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Fenton-like application to pretreated cheese whey wastewater

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ABSTRACT

Cheese whey wastewater has been treated by the Fenton-like oxidation system after being pre-processed through a coagulation – flocculation stage with $FeCl_3$ or alternatively, through a sedimentation step with $Ca(OH)_2$ plus aerobic digestion. In the first case, Fenton-like oxidation is capable of reducing the initial COD (chemical oxygen demand) to 80% of the initial value, 20% of COD shows recalcitrance to chemical oxidation regardless of the operating conditions used. In the second case, the oxidation system is capable of removing almost the total COD present in the pretreated effluent. Given the lower values of initial COD, complete COD conversion is achieved at short reaction times within minutes depending on the initial reagent concentration. Removal of Fe(III) from the oxidation treatment can be achieved by $Ca(OH)_2$ addition. Sedimentation pH significantly affects the observed settling rate. Hence, neutral conditions lead to better results than slightly acidic pHs.

1. Introduction

Dairy factories constitute a major source of food wastewaters that have been increasingly associated to the rapid oxygen consumption, eutrophication phenomena, fats flotation, foam formation, salinization, acidification, odors liberation, presence of biogenic elements, organic and inorganic contamination when discharged uncontrollably into the environment. Frequently, cheese effluents (cheese whey, second cheese whey and cheese whey wastewater) have been defined as high strength wastewaters (Kargi and Uzunçar, 2012; Prazeres et al., 2012) with maximum values of biological and chemical oxygen demand (BOD and COD) of approximately 60 and 100 g L^{-1}, respectively.

Cheese whey wastewater (CWW) is constituted by different dilutions of cheese whey and/or second cheese whey with washing water that contains, generally, acidic and alkaline chemicals used in the washing process. The high value of organic matter (COD $\approx$ 77 g L^{-1} and BOD $\approx$ 16 g L^{-1}) of the cheese whey wastewater is caused by the lactose (0.18–45 g L^{-1}), protein (1.8–34 g L^{-1}) and fat (0.08–6 g L^{-1}) contents (see Fig. 1). From Fig. 1 can be concluded that the cheese whey wastewater characterization differs considerably. Accordingly, dairy effluents characteristics depend on the final products, system type and operation methods, wastewater management, climate and washing process used in the dairy factory (Gutiérrez et al., 1991; Pattnaik et al., 2007; Prazeres et al., 2013). The milk type used in the dairy production also assumes a leading role in the wastewater contamination level. It comprises water, fat matter, nitrogenous matter, mineral salts and lactose, etc. The milk nutritional content is characteristic and specific for each species. As a rule of thumb, sheep's milk has a higher content of fat, proteins and salts, followed by goat milk and cow milk.

Additionally, high concentrations of suspended solids, chloride and sodium have also been detected in the cheese whey wastewater composition, constituting a potential environmental risk. Thus, the appropriate treatment line to the cheese whey wastewater has become a difficult task.

Raw cheese whey wastewater has been treated by means of anaerobic digestion (Gutiérrez et al., 1991; Fang, 1991; Kalyuzhnyi et al., 1997; Gavala et al., 1999), aerobic digestion (Fang, 1991; Martins and Quinta-Ferreira, 2010; Martins et al., 2010; Rivas et al., 2010, 2011), coagulation – flocculation and basic precipitation (Rivas et al., 2010, 2011). Biological processes are very effective in the organic removal (usually, COD removal $\geq$90%), despite the difficulty of maintaining stable operation conditions. Additionally, chemical processes applied to raw cheese whey wastewater

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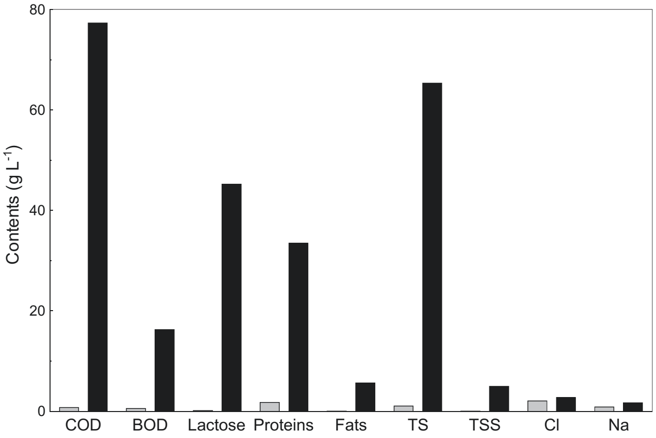

Fig. 1. Cheese whey wastewater characterization (gray color represents the minimum value and black color represents the maximum value). COD – Chemical oxygen demand; BOD – Biological oxygen demand; TS – Total Solids; TSS – Total suspended solids.

produce clarified effluents with low concentrations of suspended solids, turbidity and nutrients. Moreover, chemical processes can also reduce the organic matter to approximately half of the initial content.

Despite the considerable number of studies that can be identified dealing with the raw cheese whey wastewater treatment, the generated effluent is generally characterized by COD and BOD values exceeding the limit of direct discharge. As a consequence, different alternative treatment lines are claimed in order to allow the direct discharge or appropriate reuse. For these reasons, some authors use diluted cheese whey wastewater in anaerobic digestion (Gavala et al., 1999; Yang et al., 2003) or pretreat the CWW (to reduce the fats content) prior to the constructed wetland application by hybrid system (Comino et al., 2011). Another option for cheese whey wastewater management is the aerobic digestion of pretreated wastewater by coagulation – flocculation or precipitation (Rivas et al., 2010, 2011). However, these management mechanisms are still not sufficient to enable the effluent production according to Environmental European Legislation.

Advanced oxidation processes (AOPs) application after the chemical and/or biological processes can constitute a viable and promising alternative to eliminate this recalcitrant organic matter, principally, due to the hydroxyl radicals (HO•) formation. However, only a few studies have reported the cheese whey wastewater treatment by AOPs. In this context, Martins and Quinta-Ferreira (2010) tested some oxidation processes (O_3, O_3/H_2O_2, O_3/N-150 (Fe_2O_3-MnOx), O_3/Mn–Ce–O (70/30)) after aerobic digestion (activated sludge) of cheese whey wastewater. Unfortunately, only the following sequence: aerobic digestion (activated sludge) + (O_3/H_2O_2) provided an effluent with organic matter value below the environmental discharge limit.

Another oxidation technology that can also be used in a similar way is the Fenton process, defined as a mixture of ferrous/ferric iron (catalyst) and hydrogen peroxide (oxidizing agent) (Ortega-Gómez et al., 2012). Thus, the effluent obtained after the integrated combination of aerobic digestion (activated sludge) + Fenton process (Martins et al., 2010) presented a low COD value (0.02 g L^{-1}) and, simultaneously, a high organic matter removal was achieved in the oxidation stage (96–100%). Fenton process is an effective technology that depends on several operating variables, namely, matrix complexity, organic matter load and type, temperature, Fe^{2+}/Fe^{3+} concentration, H_2O_2 concentration, initial pH and reaction time (Rodríguez-Chueca et al., 2012).

Thus, integrated combination of different physicochemical, biological and oxidation stages must be considered to provide multiple options for cheese whey wastewater management, with the final goal of direct discharge or zero-water discharge systems implementation. The oxidation process with Fenton-like system after $FeCl_3$ coagulation–flocculation or after $Ca(OH)_2$ precipitation + aerobic digestion (activated sludge) of cheese whey wastewater has not been reported in literature. As a result, this study provides the first information about Fenton-like process as a post-treatment of pretreated cheese whey wastewater by the stages aforementioned. Hence, in this work, two main experimental series were completed. In the first one, raw CWW was firstly pretreated by $FeCl_3$ addition (9×10^{-4} M) with no pH change. Once the solid (mainly $Fe(OH)_3$) was settled down, the supernatant was oxidized in the presence of pre-calculated amounts of hydrogen peroxide and ferric chloride. In the second series, the effluent was pretreated by lime addition instead of $FeCl_3$. The supernatant was thereafter aerobically biodegraded and, finally, after solids separation, the effluent was again processed in the presence of the system H_2O_2/Fe(III).

2. Materials and methods

2.1. Raw and pretreated cheese whey wastewater

Raw cheese whey wastewater was obtained from a small “Serpa Cheese industry” located in the South of Portugal. The effluent is characterized by an elevated value of organic matter, monitored by COD (9.3–18.5 g L^{-1}) and BOD (6.9–12.9 g L^{-1}). Additionally, this effluent exhibits a whitish color with high values of total solids and turbidity in the ranges 5.7–15.1 g L^{-1} and 405–1386 NTU. Acid (3.28–4.78) and saline (7.13–10.91 dS m^{-1}) properties are commonly presented by raw cheese whey wastewater. This effluent is also rich in nutrients (g L^{-1}), such as potassium (0.228), phosphorus (0.103), calcium (0.117), magnesium (0.049), sodium (1.345) and chloride (2.706). A detailed description of the raw effluent can be found elsewhere (Rivas et al., 2010, 2011).

Prior to its use in Fenton-like process, $FeCl_3$ coagulation – flocculation and $Ca(OH)_2$ precipitation + aerobic digestion were applied to raw cheese whey wastewater at the optimal operating conditions. Pretreated cheese whey wastewater characterization is shown in Table 1. The COD value presented by the supernatant of the $FeCl_3$ coagulation–flocculation in the range 8.84–10.46 g L^{-1} implies that the generated effluent still constitutes a hazardous waste. Additionally, in spite of the high COD removal values (97–99%), when $Ca(OH)_2$ precipitation + aerobic digestion were used, the final effluent yet presented an inadmissible COD content, requiring a post-treatment.

2.2. Analytical procedures

Cheese whey wastewater was characterized and immediately frozen to avoid degradation by intrinsic biological community. Raw and pretreated cheese whey wastewater characterization was performed by determination of the principal contamination indicators. pH and redox potential were monitored in a WTW InoLab apparatus. Conductivity and turbidity were quantified in a Jenway 4510 pH meter and WTW Turb550 turbidimeter, respectively. COD, solids, ammonium and Kjeldahl nitrogen were determined by standards methods (APHA, 1998). BOD and chloride were analyzed by respirometric and Mohr methods, respectively. Phosphorus was evaluated from colorimetric method by the reaction of orthophosphates with vanadate-molybdate reagent (APHA, 1998) after calcination at 600 °C plus dry digestion. For oil and fats measurement the gravimetric method after Soxhlet extraction (Sawyer

Table 1
Characterization of the pretreated cheese whey wastewater by $FeCl_3$ coagulation − flocculation and $Ca(OH)_2$ precipitation + aerobic digestion.

Parameter	Units	$FeCl_3 - P_{treat}$[a]		$Ca(OH)_2$ + aerobic digestion − P_{treat}[b]	
		Interval	Average	Interval	Average
pH	–	4.19–4.20	4.20 ± 0.01	8.23–8.71	8.49 ± 0.14
Redox potential	mV	153.2–179.8	166.4 ± 13.3	48.7–77.6	61.1 ± 11.7
Conductivity	$dS\ m^{-1}$	14.58–14.88	14.73 ± 0.15	9.52–15.13	11.76 ± 2.44
COD	$g\ L^{-1}$	8.838–10.463	9.463 ± 0.875	0.188–0.574	0.328 ± 0.132
BOD_5 pH = 7.0	$g\ L^{-1}$	8.000–9.000	8.500 ± 0.500	0.300–0.600	0.414 ± 0.146
BOD_5/COD at pH = 7.0	–	0.76–1.02	0.91 ± 0.13	1.05–1.88	1.31 ± 0.31
Turbidity	NTU	225.8–648.8	482.6 ± 225.5	1.9–20.8	9.0 ± 6.5
Total solids	$g\ L^{-1}$	6.188–6.908	6.561 ± 0.361	–	–
Total suspended solids	$g\ L^{-1}$	0.320–0.908	0.577 ± 0.301	–	–
Chlorides	$g\ L^{-1}$	2.927–3.104	3.015 ± 0.089	–	–
Oil and fats	$g\ L^{-1}$	1.502–2.505	2.097 ± 0.527	–	–
Kjeldahl nitrogen	$g\ L^{-1}$	0.248–0.266	0.256 ± 0.009	–	–
Ammonium nitrogen	$g\ L^{-1}$	0.069–0.071	0.070 ± 0.0008	–	–
Phosphorus	$g\ L^{-1}$	0.0053–0.0068	0.0060 ± 0.0008	–	–
220 nm	cm^{-1}	0.293–0.489[c]	0.414 ± 0.106[c]	0.329–2.148[d]	0.799 ± 0.671[d]
254 nm	cm^{-1}	0.134–0.265[c]	0.217 ± 0.072[c]	0.130–0.540[d]	0.247 ± 0.136[d]
292 nm	cm^{-1}	0.083–0.191[c]	0.151 ± 0.059[c]	0.090–0.349[d]	0.174 ± 0.084[d]
386 nm	cm^{-1}	0.049–0.104[c]	0.086 ± 0.032[c]	0.034–0.123[d]	0.063 ± 0.031[d]
385 nm	cm^{-1}	0.049–0.104[c]	0.086 ± 0.032[c]	0.035–0.123[d]	0.063 ± 0.031[d]
410 nm	cm^{-1}	0.043–0.092[c]	0.075 ± 0.028[c]	0.024–0.104[d]	0.052 ± 0.027[d]

[a] Results after three replicates. (From Rivas et al., 2010).
[b] Results after seven sequences: $Ca(OH)_2$ precipitation + aerobic digestion.
[c] After 1:50 dilution with ultrapure water.
[d] After 1:3 dilution with ultrapure water.

et al., 1994) was used. The absorbance at 220 nm (low-molecular-weight compounds), 254 nm (aromatic and unsaturated compounds), 292 nm (aromatic amino acids and aliphatic volatile compounds with a conjugated chain), 385–386 nm (carbohydrates) and 410 nm (color) (APHA, 1998; Peuravuori et al., 2002; Pacheco and Peralta-Zamora, 2004; Rivas et al., 2005; Kasprzyk-Hordern et al., 2006) were measured in an Ultrospec 2100pro spectrophotometer. Hydrogen peroxide concentration was titrated in acid medium (H_2SO_4) with a standardized solution of sodium thiosulfate in the presence of potassium iodide, ammonium molybdate (catalyst) and starch as indicator (iodometric method).

2.3. *Reagents and experimental procedure*

Batch Fenton-like process experiments were carried out by using 1 L glass bottles with 300–500 mL cheese whey wastewater volume. A pH adjustment was performed using H_2SO_4 solution for the supernatant of the aerobic digestion before the application of Fenton-like process. The pre-calculated iron concentration and desired hydrogen peroxide volume were added to pretreated cheese whey wastewater. In a first approach, Fenton-like process series were operated at constant hydrogen peroxide concentration ≈ 0.20 M and different Fe(III) concentrations (0.010, 0.025, 0.050, 0.075 and 0.100 M) at initial pH = 4.22 (after $FeCl_3$ coagulation − flocculation stage) or at initial pH = 4.21 ± 0.03 (after $Ca(OH)_2$ precipitation + aerobic digestion). Following this procedure, the influence of H_2O_2 concentration was studied. Thus, Fenton-like process series were conducted at constant Fe(III) concentration = 0.050 M and different hydrogen peroxide concentrations in the range of 0.4–1.1 M.

All Fenton-like experiments were continuously stirred and performed at room temperatures (19.7 ± 2.3 °C after $FeCl_3$ coagulation − flocculation stage and 21.4 ± 1.3 °C after $Ca(OH)_2$ precipitation + aerobic digestion). Ferric chloride ($FeCl_3.6H_2O$) and hydrogen peroxide (33% V/V) used for the Fenton-like experiments were obtained from Sigma–Aldrich and used as received. To account for hydrogen peroxide COD contribution the equation proposed by Kang et al. (1999) given by: $C_{COD} = C_{CODm} - f\,C_{H2O2}$, where $f = 0.4706 - 4.06 \cdot 10^{-5}\ C_{H2O2}$ was used. In the previous expression C_{CODm} and C_{COD} stand for COD with and without considering hydrogen peroxide contribution, respectively, and C_{H2O2} is the measured hydrogen peroxide concentration. This equation was tested to be valid for H_2O_2 concentrations below 8 $g\ L^{-1}$.

Supplementary experiments were developed in order to find the iron sedimentation pH after the Fenton-like process. Sedimentation assays were completed in a normalized glass graduated cylinder.

3. Results and discussion

3.1. *Coagulation − flocculation with $FeCl_3$ + Fenton-like oxidation*

3.1.1. *Ferric iron concentration influence in the chemical oxidation process*

The first experimental series was conducted after application of the $FeCl_3$ coagulation − flocculation stage. This pretreatment was conducted under optimum conditions found in a previous paper (Rivas et al., 2010). Hence, 9×10^{-4} M of $FeCl_3$ were added to the raw CWW at the natural pH of the effluent (pH 4–5). After solids separation, the supernatant was treated by instantaneous addition of 0.2 M of hydrogen peroxide and variable amounts of Fe(III). Fig. 2 shows the results obtained for experiments conducted in the presence of 0.010, 0.025, 0.050, and 0.075 M of Fe(III). The experiment carried out with the lowest Fe(III) concentration led to a final COD conversion of roughly 80%. However, the process was extremely slow, necessitating more than one day to achieve this COD removal. From Fig. 2, a significant improvement of COD conversion is observed when increasing the initial Fe(III) concentration from 0.010 to 0.025 M. Initial Fe(III) concentrations above 0.025 M did not significantly improve the process efficiency in terms of final COD conversion, however, a slight higher H_2O_2 decomposition rate could be observed when increasing ferric iron load. Experimental data also suggest the existence of a COD fraction (around 20–30%) refractory to oxidation.

The mechanism developed in Fenton's chemistry can be summarized in the following reactions (rate constant units in mol, liter, and seconds):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\bullet} \quad k_{i2} = 76 \qquad (1)$$

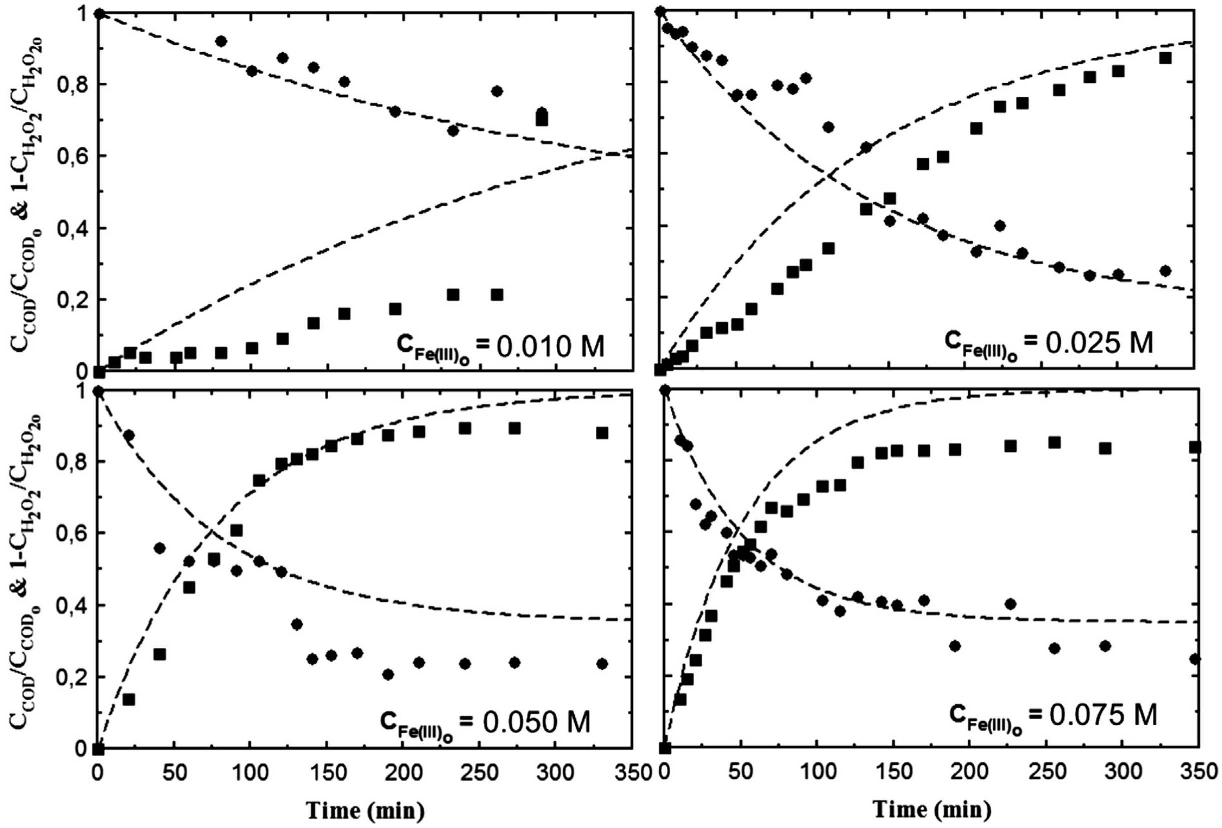

Fig. 2. Fenton-like oxidation of CWW pretreated with 9 × 10^{-4} M of $FeCl_3$. Experimental conditions: $T = 293$ K, $C_{H2O2o} = 0.2$ M, $C_{CODo} = 5.0$ g L^{-1} (average values before H_2O_2 addition). Symbols: ●, Normalized COD concentration; ■, H_2O_2 conversion. Dashed lines: model calculations.

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2^{\bullet} \quad k_{i3} = 10^{-3} - 10^{-2} \tag{2}$$

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \quad k_{p1} = 2.7 \times 10^7 \tag{3}$$

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + OH^- \quad k_{p2} = 4.3 \times 10^8 \tag{4}$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \quad k_{r1} = 10^4 \tag{5}$$

$$Fe^{2+} + HO_2^{\bullet} + H^+ \rightarrow Fe^{3+} + H_2O_2 \quad k_{01} = 1.2 \times 10^6 \tag{6}$$

$$Fe^{3+} + {}^{\bullet}O_2^- \rightarrow Fe^{2+} + O_2 \quad k_{r2} = 1.5 \times 10^8 \tag{7}$$

$$Fe^{2+} + {}^{\bullet}O_2^- + 2H^+ \rightarrow Fe^{3+} + H_2O_2 \quad k_{02} = 10^7 \tag{8}$$

$$HO_2^{\bullet} \rightarrow {}^{\bullet}O_2^- + H^+ \quad \mathrm{k_d} = 8 \times 10^5 \tag{9}$$

$${}^{\bullet}O_2^- + H^+ \rightarrow HO_2^{\bullet} \quad k_{dr} = 5 \times 10^{10} \tag{10}$$

$$COD + HO^{\bullet} \rightarrow Products \quad k_h = 10^8 - 10^{-10} \tag{11}$$

In order to simulate the process, the above set of reactions was considered in the application of the mass balance to a discontinuous batch reactor. The system of first order differential equations was numerically solved by fixing $k_{i3} = 1.5 \times 10^{-3}$ M^{-1} s^{-1} and $k_h = 10^9$ M^{-1} s^{-1}. Dashed lines in Fig. 2 show the theoretical profiles in terms of COD depletion and H_2O_2 conversion. As observed from the figure, with some exceptions in H_2O_2 profiles, the simple mechanism derived from reactions (1)–(11) could acceptably simulate the process under the operating conditions investigated. Analogously to experimental data, the model also predicts the accumulation of COD at the end of the process. However, unreacted COD can be the consequence of a H_2O_2 shortage. In an attempt to corroborate the existence of this recalcitrant fraction, a second series of experiments was conducted by assessing the influence of initial hydrogen peroxide concentration.

3.1.2. Hydrogen peroxide concentration influence in the chemical oxidation process

Additional experiments conducted in the presence of 0.42, 0.61, 0.77, 0.82 and 1.07 M in H_2O_2 initial concentrations were completed. Fig. 3 illustrates the results obtained in terms of total COD depletion (COD corresponding to CWW + remaining H_2O_2). Given the high H_2O_2 concentration used in this experimental series, corrected COD could not be calculated for all data points and expressions for determination of the hydrogen peroxide COD contribution were only used to approximate the final COD value corresponding to CWW. An attempt to experimentally obtain the ratio H_2O_2/COD in this effluent also failed for H_2O_2 concentrations above 8–10 g L^{-1}.

Fig. 3 shows a general trend characterized by an initial induction period followed by a fast COD depletion. However, these results are the consequence of H_2O_2 decomposition curves. Reliable final COD values could be obtained when hydrogen peroxide concentration was sufficiently low. In all cases, recalcitrant COD values constituted roughly 20–30% of the initial CWW organic load, corroborating the fraction of unreacted COD. Also, it should be highlighted that COD stationary values were achieved in a short period of time, undoubtedly due to the high H_2O_2 concentrations used.

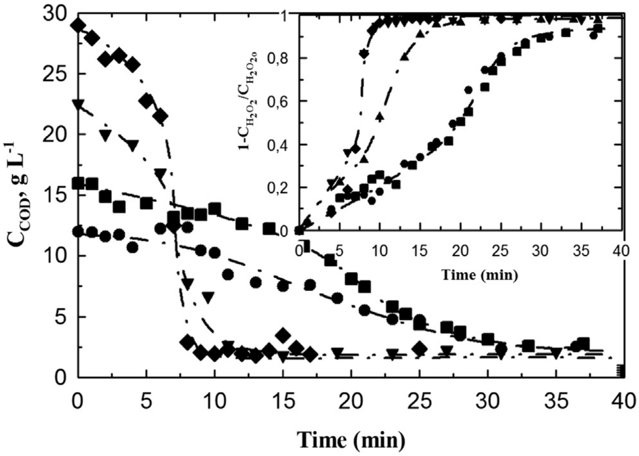

Fig. 3. Fenton-like oxidation of CWW pretreated with 9 × 10^{-4} M of $FeCl_3$. Experimental conditions: $T = 293$ K, $C_{Fe(III)o} = 0.050$ M. Symbols: •, $C_{H2O2o} = 0.42$ M; ■, $C_{H2O2o} = 0.61$ M; ▲, $C_{H2O2o} = 0.77$ M; ▼, $C_{H2O2o} = 0.82$ M; ◆, $C_{H2O2o} = 1.07$ M.

The influence of H_2O_2 concentration in this system could be theoretically obtained. Fig. 4 shows the results obtained (20% of recalcitrant COD has been considered). As observed, oxidizable COD removal is highly influenced by H_2O_2 concentration. Additionally, hydrogen peroxide conversions do follow an S-shape pattern (initial values above 0.4 M) increasing its rate when COD depletion comes to a halt. The latter results were also experimentally observed (see Fig. 3 inset).

3.2. Precipitation with $Ca(OH)_2$ + aerobic degradation + Fenton-like oxidation

As stated previously, the combination of a $FeCl_3$ coagulation – flocculation pre-stage plus oxidation by the system Fe(III)/H_2O_2 leads to residual COD values in the interval 1.100–1.300 g L^{-1} in the best of cases. This organic load is too high to consider direct disposal of treated CWW into natural water ecosystems or public sewage system. Accordingly, an additional aerobic biodegradation stage was contemplated before the final chemical oxidation. Simultaneously, based on previous studies (Rivas et al., 2011), the pretreatment with $FeCl_3$ was replaced by a pre-sedimentation stage with $Ca(OH)_2$.

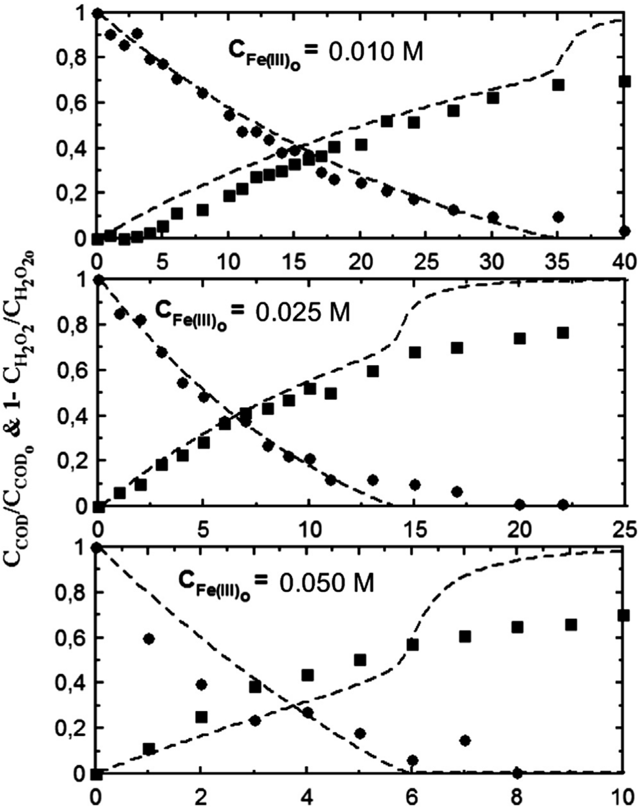

Fig. 5. Fenton-like oxidation of CWW pretreated with $Ca(OH)_2$ precipitation plus aerobic digestion. Experimental conditions: $T = 293$ K, $C_{H2O2o} = 0.2$ M, $C_{CODo} = 2.5$ g L^{-1} (average values before H_2O_2 addition). Symbols: •, Normalized COD concentration; ■, H_2O_2 conversion. Dashed lines: model calculations.

3.2.1. Ferric iron concentration influence in the chemical oxidation process

Fig. 5 displays the results obtained after Fenton-like application to the supernatant obtained from the aerobic digestion step (activated sludge). As observed, the effluent was more easily oxidized by the system Fe(III)/H_2O_2 due to the lower initial organic load, and likely, due to the removal of recalcitrant compounds in the previous aerobic digestion. Hence, COD effluent is lowered below the detection limit in few minutes when Fe(III) concentrations used are in the interval 0.010–0.075 M. Again the reaction mechanism represented by equations (1)–(11) was capable of acceptably

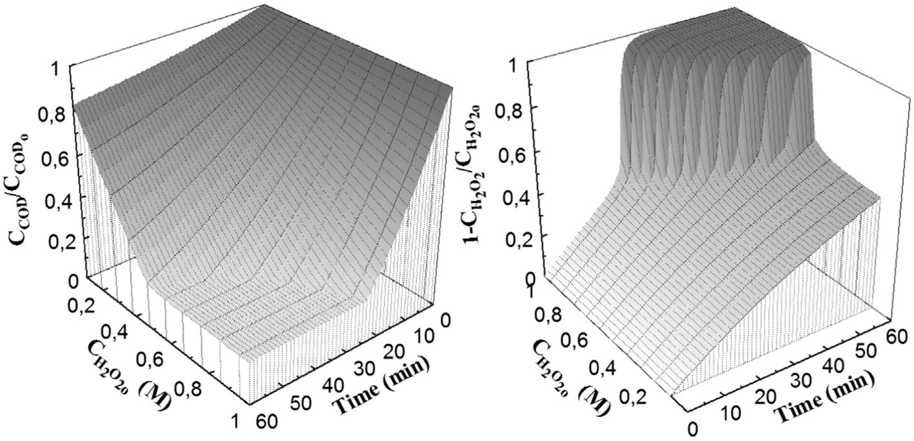

Fig. 4. Fenton-like oxidation of CWW pretreated with 9 × 10^{-4} M of $FeCl_3$. Experimental conditions: $T = 293$ K, $C_{Fe(III)o} = 0.050$ M. Theoretical COD removal and H_2O_2 conversion as a function of initial hydrogen peroxide concentration.

simulating the process, however, in this experimental series, the value of k_{i3} that best fitted the data was one order of magnitude higher ($k_{i3} = 1.5 \times 10^{-2}\ \mathrm{M^{-1}\ s^{-1}}$) than the value previously used. This is not unusual since the rate constants of the initiation reactions in Fenton's chemistry highly depend on the chelating agents present in the media, i.e., the complex formed by Fe(II) and Fe(III) (Rivas et al., 2001). In general, COD profiles are well simulated although the model predicts a fast hydrogen peroxide conversion when COD has disappeared. The latter fact is not experimentally observed. Some minor discrepancies between real COD of the effluent and calculations in corrected COD should not be ruled out.

3.2.2. Hydrogen peroxide concentration influence in the chemical oxidation process

Although the hydrogen peroxide concentration of 0.2 M leads to acceptable results in terms of COD conversion and depletion rate, to complete this study a new experimental series was carried out by increasing this concentration in the range 0.37–1.13 M Fig. 6 shows the results in terms of total COD degradation profiles.

As expected, increasing values of initial H_2O_2 concentration led to faster decomposition rates and COD removals. Hence, the highest H_2O_2 concentration tested reduced the COD levels below the detection limit in just 4 min. Moreover, peroxide conversion also approached values close to 100% in just 5–6 min.

3.3. Removal of Fe(III) after Fenton-like oxidation. $Ca(OH)_2$ addition

Final disposal of treated CWW needs pH adjustment and Fe(III) elimination. Accordingly, different amounts of $Ca(OH)_2$ were added to processed CWW to achieve a final pH in the interval 4.5–7.5. Once the solid was formed, the settling properties of the formed sludge were evaluated. Fig. 7 shows the solid–water interface decrease as a function of time corresponding to effluents treated with different amounts of Fe(III).

From this figure two main conclusions can be withdrawn. Hence, the amount of Fe(III) used in the oxidation process significantly influences the settling ratio of the generated sludge. Logically, the higher the solid concentration, the lower the sedimentation rate. This also affects the sludge volumetric index found at large times. Additionally, pH also exerts a significant effect in the sedimentation process. In experiments carried out with the lowest Fe(III) concentration, the final volume occupied by the sludge is similar regardless of the media pH, however the sedimentation rate is higher as the pH is increased. In experiments with the highest Fe(III) concentration, both the sedimentation rate and sludge volumetric index are improved under less acidic conditions.

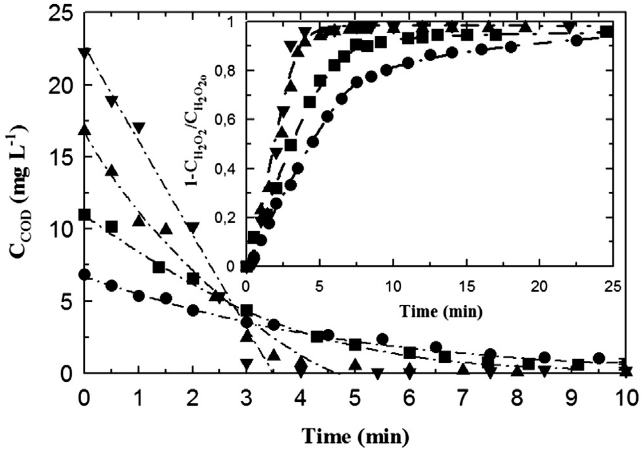

Fig. 6. Fenton-like oxidation of CWW pretreated with $Ca(OH)_2$ precipitation plus aerobic digestion. Experimental conditions: $T = 293$ K, $C_{Fe(III)o} = 0.050$ M. Symbols: ●, $C_{H2O2o} = 0.37$ M; ■, $C_{H2O2o} = 0.52$ M; ▲, $C_{H2O2o} = 0.82$ M; ▼, $C_{H2O2o} = 1.13$ M.

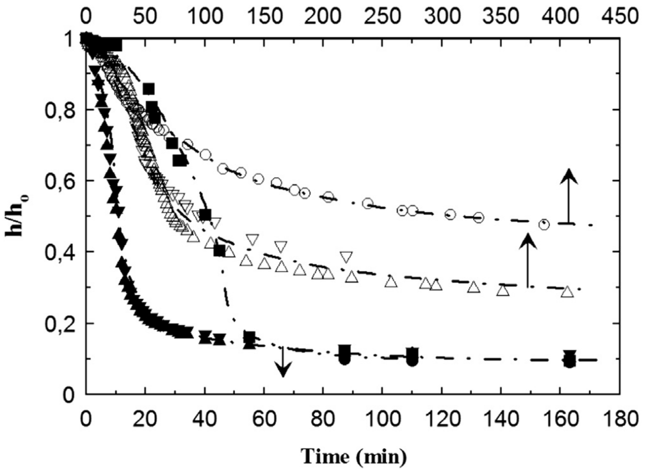

Fig. 7. Settling properties of sludge from Fenton-like treated CWW. Solids symbols correspond to $C_{H2O2o} = 0.2$ M + 0.010 M of Fe(III), open symbols correspond to $C_{H2O2o} = 0.2$ M + 0.050 M of Fe(III). Precipitation pH after $Ca(OH)_2$ addition: ●, 4.5; ■, 5.5; ▲, 6.5; ▼, 7.5.

4. Conclusions

From the results found in this study the following conclusions are withdrawn:

- $FeCl_3$ pretreated CWW can be oxidized by means of the Fenton-like system H_2O_2/Fe(III) reducing the organic load up to 80% of its initial value. However, the remaining recalcitrant COD is above the limit for direct discharge.
- If raw CWW is pretreated by $Ca(OH)_2$ precipitation plus aerobic digestion, the final oxidation system is capable of almost removing the total COD content of the effluent, rendering a relatively clean wastewater suitable for other uses.
- Fe(III) removal after the oxidation stage can be conducted by $Ca(OH)_2$ addition to form $Fe(OH)_3$. Good settling properties are obtained when increasing the precipitation pH from 4.5 to 7.5.

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