




Article

Persulfate Process Activated by Homogeneous and Heterogeneous Catalysts for Synthetic Olive Mill Wastewater Treatment

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Abstract: Wastewaters from the olive oil industry are a regional environmental problem. Their phenolic content provides inherent toxicity, which reduces the treatment potential of conventional biological systems. In this study, Sulfate Radical based Advanced Oxidation Processes (SRbAOPs) are compared with advanced oxidation processes (namely Fenton's peroxidation) as a depuration alternative. Synthetic olive mill wastewaters were submitted to homogeneous and heterogeneous SRbAOPs using iron sulfate and solid catalysts (red mud and Fe-Ce-O) as the source of iron (II). The homogenous process was optimized by testing different pH values, as well as iron and persulfate loads. At the best conditions (pH 5, 300 mg/L of iron and 600 mg/L of persulfate), it was possible to achieve 39%, 63% and 37% COD, phenolic compounds and TOC removal, respectively. The catalytic potential of a waste (red mud) and a laboratory material (Fe-Ce-O) was tested using heterogenous SRbAOPs. The best performance was achieved by Fe-Ce-O, with an optimal load of 1600 mg/L. At these conditions, 27%, 55% and 5% COD, phenolic compounds and TOC removal were obtained, respectively. Toxicity tests on *A. fischeri* and *L. sativum* showed no improvements in toxicity from the treated solutions when compared with the original one. Thus, SRbAOPs use a suitable technology for synthetic OMW.

Keywords: sulfate radical based advanced oxidation process; synthetic olive mill wastewater; toxicity; homogeneous catalysis; heterogeneous catalysis



Citation: Domingues, E.; Silva, M.J.; Vaz, T.; Gomes, J.; Martins, R.C. Persulfate Process Activated by Homogeneous and Heterogeneous Catalysts for Synthetic Olive Mill Wastewater Treatment. *Water* **2021**, *13*, 3010. <https://doi.org/10.3390/w13213010>

Academic Editor: Jiangyong Hu

Received: 29 September 2021

Accepted: 25 October 2021

Published: 27 October 2021

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1. Introduction

The discharge of industrial wastewaters into water resources, without any type of treatment, is an unfortunate reality. This limits access to quality water. A problematic industry is olive oil production. This industry generates a large amount of contaminated liquid effluent that is highly difficult to treat. Olive mill wastewater (OMW) is a serious environmental problem, produced in olive mills either by the discontinuous press method or by the continuous centrifugation method for olive oil extraction and olive washing processes. However, it is worthy to mention that the European Union (EU) does not have specific legislation with regard to OMW treatment, leaving it to Member States to establish their own legislation.

During olive oil production, large quantities of olive mill wastewaters and residues—olive pomace (OP)—are generated. OP is currently sent to extraction units, where olive oil extraction industry wastewaters (OOEIW) are also produced. OMW is a dark, odorous, turbid and highly polluted wastewater due to the wide variety of contaminants it contains [1]. According to its age and the production process, the color of OMW varies from dark red to black. This dark colored wastewater, with very large contents of organic matter, recalcitrant/toxic components such as phenolic compounds (polyphenols, tannins),

sugars, proteins, and a considerable salt concentration, is a substantial pollutant and is environmentally hazardous [2–5]. Given the lack of technologies capable of treating these wastewaters due to their characteristics, the most common practice is to proceed with their disposal in ponds; the paste resulting from this process is discharged into the soil. However, these wastewaters are a source of phenolic compounds and, given their toxicity to both aquatic and human life, they are considered an environmental problem.

Fenton's process, an advanced oxidation process (AOP) is specified in the literature as interesting alternative for agro-industrial wastewater treatment [6,7]. However, Sulfate Radical based Advanced Oxidation Processes (SRbAOPs) have been the subject of recent investigations to overcome some of the disadvantages of Fenton's process [8].

SRbAOPs can be applied to remove or degrade resistant pollutants, such as antibiotic-resistant microorganisms, drugs, and non-biodegradable organic matter [9].

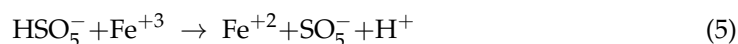
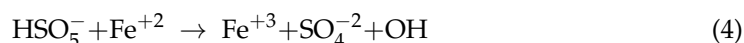
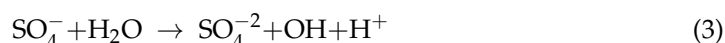
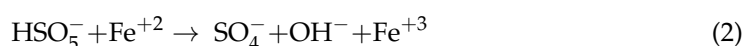
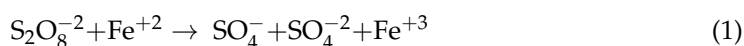
The sulfate radicals ($\text{SO}_4^{\cdot-}$) bind with the pollutants by removing hydrogen from the saturated carbon and adding it in the double bonds or by electron transfer, causing partial or total mineralization of the organic matter [10].

The use of SRbAOPs has some advantages over the Fenton method, such as

- Sulfate radicals have a higher stability and thus a longer life span than the hydroxyl radical OH^\bullet , which is the radical formed in the Fenton process;
- The oxidant agent necessary to generate SO_4^- is solid at room temperature, which facilitates its transport and storage;
- The range of pH values of the SRbAOP is wider than the one used in the Fenton process;
- Sulfate radicals have a bigger solubility in aqueous solution than OH^\bullet ; and
- The hydroxyl radicals react through unselective multi-step pathways, which limits the process efficiency [11–13].

However, some authors have reported that although sulfate radicals have a greater stability and have an oxidation potential similar to hydroxyl radicals, the reaction rate between SO_4^- and organic matter is slower than the one observed between OH^\bullet and organic compounds [14,15]. Nevertheless, other authors have found that the reaction between the organic matter and the sulfate radicals is faster than the one with hydroxyl radicals [11]. The oxidation efficiency of free sulfate radical ($\text{SO}_4^{\cdot-}$) is made clear by its oxidation potential ($E_0 = 2.6 \text{ V}$), which is the third highest after fluorine ($E_0 = 3.6 \text{ V}$) and OH^\bullet ($E_0 = 2.8 \text{ V}$) [16].

Sulfate radicals are generated through the activation of an oxidant agent, like persulfate ($\text{PS-S}_2\text{O}_8^{2-}$) or peroxymonosulfate (PMS-HSO_5^-). Regarding the activation of PS and PMS through catalytic processes, the most common is the use of Fe (II), as shown in Equations (1) and (2). It is important to note that during the activation process, in addition to the formation of sulfate radicals, other radicals can be formed, as described in Equations (3)–(5) [9,17,18].



The activation of PS and PMS can be carried out in homogeneous or heterogeneous systems. In homogeneous systems, there is less resistance to mass transfer, and consequently, the reaction rate is faster. Nevertheless, some unwanted side reactions take place, and ferrous sludge is formed. Heterogeneous systems emerged with the aim of eliminating the disadvantages of homogeneous systems, namely the formation of iron sludge [17,18]. Persulfate decontamination technologies, whether using radical driven processes or di-

rect electron transfer, have proven to be very powerful processes for the treatment of a wide range of pollutants, namely halogenated olefins, BTEXs (benzene, toluene, ethylbenzene and xylenes), perfluorinated chemical products, phenols, pharmaceutical products, inorganics, and pesticides [19].

The use of iron-rich residues as catalysts in this process can be an interesting environmental approach. Red mud is a low-cost catalyst, and it was innovatively applied in the Fenton process with the objective of reducing the operation costs and reusing a waste that is currently produced in large quantities. Red mud is the iron-rich waste formed during aluminum oxide production by the bauxite leaching process (Bayer process) [20]. In another perspective, Fe-Ce-O was studied because ceria-based iron catalysts have shown good performance in enhancing the removal of organic compounds, reducing toxicity, and improving biodegradability in the depuration of phenolic wastewaters with the ozonation process [21].

Bearing all this in mind, the objective of the present work is to evaluate the applicability of SRbAOPs in the treatment of synthetic olive oil wastewater. More specifically, the applicability of metal-activated persulfate as a source of radical sulfates is analyzed. Homogeneous SRbAOPs are compared with the heterogeneous process. Moreover, the results are compared with Fenton's peroxidation, considering the pollutants' abatement but also the toxic impact of the treated samples.

To the best of our knowledge, the degradation of synthetic OMW has not been carried out by PS oxidation through the application of iron as an activator. In the present study, the degradation of synthetic OMW by PS oxidation, using homogeneous (Iron (II) Sulfate Heptahydrate) is studied for the first time. Moreover, new solid catalysts (red mud and Fe-Ce-O) were also innovatively tested as activators of PS.

2. Materials and Methods

2.1. Reagents and Materials

The synthetic OMW consists of a solution of five phenolic compounds (Trans-cinnamic acid, 3,4-Dihydroxybenzoic, 4-Hydroxybenzoic, 3,4,5-Trimethoxybenzoic, and 3,4-Dimethoxybenzoic) dissolved in ultrapure water, with a concentration of 100 mg/L each. All phenolic acids were purchased from Sigma-Aldrich (Velp Scientifica, Taufkirchen, Germany).

2.2. Heterogeneous Catalyst Preparation and Characterization

2.2.1. Red Mud

The red mud was supplied by a Greek aluminum producer, and it was prepared for used in accordance with [20]: grounded and sieved (diameter < 0.105 μm) after drying at 105 °C for 24 h.

Red mud elemental composition was determined by atomic absorption. First, the solid sample was digested (HCl, 6 M). The insoluble compounds were separated by vacuum filtration, and the filtrate was transferred to a 100 mL flask to which ultrapure water was added until the volume was adjusted. The solution was then characterized by atomic absorption to determine its content in metal elements.

2.2.2. Fe-Ce-O

Fe-Ce-O is a solid prepared in the laboratory, according to [22], composed of a molar ratio Fe/Ce equal to 70/30. The catalyst precursors were $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Panreac, Barcelona). After co-precipitation, the solution was filtered and washed 5 times with ultrapure water, and the resulting precipitate was dried at 105 °C for 3 h. Then, the sample was calcined for 3 h at 300 °C, and finally it was ground manually and sieved (diameter < 0.105 μm).

It should be noted that Fe-Ce-O 70/30 was selected as a heterogeneous iron-based catalyst for this study due to its good performance in the Fenton process [23]. In addition, the choice of calcification temperature was also based on the results obtained in a previous work [24] when applying Fe-Ce-O 70/30 in the Fenton process.

2.3. Sulfate Radical Based Advanced Oxidation Process Experiments

The SRbAOP experiments took place in a 500 mL spherical reactor made of glass. To this reactor, 250 mL of synthetic OMW was added and subjected to an agitation of 300–500 rpm in homogeneous catalysis, and 800–1000 rpm in heterogeneous catalysis, by magnetic agitation. Then, the catalyst was added, followed by pH correction, by pouring drops of a NaOH and a H₂SO₄ solution. The reaction was then started through the addition of the oxidant agent (PS). To stop the reaction, after 30 min, the pH was changed to 7 by pouring drops of NaOH and H₂SO₄. Then, the solution was centrifuged at 4000 rpm in a Nahita centrifuge model 2655 for 5 min, and finally it was filtered through a 0.45 µm cellulose acetate filter.

After the reaction stopped, the efficiency of the treatment applied was analyzed in terms of the reduction of the chemical oxygen demand (COD), biological oxygen demand (BOD₅), total organic carbon (TOC), and the concentration of phenolic compounds. The experimental procedure described above, from the formulation of the OMW to the analysis of the efficiency of the process, is outlined in Figure 1.

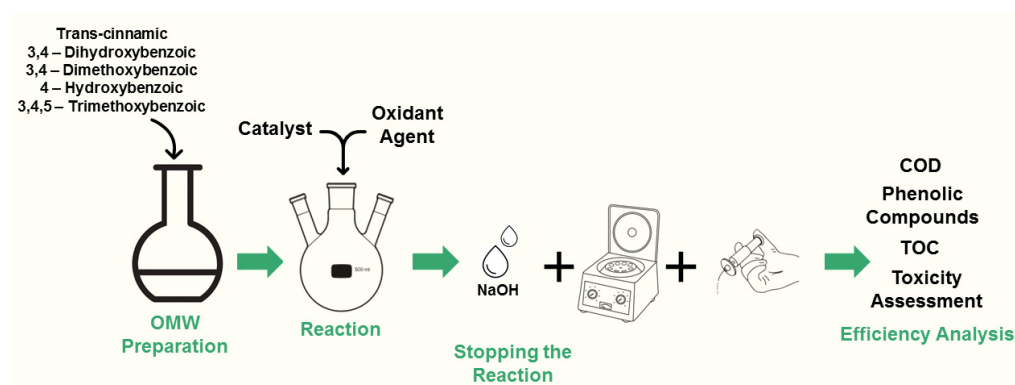


Figure 1. Outline of the experimental procedures.

2.4. Analytical Techniques

To analyze the COD, the 5220 D method was applied [25]. For the application of this method, samples of the treated OMW were diluted by a factor of 10. Then, 2.5 mL of the diluted OMW was introduced into the digestion vessels along with 1.5 mL of the digestion solution and 3.5 mL of the acid solution. Afterwards, the vessels were introduced in the ECO 25 (Velp Scientifica, Taufkirchen, Germany) digester at 150 °C for 2 h. Finally, the vessels were cooled slowly to room temperature over 1 h. After cooling, the absorbance of the samples was read in the PhotoLab S6 (WTW) filter photometer at 445 nm. All samples were analyzed at least in duplicate.

The phenolic content was obtained throughout the Folin–Ciocalteu method [26]. For the application of this method, 20 µL of the treated OMW was placed in cuvettes with 1.58 mL of distilled water, 100 µL of the Folin–Ciocalteu (Panreac, Darmstadt, Barcelona) reagent, and 300 µL of a saturated solution of sodium carbonate (Na₂CO₃). After 2 h in the dark, the absorbance of the samples was read in the T60 UV/VIS (PG Instruments, Leicestershire, UK) spectrophotometer at 765 nm. All samples were analyzed in duplicate.

To analyze the TOC, the 5310 B method was applied [25]. For the application of this method, the sample had to be homogenized and diluted, as necessary. The sample was then injected, and the inorganic and organic carbon were measured via a nondispersive infrared analyzer. This analysis was carried out in an SSM-5000A (Shimadzu, Tochigi, Japan).

The respirometry (BOD₅) measurement is a pressure measurement. If oxygen is consumed in a closed vessel at a constant temperature, a negative pressure develops. If a gas is released, an overpressure develops. The OxiTop[®] measuring head measures and stores this pressure for the whole duration of a measurement once started. The OxiTop[®] OC 110 controller collects the pressure values from the measuring heads and processes them.

HPLC was applied to evaluate the individual degradation of the five phenolic acids present in OMW and identify intermediate compounds. HPLC was applied according to Domingues et al. [27], and a C18 column (SiliaChrom) at 40 °C was used. The mobile phase had a flow rate of 0.5 mL/min and consisted of a 50/50 mixture of methanol and acidified water, with 1% orthophosphoric acid. The peak determination occurred at 255 nm.

The purpose of atomic adsorption was to characterize the red mud as well as to identify and quantify metal leaching during heterogeneous catalysis. The analyses were performed according to the 3111 B method, in accordance with Baird et al. [25]. For the application of this method, standard solutions of the metals were prepared according to the method mentioned above. The samples for the leaching analysis were prepared according to the 3030 C method. For this method, ContrAA 300 (Analytik Jena GmbH, Jena, Germany) equipment was used.

2.5. Toxicity Assessment

To assess the toxicity of treated wastewater, the sensitivity of species such as *Aliivibrio fischeri* bacteria and *Lepidium sativum* was analyzed, as described by Domingues et al. [20] and Baird et al. [25].

Regarding the toxicity studies carried out on *A. fischeri*, the luminescence inhibition was analyzed and compared with a blank, according to the 8050 method described by Bair et al. [25]. The blank consists of a solution with 2% NaCl that is suitable for the growth of bacteria.

The inhibition effect was measured after 15 and 30 min of contact of the bacteria with the treated and untreated wastewater, using a Lumistox 300 (Dr. Lange) luminometer. Before starting the tests, all samples had their pH corrected to a value between 6.5 and 7.5.

The toxicity tests with *L. sativum* consisted of the introduction of 10 seeds evenly separated in filters placed in Petri dishes. Afterwards, the filters were wet with 5 mL of treated and untreated wastewater and with distilled water (blank). Then the Petri dishes were placed in an oven at 27 °C for 48 h. These experiments were carried out in duplicate, and before starting the tests, all samples had their pH corrected to a value between 6.5 and 7.5. These tests allowed us to determine the germination index (GI), according to Trautmann and Krasny [28]. The GI was determined by Equations (6)–(8), where L_s and L_0 correspond to the average radical length of the sample and the blank, respectively, and G_s and G_0 correspond to the average germination of the sample and the blank, respectively.

$$GI = \frac{G \times L}{10000} \quad (6)$$

$$G = \frac{G_s}{G_0} \times 100 \quad (7)$$

$$L = \frac{L_s}{L_0} \times 100 \quad (8)$$

3. Results

3.1. Synthetic Olive Mill Wastewater Characterization

The characterization of the synthetic OMW was made based on the following parameters: pH, chemical oxygen demand (COD), total organic carbon (TOC), and phenolic compounds (Table 1).

Table 1. Synthetic OMW characterization.

Parameter	COD (mg/L)	TOC (mg/L)	Phenolic Compounds (mg/L)	pH
Value	800 ± 64	284 ± 23	300 ± 24	3.5 ± 0.2

3.2. Homogenous Catalysis

The performance of the SRbAOPs based on iron-activated persulfate, in homogeneous catalysis and using iron sulfate as a catalyst, was optimized and analyzed in terms of the results obtained regarding the removal of organic matter and toxicity.

Before optimizing the operating conditions of homogeneous catalysis, the need for persulfate activation was investigated. Thus, an experiment involving the addition of persulfate (600 mg/L) to the effluent at pH 5 was tested. At these conditions, it was possible to obtain a COD removal of $4.08 \pm 0.44\%$ after 60 min of reaction. These results evidence the need for persulfate activation. In fact, Chueca et al. [29] attained up to 87% of COD removal in the treatment of synthetic wastewater from the wine industry with iron activated persulfate. In this context, the need for persulfate activation is clear. At homogeneous conditions, iron sulfate was selected as the iron source for persulfate activation.

To optimize the operating conditions of the homogenous process, pH, persulfate load, and iron concentration were selected as operation variables.

Regarding the pH tests, the initial concentrations of iron and persulfate (PS) were kept constant and equal to 200 mg/L and 600 mg/L, respectively. pH ranged within 3–11. Figure 2 represents the pH influence on COD and phenolic compound removal after 30 min of reaction.

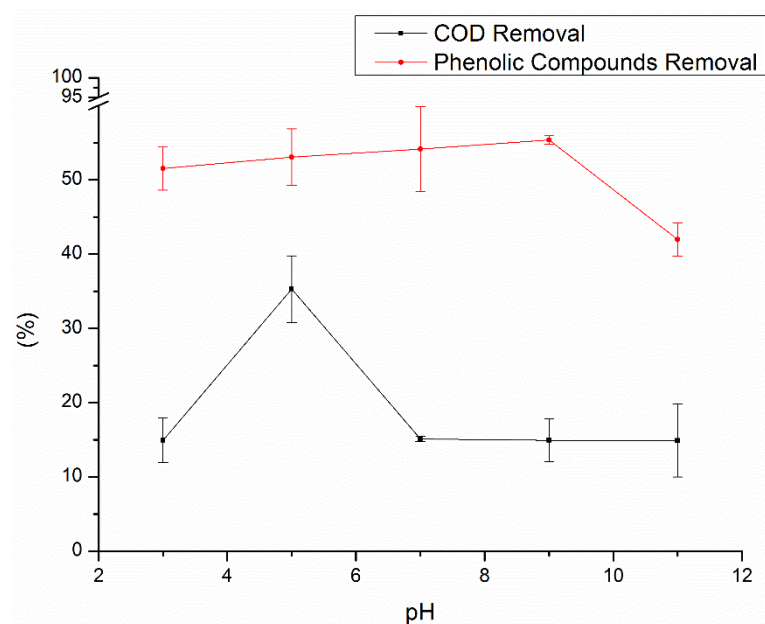


Figure 2. pH influence on COD removal and phenolic compound removal (30 min of reaction, $[\text{Fe}^{2+}] = 200 \text{ mg/L}$ and $[\text{PS}] = 600 \text{ mg/L}$).

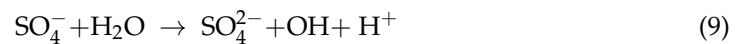
By analyzing Figure 2, it is concluded that a pH value of 5 makes it possible to obtain a maximum COD removal of approximately 35%, while the remaining tested pH values allowed a COD removal of approximately 15%. However, it also can be observed that the pH value does not have a significant influence on the removal of phenolic compounds (around 50%). The exception is pH 11, which slightly decreases the removal efficiency of these compounds.

The low COD removal obtained for a pH of 3 can be justified by the scavenger effect that H^+ causes on the sulfate radical. On the other hand, the low COD removal at alkaline conditions may be caused by the formation of HO^* , which, although having an oxidation redox similar to sulfate radicals, has a shorter life span [30,31] which may make it less available for reaction.

Bearing in mind COD and phenolic content removal, a pH of 5 was selected as the optimal value. The result obtained agrees with that obtained by Chueca et al. [29,32],

which, among the few studies found, focused on the treatment of wastewaters from the agro–food industry by iron-activated PS. Although the result obtained was as expected, the discrepancy between the efficiency of COD removal between pH 5 and the remaining values was unexpected, since it was reported by Ioannidi et al. [12] that the SRbAOP has a wide operating range of pH values.

With the pH tests, it was also found that, with the course of the reaction, regardless of the initial pH, the pH of the medium decreased. This can be justified by the reaction of the sulfate radical with OH^- and the consequent formation of H^+ , as represented in Equation (9) and mentioned by Fan et al. [33].



To test the effect of the persulfate, the initial concentrations of iron and the pH value were kept constant and equal to 200 mg/L and 5, respectively. The persulfate load was analyzed within the range of 400–800 mg/L. Figure 3a–d represent the PS load influence on COD and phenolic compound removal, respectively.

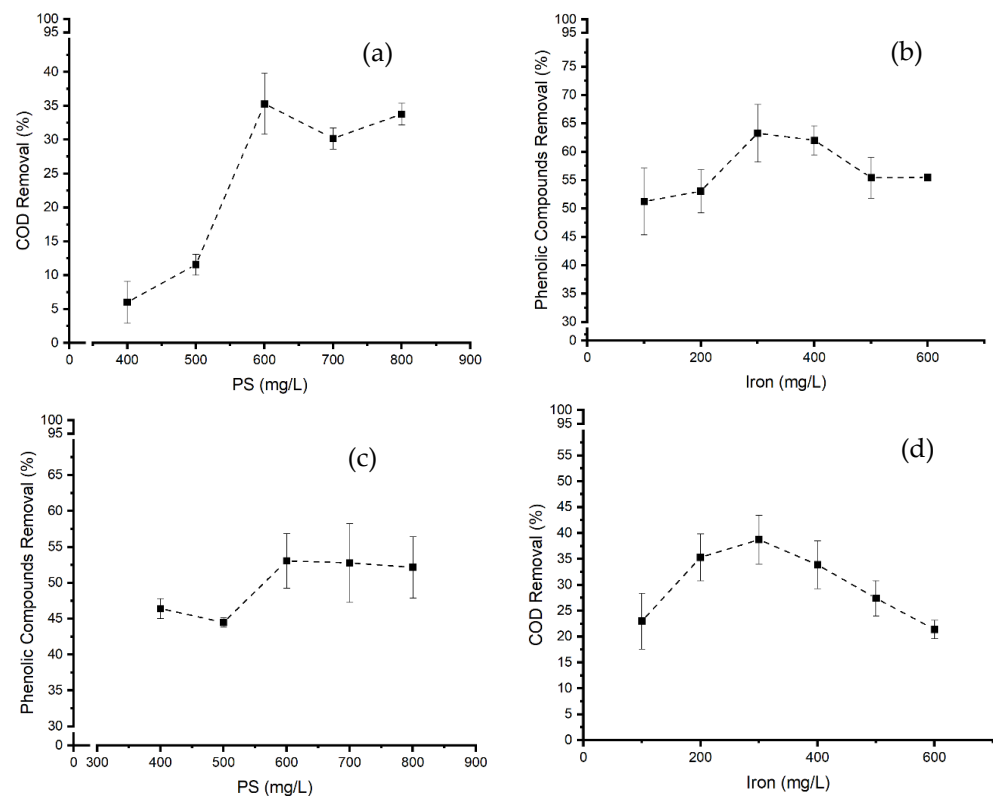


Figure 3. Persulfate and iron load influence on COD removal and phenolic compound removal. (a) Persulfate COD removal, (b) iron phenolic compound removal, (c) Persulfate phenolic compound removal (d) iron COD removal.

Through Figure 3a, it is concluded that a persulfate concentration of 600 mg/L allowed us to obtain a maximum COD removal of approximately 35%. From 400 to 600 mg/L, there was an increase in the COD removal efficiency, and from this point onwards an increase in the PS concentration led to a plateau, with COD removal barely changing. A PS concentration of 600 mg/L also allowed the maximum phenolic compound removal, approximately 53% (Figure 3b). After this, the phenolic content removal did not significantly change with the increasing concentration of the oxidant. It was expected that the increase in PS concentration would result in a scavenger effect, that is, a decrease in removal efficiency. However, this was not the case, perhaps because, as mentioned by Xiao et al. [17], the PS

scavenger effect is not very noticeable, and the PS load may not have increased enough to detect this phenomenon.

Iron load tests (Figure 3c,d) were performed keeping the initial concentrations of persulfate and the pH value constant at 600 mg/L and 5, respectively. Iron load was evaluated within the range of 100–600 mg/L.

From Figure 3c,d, it is concluded that the optimal concentration of iron is 300 mg/L, as this load results in the more pronounced removal of COD and phenolic compounds: 39% and 63%, respectively. COD and phenolic content removal increased with an increase in the iron load from 100 to 300 mg/L. From this point onwards, an increase in the catalyst load resulted in a decrease in the removal efficiency of the process.

3.2.1. Toxicity Assessment

In order to evaluate the effect of the treatment on the wastewater toxicity, the treated samples' GI was compared with the initial effluent. For the toxicity assessment with *L. sativum*, samples from the reactions that operated with a PS concentration of 500, 600, and 700 mg/L were analyzed. The results of these experiments are presented in Table 2.

Table 2. Germination index results for *L. sativum* for different conditions.

Type of Effluent	Synthetic Effluent	400 mg/L	500 mg/L	600 mg/L	700 mg/L	800 mg/L
GI (%) *	30.6 ± 3.2	–	46.1 ± 11.5	39.9 ± 11.5	29.7 ± 16.6	–
GI (%) **	30.6 ± 3.2	47.3 ± 19.3	42.7 ± 15.1	39.2 ± 10.0	33.8 ± 0.5	43.6 ± 1.0
GI (%) ***	30.6 ± 3.2	39.9 ± 11.5	33.1 ± 6.9	34.1 ± 0.4	–	–

* Germination index results for *L. sativum* for a PS concentration of 500, 600, and 700 mg/L; Iron = 200 mg/L; pH 5. ** Influence of the PS load without iron on *L. sativum* growth. *** Germination index results for *L. sativum* for an iron concentration of 200, 300, and 400 mg/L.

From the analysis of Table 2, it can be observed that the treated samples have a higher or equal GI than that of the untreated wastewater. In this scenario, in accordance with Trautmann and Krasny [28], the treated sample with a PS load of 500 mg/L showed a strong inhibition towards plant growth, the sample with a PS load of 600 mg/L showed a severe inhibition, and the sample with a PS load of 700 mg/L showed a severe inhibition.

Considering the decrease in GI with the increase in the PS load, the individual influence of the PS load on the toxicity of *L. sativum* was also analyzed. For this, ultrapure water with different PS concentrations was used in the germination tests. These results are shown in Table 2. It seems that all samples have a higher GI than the untreated wastewater. Thus, considering the PS load and the organic matter concentration present in the sample, it seems that the toxic effect of persulfate introduced in the solution is less than that of the phenolic compounds present in the wastewater. It is also concluded that an increase in PS load results in a slight decrease of the GI, that is, an increase in the toxic effect. Among all samples, only the two with the lowest PS load (400 and 500 mg/L) are classified, according to Trautmann and Krasny [28], as having strong inhibition, whereas the rest are classified as having a severe inhibition.

By comparing the results of Table 2, it is possible to conclude that the increase in PS concentration does not justify the decrease in GI and, consequently, the increase in toxicity. Thus, intermediate and/or secondary compound formation during the oxidation treatment are also a reason for the toxic character of the treated samples.

To evaluate the effect of iron load on the treated wastewater's toxic character, toxicity tests were carried out on *L. sativum* using the samples of the reactions that operated with an iron load of 200, 300, and 400 mg/L. Results are shown Table 2. It can be observed that the treated samples have a higher—but similar—GI than that of the untreated wastewater. In this scenario, in accordance with Trautmann and Krasny [28], all samples show a strong inhibition towards plant growth.

3.2.2. Homogeneous SRbAOP Performance under the Optimal Operating Conditions

From the experiments described above, it can be concluded that the optimal conditions involve the use of 600 mg/L of PS and 300 mg/L of iron. This means an optimal mass ratio between the PS load and the iron load of two, which is equivalent to use a molar ratio of 0.58. This conclusion does not line up with the recommendation of Rodriguez et al. [34] and Xiao et al. [17], which is the use of a molar ratio between the PS load and the iron load of one. This phenomenon can be justified by the occurrence of secondary reactions that consume iron (II), as in the case of the reaction between iron and dissolved oxygen [17].

Knowing the optimal ratio between the reagents, the influence of the increased loads of reactants was analyzed, keeping this ratio constant. For these tests, the initial pH value was kept constant at five, and the following pairs of values were used for the concentration of PS and iron, respectively, in mg/L: (600; 300), (1200; 600), (1800; 900), (2400; 1200). Figure 4 shows the influence of these loads on COD and phenolic compound removal.

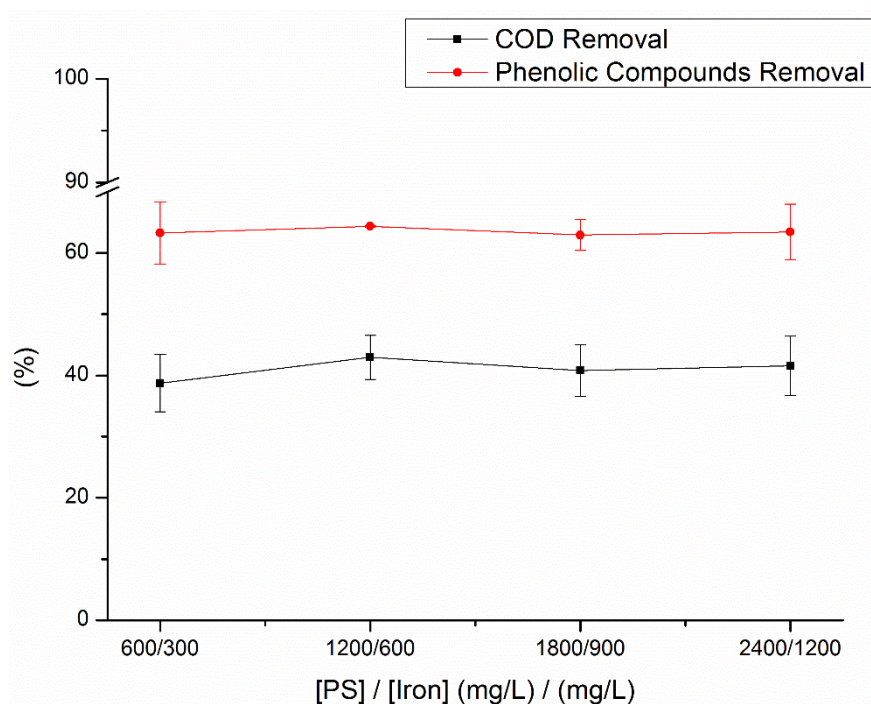


Figure 4. Persulfate and iron load influence on COD removal and phenolic compound removal. (30 min of reaction at pH 5).

From the analysis of Figure 4, it is possible to conclude that an increase in the loads of persulfate and of iron, maintaining the proportion between them, does not result in a significant increase in the removal of COD or the removal of phenolic compounds. Therefore, it can be said that the optimum concentration of reagents to be introduced is 600 mg/L of PS and 300 mg/L of iron, as previously discussed.

As in previous experiments, the toxicity of treated wastewater was analyzed. In this case, for the tests with *L. sativum*, samples of the reactions that operated with the pairs of values (600; 300) and (1200; 600) were evaluated, and the results are shown in Table 3.

Table 3. Germination index results for *L. sativum*, for a persulfate an iron load of (600; 300) and (1200; 600) mg/L.

Type of Effluent	Synthetic Effluent	(600; 300) mg/L	(1200; 600) mg/L
Germination Index (%)	30.6 ± 3.2	33.1 ± 6.9	32.8 ± 1.6

From the analysis of the Table 3, it can be observed that the treated samples have a similar GI to that of the untreated wastewater, which may be caused by the formation of intermediate compounds with a higher or similar toxicity to the original compounds present in the OMW. In this scenario, in accordance with Trautmann and Krasny [28], all samples showed a strong inhibition towards plant growth.

As mentioned above, a pH value of 5, an iron concentration of 300 mg/L, and a PS concentration of 600 mg/L are the optimal parameters for the treatment process under analysis. Under these conditions, it is possible to achieve a COD removal of $38.74 \pm 4.70\%$, a removal of phenolic compounds of $63.19 \pm 5.09\%$, and a removal of TOC of $36.98 \pm 7.21\%$. Thus, the treated wastewater under the best operating conditions has, approximately, a COD load of 520 ± 40 mg/L, a TOC load of 179.3 ± 20.5 mg/L, and a concentration of phenolic compounds of 129 ± 18 mg/L.

Therefore, considering the environmental limit values (ELVs) for the discharge of OMW in water resources, as represented in Table 4, the effluent resulting from the treatment process is not in a condition to be discharged.

Table 4. ELV for OMW discharge (Adapted from [35]).

Parameter	Portugal	Spain	Greece	Italy
COD (mg/L)	150	160–500	45–180	160
BOD ₅ (mg/L)	40	40–300	15–60	40
Phenolic Compounds (mg/L)	0.5	0.5–1	0.005–0.5	0.5
pH	6–9	5.5–9.5	6–9	5.5–9.5

In addition, under the optimal operating conditions, the treated OMW still has high levels of toxicity for *A. fischeri* (bacteria). After 15 min of contact with the solution, the luminescent activity of the bacteria was inhibited by $64.82 \pm 2.85\%$ and, after 30 min, by $69.16 \pm 3.20\%$. For the same contact times, the untreated wastewater inhibited microbial activity by $60.38 \pm 0.31\%$ and $61.29 \pm 0.54\%$, respectively. Regarding the toxic effect on the species *L. sativum* (plant), as mentioned before, the untreated OMW showed a GI of $30.6 \pm 3.2\%$, while the treated wastewater had a GI of $33.1 \pm 6.9\%$. All the values mentioned above are shown in Table 5.

Table 5. Luminescence inhibition and germination index results for bacteria and *L. sativum*, respectively, for the untreated OMW and the treated wastewater under the optimal conditions.

Type of Solution	<i>Bacteria A. fischeri</i>		<i>L. sativum</i>
	Inhibition (15 min)	Inhibition (30 min)	GI
Untreated OMW	$60.38 \pm 0.31\%$	$61.29 \pm 0.54\%$	$30.6 \pm 3.2\%$
Treated OMW	$64.82 \pm 2.85\%$	$69.16 \pm 3.20\%$	$33.1 \pm 6.9\%$

The performance of the process under the optimum conditions was further analyzed considering the individual degradation of each of the five phenolic compounds present in the OMW. This analysis was performed based on the variation of the peak area, obtained using high performance liquid chromatography (HPLC), over time. The results of this analysis are shown in Figure 5.

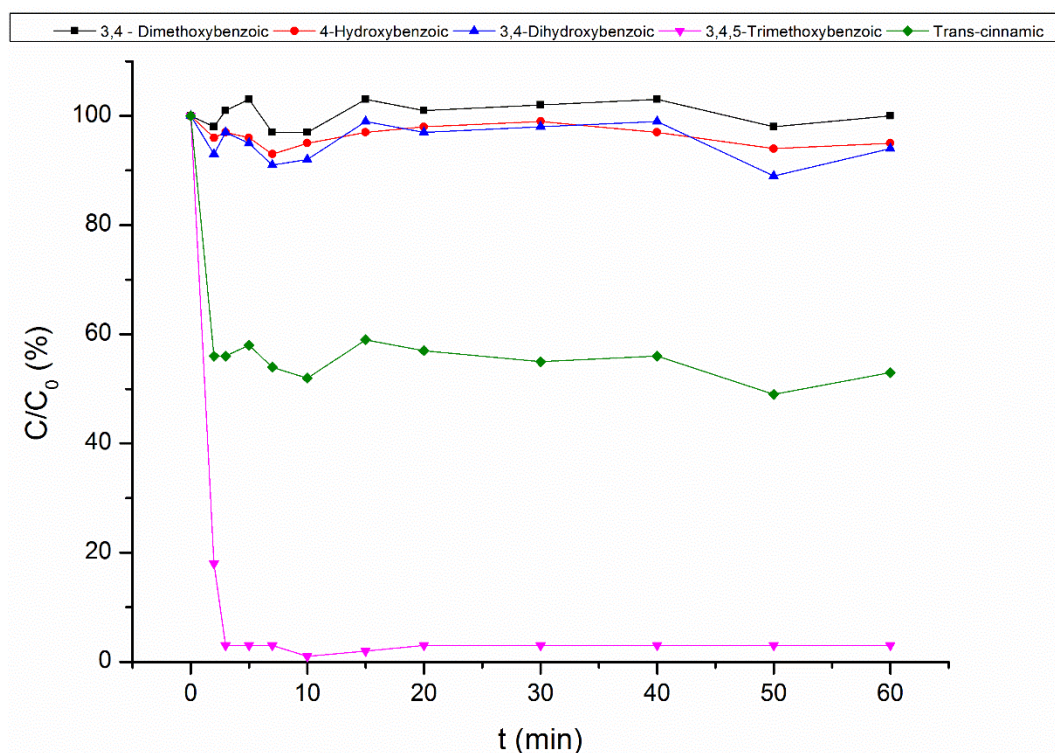


Figure 5. Individual degradation of the five phenolic compounds by the optimized SRbAOP.

The analysis of Figure 5 shows that the SRbAOP can fully degrade the 3,4,5-trimethoxybenzoic compound and can degrade the trans-cinnamic compound by 50%, but cannot degrade the remaining three compounds. Such behavior may be due to the higher selectivity of sulfate radicals towards certain organic compounds when compared to that of the hydroxyl radicals, as mentioned by Brienza et al. [11]. It should be noted that, although only two of the five phenolic compounds present in the OWM were degraded, these were the most complex compounds in the mixture in terms of chemical structure, as they were the ones with the most or the longest substitutes. It is also noted that the compounds were degraded in the first 5 min of the reaction, suggesting that this is a process of rapid and selective degradation.

Based on the HPLC results, it was also found that, along the reaction, other peaks appear in the chromatogram in addition to those used in the formulation of synthetic OWM. These peaks were formed during the reaction, and that they did not exist in the initial samples, which allows us to conclude that they are representative of intermediate compounds. Based on the database of the equipment used, it was found that these peaks may correspond to hydroquinone and 2-phenylhydroquinone, as mentioned by Santos et al. [36] and Enguita and Leitão [37], which may suggest that the toxicity of wastewater does not decrease with the treatment, although there is a reduction in the content of organic matter.

3.2.3. Comparison with the Fenton Process

As the Fenton process is an advanced oxidation process very much studied for the abatement of agro-industrial wastewaters, with an operation comparable to SRbAOP, the performance of both technologies was analyzed.

Rossi [38] studied the applicability of the Fenton process in the treatment of synthetic wastewater like the one used in this work. It is possible to verify that, to achieve a removal of COD and phenolic compounds using the Fenton process (Table 6) similar to that achieved using the SRbAOP, it is necessary to introduce 100 mg/L of Fe^{2+} and 830 mg/L of H_2O_2 . It

should be noted that these are not the optimal conditions for the Fenton process analyzed in the cited study.

Table 6. Comparison between the Fenton process and the SRbAOP, in a homogeneous system.

Process	Process Conditions	Results	Reference
Fenton	[Fe ²⁺] = 100 mg/L [H ₂ O ₂] = 830 mg/L pH = 3	~40% COD removal ~85% phenolic compounds removal	[38]
Fenton	[Fe ²⁺] = 25 or 50 mg/L [H ₂ O ₂] = 3 or 2 g/L pH = 3	~40% TOC removal ~100% phenolic compounds removal	[39]
SRbAOP	[Fe ²⁺] = 300 mg/L [S ₂ O ₈ ²⁻] = 600 mg/L pH = 5	~40% COD removal ~37% TOC removal ~63% phenolic compounds removal	This work
Fenton	H ₂ O ₂ /Fe ²⁺ = 15 H ₂ O ₂ /COD = 1.75 pH = 3.5 T = 30 °C	70% COD removal	[6]

Esteves et al. [39] also studied the applicability of the Fenton process in the treatment of a similar synthetic effluent. It is possible to verify that, to achieve the same TOC removal efficiency as in the SRbAOP with the Fenton process, it is necessary to introduce, in the system, 3 g/L of H₂O₂ and 25 mg/L of iron or 2 g/L of H₂O₂ and 50 mg/L of iron (Table 6). It should be noted that these are not the optimal conditions for the Fenton process analyzed in the cited study.

Lucas and Peres [6] studied the effect of pH, temperature, H₂O₂/Fe²⁺ molar ratio, and H₂O₂/COD weight ratio for Fenton's peroxidation of OMW (collected in Portugal and diluted to an initial COD ~2 g/L). The authors verified that the best operating conditions (pH 3.5, 30 °C, H₂O₂/Fe²⁺ = 15, and H₂O₂/COD = 1.75) led to 70% COD removal. This was a real effluent diluted to achieve twice the COD of the synthetic effluent studied in this work.

From the analysis of Table 6, it appears, according to Rossi [38] and Esteves et al. [39], that for the same treatment efficacy, the Fenton process produces less sludge, since it uses a lesser amount of catalyst. However, it requires a greater amount of oxidizing agent, which may increase the operating costs.

3.3. Heterogenous Catalysis

In this section, the performance of SRbAOP based on metal-activated persulfate, in heterogeneous catalysis, using red mud and Fe-Ce-O as a catalyst, is optimized and analyzed in terms of the results obtained regarding the removal of organic matter and toxicity.

3.3.1. Catalysts Characterization

For a correct analysis of the treatment process using heterogeneous catalysis, it is essential to know the physical and chemical characteristics of the selected catalysts.

The characterization of the Fe-Ce-O and the red mud was previously described by Rossi et al. [24] and Domingues et al. [20], respectively. Table 7 summarizes the characterization of these catalysts in terms of their surface area, pore size, chemical composition, and particle size and Table 8 presents the red mud chemical characterization

Table 7. Red mud and Fe-Ce-O characterization.

Catalyst	Surface Area (m ² /g)	Porosity	Chemical Composition
Fe-Ce-O	188	0.58	Fe/Ce 70/30 (mol/mol)
Red Mud	0.6	–	*

* The red mud chemical characterization is presented in Table 8.

Table 8. Red mud chemical composition.

Chemical Element	m _{chemical element} /m _{red mud}
Copper	43 ppm
Iron	5.9%
Zinc	17 ppm
Nickel	726 ppm
Chromium	862 ppm
Lead	53 ppm
Manganese	175 ppm
Magnesium	943 ppm
Calcium	3.4%
Sodium	1.9%
Potassium	0.29%

As previously mentioned, the red mud and the Fe-Ce-O were sieved, so the catalyst particles used had a diameter of <0.105 µm.

3.3.2. Heterogeneous SRbAOP Analysis

Two iron catalysts (red mud and Fe-Ce-O) were tested regarding their ability to activate persulfate. In both scenarios, the initial pH value and the PS load were kept constant and equal to 5 and 600 mg/L, respectively, and the catalyst load was optimized; see Figure 6.

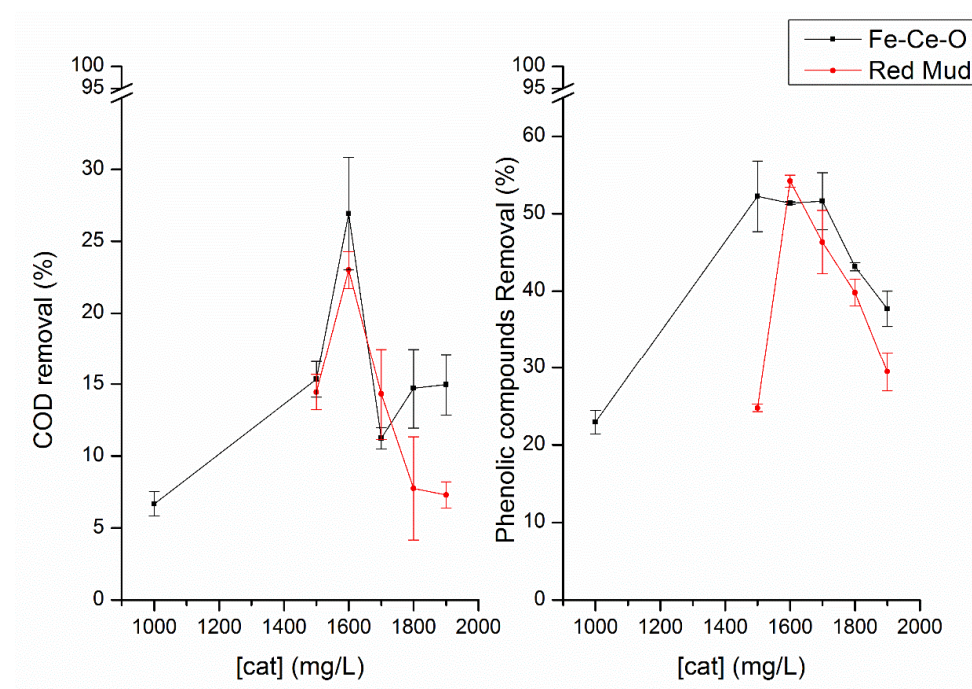


Figure 6. Catalyst load influence on COD removal and phenolic compound removal. (30 min of reaction, pH 5, and (PS) = 600 mg/L).

Regarding the red mud tests, the following red mud loads analyzed were 1500, 1600, 1700, 1800, and 1900 mg/L; for Fe-Ce-O tests, the loads were 1000, 1500, 1600, 1700, 1800, and 1900 mg/L. The effects of heterogeneous SRbAOPs were studied in terms of COD and phenolic compound removal.

From the analysis of Figure 6, it is possible to conclude that a red mud load of 1600 mg/L makes it possible to obtain the maximum COD and phenolic compound removal, of approximately 23% and 55%, respectively. From this point forward, an increase of the red mud load results in a decrease of the process efficiency.

A load of 1600 mg/L of Fe-Ce-O allows for the maximization of the COD and phenolic compound removal, achieving, approximately, 27% and 55% COD and phenolic compound removal, respectively. It is also verified that an increase in Fe-Ce-O load from 1000 to 1600 mg/L results in a COD removal increase, and from this point onward, an increase in the catalyst load induces a decrease in the COD removal.

In order to evaluate the toxic impact of the treated wastewater, *A. fischeri* luminescence inhibition provoked by treated samples at the optimal conditions was compared to the untreated simulated OMW (Table 9).

Table 9. Luminescence inhibition results for bacteria and GI for *L. sativum* for the untreated OMW and the treated wastewater with red mud and Fe-Ce-O (30 min of reaction, pH 5, (PS) = 600 mg/L and (cat) = 1600 mg/L).

Type of Solution	Bacteria <i>A. fischeri</i>		<i>L. sativum</i>
	Inhibition (15 min)	Inhibition (30 min)	GI
Untreated OMW	60.38 ± 0.31%	61.29 ± 0.54%	30.6 ± 3.2%
Treated OMW (red mud)	61.25 ± 1.64%	65.49 ± 1.59%	0.8 ± 1.2%
Treated OMW (Fe-Ce-O)	88.97 ± 6.16%	95.13 ± 5.63%	23.4 ± 1.4%

Treated wastewater has a toxicity towards the bacteria comparable to the untreated OMW. In Table 9, it can be observed that the treated samples have a lower GI than that of the untreated wastewater. As the results from the toxicity tests for the treated samples may be influenced by the presence of metals leached from the catalysts, the amount of iron dissolved in the effluent after the reaction was evaluated. This is also an important issue regarding the catalyst's stability and reutilization. For red mud, under optimal operating conditions, iron leaching of 13.08 ± 4.99 mg/L was observed, which means that, for every milligram of catalyst introduced in the system, 0.008 ± 0.003 mg of iron are leached. Regarding Fe-Ce-O, at the optimal conditions, an iron leaching of 42.32 ± 2.51 mg/L was observed, which means that, for every milligram of catalyst added, there is a leaching of 0.027 ± 0.002 mg of iron.

There are several studies in the literature focusing on the toxicity of phenolic wastewater in different oxidation treatments, such as ozonation and photocatalytic treatment. After the photocatalytic treatment of wastewaters containing different aromatic compounds, the early intermediates were more toxic and less biodegradable than the original pollutants [36]. Those authors reported that an improvement in the BOD/TOC ratio and in toxicity were observed only when mineralization of at least 80% of the initial TOC was reached. Some studies [40–42] have shown that major intermediates of phenol oxidation in AOPs can be categorized as readily biodegradable compounds (acetic, fumaric, propionic, formic, and succinic acids), nonbiodegradable compounds but without inhibitory or toxic effect over the biomass (maleic, oxalic, and malonic acids), toxic compounds (p-benzoquinone and hydroquinone), and finally inhibitory compounds (catechol) for biodegradation [41]. These results may agree with what happens with persulfate. The mineralization is not very high under the conditions studied, and in addition the reaction time was only 30 min. Thus, in line with what has been reported for other oxidation processes, in our case, toxic intermediates (such as hydroquinone) could also be formed. The analytic techniques applied only allowed us to identify hydroquinone, but surely other toxic intermediates (unidentified)

were produced. The amount and type of intermediates formed are surely dependent on the conditions applied (such as the type of catalysts). So, even if hydroquinone was not identified in the heterogeneous oxidation, other toxic intermediates that were not identified were produced. This may explain the lack of variation of toxicity during those processes.

Considering the red mud chemical composition, in Table 8, the optimal red mud load corresponds to 94.4 mg/L. Therefore, the molar ratio between PS and iron is 1.85, which does not follow the recommendation by Xiao et al. [17] and Rodriguez et al. [34]; the conclusions of these authors also do not apply to systems activated by Fe (II). According to Wu et al. [43], who studied the activation of PS by Fe (III), a molar ratio of two between PS and iron is more appropriate for these systems, which is close to the value reached in this work.

Considering the Fe-Ce-O composition present in Table 8, the introduction of the optimal Fe-Ce-O load results on an input of iron, into the system, of 480 mg/L. Thus, the molar ratio between PS and iron is 0.36, which does not follow the recommendations of Wu et al. [43], in iron (III)-activated PS systems, a molar ratio of two between the PS and iron should be adopted. Therefore, the system may be suffering from a lack of PS.

Finally, the performance of heterogeneous SRbAOP was compared with the Fenton process using the same catalysts. The comparison with the literature results is given in Table 10.

Table 10. Comparison between the Fenton process and the SRbAOP, using red mud as the catalyst.

Process	Process Conditions	Results	Reference
Fenton	[red mud] = 1000 mg/L [H ₂ O ₂] = 25 mg/L pH = 3	~5% TOC removal 25% TOC removal can be achieved with 100 mg/L of H ₂ O ₂ For 100 mg/L of H ₂ O ₂ : GI ~50% Bacterial inhibition = 100%	[20]
SRbAOP	[red mud] = 1600 mg/L [Fe ⁺³] = 100 mg/L [S ₂ O ₈ ⁻²] = 600 mg/L pH = 5	~23% COD removal ~1% TOC removal ~55% phenolic compound removal GI = 0.8 ± 1.2 % Bacterial inhibition of ~61–65 %	This work
Fenton	[Fe-Ce-O] = 1500 mg/L [H ₂ O ₂] = 3910 mg/L pH = 4	~25% COD removal ~100% phenolic compound removal	[22]
Fenton	[Fe-Ce-O] = 500 mg/L [H ₂ O ₂] = 8296 mg/L pH = 3	~5% TOC removal ~44% phenolic compound removal	[23]
SRbAOP	[Fe-Ce-O] = 1600 mg/L [Fe ⁺³] = 480 mg/L [S ₂ O ₈ ⁻²] = 600 mg/L pH = 5	~27% COD removal ~5% TOC removal ~55% phenolic compound removal	This work

From the analysis of Table 10, it appears that to achieve a similar removal of TOC in the Fenton process with red mud, less catalyst and less oxidizing agent are used. Whereas, regarding Fe-Ce-O, it is noted that for the Fenton process to achieve the same removal efficiency for TOC and phenolic compounds, a smaller amount of catalyst and a greater amount of oxidant are required. If one bears in mind COD abatement, to reach the same efficiency, the Fenton process requires a higher amount of oxidant and catalyst compared to SRbAOP.

3.4. Comparison between the Homogeneous and Heterogeneous Processes

All the catalysts used in the PS activation were compared to evaluate the best catalysis mode. This evaluation was done based on the optimal operating conditions for each catalyst and the results; both are shown in Table 11.

Table 11. Comparison between the different catalysts.

Catalyst	Optimal Conditions	Results
Iron (II) Sulfate	[Iron] = 300 mg/L [PS] = 600 mg/L pH = 5	~39% COD removal ~63% phenolic compound removal ~37% TOC removal GI ~33% Bacterial Inhibition ~65–69%
Red Mud	[Red Mud] = 1600 mg/L [Iron] = 94.4 mg/L [PS] = 600 mg/L pH = 5	~23% COD removal ~55% phenolic compound removal ~1% TOC removal 0.008 ± 0.003 mg iron leaching/mg catalyst GI ~1% Bacterial Inhibition ~61–65%
Fe-Ce-O	[Fe-Ce-O] = 1600 mg/L [Iron] = 480 mg/L [PS] = 600 mg/L pH = 5	~27% COD removal ~55% phenolic compound removal ~5% TOC removal 0.027 ± 0.002 mg iron leaching/mg catalyst GI ~23% Bacterial inhibition ~89–95 %

The homogeneous catalysis exhibits the best performance regarding removal efficiency as well as toxicity. These results were expected as, in homogenous systems, the mass transfer resistance is smaller. Even so, the discrepancy between the removal efficiency in heterogeneous catalysis and in homogeneous catalysis is not that significant.

Regarding the heterogenous catalysts, Fe-Ce-O shows the best COD removals results and toxicity results. Thus, Fe-Ce-O is better than red mud for PS activation. The use of heterogeneous catalysts allows the catalysts' recovery and reuse. In addition, it avoids iron sludge formation and management, which are required in homogeneous systems.

An interesting result is the fact that the use of 100 mg/L of iron (II) in the homogeneous systems shows the same efficiency as 1600 mg/L of red mud (94.4 mg/L of iron (III)). Bearing in mind that the same amount of iron (II) and iron (III) provide the same degradation efficiency of organic matter, the theory, mentioned by Xiao et al. [11], that Fe (III) is less efficient in the activation of PS seems to be contradicted. However, since the sludge is composed of other metals in addition to iron, these may also be acting in the persulfate activation process. Fan et al. [33] and Hoa et al. [31] found that PS can also be activated by manganese, aluminum, zinc, and copper, all of which are present in the red mud.

Comparing the red mud optimum with the Fe-Ce-O optimum, since the removal efficiencies are similar, it is verified that the synergistic effect between the iron and the cerium may be as efficient as using various metals.

4. Conclusions

SRbAOP is a selective and fast process, since, when applied to the treatment of synthetic wastewater, it was able to degrade 100% of the compound with more substitutes and 50% of the compound with the longest substitute, in 5–10 min. However, it was not able to degrade the remaining compounds.

Homogeneous SRbAOP applied to synthetic wastewater allowed a removal of 39% of the COD, 63% of the phenolic compounds, and 37% of the TOC at the best operating conditions (pH = 5, (Fe²⁺) = 300 mg/L, (PS) = 600 mg/L). In terms of toxicity, in the optimum operating conditions, the treated effluent has a similar toxicity to the original for both the bacteria *A. fischeri* and the plant *L. sativum*, which may be due to the formation of intermediate compounds, such as hydroquinone.

As for the heterogeneous SRbAOP, among the catalysts tested (red mud and Fe-Ce-O), Fe-Ce-O showed the best results, since it allowed achievement of the lowest toxicity, the highest COD removal, and the lowest leaching, under the optimal operating load of

1600 mg/L. However, the toxicity of the treated wastewater was higher than that of the untreated wastewater.

Among the heterogeneous and the homogeneous SRbAOPs, the homogenous had the best efficiency and led to the lowest toxicity. However, the efficiencies between the two processes were similar. In this context, the use of heterogeneous catalysts may be preferable, since it allows catalyst recovery and reuse while avoiding iron sludge formation and management.

The increased interest in the subject of persulfate-based treatment processes, especially in persulfate forms of activation, reveals that these technologies are promising. The evaluation of persulfate technology as a substitute for the Fenton process, which is already well established in the industry, requires a careful analysis of various factors, such as water matrix effects, byproduct formation, toxicological consequences, costs, and engineering challenges. In fact, persulfate could be an alternative to Fenton's process for the treatment of olive mill wastewater. However, the process must still be studied using other activators, such as thermal, electro activation, and other catalysts.

Author Contributions: Writing—original draft preparation, E.D.; Conceptualization, E.D.; Methodology, E.D., M.J.S. and T.V.; Funding acquisition, E.D., J.G. and R.C.M.; Data curation, E.D., M.J.S. and T.V.; Investigation, E.D.; Writing—review and editing, J.G. and R.C.M.; Supervision, R.C.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the European Union through the European Regional Development Fund (FEDER) within the framework COMPETE2020 by the financial support of the project POCI-01-0247-FEDER-033193 (SERENA—Development of a sludge free Fenton-integrated treatment methodology for olive mill wastewaters: a water recovery). Eva Domingues acknowledges FCT (Fundação para a Ciência e Tecnologia, Portugal) for the PhD Grant (SFRH/BD/144096/2019). João Gomes gratefully acknowledges the Foundation for Science and Technology (FCT Portugal) for the financial support (CEECIND/01207/2018). Thanks are due to FCT/MCTES for the financial support to CIEPQPF (UIDB/00102/2020).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

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

Abbreviations

AOP	Advanced oxidation process
BOD5	Biological oxygen demand
COD	Chemical oxygen demand
EU	European Union
GI	Germination Index
OMW	Olive mil wastewater
OP	Olive pomace
OOEIW	Olive oil extraction industry wastewaters
PMS	Peroxymonosulfate
PS	Persulfate
SRbAOP	Sulfate Radical based Advanced Oxidation Process
TOC	Total organic carbon

References

1. Alver, A.; Bastuk, E.; Kiliç, A.; Karatas, M. Use of advance oxidation process to improve the biodegradability of olive oil mill effluents. *Process Saf. Environ. Prot.* **2015**, *98*, 319–324. [[CrossRef](#)]
2. Ochando-Pulido, J.M.; Martinez-Ferez, A. Operation setup of a nanofiltration membrane unit for purification of two-phase olives and olive oil washing wastewaters. *Sci. Total Environ.* **2018**, *612*, 758. [[CrossRef](#)]
3. Ochando-Pulido, J.M.; Pimentel-Moral, S.; Verardo, V.; Martinez-Ferez, A. A focus on advanced physico-chemical processes for olive mill wastewater treatment. *Sep. Purif. Technol.* **2017**, *179*, 161. [[CrossRef](#)]

4. Flores, N.; Brillas, E.; Centellas, F.; Rodríguez, R.M.; Cabot, P.L.; Garrido, J.A.; Sirés, I. Treatment of olive oil mill wastewater by single electrocoagulation with different electrodes and sequential electrocoagulation/electrochemical Fenton-based processes. *J. Hazard. Mater.* **2018**, *347*, 58. [[CrossRef](#)] [[PubMed](#)]
5. Gürsoy Haksevenler, B.H.; Arslan Alaton, I. Evidence of inert fractions in olive mill wastewater by size and structural fractionation before and after thermal acid cracking treatment. *Sep. Purif. Technol.* **2015**, *154*, 176. [[CrossRef](#)]
6. Lucas, M.S.; Peres, J.A. Removal of COD from olive mill wastewater by Fenton's reagent: Kinetic study. *J. Hazard. Mater.* **2009**, *168*, 1253–1259. [[CrossRef](#)] [[PubMed](#)]
7. Amor, C.; Marchão, L.; Lucas, M.S.; Peres, J.A. Application of Advanced Oxidation Processes for the Treatment of Recalcitrant Agro-Industrial Wastewater: A Review. *Water* **2019**, *11*, 205. [[CrossRef](#)]
8. Rodríguez, S.; Lorenzo, D.; Santos, A.; Romero, A. Comparison of real wastewater oxidation with Fenton/Fenton-like and persulfate activated by NaOH and Fe(II). *J. Environ. Manag.* **2020**, *255*, 109926. [[CrossRef](#)]
9. Qiu, Q.; Guoxiang, L.; Yi, D.; Yaoyang, X.; Peng, B. Removal of antibiotic resistant microbes by Fe (II)-activated persulfate oxidation. *J. Hazard. Mater.* **2020**, *396*, 122733. [[CrossRef](#)] [[PubMed](#)]
10. Genç, N.; Durma, E.; Ciciğun, H.K.K. Response Surface Modeling and Optimization of Microwave-Activated Persulfate Oxidation of Olive Oil Mill Wastewater. *Clean Soil Air Water* **2020**, *48*, 1. [[CrossRef](#)]
11. Brienza, M.; Katsoyiannis, I. Sulfate Radical Technologies as Tertiary Treatment for the Removal of Emerging Contaminants from Wastewater. *Sustainability* **2017**, *9*, 1604. [[CrossRef](#)]
12. Ioannidi, A.; Oulego, P.; Collado, S.; Petala, A.; Arniella, V.; Frontistis, Z.; Angelopoulos, G.N.; Diaz, M.; Mantzavinos, D. Persulfate activation by modifies red mud for the oxidation of antibiotic sulfamethoxazole in water. *J. Environ. Manag.* **2020**, *270*, 110820. [[CrossRef](#)]
13. Gormez, F.; Gormez, O.; Yabalak, E.; Gormen, B. Application of the central composite design to mineralization of olive mill wastewater by electro/Fe (II)/persulfate oxidation method. *SN Appl. Sci.* **2020**, *2*, 178. [[CrossRef](#)]
14. Waclawek, S.; Lutze, H.V.; Grubel, K.; Padil, V.V.T.; Cernik, M.; Dionysiou, D.D. Chemistry of persulfates in water and wastewater treatment: A review. *Chem. Eng. J.* **2017**, *330*, 44–62. [[CrossRef](#)]
15. Giannakis, S.; Lin, K.Y.A.; Ghandari, F. A review of the recent advances on the treatment of industrial wastewaters by Sulfate Radical-based Advanced Oxidation Processes (SR-AOPs). *Chem. Eng. J.* **2021**, *406*, 127083. [[CrossRef](#)]
16. Usman, M.; Cheema, S.A.; Farooq, M. Heterogeneous Fenton and persulfate oxidation for treatment of landfill leachate: A review supplement. *J. Clean. Prod.* **2020**, *256*, 120448. [[CrossRef](#)]
17. Xiao, S.; Cheng, M.; Zhong, H.; Liu, Z.; Liu, Y.; Yang, X.; Liang, Q. Iron-mediated activation of persulfate and peroxymonosulfate in both homogeneous and heterogeneous ways: A review. *Chem. Eng. J.* **2020**, *384*, 123265. [[CrossRef](#)]
18. Manos, D.; Miserli, K.; Konstantinou, I. Perovskite and Spinel Catalysts for Sulfate Radical-Based Advanced Oxidation of Organic Pollutants in Water and Wastewater Systems. *Catalysts* **2020**, *10*, 1299. [[CrossRef](#)]
19. Lee, J.; von Gunten, U.; Kim, J.H. Persulfate-Based Advanced Oxidation: Critical Assessment of Opportunities and Roadblocks. *Environ. Sci. Technol.* **2020**, *54*, 3064–3081. [[CrossRef](#)]
20. Domingues, E.; Assunção, N.; Gomes, J.; Lopes, D.V.; Frade, J.R.; Quina, M.J.; Quinta-Ferreira, R.M.; Martins, R.C. Catalytic Efficiency of Red Mud for the Degradation of Olive Mill Wastewater through Heterogeneous Fenton's Process. *Water* **2019**, *11*, 1183. [[CrossRef](#)]
21. Martins, R.C.; Quinta-Ferreira, R.M. Screening of Ceria-Based and Commercial Ceramic Catalysts for Catalytic Ozonation of Simulated Olive Mill Wastewaters. *Ind. Eng. Chem. Res.* **2009**, *48*, 1196–1202. [[CrossRef](#)]
22. Martins, R.C.; Gomes, T.; Quinta-Ferreira, R.M. Fenton's Depuration of Weathered Olive Mill Wastewaters over a Fe-Ce-O Solid Catalyst. *Ind. Eng. Chem. Res.* **2010**, *49*, 9043–9051. [[CrossRef](#)]
23. Martins, R.C.; Amaral-Silva, N.; Quinta-Ferreira, R.M. Ceria based solid catalysts for Fenton's depuration of phenolic wastewaters, biodegradability enhancement and toxicity removal. *Appl. Catal. B-Environ.* **2010**, *99*, 135–144. [[CrossRef](#)]
24. Rossi, A.F.; Amaral-Silva, N.; Martins, R.C.; Quinta-Ferreira, R.M. Heterogeneous Fenton using ceria-based catalysts: Effects of the calcination temperature in the process efficiency. *Appl. Catal. B-Environ.* **2012**, *111–112*, 254–263. [[CrossRef](#)]
25. Baird, R.B.; Eaton, A.D.; Rice, E.W. Standard Methods for the Examination of Water and Wastewater. *J. Am. Public Health Assoc.* **2017**, *23*.
26. Lamuela-Raventós, R.M. Folin-Ciocalteu method for the measurement of total phenolic content and antioxidant capacity. In *Measurement of Antioxidant Activity & Capacity: Recent Trends and Applications*; Apak, R., Capanoglu, E., Shahidi, F., Eds.; Wiley: Hoboken, NJ, USA, 2017.
27. Domingues, E.; Rodriguez, F.; Gomes, J.; Quina, M.J.; Castro-Silva, S.; Martins, R.C. Screening of low-cost materials as heterogeneous catalysts for olive mill wastewater Fenton's peroxidation. *Energy Rep.* **2020**, *6*, 161–167. [[CrossRef](#)]
28. Trautmann, N.-M.; Krasny, M.E. *Composting in the Classroom—Scientific Inquiry for High School Students*; Cornell Waste Management Institute, Cornell Center for the Environment: Ithaca, NY, USA, 2017.
29. Chueca, J.R.; Amor, C.; Mota, J.; Lucas, M.S.; Peres, J.A. Oxidation of winery wastewater by sulphate radicals: Catalytic and solar photocatalytic activations. *Environ. Sci. Pollut. Res.* **2017**, *24*, 22414–22426. [[CrossRef](#)] [[PubMed](#)]
30. Ghanbari, F.; Moradi, M. Application of peroxymonosulfate and its activation methods for degradation of environmental organic pollutants: Review. *Chem. Eng. J.* **2017**, *310*, 41–62. [[CrossRef](#)]

31. Hoa, N.T.; Nguyen, H.; Nguyen, L.; Do, K.N.; Vu, L.D. Efficient removal of ciprofloxacin in aqueous solutions by zero-valent meta-activated persulfate oxidation: A comparative study. *J. Water Proc. Eng.* **2020**, *35*, 101199. [[CrossRef](#)]
32. Chueca, J.R.; Amor, C.; Silva, T.; Dionysiou, D.D.; Puma, G.L.; Lucas, M.S.; Peres, J.A. Treatment of winery wastewater by sulphate radicals: HSO₅⁻/transition metal/UV-A LEDs. *Chem. Eng. J.* **2017**, *310*, 473–483. [[CrossRef](#)]
33. Fan, Z.; Zhang, Q.; Li, M.; Sang, W.; Qiu, Y.; Xie, C. Activation of persulfate by manganese oxide-modified sludge-derived biochar to degrade Orange G in aqueous solution. *Environ. Pollut. Bioavailab.* **2019**, *31*, 70–79. [[CrossRef](#)]
34. Rodriguez, S.; Santos, A.; Romero, A.; Vicente, F. Kinetic of oxidation and mineralization of priority and emerging pollutants by activated persulfate. *Chem. Eng. J.* **2012**, *213*, 225–234. [[CrossRef](#)]
35. Halalsheh, M.; Kassab, G.; Shatanawi, K. Impact of legislation on olive mill wastewater management: Jordan as a case study. *Water Policy* **2021**, *23*, 343–357. [[CrossRef](#)]
36. Santos, A.; Yustos, P.; Quintanilla, A.; Rodríguez, J.J. Evolution of Toxicity upon Wet Catalytic Oxidation of Phenol. *J. Environ. Sci. Technol.* **2004**, *38*, 133–138. [[CrossRef](#)] [[PubMed](#)]
37. Enguita, F.; Leitão, A.L. Hydroquinone: Environmental Pollution, Toxicity and Microbial Answers. *Biomed. Res. Int.* **2013**. [[CrossRef](#)]
38. Rossi, A.F. Fenton's Process Applied to Wastewaters Treatment—Heterogeneous and Homogeneous Catalytic Operation Modes. Ph.D. Thesis, Chemical Engineering, Coimbra University, Coimbra, Portugal, 2014.
39. Esteves, B.M.; Rodriguez, C.S.D.; Madeira, L.M. Synthetic olive mill wastewater treatment by Fenton's process in batch and continuous reactors operation. *Environ. Sci. Pollut. Res.* **2018**, *25*, 34826–34838. [[CrossRef](#)]
40. Moussavi, G.; Khavanin, A.; Alizadeh, R. The investigation of catalytic ozonation and integrated catalytic ozonation/biological processes for the removal of phenol from saline wastewaters. *J. Hazard. Mater.* **2009**, *171*, 175–181. [[CrossRef](#)]
41. Suarez-Ojeda, M.E.; Carrera, J.; Metcalfe, I.S.; Font, J. Wet air oxidation (WAO) as a precursor to biological treatment of 10 Journal of Engineering substituted phenols: Refractory nature of the WAO intermediates. *Chem. Eng. J.* **2008**, *144*, 205–212. [[CrossRef](#)]
42. Liotta, L.F.; Gruttadauria, M.; di Carlo, G.; Perrini, G.; Librando, V. Heterogeneous catalytic degradation of phenolic substrates: Catalysts activity. *J. Hazard. Mater.* **2009**, *162*, 588–606. [[CrossRef](#)]
43. Wu, Y.; Prulho, R.; Brigante, M.; Dong, W.; Hanna, K.; Mailhot, G. Activation of persulfate by Fe(III) species: Implications for 4-tert-butylphenol degradation. *J. Hazard. Mater.* **2016**, *322*, 380–386. [[CrossRef](#)] [[PubMed](#)]