CELLULOSE CHEMISTRY AND TECHNOLOGY

OPTIMIZATION OF A PHOTOCATALYTIC PROCESS FOR REMOVAL OF PHENOLIC COMPOUNDS FROM WASTEWATER GENERATED IN THE PRODUCTION OF CELLULOSE FROM *PINUS RADIATA* AND *EUCALYPTUS GRANDIS* WOOD

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Received November 18, 2023

This study aimed to improve the sustainability of the kraft pulp production process by recovering *Pinus radiata* and *Eucalyptus grandis* wastewater generated during the bleaching process. The effluents were obtained from the first alkaline extraction stage (E_0) of the ECF bleaching sequence used to produce white Kraft cellulose, considering that this stage is where the highest contamination by phenolic compounds occurs and the effluent exhibits an intense color. A photochemical oxidation system, utilizing $TiO_2/S_2O_8^{2-}/UV$, was implemented to generate *in situ* two highly oxidizing radical species, with high redox potential, a hydroxyl radical (HO• 2.8 eV) and a sulfate radical ($SO_4^{\bullet-}$ 2.5-3.1 eV), which promote rapid degradation of contaminants. To obtain the optimal response, we employed the 2^n model to construct a matrix of 15 experiments, utilizing the Box-Behnken design. According to the experimental variables studied, phenolic compounds were completely removed from the Eucalyptus effluent (0.0312 min^{-1}) and 80% of them were removed from the pine effluent (0.0102 min^{-1}), at pH 5.0 with 0.6 gL^{-1} of persulfate and 1.0 gL^{-1} of titanium dioxide. Under these conditions, the bioavailability of effluents from *Pinus radiata* and *Eucalyptus grandis* increases from 0.16 and 0.26 to 0.90, after the treatment. The excellent bioavailability of the effluents obtained after the treatment demonstrates that the process used is efficient in recovering wastewater from the pulp industry and that the treated water could be reused in the same process or returned to the ecosystem, without harming the environment.

Keywords: pulp and paper mill effluents, phenolic compounds, biodegradability, design, Box-Behnken design, response surface methodology

INTRODUCTION

Due to the increasing scarcity of water resources globally, it is necessary to explore alternatives for reclaiming wastewater, which can be then reused in industrial processes to reduce the consumption of clean water, or if treated, can be returned to the ecosystem to maintain aquifers, without causing ecological damage.[1,2] Various alternatives studied, known as clean technologies, include advanced oxidation processes (AOPs).[3-7] These processes are efficient, as they can eliminate all types of contaminants in short treatment times, due to the *in situ* generation of highly reactive species, unlike conventional treatments, which require long treatment times and high investment, without achieving adequate results.[8,9,10]

The advanced technologies target the eradication of pollutants, pathogens, and other contaminants from the water, guaranteeing its safety for reuse, and without any threat to human health or the environment. This reduces the pressure on fresh water resources and diminishes the environmental pollution that results from the discharge of untreated wastewater. Undoubtedly, advanced oxidation processes have been extensively studied for their rapid and effective degradation of high levels of pollutants present in wastewater.[11-15] The decomposition of organic matter is achieved by the on-site generation of the persulfate radical and the hydroxyl radical, which are highly reactive and non-selective species. Persulfate acts as an electron acceptor on the semiconductor surface, producing the sulfate radical. The interaction of these two species synergistically accelerates the degradation of contaminants,[16,17,18] resulting in an efficient process for the degradation of effluents from the pulp industry.

In the following equations (1-6), the radical generation system in the photocatalytic process is illustrated. As observed, the first step involves the activation of the semiconductor, in this case, titanium dioxide, through UV radiation (Eq. 1), generating an electron-hole pair in the semiconductor. The electrons in the semiconductor migrate towards the semiconductor's surface, conduction band (CB), where they are captured by persulfate to prevent electron-hole recombination (Eq. 2). This is crucial because organic matter is anchored in the hole (h^+) or valence band (VB) of the semiconductor to be degraded by the radicals. Simultaneously, persulfate captures the electrons, producing sulphate radicals, which, in turn, generate more hydroxyl radicals (Eqs. 3-5). These hydroxyl radicals are the most reactive species for degrading organic matter (O.M.) (Eq. 6).

$$TiO_2 + UV \rightarrow e^-_{CB} + h^+_{VB} \quad (1)$$
$$S_2O_8^{2-} + e^-_{CB} \rightarrow SO_4^{\bullet -} + SO_4^{2-} \quad (2)$$
$$SO_4^{\bullet -} + H_2O \rightarrow \bullet OH + SO_4^{2-} + H^+ \quad (3)$$
$$S_2O_8^{2-} + h\nu \rightarrow 2\,SO_4^{\bullet -} \quad (4)$$
$$SO_4^{\bullet -} + H_2O \rightarrow SO_2^{-2} + \bullet\,OH + H^+ \quad (5)$$
$$\bullet OH + \text{O.M.} \rightarrow \text{O.M. oxidized} + H_2O \quad (6)$$

It should be noted that the use of advanced oxidation processes is crucial in industrial wastewater treatment, especially when dealing with difficult and persistent pollutants, which conventional treatment methods fail to remove.[19-23]

The appropriate treatment of industrial wastewater to reduce pollution is the objective of using the photocatalytic system in this study, which utilizes both a semiconductor and an oxidant activated by UV radiation, as an alternative to pollution reduction and water resource conservation, focused on industries that consume a high percentage of clean water and generate equally high percentages of water contaminated with highly toxic compounds. It is well known that the effluents of the pulp and paper industry contain high concentrations of organic matter, resulting in high levels of color, chemical oxygen demand and high toxicity. Thus, in order to ensure the protection of ecosystems, it is vital to remove contaminants from these effluents before their discharge into the environment.[24,25,26] This study focuses on an advanced oxidation technique, using *in situ* production of sulphate radicals and hydroxyl radicals, for the removal of phenolic compounds from real effluent samples collected from a pulp mill.

EXPERIMENTAL

Advanced oxidation process

In this study, we worked with two real effluents: *Pinus radiata* effluent and *Eucalyptus grandis* effluent. These were obtained from the first alkaline extraction stage (E_0) of the ECF bleaching sequence used in the process of obtaining white Kraft cellulose.

The treatment process involved a photochemical oxidation system, utilizing $TiO_2/S_2O_8^{2-}/UV$. The treatments were carried out in a cylindrical reactor coupled with a UVC-254 nm mercury lamp. For the treatment optimization, an experimental matrix of 15 experiments was used with a Box Benhken design. For the experimental model, three variables were studied: pH, titanium dioxide dosage, and persulfate dosage. For each experiment, the pH was adjusted according to the experimental matrix using a pH meter (Model 211).

After each experiment, the samples were analyzed to determine the removal of phenolic compounds (λ = 280 nm) utilizing a Spectroquant Pharo 300 Spectrophotometer (Merck).

After developing the experimental matrix, response surfaces were obtained for the design, from which the optimal values of the studied variables, allowing the greatest degradation of the effluent, were obtained. Subsequently, with these values, the reaction kinetics was studied to observe over time whether there is a greater degradation of the phenolic compounds in the effluent.

Chemical Oxygen Demand (COD, mg O_2/L) was determined following the standardized method ISO 15705, using a Spectroquant® NOVA 60 Spectrophotometer. Total phenols were determined by the standarized ISO 8466-1 and DIN 38402 A 51 method, and TOC (Total Organic Carbon) – by ISO 84661-1 and DIN 38402 A51 method.

Bacterial growth

To assess bacterial growth, we employed the serial dilution method. This involved standardizing the treatments using the McFarland scale with optimal values. Inoculated plates were then incubated upside down at 37 °C for 24 hours. To determine bacterial counts, viable bacterial colonies were counted every 24 hours over a period of 120 hours. The results were expressed in terms of colony-forming units (CFU mL^{-1}). This procedure enabled us to monitor bacterial proliferation over time and assess the impact of treatment conditions on bacterial populations.

RESULTS AND DISCUSSION

The pulp manufacturing industry, whose main objective is paper production, primarily employs two plantation species: *Eucalyptus grandis* and *Pinus radiata*. This study compared effluents obtained from the pulping processes of both species to assess the effectiveness of phenolic compound degradation in each wastewater stream. The treatment of the effluent samples was accomplished using the advanced oxidation process, which integrates titanium dioxide, persulfate, and UV radiation.

Initially, we analyzed each effluent to determine the level of organic load present. As shown in Table 1, the effluent from the *Pinus radiata* process had higher chemical oxygen demand (COD) and color. This is because pine wood contains a higher concentration of tannins than eucalyptus wood.[27,28]

By evaluating these characteristics, we can acquire an understanding of the unique qualities of each effluent and comprehend their potential reaction to the advanced oxidation treatment process. The removal of phenolic compounds from cellulose bleaching effluents is a critical stage in wastewater treatment because of the adverse environmental effects of these compounds. Phenolic compounds are toxic and may persist in aquatic ecosystems, affecting water quality and marine life.[29,30]

Table 1
Initial characterization of each effluent

Parameters	*Pinus radiata*	*Eucalyptus grandis*
Color Pt-Co (mgL^{-1})	1726	1280
pH	12.89	11.73
COD (mgL^{-1})	1169	904
Total phenols (mgL^{-1})	3600	3573

The advanced oxidation process, incorporating titanium dioxide, persulfate, and UV radiation, has been demonstrated as a promising approach for degrading phenolic compounds in effluents from white pulp mills.[31-38] This process generates reactive radicals that degrade complex organic molecules, transforming them into simpler and harmless substances. By efficiently degrading phenolic compounds, both the toxicity and the color of the effluent are simultaneously reduced, which are essential parameters for determining the subsequent reuse of water.

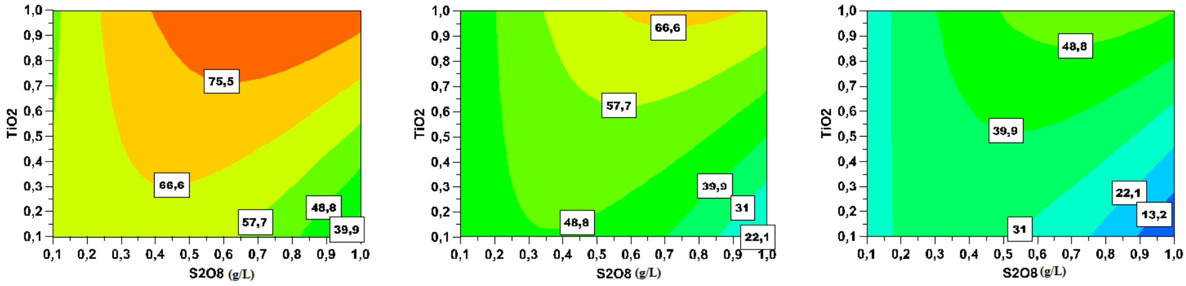
Table 2 presents the full factorial experimental design carried out with three levels to enhance the treatment of both effluents. The experimental variables were varied between their minimum (-1) and maximum (+1) values to evaluate their impact on the treatment process, and the response was determined as the percentage of phenolic compounds removal from each effluent. The experimental design is a valuable tool for comprehensively examining the impacts of several variables on treatment effectiveness. By systematically adjusting the variables within their specified ranges, it is possible to determine the most effective conditions for phenolic compounds removal from effluents.[39-42]

Figure 1 shows the response surface plots provided by the model for the efficiency of phenolic compound removal from *Pinus radiata* effluent. Changes in experimental variables, TiO_2 and $S_2O_8^{2-}$ concentration, influenced by the changes in pH, are observed. This visualization enables observation of trends and interactions between variables, facilitating the understanding of the ideal conditions to achieve the highest efficiency in the degradation of phenolic compounds. This result proves useful for decision-making and treatment process improvement, as it shows that the maximum removal rate is achieved at pH 5.0. Additionally, a specific point in the orange area is observed, where a combination of TiO_2 (concentration ranging between 0.7 to 1.0 g/L) and persulfate (concentration ranging between 0.4 to 1.0 g/L) successfully eliminates phenolic compounds.

In Figure 2, the precise identification of the optimal value for each experimental variable is observed. It is shown that an increase in persulfate concentration results in greater removal of phenolic compounds; however, this reaches a maximum of 0.6 g/L. At the same time, it is observed that elimination increases as TiO_2 is increased, and removal rates reach between 70% and 80% with 0.8 g/L and 1.0 g/L of TiO_2 respectively. This result is consistent with the principles of photocatalytic oxidation utilizing TiO_2 and persulfate. When TiO_2 absorbs luminous energy, the semiconductor material generates electron-hole pairs. These holes from the valence band serve as powerful oxidizing agents capable of degrading organic compounds, such as phenolic compounds.[43,44] The presence of persulfate enhances the oxidation process because persulfate radicals, formed *in situ*, act as electron acceptors on the semiconductor surface and prevent electron-hole recombination. This is critical because recombination would reduce the effectiveness of the oxidation process.[45]

Table 2
Experimental design for optimizing phenolic compounds removal from effluents using the $TiO_2/S_2O_8^{2-}$/UV photocatalytic process

Exp.	Run	$S_2O_8^{2-}$ (gL^{-1})	TiO_2 (gL^{-1})	pH	Removed phenolics from *Pinus radiata* effluent (%)	Removed phenolics from *Eucalyptus grandis* effluent (%)
1	13	0.1 (-1)	0.1 (-1)	8 (0)	44.12	45.20
2	2	1.0 (+1)	0.1 (-1)	8 (0)	18.63	23.60
3	7	0.1 (-1)	1.0 (+1)	8 (0)	41.18	45.72
4	12	1.0 (+1)	1.0 (+1)	8 (0)	64.38	66.50
5	6	0.1(-1)	0.55 (0)	5 (-1)	58.5	62.4
6	14	1.0 (+1)	0.55 (0)	5(-1)	59.1	62.8
7	15	0.55 (0)	0.55 (0)	11(+1)	25.2	27.3
8	4	0.55(0)	0.55 (0)	11(+1)	26.4	25.3
9	10	0.55(0)	0.1 (-1)	5(-1)	58.7	67.7
10	1	0.55(0)	1.0 (+1)	5(-1)	79.9	79.8
11	9	0.55(0)	0.1(-1)	11(+1)	31.8	27.1
12	11	0.55 (0)	1.0 (+1)	11(+1)	49.7	59.0
13	5	0.55 (0)	0.55 (0)	8(0)	57.2	67.5
14	3	0.55 (0)	0.55 (0)	8(0)	58.2	66.8
15	8	0.55 (0)	0.55 (0)	8(0)	56.2	67.4



pH=5.0 pH = 8.0 pH =11

Figure 1: Response surface plots provided by the model for the efficacy of phenolic compounds removal from *Pinus radiata* pulp and paper mill wastewater using the $TiO_2/S_2O_8^{2-}$/UV process

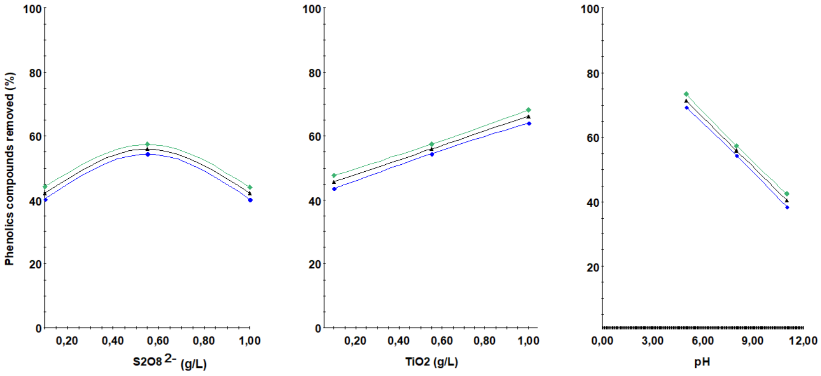


Figure 2: Optimal values for each experimental variable in the removal of phenolic compounds from *Pinus radiata* pulp and paper mill effluent

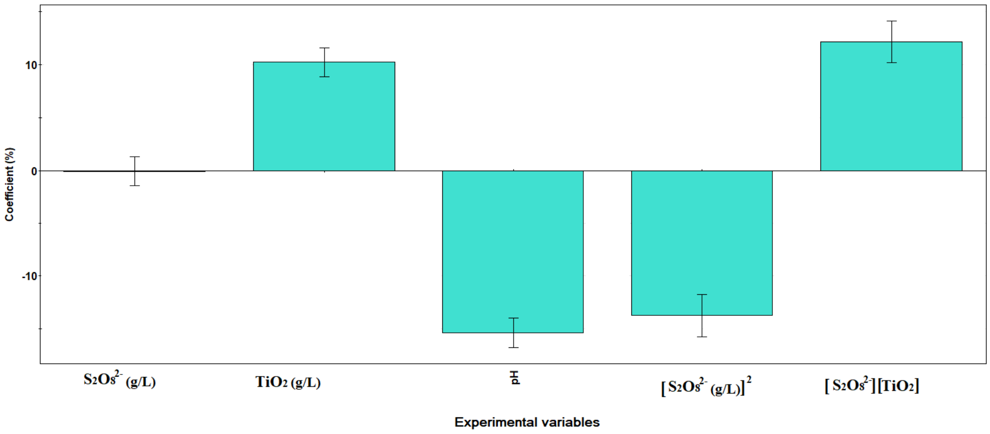


Figure 3: Polynomial response of the experimental design for the phenolic compounds' removal from the *Pinus radiata* effluent

Figure 3 illustrates the graph of the polynomial equation for the response of the experimental design, where the interaction between the experimental variables is observed: Y (%) = 55.95 (±0.65) + 10.2 [TiO_2](±0.61) – 0.06 [$S_2O_8^{2-}$](±0.61) -15.4 pH (±0.61) -13.8[$S_2O_8^{2-}$]^2 (±0.81) + 12.2 [TiO_2] [$S_2O_8^{2-}$] (±0.86); ($p \leq 0.0001$, 95% of confidence level, $R^2 = 0.996$, $Q^2 = 0.982$).

The design suggests maintaining more acidic pH levels for optimal results, and it is observed that the interaction of the three experimental variables allows for the maximum degradation of compounds in the effluent. Both the fraction of the variation of the response explained by the model (R^2 = 0.996) and the variation of the response predicted by the model (Q^2 = 0.982) are close to 1, indicating that it is a suitable model.

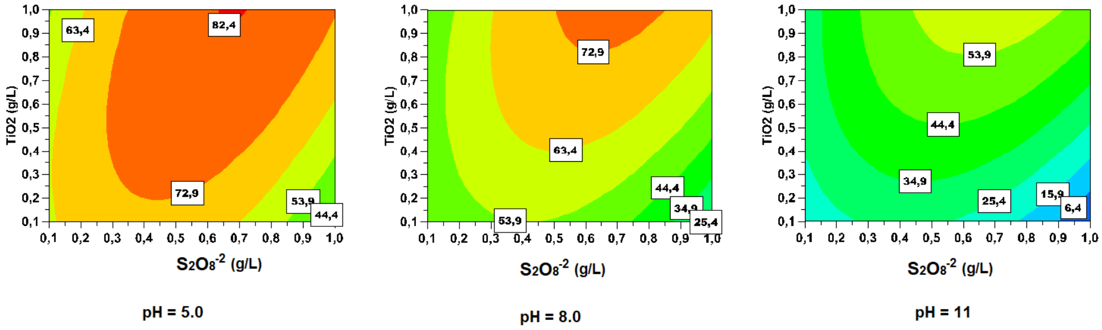


Figure 4: Response surface provided by the model for the efficacy of eliminating phenolic compounds from *Eucalyptus grandis* pulp and paper mill effluent with $TiO_2/S_2O_8^{2-}$/UV

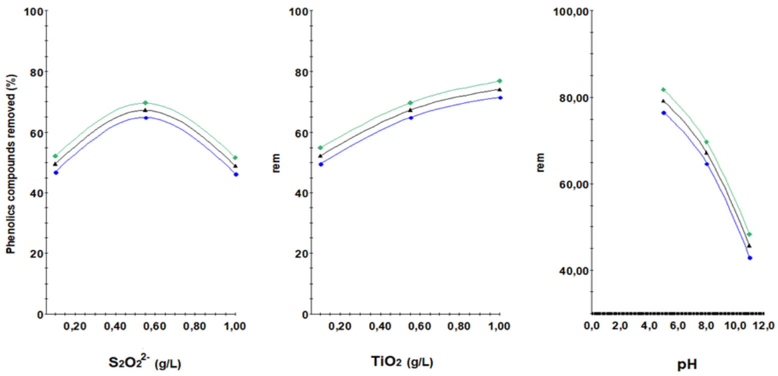


Figure 5: Optimal values for each experimental variable in removing of phenolic compounds from *Eucalyptus grandis* pulp and paper mill effluent

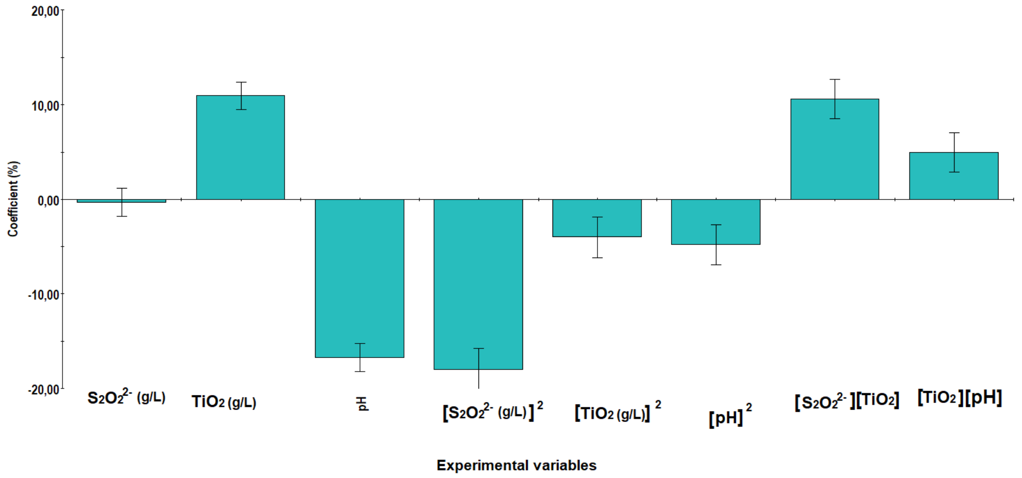


Figure 6: Polynomial response of the experimental design for the removal of phenolic compounds from *Eucalyptus grandis* pulp and paper mill effluent

The effluent generated in the eucalyptus cellulose bleaching process contains a lower concentration of organic compounds than the effluent generated in pine cellulose production, this is due to the different characteristics of each species.

This can be attributed to the lower amount of lignocellulosic compounds present in eucalyptus wood, compared with *Pinus radiata*. Nevertheless, the organic compounds present in the effluent exhibit equal difficulty in degradation. Figure 4 shows that the process of removing organic matter exhibits similar behavior to the degradation of organic matter in *Pinus radiata* effluent. The optimal experimental conditions include: 0.6 g/L of persulfate, 1.0 g/L of titanium dioxide, and pH 5.0, resulting in a removal rate over 80%. In Figure 5, the exact identification of the optimal value for each experimental variable is observed.

An empirical relationship between the response and the variables is expressed by the polynomial equation, where the synergisms between experimental variables and the parameters of the equation can be observed, as graphed in Figure 6: $Y (\%) = 67.2 (\pm 0.99) + 10.9 [TiO_2](\pm 0.60) - 0.3 [S_2O_8^{2-}](\pm 0.60) - 16.8\ pH (\pm 0.60) - 4[TiO_2]^2(\pm 0.90) - 18[S_2O_8^{2-}]^2 (\pm 0.90) - 4.8\ pH^2 (\pm 0.90) + 10[TiO_2] [S_2O_8^{2-}] (\pm 0.85) + 4.95[TiO_2]pH$; ($p \leq 0.0001$, 95% of confidence level, $R^2 = 0.997$, $Q^2 = 0.967$).

At lower pH levels, the removal rate increases, but reaches a maximum due to the quadratic variable. Similarly, the concentration of the semiconductor follows the same trend. Additionally, it can be observed that the maximum removal rate takes place when the pH is around the isoelectric point of the semiconductor.[46,47]

To investigate whether a lower pH could result in higher removal, we conducted a new optimization with pH levels ranging from 2 (-1) to 5 (+1) (Table 3). The hypothesis was that the positively charged semiconductor could attract a greater concentration of phenolic compounds and make degradation more feasible. The results confirm the initial hypothesis that the highest removal is obtained at pH 5.0. It is noted that a higher concentration of persulfate is required to achieve optimal removal at more acidic pH levels for both effluents. This is evident in both effluents, as indicated by the data presented in the response surface and polynomial graphs, for both *Pinus radiata* effluent (Figs. 7, 8, 9) and *Eucalyptus grandis* effluent (Figs. 10, 11, 12).

Using the optimized variables, degradation tests were conducted to investigate if the removal rate increases with longer treatment times. Figure 13 shows a comparison between the treatment under study and other oxidation processes. It was found that the use of TiO_2 in combination with persulfate achieved the highest efficiency. However, it was also observed that the removal of phenolic compounds reaches only 80% after prolonged treatment time, which aligns with the response given by the experimental design. In the case of the *Eucalyptus grandis* effluent, Figure 14 shows that 100% removal is achieved with a longer treatment time, indicating that the organic matter in this type of effluent is at a lower concentration.

Table 3
Experimental design for the optimal removal of phenolic compounds in both effluents from pH 2 (-1) to 5 (+1)

Exp.	Run	pH	TiO_2 (gL^{-1})	$S_2O_8^{2-}$ (gL^{-1})	Removed phenolics from *Pinus radiata* effluent (%)	Removed phenolics from *Eucalyptus grandis* effluent (%)
1	7	2.0 (-1)	0.7 (-1)	0.7(0)	71.4	62.4
2	6	5.0 (+1)	0.7 (-1)	0.7(0)	52.9	79.0
3	13	2.0 (-1)	1.0 (+1)	0.7(0)	67.4	62.1
4	4	5.0 (+1)	1.0 (+1)	0.7(0)	65.3	79.7
5	3	2.0 (-1)	0.85 (0)	0.4 (-1)	59.1	66.6
6	12	5.0 (+1)	0.85 (0)	0.4 (-1)	65.6	96.5
7	9	2.0 (-1)	0.85 (0)	1.0 (+1)	79.0	88.8
8	11	5.0 (+1)	0.85 (0)	1.0 (+1)	52.8	95.5
9	14	3.5 (0)	0.70 (0)	0.4 (-1)	63.9	79.0
10	2	3.5 (0)	1.0 (+1)	0.4 (-1)	71.4	80.8
11	5	3.5 (0)	0.7 (-1)	1.0 (+1)	68.8	88.4
12	1	3.5 (0)	1.0 (+1)	1.0 (+1)	70.0	91.3
13	10	3.5 (0)	0.85 (0)	0.7 (0)	67.7	54.2
14	8	3.5 (0)	0.85 (0)	0,7(0)	69.3	55.9
15	15	3.5 (0)	0.85 (0)	0.7(0)	68.5	54.6

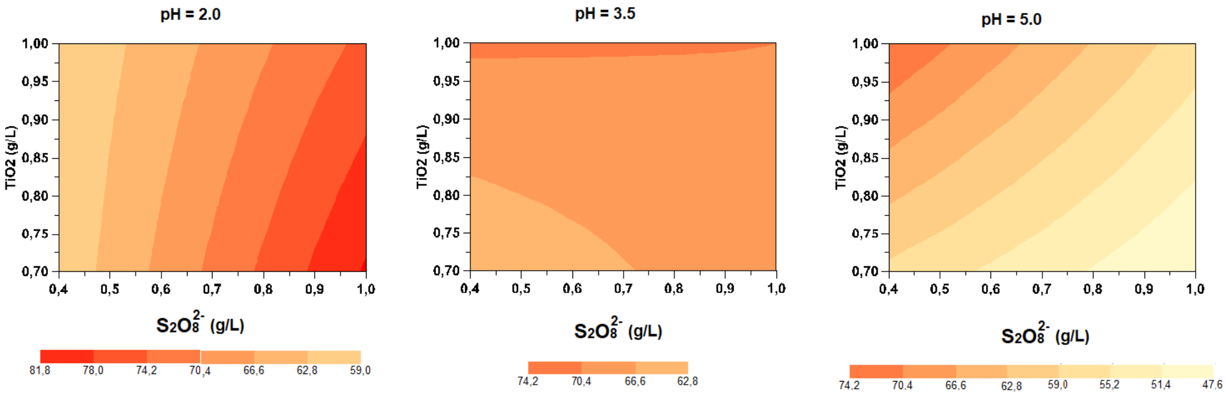


Figure 7: Response surface plots provided by the model for the efficiency of phenolic compounds removal from *Pinus radiata* pulp and paper mill effluent

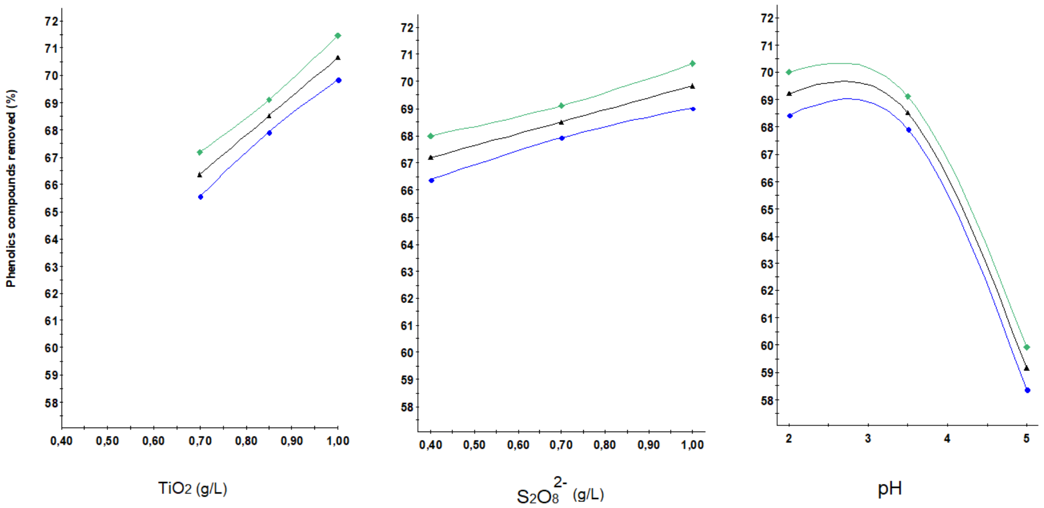


Figure 8: Optimal value for each experimental variable for the removal of phenolic compounds from *Pinus radiata* pulp and paper mill effluent

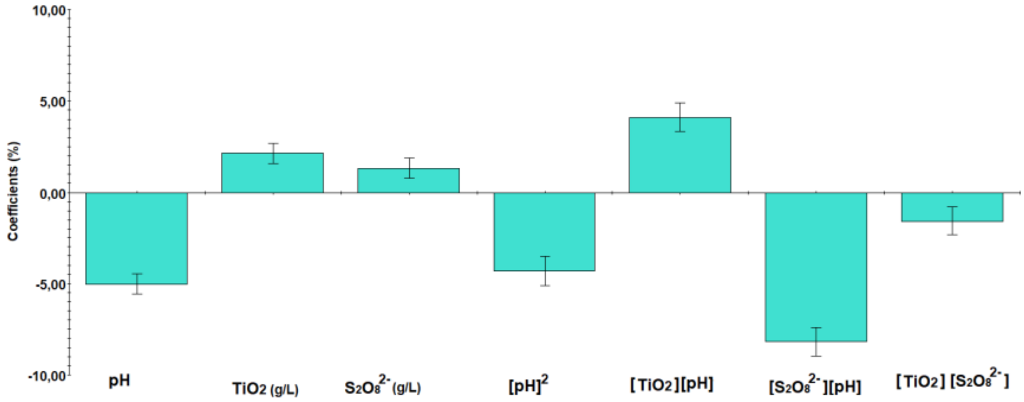


Figure 9: Polynomial response of the experimental design for the removal of phenolic compounds from *Pinus radiata* pulp and paper mill effluent; Y (%) = 68.5 (± 0.25) + 2.1 $[TiO_2]$ (±0.23) + 1.3$[S_2O_8^{2-}]$(±0.23) -5.0 pH (±0.23) -1.6$[TiO_2]$ $[S_2O_8^{2-}]$ (±0.30) + 4.1$[TiO_2]$pH(± 0.33)-8.2$[S_2O_8^{2-}]$pH(±0.33) -4.3 pH^2 (±0.34); ($p \leq 0.0001$, 95% of confidence level, $R^2 = 0.995$, $Q^2 = 0.978$)

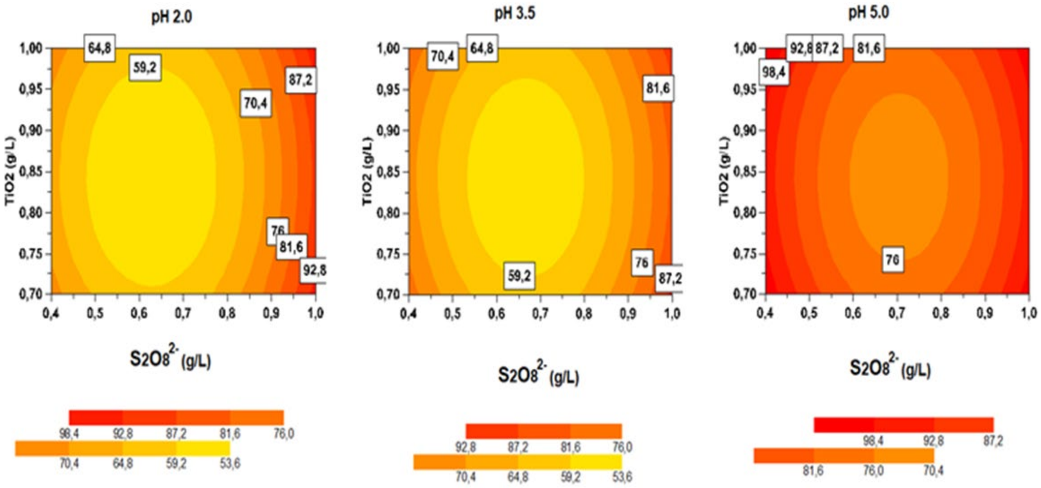


Figure 10: Response surface provided by the model for the efficiency of phenolic compounds removal from *Eucalyptus grandis* pulp and paper mill effluent

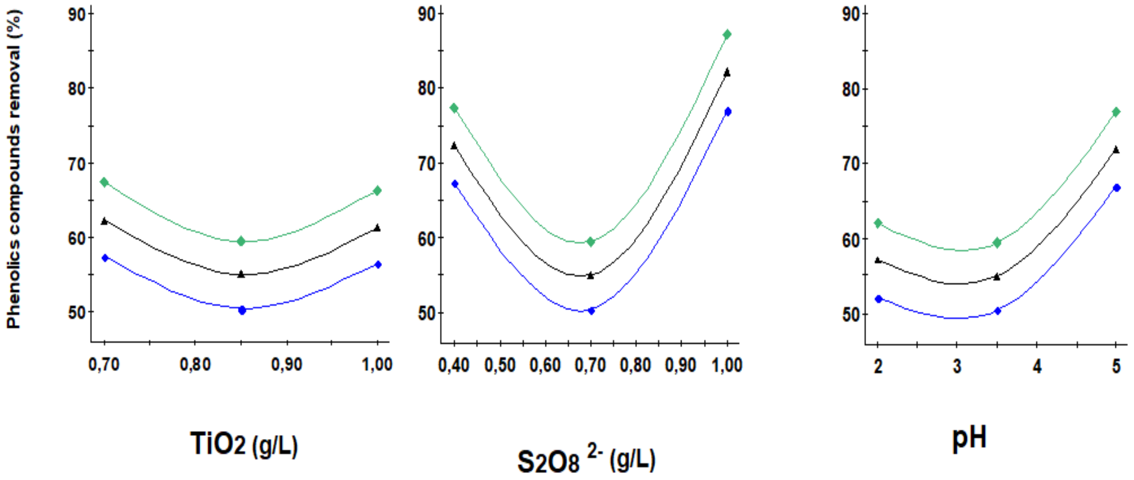


Figure 11: Optimal value for each experimental variable in the removal of phenolic compounds from *Eucalyptus grandis* pulp and paper mill effluent

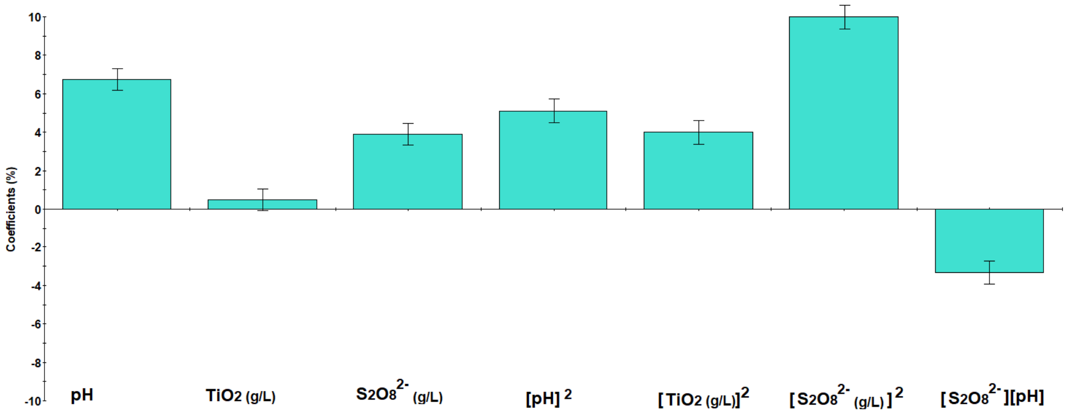


Figure 12: Polynomial response of the experimental design for the removal of phenolic compounds from *Eucalyptus grandis* pulp and paper mill effluent; Y (%) = 54.9 (± 0.51) + 0.5 $[TiO_2]$(±0.24) + 3.9 $[S_2O_8^{2-}]$(±0.24) +6.7 pH (±0.24) + 4$[TiO_2]^2$(±0.26) + 13.1$[S_2O_8^{2-}]^2$ (±0.26) - 3.3$[S_2O_8^{2-}]$pH(±0.25) - 5.1 pH^2 (±0.26); ($p \leq 0.0001$, 95% of confidence level, $R^2 = 0.998$, $Q^2 = 0.922$)

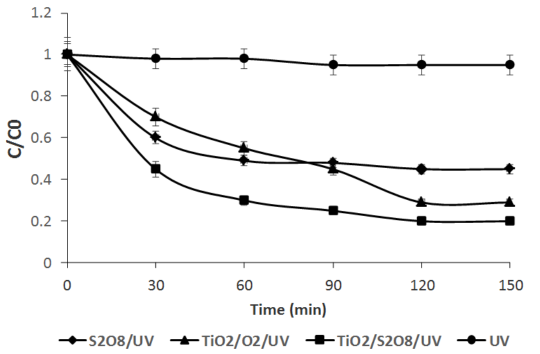


Figure 13: Phenolic compounds removed over time from the *Pinus radiata* pulp and paper mill effluent using the studied system, compared with other AOP treatments

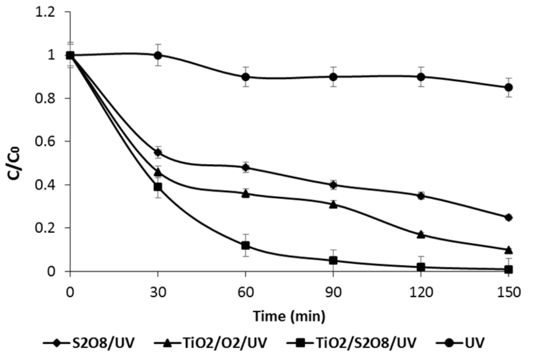


Figure 14: Organic matter removed over time from the *Eucalyptus grandis* pulp and paper mill effluent using the studied system, compared with other AOP treatments

Table 4 shows the rate constants for the removal of phenolic compounds with the different treatments in both effluents. The photocatalytic system studied exhibits a faster removal rate in both effluents, compared to the other treatments. In the case of the *Eucalyptus grandis* effluent, the removal rate of the compounds is even faster, achieving a greater removal in the same treatment time than in the case of the *Pinus radiata* effluent. This confirms that treating *Pinus radiata* effluent is more complex, compared to the eucalyptus effluent, because it contains a higher concentration of phenolic compounds.

Table 4
Rate constants obtained for each effluent with different AOP systems at optimized experimental variables

AOP system	*Eucalyptus grandis*		*Pinus radiata*	
	Kv x min^{-1}	R^2	Kv x min^{-1}	R^2
$TiO_2/S_2O_8^{2-}$/UV	0.0312	0.995	0.0102	0.85
TiO_2/O_2/UV	0.014	0.962	0.0086	0.97
$S_2O_8^{2-}$/UV	0.0081	0.930	0.0047	0.90
UV	0.0011	0.834	0.0004	0.86

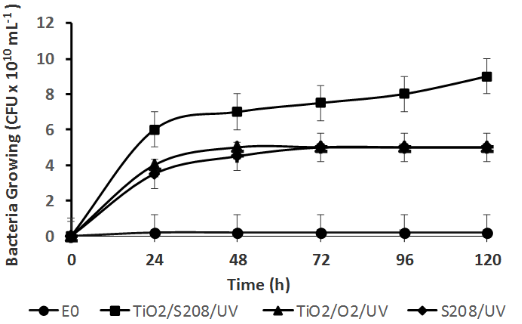


Figure 15: Bioavailability of residual organic matter in *Pinus radiata* effluent after each AOP treatment compared to the initial effluent

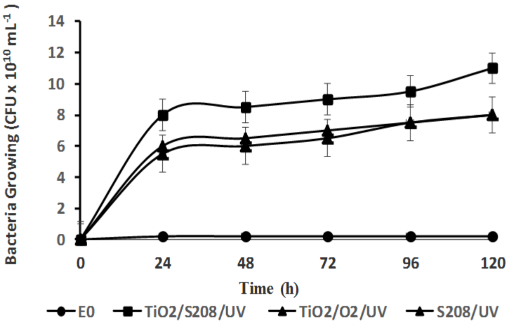


Figure 16: Bioavailability of residual organic matter in *Eucalyptus grandis* effluent after each AOP treatment compared to the initial effluent

Table 5
Summary of parameter values obtained after treatment with the $TiO_2/S_2O_8^{2-}/UV$ photocatalytic system

Parameters	*Eucaliptus grandis* (removed %)	*Pinus radiata* (removed %)
COD (mg O_2/L)	85.3	65.5
TOC (mg C/L)	76.9	58.9
Total phenols (mg/L)	100	80.0
Color (mg Pt-Co/L)	100	85.5

To observe whether the residual organic matter remained bioavailable after each treatment, a bacterial inoculum obtained from the environment was added to the effluent, and its evolution was monitored for 5 days. As shown in Figures 15 and 16 for each effluent, the highest bacterial growth occurred where the system under study was used for treatment, indicating that microorganisms did not grow in the initial effluents. This confirms that, before the treatment, the effluents contain organic compounds that can be harmful to the environment, but after adequate treatment, the organic matter becomes bioavailable and the high color of these effluents has been eliminated.[48,49]

Table 5 shows a summary of the parameter values obtained after the treatment of the effluent samples with the $TiO_2/S_2O_8^{2-}/UV$ photocatalytic system. As observed, the system effectively improved the quality of each effluent, resulting in water with a high level of bioavailability in a short treatment time. The bioavailability, determined as TOC/COD, increases after the treatment from the initial value of 0.16 to 0.90 for the *Pinus radiata* effluent, and from 0.26 to 0.90 for the *Eucalyptus grandis* effluent. Thus, in both cases, the bioavailability of the organic matter in the initial effluent is low and increases significantly after the treatment. Values close to 0.90 indicate that the treatment was efficient in achieving a very good bioavailability of the effluents.[50]

CONCLUSION

The advanced oxidation process using the $TiO_2/S_2O_8^{2-}/UV$ photocatalytic system is an effective approach to treating effluents with high levels of complex organic matter. The treatment is efficient in mineralizing organic matter, meaning it transforms it into carbon dioxide and water. This is observed in the determination of TOC, which in the case of the pine effluent was reduced by 58.9% and in the treatment of the eucalyptus effluent was reduced by 76.9%. The efficiency of the studied system is also reflected in the removal of color and phenolic compounds, and in the case of the eucalyptus effluent, these parameters were eliminated by 100%.

The process significantly improved the bioavailability of organic matter in both *Pinus radiata* and *Eucalyptus grandis* effluents. The values obtained of 0.9 indicate that the treatment was effective in achieving the bioavailability of organic matter in the effluents.

The favorable results are achieved by identifying the appropriate combination of experimental variables through the implementation of experimental design.

Photocatalytic processes prove to be effective in treating complex effluents, allowing for their safe discharge into the environment or reuse. These results highlight the efficiency of photocatalysis as a viable treatment option.

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