic content (TPh), the Colorimetric Folin and Ciocalteu method was employed. It is based on the reduction of a phosphomolybdic-phosphotungstic acid complex by phenolic compounds, resulting in a blue-colored complex that can be quantified using a spectrophotometer, where the quantity of phenolic compounds in the sample can be calculated based on a standard curve generated using known concentrations of a standard phenolic compound, such as gallic acid [45]. The removal efficiency was determined with Equation (1).

$$\text{Removal efficiency (\%)} = \frac{\text{Concentration}_{\text{initial}} - \text{Concentration}_{\text{final}}}{\text{Concentration}_{\text{initial}}} \times 100 \quad (1)$$

Each PS absorbs radiation with a specific wavelength, measured by the absorbance of AlPcS₄, ZnPcS₄, TPP, and RB at 675 nm, 765 nm, 515 nm, and 547 nm, respectively. The concentration of PS was monitored using photometric methods, where the absorbance of a sample was measured in a cuvette of 2 mL against the wastewater sample before adding PS [39,46]. Monitoring the PS concentration over reaction time allows access to PS bleaching.

2.2. Photosensitizers and Wastewater

For this work, four PS were evaluated, namely, Rose Bengal (RB) (Fluka), Al(III) phthalocyanine chloride tetrasulfonic acid (AlPcS₄) (a mixture of Regio isomers, Frontier Scientific, Newark, DE, USA), Zinc(II) phthalocyanine tetrasulfonate tetrasodium salt (ZnPcS₄) (Frontier Scientific, Newark, DE, USA), and Tetraphenylporphyrin (TPP), to remove total phenolic content (TPh) and Chemical Oxygen Demand (COD).

Complex compounds like phthalocyanines and porphyrins are used as photosensitizers in photosensitive oxidation processes. Dyes, such as Rose Bengal, are also being investigated for their potential use. Phthalocyanines are a group of macrocyclic and aromatic organic compounds with a wide range of applications, particularly in photochemistry. While all transition metals can form coordination complexes with phthalocyanines, only zinc, aluminum, and titanium form complexes that react with solar radiation, producing metallophthalocyanines [47,48].

The emission of energy by the photosensitizer and the subsequent excitation of molecular oxygen in wastewater to singlet oxygen are influenced by the degree of sulfation. The negative charge of phthalocyanines enables their solubility in water, but it is important to ensure they are in their monomeric form to prevent cluster formation. By reducing their aggregation, sunlight can more efficiently excite the photosensitizer. Therefore, it is essential to synthesize phthalocyanine complexes that are both soluble and in their monomeric form when in contact with water [39,47,48].

The central ion's nature plays a crucial role in the effectiveness of photosensitizers. Heavy metal ions or paramagnetic metal ions increase the photosensitizer's yield as a triplet but reduce its lifetime in the singlet state. When phthalocyanines or porphyrins are used to sensitize a photo-redox reaction, the active sensitizer that initiates the reaction is the photosensitizer in the triplet state. Therefore, a longer triplet state lifetime for the photo-

sensitizer is beneficial, as it increases the likelihood of diffusion shocks between the excited photosensitizer and potential inhibitors. Organic compounds containing double bonds, such as phenolic compounds, are potential inhibitors that compete with the photosensitizer by absorbing solar radiation [48].

Figure 3 shows the absorption spectra of zinc and aluminum phthalocyanine are very similar, with both photosensitizing agents behaving the same when in contact with radiation.

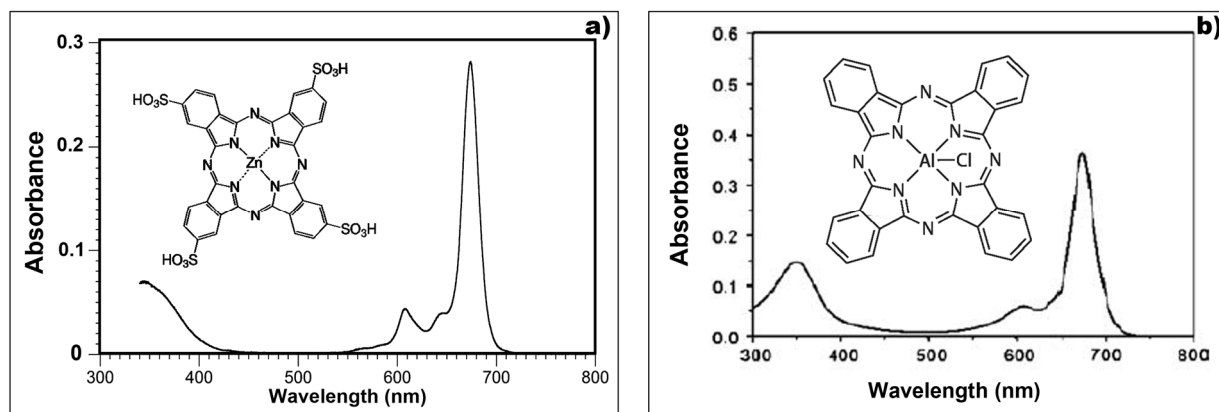


Figure 3. Molecular structure and absorption spectrum of ZnPcS₄ (a) and AlPcS₄ (b) (data from software PhotochenTM [49]).

The molecular structure of porphyrins, like phthalocyanines, includes a porphyrin skeleton (C₂₀H₁₄N₄) consisting of a heterocyclic aromatic ring with at least two different chemical elements at its vertices [50–52]. The most common porphyrins have symmetrical groups attached to the aromatic ring, such as tetraphenyl porphyrin (TPP), presented in Figure 4. These molecules are sensitive to changes in acidity and can break their coordination bond with metal ions. Porphyrins are also soluble in water and can be modified by sulfation or carboxylation, which affects their solubility. Compared to the phthalocyanine family, porphyrins have lower light absorption and do not extend into the near-infrared zone of visible radiation. They only absorb 37% of available solar radiation when exposed to sunlight [48]. However, porphyrins have a longer lifespan in the triplet state than phthalocyanine, which makes them more efficient in exciting molecular oxygen and producing oxygen singlets. This property makes them favorable for use as photosensitizers, despite their lower absorption of solar radiation [47].

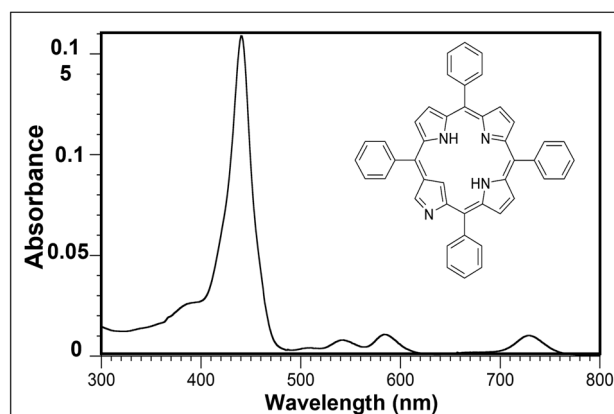


Figure 4. Molecular structure and absorption spectrum of TPP (data from software PhotochenTM [49]).

Like phthalocyanine and porphyrin, Rose Bengal's complex molecular structure is depicted in Figure 5. However, its absorption spectrum absorbs radiation with a wavelength

of up to 600 nm, with the highest peak of absorption occurring at 547 nm. Nonetheless, Rose Bengal is an efficient photosensitizer, as it has a high quantum yield and transfers energy effectively to molecular oxygen in the triplet state, producing oxygen singlet. The increased generation of oxygen singlet makes it effective for oxidizing and decomposing organic matter in the effluent. Rose Bengal is used at a maximum concentration of 10^{-5} M when degrading chlorophenols, an endocrine-disrupting compound, to avoid aggregation and decrease in quantum yield. However, this photosensitizer requires an alkaline solution and is not very stable, undergoing self-degradation during irradiation, also known as photobleaching [53].

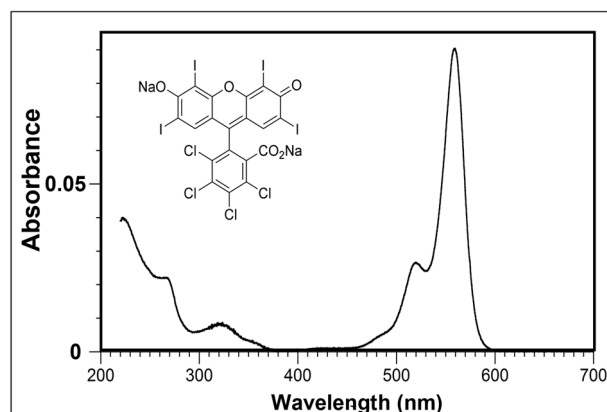


Figure 5. Rose Bengal molecular structure and absorption spectrum (data from software PhotochenTM [49]).

The wastewater was collected from the treated wastewater storage tank of a conventional activated sludge wastewater treatment plant of a winery facility in the Ribatejo region of Portugal and stored at a temperature of 4 °C. Table 1 presents the average wastewater characterization.

Table 1. Average characterization of the wastewater after biological treatment.

| COD (mg O ₂ /L) | BOD (mg O ₂ /L) | TSS (mol/L) | TPh (mg/L) | pH |
|-------------------------------|-------------------------------|----------------|---------------|-------------|
| 125 ± 65.0 | 17.8 ± 5.23 | 26.6 ± 5.35 | 21.9 ± 1.90 | 7.45 ± 0.45 |

2.3. Experimental Methodology

A glass reactor with a cylinder volume of 0.5 L was utilized. An air bomb supplied the oxygen with an airflow of 4.5 L/min. Before being added to the reactor, the wastewater pH was adjusted to the desired value by adding sodium hydroxide (NaOH) or sulfuric acid (H₂SO₄). The aerator was connected, and an established amount of PS solution was introduced according to the desired PS concentration. This process was carried out carefully to avoid direct contact with the reactional medium and solar radiation. After starting the stopwatch, an initial sample was removed, and the reactor was placed directly in contact with sunlight. Pasteur pipettes of 3 mL were used to collect samples, and 9 mL of sampling were collected during the assay time (180 min).

3. Results and Discussion

The experimental work was divided into three main sections. Firstly, the sunlight degradation effect in the wastewater (photolysis) was evaluated by putting the wastewater under direct sunlight. After that, the photooxidation of each PS at constant pH and PS concentration was evaluated. Finally, the effect of initial pH on the photooxidation and the initial concentration of PS was studied.

3.1. Photolysis

The reactor was filled with wastewater and put under direct sunlight to assess the solar effect on COD and TPh degradation. The assay was duplicated, with an average solar radiation of 501 W/m^2 . Figure 6 presents the effect of sunlight on the degradation of COD and TPh.

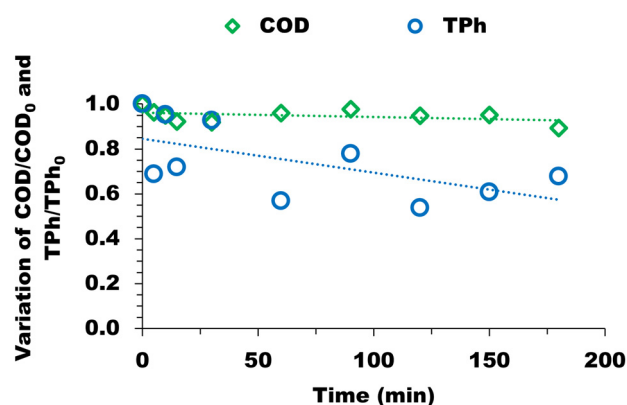


Figure 6. Variation of the ratios COD/COD₀ and TPh/TPh₀ during the photolysis assay.

From Figure 6, one can perceive that the COD shows a slight variation ($\approx 11\%$) during the 180 min of the experiment when compared with the TPh ($\approx 32\%$). The observed variation can be attributed to dissolved organic matter (DOM), which can act as a sensitizer in indirect photodegradation. This process generates reactive species that can effectively mineralize phenolic compounds [26,46,54]. As presented in Mostafa and Rosario-Ortiz's [34] study, when exposed to solar radiation, the organic matter in wastewater shows a higher rate of singlet oxygen formation than the one usually reported for the natural organic matter (NOM) present in aquatic systems. Therefore, the organic matter in the wastewater can absorb solar radiation, reaching the excited state of triplet organic matter and promoting singlet oxygen production [55]. O'Connor et al. concluded that the organic matter for wastewater is able to improve the yield production of $^1\text{O}_2$ and more energetic triplet excited states than NOM [55].

3.2. Photooxidation

After assessing the sunlight effect, four photosensitizers were used to evaluate which one had the best performance in removing those pollutants (COD and TPh). Each assay was duplicated on different days to maintain the same starting time for both. Table 2 presents the working conditions in each assay concerning the PS used, its molar concentration, the initial wastewater pH, and the average solar radiation.

Table 2. Working conditions for each assay.

| Assay | PS | [PS] (mol/L) | Wastewater pH | Average Solar Radiation (W/m ²) |
|-------|--------------------|--------------------|------------------|--|
| A1 | ZnPcS ₄ | 5×10^{-6} | 7.00 | 623 |
| A2 | AlPcS ₄ | | | 480 |
| A3 | RB | | | 590 |
| A4 | TPP | | | 444 |

Figure 7 shows each assay's COD, TPh variation, and PS concentration over time. From Figure 3b, the COD degradation did not show a wider variation, as in Figure 3c, where the TPh removal is noticeable for all assays. Assays A1 and A3 demonstrated higher levels of COD removal, with values of 23% and 20%, respectively. Additionally, A1 and A3 showed TPh removal rates of approximately 81% and 76%. Those removals can be related to the high singlet oxygen quantum yield associated with the RB photosensitizer and the

addition of Zn since heavy metals are expected to increase the singlet oxygen quantum yield [30,56], but also to increase the solar radiation. Based on the Miller study [53], the most significant decline in PS concentration over time resulted in a 53% reduction in RB concentration after one hour of the experiment. A similar decrease of 48% was observed in the current study after a one-hour treatment, whereas the ZnPcS₄ maintained more or less the same over time.

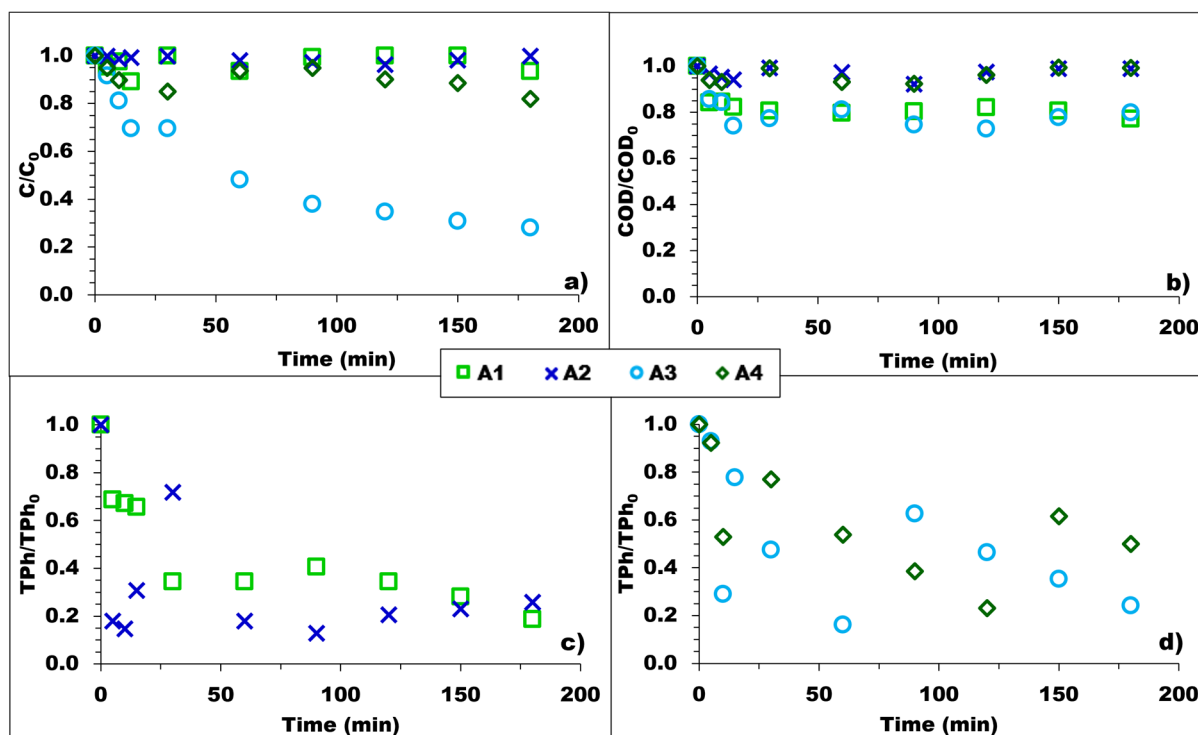


Figure 7. Photooxidation effect under different photosensitizers for assays A1 to A4: (a) variation of PS concentration during the assay time, (b) COD/COD₀ ratio and (c) TPh/TPh₀ for assays A1 and A2, and (d) TPh/TPh₀ for assays A3 and A4 over time.

Regarding the other experiments, the COD removal was similar for the A2 and A4 experiments. A2 showed a similar TPh removal to assay A3 (76%), whereas A4 presented approximately 50% removal. Regarding the variation of PS concentration, A2 presented a constant PS concentration value, whereas A4 showed a reduction of 18% in its concentration. The higher TPh removal for assays A1, A2, and A3 follows previous studies showing that using PS with RB, Zn, and Al improved the phenol mineralization compared with other PS [30,57,58]. Agreeing with the Al-Nu'airat et al. [59] study, the reaction of phenol with only ¹O₂, as the presence of •OH and phenoxy intermediates, was not found, leading to a conclusion that the ¹O₂ effectively degraded phenolic compounds.

3.3. The Effect of Initial Wastewater pH on the Photooxidation Process

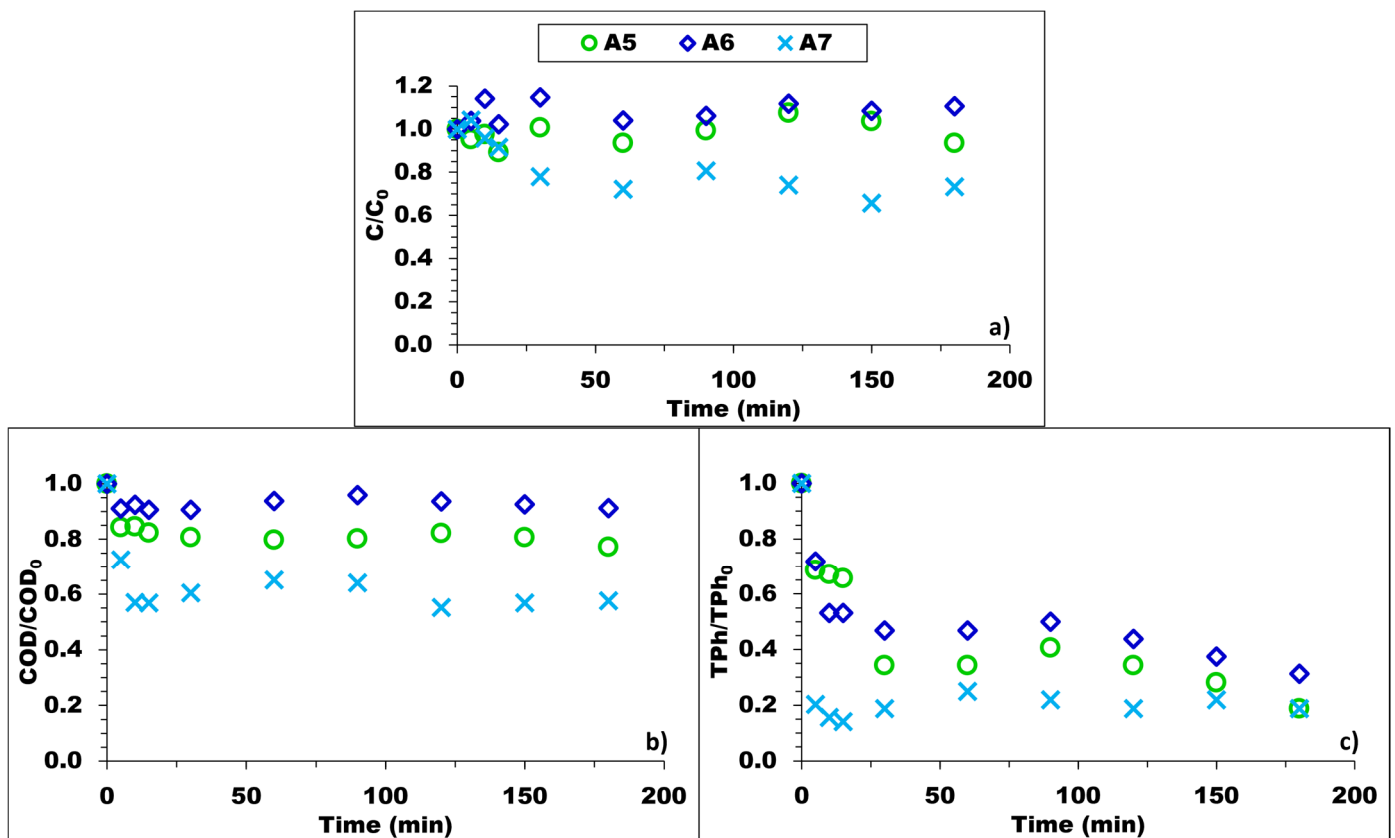
As a result of the optimal outcome obtained in assay A1, the ZnPcS₄ was utilized exclusively as the PS in subsequent experiments. The assays A5 to A7 evaluated the Ph effect on COD and TPh removal. Table 3 presents the working conditions during those assays.

The COD and TPh removals for assays A5 to A7 are presented in Figure 4, as well as the variation of PS concentration.

Table 3. Working conditions for assays A5 to A7.

| Assay | PS | [PS] (mol/L) | Wastewater pH | Average Solar Radiation (W/m ²) |
|-------|--------------------|--------------------|------------------|--|
| A5 | ZnPcS ₄ | 5×10^{-6} | 7.00 | 623 |
| A6 | | | 3.00 | 310 |
| A7 | | | 11.0 | 436 |

The pH effect is noticeable in COD and TPh removal. From Figure 8b, it is possible to conclude that a higher value of pH promotes a higher degradation of COD (42%) and TPh (81%). This finding is consistent with previous studies which indicated that lower pH values reduced the activity of the photooxidation process, leading to lower removal rates [57]. In Figure 8c, one can observe the pH effect on the phenol degradation. Previous studies reported that the TPh degradation strongly relies on the solution pH, as its degradation rate increases with the pH value [58]. As reported by Aimeur et al. [43], using a pH of 12 improved the phenol degradation, reaching complete phenolic compounds removal. In the first minutes of the reaction, the removal of TPh reaches its maximum for assay A7. Assay A6 needs the total experimental time to reach the maximum TPh removal (69%). The pH effect on phenolic compounds removal was also studied by Wenk et al. [54], where authors stated that phenol degradation is highly dependent on Ph values. According to the author's findings, as the pH of the system increased from 0 to 10, the redox potential of TPh also increased. The same is visible during this work, as the pH increase highly influences the phenol removal.

**Figure 8.** Photooxidation regarding the PH variation effect for assays A5 to A7: (a) variation of PS concentration during the assay time, (b) COD/COD₀ ratio, and (c) TPh/TPH₀ ratio over time.

Another visible effect of the change in pH is the bleaching of the PS: the higher the pH of the solution, the more degradation the PS presents (Figure 8a). For assay A6, where the

pH used was 3, the PS concentration was almost constant during the assay, mainly due to the difficulty of PS dissolution in an aquatic acid medium. Due to that, the PS concentration increased due to non-homogenous samples. By analyzing those results, a pH near 7 is preferable, as the PS bleaching is lower compared with higher pH values, and the reached TPh removals were almost the same (81%).

3.4. The Effect of the Initial PS Concentration on the Photooxidation Process

To optimize the photooxidation process, the PS concentration must be taken into account. The following assay set was established to access the PS concentration effect in COD and TPh removal. Table 4 presents the operating conditions of those assays.

Table 4. Operating conditions for assays A8 to A9.

| Assay | PS | [PS] (mol/L) | Wastewater pH | Average Solar Radiation (W/m ²) |
|-------|--------------------|---------------------|---------------|---|
| A8 | ZnPcS ₄ | 5×10^{-6} | 7 | 623 |
| A9 | | 3×10^{-6} | | 378 |
| A10 | | 10×10^{-6} | | 436 |

Figure 9 shows the COD and TPh removal under different PS concentrations and the PS concentration during the assays. The results obtained from the experiment revealed that the COD removal rates for all the assays were relatively similar (as shown in Figure 5b). However, it is worth noting that after a 30-min exposure to sunlight, a minor decrease in COD removal was observed for assay A10 (approximately 30%). It took a longer duration of 180 min for this assay to achieve the highest possible COD removal rate, which was measured at 40%.

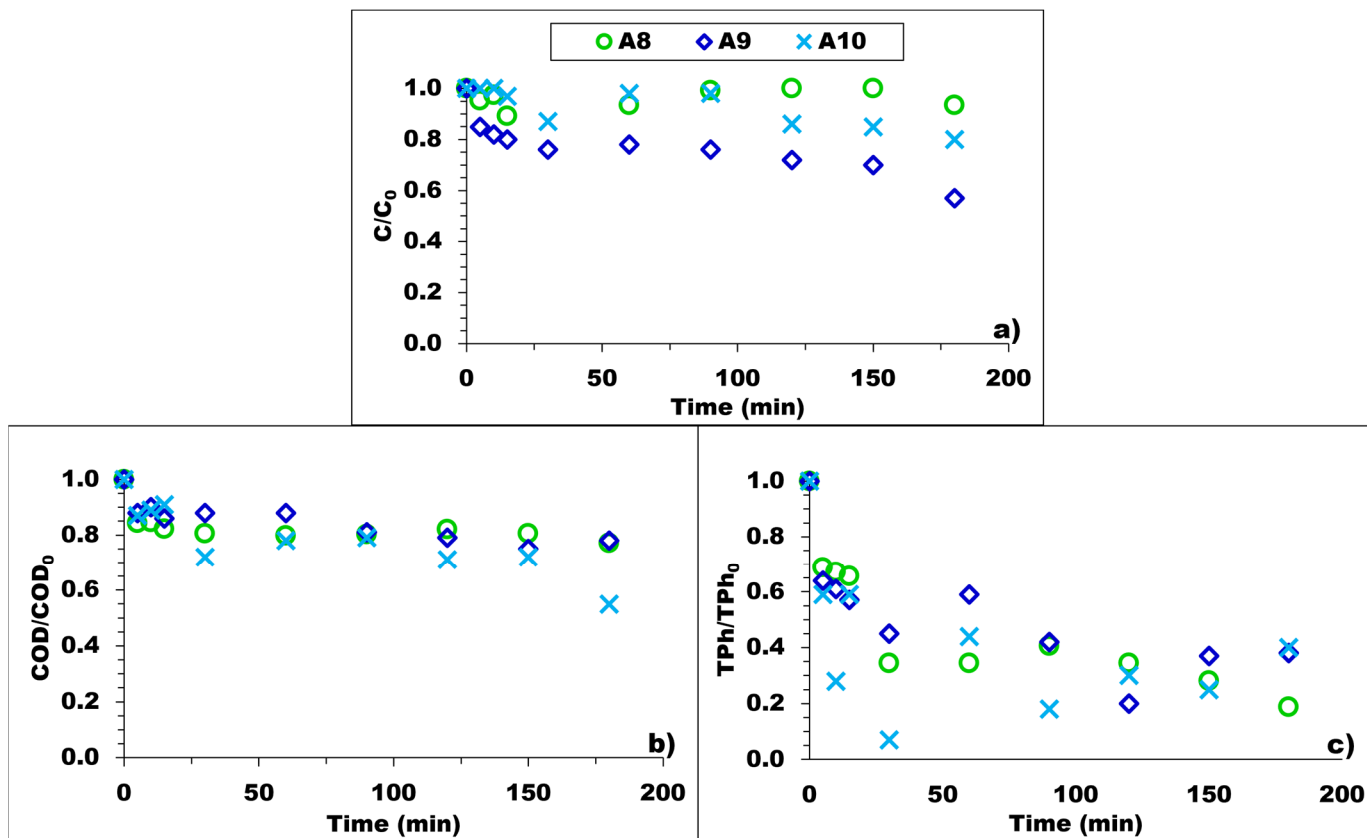


Figure 9. Photooxidation of assays A8 to A10 regarding the variation of PS: (a) variation of PS concentration during the assay time, (b) COD/COD₀ ratio, and (c) TPh/TPH₀ ratio over time.

Upon conducting the experiment on phenolic compounds, it was observed that after a duration of 30 min, the removal rates for assays A8, A9, and A10 reached 70%, 50%, and 90%, respectively (as depicted in Figure 9c). Notably, the assay with low PS concentration (A9) exhibited higher PS bleaching than the other assays. In particular, during the initial 30-min duration of the experiment, assay A8 did not display any signs of PS bleaching (as demonstrated in Figure 9a), which contrasts with the observations made for assays A9 and A10.

This fact agrees with what was stated by Aimeur et al. [43]; phenol degradation was not affected by molar ratios of [PS]/phenol ≥ 1 ; otherwise, for ratios lower than 1, the kinetics of phenol degradation decrease.

Once the main goal of the work is to recover the treated wastewater, it is important to evaluate the toxicological effect of the zinc compounds. Some authors have studied the neurotoxicity of zinc, showing promising results [60–62]. Besides affecting neuronal signaling, Morris and Levenson concluded that zinc-mediated neurotoxicity is also associated with regulating mitochondrial function and energy production. Additionally, the aggregation of amyloid beta peptides in Alzheimer's disease is another mechanism that contributes to this phenomenon [60]. Another application of metallated porphyrins and phthalocyanines is used in photodynamic therapy, where zinc showed promising results [63,64]. However, as the matrix used in this study may contain other substances, neurotoxicological studies with this matrix need to be conducted.

4. Conclusions

Using photosensitizers activated by sunlight presents a promising alternative for removing residual pollutants from wastewater that has undergone prior biological wastewater treatment. In this study, various photosensitizers (PS) were tested for their effectiveness in removing chemical oxygen demand (COD) and total phenols (TPh) from wastewater. Rose Bengal and ZnPcS₄ were found to be the most effective, achieving removal rates of 20% and 76% for COD and 23% and 81% for TPh, respectively. However, it was observed that Rose Bengal had a lower photostability compared to ZnPcS₄.

The effects of pH and PS concentration on the removal of TPh were further investigated using ZnPcS₄. It was found that the removal of TPh was highly dependent on the pH of the solution, with alkaline solutions being more effective due to an improved singlet oxygen quantum yield, which enhances the oxidation rate. At a pH lower than 7, the removal of COD and TPh was lower, at 9% and 69%, respectively. However, at a higher pH, the removal of COD and TPh improved significantly, reaching 42% and 81%, respectively. Nonetheless, the degradation of the PS was observed to be higher at pH levels other than 7. Therefore, it is recommended to maintain a pH of approximately 7 for optimal performance.

Regarding the effect of PS concentration, it was observed that a molar concentration of 5×10^{-6} mol/L demonstrated the best overall performance for the removal of TPh. These findings provide valuable insights into the optimization of solar-based wastewater treatment systems, which can potentially help mitigate environmental pollution. They promote water reuse, reducing the water footprint of winemaking industries.

Author Contributions: Conceptualization, D.G., R.C.M., A.N. and S.C.-S.; validation, R.C.M. and S.C.-S.; investigation, D.G.; resources, M.G.; data curation, D.G., R.C.M., S.C.-S. and A.D.S.; writing—original draft preparation, A.D.S.; writing—review and editing, A.D.S., A.N., M.G., R.Q.-F. and L.M.C.; visualization, A.D.S. and A.N.; supervision, R.C.M. and S.C.-S.; project administration, R.C.M., A.N., S.C.-S. and R.Q.-F.; funding acquisition, R.C.M., A.N., S.C.-S. and R.Q.-F. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Project SAFE—Water recovery in cellars using photosensitized oxidation, grant number POCI-01-0247-FEDER-039708.

Institutional Review Board Statement: Not applicable.

Acknowledgments: Authors gratefully acknowledge Project SAFE—Water recovery in cellars using photosensitized oxidation, POCI-01-0247-FEDER-039708.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Jiménez, B.; Navarro, I. Wastewater Use in Agriculture: Public Health Considerations. In *Encyclopedia of Environmental Management, Four Volume Set*; Jorgensen, S.E., Ed.; CRC Press: Boca Raton, FL, USA, 2015; p. 15, ISBN 9781351235860.
2. Bandinelli, R.; Acuti, D.; Fani, V.; Bindi, B.; Aiello, G. Environmental Practices in the Wine Industry: An Overview of the Italian Market. *Br. Food J.* **2020**, *122*, 1625–1646. [CrossRef]
3. Oliveira, M.; Costa, J.M.; Fragoso, R.; Duarte, E. Challenges for Modern Wine Production in Dry Areas: Dedicated Indicators to Preview Wastewater Flows. *Water Supply* **2019**, *19*, 653–661. [CrossRef]
4. Kumar, A.; Arienzo, M.; Quayle, W.; Christen, E.; Grocke, S.; Fattore, A.; Doan, H.; Gonzago, D.; Zandonna, R.; Bartrop, K.; et al. *Developing a Systematic Approach to Winery Wastewater Management*; Grape and Wine Research & Development Corporation: Adelaide, Australia, 2009.
5. Oliveira, M.; Duarte, E. Winery Wastewater Treatment-Evaluation of the Air Micro-Bubble Bioreactor Performance. In *Mass Transfer-Advanced Aspects*; InTech: London, UK, 2011; pp. 79–113, ISBN 9781498728515.
6. Vlyssides, A.G.; Barampouti, E.M.; Mai, S. Wastewater Characteristics from Greek Wineries and Distilleries. *Water Sci. Technol.* **2005**, *51*, 53–60. [CrossRef]
7. Zacharof, M.P. Grape Winery Waste as Feedstock for Bioconversions: Applying the Biorefinery Concept. *Waste Biomass Valorization* **2017**, *8*, 1011–1025. [CrossRef]
8. International Organisation of Vine and Wine Wine Production-First Estimates. Available online: https://www.oiv.int/sites/default/files/documents/PPTWorld%20Wine%20Production%20Outlook_2022_Press%20Conf.pdf (accessed on 3 April 2023).
9. Rodrigues, R.P.; Gando-Ferreira, L.M.; Quina, M.J. Increasing Value of Winery Residues through Integrated Biorefinery Processes: A Review. *Molecules* **2022**, *27*, 4709. [CrossRef] [PubMed]
10. Ioannou, L.A.; Puma, G.L.; Fatta-Kassinos, D. Treatment of Winery Wastewater by Physicochemical, Biological and Advanced Processes: A Review. *J. Hazard. Mater.* **2015**, *286*, 343–368. [CrossRef]
11. European Commission. The European Green Deal. *Eur. Comm.* **2019**, *53*, 24. [CrossRef]
12. European Commission. *A New Circular Economy Action Plan For a Cleaner and More Competitive Europe*; European Commission: Brussels, Belgium, 2020.
13. Cañadas, R.; Díaz, I.; Rodríguez, M.; González, E.J.; González-Miquel, M. An Integrated Approach for Sustainable Valorization of Winery Wastewater Using Bio-Based Solvents for Recovery of Natural Antioxidants. *J. Clean. Prod.* **2022**, *334*, 130181. [CrossRef]
14. Santos, J.R.F.; Rodrigues, R.P.; Quina, M.J.; Gando-Ferreira, L.M. Recovery of Value-Added Compounds from Winery Wastewater: A Review and Bibliometric Analysis. *Water* **2023**, *15*, 1110. [CrossRef]
15. Miklas, V.; Touš, M.; Miklasová, M.; Máša, V.; Horňák, D. Winery Wastewater Treatment Technologies: Current Trends and Future Perspective. *Chem. Eng. Trans.* **2022**, *94*, 847–852. [CrossRef]
16. The Council of the European Communities. *Council Directive 91/271/EEC of 21 May 1991 Concerning Urban Waste-Water Treatment*; LEX-FAOC013224; The Council of the European Communities: Luxembourg, 1991; pp. 14–15.
17. Nidheesh, P.V.; Couras, C.; Karim, A.V.; Nadais, H. A Review of Integrated Advanced Oxidation Processes and Biological Processes for Organic Pollutant Removal. *Chem. Eng. Commun.* **2022**, *209*, 390–432. [CrossRef]
18. Kundu, D.; Dutta, D.; Samanta, P.; Dey, S.; Sherpa, K.C.; Kumar, S.; Dubey, B.K. Valorization of Wastewater: A Paradigm Shift towards Circular Bioeconomy and Sustainability. *Sci. Total Environ.* **2022**, *848*, 157709. [CrossRef]
19. Obreza, T.A.; Boman, B.J.; Kadyampakeni, D.; Zekri, M.; Morgan, K.; Vashisth, T. Fertilizer Sources and Formulations. In *Nutrition of Florida Citrus Trees*; EDIS: Miami, FL, USA, 2020; Volume 2020, pp. 39–44.
20. Etchebarne, F.; Aveni, P.; Escudier, J.-L.; Ojeda, H. Reuse of Treated Wastewater in Viticulture: Can It Be an Alternative Source of Nutrient-Rich Water? *BIO Web Conf.* **2019**, *12*, 01009. [CrossRef]
21. Milani, M.; Consoli, S.; Marzo, A.; Pino, A.; Randazzo, C.; Barbagallo, S.; Cirelli, G.L. Treatment of Winery Wastewater with a Multistage Constructed wetland System for Irrigation Reuse. *Water* **2020**, *12*, 1260. [CrossRef]
22. European Union. Regulation 2020/741. *Off. J. Eur. Union* **2022**, 1–55.
23. Salgot, M.; Folch, M. Wastewater Treatment and Water Reuse. *Curr. Opin. Env. Sci. Health* **2018**, *2*, 64–74. [CrossRef]
24. Kim, H.; Kim, W.; MacKeyev, Y.; Lee, G.S.; Kim, H.J.; Tachikawa, T.; Hong, S.; Lee, S.; Kim, J.; Wilson, L.J.; et al. Selective Oxidative Degradation of Organic Pollutants by Singlet Oxygen-Mediated Photosensitization: Tin Porphyrin versus C60 Aminofullerene Systems. *Environ. Sci. Technol.* **2012**, *46*, 9606–9613. [CrossRef]
25. Valkov, A.; Raik, K.; Mualem-Sinai, Y.; Nakonechny, F.; Nisnevitch, M. Water Disinfection by Immobilized Photosensitizers. *Water* **2018**, *11*, 26. [CrossRef]
26. Sarma, S.J.; Das, R.K.; Brar, S.K. Singlet Oxygen Production by Organic Matter and Disintegration of Pathogens and Pollutants during Wastewater Treatment: How Important? *Hydrol. Curr. Res.* **2013**, *4*, e109. [CrossRef]
27. Zhang, Y.; Sivakumar, M.; Yang, S.; Enever, K.; Ramezani-pour, M. Application of Solar Energy in Water Treatment Processes: A Review. *Desalination* **2018**, *428*, 116–145. [CrossRef]
28. Pandey, A.K.; Reji Kumar, R.; Kalidasan, B.; Laghari, I.A.; Samykan, M.; Kothari, R.; Abusorrah, A.M.; Sharma, K.; Tyagi, V.V. Utilization of Solar Energy for Wastewater Treatment: Challenges and Progressive Research Trends. *J. Environ. Manag.* **2021**, *297*, 113300. [CrossRef]

29. Tai, C.; Zhang, S.; Wang, J.; Yin, Y.; Shi, J.; Wu, H.; Mao, Y. Solar-Induced Generation of Singlet Oxygen and Hydroxyl Radical in Sewage Wastewaters. *Environ. Chem. Lett.* **2017**, *15*, 515–523. [CrossRef]
30. DeRosa, M.C.; Crutchley, R.J. Photosensitized Singlet Oxygen and Its Applications. *Coord. Chem. Rev.* **2002**, *233–234*, 351–371. [CrossRef]
31. Foszpańczyk, M.; Bilińska, L.; Gmurek, M.; Ledakowicz, S. Heterogeneous Oxidation of Phenolic Compounds with Photosensitizing Catalysts Incorporated into Chitosan. *Catalysts* **2019**, *9*, 891. [CrossRef]
32. Thandu, M.; Comuzzi, C.; Goi, D. Phototreatment of Water by Organic Photosensitizers and Comparison with Inorganic Semiconductors. *Int. J. Photoenergy* **2015**, *2015*, 521367. [CrossRef]
33. Baptista, M.S.; Cadet, J.; Di Mascio, P.; Ghogare, A.A.; Greer, A.; Hamblin, M.R.; Lorente, C.; Nunez, S.C.; Ribeiro, M.S.; Thomas, A.H.; et al. Type I and Type II Photosensitized Oxidation Reactions: Guidelines and Mechanistic Pathways. *Photochem. Photobiol.* **2017**, *93*, 912–919. [CrossRef]
34. Mostafa, S.; Rosario-Ortiz, F.L. Singlet Oxygen Formation from Wastewater Organic Matter. *Environ. Sci. Technol.* **2013**, *47*, 8179–8186. [CrossRef] [PubMed]
35. Vivar, M.; Fuentes, M.; Torres, J.; Rodrigo, M.J. Solar Disinfection as a Direct Tertiary Treatment of a Wastewater Plant Using a Photochemical-Photovoltaic Hybrid System. *J. Water Process Eng.* **2021**, *42*, 102196. [CrossRef]
36. Brkic', D.; Forzatti, P.; Pasquon, I.; Trifiro', F. Homogeneous and Heterogeneous Photo-Oxygenation of 2,3-Dimethyl-2-Butene. *J. Mol. Catal.* **1977**, *3*, 173–184. [CrossRef]
37. Tratnyek, P.G.; Elovitz, M.S.; Colverson, P. Photoeffects of Textile Dye Wastewaters: Sensitization of Singlet Oxygen Formation, Oxidation of Phenols and Toxicity to Bacteria. *Environ. Toxicol. Chem.* **1994**, *13*, 27–33. [CrossRef]
38. Faust, D.; Funken, K.H.; Horneck, G.; Milow, B.; Ortner, J.; Sattlegger, M.; Schäfer, M.; Schmitz, C. Immobilized Photosensitizers for Solar Photochemical Applications. *Sol. Energy* **1999**, *65*, 71–74. [CrossRef]
39. Ozoemena, K.; Kuznetsova, N.; Nyokong, T. Photosensitized Transformation of 4-Chlorophenol in the Presence of Aggregated and Non-Aggregated Metallophthalocyanines. *J. Photochem. Photobiol. A Chem.* **2001**, *139*, 217–224. [CrossRef]
40. Zhang, X.F.; Wang, Y.; Niu, L. Titanyl Phthalocyanine and Its Soluble Derivatives: Highly Efficient Photosensitizers for Singlet Oxygen Production. *J. Photochem. Photobiol. A Chem.* **2010**, *209*, 232–237. [CrossRef]
41. Gryglik, D.; Gmurek, M. The Photosensitized Oxidation of Mixture of Parabens in Aqueous Solution. *Environ. Sci. Pollut. Res.* **2018**, *25*, 3009–3019. [CrossRef] [PubMed]
42. Neves, C.M.B.; Filipe, O.M.S.; Mota, N.; Santos, S.A.O.; Silvestre, A.J.D.; Santos, E.B.H.; Neves, M.G.P.M.S.; Simões, M.M.Q. Photodegradation of Metoprolol Using a Porphyrin as Photosensitizer under Homogeneous and Heterogeneous Conditions. *J. Hazard. Mater.* **2019**, *370*, 13–23. [CrossRef] [PubMed]
43. Aimeur, M.; Baudu, M.; Zermane, F.; Joussein, E.; Bouras, O. Evaluation of the Use of Free or Supported Phenalenone Based on Natural Halloysite for Phenol Photodegradation in Aqueous Solution. *J. Photochem. Photobiol. A Chem.* **2021**, *404*, 112904. [CrossRef]
44. APHA; AWWA; WEF. *Standard Methods for the Examination of Water and Wastewater*, 23rd ed.; Rice, E.W., Baird, R.B., Eaton, A.D., Eds.; American Public Health Association: Washington, DC, USA; American Water Works Association: Austin, TX, USA; Water Environment Federation: Wythe, VA, USA, 2017; ISBN 9780875532875.
45. Waterhouse, A.L. Determination of Total Phenolics. *Curr. Protoc. Food Anal. Chem.* **2002**, *6*, I1.1.1–I1.1.8.
46. Remucal, C.K. The Role of Indirect Photochemical Degradation in the Environmental Fate of Pesticides: A Review. *Environ. Sci. Process. Impacts* **2014**, *16*, 628–653. [CrossRef]
47. Ion, R.-M. Porphyrins and Phthalocyanines: Photosensitizers and Photocatalysts. In *Phthalocyanines and Some Current Applications*; InTech: Jakarta Selatan, Indonesia, 2017. [CrossRef]
48. Darwent, J.R.; Douglas, P.; Harriman, A.; Porter, G.; Richoux, M.C. Metal Phthalocyanines and Porphyrins as Photosensitizers for Reduction of Water to Hydrogen. *Coord. Chem. Rev.* **1982**, *44*, 83–126. [CrossRef]
49. Lindsey, J.S.; Taniguchi, M.; Du, H. PhotochemCAD. Available online: <https://www.photochemcad.com/> (accessed on 11 April 2023).
50. Kassab, K.; Al-Herrawy, A.Z. Photosensitized Inactivation of Cyst Forms of the Freshwater Amoeba *Vahlkampfia Hartmanni* by Aluminium (III) Phthalocyanine Tetrasulfonate. *Environmentalist* **2005**, *25*, 13–18. [CrossRef]
51. Anderson, K.E.; Bloomer, J.R.; Bonkovsky, H.L.; Kushner, J.P.; Pierach, C.A.; Pimstone, N.R.; Desnick, R.J. Recommendations for the Diagnosis and Treatment of the Acute Porphyrias. *Ann. Intern. Med.* **2005**, *142*, 439. [CrossRef] [PubMed]
52. Badminton, M.N.; Elder, G.H. Molecular Mechanisms of Dominant Expression in Porphyria. *J. Inherit. Metab. Dis.* **2005**, *28*, 277–286. [CrossRef] [PubMed]
53. Miller, J.S. Rose Bengal-Sensitized Photooxidation of 2-Chlorophenol in Water Using Solar Simulated Light. *Water Res.* **2005**, *39*, 412–422. [CrossRef] [PubMed]
54. Wenk, J.; Graf, C.; Aeschbacher, M.; Sander, M.; Canonica, S. Effect of Solution PH on the Dual Role of Dissolved Organic Matter in Sensitized Pollutant Photooxidation. *Environ. Sci. Technol.* **2021**, *55*, 15110–15122. [CrossRef] [PubMed]
55. Connor, M.O.; Helal, S.R.; Latch, D.E.; Arnold, W.A. Quantifying Photo-Production of Triplet Excited States and Singlet Oxygen from Ef Fl Uent Organic Matter. *Water Res.* **2019**, *156*, 23–33. [CrossRef] [PubMed]
56. Spagnul, C.; Turner, L.C.; Boyle, R.W. Immobilized Photosensitizers for Antimicrobial Applications. *J. Photochem. Photobiol. B Biol.* **2015**, *150*, 11–30. [CrossRef]

57. Gerdes, R.; Wöhrle, D.; Spiller, W.; Schneider, G.; Schnurpfeil, G.; Schulz-Ekloff, G. Photo-Oxidation of Phenol and Monochlorophenols in Oxygen-Saturated Aqueous Solutions by Different Photosensitizers. *J. Photochem. Photobiol. A Chem.* **1997**, *111*, 65–74. [[CrossRef](#)]
58. Nowakowska, M.; Kepczyński, M. Polymeric Photosensitizers 2. Photosensitized Oxidation of Phenol in Aqueous Solution. *J. Photochem. Photobiol. A Chem.* **1998**, *116*, 251–256. [[CrossRef](#)]
59. Al-Nu'airat, J.; Dlugogorski, B.Z.; Gao, X.; Zeinali, N.; Skut, J.; Westmoreland, P.R.; Altarawneh, M. Reaction of Phenol with Singlet Oxygen. *Phys. Chem. Chem. Phys.* **2018**, *21*, 171–183. [[CrossRef](#)]
60. Morris, D.R.; Levenson, C.W. Neurotoxicity of Zinc. *Neurotox. Met.* **2017**, *18*, 303–312. [[CrossRef](#)]
61. Sousa, M.S.; Alves, J.L.; Freitas, J.C.S.; Miraldo, J.N.; Sampaio dos Aidos, F.D.S.; Santos, R.M.; Rosário, L.M.; Quinta-Ferreira, R.M.; Quinta-Ferreira, M.E.; Matias, C.M. A Model of Zinc Dynamics Evoked by Intense Stimulation at the Cleft of Hippocampal Mossy Fiber Synapses. *Brain Res.* **2023**, *1807*, 148322. [[CrossRef](#)] [[PubMed](#)]
62. Corceiro, V.N.; Bastos, F.C.; Matias, C.M.; Dionísio, J.C.; Santos, R.M.; Rosario, L.M.; Quinta-Ferreira, R.M.; Quinta-Ferreira, M.E. Sulfamethoxazole Induces Zinc Changes at Hippocampal Mossy Fiber Synapses from Pregnant Rats. *Gen. Physiol. Biophys.* **2018**, *37*, 213–221. [[CrossRef](#)] [[PubMed](#)]
63. Ding, K.; Zhang, Y.; Si, W.; Zhong, X.; Cai, Y.; Zou, J.; Shao, J.; Yang, Z.; Dong, X. Zinc(II) Metalated Porphyrins as Photothermogenic Photosensitizers for Cancer Photodynamic/Photothermal Synergistic Therapy. *ACS Appl. Mater. Interfaces* **2018**, *10*, 238–247. [[CrossRef](#)] [[PubMed](#)]
64. Huang, K.; Zhang, H.; Yan, M.; Xue, J.; Chen, J. A Novel Zinc Phthalocyanine-Indometacin Photosensitizer with “Three-in-One” Cyclooxygenase-2-Driven Dual Targeting and Aggregation Inhibition for High-Efficient Anticancer Therapy. *Dye. Pigment.* **2022**, *198*, 109997. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.