catalysts

MDPI

Article

Table Olive Manufacturing Wastewater Treatment Using the Peroxymonosulfate/Fe(III) System

Francisco Javier Rivas *, Fernando J. Beltrán and Olga Gimeno

Departamento de Ingeniería Química y Química Física, Instituto Universitario de Investigación IACYS, Universidad de Extremadura, Avenida de Elvas s/n, 06006 Badajoz, Spain; ogimeno@unex.es (O.G.)
* Correspondence: fjrivas@unex.es; Tel.: +34-924289300

Abstract: Wastewater generated in table olive manufacturing processes (WWTOMP) is a seasonal waste difficult to manage due to the high salinity content. The treatment of WWTOMP has been accomplished by including a precoagulation stage with aluminum sulfate, oxidation using the peroxymonosulfate/Fe(III) system, and a final aerobic biological stage. The optimum conditions of precoagulation led to a chemical oxygen demand removal rate of roughly 30–35% without the need for pH adjustment. The peroxymonosulfate(PMS)/Fe(III) system was thereafter applied to the effluent after coagulation. The addition of PMS lowered the initial pH to acidic conditions (pH = 1.5–2.0). Under these operating conditions, the initial PMS concentration and the initial Fe(III) dose showed optimum values. An excess of the oxidant and/or the catalyst partially inhibited the process efficiency, and pH exerted a significant influence. COD removal was substantially increased as the pH of the solution was moved toward circumneutral values in the interval 5–4. Moreover, at pH values of 5 and 7, PMS was capable of reducing COD without the need for Fe(III) presence. The direct oxidation of organics by PMS or the generation of chloride-based oxidants (Cl_2 or HClO) is suggested to occur in parallel to the radical attack from PMS decomposition. An attempt to biologically reduce the final COD to discharge limits failed, mainly due to the high salinity content; however, the 1:2 dilution led to the reduction in COD from 6 to 2 g L^{-1}. Acclimated sludges or saline content reduction should be first considered.

Keywords: table olive wastewater; monopersulfate; ferric iron catalysis; oxone; sulfate radicals

check for updates

Citation: Rivas, F.J.; Beltrán, F.J.; Gimeno, O. Table Olive Manufacturing Wastewater Treatment Using the Peroxymonosulfate/Fe(III) System. *Catalysts* **2024**, *14*, 121. https://doi.org/10.3390/catal14020121

Academic Editor: John Vakros

Received: 11 January 2024
Revised: 25 January 2024
Accepted: 26 January 2024
Published: 2 February 2024

1. Introduction

In the quest for effective and sustainable wastewater treatment strategies, sulfate radicals have emerged as a promising tool, offering a versatile and powerful approach to address the complex challenges associated with real wastewater. The use of sulfate radicals involves advanced oxidation processes (AOPs), harnessing their strong oxidative potential to degrade and transform a wide range of pollutants present in wastewater. This innovative technique has garnered considerable attention in recent years due to its efficacy in treating diverse contaminants, its applicability to various industrial effluents, and its potential for reducing the environmental impact of wastewater discharge.

The generation of sulfate radicals can be accomplished through various methods, including the excision of the persulfate (PS) or the peroxymonosulfate (PMS) molecule [1]. In the literature, activation through radiation [2], heat [3], homogeneous or heterogeneous catalysts [4], etc., has been reported. Metal homogeneous activation is normally accomplished in the presence of cations at a low valence state, which transfer an electron to the PS/PMS molecule to generate the corresponding radicals:

$$HSO_5^{-} + M^{+n} \rightarrow OH^{-} + M^{+(n+1)} + SO_4^{-\bullet} \quad (1)$$

$$HSO_5^{-} + M^{+n} \rightarrow M^{+(n+1)} + HO^{\bullet} + SO_4^{2-} \quad (2)$$

Hydroxyl and/or sulfate radicals can oxidize a number of organic and inorganic substances, leading to the generation of simpler and more biodegradable final products or even mineralization to carbon dioxide and water [5]. Additionally, PS and/or PMS can directly oxidize contaminants through a nonradical pathway [6].

The use of homogeneous catalysis has been proven to be more efficient than heterogenous catalysts [1]; however, the toxicity and cost associated with transition metals is a substantial drawback in terms of real scaling up and application. In this sense, the use of iron as a homogeneous catalyst can be suggested due to its wide availability and low toxicity compared to other more costly or harmful metals such as cobalt, silver, copper, etc.

The Fe(II)/PMS system has been widely used in the treatment of selected pollutants [7] with a variety of results. As a rule of thumb, the main disadvantage of this system is the fast consumption of Fe(II), leading to the generation of Fe(III) and the precipitation of Fe(II) or Fe(III) depending on pH conditions, which would eventually remove the catalyst from the media. To avoid the previous negative effects, some authors have proposed the use of chelating agents capable of simultaneously promoting the redox cycle Fe(II)/Fe(III) [8,9]. Hence, natural polyphenols extracted from plants with strong electron-donating capacity can address both functions, i.e., iron complexation and Fe(III) reduction capacity [10].

Table olive manufacturing generates several effluents with a high contaminant load. During the manufacturing process, washing water, debittering aqueous solutions, brines, etc., are produced and mixed at the end of the plant production process. The characteristics of wastewater from table olive production can vary depending on the specific processing methods employed, but they generally share some common features.

Wastewater from table olive production often contains high concentrations of brine, which is used in the curing process to reduce bitterness and enhance flavor. Brine can contribute to elevated salinity levels in wastewater. Additionally, the processing of table olives involves various steps such as washing, fermentation, and packaging. As a result, wastewater may contain organic matter such as olive residues, fermentation byproducts, and other organic compounds, including a high content of polyphenols [11]. Polyphenolic compounds, which are natural antioxidants found in olives, can be present in wastewater. In terms of the base of their structure, phenolic compounds can be classified as those derived from cinnamic acid (p-coumaric acid, caffeic acid, ferulic acid, and synaptic acid) and those derived from benzoic acid (p-hydroxybenzoic acid, protocatechuic, vanillic acid, veratric acid, gallic acid, and syringic acid) [12]. These compounds may contribute to color and can pose challenges in terms of biological treatment and disposal.

The pH of wastewater can be influenced by the presence of organic acids used in the curing process. Olive processing methods such as lactic acid fermentation can contribute to acidity in the wastewater. Olive fruit contains oil, and the processing steps involved may lead to the presence of fats and lipids in the wastewater. The oil content can affect the overall characteristics of the wastewater. The presence of compounds such as polyphenols and residual olive material can contribute to color and turbidity in the wastewater. This may necessitate additional treatment for aesthetic reasons and to meet discharge standards.

Considering the abovementioned findings, and given the beneficial effect of the presence of phenolic compounds in the Fe(II)/Fe(III)/PMS system, it was assumed that the application of this treatment could be a promising option to reduce the organic load of wastewaters containing high concentrations of polyhydroxyphenols, as is the case with the effluent generated in the table olive manufacturing industry. Hence, a first attempt was made to investigate the influence of the main operating parameters, and the resulting conclusions and perspectives are stated in this article.

2. Results and Discussion

2.1. Preliminary Coagulation–Flocculation Stage

Before the application of the Fe(III)/PMS system, wastewater organic content was reduced using a simple precipitation process in the presence of $Al_2(SO_4)_3$. The coagulation–flocculation stage can be easily implemented with no special requirements in terms of technology. Aluminum sulfate was chosen as the most effective coagulant. A first series was carried out by varying the coagulant dose at pH 6.5. The optimum pH for aluminum sulfate as a coagulant in water treatment typically falls within the range of 6.0 to 7.5. However, it should be noted that the effectiveness of aluminum sulfate as a coagulant can be influenced by the specific water quality and characteristics of the system being treated [13]. Figure 1 shows the removal of the chemical oxygen demand (COD) and turbidity in the jar test experiments conducted in the presence of increasing doses of aluminum sulfate.

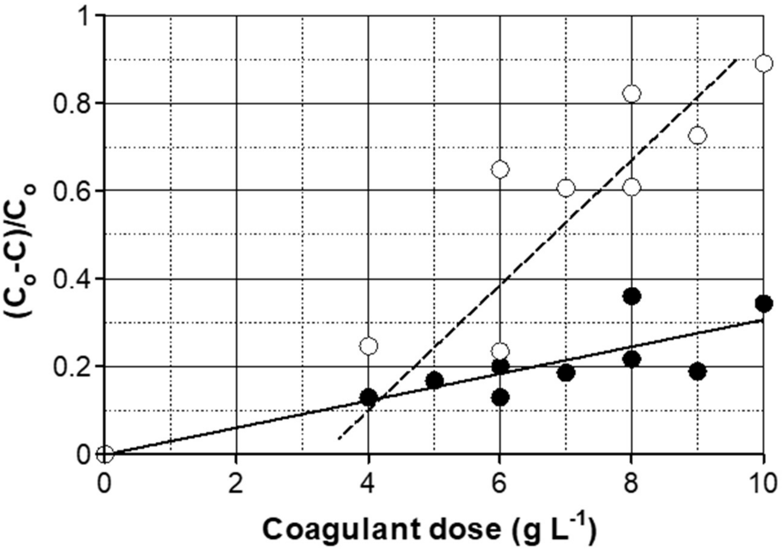

Figure 1. Coagulation–flocculation applied to wastewater from table olive manufacturing. COD (●) and turbidity (○) removal in the presence of different doses of aluminum sulfate. C_{COD_o} = 28.6 g L^{-1}, Turbidity_o = 170 NTU, pH = 6.5; T = 20 °C.

As observed in Figure 1, the coagulant dose exerted a positive influence both in COD and turbidity removal processes. Hence, with the highest coagulant concentration, COD elimination was approximately 30%, and turbidity decay was 90%. Data in the literature are scarce, but similar values have been reported in studies on wastewater of an analogous nature. For instance, Aldana and coworkers reported a 20% COD elimination rate and 50% turbidity removal using effluent from a black table olive processing plant [14]. Ferrer-Polonio et al. found a negligible COD reduction after applying commercial coagulants to wastewater from the production of green table olives; however, these authors used very low doses of the coagulants–flocculants tested [15].

Most of the works, however, are published on the effluents used in wastewater treatment from olive oil production [12], which have significantly different properties from the effluents generated in table olive production [15], including a higher organic load and much lower conductivity.

Experiments shown in Figure 1 were carried out at pH 6.5. In this pH range, aluminum sulfate undergoes hydrolysis, forming aluminum hydroxide flocs, ensuring the formation of stable and well-settling flocs. However, the optimum pH also depends on the wastewater nature and the characteristics of the substances present. Accordingly, a new series of experiments was performed by adjusting the initial pH to different values.

As inferred from Figure 2, the turbidity removal efficacy increased as the coagulation pH moved toward more basic conditions. These results are in line with those reported by Ferrer-Polonio and co-workers [15]. These authors reported an increase in turbidity removal from 40% to almost 100% when increasing the coagulation pH from 4.0 to 9–11. Contrarily, COD elimination slightly decreased as the pH was adjusted to the basic zone. In this scenario, it was decided to carry out the process at the natural pH of wastewater, which, after coagulant addition, decreased to a pH value of roughly 5.0. At this pH, maximum

COD was eliminated (around 30–35%) without the need for pH adjustment, thus reducing chemical usage. The use of flocculants did not improve the process, so this addition was not considered. After the coagulation stage, the supernatant phenolic content decreased by 60% compared to the untreated effluent.

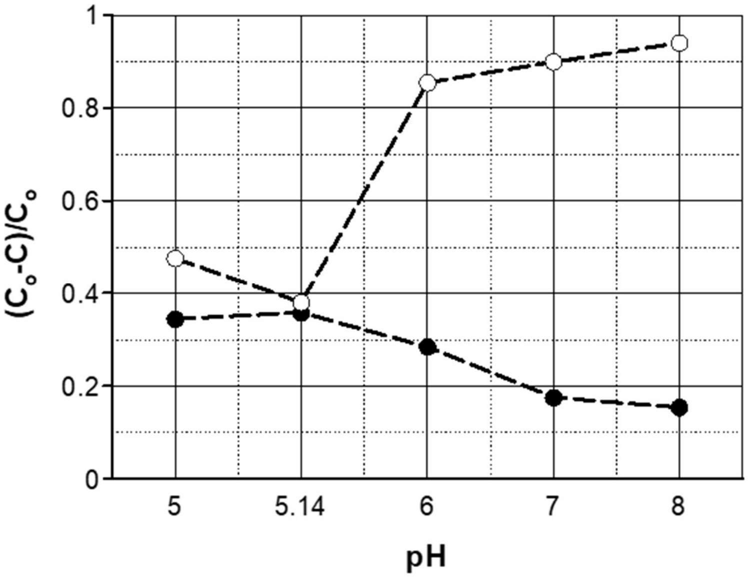

Figure 2. Coagulation–flocculation applied to wastewater from table olive manufacturing. COD (●) and turbidity (○) removal at different pH. C_{COD_o} = 28.6 g L^{-1}, Turbidity_o = 170 NTU, T = 20 °C, $C_{Al2(SO4)3}$ = 8.0 g L^{-1}.

2.2. *Application of the Fe(III)/PMS System*

2.2.1. Influence of Initial PMS Concentration

In order to decrease the COD of the effluent obtained after the precipitation stage, the feasibility of the Fe(III)/PMS system was investigated. To avoid the use of excessive quantities of PMS, an initial dilution of 1:10 with tap water was prepared using the coagulated supernatant obtained in the previous stage.

Hence, a first series of experiments was carried out at different initial concentrations of PMS in the presence of 3.0×10^{-3} in Fe(III) under uncontrolled pH conditions. These operating conditions were chosen according to previous studies dealing with the treatment of similar effluents with Fenton's reagent [16].

The results in Figure 3, obtained under different concentrations of initial PMS concentration, indicate the existence of an optimum in the initial PMS load under the operating conditions investigated.

The PMS/Fe(II)/Fe(III) system is assumed to behave analogously to Fenton´s chemistry [15], i.e., through generation of highly reactive radicals:

$$\mathrm{Fe(II)} + \mathrm{HSO_5^-} \rightarrow \left\{ \begin{array}{l} \mathrm{SO_4^{-\bullet}} + \mathrm{Fe(III)} + \mathrm{HO^-} \\ \mathrm{SO_4^{2-}} + \mathrm{Fe(III)} + \mathrm{HO^\bullet} \end{array} \right. \quad k = 3 \times 10^4 \mathrm{M^{-1}s^{-1}} \tag{3}$$

However, if no Fe(II) is present from the start, a previous reduction of Fe(III) to Fe(II) is required. This stage is believed to occur due to the presence of phenolic substances in the effluent to be treated [17,18]:

$$\mathrm{Phen} + \mathrm{Fe(III)} \rightleftarrows \mathrm{Phen} \equiv \mathrm{Fe(III)} \tag{4}$$

$$\mathrm{Phen} \equiv \mathrm{Fe(III)} \rightleftarrows \mathrm{Fe(II)} + \mathrm{Semiquinone^\bullet} \tag{5}$$

$$\mathrm{Semiquinone^\bullet} + \mathrm{Fe(III)} \rightleftarrows \mathrm{Fe(III)} + \mathrm{Benzoquinone} \tag{6}$$

Once radicals are formed, these species may attack the COD content of the effluent (Reactions (7) and (8)) to generate oxidized molecules with a lower COD value or even lead to CO_2 and water. An excess of the oxidant, however, could compete with the target substances (M) that contribute to COD, the scavenging part of the radicals available (Reactions (9) and (10)):

$$M + SO_4^{-\bullet} \rightarrow \text{Intermediate} + SO_4^{2-} \quad (7)$$

$$M + HO^{\bullet} \rightarrow \text{Intermediate} + HO^{-} \quad (8)$$

$$SO_4^{-\bullet} + HSO_5^{-} \rightarrow HSO_4^{-} + SO_5^{-\bullet} \quad (9)$$

$$HO^{\bullet} + HSO_5^{-} \rightarrow SO_5^{-\bullet} + H_2O \quad (10)$$

The negative effect of an excess of PMS is not always detected and depends on a number of factors such as pH, target pollutants nature, temperature, etc. Hence, some works [19,20] have reported the existence of an optimum PMS concentration in effluents from the olive oil manufacturing process (synthetic or real).

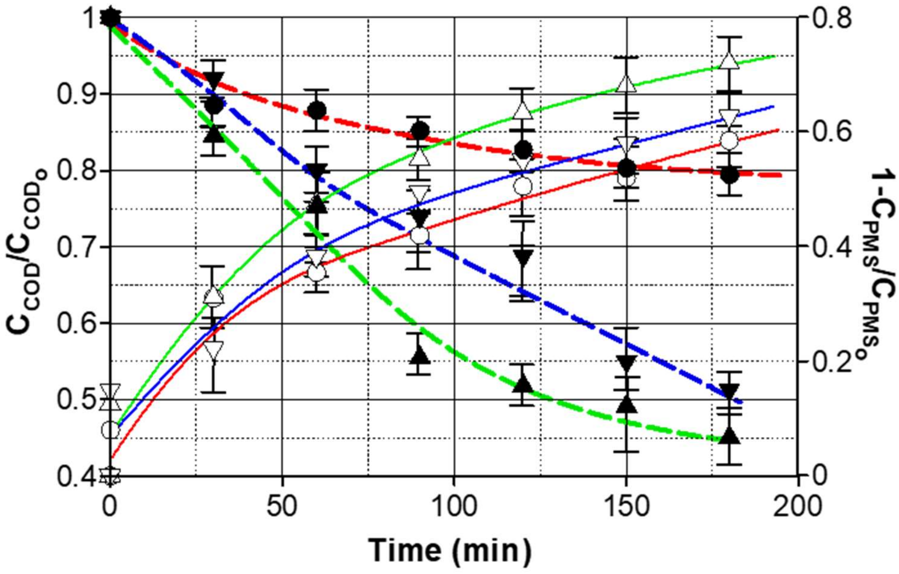

Figure 3. Removal of table olive wastewater COD using the PMS/Fe(III) system. C_{COD_o} = 2.0 g L^{-1} (averaged value), T = 20 °C, $C_{Fe(III)} = 3.0 \times 10^{-3}$, pH = 1.5 (after PMS addition), C_{PMS_o}: ●○, 0.1 M; ▲△, 0.2 M; ▼▽, 0.4 M. (Open symbols correspond to PMS conversion).

Some simple calculations (see Figure 4) suggest that PMS is inefficiently consumed when the highest initial concentration is used. The amount of monopersulfate disappearance increases as the initial concentration of this reagent is augmented; however, this is not converted to a higher rate of COD removal. Figure 4 shows the COD conversion rate relative to PMS consumption. As inferred from this figure, the lowest PMS efficiency was obtained when the highest concentration was used. As commented previously, similar results have been reported in the literature when an excess of the oxidant is added to the reaction media, although different trends are experienced depending on the operating conditions used and the matrix nature to be treated [21].

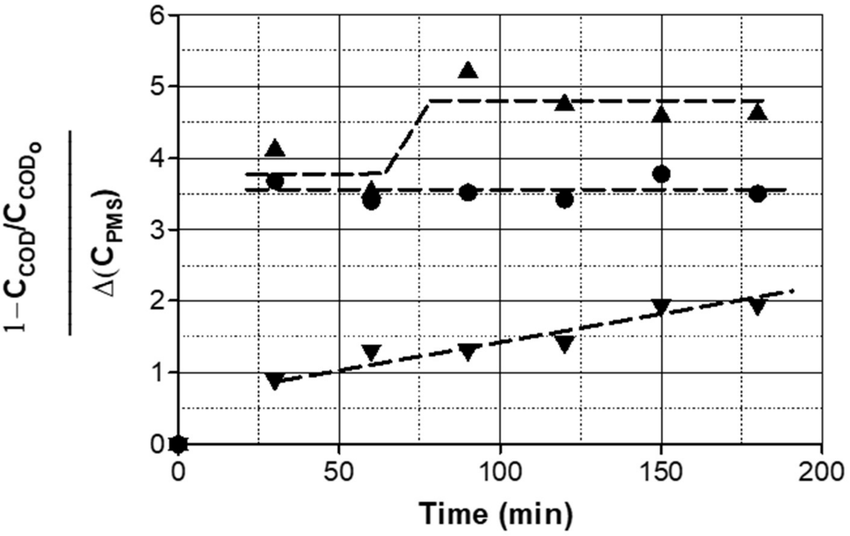

Figure 4. Treatment of table olive wastewater using the PMS/Fe(III) system. PMS efficiency in COD removal. C_{CODo} = 2.0 g L^{-1} (averaged value), T = 20 °C, $C_{Fe(III)} = 3.0 \times 10^{-3}$, pH = 1.5 (after PMS addition), C_{PMSo}: ●, 0.1 M; ▲, 0.2 M; ▼, 0.4 M.

2.2.2. Influence of Initial Fe(III) Concentration

The next series of experiments was conducted to assess the influence of the initial Fe(III) concentration in the range 1.0–6.0 × 10^{-3} M while keeping constant the rest of the operating parameters. Figure 5 shows the results obtained in this series. As observed, no significant differences could be observed in the range of Fe(III) concentrations tested. A certain negative effect may be envisaged when the highest Fe(III) concentration was used; however, the sporadic results obtained do not allow us to categorically point to the scavenging effect of the iron excess due to Reactions (11) and (12).

$$SO_4^{-\bullet} + Fe(II) \rightarrow SO_4^{2-} + Fe(III) \tag{11}$$

$$HO^{\bullet} + Fe(II) \rightarrow HO^{-} + Fe(III) \tag{12}$$

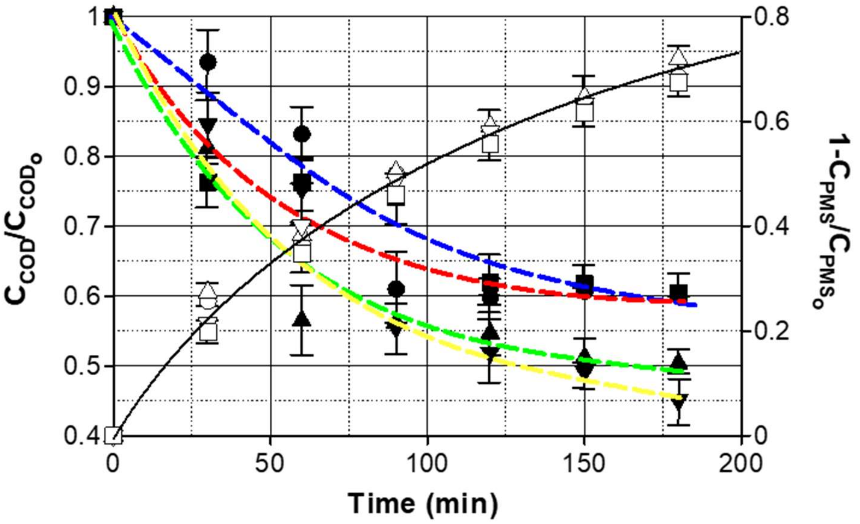

Figure 5. Treatment of table olive wastewater using the PMS/Fe(III) system. Initial Fe(III) influence. C_{CODo} = 2.0 g L^{-1} (averaged value), T = 20 °C, C_{PMSo} = 0.2 M, pH = 1.5 (after PMS addition), $C_{Fe(III)}$ = M × 10^3: ●○, 1.0; ▲△, 3.0; ■□, 6.0; ▼▽, 10.0. (Open symbols: PMS conversion).

The low influence of iron dose was also reported by other authors after applying the Fe(II)/PMS technology to olive mill wastewater [20].

Unexpectedly, based on Reaction (3), iron concentration did not influence the PMS conversion rate, suggesting the existence of a parallel reaction mechanism not involving the activation through iron species.

Nevertheless, no outstanding results were obtained, and the final COD value after 3 h of treatment did not suggest the addition of Fe(III) or the application of the PMS/Fe(III) system.

2.2.3. pH Influence

A final attempt was finally made by increasing the pH of the experiments after PMS addition. In case of acceptable results at circumneutral pH, a final biological process could be carried out to comply with the regulations of direct discharge.

Figure 6 shows the results obtained in the interval of pH values 1.5–7.0.

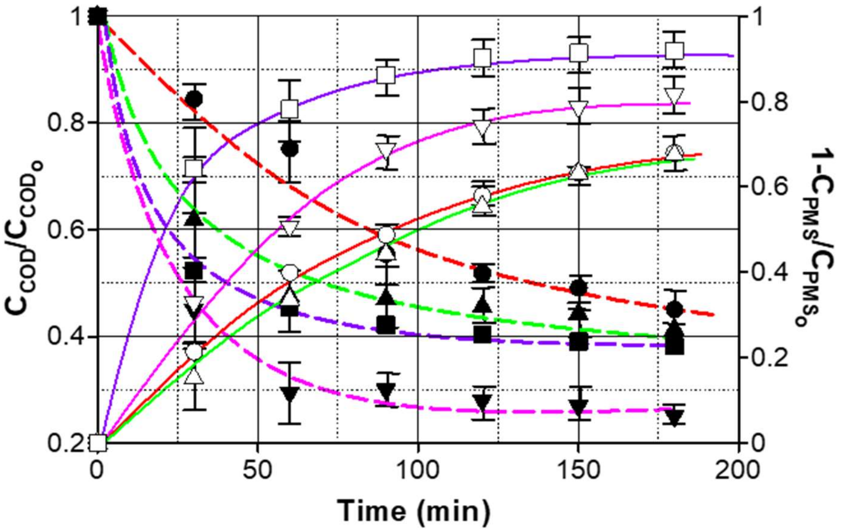

Figure 6. Treatment of table olive wastewater using the PMS/Fe(III) system. Initial pH influence. C_{CODo} = 2.0 g L^{-1} (averaged value), T = 20 °C, C_{PMSo} = 0.2 M, $C_{Fe(III)}$ = 0.03 M, pH (after PMS addition): ●○, 1.5; ▲△, 3; ▼▽, 5.0; ■□, 7.0. (Open symbols: PMS conversion).

As observed from Figure 6, pH exerted a substantial influence both in COD elimination and PMS uptake. Considering the data obtained, pH positively influenced COD conversion when increasing this parameter from 1.5 to 5.0. A further increase to pH 7.0, however, resulted in the partial inhibition of the process. The pH effect raises some controversy in the specialized literature. The following statements were found in the literature:

- Some authors claim that high pH has a negative effect due to the self-decomposition of PMS through a nonradical pathway with oxygen evolution, showing maximum decomposition at pH 9.0 [22,23].
- A pH level of above 3.0 may lead to Fe(III) precipitation, thus inhibiting its catalytic role in PMS decomposition.
- For pH below 5.0, radicals can be scavenged by protons [24].
- The efficacy of the PMS/Fe(III)/Fe(II) system at low pH can be reduced due to the formation of iron aquocomplexes (the reduction of the available free iron) [24].
- The reactivity of target pollutants can significantly differ depending on the major structure present (protonated, neutral, or ionic forms). This is especially relevant in phenol-type substances.
- Extremely acidic pH may prompt proton bonding to the O−O bond of PMS, diminishing and inhibiting the decomposition with Fe(II) [25].

According to all the above statements, a dual influence of pH can be expected depending on the predominant effect. Thus, in this particular case, the precipitation of iron species is believed to be avoided due to the formation of stable complexes with the phenolic content of the wastewater (no apparent particulate formation was observed). Additionally, given the complex nature of the effluent, the reactivity of the protonated/neutral/ionic forms of the organics present is unknown. However, it seems clear that as pH increases, the inefficient PMS decomposition proceeds to a higher extent.

Figure 7 shows an optimum PMS uptake in the experiment conducted at pH 3, decreasing thereafter when this parameter was increased to 5 and 7. This effect was specifically observed in the first hour of the process.

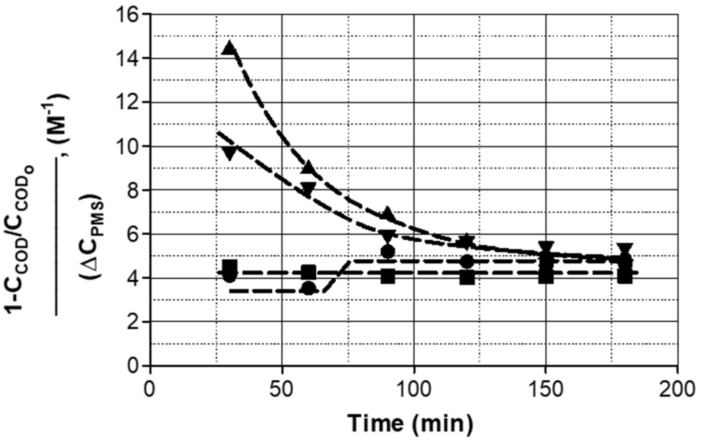

Figure 7. Treatment of table olive wastewater by the PMS/Fe(III) system. PMS efficiency in COD removal. Initial pH influence. C_{CODo} = 2.0 g L^{-1} (averaged value), T = 20 °C, C_{PMSo} = 0.2 M, $C_{Fe(III)}$ = 0.03 M, pH (after PMS addition): ●, 1.5; ▲, 3; ▼, 5.0; ■, 7.0.

As stated previously, since no differences in PMS conversion were obtained for the experiments carried out at different Fe(III) doses, it was hypothesized that other parallel routes of COD elimination may coexist. Accordingly, a series of experiments was performed at different pH values in the presence and absence of Fe(III).

As inferred from Figure 8, PMS was capable of directly removing COD from the media with no need for Fe(III) mediated activation. The direct PMS elimination of COD was more efficient at pH 5 compared to the results obtained at pH 7, although differences could be considered negligible with a final COD conversion rate of approximately 65–70% after 180 min of treatment.

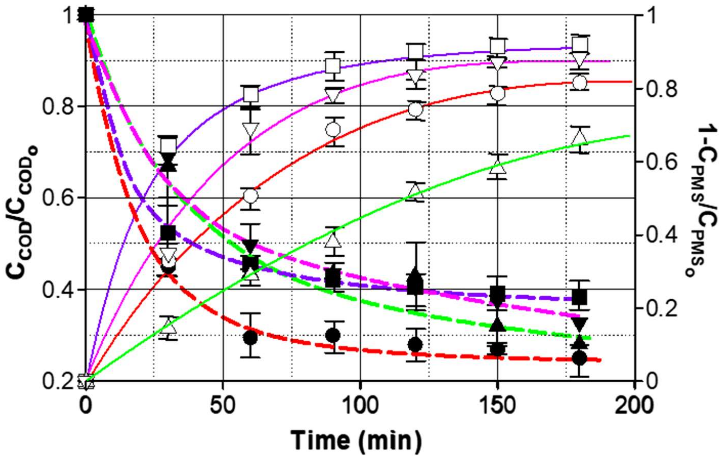

Figure 8. Treatment of table olive wastewater using the PMS/Fe(III) system. Initial pH and Fe(III) influence. C_{CODo} = 2.0 g L^{-1} (averaged value), T = 20 °C, C_{PMSo} = 0.2 M. ●○, $C_{Fe(III)}$ = 0.03 M, pH = 5.0; ■□, $C_{Fe(III)}$ = 0.03 M, pH = 7.0; ▲△, $C_{Fe(III)}$ = 0.0 M, pH = 5.0; ▼▽, $C_{Fe(III)}$ = 0.0 M, pH = 7.0. (Open symbols: PMS conversion).

The presence of Fe(III) slightly accelerated the COD removal rate, although this improvement was more significant at pH 5.0. More clear trends were observed in PMS evolution. Therefore, as the pH increased, so did the conversion rate of PMS. This behavior could be verified in the presence or absence of Fe(III). Comparing the data obtained at the same pH, we found that the presence of Fe(III) involved an increase in the PMS removal rate, suggesting the coexistence of two mechanisms in COD transformation: a likely direct oxidation process by peroxymonosulfate and indirect oxidation through the radicals generated after PMS scission.

Monopersulfate can oxidize organic molecules without the need for activators. The hydroxylation of dicarbonyl groups has been previously reported in the literature [26]. Additionally, other studies highlight its potential for oxidizing nitrogen-containing compounds [27,28]; oxygenating C–H bonds; and cleaving olefins, ketones, and more [29].

The oxygenation of PMS-attacked molecules leads to the observed COD reduction; however, pH plays a crucial role since the selective reaction of PMS highly depends on the predominant species of the organic molecules (protonated, neutral, or ionic forms) [30].

Given the high concentration of chlorides, a third pathway could be postulated. Peroxymonosulfate is capable of oxidizing Cl^- ions to HClO and/or molecular chlorine [31,32].

$$HSO_5{}^- + Cl^- \leftrightarrows SO_4{}^{2-} + HClO \tag{13}$$

$$H^+ + HClO + Cl^- \leftrightarrows H_2O + Cl_2 \tag{14}$$

Chlorine or hypochlorite can thereafter reduce substances (M) contributing to COD:

$$HClO/Cl_2 + M \rightarrow \text{Products} \tag{15}$$

Regardless, even under optimal conditions, the resulting COD still exceeded the discharge limit, necessitating the implementation of a final polishing process. The biodegradability of the effluent was tested in the presence of an unacclimated activated sludge collected from the secondary tank of a municipal wastewater plant.

In this case, raw wastewater was first subjected to filtration + coagulation + monopersulfate oxidation in the absence of iron + 1:2 dilution with tap water. Polyphenols are toxic to microorganisms, which is why the previous oxidative process should hopefully eliminate these compounds before the application of the activated sludge biodegradation. The obtained final effluent presented an initial COD of 6130 ppm with a reduction of 66.7% regarding the raw wastewater effluent COD before dilution and an 82% decrease after 1:2 dilution. The results are shown in Figure 9.

The use of nonacclimated microorganisms applied to an effluent with this extent of high NaCl content did meet expectations. However, Figure 9 corroborates the results indicating that, after an initial induction period, the aerobic biodegradation of the effluent could reduce the COD by an additional 60%, yielding a final COD of 2.4 g L^{-1}. Unfortunately, the settling properties of the activated sludge gradually deteriorated, likely due to the accumulation of filamentous or dead microorganisms because of the extreme saline conditions. In fact, an experiment conducted with no dilution (initial COD = 11.4 g L^{-1}) did result in the total mortality of the microorganisms. However, this was just the first attempt to determine the potential biodegradability of this effluent. The possible use of acclimated microorganisms would hopefully lead to better results.

The concentration of added sulfate was below the amount of NaCl present (around 30 g L^{-1} for raw wastewater and 15 g L^{-1} for the 1:2 dilution used in biodegradation experiments). We believe that the inhibition of the aerobic process is likely due to sodium chloride rather than added sulfates. Nevertheless, the influence of the sulfates should not be overlooked, and a more rigorous study should be performed to optimize the process.

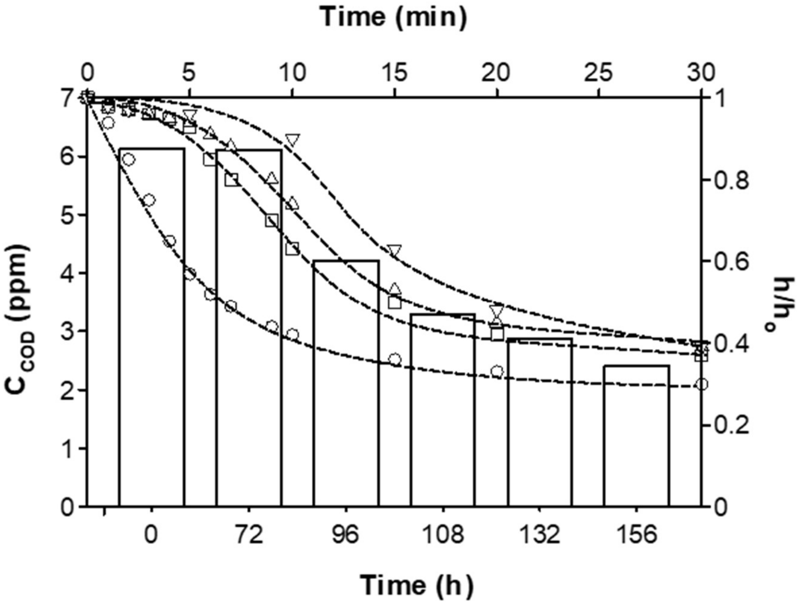

Figure 9. Aerobic biodegradation of table olive wastewater after filtration + coagulation + PMS addition. C_{CODo} = 6.1 g L^{-1}, T = 20 °C, pH = 7.0. (mixed liquor volatile suspended solids) MLVSS = 2.4 g L^{-1}. Bars (left and bottom axis): COD evolution. Symbols (up and right axis) for normalized height of solids in settling runs: ○, after 0.0 h; □, after 72 h; △, after 96 h; ▽, after 108 h.

The activated sludge process can be influenced by the presence of sulfates impacting both the microbiological and chemical aspects of the system. Hence, the microbial reduction of sulfates in the activated sludge process can result in the formation of sulfides and the release of hydrogen sulfide gas. Moreover, elevated sulfate concentrations can directly harm the microorganisms responsible for breaking down organic matter in the activated sludge system, potentially reducing the efficiency of the biological treatment. The presence of sulfates can influence the precipitation of solids, such as metal sulfides or insoluble salts, potentially affecting the separation of solids within the activated sludge process.

3. Materials and Methods

3.1. Wastewater Characterization

Wastewater was provided by an agricultural cooperative located in Almendralejo, Badajoz (southwestern Spain). Wastewater was a mixture of effluents generated in all stages of table olive manufacturing (washing of fruits, debittering of olives, fermentation, and packing). The main characteristic of this wastewater is its high NaCl content, which hinders biological or chemical treatment. Some of the main properties of the effluent are displayed in Table 1.

Table 1. Table olive wastewater characteristics.

pH	8.02 ± 0.001
Conductivity, mS/cm	74.8 ± 0.7
Total organic carbon, ppm	10,400 ± 150
Inorganic carbon, ppm	242.5 ± 0.1
Nitrates, ppm	92 ± 1.53
Polyphenols (ppm gallic acid)	1081 ± 31
Chemical oxygen demand, ppm	34,033 ± 1318
Turbidity, NTU units	187 ± 9.6

3.2. Analytical Procedure

Turbidity, pH, and conductivity were analyzed with a Hanna HI 93414 turbidity meter (Hanna Instruments, Madrid, Spain) and a Hanna HI 255 Combined Meter pH/mv and EC/TDS/NaCl, respectively (Hanna Instruments, Madrid, Spain). The chemical oxygen demand (COD) was determined following the standard dichromate reflux method using the Hach–Lange commercial cuvettes (VWR, Madrid, Spain) and a Hach DR3900 spectrophotometer (VWR, Madrid, Spain) [33]. The positive interference derived from the presence of peroxide substances was corrected by subtracting the COD value generated for these materials (a previous calibration process was carried out). Total organic carbon (TOC) and inorganic carbon (IC) were measured with a TOC-VCSH Shimadzu analyzer (Kyoto, Japan). Phenolic content in wastewater was evaluated using the Folin–Ciocalteu colorimetric method, and the results were stated as phenol equivalents [34]. Nitrate concentration was analyzed using a UV spectroscopy method based on The American Public Health Association protocol since nitrate absorbs at 210 nm. This protocol measured the differences in sample absorbances at 220 and 275 nm (the rate at which nitrate does not absorb) [35]. The absorbance of samples at 220 and 275 nm was determined by means of a Thermo Scientific UV-VIS 201 Evolution spectrophotometer (Waltham, MA, USA). Potassium monopersulfate (PMS) was determined via iodometric titration.

3.3. Materials and Methods

All chemicals were supplied by PanReac (Madrid, Spain) and used without further purification. Table olive wastewater (WWTOMP, ADIADA SL, Almendarlaejo, Spain) was previously filtered through vacuum filtration to remove the suspended solids. Next, coagulation and further sedimentation experiments were carried out in an OVAN JT60E (OVAN, Barcelona, Spain) jar test model equipped with six cylindrical beakers with 600 mL of capacity. Agitation was mechanically performed by using an impeller with a 1 cm × 5 cm blade. For this purpose, 400 mL of filtered wastewater was placed in a glass beaker, and the coagulant (aluminum sulfate) was added with fast stirring (120 rpm) for a period of three minutes. Then, speed was adjusted to slow mixing (30 rpm) for 20 min. Finally, agitation was switched off, allowing for the settling of coagulated particles for 24 h. PMS oxidation experiments were carried out in 1 L glass recipient under magnetic stirring with coagulated WWTOMP diluted ten times with tap water. Systematically, samples were withdrawn and immediately evaluated after sampling. The fast analysis of samples allowed us to avoid the use of scavenging reagents.

Author Contributions: Conceptualization, F.J.B. and F.J.R.; methodology, O.G.; software, O.G.; validation, O.G. and F.J.R.; formal analysis, F.J.B.; investigation, O.G.; resources, F.J.B.; data curation, F.J.R.; writing—original draft preparation, F.J.R.; writing—review and editing, F.J.R. and F.J.B.; visualization, O.G.; supervision, F.J.R.; project administration, O.G.; funding acquisition, O.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Junta de Extremadura through the program INVESTIGO (grant PI-0121-22).

Data Availability Statement: The data presented in this study are available upon request from the corresponding author (accurately indicating status).

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

References

1. Giannakis, S.; Lin, K.-Y.A.; Ghanbari, 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]
2. Berruti, I.; Nahim-Granados, S.; Abeledo-Lameiro, M.J.; Oller, I.; Polo-López, M.I. Peroxymonosulfate/Solar Process for Urban Wastewater Purification at a Pilot Plant Scale: A Techno-Economic Assessment. *Sci. Total Environ.* **2023**, *881*, 163407. [CrossRef]
3. Yin, L.; Wei, J.; Qi, Y.; Tu, Z.; Qu, R.; Yan, C.; Wang, Z.; Zhu, F. Degradation of Pentachlorophenol in Peroxymonosulfate/Heat System: Kinetics, Mechanism, and Theoretical Calculations. *Chem. Eng. J.* **2022**, *434*, 134736. [CrossRef]
4. Al Hakim, S.; Baalbaki, A.; Tantawi, O.; Ghauch, A. Chemically and Thermally Activated Persulfate for Theophylline Degradation and Application to Pharmaceutical Factory Effluent. *RSC Adv.* **2019**, *9*, 33472–33485. [CrossRef] [PubMed]
5. Rodríguez-Chueca, J.; Garcia-Cañibano, C.; Sarro, M.; Encinas, Á.; Medana, C.; Fabbri, D.; Calza, P.; Marugán, J. Evaluation of Transformation Products from Chemical Oxidation of Micropollutants in Wastewater by Photoassisted Generation of Sulfate Radicals. *Chemosphere* **2019**, *226*, 509–519. [CrossRef]

6. Zhang, S.; Xie, Y.; Manoli, K.; Ji, Y.; Yu, X.; Feng, M. Degradation of Methotrexate by Unactivated and Solar-Activated Peroxymonosulfate in Water: Moiety-Specific Reaction Kinetics and Transformation Product-Associated Risks. *Water Res.* **2023**, *246*, 120741. [CrossRef]
7. Hou, K.; Pi, Z.; Chen, F.; He, L.; Yao, F.; Chen, S.; Li, X.; Dong, H.; Yang, Q. Sulfide Enhances the Fe(II)/Fe(III) Cycle in Fe(III)-Peroxymonosulfate System for Rapid Removal of Organic Contaminants: Treatment Efficiency, Kinetics and Mechanism. *J. Hazard. Mater.* **2022**, *435*, 128970. [CrossRef] [PubMed]
8. Pan, Y.; Qin, R.; Hou, M.; Xue, J.; Zhou, M.; Xu, L.; Zhang, Y. The Interactions of Polyphenols with Fe and Their Application in Fenton/Fenton-like Reactions. *Sep. Purif. Technol.* **2022**, *300*, 121831. [CrossRef]
9. Shi, X.; Li, Y.; Zhang, Z.; Sun, L.; Peng, Y. Enhancement of Ciprofloxacin Degradation in the Fe(II)/Peroxymonosulfate System by Protocatechuic Acid over a Wide Initial pH Range. *Chem. Eng. J.* **2019**, *372*, 1113–1121. [CrossRef]
10. Zhang, L.; Qian, Z.; Wang, L.; Jin, P.; Yang, S. Gallic Acid Enhanced Bisphenol A Degradation through Fe^{3+}/Peroxymonosulfate Process. *Water Supply* **2022**, *22*, 4852–4863. [CrossRef]
11. Rincón-Llorente, B.; la Lama-Calvente, D.; Fernández-Rodríguez, M.J.; Borja-Padilla, R. Table Olive Wastewater: Problem, Treatments and Future Strategy. A Review. *Front. Microbiol.* **2018**, *9*, 1641. [CrossRef]
12. Achak, M.; Elayadi, F.; Boumya, W. Chemical Coagulation/Flocculation Processes for Removal of Phenolic Compounds from Olive Mill Wastewater: A Comprehensive Review. *Am. J. Appl. Sci.* **2019**, *16*, 59–91. [CrossRef]
13. Brandt, M.J.; Johnson, K.M.; Elphinston, A.J.; Ratnayaka, D.D. Chapter 8—Storage, Clarification and Chemical Treatment. In *Twort's Water Supply*; Brandt, M.J., Johnson, K.M., Elphinston, A.J., Ratnayaka, D.D., Seventh, E., Eds.; Butterworth-Heinemann: Boston, MA, USA, 2017; pp. 323–366. ISBN 978-0-08-100025-0.
14. Aldana, J.C.; Acero, J.L.; Álvarez, P.M. Membrane Filtration, Activated Sludge and Solar Photocatalytic Technologies for the Effective Treatment of Table Olive Processing Wastewater. *J. Environ. Chem. Eng.* **2021**, *9*, 105743. [CrossRef]
15. Ferrer-Polonio, E.; Iborra-Clar, A.; Mendoza-Roca, J.A.; Pastor-Alcañiz, L. Fermentation Brines from Spanish Style Green Table Olives Processing: Treatment Alternatives before Recycling or Recovery Operations. *J. Chem. Technol. Biotechnol.* **2016**, *91*, 131–137. [CrossRef]
16. Rivas, F.J.; Beltrán, F.J.; Gimeno, O.; Alvarez, P. Treatment of Brines by Combined Fenton's Reagent–Aerobic Biodegradation: II. Process Modelling. *J. Hazard. Mater.* **2003**, *96*, 259–276. [CrossRef] [PubMed]
17. Duesterberg, C.K.; Waite, T.D. Kinetic Modeling of the Oxidation of P-Hydroxybenzoic Acid by Fenton's Reagent: Implications of the Role of Quinones in the Redox Cycling of Iron. *Environ. Sci. Technol.* **2007**, *41*, 4103–4110. [CrossRef] [PubMed]
18. Kilic, M.Y.; Abdelraheem, W.H.; He, X.; Kestioglu, K.; Dionysiou, D.D. Photochemical Treatment of Tyrosol, a Model Phenolic Compound Present in Olive Mill Wastewater, by Hydroxyl and Sulfate Radical-Based Advanced Oxidation Processes (AOPs). *J. Hazard. Mater.* **2019**, *367*, 734–742. [CrossRef] [PubMed]
19. Vaz, T.; Domingues, E.; Gomes, J.; Martins, R.C. Evaluation of the Activation Procedure on Oxone Efficiency for Synthetic Olive Mill Wastewater Treatment. *Catalysts* **2022**, *12*, 291. [CrossRef]
20. Can-Güven, E.; Bayrak, Ş.; Dokuyucu, B.; Yazici Guvenc, S.; Varank, G. Hybrid Treatment of Olive Mill Wastewater by Iron-Catalyzed Percarbonate and Peroxymonosulfate Oxidation Followed by Electrooxidation. *J. Water Process Eng.* **2023**, *54*, 104018. [CrossRef]
21. Rivas, F.J. Monopersulfate in Water Treatment: Kinetics. *J. Hazard. Mater.* **2022**, *430*, 128383. [CrossRef] [PubMed]
22. Wang, Y.R.; Chu, W. Degradation of 2,4,5-Trichlorophenoxyacetic Acid by a Novel Electro-Fe(II)/Oxone Process Using Iron Sheet as the Sacrificial Anode. *Water Res.* **2011**, *45*, 3883–3889. [CrossRef]
23. Rastogi, A.; Al-Abed, S.R.; Dionysiou, D.D. Sulfate Radical-Based Ferrous–Peroxymonosulfate Oxidative System for PCBs Degradation in Aqueous and Sediment Systems. *Appl. Catal. B Environ.* **2009**, *85*, 171–179. [CrossRef]
24. 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]
25. Wang, Y.; Tian, D.; Chu, W.; Li, M.; Lu, X. Nanoscaled Magnetic $CuFe_2O_4$ as an Activator of Peroxymonosulfate for the Degradation of Antibiotics Norfloxacin. *Sep. Purif. Technol.* **2019**, *212*, 536–544. [CrossRef]
26. Yu, J.; Cui, J.; Zhang, C. ChemInform Abstract: A Simple and Effective Method for α-Hydroxylation of β-Dicarbonyl Compounds Using Oxone as an Oxidant Without a Catalyst. *Eur. J. Org. Chem.* **2010**, *2010*, 7020–7026. [CrossRef]
27. Priewisch, B.; Rück-Braun, K. Efficient Preparation of Nitrosoarenes for the Synthesis of Azobenzenes. *J. Org. Chem.* **2005**, *70*, 2350–2352. [CrossRef]
28. Fields, J.D.; Kropp, P.J. Surface-Mediated Reactions. 9. Selective Oxidation of Primary and Secondary Amines to Hydroxylamines1. *J. Org. Chem.* **2000**, *65*, 5937–5941. [CrossRef]
29. Yan, J.; Travis, B.R.; Borhan, B. Direct Oxidative Cleavage of Alpha- and Beta-Dicarbonyls and Alpha-Hydroxyketones to Diesters with $KHSO_5$. *J. Org. Chem.* **2004**, *69*, 9299–9302. [CrossRef]
30. Rivas, F.J.; Gimeno, O.; Borallho, T. Aqueous Pharmaceutical Compounds Removal by Potassium Monopersulfate. Uncatalyzed and Catalyzed Semicontinuous Experiments. *Chem. Eng. J.* **2012**, *192*, 326–333. [CrossRef]
31. Fortnum, D.H.; Battaglia, C.J.; Cohen, S.R.; Edwards, J.O. The Kinetics of the Oxidation of Halide Ions by Monosubstituted Peroxides. *J. Am. Chem. Soc.* **1960**, *82*, 778–782. [CrossRef]
32. Rivas, F.J.; Solís, R.R. Chloride Promoted Oxidation of Tritosulfuron by Peroxymonosulfate. *Chem. Eng. J.* **2018**, *349*, 728–736. [CrossRef]

33. Moore, W.A.; Kroner, R.C.; Ruchhoft, C.C. Dichromate Reflux Method for Determination of Oxygen Consumed. *Anal. Chem.* **1949**, *21*, 953–957. [CrossRef]
34. Singleton, V.L.; Orthofer, R.; Lamuela-Raventós, R.M. Analysis of Total Phenols and Other Oxidation Substrates and Antioxidants by Means of Folin-Ciocalteu Reagent. In *Oxidants and Antioxidants Part A*; Academic Press: Cambridge, MA, USA, 1999; Volume 299, pp. 152–178. ISBN 0076-6879.
35. Eaton, A.D.; Franson, M.A.H.; Association, A.P.H.; Association, A.W.W.; Federation, W.E. *Standard Methods for the Examination of Water and Wastewater*; Apha, Standard Method for the Examination Fo Water and Waste; American Public Health Association: Washington, DC, USA, 2005; ISBN 9780875530475.