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Oil removal from fishmeal mill wastewater by the Fe°/UV process: optimization by experimental design

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ABSTRACT

Oil is one of the most difficult to eliminate pollutant present in the fishmeal mill wastewater industry, due to its physical properties which allow it to expand in a fine layer on the water's surface, inhibiting light penetration, and gaseous exchange between the water–air phases. This alters photosynthesis, which reduces dissolved oxygen content, with consequent modifications on the structure of the food chain. In order to reduce oils from wastewater, we used elementary iron in catalytic suspension with ultraviolet radiation (254 nm). The reaction was carried out in a cylindrical quartz reactor. The efficiency of the studied system was determined by means of multivariate analysis with the statistical program MODDE 7.0, where the experimental variables were pH and reaction time. The response of the treatment was given by the percentage of oil removal. The optimal experimental value obtained was 96% of oil removal, under conditions of $pH = 4.8$ and 40 min of reaction time. Total organic carbon reduction, measured as total organic carbon, reached 70.9%. Additionally, we achieved reduction of chemical oxygen demand and biological oxygen demand of 78.18 and 70%, respectively, under optimal variable conditions. Under the same conditions, the disinfection capacity of the system reached nearly 100%. Based on these results, we affirm that the Fe°/UV treatment is efficient in the removal of fish oil from fishmeal mill wastewater, thus avoiding effluent filtration, which is necessary in treatments that use iron salts, such as the traditional Photo-Fenton reaction.

Keywords: Experimental design; Fishmeal mill wastewater; Oil; Response surface methodology; Zero-valent iron

1. Introduction

Industrial residual waters are those that come from any economic activity whose process of production, transformation, or manipulation utilizes water. In coastal environments, fishing industries frequently spill effluents into nearshore waters. These effluents have a high organic charge, with oils being one of the polluting agents causing the greatest problems for the industrial process, due to their very complex removal. When oils are present in high concentrations in fishing effluents, they can cause serious alterations to marine ecosystems, where they accumulate on the water surface, forming fine oil layers that inhibit light penetration and gaseous exchange between the water–air phases, with direct effects on dissolved oxygen content and, consequently, on phytoplanktonic productivity, giving rise to anaerobic processes [1–4].

High-organic matter in effluents can be measured by chemical parameters, such as biological oxygen demand (BOD_5), chemical oxygen demand (COD), and

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total organic carbon (TOC), all of which consider water quality and, thus, make it possible to determine the effect of effluents in the ecosystem with greater certainty. The excess of organic matter on the water's surface causes a decrease in oxygen concentrations due to nitrogen biodegradation of organic waste (nitrification process). In this process of high oxygen demand, ammonia successively oxidizes to nitrites and nitrates, causing serious contamination problems which alter organism life. The level of pollution produced by fishing activities is high year round, which also poses problems for the health of the human population living in the surrounding areas, generates risks for local production, and negatively effects environmental quality. Chilean law number 19.300, regarding the general environmental framework of the country, specifies the maximum allowable limits of oils in liquid waste discharged into waters (20 mg/L within the littoral protection zone, which is 20 mg/L; 50 mg/L in inland water bodies).

Many reports have focused on the study of new chemical oxidation technologies as a pretreatment for nonbiodegradable or toxic wastewater, combined with a conventional biological treatment [5–11]. The objective of this study is to evaluate an amiable technology that allows for the efficient removal of organic matter present in fishmeal effluent. In particular, we aimed to evaluate the feasibility of enhancing the biodegradability of fishmeal effluent using zero-valent iron activated by UV radiation, as a photocatalytic system [12–14]. This process is part of the so-called advanced oxidation processes (AOP_S), which are based on the *in situ* production of hydroxyl radicals ($HO^\bullet$), which are a powerful oxidant (2.8 eV), extremely reactive, and nonselective, attacking organic molecules until they are mineralized, as is described by Eqs. (1)–(3) [15,16].

$$Fe^\circ + H_2O + hv \rightarrow Fe^{2+} + {}^\bullet OH + H^+ \tag{1}$$

$$Fe^{2+} + {}^\bullet OH + H^+ \rightarrow Fe^{3+} + H_2O + hv \tag{2}$$

$$Fe^{3+} + R^\bullet \rightarrow Fe^{2+} + \text{oxidation products} \tag{3}$$

2. Experimental

2.1. Sample

Effluent was obtained from the general emissary of a fishmeal mill, where all of the industrial liquids from different stages of the fishmeal production process converge.

2.2. Oxidation process

The Fe°/UV method was carried out in a 200 mL cylindrical quartz reactor with the addition of 1 g of zero-valent iron (10 μm, Merck). The system was kept in constant agitation. UV radiation was provided through a 254 nm lamp (HP, 30 W).

2.3. Analytical methods

COD ($mg\,O_2\,L^{-1}$) was determined in a NOVA-60 photometer using standard method 5220D. For TOC ($mg\,L^{-1}$) analysis, the samples were filtered with 0.22 μm filters, acidified with hydrochloric acid and injected in a TOC analyzer (Shimadzu 5,000). BOD_5 was determined with an oxygen partial pressure sensor (OXITOP), using standard method 5210-D. The pH was measured with an electrode (bifunction Sen Tix WTW Inolab). Oil concentration was determined at 530 nm in a UV–visible spectrophotometer (model Spectrum UV 1600). Iron concentration was determined in a NOVA-60 photometer using merck spectroquant test (0.010–5.0 $mg\,L^{-1}$).

2.4. Multivariate analysis

For the fish oil sample, degradation was optimized as follows: pH 3 (−1) to 5 (+1) and time of reaction in minutes between 30 (−1) and 120 (+1), while maintaining the iron concentration constant to ensure a high iron concentration in the solution. Statistical analyses were performed using MODDE 7.0 software, which utilizes a response surface to evaluate the effect of the interaction between variables. In order to determine the optimal response, we obtained a model of 11-type star experiments to determine the influence of the variables, where the general response polynomial is a quadratic polynomial described by Eq. (4).

$$Y(\%) = B_0 + B_1X_1 + B_2X_2 + B_{11}X_1^2 + B_{22}X_2^2 + B_{12}X_1X_2 \tag{4}$$

where Y is the percentage of response (i.e. reduction); B_0 is the average value of the experimental response; B_1 is the main effect of the variables; B_2 is the quadratic effect of the variables; and B_{12} is the first-order interaction effect between the variables.

The experimental matrix (Table 1) generated by the experimental design indicates the interaction between the values (minimum (−1), maximum (1), and central points (0)).

Table 1
Initial characteristics of fishmeal mill effluent

Parameters	Effluent
pH	7.6
Oil ($mg\,L^{-1}$)	1,600
TOC ($mg\,L^{-1}$)	1,728
BOD_5 ($mg\,O_2\,L^{-1}$)	3,000
COD ($mg\,O_2\,L^{-1}$)	5,562

3. Results and discussion

The initial chemical parameters of the effluent were measured and found to be high (Table 1), particularly COD, which means that the effluent cannot be discharged directly into the environment without treatment. In order to evaluate the efficiency of the Fe°/UV treatment system, we used experimental design. The experimental matrix and the corresponding responses (observed response and predicted response) are presented in Table 2. The difference between the observed response and predicted response gives the error for each of the variable combinations. The response was measured as the percentage of oil was removed from the effluent. The optimal values of the experimental variables were obtained from the regression equation and analysis of the response surface, where we observed two maximum responses indicated in the red zone (Fig. 1), one at a more acidic pH, which required a longer treatment time, and another under conditions of minor acidification (pH 4.8), which required only 40 min of reaction. This result is in agreement with the characteristics of the surface of iron, which, in water, can exhibit metal-like or ligand-like coordination properties depending on the solution. At low pH ($<pH_{zpc} = 8$), iron is positively charged and attracts anionic ligands, including key environmental species, such as sulfate and phosphate [16]. Therefore, we selected the best variable combination to be at low activation time and minor acidification, which decrease operational costs. Optimal conditions attained 97% of oil removal, with a 95% confidence interval. The mathematical model was validated by means of statistical analysis, indicating the relationship between variances (Fig. 2). The lack of fit (model error) was compared with the pure error. The model for the oil removal response showed no lack of fit.

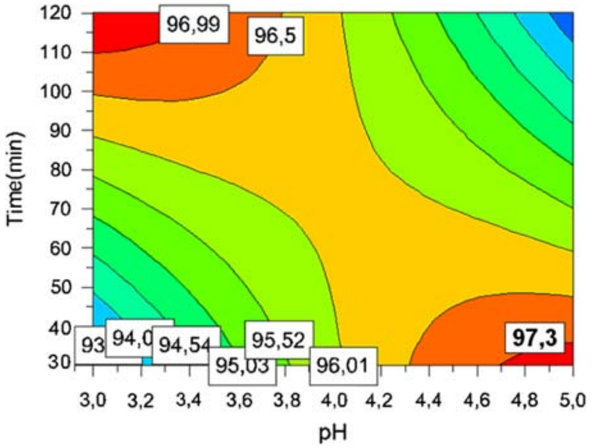

Fig. 1. Response surface for oil removal optimization from fishmeal mill effluent using the Fe°/UV treatment.

In the validation of the model, we considered the following hypotheses:

Table 2
Experimental matrix and responses (observed and predicted) for oil removal using the Fe°/UV treatment system

Experiment	Order run	Experimental variables					
		pH		Time (min)		Response (%)	
						Observed	Predicted
1	11	3	−1	30	−1	95.8	93.1
2	8	5	1	30	−1	96.6	97.2
3	9	3	−1	120	1	99.0	97.5
4	4	5	−1	120	1	91.5	93.2
5	10	2,586	−1.41	75	0	91.7	94.6
6	3	5,414	1.41	75	0	96.3	94.5
7	6	4	0	11.37	−1.41	94.5	95.8
8	7	4	0	138.63	1.41	96.3	96.0
9	5	4	0	75	0	95.0	96.1
10	2	4	0	75	0	95.3	96.1
11	1	4	0	75	0	94.6	96.1

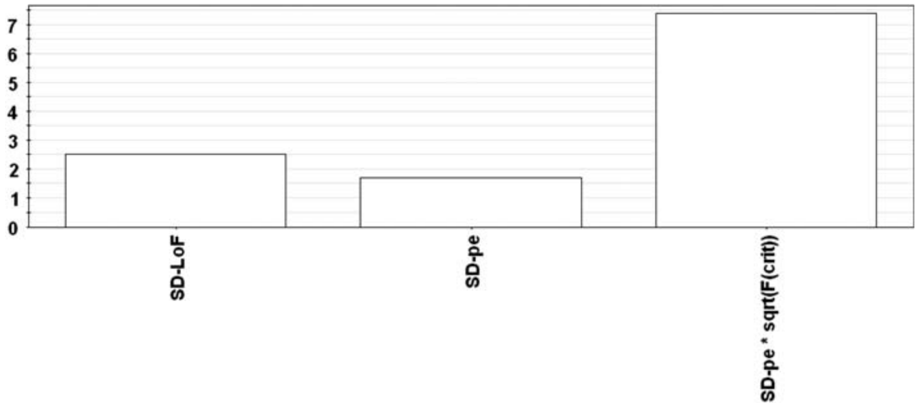

Fig. 2. Optimal estimation of the experimental variables (pH and reaction time) on oil removal. The first bar represents the standard deviation of the lack of fit. The second bar indicates pure error. The third bar represents the standard deviation of the pure error multiplied by the square root of the critical *F* value (i.e. the value of the *F* distribution for which the standard deviation of the lack of fit is significant at the 95% level), hence when the first bar is larger than the third bar, this indicates that the model has a significant lack of fit.

The null hypothesis H_0: $\mu_1 = \mu_2$ proposes that the variances between the model and residual are equal, thus, the model does not contain intrinsic errors (residuals).

The alternate hypothesis H_1: $\mu_1 \neq \mu_2$ proposes that the model and residual variances differ.

Prior to analyses, we evaluated the model assumption that the variances of lack of fit (model error) and pure error (replicate error) are equal. In order for the alternative hypothesis to be supported, the experimental *F* must be greater than the critical *F*.

Regression analysis showed that total oil degradation initially increased with removal time and pH, reaching a maximum and later decreasing as a quadratic function of pH (Fig. 1; adjusted $F_{5,5} = 27.8$; $p < 0.001$). Model fit was good and presented no significant difference from the predicted model values (adjusted $R^2 = 0.93$; $Q^2 = 0.80$; lack of fit $F_{5,5} = 1.6$; $p = 0.41$). The experimental matrix for a polynomial response was solved, whose expression is represented by Eq. (5).

$$Y(\%) = 96.11 + 0.8X_1(\pm 0.87) + 0.5X_2(\pm 0.87) - 1.65X_1^2(\pm 0.93) + 0.38X_2^2(\pm 0.93) - 2.5X_1X_2(\pm 1.38) \quad (5)$$

where $Y(\%)$ = total oil removal in percentage; X_1 = pH of the solution; and X_2 = reaction time in minutes.

From analysis of the polynomial, it can be deduced that oil removal depends on both variables. This is also observed in Fig. 3, where the effects of pH and reaction time are clearly positive. The effects of the variables and the optimized reaction can be corroborated following the reaction kinetics. The system efficiency for the treatment is observed in Fig. 4,

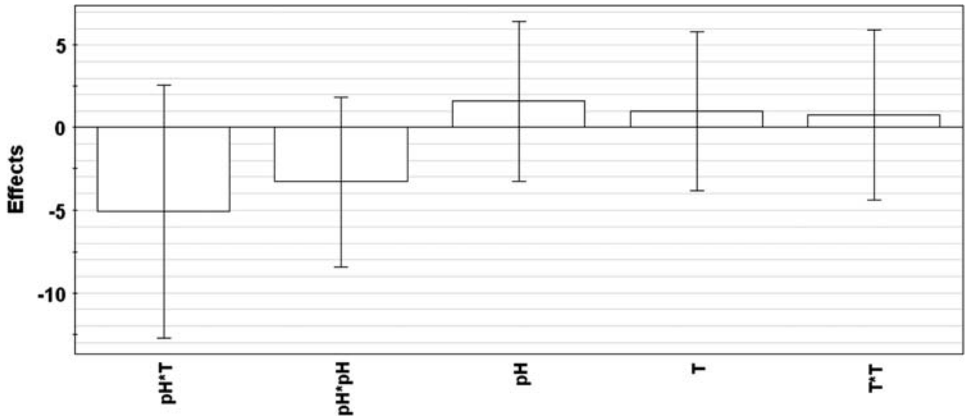

Fig. 3. Analysis of the influence of parameters on oil removal. Bars represent the 95% confidence intervals.

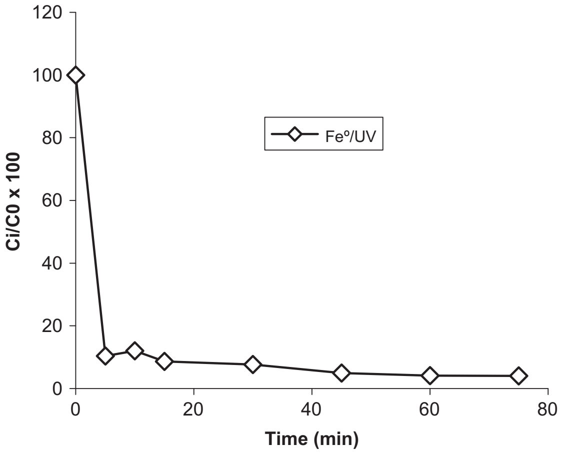

Fig. 4. Kinetics of oil removal using the optimized Fe˚/UV system.

where during the first minutes of reaction oil removal reached 89%, later attaining 96% of oil removal at 40 min of treatment, and remaining constant over longer time periods. The obtained results are in agreement with the cited literature [17], where a review of water purification by different methods, found that the Fenton reaction is carried out in two steps; where the first stage is faster than the other oxidation processes, and in the second phase the speed of degradation diminishes. Other researchers have studied the reduction of olive oil in residual waters using the Fenton reaction, reaching 95% oil reduction in 2 h of treatment [18].

Under optimal treatment conditions, the kinetics of COD and BOD_5 removal, respectively, follow the same tendency, with oil reduction reaching 50% after 5 min of treatment, and greater reductions with increasing time of treatment. Under these conditions, we obtained a 78.18% reduction in COD and 70% reduction in BOD_5 (Fig. 5).

Researchers using electrocoagulation for the decolorization of colorant contaminated water [19] obtained similar values of COD reduction, where they report the operational parameters for reduced COD at 75%. Other studies that applied chemical and biological treatments to olive mill wastewater were also able to reduce COD by 75%, in four days. Treatments using the Fenton reaction, combined with an anaerobic treatment, were able to reduce COD in olive oil mill wastewater by 76% in 48 h of hydraulic retention time, improving the effluent biodegradability [20,21]. A comparison of the system used in our study with those used by other researchers for COD removal from wastewater containing oils demonstrates the efficiency of the system for removing COD from fishmeal wastewater, where high efficiency is reached in a short time period and without the use of iron salts in solution.

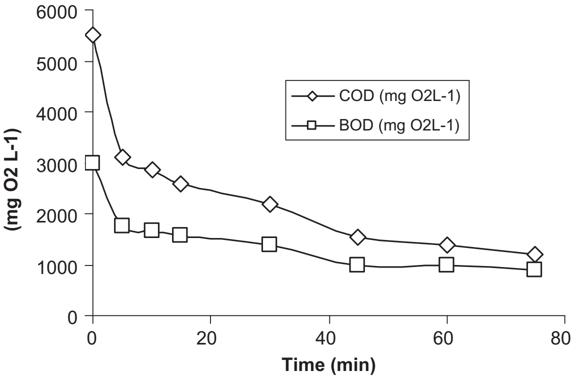

Fig. 5. Behavior of COD and BOD_5 for the optimized variables using the Fe˚/UV process.

Furthermore, following the optimized treatment, fishmeal mill effluent biodegradability increased, which is expressed by the BOD_5/COD ratio, which ranged from 0.55 to 0.75 (Fig. 6). This increase in biodegradability is very promising, compared with other studies where the researchers performed olive mill wastewater degradation using homogeneous and heterogeneous photocatalytic oxidation, and biodegradability ranged from 0.66 to 0.8 [22]. When high biodegradability is achieved the effluent can be submitted to biological treatment without problems or can even be discharged into the environment without later consequences. Authors such as Bali et al. [10], have suggested the combination of AOP with biological treatment as a promising alternative which should be developed as a potential method for water purification. Biological treatment itself presents some disadvantages, where the principal criticism is that this process is not destructive and only transfers the contamination from one stage to another, which does not resolve the problem of pollution [23].

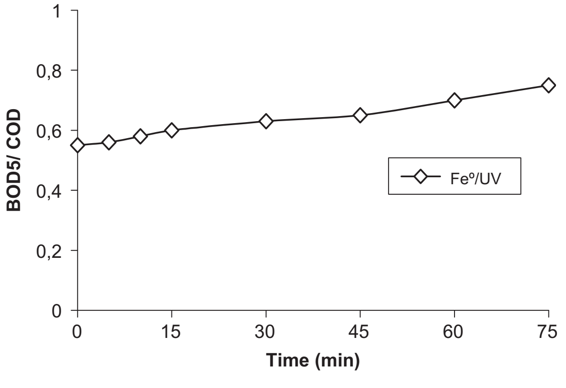

Fig. 6. Biodegradability enhancement of fishmeal mill effluent using the optimized variables.

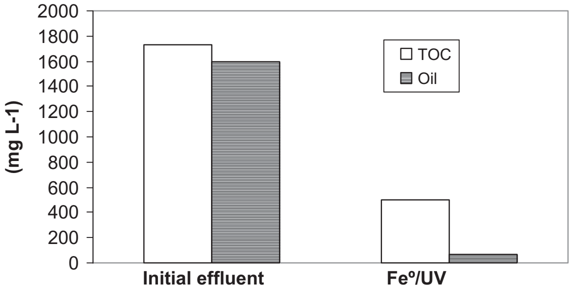

Fig. 7. Mineralization of oils from fishmeal mill effluent using the optimized Fe°/UV process.

Finally, TOC reduction reached 70.9% under the studied optimal conditions (Fig. 7). In this sense, mineralization is a parameter that evidences the efficiency of the Fe°/UV treatment in reducing the organic matter of the fishmeal mill wastewater, where further reduction demonstrates the efficiency of the Fe°/UV system.

4. Disinfection

Once the optimal conditions were determined, we carried out tests to evaluate whether the photocatalytic system is able to disinfect. Indeed, disinfection of the fishmeal effluent was observed (Fig. 8), where the number of colony forming units (CFU mL^{-1}) decreased as reaction time increased. The Fe°/UV system produced the most efficient and stable reduction over the time, attaining nearly 100% reduction of CFU at optimal time. Park et al. [24] observed that fecal coliform removal using Photo-Fenton treatment is more effective when the Fenton reaction is used alone, achieving 99.4 and 96% reduction of CFU in 80 min, respectively. This is logical since UV light acts as a disinfectant and is widely used in biological filters for water contaminated with viruses or bacteria. Water disinfection has the similar objective of the inactivation of micro-organisms present in the medium, decreasing the probability of disease transmission, and improving the handling of the treated water. The Fe°/UV system is based on the use of UV radiation, and is shown to be an efficient alternative for increasing the application of residual water treatment, achieving both organic matter mineralization and water disinfection.

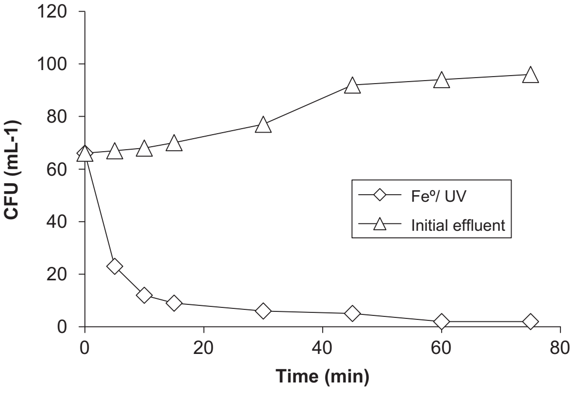

Fig. 8. Disinfection kinetics of the photocatalytic treatments applied to fishmeal effluent. CFU are colony forming units.

5. Conclusion

The Fe°/UV system is an efficient treatment for the reduction of oil from fishmeal mill wastewater, achieving good organic matter mineralization, and improving effluent biodegradability and disinfection. Multivariate analysis allowed detection of the synergism between the variables pH and reaction time, in order to determine the optimum conditions for the process. The optimal pH determined is ideal for treating fishmeal wastewater given that it is near the initial pH of the effluent, reducing the cost of reagents for pH adjustment. On the other hand, at higher pH, the iron complexes precipitate inhibiting the catalytic reaction of the iron. Finally, the addition of 1 g of iron ensured that the initial COD was reduced from 5,562 $mg\,O_2\,L^{-1}$ to 1,218 $mg\,O_2\,L^{-1}$.

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