Chemical Oxidation of Fish Canning Wastewater by Fenton's Reagent

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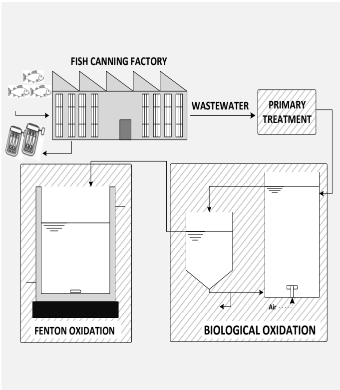

The fish canning industry generates large volume of wastewater for which the treatment is particularly difficult due to the high content of organic matter and salts and to the significant amount of oil and grease they present.
In this work, a closed jacketed batch reactor was used to study the feasibility of applying a Fenton reaction step after an activated sludge biological treatment. For this purpose and in order to find optimal conditions, a 3^3 Box-Behnken full factorial design was used. The predicted optimum value (64% DOC degradation) was found for hydrogen peroxide concentration of 1520 mg/L, iron concentration of 338 mg/L and pH 3.2.

Introduction

Fish-processing industry consumes huge quantities of water, producing large amounts of wastewaters, from factory cleaning and raw materials washing [1]. These effluents have quite a high organic load and also high levels of salinity. Cooking effluents also contain highest organic matter load. The high salinity (Na^+, Cl^-, SO_4^{2-}) is caused both by the raw material and the seawater, used in the process [2]. The level of total soluble and suspended chemical oxygen demand (COD) varies largely between factory and fish type [3]. It is also known a frequent change of products to be treated, with variation in flows and composition, which implies changes in wastewater characteristics. These variable operating conditions makes very difficult to design a common treatment plant for all of the wastewaters produced in a single unit. A treatment process suitable to treat or even valorise and recycle this wastewater must be found, or it can difficult the evolution of the small and medium size units, since they often cannot afford a plan for managing this effluent.

Biological treatment is the most common process used to treat organic-containing wastewaters [4]. These processes are frequently used since they are more economic and environmental friendly, using optimized natural pathways to actually destroy pollution, not only transform it into another form [5]. However, some compounds persist after the biological treatment and the oxidative processes arise as good methods to treat the remaining recalcitrant organic matter. The Fenton reagent (Fe^{2+}/H_2O_2) is currently accepted as one of the most effective methods for the oxidation of organic pollutants [6]. Oxidation of organic substrates by Fenton's reagent has been studied since 1894 [7]. It is currently known that the efficiency of the Fenton's reaction depends mainly on H_2O_2 concentration, Fe^{2+}/H_2O_2 ratio, pH and reaction time. The initial concentration of the pollutant and its characteristics, as well as temperature, also have a substantial influence on the final efficiency [6].

The experimental design and response surface methodology (RSM) are useful statistical techniques to identify and optimize factors that influence a particular process, with reduced number of experiments to be performed. Additionally, the relative significance of the factors and possible synergic or antagonistic interactions that may exist between them can be evaluated [8]. This multivariate technique fits the experimental data to a theoretical model through a response function, estimating this way the model coefficients. The adequacy of the model is evaluated by the coefficient of determination R^2.

The most common design of RSM is Box-Behnken design (BBD) [8, 9], which is well suited for fitting a quadratic surface, since it considers three levels per factor and fills in the combinations of center and extreme levels in which the optimal conditions for an experiment are found [10, 11]. This design has been widely applied in optimization of several treatment processes [12-14] because of its reasoning design and excellent outcomes.

Advanced oxidation of fish canning wastewaters by Fenton's reagent has not been reported in the literature. Therefore, the major objective of this study is to investigate the total or partial mineralization and the reduction of recalcitrant organic compounds by Fenton's reagent of a previously biologically treated fish canning wastewater in terms of dissolved organic carbon (DOC). The effects of initial pH, Fe(II) and H_2O_2

concentrations on the reaction were investigated by using a 3^3 Box-Behnken full factorial design with RSM. Optimal values of the operating parameters maximizing DOC removals were determined.

Materials and methods

Fish-processing wastewater

The clarified fish processing wastewater was obtained after a biological treatment (with a final DOC of about 50 mg/ L, a COD of about 220 mg/L and a biochemical oxygen demand (BOD_5) of about 0.8 mg/L) and used for chemical oxidation, with Fenton's reagent.

Fenton Trials

Chemical oxidation was performed in a closed jacketed batch reactor (1 L capacity), which contained 500 mL of the previously biologically treated effluent. The reactor operated under constant stirring, accomplished through a magnetic bar and a Falc magnetic stirrer. The temperature of the reaction mixture was kept constant at 33 ºC by coupling the reactor to a thermostatic bath. Reagents employed in the oxidation process were $FeSO_4 \cdot 7H_2O$ (Panreac) and H_2O_2 (30 wt.%, from Riedel-de Haën). The pH in the reaction mixture was adjusted to the desired value using H_2SO_4 (95–97%, Fluka).

Before each run, the effluent was put in the reactor, and the temperature stabilized. The catalyst (iron sulphate) was introduced after pH adjustment to avoid iron precipitation. Time zero of the runs was defined as the moment of hydrogen peroxide solution addition. The reaction was stopped reducing H_2O_2 with Na_2SO_3 (Merck) in excess. To measure the solution temperature and pH, a thermocouple and a pH electrode (WTW, Sentix 41 model), connected to a pH-meter from WTW (model inolab pH Level 2), were used, respectively.

Analytical Methods

The DOC was determined by catalytic oxidation followed by quantification of the CO_2 formed through infra-red spectrometry (NDIR), as described in Method No. 5310D of the Standard Methods for the Examination of Water and Wastewater [15]. For that, a Shimadzu 5000A Total Organic Carbon (TOC) analyzer was used. TOC values reported represent the average of at least two measurements; in most cases each sample was injected three times, validation being performed by the apparatus only if CV was smaller than 2%.

Standard methods for the examination of wastewater [15] were also adopted for the measurement of COD and BOD_5.

Factorial design

A 3^3 Box-Behnken full factorial design, including three replicates at central point, was carried out in order to analyse the influence of the factors pH, Fe(II) and H_2O_2 concentrations on the DOC abatement of a fish canning wastewater by Fenton's reaction. The ranges studied for each of the factors were established according to studies already carried out in the group [16, 17]. The low level (-1), high level (+1) and the middle point (0) of each factor are listed in Table 1. Table 2 gives the experimental design matrix.

Table 1. Factor levels for a 3^3 Box-Behnken factorial design.

Factors	Parameters	Coded level		
		+1	0	-1
X_1	$[H_2O_2]$ (mg/L)	2000	1000	100
X_2	[Fe(II)] (mg/L)	400	200	50
X_3	pH	3.5	3.0	2.5

Table 2. Box-Behnken design matrix with experimental results and predicted values for fish canning wastewater DOC oxidation.

Run	Factors			DOC removal (%)	
	X_1 (mg/L)	X_2 (mg/L)	X_3	Actual Value	Predicted Value
1	100	50	2.5	23.9	19.7
2	100	50	3.0	22.6	24.1
3	100	50	3.5	5.0	12.3
4	100	200	2.5	41.2	39.4
5	100	200	3.0	46.3	46.8
6	100	200	3.5	42.7	38.1
7	100	400	2.5	26.5	36.7
8	100	400	3.0	53.9	48.2
9	100	400	3.5	46.6	43.4
10	1000	50	2.5	26.6	24.7
11	1000	50	3.0	33.7	31.4
12	1000	50	3.5	26.4	21.9
13	1000	200	2.5	50.1	46.1
14	1000	200	3.0	49.6	55.8
15	1000	200	3.5	49.8	49.3
16	1000	400	2.5	48.0	45.6
17	1000	400	3.0	65.4	59.4
18	1000	400	3.5	51.1	56.9
19	2000	50	2.5	10.3	17.9
20	2000	50	3.0	29.2	27.2
21	2000	50	3.5	21.5	20.2
22	2000	200	2.5	44.4	41.2
23	2000	200	3.0	52.0	53.5
24	2000	200	3.5	53.4	49.6
25	2000	400	2.5	43.5	43.2

26	2000	400	3.0	62.7	59.5
27	2000	400	3.5	54.8	59.6
28	1000	200	3.0	54.8	55.8
29	1000	200	3.0	47.1	55.8

The experimental Box-Behnken design, analysis of variance (ANOVA) and 3D response surface were carried out using the software Statistica v7.0 (Statsoft Inc.). Eq. (1) describes the regression model of the present system, which includes the interaction terms:

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad (1)$$

where Y is the predicted response, *i.e.* the DOC removal; X_1, X_2 and X_3 are the coded levels of the independent factors H_2O_2 concentration, Fe(II) concentration and pH. The regression coefficients are: β_0 the intercept term; β_1, β_2 and β_3 the linear coefficients; β_{12}, β_{13}, β_{23} the interaction coefficients and β_{11}, β_{22}, β_{33} the quadratic coefficients. The model evaluates the effect of each independent factor on the response.

Results and discussion

The characteristics of the biologically treated wastewater show the high recalcitrant nature of the organic compounds present in it, which is reflected by its very low BOD_5/COD ratio (< 0.005). For treatment of such a wastewater, an advanced oxidation process, such as Fenton's reagent, seems to be a suitable option.

The performance and optimization of Fenton treatment was investigated applying a Box-Behnken full factorial design with three factors: hydrogen peroxide concentration, iron concentration and pH. The results from the 29 experiments are presented in Table 2. Using the experimental data, the second order polynomial model (Eq. (1)) was fitted to these results and obtained in terms of coded factors:

$$Y = -250.3 - 0.001X_1 + 0.133X_2 + 184.2X_3 - 32.35X_3^2 + 0.005X_1X_3 + 0.04X_2X_3 \quad (2)$$

The DOC oxidation results predicted by the model presented above, at each experimental point, are presented in Table 2. The statistical significance of the polynomial model for the experimental responses was evaluated by ANOVA. According to the ANOVA results (Table 3), the quadratic model, including linear interactions, fitted adequately to the experimental data giving a coefficient of determination, R^2, of 0.9061.

The regression coefficients and the interaction between each independent factor can be considered statistically significant for *p-values* lower than 0.05, with 95% of confidence interval. The Pareto chart also displays the statistically relevant effect of each factor on the response and it is a practical mode to view the results. These are sorted from the largest to the smallest, and the effects to the right of the divisor line are significant. Thus, according to the ANOVA results (Table 3) and to the Pareto chart (Figure 1), it is possible to observe that the linear and quadratic terms of iron concentration (X_2) are the factors that most affect the reduction of DOC of the fish canning wastewater in study by Fenton's reagent. However, both terms of hydrogen peroxide concentration (X_1) and the quadratic term of pH (X_3) also have an effect on the reaction whilst the interaction between the three factors and the linear term of pH do not affect the oxidation.

Table 3. Analysis of variance (ANOVA) for the fitted quadratic polynomial model for optimization of DOC oxidation by Fenton's reagent of a fish canning wastewater.

Source	Sum of squares (SS)	df[a]	Mean square (MS)	*F*-value	*p*-value
(1) X_1 (L[b])	233.0	1	233.0	7.3	0.0142
X_1 (Q[c])	225.2	1	225.2	7.0	0.0156
(2) X_2 (L)	3581.2	1	3581.2	112.1	0.0000
X_2 (Q)	1022.6	1	1022.6	32.0	0.0000
(3) X_3 (L)	91.2	1	91.2	2.9	0.1074
X_3 (Q)	435.0	1	435.0	13.6	0.0016
1L by 2L	51.6	1	51.6	1.6	0.2194
1L by 3L	71.5	1	71.5	2.2	0.1511
2L by 3L	150.9	1	150.9	4.7	0.0426
Error	607.1	19	32.0		
Total SS	6462.7	28			

R^2 = 0.9061; adj R^2 = 0.8616
[a] df: degrees of freedom
[b] L: linear
[c] Q: quadratic

The effects of the independent factors and their interaction on the oxidation are also represented by RSM, with which is also possible to predict the response and to determine the optimum values of the reaction. The response surface plots (Figure 2) show the DOC removal as function of two factors, whilst the third was kept at a constant level. By these plots is then possible to clearly observe that the optimum conditions for obtaining the maximum degradation are within the experimental ranges tested.

Then, the surface plots show the increase of DOC degradation with the increase of iron concentrations. Plots 2a and 2c (Figure 2) clearly show that the DOC degradation by Fenton's reagent was sensitive even to small alterations of iron concentration. The DOC degradation of the fish canning wastewater was increased up to a critical iron concentration and thereafter the DOC degradation decreased. The existence of an optimal iron concentration is explained by the reaction of the excess of iron ions with the hydroxyl radical (Eq. (3)), thereby decreasing the concentration of radicals available and limiting the oxidation of organic compounds [18].

$$HO\cdot + Fe^{2+} \rightarrow OH^{-} + Fe^{3+} \qquad (3)$$

Furthermore, the high concentrations of iron are not desirable for two practical reasons: the reagent cost and the need of iron sludge treatment, that means also higher costs [19].

As it can be seen from plot 2b (Figure 2), the hydrogen peroxide concentration and the pH factors did not seem to play an important role on the degradation in the treated range. But it is possible to observe the existence of an optimum hydrogen peroxide concentration, that is justified by parallel reactions between the H_2O_2 in excess and the hydroxyl radical, generating $HO_2^{\cdot}$ species with a lower oxidation potential [20].

The adequacy of the proposed model (Eq. (2)) for organic matter degradation of pre-treated fish canning wastewaters by Fenton's reagent was evaluated at the optimum operating conditions. According to the model the optimum conditions were: hydrogen peroxide concentration of 1520 mg/L, iron concentration of 338 mg/L and pH 3.2, predicting above 64% DOC reduction. Under these optimal conditions, new experiments were conducted in triplicate and a DOC abatement of 64.4% was achieved, which is in good agreement with the degradation predicted by the model. Furthermore, for the entire range of the tested factors, the experimental results are very close to the predicted values obtained from the model.

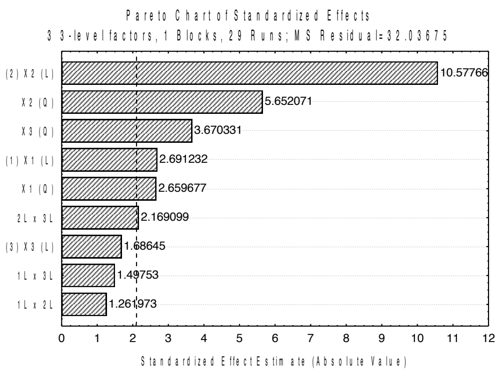

Figure 1. Pareto chart of standardised effects for 3^3 Box-Behnken factorial design. (1) H_2O_2 concentration; (2) Fe(II) concentration; (3) pH.

The observed maximum of DOC degradation at pH 3.2 is in agreement with the values founded in the literature for other wastewaters treated by Fenton's reagent [19, 21, 22]. The high reagents concentrations necessary to obtain some organic matter degradation can be explained firstly by the nature of the effluent, which has already been biologically treated and contains predominantly recalcitrant matter and then, by the high salt concentration, which decreases the process efficiency due to chloride ions, that are able to trap hydroxyl radicals, producing hypochlorous acid precursors or to react with the hydroxyl radicals producing less reactive radicals [23]. So the concentration of Fenton's reagent employed must be enough to overcome the restrictions imposed by the salinity.

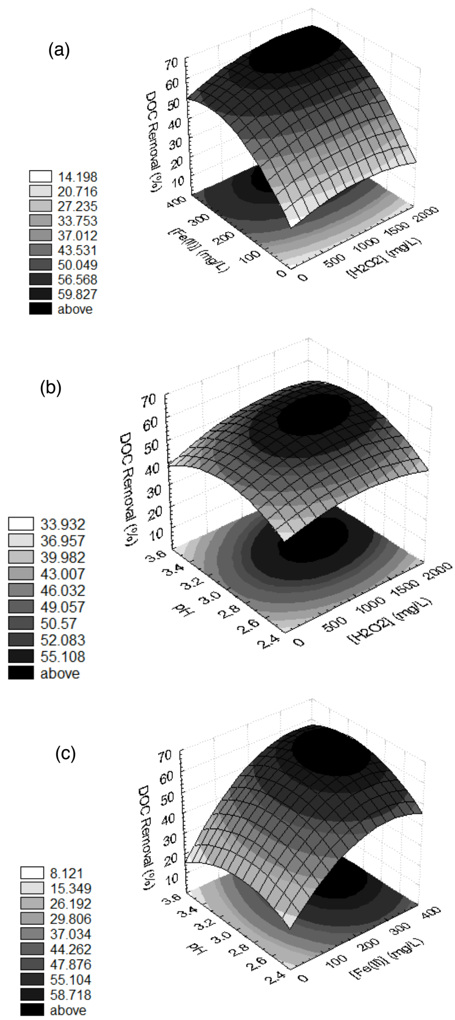

Figure 2. Response surface plots for DOC removal of a fish canning wastewater by Fenton's reagent as a function of: (a) H_2O_2 and Fe(II) concentration at pH 3; (b) H_2O_2 concentration and pH at 200 mg/L of Fe(II); (c) pH and Fe(II) concentration at 1000 mg/L of H_2O_2.

Figure 3 shows the DOC removal by Fenton oxidation and the corresponding pH variation over time, under the optimal conditions found. It is possible to observe that the decomposition was performed in two stages: via a rapid first-stage (up to 2 min) followed by a slow second-stage (from 2 min to end). This profile of degradation was found in literature and had been recognized in various Fenton processes [24-27]. During the first 2 minutes of the reaction, rapid pollutant degradation is attributed to high ·OH concentrations, as a result of greater amounts of Fe^{2+} catalysts in the solution that reacts with H_2O_2. At the second stage, Fe^{3+} ions were combined with H_2O_2 to produce weaker oxidant radicals compared to ·OH in addition to their slower rate of production [26].

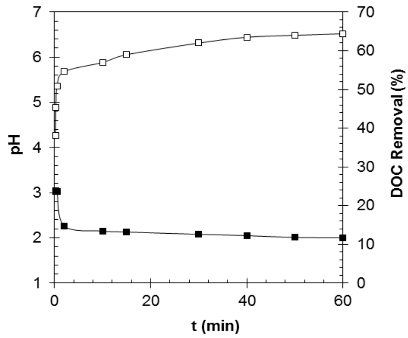

Figure 3. Time course of pH variation (■) and DOC removal (□). Each point represents the average of three replicates (S.D. <10% of the mean).

The pH, which was not corrected during each experiment, had a similar profile to the DOC abatement but in the reverse direction, decreasing until the end. Detailed kinetic study is very difficult to perform for Fenton process in this kind of effluents due to complexity of chemical compounds formed as intermediates during the reaction [28] and to the high initial reaction velocity. However, it was attempted to fit the experimental results to a parallel decay kinetic model (Eq. 4), which simulates the two different stages observed:

$$DOC_t = C_0.p.\exp(-k_1.t)+C_0.(1-p).\exp(-k_2.t) \quad \text{(Eq. 4)}$$

where DOC_t is the DOC concentration (mg/L) at time *t*, C_0 is the DOC initial concentration (49.43 mg/L), *p* represents a fraction of C_0, k_1 and k_2 are the decay kinetic constants and *t* is the time (min).

Using the program Fig.P - The Scientific Fig. Processor, v. 2.98, Biosoft, the kinetic constants of the model were achieved, leading to the model present in the Eq. (5) with a coefficient of correlation R^2 of 0.997.

$$DOC_t = 22.47\exp(-0.005t)+26.96\exp(-7.04t) \quad \text{(Eq. 5)}$$

In order to evaluate the adequacy of the proposed model for the kinetics of DOC removal of a fish canning wastewater previously biologically treated by Fenton's oxidation, the time course calculated by the kinetic model was compared with the experimental one (Figure 4). The close correlation between the predicted and the experimental results seems to support the reliability of the established model.

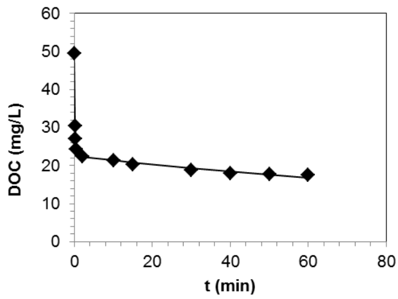

Figure 4. Comparison of experimental (◆) and simulated (continuous line) time courses of DOC removal by Fenton oxidation of a fish canning wastewater previously biologically treated, with initial DOC concentration of 49.43 mg/L

Conclusions

The overall results of this study indicate that the application of Fenton's reagent is a feasible method to partially treat fish canning wastewaters, allowing achieve a satisfactory decrease of DOC. However, the excessive reagent concentrations required, along with the fact that the optimum predicted organic matter degradation (above 64 %) only lead to DOC values of about 20 mg/L, may be valid reasons to dismiss this chemical step from the treatment process, since there are several associated costs and the DOC values attained only with the biological treatment are adequate for a further treatment, for instance, reserve osmosis for effluent recycling.

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