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Chemical oxidation of fish canning wastewater by Fenton's reagent

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ABSTRACT

The fish canning industry generates large volumes 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 (63% DOC degradation) was found for hydrogen peroxide concentration of 1558 mg/L, iron concentration of 363 mg/L and pH 3.2.

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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 from fish canning industry also show a marked organic matter load. The high salinity (Na^+, Cl^-, SO_4^{2-}) is caused both by raw material and brine, 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 flow rates and composition, which implies changes in wastewater characteristics. These variable operating conditions difficult the planning of a common treatment plant for all of the wastewaters produced in a single unit. A treatment process suitable to treat or even valorize and recycle this wastewater must be found, or it can be difficult the evolution of the small and medium size units, since they often cannot afford a plan for managing their effluents.

Biological treatment is the most common process used to treat organics-containing wastewaters [4]. The biological processes are frequently employed 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 refractory compounds persist after the biological treatment and chemical 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 pollutants and their characteristics, as well as temperature, also have a substantial influence on the overall efficiency [6].

The experimental design and response surface methodology (RSM) are useful statistical techniques to identify and optimize factors that influence a particular process, through a reduced number of experiments to be performed. Additionally, the relative significance of the factors and possible synergistic 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 the optimization of several treatment processes [12–14] because of its reasoning strategy and excellent outcomes.

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Advanced oxidation of fish canning wastewaters by Fenton's reagent has not been yet 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), with the aim to meet the emission limit values for discharge into water bodies established by Decree-Law No. 236/98 ($COD \leq 150$ mg/L). 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 with a final dissolved organic carbon (DOC) of about 50 mg/L, a chemical oxygen demand (COD) of about 220 mg/L, a biochemical oxygen demand (BOD_5) of about 0.8 mg/L, a conductivity of 30–40 mS/cm and a pH between 7 and 8 was obtained after a biological treatment 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, for 1 h. 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 °C 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 into 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 after 1 h by reducing H_2O_2 with Na_2SO_3 (Merck) in excess. Any remaining sulphite was oxidized by bubbling O_2. 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 non-dispersive infra-red spectrometry (NDIR), as described in Method No. 5310 D of the Standard Methods for the Examination of Water and Wastewater [15]. For that, a Shimadzu 5000A Total Organic Carbon (TOC) analyzer was used. DOC 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 coefficient of variation (CV) was smaller than 2%.

Standard methods for the examination of wastewater [15] were also adopted for the measurement of COD and BOD_5 (methods 5220 C and 5210 B, respectively).

Factorial design

A 3^3 Box–Behnken full factorial design, including three replicates at central point, was carried out in order to analyze 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. However, first of all, in order to decide the factor values to study, the stoichiometric H_2O_2 requirements for sample degradation were determined taking into account the COD value. After this, the initial Fe(II) concentration was established by varying the molar $[Fe(II)]/[H_2O_2]$ ratio from 1/2 to 1/65. Nevertheless, perhaps because of the high variability of the real wastewater that is being studied, the optimum conditions determination was not easy, but it seemed that there was a trend toward higher values of H_2O_2. So, it was decided to start with a Box–Behnken factorial design only with 2 factors (H_2O_2 and Fe(II) concentrations) to analyze the results trend. With that help and knowing the normal pH values range for Fenton's reagent wastewater treatment [16,17], a Box–Behnken full factorial design with 3 factors and 3 levels was done later, in order to define the reaction optimum conditions and to analyze the factors influence. Each independent variable was coded at three levels between −1 (low level), 0 (middle point) and +1 (high level). The coding of the variables was done by Eq. (1) [18]:

$$x_i = \frac{X_i - X_z}{\Delta X_i}, \quad i = 1, 2, 3, \ldots, k \tag{1}$$

where x_i, is the dimensionless value of an independent variable, X_i is the real value of an independent variable, X_z is the real value of an independent variable at the center point and ΔX_i is the step change of the real value of the variable i corresponding to a variation of a unit for the dimensionless value of the variable i. The levels of each factor are listed in Table 1. Table 2 gives the experimental design matrix.

The experimental Box–Behnken design, analysis of variance (ANOVA) and 3D response surface were carried out using the software Statistica v12.0 (Statsoft Inc.). Eq. (2) describes the regression model of the present system, which includes the interaction terms:

$$Y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{33} x_3^2 \tag{2}$$

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, respectively). 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

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	1050	100
X_2	[Fe(II)] (mg/L)	400	225	50
X_3	pH	3.5	3.0	2.5

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