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Implementation of Fenton process on wastewater from a cheese-making factory

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ABSTRACT

In this work, the performance of Fenton oxidation on whey, the high strength fraction of cheese-dairy wastewater, was studied. For this reason, factorial experimental design was used to study the main variables affecting the Fenton process, as well as their interactions. A 2^4 factorial design was performed in order to estimate the effects of the following parameters: the ratio $FeSO_4 \cdot 7H_2O/H_2O_2$ (X_1), the hydraulic retention time (X_2), the pH (X_3), and the temperature (X_4). The oxidation was carried out batch wise in an agitated, temperature- and pH-controlled glass reactor. At the end of the experiment, samples were taken from the effluent of the reactor and were analyzed in terms of COD, TOC, total Kjeldahl Nitrogen (TKN), total phosphorous, and fats and oils. The highest percentage of TOC efficiency measured was 33% in the experimental point (X_1, X_2, X_3, X_4) = (2/3, 1, 3.4, 20). Concentration of fats presented high reduction that reached 57%. Phosphorous removal was also high in all experiments, while nitrogen removal did not have high fluctuations. The results from the statistical processing of the experimental data enlightened the oxidation mechanism.

Keywords: Cheese-dairy wastewater; Factorial experiment; Fats and oils; Fenton oxidation; TOC removal

1. Introduction

Whey is the liquid residue obtained when casein and fat are separated by coagulation from the milk. Whey contains lactose (70–75%) and soluble proteins (10–15%) which result in a high chemical oxygen demand (COD) (50–70 g/L). At large milk processing plants, whey is usually dried and used as feedstock for animal feeding or more recently, by the agrofood and pharmaceutical industries. However, at small-scale milk farms or cheese production facilities, which are common in isolated rural areas, whey is not recuperated and has to be treated along with the other wastewaters generated from the installation, since the small quantity produced does not justify the significant cost of the equipment needed for the preparation of

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whey powder [1,2]. The final COD after mixing of the whey wastewater with the washing waters results in an effluent with high organic load requiring treatment before discharge. The choice of the treatment technique should address both the high organic load of the wastewater and the seasonal operation of the production plants.

Conventional anaerobic treatment processes are often used for treating dairy wastewater. Particularly anaerobic filters and UASB reactors are the most common reactor configurations employed. In fact, the UASB reactors are very suitable for treating food industry wastewaters, since they can treat large volumes of wastewaters in a relatively short period of time. Nevertheless, according to Burak et al. [3], more research should be directed towards treatment of dairy wastewaters in pilot and full-scale UASB reactors in the near future, to make use of these potential advantages outlined. Lipid degradation and inhibition in single-phase anaerobic systems is frequently discussed in literature, since lipids are potential inhibitors in anaerobic systems which can often be encountered by environmental engineers and wastewater treatment plant operators. Moreover, high concentrations of suspended solids in dairy waste streams can also affect the performance of conventional anaerobic treatment processes adversely, particularly the most commonly used upflow anaerobic filters [4].

This study aimed at examining the potential of applying Fenton oxidation as a pretreatment stage of cheese-dairy wastewater.

2. Materials and methods

2.1. Raw material

The cheese-dairy wastewater originated from a cheese-making factory with a capacity of 150tn cheese/year situated in Viotia, Greece. Table 1 presents the mean values and their standard deviation around the mean value for all the parameters of the raw wastewater during an operation cycle of the cheese-making factory.

Table 1
Cheese-dairy wastewater characteristics

Parameter	Mean value
pH	4.0 ± 0.3
COD (mg/L)	20,314 ± 9,186
TOC (mg/L)	7,920 ± 3,427
SS (g/L)	5.0 ± 4.4
VSS (g/L)	5.0 ± 4.3
Total Kjeldahl nitrogen (mg/L)	285 ± 118
Total phosphorous (mg/L)	85 ± 35
Fats and oils (mg/L)	1,931 ± 1,391

The characteristics of the raw wastewater have serious fluctuations during the operation of the cheese-making factory. From the data presented in Table 1, the high organic load of the wastewater is obvious. Furthermore, the concentration of fats and oils that equals to 2 g/L is indicative that the direct biological treatment of such a wastewater would be inefficient. The high values of the pollution parameters of cheese-dairy wastewater are mainly attributed to the whey. For this reason, in the present study, whey was used as raw material for the Fenton oxidation experiments. The composition of the whey used was COD 64,600 mg/L, TOC 20,135 mg/L, TKN 1,021 mg/L, TP 285 mg/L, and fats and oils 2.4 g/L.

2.2. Experimental procedure

The collected whey was preserved in the fridge in order to avoid any kind of degradation and was subjected to Fenton oxidation treatment. The oxidation was carried out batch wise in an agitated (120 rpm) temperature and pH controlled glass reactor of 500 mL capacity. Initially, the wastewater sample was set at the desired temperature. Next, the Fenton reagents were added according to their relative ratio. As ferrous salt, $FeSO_4{\cdot}7H_2O$ was used and the hydrogen peroxide was of 60% concentration. After oxidation, a part of the oxidation mixture was analyzed for fats and oils. The rest of the sample was filtered and the filtrate was analyzed in terms of COD, TOC, Total Kjeldahl Nitrogen (TKN), and Total Phosphorous. Total organic carbon (TOC) was analyzed with a TOC Analyzer Dohrmann DC-80 (detection limit lower than 1 mg/L) after acidifying the sample. The other pollution parameters were analyzed according to the standard methods for examination of water and wastewater [5].

2.3. Factorial design

The aim of the experimental procedure was to determine the influence of some basic process parameters on the effectiveness of the oxidation treatment in terms of % COD, TOC, TKN, TP, and fats removal. These parameters were the ratio of ferrous sulfate heptahydrate concentration to hydrogen peroxide concentration, the hydraulic retention time, the pH, and the temperature. These parameters are referred to as "controlling parameters" of the system. The effect of the controlling parameters on the optimization parameter was estimated by performing a 2^4 factorial experiment.

Table 2
Controlling parameters and their levels in the factorial experiment

	Controlling parameters		Variation intervals		
	Units	Representation As	−1 Level	0 Level	+1 Level
$FeSO_4{\cdot}7H_2O/H_2O_2$	$g/L(mL/L)^{-1}$	X_1	2/3	3/3	4/3
HRT	H	X_2	1	3	5
pH		X_3	3.4	3.8	4.2
Temperature	ºC	X_4	20	25	30

In general, by using a 2^n factorial design, n controlling parameters interrelate to an optimization parameter through an appropriate linear model. Their significance can also be estimated and assessed [6,7]. The levels of the controlling parameters are given on Table 2. The experimental area of the factorial design was predetermined in previous preliminary trials. In the 2^4 factorial design, 16 experiments were carried out. Three extra experiments in the center of the design (level 0) were also conducted for statistical purposes. Each experiment was repeated three times and the results presented are the mean values.

From these data, a mathematical model was constructed. Its adequacy was checked by the Fisher criterion. According to the latter, the following ratio should follow the F-distribution with level of importance $p = 5\%$:

$$F = \frac{\varsigma^2_{\mathrm{ad}}}{\varsigma^2_Y}, \tag{1}$$

where ς^2_Y is the standard deviation and $\varsigma^2_{\mathrm{ad}}$ is the adequacy deviation and is calculated by the following equation:

$$\varsigma^2_{\mathrm{ad}} = \frac{\sum_{i=1}^{N}(Y_i - \hat{Y}_i)^2}{F}, \tag{2}$$

where Y_i is the experimental i value, $\hat{Y}_i$ is the estimated i value from the model determined, F is the number of degrees of freedom, and N is the number of trials.

As far as the determination of statistically important parameters is concerned, the procedure mentioned below was followed. The coefficient deviation is defined as:

$$\varsigma^2(b_j) = \frac{\varsigma^2_Y}{N}, \tag{3}$$

where N is the number of trials.

The importance of the coefficient was checked by:

$$t = \frac{|b_j|}{\varsigma(b_j)}, \tag{4}$$

where b_j is the j linear coefficient.

The "t" should follow the Student distribution for importance level $p = 5\%$ and degrees of freedom of those of the deviation ς^2_Y.

3. Results

In Table 3, the results of the factorial experiment regarding % TOC, % COD, % TKN, % TP, and % fats removal efficiency for the treated whey are presented.

It is worth noticing that the Fenton oxidation process was in some cases effective, since the % TOC removal efficiency reached 33%, the % COD removal efficiency 35%, the % TKN removal efficiency 51%, the % TP removal efficiency 63%, and last but not least the % fats removal efficiency reached the high percentage of 57%. From the experimental results, it is clear that Fenton oxidation managed to oxidize fats either partially, by converting them to soluble organic compounds or totally, by full mineralization. The concentrations of the other parameters such as TOC, COD, TKN, and TP may have presented an increase which is also in accordance with the assumption that complex chemical components, insoluble in water, break down into water soluble fragments. By all the facts mentioned above, the beneficial effect of fenton oxidation is obvious.

3.1. TOC removal

According to the results of the factorial experiment and by following a specific analytical procedure [6,7], the following linear model, interrelating the % TOC removal efficiency (Y_1) with the controlling parameters of the system, was estimated:

Table 3
Percentage removal efficiency results of the factorial experiment

Trial	X_1	X_2	X_3	X_4	% TOC efficiency Y_1	% COD efficiency Y_2	% TKN efficiency Y_3	% TP efficiency Y_4	% fats efficiency Y_5
1	+	+	+	+	−0.4	21.5	22.7	40.5	7.0
2	−	+	+	+	6.9	30.2	33.6	46.4	5.2
3	+	−	+	+	11.2	30.5	21.9	36.0	7.0
4	−	−	+	+	6.2	15.5	15.2	43.1	41.1
5	+	+	−	+	9.3	34.5	21.0	53.4	3.3
6	−	+	−	+	8.3	19.8	30.3	54.5	35.3
7	+	−	−	+	12.2	33.6	34.6	63.4	5.7
8	−	−	−	+	13.8	13.6	49.1	61.3	57.2
9	+	+	+	−	−0.4	21.4	24.9	38.1	51.5
10	−	+	+	−	30.9	16.4	16.2	49.4	8.8
11	+	−	+	−	19.3	9.0	25.8	35.7	2.3
12	−	−	+	−	30.8	7.7	−19.2	44.1	15.5
13	+	+	−	−	11.6	32.5	35.0	58.1	21.3
14	−	+	−	−	22.0	14.9	25.6	51.0	14.7
15	+	−	−	−	7.6	24.1	42.5	60.8	13.2
16	−	−	−	−	33.0	10.8	30.0	58.4	2.4
17	0	0	0	0	7.1	14.6	51.2	55.7	71.6
18	0	0	0	0	4.3	14.9	19.3	53.9	68.7
19	0	0	0	0	6.1	13.2	44.3	50.6	72.1

$$\begin{aligned} Y_1 = {} & 13.894 - 5.094X_1 - 2.869X_2 - 0.831X_3 \\ & - 5.456X_4 - 0.906X_1X_2 - 0.548X_1X_3 \\ & + 4.731X_1X_4 - 0.943X_2X_3 + 0.456X_2X_4 \\ & + 1.631X_3X_4 + 3.106X_1X_2X_3 + 0.306X_1X_2X_4 \\ & + 0.331X_1X_3X_4 + 0.631X_2X_3X_4 \\ & + 1.243X_1X_2X_3X_4 \end{aligned} \tag{5}$$

The significance of the linear coefficients and their interactions was checked though statistical analysis. It was proved that the most significant linear parameters ($p < 5\%$) were the ratio of ferrous sulfate heptahydrate concentration to hydrogen peroxide concentration (X_1), the hydraulic retention time (X_2), and the temperature (X_3). The minus (−) in the above equation indicates that an increase of the controlling parameter leads to a lower % TOC efficiency and, consequently, to a less effective oxidation. Oxidation process includes two different steps, which can be performed either sequential or in parallel. One step is the breaking down of complex organic substances to smaller molecules and the other one is the mineralization of organic compounds. TOC removal expresses the mineralization efficiency of the oxidation process. From equation 6, it can be concluded that high temperature (30˚C) leads to lower TOC removal. This fact may be due to hydrogen peroxide deactivation. This implies that temperature of 30˚C was not favorable for the mineralization step but it did not inhibit the whole oxidation process since elevated efficiencies for the rest of the examined parameters were achieved. The influence of the controlling parameter of pH alone was not significant. However, it was shown through statistical analysis that the interaction of pH with Fenton's reagents ratio and HRT, as well as that of reagent's ratio and temperature should be accounted for. Thus, the model was simplified to the following:

$$\begin{aligned} Y_1 = {} & 13.894 - 5.094X_1 - 2.869X_2 - 5.456X_4 \\ & + 4.731X_1X_4 + 3.106X_1X_2X_3 \end{aligned} \tag{6}$$

The adequacy of the mathematical model was checked by the Fisher criterion.

Adequacy of the simplified model: $F_{exp} = 16.2 > F_{tab} = 19.4$
where F_{exp} = the experimental value of the Fisher criterion and F_{tab} = the value of the Fisher criterion from the statistical tables.

As it is obvious, the simplified model is adequate and thus could be used for TOC removal prediction in the controlling parameters examined range.

In the experimental range studied, the higher % TOC efficiency measured was 33% in the experimental point (X_1, X_2, X_3, X_4) = (2/3, 1, 3.4, 20).

3.2. COD removal

The experimental results were analyzed as far as COD efficiency is concerned in the same way as described in Section 3.1. The following linear model was estimated, interrelating the % COD removal efficiency (Y_2) with the controlling parameters of the system:

$$\begin{aligned} Y_2 = {} & 21.000 + 4.886X_1 + 2.900X_2 - 1.975X_3 \\ & + 3.900X_4 - 1.312X_1X_2 - 3.313X_1X_3 \\ & + 0.236X_1X_4 + 0.450X_2X_3 - 1.300X_2X_4 \\ & + 1.500X_3X_4 - 1.188X_1X_2X_3 - 2.313X_1X_2X_4 \\ & + 0.238X_1X_3X_4 - 0.625X_2X_3X_4 \\ & - 1.113X_1X_2X_3X_4 \end{aligned} \tag{7}$$

The significance of the linear coefficients and their interactions was checked though statistical analysis. It was proved that only the interactions X_1X_4 and X_2X_3 were not statistically significant. Thus, the derived model is the following:

$$\begin{aligned} Y_2 = {} & 21.000 + 4.886X_1 + 2.900X_2 - 1.975X_3 \\ & + 3.900X_4 - 1.312X_1X_2 - 3.313X_1X_3 \\ & - 1.300X_2X_4 + 1.500X_3X_4 - 1.188X_1X_2X_3 \\ & - 2.313X_1X_2X_4 + 0.238X_1X_3X_4 - 0.625X_2X_3X_4 \\ & - 1.113X_1X_2X_3X_4 \end{aligned} \tag{8}$$

However, excess hydrogen peroxide interfered with the measurement of COD. The residual hydrogen peroxide could consume $K_2Cr_2O_7$, leading to the increase of COD [8]. This fact could seriously influence the experimental results and thus, the TOC removal model could better describe the oxidation process as far as organic pollutants are concerned.

3.3. TKN removal

The mathematical model describing the TKN removal (Y_3) is the following:

$$\begin{aligned} Y_3 = {} & 25.575 + 2.975X_1 + 0.587X_2 - 7.936X_3 \\ & + 2.975X_4 - 3.238X_1X_2 - 3.213X_1X_3 \\ & - 6.475X_1X_4 + 6.125X_2X_3 - 2.238X_2X_4 \\ & + 2.737X_3X_4 - 3.500X_1X_2X_3 + 1.688X_1X_2X_4 \\ & + 0.763X_1X_3X_4 + 0.325X_2X_3X_4 \\ & + 0.650X_1X_2X_3X_4 \end{aligned} \tag{9}$$

The analysis for the statistically significant linear coefficients and their interactions revealed that none of the coefficients was significant. This fact means that within the experimental range examined, the TKN removal fluctuates around 25.6% according to Eq. (9). At the center point run TKN removal was 38.2% ± 16.7%. The high standard error near 45% of the average should be pointed out. In trial, 12 (X_1, X_2, X_3, X_4) = (2/3, 1, 4.2, 30), TKN removal was −19.2%, which means that nitrogen concentration was not decreased but significantly increased. In the same trial, TOC, TP, and fats and oils efficiencies were 30.8, 44.1, and 15.5%, respectively. The high TOC and fats and oils removal imply that oxidation and mineralization of complex organic compounds took place. Their mineralization led to nitrogen and phosphorus release. Phosphorus was removed probably by precipitation (Section 3.4), while nitrogen dissolved in the reaction mixture without being further oxidized. This was only the case in trial 12, since in all other trials nitrogen was removed as well. According to Pignatello et al. [9], when the organic substrate contains heteroatoms, mineralization often leads to the formation of inorganic acids (HCl, HNO_3, NH_4^+, H_2SO_4, etc.). Nitrogen-containing compounds may form HNO_3 exclusively or a mixture of NH_4^+ and HNO_3. Redox interconversion of NH_4^+ and NO_3^- during HO-intiated reactions involve a number of intermediate steps and species (e.g., NH_2OH, $NH_2^{\cdot}$, NO·) whose importance is governed by pH and presence of electron, proton, or hydrogen donors or acceptors, and O_2 (Gonzalez et al., 2004).

3.4. TP removal

Phosphorous removal (Y_4) could be described according to the factorial experiment results analysis by the following mathematical model:

$$\begin{aligned} Y_4 = {} & 49.638 - 1.388X_1 - 0.713X_2 - 7.975X_3 \\ & + 0.1875X_4 - 0.013X_1X_2 - 2.700X_1X_3 \\ & - 0.113X_1X_4 + 2.650X_2X_3 - 0.413X_2X_4 \\ & - 0.350X_3X_4 - 0.200X_1X_2X_3 - 0.237X_1X_2X_4 \\ & + 0.950X_1X_3X_4 + 0.425X_2X_3X_4 \\ & + 0.750X_1X_2X_3X_4 \end{aligned} \tag{10}$$

The significance of the linear coefficients and their interactions was checked through statistical analysis. It was proven that the only significant linear parameters ($p < 5\%$) was the pH. Thus, the final simplified model is:

$$Y_4 = 49.638 - 7.975X_3 \tag{11}$$

From the equation above, it is obvious that phosphorus removal is favored under acidic conditions, since the lower the pH, the higher the TP removal. Generally phosphorus removal was high, reaching 63.4% at the experimental point (X_1, X_2, X_3, X_4) = (4/3, 1, 3.4, 30).

According to Pignatello et al. [9], Fenton and photo-Fenton oxidations of organic compounds are inhibited in varying degrees by phosphates, depending on their concentrations. Such anions may be present initially in the wastewater or formed as end products from the compounds undergoing degradation. Phosphate inhibition is mainly due to precipitation of iron. Iron(III) forms complexes with phosphate that are quite insoluble in neutral or mildly acidic solution. The latter is in accordance with the experimental results of this study since phosphorous removal is enhanced as pH decreases. Consequently, the high percentages of phosphorous removal should be considered as an inhibition factor for organic pollutants oxidation and should be seriously accounted for the whole process design.

3.5. Fats removal

According to the results of the factorial experiment and by following a specific analytical procedure [6,7], the following linear model was estimated, interrelating the fats removal (Y_5) with the controlling parameters of the system:

$$\begin{aligned} Y_5 = 18.219 &- 4.306X_1 + 0.169X_2 + 0.919X_3 \\ &+ 2.006X_4 + 6.694X_1X_2 + 3.956X_1X_3 \\ &- 10.169X_1X_4 + 0.656X_2X_3 - 7.693X_2X_4 \\ &- 4.231X_3X_4 + 4.781X_1X_2X_3 + 0.231X_1X_2X_4 \\ &+ 2.444X_1X_3X_4 - 2.106X_2X_3X_4 \\ &- 2.731X_1X_2X_3X_4 \end{aligned} \tag{12}$$

The significance of the linear coefficients and their interactions was checked through statistical analysis. Apart from hydraulic retention time, all other controlling parameters were statistically significant. The model was turned to the following:

$$\begin{aligned} Y_5 = 18.219 &- 4.306X_1 + 0.919X_3 + 2.006X_4 \\ &+ 6.694X_1X_2 + 3.956X_1X_3 - 10.169X_1X_4 \\ &- 7.693X_2X_4 - 4.231X_3X_4 + 4.781X_1X_2X_3 \\ &+ 2.444X_1X_3X_4 - 2.106X_2X_3X_4 \\ &- 2.731X_1X_2X_3X_4 \end{aligned} \tag{13}$$

Fats removal is improved as Fe/H_2O_2 ratio and pH decreases and as temperature increases. This fact is in accordance with literature, since fats are hydrolyzed under acidic conditions and high temperature.

In the experimental range studied, the highest % fats removal efficiency measured was 57.2% in the experimental point (X_1, X_2, X_3, X_4) = (2/3, 1, 3.4, 30). Nevertheless, at the center point run, fats removal reached $70.8 \pm 1.8\%$. This fact reveals that optimum conditions for fats oxidation are near the center point (X_1, X_2, X_3, X_4) = (3/3, 3, 3.8, 25). A factorial design with more narrow levels could reveal the real optimum. Further investigation should be conducted in this direction.

4. Conclusions

Cheese-dairy wastewater is a high-strength wastewater, containing high concentrations of lipids and fats. Subsequently, the need for the management of such wastewater becomes urgent because not only there are many cheese-dairy industries operating, producing large volumes of wastewater, but also their wastewaters are not amenable to conventional biological treatment.

Chemical oxidation is a method that has not been utilized for the treatment of this type of wastewater. In this study, whey, the most polluting fraction of cheese-dairy wastewater, was treated by a Fenton oxidation procedure in order either to break down the large molecules of fats or to mineralize organic pollutants. Mineralization efficiency measured as total organic carbon removal reached 33%. On the other hand, in some cases, the % fats removal efficiency was much higher, reaching 57%. Thus, the fenton oxidation step seems to meet its main goal: to break down complex chemical components, insoluble in water, into water soluble fragments. The optimum conditions achieved for the oxidation of whey were found to be in terms of % fats removal: ferrous sulfate to hydrogen peroxide ratio 2/3, hydraulic retention time 1 h, pH 3.4, and temperature 30˚C.

Conclusively, Fenton oxidation could be an effective method for the treatment of wastewater containing high concentrations of fats such as cheese-dairy wastewater and could also be used as a pretreatment stage for a biological treatment. The feasibility of the pretreatment method by its incorporation in an integrated plant could be the aim of a future work. Technical and economical aspects should be evaluated.

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