

Combination of Coagulation-Flocculation-Decantation with Sulfate Radicals for Agro-Industrial Wastewater Treatment [†]

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Abstract: In this work, the effect of the combined coagulation-flocculation-decantation (CFD) with sulfate radical oxidation process on the treatment of two winery wastewaters (WW1 and WW2) was investigated. The oxidation process was optimized by application of a Box-Behnken design of Response Surface Methodology. Under the best CFD conditions: [potassium caseinate] = 0.4 g/L, [bentonite] = [PVPPP] = 0.1 g/L, pH = 3.0, rapid mix (rpm/min) = 150/3, slow mix (rpm/min) = 20/20, sedimentation time = 12 h, and oxidation conditions: [sodium persulfate (SPS)] = 51.9 mM, [Fe²⁺] = 0.90 mM, pH = 3.0, radiation UV-A (365 nm), time = 300 min it was achieved a total organic carbon (TOC) and a chemical oxygen demand (COD) of 38.9 and 45.3%, respectively, for WW 1 and 51.2 and 73.3%, respectively for WW2. The combined process shows a good potential for WW treatment.

Keywords: Box-Behnken; coagulation-flocculation-decantation; sulfate radical oxidation; winery wastewater

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1. Introduction

Portugal is a Mediterranean wine producer, with an approximated vineyard area of 191,000 ha and a wine production value of 6.4 MhL, in 2020 [1]. This high production of wine leads to the generation of huge volumes of wastewater, due to the cleaning of tanks, washing of floors and equipment, rinsing of transfer lines, barrel cleaning, off wine and product losses, bottling facilities and filtration units [2]. In order to treat the winery wastewater, a coagulation-flocculation-decantation (CFD) process can be applied. The CFD process is known as one of the most mature and effective process, which can remove most of the colloids and suspended solids in the wastewater by forming flocs. Generally, the CFD mechanisms can be categorized as the following kinds: (1) simple charge neutralization, (2) charge patching, (3) bridging and (4) sweeping [3]. Another effective treatment that can be applied for winery wastewater treatment is the sulfate radical-based advanced oxidation processes (SR-AOPs), where the generation of sulfate radical is promoted, alone or jointly with hydroxyl radicals. As oxidants, it can be applied peroxymonosulfate (PMS) and peroxydisulfate (PDS), with a redox potential of 1.82 and 2.01 V, respectively [4]. The sulfate radicals can be activated by several methods, including metal or non-metal catalysts, heat, UV or visible light, microwave, ultrasound, electrochemistry, alkali and photo-catalytic activation [5]. The aim of this work is (1) to apply oenological coagulants potassium caseinate, bentonite and polyvinylpolypyrrolidone to increase the efficiency of SR-AOPs for the treatment of winery wastewater, (2) to apply a Box-Behnken

design of Response Surface Methodology to optimize the SR-AOP and (3) to evaluate the efficiency of combined CFD-SR-AOP process in WW treatment.

2. Material and Methods

2.1. Reagents

Ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was supplied by Panreac, Barcelona, Spain, sodium persulfate (SPS) was supplied by Merck, Darmstadt, Germany and hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$, HA) was acquired by Sigma-Aldrich, St. Louis, MO, USA.

2.2. Analytical Techniques

Two different winery wastewaters (WW) were studied, and different physical–chemical parameters were monitored in order to characterize the WW, including the chemical oxygen demand (COD), the biochemical oxygen demand (BOD_5), the total organic carbon (TOC) and the total polyphenols. The main chemical parameters measured are shown in Table 1.

Table 1. Characterization of winery wastewaters (WW1 and WW2).

Parameter	Winery Wastewater	
	WW1	WW2
pH	3.74 ± 0.04	3.84 ± 0.04
Conductivity ($\mu\text{S}/\text{cm}$)	238 ± 3.4	245 ± 2.9
Turbidity (NTU)	327 ± 4	643 ± 7
Total suspended solids (mg/L)	779 ± 15	1559 ± 36
Chemical oxygen demand (mg O_2/L)	1119 ± 24	4640 ± 82
Biochemical oxygen demand (mg O_2/L)	588 ± 21	1813 ± 45
Total organic carbon (mg C/L)	464 ± 4	997 ± 9
Total polyphenols (mg gallic acid/L)	22.5 ± 1.4	42.9 ± 2.6
Ferrous iron (mg Fe/L)	0.10 ± 0.02	0.10 ± 0.02
Biodegradability index – BOD_5/COD	0.53 ± 0.04	0.39 ± 0.03

2.3. Coagulation-Flocculation-Decantation Set-Up

The coagulation-flocculation-decantation experiments were performed in a conventional model jar-test apparatus (ISCO JF-4, Louisville, KY, USA), and the process was optimized as follows:

(1) [potassium caseinate] = 0.4 g/L, [bentonite] = [PVPP] = 0.1 g/L, pH = 3.0, rapid mix (rpm/min) = 150/3, slow mix (rpm/min) = 20/20, sedimentation time = 12 h.

2.4. Sulfate Radical Oxidation Set-Up

Batch experiments for oxidation process were performed with UV-A LEDs lamps. The reactor was loaded with 500 mL of winery wastewater and continuous mixing was maintained by means of a magnetic stirrer. The oxidation process was optimized by application of a Box-Behnken design of Response Surface Methodology. In the Box-Behnken, three variables were studied (SPS, Fe^{2+} and HA) under three levels (Table 2) for a total of 15 assays, under fixed conditions as follows: pH = 3.0, Temperature = 298 K, time = 300 min.

Table 2. Values of operating parameters at 3 levels in Box-Behnken design.

Parameters	Code	Levels		
		-1	0	1
[SPS] mM	X ₁	15	45	75
[Fe ²⁺] mM	X ₂	0.25	1.00	1.75
[HA] mM	X ₃	0.00	4.38	8.75

2.5. Statistical Analysis

The Box-Behnken design of Response Surface Methodology was performed by Minitab Statistical Software 2018 (State College, PA, USA). All the experiments were performed in triplicate and the observed standard deviation was always less than 5% of the reported values and average values were compared using Tukey’s test.

3. Results and Discussion

3.1. Box-Behnken Design

The Box-Behnken design was used to study the combinational effect of 3 influencing factors, i.e., SPS concentration (X₁), Fe²⁺ concentration (X₂), and HA concentration (X₃) on the TOC and COD removal of WW1. Based on the experimental data obtained in Table 3, a second-order polynomial model has been developed using Box-Behnken design to find the functional association between independent variables and responses, as observed in Equation 1 and Equation 2, as follows:

$$TOC = 4.65 + 1.186 X_1 - 2.99 X_2 - 4.94 X_3 - 0.01356 X_1 * X_1 - 3.40 X_2 * X_2 + 0.185 X_3 * X_3 + 0.1568 X_1 * X_2 - 0.0116 X_1 * X_3 + 2.095 X_2 * X_3 \tag{1}$$

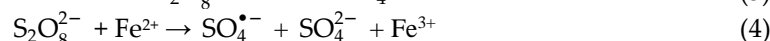
$$COD = 26.86 + 0.488 X_1 + 6.0 X_2 - 1.50 X_3 - 0.00463 X_1 * X_1 - 4.74 X_2 * X_2 - 0.152 X_3 * X_3 + 0.067 X_1 * X_2 + 0.0057 X_1 * X_3 + 1.600 X_2 * X_3 \tag{2}$$

A plot between predicted versus experimental data from TOC and COD results showed a straight line and a R² of 0.876 and 0.943, respectively. Therefore, the values obtained from the developed model have high degree of correlation with the experimental results.

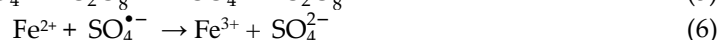
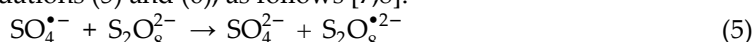
Table 3. Experimental and predicted percentage of TOC and COD removal for the generated runs in Box-Behnken design. a—all statistical experiments were conducted under the same operational conditions.

Assay	Coded Level			TOC Removal		COD Removal	
	X1	X2	X3	Observed	Predicted	Observed	Predicted
SR – 1	45	1.75	8.75	25.5	25.8	44.0	42.6
SR – 2	75	0.25	4.38	1.0	0.0	38.0	34.0
SR – 3	15	0.25	4.38	2.8	2.5	28.0	27.3
SR – 4	45	0.25	0.00	31.6	31.4	40.0	41.4
SR – 5	45	1.75	0.00	29.1	27.3	44.0	40.6
SR – 6 ^a	45	1.00	4.38	27.2	20.0	47.0	42.3
SR – 7	75	1.00	8.75	4.9	4.4	36.0	36.6
SR – 8	15	1.00	8.75	4.7	3.1	28.0	25.4
SR – 9	45	0.25	8.75	0.5	2.3	19.0	22.4
SR – 10	75	1.00	0.00	21.2	22.7	41.0	43.6
SR – 11 ^a	45	1.00	4.38	18.0	20.0	40.0	42.3
SR – 12	15	1.75	4.38	3.8	5.1	30.0	34.0
SR – 13 ^a	45	1.00	4.38	15.0	20.0	40.0	42.3
SR – 14	75	1.75	4.38	16.1	16.4	46.0	46.8
SR – 15	15	1.00	0.00	14.8	15.4	36.0	35.4

After performance of the experimental Box-Behnken design, optimization plots for the treatment of the WW were generated, in order to comprehend the best factorial combination, with the objective to maximize the response for TOC and COD removal. In accordance with the statistical model, the following operational conditions were obtained: [SPS] = 51.96 mM, [Fe²⁺] = 0,90 mM, pH = 3.0, radiation UV-A (365 nm), Temperature = 298 K, t = 300 min, and it was achieved a TOC and COD removal of 19.7 and 31.2%, respectively. The organic carbon removal was explained due to the activation of persulfate by the Fe²⁺ catalyst and the UV-A radiation, as observed in Equation 3 and Equation 4, as follows [6]:



The employment of higher concentrations of SPS and Fe²⁺ leads to scavenging reactions, as observed in Equations (5) and (6), as follows [7,8]:



3.2. Combination of Coagulation-Flocculation-Decantation and Oxidation Processes

A pre-treatment with coagulation-flocculation-decantation was performed on the WW1 to evaluate the effect in the oxidation process. As observed in Figure 1, the CFD process achieved a turbidity, TSS, total polyphenols, TOC and COD removal of 99.6, 95.5, 99.9, 8.8 and 12.4%, respectively. With performance of oxidation process, it was observed a significant increase to 99.9, 95.8, 99.9, 38.9 and 45.3% removal, respectively. Considering the efficiency of the combined processes, it was used the same operational conditions to treat WW2, a wastewater with higher organic load. With performance of CFD process it was observed a removal of 99.6, 97.7, 93.6, 19.9 and 31.8%, respectively. With the application of oxidation process, it was observed a significant increase to 99.9, 97.8, 99.9, 51.2 and 73.3% removal, respectively. These results were similar to those of Jaafarzadeh et al., [9], who observed that performance of CFD process before oxidation with sulfate radicals increased the removal of organic matter from pulp and paper wastewater.

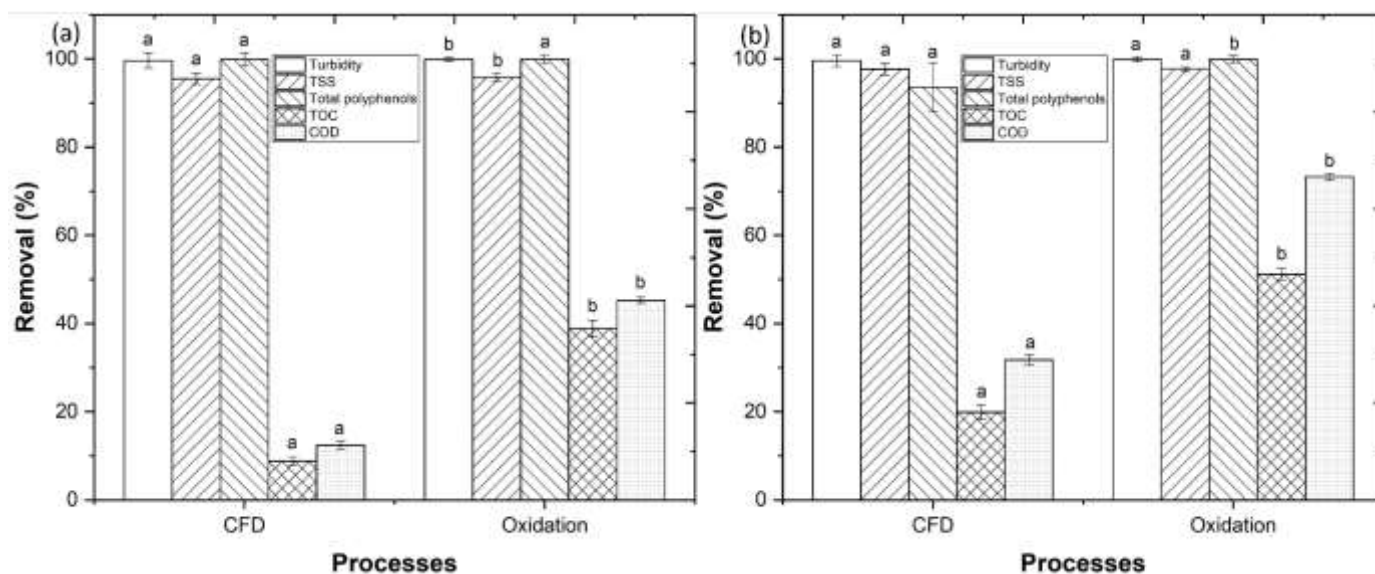


Figure 1. Assessment of the CFD and oxidation processes efficiency in the treatment of (a) WW1 and (b) WW2. Means in bars with different letters represent significant differences ($p < 0.05$) within each parameter (turbidity, TSS, total polyphenols, TOC and COD) by comparing wastewaters.

4. Conclusions

In this work, it was optimized the sulfate radical oxidation process by a Box-Behnken design. To increase the oxidation process efficiency, it was performed a pre-treatment with CFD process to wastewaters WW1 and WW2. Based in the results, it is concluded:

1. With the optimization performed by the Box-Behnken design, it is achieved a TOC and COD removal of 19.7 and 31.2%, respectively;
2. The application of CFD process to WW1 and WW2 achieves a high removal of turbidity, TSS and total polyphenols;
3. The combination of CFD-oxidation processes achieves a high TOC and COD removal for the treatment of WW2 (51.2 and 73.3%, respectively).

Based in the results, it is concluded that the combination of CFD-oxidation processes is an efficient technique for the treatment of winery wastewater with high organic load.

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References

1. Jorge, N.; Teixeira, A.R.; Matos, C.C.; Lucas, M.S.; Peres, J.A. Combination of Coagulation–Flocculation–Decantation and Ozonation Processes for Winery Wastewater Treatment. *Int. J. Environ. Res. Public Health* **2021**, *18*, 8882. <https://doi.org/10.3390/ijerph18168882>.
2. Ioannou, L.A.; Puma, G.L.; Fatta-Kassinos, D. Treatment of Winery Wastewater by Physicochemical, Biological and Advanced Processes: A Review. *J. Hazard. Mater.* **2015**, *286*, 343–368. <https://doi.org/10.1016/j.jhazmat.2014.12.043>.
3. Zhao, C.; Zhou, J.; Yan, Y.; Yang, L.; Xing, G.; Li, H.; Wu, P.; Wang, M.; Zheng, H. Application of Coagulation/Flocculation in Oily Wastewater Treatment: A Review. *Sci. Total Environ.* **2021**, *765*, 142795. <https://doi.org/10.1016/j.scitotenv.2020.142795>.
4. Giannakis, S.; Lin, K.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. <https://doi.org/10.1016/j.cej.2020.127083>.
5. Ike, I.A.; Foster, S.L.; Shinn, S.R.; Watson, S.T.; Orbell, J.D.; Greenlee, L.F.; Duke, M.C. Advanced Oxidation of Orange G Using Phosphonic Acid Stabilised Zerovalent Iron. *J. Environ. Chem. Eng.* **2017**, *5*, 4014–4023. <https://doi.org/10.1016/j.jece.2017.07.069>.
6. Qi, C.; Liu, X.; Ma, J.; Lin, C.; Li, X.; Zhang, H. Activation of Peroxymonosulfate by Base: Implications for the Degradation of Organic Pollutants. *Chemosphere* **2016**, *151*, 280–288. <https://doi.org/10.1016/j.chemosphere.2016.02.089>.
7. Zhi, D.; Lin, Y.; Jiang, L.; Zhou, Y.; Huang, A.; Yang, J.; Luo, L. Remediation of Persistent Organic Pollutants in Aqueous Systems by Electrochemical Activation of Persulfates: A Review. *J. Environ. Manage.* **2020**, *260*, 110125. <https://doi.org/10.1016/j.jenvman.2020.110125>.
8. Liu, H.; Bruton, T.A.; Li, W.; Buren, J. Van; Prasse, C.; Doyle, F.M.; Sedlak, D.L. Oxidation of Benzene by Persulfate in the Presence of Fe (III)-and Mn (IV)-Containing Oxides: Stoichiometric Efficiency and Transformation Products. *Environ. Sci. Technol.* **2016**, *50*, 890–898. <https://doi.org/10.1021/acs.est.5b04815>.
9. Jaafarzadeh, N.; Ghanbari, F.; Alvandi, M. Integration of Coagulation and Electro-Activated HSO₅⁻ to Treat Pulp and Paper Wastewater. *Sustain. Environ. Res.* **2017**, *27*, 223–229. <https://doi.org/10.1016/j.serj.2017.06.001>.