

Modeling of Chemical Oxygen Demand and Total Suspended Solids Removal Using the Fenton Process

Lorgio Valdiviezo-Gonzales^{a*}, Valeria D. Justiniano^b, Kiara Ñ. Berlanga^b, julio M. Molina^b, Rita J. Cabello Torres^b, Fernando García Avila^c

^a Universidad Tecnológica del Perú, UTP, campus San Juan de Lurigancho, Lima-Perú.

^b Universidad César Vallejo, Campus San Juan de Lurigancho, Lima, Peru.

^c Universidad de Cuenca, Grupo de Evaluación de Riesgos Ambientales en Sistemas de Producción y Servicios (RISKEN), Cuenca, Ecuador

lvaldiviez@utp.edu.pe

Predictive mathematical models were developed for removing Chemical Oxygen Demand (COD) and Total Suspended Solids (TSS) and optimizing the main operating parameters of the Fenton process, applied to effluents from a fish canning industry. The maximum removals obtained for COD and TSS were 89.2 % and 76.1 %, respectively. The optimum doses for COD removal were: 200 mg/L FeSO₄ 7H₂O and 1,000 mg/L H₂O₂ at pH 2.5. While for TSS removal the optimum parameters were 1 200 mg/L H₂O₂, 300 mg/L FeSO₄ 7H₂O, and pH 3. The adjusted R² values of the COD and TSS removal models were 70.64 % and 98.01 %, respectively, indicating that the models obtained are acceptable in the prediction of both parameters.

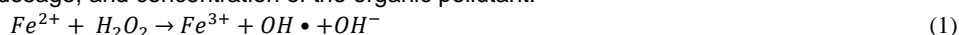
1. Introduction

In Peru, an average of 2 217 946 m³/day of wastewater is generated, which is discharged to the sewage network, of this volume 68% does not receive treatment (OEFA, 2014).

Regarding the treatment of effluents from fish canning industries, biological treatments including aerobic and anaerobic processes such as activated sludge, aeration lagoons, trickling filter (Parvathy et al. 2017), Constructed Wetland (Salim et al. 2021), unconventional methods such as a hydrodynamic cavitation reactor (Dhanke et al. 2020) have been reported.

However, the fish cannery under study discharges its treated water into the sewage system through a three-stage treatment system: pretreatment, primary treatment, and secondary treatment (Figure 1). According to previous analyses, this treatment does not allow compliance with the Maximum Allowable Values (VMA in Spanish), regarding Chemical Oxygen Demand (COD) and Oils and Fats (O&F) established at 1000 mg/L and 100 mg/L, respectively (MVCS, 2019), exceeding the COD value by up to three times.

Consequently, the present study evaluates an alternative to the current treatment, including the Fenton process. This process is based on the combination of iron (II) sulfate (FeSO₄) and hydrogen peroxide (H₂O₂) and pH values from 2 to 4 (Cristovao et al. 2014). Fenton is part of the so-called Advanced Oxidative Processes (AOPs) based on the formation of hydroxyl radicals (OH·) (Kanafin et al. 2022), through the reaction of an oxidizing agent (H₂O₂) and a catalyst (Fe²⁺), (1)-(3) (Vorontsov 2019). OH· acts as a powerful oxidant capable of degrading organic compounds, via redox reactions (4), dehydrogenation (5), and/or hydroxylation (6) (Zhang et al. 2019). Likewise, the most influential parameters in the Fenton process are pH, iron dosage, hydrogen peroxide dosage, and concentration of the organic pollutant.



2. Materials and methods

2.1 Sample collections, experimental design, and statistical analysis

In this study, were collected 51 L of effluent from the production process of a company dedicated to the production of canned fish located in the district of Chancay, Lima (Peru). Sampling was performed (Figure 1) considering the techniques established in R.M 061-2016-PRODUCE (SNP, 2016).

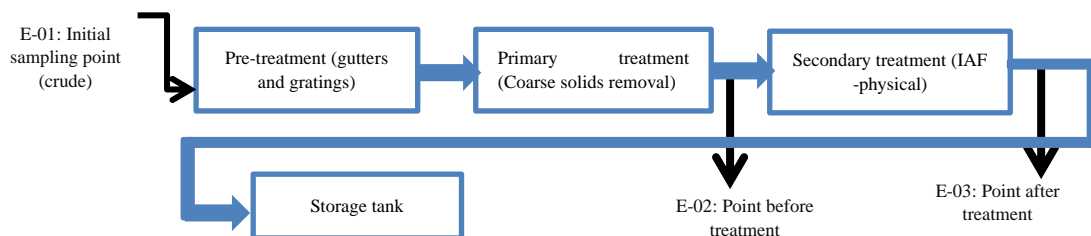


Figure 1. Effluent treatment system and sampling points

The Box - Behnken design (response surface methodology) was applied, supported by Minitab software (Version 19). The effect of the combination of three independent variables was evaluated: Iron II sulfate heptahydrate, hydrogen peroxide, and pH, with symbols A, B, and C (see Table 1). Three levels were evaluated for each variable: low level (-), intermediate level (0), and high level (+).

Table 1. Parameters and levels evaluated.

Operating conditions	symbol	Level Code		
		-	0	+
FeSO ₄ 7H ₂ O (mg/L)	A	200	250	300
H ₂ O (mg/L)	B	1000	1200	1400
pH	C	2,5	3	3,5

To evaluate the current treatment's efficiency, samples were collected at three points, as shown in Figure 1. The sampling points described were: a sampling of the crude oil (E-1), sampling before secondary treatment (E-2), and sampling after secondary treatment (E-3). The response variables were fitted by a second-order model using a polynomial quadratic equation, as presented in (7) (Varank et al. 2016):

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^k \sum_{j=1}^k \beta_{ij} X_i X_{ij} + \varepsilon \quad (7)$$

Where Y is the expected response, (COD and TSS); X_i and X_j, are the independent variables (factors); β_i, β_{ii}, and β_{ij} are the linear, quadratic coefficients and interaction effects, k is the number of independent variables and ε is the random error. The model evaluates the effect of each independent factor on the response variable (Varank et al. 2016). The mathematical model was evaluated by applying the analysis of variance (ANOVA), this statistical technique allows for evaluating the inclusion or exclusion of linear, quadratic terms and interactions, based on the p-value and F-value. Likewise, to determine the fit of the model to the experimental data, the R-squared and adjusted R-squared statistics were applied.

2.2 Experimental Procedure and parameter analysis

The experimental assays were carried out in a programmable flocculator, (VELP brand, model JLT6) each experiment with a sample volume of 0.5 L. Previously the pH (pH-meter, HANNA, model HI 8424) of the samples was adjusted (interval of 2.5 - 3.5), using hydrochloric acid at 4% (HCl, 37% w/w), then iron (II) sulfate heptahydrate (FeSO₄ 7H₂O, 99.6% w/w) was added and homogenized for 3 minutes at 100 rpm and then decreased to 30 rpm for 3 minutes, leaving it to rest for 10 minutes; Finally, hydrogen peroxide (H₂O₂, 30% w/w) was added and the solution was stirred for 35 minutes at 30 rpm.

The reaction was stopped by increasing the pH with sodium hydroxide (3 M, 98.9% w/w) to pH 10-11 and adding 0.25 g of manganese (II) oxide (91% w/w purity, JT Baker), then allowed to stand for 10 minutes for sedimentation, finally, COD and TSS were measured.

The experimental sequence was carried out according to the matrix presented in Table 2.

In each sample, the reduction of COD (APHA-AWWA-WEF, Colorimetric Closed Reflux Method) and TSS (APHA-AWWA-WEF, Gravimetric Filtration Method) was verified, subsequently, the comparison was made with

the VMA established in D.S 010 - 2019 - VIVIENDA (MVCS, 2019), in addition, the optimum pH values and doses of catalyst and oxidant were determined through the response surface methodology

Table 2. Experimental matrix, Box Behnken design for the optimization of the Fenton process

Experiment	A	B	C	FeSO ₄ 7H ₂ O (mg/L)	H ₂ O ₂ (mg/L)	pH
1	0	-	-	250	1000	2,5
2	0	-	+	250	1000	3,5
3	0	+	-	250	1400	2,5
4	0	+	+	250	1400	3,5
5	-	0	-	200	1200	2,5
6	-	0	+	200	1200	3,5
7	+	0	-	300	1200	3,0
8	+	0	+	300	1200	3,5
9	-	-	0	200	1000	3,0
10	-	+	0	200	1400	3,0
11	+	-	0	300	1000	3,0
12	+	+	0	300	1400	3,0
13	0	0	0	250	1200	3,0
14	0	0	0	250	1200	3,0
15	0	0	0	250	1200	3,0

3. Results

The results of the initial monitoring are presented in Table 3. The comparison of the COD, TSS, and O&F parameters of the treated effluent with the maximum admissible values (E-3 and VMA), allows for observing the ineffectiveness of the current treatment, concerning COD and O&F. Consequently, this study aims to improve the quality parameters to comply with the VMA in force. The results obtained by applying the Box - Behnken design are presented in Figure 2. It shows both values experimental (Figure 2a) and predicted (Figure 2b) plotted to improve their comparison.

Table 3. Initial sampling results of current effluent treatment

parameter	Sample Point			VMA
	1	2	3	
COD (mg/L)	12,200	5,600	3145,6	1,000
O&F (mg/L)	5,131	2,516	184	100
TSS (mg/L)	581	284	175	500
Turbidity (NTU)	610	198	14,4	...
Conductivity (µS/cm)	892,000	198,000		...

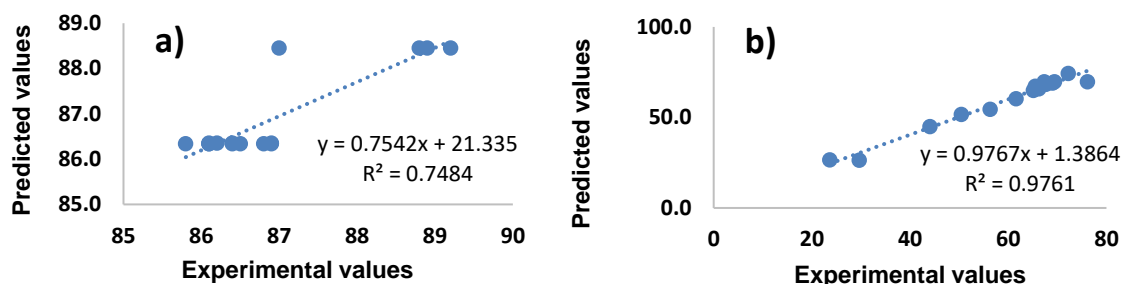


Figure 2: Experimental vs. estimated values for a) COD and b) TSS

Figure 2 shows R² values of 0.7484 and 0.9761 for COD and TSS, ie, both models obtained allow obtaining estimated values very close to the experimental values. The models are represented by equations (8) and (9).

$$\% \text{ DQO} = 118,21 - 0,2340 A + 0,000426 A * A \quad (8)$$

$$\% \text{ SST} = -528 + 0,835 A - 0,115 B + 351,2 C - 0,000159 B * B - 55,72 C * C + 0,000670 A * B - 0,4930 A * C + 0,1035 B * C \quad (9)$$

3.1 COD removal

As presented in the Pareto diagram (Figure 3a), the parameter with the greatest influence on the process is the catalyst (A: FeSO₄ 7H₂O). This result is supported by the ANOVA analysis (Table 4), allowing to discard of some terms of the equation and expressing the model as a function of the catalyst and its interaction (A and AA), as presented in (8). Likewise, the value of F (23.91) confirms the significance of this parameter.

Therefore, it is possible to observe that the linear and quadratic terms of FeSO₄ 7H₂O (A) and (AA) are the factors that most affect COD reduction, while the pH and H₂O₂ factors do not have a significant effect on COD removal. The catalyst has the function of accelerating the reaction but does not intervene in the spontaneity of the process. Therefore, the positive effect observed could be related to the increase in pH to 10 or 11 at the end of the treatment, which favors the formation of Fe(OH)₂ or Fe(OH)₃ that acts as a coagulant and favors the sedimentation of suspended organic matter. This synergistic effect of the Fenton process has been reported by (Lin et al. 2022).

Cristovao et al. (2014) reported optimum operating conditions of the Fenton process in COD removal (63%) at pH = 3.2; H₂O₂= 1558 mg/L and FeSO₄.7H₂O= 363 mg/L with a time of 1 h. The present study obtained a maximum COD removal of 89.2 % with lower reagent and time consumption. Relatively short reaction times were also reported by Vorontsov (2019).

In COD removal, the optimum catalyst value was 200 mg/L FeSO₄.7H₂O (minimum level), indicating that an excess of catalyst produces OH· radical trapping effect. Consequently, excess iron hurts the efficiency of the process, as presented in (2).

The contour plots (Figures 4a and 4b) show the COD removal as a function of three evaluated factors. According to the model, the optimum conditions were: pH 2.5; 200 mg/L FeSO₄.7H₂O, and H₂O₂ 1000 mg/L. The maximum COD removals are reached with the lowest iron concentrations. H₂O₂ concentration and pH do not represent a significant effect on COD reduction.

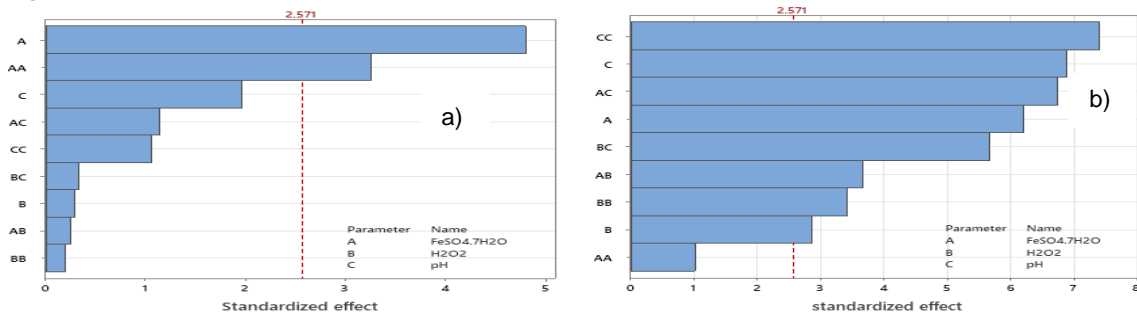


Figure 3: Standardized Pareto plot for a) COD and b) TSS removal.

Table 4. Analysis of variance for COD removal, considering parameters of major influence.

Source	COD		Source	TSS	
	F value	p Value		F value	p Value
A	23,91	0,000	A	38.23	0,000
A*A	11,78	0,005	B	8,15	0,029
Lack of adjustment	5,97	0,152	C	47.03	0,000
			B*B	11,17	0,016
			C*C	53.65	0,000
			A*B	13.36	0,011
			A*C	45.43	0,001
			B*C	31.89	0,001
			Lack of adjustment	0.45	0,774

3.2 Total suspended solids

The Pareto diagram (Figure 3b) indicates that all factors and interactions are significant, except for the interaction AA (Iron (II) sulfate * Iron (II) sulfate). This was confirmed by observing the p-value in the ANOVA presented in Table 4. Also, the response surface plots (Figure 4c-4e) show that the highest TSS removals are achieved when the pH, catalyst, and oxidant levels are high. Also, the model indicates that the optimum process conditions are: pH 3; 300 mg/L FeSO₄.7H₂O, and 1200 mg/L H₂O₂.

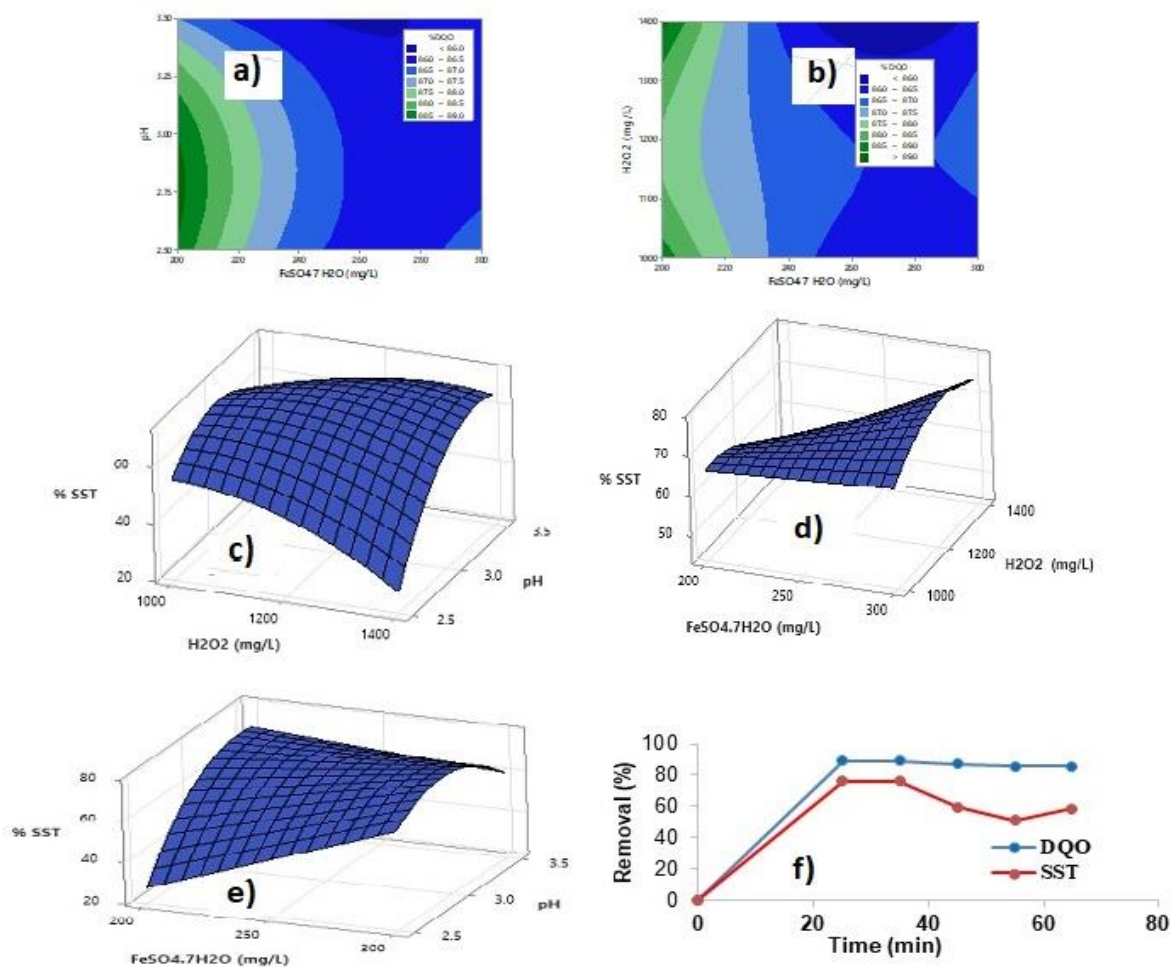


Figure 4. Contour plot, a) influence of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and pH on COD removal by the Fenton process: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_2O_2 , and pH. Response surface for TSS removal c) effect of pH and H_2O_2 d) effect of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and H_2O_2 e) effect of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and pH f) Effect of reaction time

3.3 Effect of reaction time

The results obtained regarding the effect of reaction time are presented in Figure 4f. It can be observed that the maximum COD and TSS removal is reached in the first 25 minutes, after this time the values are almost constant in the case of COD and have a tendency to reduce the TSS removal.

The final parameters of COD, TSS, O&F, and residual iron, as well as the optimum conditions, are presented in Table 5.

Table 5. Optimal conditions and final effluent quality

Parameter	Optimal operating conditions	Quality parameters (mg/L)			
SST	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 300 mg/L; H_2O_2 1200 mg/L y pH 3	COD	SST	O&F	Fe (residual)
		644	96	42,8	0,972
DQO	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 200 mg/L; H_2O_2 1000 mg/L y pH 2,5	767,2	77,8	60,4	0,894

ECA's Category 1, Subcategory A3, Iron= 5mg/L (MINAM 2017).

In the conditions of maximum COD and TSS removal, the quality parameters obtained allow compliance with the currently established VMA (see Table 3). The optimum pH in this study was 2.5 and 3 for COD and TSS respectively, similar to that mentioned by Matavos-Aramyan and Moussavi (2017) who conclude that the optimum pH range of the Fenton process is 2.5 - 4.

This is because the Fenton process works in acidic media, favoring the formation of hydroxyl radicals (OH \cdot). Higher pH values are related to the loss of the catalyst (Fe $^{2+}$ to Fe $^{3+}$) and consequently lower removals. The optimum H $_2$ O $_2$ concentration for COD and TSS removal was 1000 and 1200 mg/L, higher values (1558 mg/L) were reported by Cristovao et al. (2014) for the treatment of an effluent similar to this study. Usually, the increase of the oxidant has an impact on an increase in the removal efficiencies, however, excessive use can hurt the process (3).

4. Conclusion

The optimum parameters for obtaining maximum COD removal, according to the range evaluated, were: pH = 2.5, H $_2$ O $_2$ = 1000 mg/L, and FeSO $_4$ 7H $_2$ O = 200 mg/L, while for TSS removal: pH = 3, FeSO $_4$ 7H $_2$ O = 300 mg/L and H $_2$ O $_2$ = 1200 mg/L. Likewise, the time was set at 25 minutes. The operating conditions described allowed removals of up to 89.2 % of COD and 76.1 % for TSS, reaching the VMAs currently established.

The concentration of residual iron is 0.972 mg/L and 0.894 mg/L, when the initial concentrations of catalyst were 200 and 300 mg/L, indicating that when the pH increases between 10 and 11 in the solution, Fe precipitates as hydroxide and performs a coagulant function, in addition, the final concentrations indicate that the effluent is of good quality, also, regarding this parameter (ECA waters: Category 1, Subcategory A3).

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