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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 the sulfate radical oxidation process on the treatment of two winery wastewaters (WW1 and WW2) was investigated. The oxidation process was optimized by the application of a Box–Behnken design of the Response Surface Methodology. Under the best CFD conditions: [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, and oxidation conditions: [sodium persulfate (SPS)] = 51.9 mM, [Fe^{2+}] = 0.90 mM, pH = 3.0, radiation UV-A (365 nm), time = 300 min, a total organic carbon (TOC) and a chemical oxygen demand (COD) of 38.9 and 45.3%, respectively, were achieved 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]. A coagulation–flocculation–decantation (CFD) process can be applied to treat the winery wastewater. 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: (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 process (SR-AOPs), where the generation of sulfate radicals is promoted, alone or jointly with hydroxyl radicals. The oxidants, peroxymonosulfate (PMS) and peroxydisulfate (PDS) can be applied, with a redox potential of 1.82 and 2.01 V, respectively, to generate the sulfate radicals [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 the 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 ($FeSO_4 \cdot 7H_2O$) was supplied by Panreac, Barcelona, Spain, sodium persulfate (SPS) was supplied by Merk, Darmstadt, Germany and hydroxylamine hydrochloride ($NH_2OH \cdot HCl$, 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 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 (µS/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 the 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 the following fixed conditions: 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, 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 three influencing factors, i.e., SPS concentration (X_1), Fe^{2+} concentration (X_2), and HA concentration (X_3), on the TOC and COD removal of WW1. Based on the experimental data obtained in Table 3, a second-order polynomial model was developed using a Box–Behnken design to find the functional association between independent variables and responses, as observed in Equations (1) and (2):

$$\begin{aligned} TOC = 4.65 + 1.186\,X_1 - 2.99\,X_2 - 4.94\,X_3 - 0.01356\,X_1 \times X_1 - 3.40\,X_2 \times X_2 + 0.185\,X_3 \times X_3 + \\ 0.1568\,X_1 \times X_2 - 0.0116\,X_1 \times X_3 + 2.095\,X_2 \times X_3 \end{aligned} \quad (1)$$

$$\begin{aligned} COD = 26.86 + 0.488\,X_1 + 6.0\,X_2 - 1.50\,X_3 - 0.00463\,X_1 \times X_1 - 4.74\,X_2 \times X_2 - 0.152\,X_3 \times X_3 + \\ 0.067\,X_1 \times X_2 + 0.0057\,X_1 \times X_3 + 1.600\,X_2 \times X_3 \end{aligned} \quad (2)$$

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

A plot between predicted versus experimental data from TOC and COD results showed a straight line and an R^2 of 0.876 and 0.943, respectively. Therefore, the values obtained from the developed model have high degree of correlation with the experimental results.

After the performance of the experimental Box–Behnken design, optimization plots for the treatment of the WW were generated to comprehend the best factorial combination, with the objective of maximizing the response for TOC and COD removal. In accordance with the statistical model, the following operational conditions were obtained: [SPS] = 51.96 mM, $[Fe^{2+}]$ = 0.90 mM, pH = 3.0, radiation UV-A (365 nm), Temperature = 298 K, t = 300 min, and a TOC and COD removal of 19.7 and 31.2%, respectively, was achieved. The organic carbon removal was explained due to the activation of persulfate by the Fe^{2+} catalyst and the UV-A radiation, as observed in Equations (3) and (4) [6]:

$$S_2O_8^{2-} + hv \rightarrow 2SO_4^{\bullet-} \quad (3)$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\bullet -} + SO_4^{2-} + Fe^{3+} \quad (4)$$

The employment of higher concentrations of SPS and Fe^{2+} leads to scavenging reactions, as observed in Equations (5) and (6), [7,8]:

$$SO_4^{\bullet -} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet 2-} \quad (5)$$

$$Fe^{2+} + SO_4^{\bullet -} \rightarrow Fe^{3+} + SO_4^{2-} \quad (6)$$

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 the oxidation process, it a significant increase to 99.9, 95.8, 99.9, 38.9 and 45.3% removal, respectively, was observed. Considering the efficiency of the combined processes, the same operational conditions were used to treat WW2, a wastewater with higher organic load. With the CFD process, a removal of 99.6, 97.7, 93.6, 19.9 and 31.8%, respectively. With the application of oxidation process, a significant increase to 99.9, 97.8, 99.9, 51.2 and 73.3% removal, respectively, was observed. These results were similar to those of Jaafarzadeh et al. [9], who observed that using the CFD process before oxidation with sulfate radicals increased the removal of organic matter from pulp and paper wastewater.

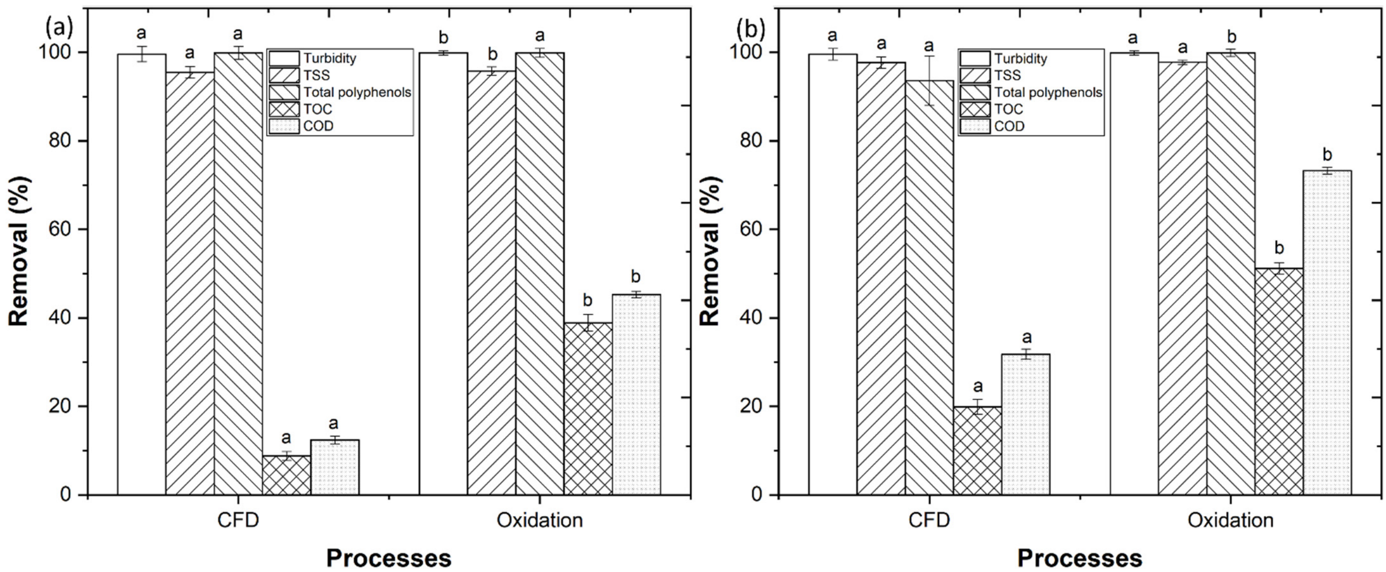

Figure 1. Assessment of the CFD and oxidation processes efficiency in the treatment of (**a**) WW1 and (**b**) WW2. Means in bars with different letters represent significant differences ($p < 0.05$) within each parameter (turbidity, TSS, total polyphenols, TOC and COD) by comparing wastewaters.

4. Conclusions

In this work, the sulfate radical oxidation process was optimized using a Box–Behnken design. To increase the oxidation process efficiency, a pre-treatment was carried out using the CFD process to wastewaters WW1 and WW2. Based on the results, the following is concluded:

1. With the optimization performed by the Box–Behnken design, a TOC and COD removal of 19.7 and 31.2%, respectively, is achieved;
2. The application of the CFD process to WW1 and WW2 achieves high levels of 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 on the results: it is concluded that the combination of CFD and oxidation processes is an efficient technique for the treatment of winery wastewater with a high organic load.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ECP2022-12610/s1.

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