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Optimization of Heterogeneous Photosensitized Oxidation for Winery Effluent Treatment

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Abstract: In this study, the heterogeneous photosensitized oxidation treatment of winery effluents was optimized using chitosan carriers immobilized with Zn(II) Phthalocyanine tetrasulfonic acid. The influence of main operating parameters such as initial pH, aeration flow rate, photocatalyst load, and concentration of the photosensitizer used in the photocatalysts' preparation was investigated. Results for chemical oxygen demand (COD) and phenolic content (TPh) removals are presented for each of the tests performed. Best reductions were obtained after 30 min of treatment in natural sunlight at an initial pH of 4.0 and an aeration flow of 2.8 L/min since it allowed reductions of 45% for COD and 73% for phenolic content (TPh). In addition, the possibility of reusing the photocatalysts during several cycles was also assessed, where an acidic initial pH allowed their reuse, being the only pH value studied where the leaching of the photosensitizer was not observed. In these conditions, the same photocatalysts were reused for six reaction cycles, and efficiency started to decrease after the third use. Thus, a greater mass and concentration of photosensitizer contributed to a superior reduction in organic matter. The results show that heterogeneous photosensitized oxidation using sunlight radiation as an energy source is an interesting approach for obtaining reusable water from winery effluents.

Keywords: photosensitized oxidation; photosensitizer; chitosan; wastewater treatment; water reuse; winery industry

1. Introduction

Water is an essential asset to life and the environment. Given its versatility, water has been excessively used, which results in a gradual decrease in the availability of good-quality water [1]. Among all the activities, the agriculture sector is the one that contributes the most to water consumption since it is responsible for 70% of all consumption [2]. The winery industry, included in this sector, is one major water consumer since the water needed per liter of wine produced can vary between 0.5 and 14 L. In addition, it is also important to consider the environmental impacts of this industry since it is estimated that the production of waste varies between 1.3 kg and 1.5 kg per liter of wine produced, of which 75% represents wastewater. The volume and composition of this wastewater are essentially associated with cleaning operations [3], and it also depends on the production season, be it the harvest or the bottling season [4]. The composition of winery wastewater consists of ethanol, sugars, esters, organic acids, and phenolic compounds [5]. The phenolic compounds mainly present in winery wastewater include flavanols (quercetin, kaempferol, and myricetin), catechins, benzoic acids (gallic, protocatechuic, 4-hydroxybenzoic, syringic, and gentisic), and cinnamic acids (p-coumaric) [6]. Its presence in the winery wastewater may hamper the biological treatment since these compounds are classified as biorefractory, i.e., are not

completely degraded by the biological treatments. Thus, if the aim is to reach reusable water from this effluent, it is necessary to develop an alternative treatment capable of removing these compounds efficiently, complementing the conventional activated sludges. The aim is to reduce the potential impacts related to this effluent, such as human health problems, like necrosis, and fauna and flora problems, such as pollution of water courses, soil and vegetation degradation, bad odor release, and plant growing inhibition [7]. Considering the aforementioned aspects and taking into account the high volume of wastewater produced by this industry [3], it would be interesting if the treatment applied could enable the reuse of this wastewater, allowing the diminishing of the environmental impacts and the water footprint of the winery industry [8].

Advanced Oxidation Processes (AOPs) have been shown to be efficient in organic matter removal [9]. These techniques are characterized by the generation of free radicals in situ, like the hydroxyl radical (HO•), known for its high oxidant power, which oxidizes organic matter until complete mineralization into carbon dioxide and water [10]. Examples of AOPs are the Fenton process, ozonation, and photocatalysis. The Fenton process uses the Fe^{2+} ion as a catalyst and hydrogen peroxide (H_2O_2) as an oxidant to form the HO• radical, which will successively oxidize and degrade organic matter [11]. Ozonation uses ozone (O_3) as an oxidant, which could react directly with organic matter (direct oxidation) or can be decomposed in HO•, which is responsible for the oxidation of pollutants (indirect oxidation) [12]. Photocatalysis uses heterogeneous photocatalysts that increase the reaction velocity [13] to remove organic and inorganic matter through the HO• radical [14]. A review of these processes was carried out by Ma et al. [12], where they investigated their efficiency on different types of effluents. All the processes studied in this work showed good COD removal for different effluents. However, it is stated that the application of this type of process at an industrial level can cause some drawbacks, as it can increase operational costs. In the work reported by Gmurek et al. [15], the authors presented the photosensitized oxidation treatment as an alternative to the AOPs as a way to reduce associated costs.

Photosensitized oxidation is a promising photochemical method for the removal of compounds that are difficult to degrade. Its application only requires three components: a radiation source, air or oxygen, and a photosensitizer (PS) [16]. Photosensitizers are chemical agents that are easily excited by the action of visible light and, when reacting with molecular oxygen, form singlets of oxygen ($^1O_2$), a strongly reactive species with the ability to oxidize resistant compounds [17]. The ideal photosensitizer must present high adsorption capacity in the region of the applied light spectrum, a long lifespan in the triplet state, and high photostability [18].

Photosensitized oxidation initiates by the absorption of radiation by the photosensitizer, allowing a photon transition from its ground state (PS^0) to the singlet excited state ($^1PS^*$). The transition from the latter to the triplet excited state ($^3PS^*$) happens due to a phenomenon of intersystem crossing (ISC), which represents the transition between two distinct electronic states without the presence of radiation [15].

Photosensitized oxidation involves two reactional mechanisms: type I and type II. In the type I mechanism, or radical photooxidation, radical ions are formed, which allow the oxidation of the substrate. The type II mechanism, or photooxidation by the oxygen singlet, comprises the transfer of energy from $^3PS^*$ to molecular oxygen, forming the oxygen singlet, which will act as an oxidizing agent responsible for substrate degradation [19]. This treatment can be applied in a homogeneous medium if the photosensitizer is dissolved directly in the effluent, or in a heterogeneous medium if the photosensitizer is immobilized in specific carriers [20]. While most works found in the literature involve the use of homogeneous photosensitizers, this still presents a crucial drawback that is related to the impossibility of recovering and reusing the catalyst [21]. The use of photocatalysts in the heterogenous system allows its easy separation from the reaction medium, enabling its future reuse [22] while improving the sustainability of the process [21]. It also reduces the photosensitizer photobleaching, which can happen after successive cycles of energy

absorption and emission, where the photosensitizer no longer absorbs energy, consequently stopping the production of oxygen singlets and the oxidation of organic matter [23].

This work aims to develop and optimize the heterogeneous photosensitized oxidation process to further eliminate organic matter and phenolic compounds still existing in wastewater from the winery industry after secondary treatment. Therefore, it is necessary to use a suitable photosensitizer as well as a carrier for photosensitizer immobilization.

Based on our previous studies [23], the Zn(II) Phthalocyanine tetrasulfonic acid (ZnPcS$_4$) has been selected as the most suitable photosensitizer when compared with other photosensitizers like Rose Bengal (RB), Al(III) phthalocyanine chloride tetrasulfonic acid (AlPcS4), and tetraphenylporphyrin (TPP), since it allowed greater reductions in COD and TPh, in addition to presenting greater photostability. The structural formula of ZnPcS$_4$ is presented in Figure 1. The degradation of a phenolic compound, such as 4-chlorophenol, was studied by Ozoemena et al. [24] using metallic phthalocyanines as photosensitizers such as AlPcS$_4$, ZnPcS$_4$, the respective mixture (AlPcS$_{mix}$ and ZnPcS$_{mix}$), and octacarboxylated phthalocyanines (AlOCOc and ZnOCPc) with pH variation. The mixture of phthalocyanines showed the best removal of pollutants for a pH of 10, while aluminum phthalocyanines showed higher stability when exposed to visible light. Thus, Gryglik et al. [25] studied the degradation of 2,4-dichlorophenol using homogeneous photosensitizers such as RB, AlPcS$_4$, ZnPcS$_4$, and meso-tetraphenylporphyrin-4,4′ (TPPS$_4$) with pH and O$_2$ concentration variation. All of the studied photosensitizers presented a removal efficiency of 100%, except for ZnPcS$_4$, which only removed 50% of this pollutant. Overall, the best results were obtained in an alkaline medium, using a higher O$_2$ concentration in the reaction mixture and sunlight.
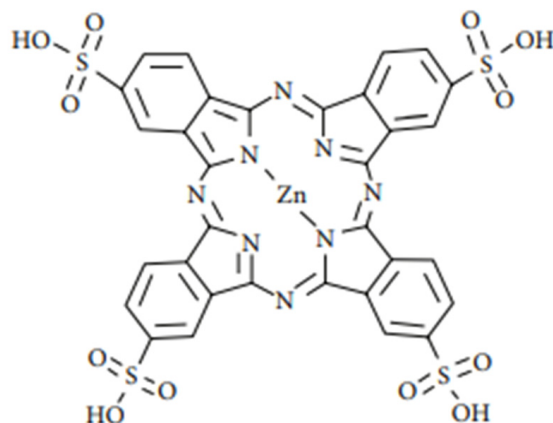

Figure 1. Structural formula of ZnPcS$_4$. Adapted from [25].

The immobilization of the chosen photosensitizer (ZnPcS$_4$) in chitosan carriers exhibited superior photocatalytic activity in our previous studies, the results of which have not yet been published. Chitosan is a natural biopolymer derived from chitin, consisting of hydroxyl (R-OH) and amine (R-NH$_2$) functional groups. It is a natural polysaccharide extracted from crustaceans such as shrimp or from the exoskeleton of arthropods and from the cell walls of yeast and fungi [26]. It is a low-cost, biodegradable, renewable, non-toxic, biocompatible, and chemically stable material, making it a viable option for complying with sustainable practices. These characteristics have contributed to the use of chitosan as a carrier in photosensitized oxidation reactions, allowing its reuse and reducing the photosensitizer leaching [27].

The efficiency of photosensitizers in a heterogeneous medium was investigated by Gmurek et al. [28], where two photosensitizers (AlPcS$_4$ and ZnPcS$_4$) were immobilized in chitosan carriers. The effectiveness of these photocatalysts was evaluated by the degradation of two pollutants, such as 2,4-dichlorophenol and benzylparaben. The results showed that these photocatalysts are able to remove 100% and 70% of the pollutants studied, respectively, while using AlPcS$_4$ and ZnPcS$_4$ as photosensitizers, respectively. The authors

also concluded that a greater amount of photosensitizer contributes to the greater removal of pollutants. This study emphasizes the importance of multiple uses of photocatalysts, as it is important for the development of this technology, as well as for economic reasons. The removal of the same pollutants while using the same photosensitizers immobilized in chitosan carriers was also studied by Olak-Kucharczyk et al. [29], where they achieved 100% removal for both cases. In this study, the effect of temperature on pollutant removal was also evaluated, where they concluded that the photosensitized oxidation process can occur both in summer and in winter.

To our knowledge, this is the first paper to deal with the application of heterogenous photosensitized oxidation for effluent purification. Up to now, this process has been employed mainly for the model aqueous environment [16,25]. However, there is a lack of information about its applicability in a highly polluted environment. Therefore, the main aim was the optimization of key parameters such as initial pH, aeration rate, the concentration of the photosensitizer solution, and photocatalyst load in the photosensitized decontamination of winery effluents. The possibility of reusing the photocatalyst during several cycles was also assessed. Treated wastewater characterization over time was performed through Chemical Oxygen Demand (COD) and Total Phenolic Content (TPh) values to evaluate the feasibility of this technique in the treatment of winery wastewater. In addition, were also determined other parameters, like Biochemical Oxygen Demand (BOD), total suspended solids (TSS) content, and toxicity level, to evaluate the treatment's capacity to reach the limits imposed in the legislation for water reuse [30].

2. Materials and Methods

2.1. Materials

The effluent used in the present work was collected at the exit of the Wastewater Treatment Plant (WWTP) of a Portuguese wine cellar located in the Douro region, from now on called E1. This sample was stored in the dark at 4 °C. The physicochemical characterization of this effluent is shown in Table 1.

Table 1. Physicochemical characterization of the studied effluent.

Effluent	pH	COD (mg_{O2}/L)	BOD$_5$ (mg_{O2}/L)	TPh (mg_{EAG}/L)	TSS (mg/L)	Toxicity Inhibition (%)
E1	8.7	133	30	38.7	52.04	76.6 (Very strong)

Zn(II) Phthalocyanine tetrasulfonic acid (ZnPcS$_4$), used as a photosensitizer, was purchased from Frontier Scientific. Chitosan from shrimp cells (degree deacetylation $\geq$ 75%) used as a photosensitizer carrier was purchased from Sigma-Aldrich.

2.2. Methods

Photocatalyst preparation was divided into two procedures: chitosan carrier preparation and photosensitizer immobilization. Chitosan carriers were produced by the phase inversion method described elsewhere [31], where an aqueous solution of chitosan in acetic acid was prepared. Firstly, two solutions of 100 mL each were prepared: one of chitosan at 6% (*w/w*) and the other of acetic acid at 8% (*v/v*). The second solution is then slowly added to the first one, with stirring. Then, the resulting mixture is left in the dark for 24 h to undergo the degassing process. After this process, the chitosan solution was dropped by a syringe into a solution of NaOH at 10% (*w/w*), with constant magnetic stirring, to obtain the chitosan particles. These particles were kept in the solution for 1 h so that they settled at the bottom of the beaker, suggesting that reticulation was accomplished and that the carriers were viable. Before the immobilization step, these carriers were washed in sequential deionized water baths until the pH of the washing water equaled the pH of the water before washing, allowing them to be stored at a neutral pH and at a temperature between 3 °C and 4 °C. Photosensitizer immobilization was carried out by an adsorption

process, where a standard photosensitizer aqueous solution with a known concentration (90 ppm, 130 ppm, or 180 ppm, depending on the tests performed) was mixed with the chitosan carriers in a 1:1 relation, i.e., for every 1 g of carriers, 1 mL of photosensitizer solution is required. The immobilization process was completed after 24 h in the dark, and then the photocatalysts were submitted to sequential baths in deionized water to remove the portion of photosensitizer that was not immobilized. Samples from these baths were collected to evaluate the immobilization efficiency by measuring their absorbance in the Lan Techniques spectrophotometer (SP-2100UV). All prepared photocatalysts showed a photosensitizer adsorption efficiency greater than 97%. After these two steps, the photocatalysts were prepared and ready to use.

The photosensitized oxidation process was carried out in a glass graduated cylinder with a volume of 250 mL, from now on called reactor. Firstly, the effluent pH was adjusted with sulfuric acid (H_2SO_4) to decrease its initial value until it reached the desired value, between 4.0 and 8.7, depending on the experiments performed. A volume of 150 mL of the effluent was added into the reactor, followed by the photocatalysts, previously weighted according to the intended load. Then, the reaction mixture was aerated by an air pump and was submitted to natural sunlight, which was the source of radiation used to excite the photosensitizer. The reaction took place during 30 min of solar exposure, and samples were collected periodically. After the reaction, the photocatalysts were collected by filtration from the reaction mixture.

The reaction evolution was evaluated by determining COD and TPh. Chemical oxygen demand was determined by the dichromate method, which is based on the method approved by USEPA 410.4 for COD quantification of superficial and residual waters [32] using a Hanna Instruments COD reactor (HI-839800) and a Wastewater Treatment Photometer (HI-83224). Total phenolic content was evaluated using the Folin–Ciocalteu reagent, according to the procedure described elsewhere [33], using the Lan Techniques spectrophotometer (SP-2100UV) to measure the absorbance of each sample. Biochemical Oxygen Demand was quantified by measuring dissolved oxygen before and after five days of incubation of a culture of microorganisms at 22 °C, using the Hanna Instruments dissolved oxygen meter (HI-98198), as described in Section 5210 of Standard Methods for the Examination of Water and Wastewater, published by the American Public Health Association (APHA) [34]. The solid content was analyzed by the procedure described in Section 2540 of Standard Methods for the Examination of Water and Wastewater, published by the American Public Health Association (APHA) [35], where the total solids present in the effluent are determined. These represent the organic and inorganic matter that remains in the sample after evaporation at 105 °C, using a stove (BINDER E 28), and 550 °C, using a muffle (P-SELECTA SELECT-HORN), respectively. Toxicity was evaluated by the growth inhibition of *Nasturtium officinalis* roots, following the procedure described elsewhere [36].

In addition, an adsorption test was performed to evaluate the efficiency of the photosensitized oxidation process. This test was carried out since the chitosan carriers have high porosity, which can lead to the adsorption of contaminants on their surface without being oxidized and consequently to the fouling of the catalyst, leading to its deactivation and shortening its lifetime [37]. The adsorption test was performed like the photosensitized oxidation process, but requires a dark environment to avoid photolysis and/or photocatalysis.

3. Results and Discussion

3.1. Adsorption Test

The influence of adsorption on the photosensitized oxidation process was evaluated at the initial pH of E1. It was found that there is no significant adsorption of contaminants on the immobilized carrier, as it only decreased 6% of COD and nothing of TPh. This may be associated with the fact that the catalysts' active sites were occupied by the photosensitizer; therefore, there were no sites available to adsorb the contaminants present in winery wastewater. This agrees with the study of Chang et al. [38], where the active sites of the

catalyst were occupied with H_2O, which led to a decrease in efficiency, since the pollutant was not absorbed as the H_2O blocked the active sites.

3.2. Influence of pH

One of the most essential parameters in water treatment when using photosensitized oxidation is the pH value [28]. Therefore, to evaluate the influence of pH in the photosensitized oxidation process, experiments were carried out at different pH values that vary between 4.0 and 8.7. Each assay performed under given conditions was duplicated. Table 2 presents the working conditions during those assays regarding the initial wastewater pH, photocatalyst load, concentration of the photosensitizer solution used in the immobilization process, aeration flow, and the average solar radiation.

Table 2. Working conditions of the experiments with pH variation.

pH	Photocatalyst Load (g/mL)	Concentration PS Solution (ppm)	Aeration Flow (L/min)	Average Solar Radiation (W/m^2)
8.7				666
7.0				660
6.0	0.167	90	2.8	833
4.0				719

Figure 2 shows that an acidic medium (pH 4.0) favors the removal of COD and TPh since it enables a reduction of 45% and 73%, respectively, after only 30 min of treatment. These reductions were higher than the ones verified in the adsorption process, suggesting that both COD and TPh parameters are being oxidized by the photosensitized oxidation process. It should be noted that the use of an acidic medium in this treatment, which aims to reuse water, needs to have a neutral pH to comply with Portuguese legislation for water reuse for irrigation (pH between 6.0 and 9.0) [30]. Thus, after treatment, it may be necessary to adjust the pH, which can increase operating costs. In the work reported by Gmurek et al. [28], it is stated that an alkaline pH increases the degradation of one phenolic compound, reaching its complete removal. Agreeing with Olak-Kucharczyk et al. [29], they achieved complete removal of the same phenolic compound for a pH value of 9.0. Although the conclusions drawn from the literature are not consistent with those obtained in this work, it is important to consider that there was a high leaching of photosensitizer from chitosan supports when tests were carried out at pH values above 6.0 (data not shown). As reported by Cuthbert et al. [39], the lack of covalent bonds can result in the leaching of the photosensitizer, leading to a decrease in reaction performance, which may explain the low oxidation efficiency observed for initial pH equal to or greater than 6.0.
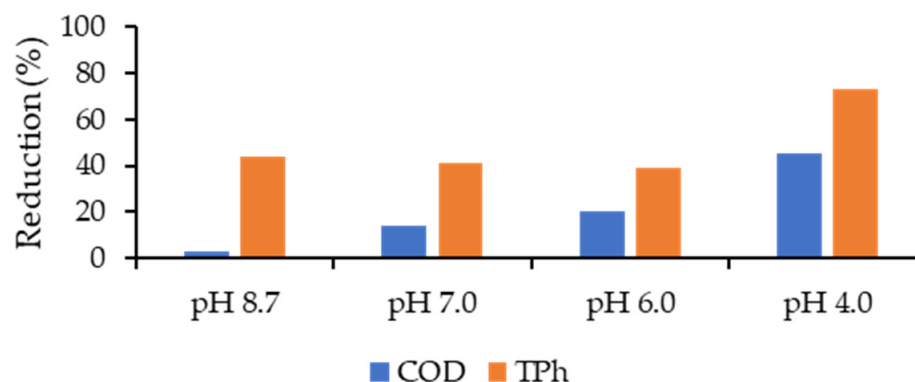

Figure 2. COD and TPh reduction with pH of the reaction mixture.

Other physicochemical parameters were also determined, such as BOD_5, TSS, and toxicity, to assess the differences between the initial and final effluent (Table 3). Despite the

interesting reduction obtained for COD and TPh, these results show a slight increase in suspended solid content at pH 4.0, which can be explained by the partial disintegration of chitosan carriers observed at this pH. Regarding BOD_5, the photosensitized oxidation treatment allowed a reduction in this parameter for both pH 8.7 and 6.0 while allowing for compliance with Portuguese legislation for this parameter of water reuse for irrigation (10 mg_{O2}/L) [30] to a pH of 6.0. On the other hand, results for toxicity levels show an improvement in these levels for experiments carried out at pH 8.7 and 4.0 when compared with the initial effluent, agreeing with the study by Foszpańczyk et al. [40], where toxicity levels decreased after 180 min of photosensitized oxidation treatment. In another work, Foszpańczyk et al. [16] studied the removal and toxicity levels of 10 aqueous contaminants, including phenolic compounds and parabens. Using chitosan carriers and sunlight, they removed over 50% of all pollutants and lowered the toxicity levels of 7 of those 10, as they presented lower toxicity than their parent compounds.

Table 3. Physicochemical parameters of the treated effluent with pH variation.

Parameters	pH	BOD_5 (mg_{O2}/L)	TSS (mg/L)	Toxicity Level
				Inhibition (%)
Initial Effluent	8.7	30	52.04	76.6 (Very strong)
Treated Effluent	8.7	19	10.20	29 (moderate)
	7.0	- [i]	-	-
	6.0	8	-	-
	4.0	-	114.3	56 (strong)

Note(s): [i] Dash (-) means that no values were determined.

Suzuki et al. [41] investigated the use of three oxidants (O_3, UV radiation, and a photocatalyst) for phenol degradation. These technologies were implemented separately and combined to minimize the associated costs. The results show that all oxidants are effective in removing 100% of the phenol content, except ozone alone. However, this type of technology is usually associated with higher costs, which represents a disadvantage when implemented on a larger scale. Martins and Ferreira [42] investigated the Fenton process and ozonation as a post-treatment to complement the activated sludge process used in phenolic effluents. The authors found that Fenton was a viable option as it allowed the removal of all phenolic content. That said, it is possible to conclude that other types of AOPs are also feasible options to remove all phenolic content. However, it is important to consider the high costs associated with them in the case of future applications.

3.3. Influence of Aeration Flow

The amount of oxygen present in the air represents one of the main components of the photosensitized oxidation process application, as it is directly related to the production of singlet oxygen [28]. Therefore, it is relevant to evaluate the influence of the aeration flow parameter in organic matter removal. As the results obtained here may be of some interest for a future industrial application, only the atmospheric air was evaluated as a source of oxygen, since the use of oxygen in other concentrations, like pure oxygen, would entail higher costs [43]. In addition to the oxygen concentration, different flow rates can also promote agitation of the reaction mixture [44]. Therefore, the efficiency of the process for two different aeration flow rates using atmospheric air was compared, resulting in measurements of 2.8 L/min and 4.8 L/min. Each experiment performed under given conditions was duplicated, and its working conditions are presented in Table 4.

Table 4. Working conditions of the experiments performed with aeration flow variation.

pH	Photocatalyst Load (g/mL)	Concentration PS Solution (ppm)	Air Flow (L/min)	Average Solar Radiation (W/m^2)
4.0	0.167	90	2.8 4.8	719 724

Figure 3 shows the effect of the aeration flow on the degradation of COD and TPh. The results obtained show a slight increase in the reduction in COD and TPh with the rise of the aeration flow since a flow of 4.8 L/min removed 46% of COD and 75% of TPh, while a flow of 2.8 L/min removed 45% of COD and 73% of TPh. Although a higher aeration flow contributes to a slightly superior removal of organic matter, the reduction is not significant to justify the use of a bigger aeration flow, which would translate into higher investment and operational costs [43]. Gmurek et al. [28] studied the influence of oxygen content using argon, air, pure oxygen, and an O_2/N_2 mixture. Argon did not promote any contaminant removal, while air removed about 50% of them. Regarding pure oxygen and the O_2/N_2 mixture, removals above 70% were obtained for both situations. The authors also state that above a certain concentration of oxygen, there is no influence on the reaction rate, as saturation of the reaction mixture is observed. That being said, the most viable option in the forthcoming stages will be the aeration flow of 2.8 L/min since, in addition to allowing good reductions, it also allows a reduction in the costs associated with photosensitized oxidation treatment.
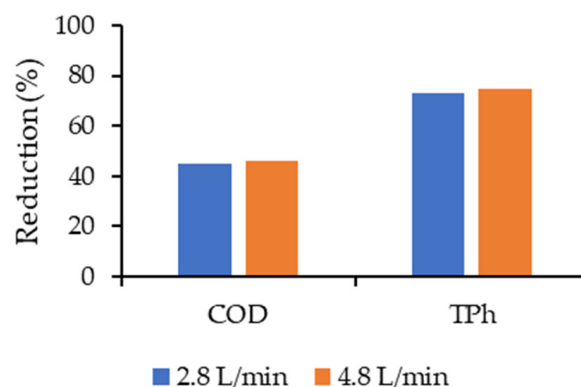
Figure 3. COD and TPh reduction with the aeration flow.

Another physicochemical parameter, such as BOD_5, was also determined. However, this value was only determined for the assay performed with an aeration flow of 4.8 L/min, where a value of 4 mg_{O2}/L was obtained. However, as the reductions obtained for both aeration flows are similar, this BOD_5 value could be compared to those presented in Table 3, which corresponds to the values obtained with an aeration flow of 2.8 L/min. This BOD_5 value of 4 mg_{O2}/L (that was obtained with an initial pH of 4.0) suggests that there is a decrease in the BOD_5 value as the pH becomes more acidic, fulfilling the Portuguese legislation for water reuse for irrigation (10 mg_{O2}/L) [30].

3.4. Photocatalyst Reuse

The photosensitized oxidation treatment in a heterogeneous medium is based on the use of catalysts in an insoluble form, easily separated from the treated effluents. In these cases, it is relevant to understand its activity and lifetime since stability is a key factor when selecting a heterogeneous catalyst [28]. Since a pH of 4.0 was the only situation where no photosensitizer leaching was observed (data not shown), it was considered that these photocatalysts could be reused for this pH value. Therefore, the possibility of reuse was evaluated by performing successive tests with the same particles and under the same operational conditions (presented in Table 5). Each experimental test performed was

named a "cycle" for clarity purposes. After each cycle, the photocatalysts were collected by filtration from the reaction mixture. The recovered photocatalysts were added to a new reaction mixture to start the next cycle under the same operating conditions.

Table 5. Working conditions of the experiments performed while reusing photocatalysts.

Cycle	pH	Photocatalyst Load (g/mL)	Concentration PS Solution (ppm)	Air Flow (L/min)	Average Solar Radiation (W/m^2)
1					724
2					794
3					778
4	4.0	0.167	90	4.8	759
5					822
6					334
7					776

Figure 4 shows the results obtained in these experiments, where a downward trend in the reduction in COD and TPh over the cycles is observed. COD reduction is constantly maintained and over 40% until the third cycle, diminishing until it reaches a value of 12%. Although TPh reduction presents a downward trend, the TPh removal is always superior to 60%. Furthermore, in these tests, it was verified that the chitosan beads suffered some disintegration over time, which resulted in a slight leaching of the photosensitizer (represented by photosensitizer concentration along the time), which could have caused the decrease in COD and TPh reduction over the cycles, since the evolution of the reaction is directly related with the progressive loss of photosensitizer concentration [45]. Therefore, based on these results, one can conclude that the photocatalysts can be reused up to three times using these operational conditions without significantly affecting the reduction efficiency.
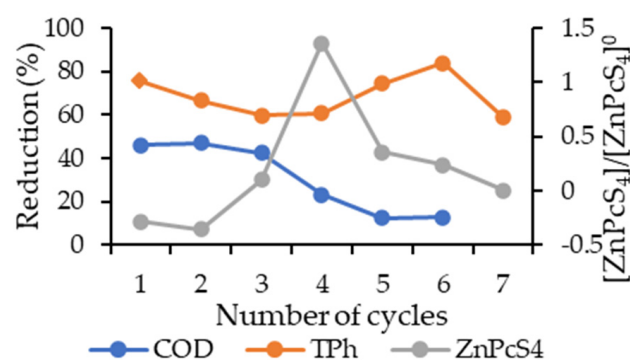

Figure 4. COD and TPh reduction evolution and leaching of ZnPcS$_4$, with the number of cycles.

The viability study of photocatalysts through their reuse has been investigated in several studies as it is of interest from an environmental and economic point of view in case of future implementation in industrial applications [46]. The research presented by Gmurek et al. [28] demonstrated that the photocatalysts of chitosan can be reused up to 8 or 10 times, depending on the immobilized photosensitizer, AlPcS$_4$ or ZnPcS$_4$, respectively, as well as the pollutant, phenol or paraben, respectively. This agrees with Foszpańczyk et al. [16] study, where they demonstrated the viability of chitosan carriers as a reusable green catalyst for 12 successive cycles. The phenol degradation rate showed a decrease in the 5th and 12th cycles, which the authors claim may be associated with the accumulation of intermediates in the active sites of the catalyst. In the study developed by Hu et al. [47], they evaluated the possibility of the reuse of an anionic resin immobilized with AlPcS$_4$ for the removal of a phenolic compound. The authors demonstrated that the reuse of this resin in five successive cycles is only feasible in the presence of hydrogen peroxide (H$_2$O$_2$) since this compound eliminates the intermediates formed during the reaction. Although several studies evaluate the reuse of photocatalysts, it is important to consider that the

results obtained depend on the photosensitizer, the carrier, and of course, the contaminant that is being treated [28].

3.5. Influence of Photocatalyst Load

To evaluate the influence of photocatalyst load, several tests were carried out using 0.100 g/mL, 0.167 g/mL, and 0.267 g/mL of photocatalysts (15 g, 25 g, and 40 g, respectively, in 150 mL of effluent). Each experiment performed under a different photocatalyst load was duplicated, and its working conditions are presented in Table 6.

Table 6. Working conditions of the experiments performed with photocatalyst load variation.

pH	Photocatalyst Load (g/mL)	Concentration PS Solution (ppm)	Air Flow (L/min)	Average Solar Radiation (W/m^2)
4.0	0.100 0.167 0.267	90	2.8	677 719 787

In these experiments, an increase in TPh reduction with the photocatalyst load increase was observed (as shown in Figure 5), where a reduction of 91%, 73%, and 61% for 0.267 g/mL, 0.167 g/mL, and 0.100 g/mL of photocatalysts was obtained, respectively. However, the same results were not reached for COD reduction since a smaller reduction was obtained for 0.167 g/mL of the photocatalyst.
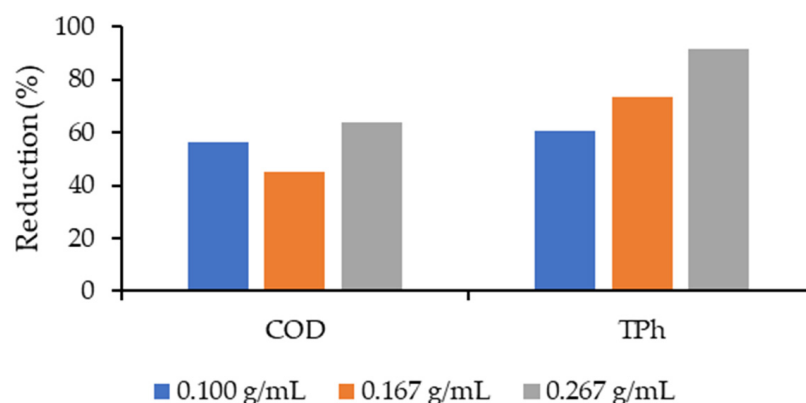

Figure 5. COD and TPh reduction with photocatalyst load.

Table 7 shows the effect of the photocatalyst load on parameters such as BOD$_5$ and TSS. These results reveal that using 0.100 g/mL or 0.167 g/mL of photocatalysts does not contribute to a difference in BOD$_5$ values (5 mg$_{O2}$/L and 4 mg$_{O2}$/L, respectively). Lastly, a slight increase was observed in suspended solid content only for 0.167 g/mL.

Table 7. Physicochemical parameters of the treated effluent with the photocatalyst load.

Parameters	Photocatalyst Load (g/mL)	BOD$_5$ (mg$_{O2}$/L)	TSS (mg/L)	Toxicity Level Inhibition (%)
Initial Effluent	-- [i]	30	52.04	76.6 (Very strong)
Treated Effluent	0.100 0.167 0.267	5 4 [ii] -	52.38 114.3 40.47	29 (moderate) - [iii] -

Note(s): [i] Double dash (--) means that it does not apply. [ii] This value corresponds to that obtained with an aeration flow of 4.8 L/min (see Section 3.3). [iii] Dash (-) means that no values were determined.

Overall, these results show a higher efficiency for the tests performed using 0.267 g/mL of the photocatalyst, agreeing with the study of Gmurek et al. [28], where an increase in catalyst load from 15.8 g to 70 g allowed a reduction improvement from 30% to 60%. However, for the COD parameter, a greater reduction for a higher mass was not achieved in tests performed with 0.167 g/mL of photocatalysts, which may be associated with experimental errors. That said, the results are not conclusive about the most effective photocatalyst load.

3.6. Influence of Photosensitizer Concentration

In this section, the influence of the concentration of the photosensitizer solution used for the immobilization process of the chitosan carriers was assessed. Thus, three different concentrations were studied: 90 ppm, 130 ppm, and 180 ppm. Each assay performed under given conditions was duplicated. Table 8 present the working conditions during those assays.

Table 8. Working conditions of the experiments performed with concentration of PS solution variation.

pH	Photocatalyst Load (g/mL)	Concentration PS Solution (ppm)	Air Flow (L/min)	Average Solar Radiation (W/m^2)
4.0	0.167	90	2.8	719
		130		787
		180		730

Figure 6 shows an increase in COD reduction for superior concentrations: 45%, 50%, and 51% for 90 ppm, 130 ppm, and 180 ppm, respectively. The same tendency was identified for TPh removal, except for 130 ppm (which may be associated with experimental errors), reaching a reduction of 73% and 83% for a concentration of 90 ppm and 180 ppm, respectively. The effect of the immobilized photosensitizer concentration was assessed by Hu et al. [47], who demonstrated an increase in the reaction rate with concentration until it reached 1.0 wt%. A further increase in concentration did not promote a higher reaction rate, suggesting that higher concentrations can lead to light shielding on the catalyst surface.
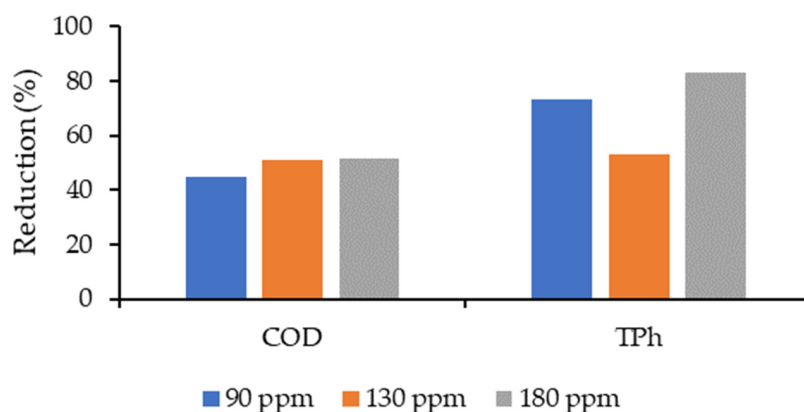

Figure 6. COD and TPh reduction with photosensitizer concentration.

The results obtained for BOD$_5$, TSS, and toxicity are shown in Table 9. With regard to the TSS content, an increase is observed only for a concentration of 90 ppm, which suggests a growth of this parameter with the reduction in the photosensitizer concentration. The results obtained for BOD$_5$ reveal an increasing trend with photosensitizer concentration. Regarding toxicity results, it is possible to verify that a higher concentration reduces the toxicity of the effluent.

Table 9. Physicochemical parameters of the treated effluent with the concentration of PS solution.

Parameters	Concentration PS Solution (ppm)	BOD$_5$ (mg$_{O2}$/L)	TSS (mg/L)	Toxicity Level
				Inhibition (%)
Initial Effluent	-- [i]	30	52.04	76.6 (Very strong)
Treated Effluent	90	4 [ii]	114.3	56 (strong)
	130	19	42.86	18 (weak)
	180	20	35.71	- [iii]

Note(s): [i] Double dash (--) means that it does not apply. [ii] This value corresponds to that obtained with an aeration flow of 4.8 L/min (see Section 3.3). [iii] Dash (-) means that the value was not determined.

Overall, the results show a higher reduction in all parameters in the tests performed with an immobilization concentration of 180 ppm. However, the results obtained for a concentration of 130 ppm are very similar to those for 180 ppm, which could be related to the light shielding reported by Hu et al. [47], so a higher concentration does not seem to be of great interest from a techno-economic point of view. Although the values obtained for 180 ppm seem to be promising in what concerns COD and TPh reductions, which lead to a significant decrease in the toxicity level, the BOD$_5$ parameter now presents a value above the limit imposed by Portuguese legislation (10 mg$_{O2}$/L) [30]. In addition, keeping in mind that these results may have some associated experimental errors, further tests should be performed in the future to clarify the influence of photosensitizer concentration.

4. Conclusions

This study evaluated the application of photosensitized oxidation in the treatment of winery wastewater, assessing the influence of initial pH, aeration flow, photocatalyst reuse, photocatalyst load, and concentration of the photosensitizer solution.

An initial pH of 4.0 proved to be favorable for the removal of COD and TPh. The successive tests performed with the photocatalysts at this pH showed that they can be used up to three times without losing the reduction efficiency of the organic matter and phenolic compounds. An aeration flow of 2.8 L/min was more advantageous since it allowed a similar reduction to the one obtained for a higher rate. The increase in the photocatalyst load and the concentration of the photosensitizer solution promoted, in a general way, the reduction in COD and TPh. However, the photocatalyst load and the concentration of the PS solution used in the immobilization step must be further studied to prove the preliminary results obtained.

That being said, it was concluded that the most viable option for the application of photosensitized oxidation in the treatment of winery wastewater aiming for its reuse is the use of an initial pH of 4.0 and an aeration flow of 2.8 L/min, since it allowed an average reduction of 45% of COD and 73% of TPh after only 30 min of reaction.

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