Treatment of Cheese Whey Wastewater: Combined Coagulation–Flocculation and Aerobic Biodegradation

JAVIER RIVAS,*,[†] ANA R. PRAZERES,[‡] FATIMA CARVALHO,[‡] AND FERNANDO BELTRÁN[†]

[†]Departamento de Ingeniería Química y Química Física, Facultad de Ciencias, Avenida de Elvas s/n, 06071 Badajoz, Spain, and [‡]Escola Superior Agrária de Beja, Rua Pedro Soares, 7801-902 Beja, Portugal

Cheese wastewater has been treated by means of a coagulation–flocculation process. Three different coagulants have been used, namely, $FeSO_4$, $Al_2(SO_4)_3$, and $FeCl_3$. When $FeSO_4$ was used, the optimum conditions were obtained using 250 ppm of the salt at pH 8.5. At these conditions, 50 and 60% of chemical oxygen demand (COD) and biological oxygen demand (BOD) were reduced, respectively. $Al_2(SO_4)_3$ achieved slightly lower reductions of COD and BOD; however, the amount needed was significantly higher (1000 ppm). When $FeCl_3$ was added, similar results to those obtained with $FeSO_4$ were experienced; again, 250 ppm was enough to eliminate COD and BOD contents in the range of 40–60%, depending upon operating conditions. The sludge formed in the coagulation–flocculation process did show acceptable settling properties, which is crucial in settling tank design. A first approach to sedimentation tank design is also conducted on the basis of experimental results. The aerobic biodegradation of cheese whey wastewater achieves the reduction of the main contaminant indicators (COD and BOD) to values close to 100%; however, effluents coming from the coagulation–flocculation pre-stage necessitate half of the time required by the non-pretreated raw wastewater.

KEYWORDS: Cheese whey wastewater; coagulation–flocculation; dairy effluents; sedimentation; aerobic biodegradation

INTRODUCTION

The dairy industry involves the processing and manufacturing of raw milk into products such as yogurt, butter, cheese, etc. by means of different processes (pasteurization, chilling, etc.).

The dairy industry is the source of a significant amount of wastewater characterized by a relatively high organic load. Thus, a typical dairy agro-industry generates around 500 m³ of wastes per day on average (*1*). Key parameters of dairy effluents show a biological oxygen demand (BOD) of 0.8−2.5 kg/metric ton of milk, a chemical oxygen demand (COD) of around 1.5 times the BOD, $10^2 - 10^3$ ppm of total suspended solids (TSS), etc. Specific milk constituents contribute to contamination in the following way: 1 kg of milk fat = 3 kg of COD, 1 kg of lactose = 1.13 kg of COD, and 1 kg protein = 1.36 kg of COD.

Properties and characterization of dairy effluents depend upon the type of product manufactured, season, methodology of production, plant size, extent of pipelines, equipment washing, etc.

Cheese whey (CW) and secondary cheese whey (SCW) are characterized by a high nutritional content (lactose, soluble proteins, fats, etc.) and other components such as citric acid, lactic acid, vitamins, etc. Cheese whey wastewater (CWW) is composed of CW, SCW, and washing water. This effluent is normally treated by biological processes (*2*), in either anaerobic (*2−10*) or aerobic (*2*, *11*, *12*) conditions. Nevertheless, some drawbacks can be enumerated. For instance, when aerobic processes are applied, high dilution ratios and hydraulic retention times are required.

The uncertainty in achieving stabilized operational conditions as a result of variations in CWW composition, flow rate, or a high content in lactose might dissuade the use of aerobic biotreatment in small−medium cheese manufacturing industries (*2*, *13*, *14*). Additionally, anaerobic operational conditions exhibit the problem of sludge floatation because of the presence of fat (*15*) and the potential washout of active microbial biomass (*2*). Moreover, caseine necessitates specific microorganisms for its degradation and is not normally applied to small−medium plants.

As a consequence, alternative/complementary combinations of physical−chemical−biological processes are needed for the adequate treatment of CWW. Thus, the combination of coagulation−flocculation and aerobic biotreatment might substantially reduce the hydraulic retention time of the latter process. Hence, this work is focused on investigating the efficiency of a pretreatment coagulation−flocculation stage under different operating conditions, keeping in mind a final biological polishing step implemented in a posterior stage.

MATERIALS AND METHODS

CWW. CWW was collected from a small industry located in the Alentejo region of Portugal. This small plant produces the so-called "Serpa cheese" typical from this area in the south of Portugal. Wastewater was characterized and immediately frozen to avoid biological activity. The main properties of this effluent are displayed in **Table 1**. The relatively low pH and high salinity of the effluent are the consequence of the type of whey produced in this industry ("acid" whey) and NaCl addition during cheese production. The low lactose and protein content results for the absence of oxygen in the aeration lagoon of the cheese plant. Thus, lactose is converted to lactic acid, and caseine is precipitated because of the acidic

*To whom correspondence should be addressed. Telephone: 0034-924-289300-6951. Fax: 0034-924-289385. E-mail: fjrivas@unex.es.

Table 1. Characterization of Wastewater from the Production of "Serpa Cheese"[a]

parameter	units	interval	average value
pH		4.01–4.55	4.23 ± 0.11
redox potential	mV	−436.5–148.6	5.8 ± 169.1
temperature	°C	10–15	12 ± 1
conductivity	mS cm^{-1}	11.25–13.47	12.39 ± 1.11
COD	mg of O$_2$ L^{-1}	8838–25583	13494 ± 4270
BOD$_5$ at pH 7.0	mg of O$_2$ L^{-1}	10000–12500	11686 ± 962
BOD$_5$ at non-modified pH	mg of O$_2$ L^{-1}	2350–8400	6342 ± 2351
BOD$_{20}$ at non-modified pH	mg of O$_2$ L^{-1}	1200–12400	9520 ± 4692
BOD$_5$/COD at pH 7.0		0.79–1.17	1.05 ± 0.16
BOD$_5$/COD at non-modified pH		0.31–0.41	0.38 ± 0.05
turbidity	NTU	1331–2004	1557 ± 219
total solids	mg L^{-1}	7016–8348	7910 ± 613
total suspended solids	mg L^{-1}	1628–4780	3317 ± 1269
total dissolved solids	mg L^{-1}	4256–4850	4729 ± 264
chloride	mg L^{-1}	2119–2838	2501 ± 248
oil and fat (soluble in petroleum ether)	mg L^{-1}	1830–3758	2489 ± 711
Kjeldahl nitrogen	mg L^{-1} N–Kj	309.9–355.5	323.7 ± 18.4
ammonium nitrogen	mg L^{-1} N–NH$_3$	51.9–70.5	62.9 ± 7.3
phosphorus	mg of P L^{-1}	6.6–7.2	6.9 ± 0.3
total proteins	μg L^{-1}	938–947	943 ± 6
lactose	mg L^{-1}	178–182	180 ± 3
absorbance at 220 nm	1:50 dilution	0.609–0.878	0.736 ± 0.105
absorbance at 254 nm	1:50 dilution	0.324–0.470	0.370 ± 0.045
absorbance at 292 nm	1:50 dilution	0.248–0.359	0.285 ± 0.035
absorbance at 386 nm	1:50 dilution	0.162–0.207	0.186 ± 0.011
absorbance at 385 nm	1:50 dilution	0.156–0.207	0.172 ± 0.016
absorbance at 410 nm	1:50 dilution	0.142–0.190	0.158 ± 0.016

[a] Number of measurements: 34 for pH, 26 for COD, 16 for absorbance and turbidity, and 7 for the rest of the parameters.

conditions in the lagoon (*16*). Thus, the strong odor of the effluent is the result of the butyric acid formation from caseine decomposition and lactose degradation. Finally, the BOD/COD ratio of the effluent at pH 7 close to the maximum value of 1 indicates the biodegradability of the effluent if enough time is applied to the biotreatment.

Analytical Procedures. COD was monitored by the absorbance of the sample after dichromate digestion at 150 °C for 2 h in the presence of silver and mercury sulfates (*17*). BOD was obtained by a respirometric method (WTW OxiTop) under controlled conditions of temperature, agitation, and light absence. Microorganisms were taken from a municipal wastewater treatment plant. Turbidity was measured by a WTW Turb550 turbidimeter. Solids were analyzed after filtration of a determined volume of sample. TSS were obtained from the residue in the filtration paper (Whatman 934-AH), while total dissolved solids were calculated after evaporation of the filtrate (*17*). Both pH and redox potential were monitored in a WTW InoLab apparatus (pH electrode SenTix 41 and redox electrode SenTix RP). Conductivity was obtained in a Jenway 4510 conductivity meter. Total phosphorus was quantified by the absorbance of the sample after the reaction of orthophosphates and a solution of vanadate–molibdate (*18*). Oil and fat were determined after extraction by means of a Sohxlet apparatus, using petroleum ether as the extracting agent (*19*). Chlorides were titrated with silver nitrate in the presence of potassium chromate. Lactose was analyzed by means of the Tell reagent (*20*). Total proteins were monitored by Lowry's method. This method is based on the blue coloration of a complex formed in the reaction of Folin's reagent and proteins in alkaline conditions and in the presence of copper as a catalyst. Ammonium and Kjedahl nitrogen were quantified by following the standard methods (*17*). Absorbance at different wavelengths was measured in a Ultrospec 2100pro spectrophotometer. Wavelengths used are indicative of low-molecular-weight compounds (220 nm), aromatic and unsaturated compounds (254 nm), aromatic amino acids and aliphatic volatile compounds with a conjugated chain (292 nm), carbohydrates (385–386 nm), and color (410 nm) (*21–24*).

Reagents and Procedure. Coagulation–flocculation experiments were carried out in a jar test apparatus (Olabo ISCO) equipped with six speed regulated stirrers. Runs were completed in 0.4 L beakers under initial
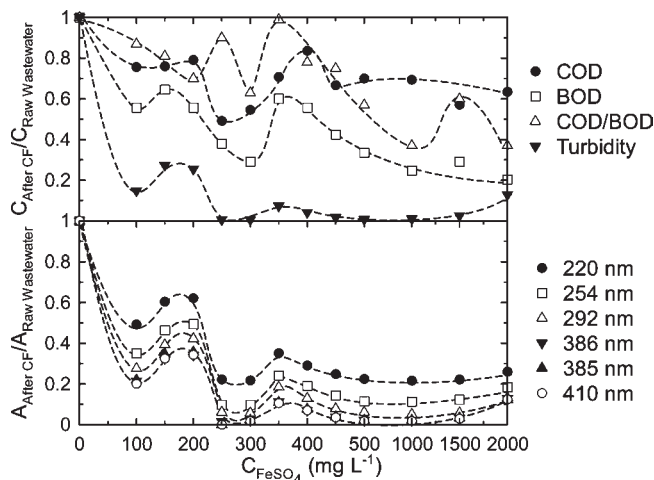

Figure 1. Coagulation–flocculation of wastewater from the production of "Serpa cheese". Effect of the FeSO$_4$ dose. (Bottom) Absorbance values after 1:50 dilution.

fast agitation (150 rpm) for 2 min and further slow agitation (20 rpm) for 20 min.

Sedimentability tests were conducted in a normalized 1 L glass probet at 34 cm high. Some runs were also conducted in a 13 L column (150 cm high and 10 cm in diameter) equipped with several sampling ports located at different positions in the column.

Activated sludge aerobic biodegradation experiments (10–12 °C at pH 7) were conducted in batch mode. The biological reactor was a 2.0 L glass recipient, continuously oxygenated by an air flow stream (40 L/h). The gaseous stream was capable of maintaining the solution well-agitated, although magnetical stirring was used to ensure the homogeneity of suspended solids. Microorganisms were taken from an activated sludge municipal wastewater plant and used after 2 days of acclimation to raw CWW.

Ferric chloride, ferrous sulfate, and aluminum sulfate were obtained from Sigma-Aldrich and used as received.

RESULTS AND DISCUSSION

Ferrous Sulfate Addition. Ferrous sulfate is a common coagulant used in wastewater treatment plants. The action of FeSO$_4$ is based on the formation of ferric hydroxides according to

$$FeSO_4 + Ca(OH)_2 \rightleftarrows Fe(OH)_2 + CaSO_4 \quad (1)$$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightleftarrows 4Fe(OH)_3 \quad (2)$$
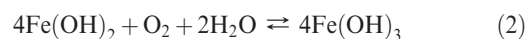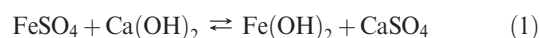
High pH (above 8.5) can be achieved by NaOH or Ca(OH)$_2$ addition; for economic reasons, the latter was used in this work.

A first squence of coagulation–flocculation experiments was conducted using different amounts of ferrous sulfate at pH 8.5. This pH value was initially used on the basis of bibliographic recommendations (*25*). **Figure 1** shows the main results obtained in terms of the removal percentage for some of the main global parameters measured (COD, BOD, turbidity, biodegradability, etc.). As inferred from this figure, it seems that an optimum in iron sulfate concentration does exist in the interval 250–325 ppm. Hence, maximum COD removals in the proximity of 50% were achieved when 250 ppm of FeSO$_4$ was used. These conditions also induced a significant decrease in BOD (60%), while the ratio BOD/COD was kept close to 0.9; i.e., the effluent can still be considered suitable for a final biodegradation stage. Turbidity was almost depleted to zero (TSS were reduced from ≈2500 to ≈100 ppm), similar to the absorbances in the ultraviolet (UV) and visible regions.

Once the optimum dose of coagulant was obtained, a second succession of experiments was conducted by varying the initial
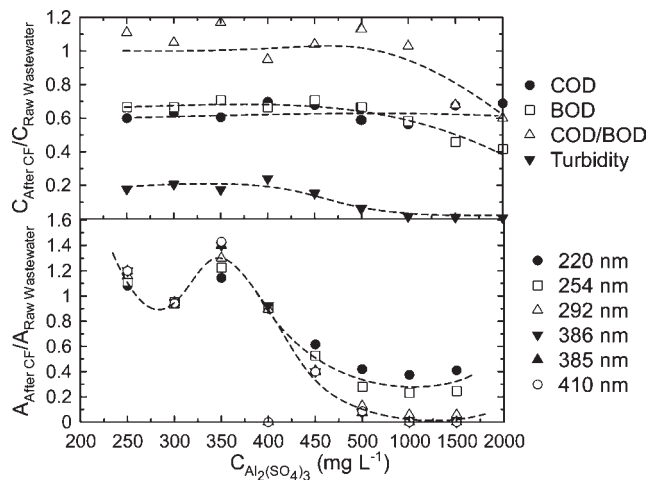
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Figure 2. Coagulation—flocculation of wastewater from the production of "Serpa cheese". Effect of the $Al_2(SO_4)_3$ dose. (Bottom) Absorbance values after 1:50 dilution.

Figure 3. Coagulation—flocculation of wastewater from the production of "Serpa cheese" by $FeCl_3$ (250 ppm). Effect of the pH adjustement. (Bottom) Absorbance values after 1:50 dilution.

pH of the raw wastewater previous to the coagulation—flocculation process. The pH interval was studied between 8.5 and 12.5. The results obtained (not shown) did not appreciably differ in the range of pH values investigated, averaging 45 and 55% of COD and BOD removals, respectively. As a consequence, pH 8.5 and 250 ppm of $FeSO_4$ were considered as the best conditions used in this work, in terms of both organic load removal and possibilities for the application of a post-biological treatment.

Aluminum Sulfate Addition. Aluminum sulfate is the most commonly used coagulant in water treatment. It is an effective coagulant for pH values ranging from 5.5 to 8.0 and can be applied as a solid or liquid. The action of aluminum sulfate comes from the following reactions:
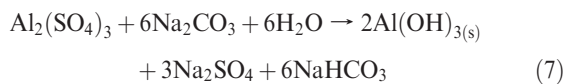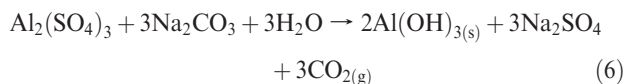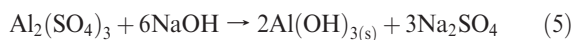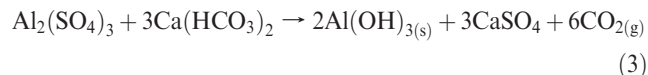
$$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \rightarrow 2Al(OH)_{3(s)} + 3CaSO_4 + 6CO_{2(g)} \quad (3)$$

$$Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_{3(s)} + 3CaSO_4 \quad (4)$$

$$Al_2(SO_4)_3 + 6NaOH \rightarrow 2Al(OH)_{3(s)} + 3Na_2SO_4 \quad (5)$$

$$Al_2(SO_4)_3 + 3Na_2CO_3 + 3H_2O \rightarrow 2Al(OH)_{3(s)} + 3Na_2SO_4 + 3CO_{2(g)} \quad (6)$$

$$Al_2(SO_4)_3 + 6Na_2CO_3 + 6H_2O \rightarrow 2Al(OH)_{3(s)} + 3Na_2SO_4 + 6NaHCO_3 \quad (7)$$

Figure 2 shows the results obtained when $Al_2(SO_4)_3$ was used as a coagulant agent at pH 7.0. As observed, the coagulant dose did not significantly affect the process efficiency. Average COD depletion was in the proximity of 40%, regardless of the amount of aluminum sulfate added. Similar results were obtained when BOD was measured, although a slight increase in BOD depletion was experienced when the highest coagulant doses were used. On the basis of absorbance and turbidity removals, the best conditions used in this work were obtained when adding around 1000 ppm of $Al_2(SO_4)_3$. Again, varying the initial pH of the sedimentation process in the interval of 6.8—7.2 did not exert any appreciable influence on the process efficacy.

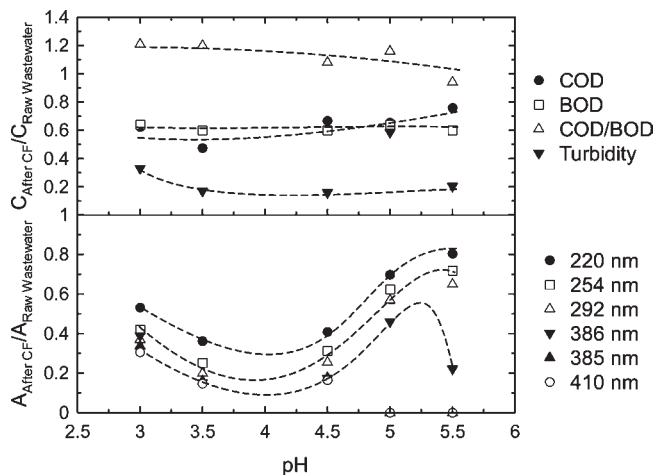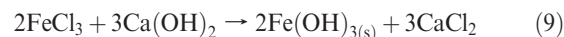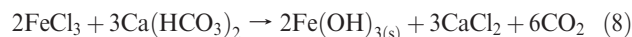**Ferric Chloride Addition.** Finally, $FeCl_3$ was tested in the coagulation—flocculation treatment of CWW. Initially, the waste-water pH was not modified and was kept at the natural value (pH 4.4) found in the lagoon.

Reactions associated with ferric chloride addition are

$$2FeCl_3 + 3Ca(HCO_3)_2 \rightarrow 2Fe(OH)_{3(s)} + 3CaCl_2 + 6CO_2 \quad (8)$$

$$2FeCl_3 + 3Ca(OH)_2 \rightarrow 2Fe(OH)_{3(s)} + 3CaCl_2 \quad (9)$$

$$FeCl_3 + 3NaOH \rightarrow Fe(OH)_{3(s)} + 3NaCl \quad (10)$$

Results obtained in this work at different pH values are displayed in **Figure 3**. The effect of the coagulant dose (results not shown) revealed a negligible effect of the coagulant dose (in the range of 250—1000 ppm) when COD was analyzed (a slight improvement was observed when 250 ppm of $FeCl_3$ was added, although this enhancement was not statistically significant). The pH effect was not remarkable with the exception of absorbance depletion profiles. It seems that the unmodified water pH is the best option to carry out the process.

From **Figures 1—3**, it is inferred that the three coagulants behave similarly; i.e., similar organic load removals (in terms of COD) are obtained. However, use of aluminum implies a higher coagulant dose to obtain the same results achieved when applying iron-based salts. **Table 2** shows the quality of the supernatant in replication experiments conducted under the best conditions found in this work. Runs were conducted in triplicate.

Sludge Sedimentability. Another important aspect to deal with in coagulation—flocculation processes is the settling properties of the sludge. **Figure 4** illustrates the sedimentation curves obtained after sludge formation by the addition of ferrous sulfate (left) and aluminum sulfate (right). In both cases, the sedimentation process could be catalogued as zone-settling type. From **Figure 4**, a higher sedimentation rate of iron hydroxide flocs is observed if compared to aluminum hydroxide flocs. When the $FeCl_3$ coagulant was used, the sedimentation was flocculent; the profiles of solid concentration—time for different heights in a cylindrical column (30 cm diameter × 150 cm height) are shown in **Figure 5**. As seen from this figure, solids at the top of the column are continuously removed throughout the whole process. The time taken to achieve complete clarification diminishes as the column zone becomes closer to the top. In contrast, solids start to accumulate in those zones located at the column bottom until a maximum in concentration is achieved; thereafter, the sedimentation velocity is faster than the accumulation rate.

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Table 2. Characterization of the Supernatant after Coagulation−Flocculation of Wastewater from the Production of "Serpa Cheese"[a]

	FeSO4		Al2(SO4)3		FeCl3		raw wastewater	
	interval	average	interval	average	interval	average	interval	average
pH	6.96−7.01	6.99 ± 0.03	6.30−6.38	6.33 ± 0.04	4.19−4.20	4.20 ± 0.01	4.24−4.27	4.25 ± 0.02
redox potential (mV)	from −486.7 to −30.7	−304.0 ± 178.2	54.0−73.2	60.7 ± 10.9	153.2−179.8	166.4 ± 13.3		86.0
conductivity (mS cm−1)	16.70−17.18	16.94 ± 0.24	16.92−17.34	17.14 ± 0.21	14.58−14.88	14.73 ± 0.15		13.47
COD (mg of O2/L)	7713−8088	7942 ± 201	8213−10025	9046 ± 915	8838−10463	9463 ± 875	13588−14213	13900 ± 442
BOD5 at pH 7.0 (mg of O2 L−1)	2500−5500	3667 ± 1607	6500−7500	7000 ± 500	8000−9000	8500 ± 500		11000
BOD/COD at pH 7.0	0.32−0.69	0.46 ± 0.20	0.70−0.84	0.78 ± 0.07	0.76−1.02	0.91 ± 0.13		0.79
turbidity (NTU)	4.5−140.1	55.4 ± 73.8	61.0−78.5	72.0 ± 9.6	225.8−648.8	482.6 ± 225.5		1714.7
total solids (mg L−1)	9520−9728	9635 ± 106	9756−9864	9823 ± 58	6188−6908	6561 ± 361	8204−8348	8283 ± 73
total suspended solids (mg L−1)	108−200	163 ± 48	204−220	212 ± 8	320−908	577 ± 301	1973−2520	2324 ± 305
total dissolved solids (mg L−1)	8264−8848	8504 ± 306	8528−8564	8549 ± 19	5220−5372	5312 ± 81	4840−4850	4847 ± 6
chlorides (mg L−1)	2128.5−217.2	2187.6 ± 51.2	2217.2−2305.8	2246.7 ± 51.2	2926.7−3104.0	3015.3 ± 88.7	2571.9−2838.0	2690.2 ± 135.5
oil and fat (mg L−1)	0−86	55 ± 48	694−900	773 ± 111	1502−2505	2097 ± 527	1830−2162	1987 ± 167
Kjeldahl nitrogen (mg L−1)	175.7−185.4	180.3 ± 4.8	170.1−181.2	177.1 ± 6.0	247.6−265.6	255.9 ± 9.1	309.9−320.9	314.5 ± 5.8
ammonium nitrogen (mg L−1)	71.9−76.1	73.8 ± 2.1	66.4−66.4	66.4 ± 0.0	69.2−70.5	69.6 ± 0.8	68.5−70.5	69.4 ± 1.0
phosphorus (mg L−1)	0.5−1.1	0.8 ± 0.3	1.3−1.7	1.6 ± 0.3	5.3−6.8	6.0 ± 0.8	6.7−7.2	7.0 ± 0.2
total proteins (μg L−1)	378−487	436 ± 55	246−660	427 ± 212	778−960	883 ± 94	938−947	943 ± 6
lactose (mg L−1)	83−101	93 ± 9	79−83	82 ± 2	225−273	253 ± 25	178−182	180 ± 3
absorbance at 220 nm	0.147−0.183	0.162 ± 0.019	0.192−0.197	0.194 ± 0.003	0.293−0.489	0.414 ± 0.106		0.642
absorbance at 254 nm	0.046−0.080	0.061 ± 0.017	0.070−0.075	0.072 ± 0.003	0.134−0.265	0.217 ± 0.072		0.368
absorbance at 292 nm	0.016−0.046	0.029 ± 0.016	0.039−0.041	0.040 ± 0.001	0.083−0.191	0.151 ± 0.059		0.280
absorbance at 386 nm	0.020−0.043	0.030 ± 0.012	0.030−0.033	0.032 ± 0.002	0.049−0.104	0.086 ± 0.032		0.179
absorbance at 385 nm	0.020−0.046	0.030 ± 0.014	0.031−0.032	0.031 ± 0.001	0.049−0.104	0.086 ± 0.032		0.181
absorbance at 410 nm	0.017−0.037	0.025 ± 0.011	0.027−0.028	0.027 ± 0.001	0.043−0.092	0.075 ± 0.028		0.164

[a] Results after three replicates.

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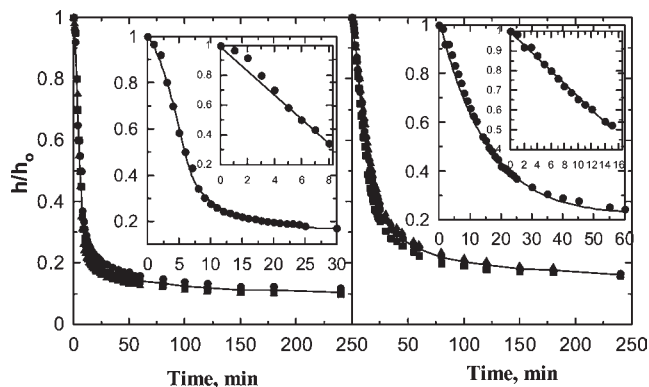*J. Agric. Food Chem.*, Vol. 58, No. 13, 2010 **7875**

Figure 4. Coagulation–flocculation of wastewater from the production of "Serpa cheese". Solids sedimentation velocity. (Left) $FeSO_4$ (250 ppm). (Right) $Al_2(SO_4)_3$ (1000 ppm).

Table 3 shows the main characteristics of the sludge obtained. As expected, given the differences between the doses added, the volume of sludge after iron-based coagulant addition is lower than the one obtained after aluminum sulfate addition. Values of organic content in the sludge (dry basis) are similar to other sludge generated in normal municipal wastewater plants (*26*). The content in organic matter, phosphorus, and nitrogen allows for the possibility of using the sludge as a fertilizer. Some studies are now being completed.

Additionally, from **Figure 4**, some previous calculations can be conducted for the design of a continuous clarifier. Thus, when the sedimentation can be catalogued as "zone-settling" type, the methods of Talmadge–Fitch or Coe–Clevenger can be applied. In the latter case, the first stage is the fitting of the curve height–time to a mathematical expression, such as the one proposed by Renko and Sirviö (*27*)

$$h(t, h_o) = \frac{\alpha X_o h_o}{\beta} + \left[h_o - \frac{\alpha X_o h_o}{\beta} \right] \exp\left(-\frac{\beta}{X_o h_o} t \right) \quad (11)$$

where t stands for time, $h(t, h_o)$ is the sludge height at time t, h_o is the initial sludge height, α and β are adjustable parameters for the sedimentation process, and X_o is the initial total solid concentration. Thus, from data taken from the left panel of **Figure 4** and the initial conditions, $h_o = 34$ cm and $X_o = 9635$ mg L^{-1}, the following values for the adjustable parameters were obtained: $\alpha = 0.73$ cm min^{-1} and $\beta = 5 \times 10^4$ mg L^{-1} cm min^{-1} ($R^2 \approx 0.98$). The solid concentration as a function of time and height can be calculated by the following expression (*28*):

$$X(t, h) = \frac{X_o h_o}{h(t, h_o) - \left[\alpha - \frac{\beta}{X_o h_o} h(t, h_o) \right] t} \quad (12)$$

To proceed with the design of a suitable sedimentation tank, two different criteria are first taken into consideration: the volumetric flow rate of wastewater and solids fed to the clarifier (m^3 day^{-1}) and the solid flow rate per surface unit in the settling tank (kg m^{-2} day^{-1}). The latter factor should be contemplated for effluents with a high solid content (> 500 ppm).

The Coe–Clevenger method involves a plot of G_B against $X(t, h)$. G_B is the solid flow rate in the clarifier because of gravity and is given by

$$G_B = X(t, h)v(t, h) \quad (13)$$

where $v(t, h)$ is the settling velocity corresponding to a sludge height of concentration $X(t, h)$. The plot G_B versus $X(t, h)$ for
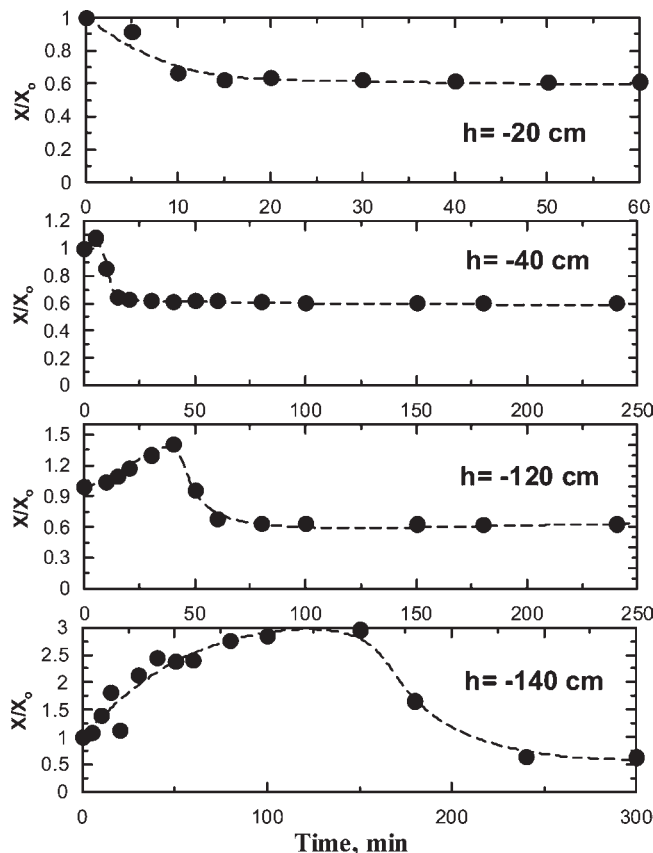

Figure 5. Coagulation–flocculation of wastewater from the production of "Serpa cheese" by $FeCl_3$ (250 ppm). Solids sedimentation in a column at different heights.

CWW treated with ferrous sulfate is shown in the top panel of **Figure 6**. Next, G_B was fitted to an adequate mathematical expression.

The design of a continuous clarifier depends upon the compacting index, γ, a design variable set from the beginning. This parameter is defined as the ratio of the solid concentration fed (X_o) to the solid concentration in the concentrated sludge (X_u) withdrawn from the clarifier. Thus, if $\gamma = 5.2$ ($X_u \approx 50\,000$ mg L^{-1}), the following step consists of plotting the tangent to the G_B curve containing the point (50\,000, 0), that is, intercepting the abscise axis at $X = 50\,000$ mg L^{-1}. Now, the y-axis intercept of this tangent gives the value G_T, which accounts for the global solid flow rate ($G_T = G_B + G_U$) because of gravity (G_B) plus the one because of the movement resulting from sludge outlet at the clarifier bottom (G_U). For $\gamma = 5.2$, this value was analytically obtained by an optimization process using Excel. Thus, a value of $G_T = 257$ kg m^{-2} day^{-1} was calculated (see the top panel of **Figure 6**).

The minimum area needed for the clarifier is given by $A_T = Q_o X_o / G_T$, with Q_o being the volumetric CWW flow rate fed. Thus, if Q_o is assumed to be 1000 m^3 day^{-1}, $A_T = 37.5$ m^2; that is, the diameter of a cylindrical clarifier should be approximately 7.0 m with an average height of 2.2 m (a 2.0 hydraulic retention time is considered).

The same calculations were carried out in the case of using aluminum sulfate. Values of $\alpha = 0.30$ cm min^{-1} and $\beta = 18.5 \times 10^3$ mg L^{-1} cm min^{-1} ($R^2 \approx 0.99$) where obtained. The G_B–X plot is shown in the bottom panel of **Figure 6**. Now, assuming a similar compacting index ($X_u \approx 50\,000$ mg L^{-1}), a value for $G_T = 74$ kg m^{-2} day^{-1} was calculated. Considering the same value of Q_o, the following results were obtained, $A_T = 133.5$ m^2; that is, the diameter of a cylindrical clarifier should be approximately

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Table 3. Sludge Characterization after Coagulation−Flocculation of Wastewater from the Production of "Serpa Cheese"[a]

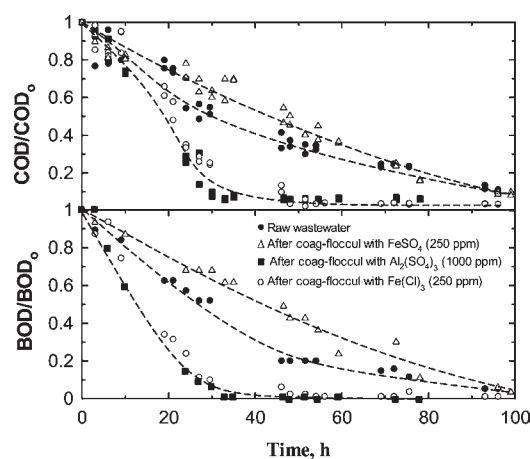|	FeSO$_4$		Al$_2$(SO$_4$)$_3$		FeCl$_3$	
	interval	average	interval	average	interval	average
sludge volume (mL of sludge/L of wastewater)	80−95	87 ± 8	130−130	130 ± 0		86
pH (ratio of sludge/water = 1:2.5)	6.67−6.97	6.81 ± 0.15	6.17−6.44	6.28 ± 0.14	4.12−4.72	4.36 ± 0.32
temperature (°C)	14−14	14 ± 0	14−14	14 ± 0	14−14	14 ± 0
conductivity (ms/cm, ratio of sludge/water = 1:2.5)	5.80−5.92	5.86 ± 0.06	5.34−5.65	5.49 ± 0.16	4.12−4.87	4.45 ± 0.38
percent dry weight (%)	4.0−4.6	4.4 ± 0.4	3.0−3.4	3.2 ± 0.2	1.5−2.0	1.7 ± 0.2
percent organic content (dry basis) (%)	65.9−69.2	67.7 ± 1.6	66.3−70.0	68.5 ± 1.9	58.2−70.6	64.4 ± 6.2
percent organic content (wet basis) (%)	2.6−3.2	3.0 ± 0.3	2.0−2.4	2.2 ± 0.2	0.9−1.4	1.1 ± 0.2
percent phosphorus (g of P/100 g of dry basis) (%)	2.7−3.1	2.9 ± 0.2	2.4−2.6	2.5 ± 0.1	1.0−1.3	1.1 ± 0.2
percent phosphorus (g of P/100 g of wet basis) (%)	0.080−0.089	0.086 ± 0.005	0.046−0.061	0.055 ± 0.008	0.010−0.019	0.013 ± 0.005
percent Kjeldahl nitrogen (g of N−Kj/100 g of wet basis) (%)	0.078−0.086	0.083 ± 0.005	0.070−0.096	0.081 ± 0.013	0.059−0.073	0.066 ± 0.007
percent ammonium nitrogen (g of N−NH$_3$/100 g of wet basis) (%)	0.050−0.052	0.051 ± 0.001	0.016−0.018	0.017 ± 0.001	0.003−0.005	0.004 ± 0.001
sedimentation type	zone settling		zone settling		flocculent	

[a] Results after three replicates.
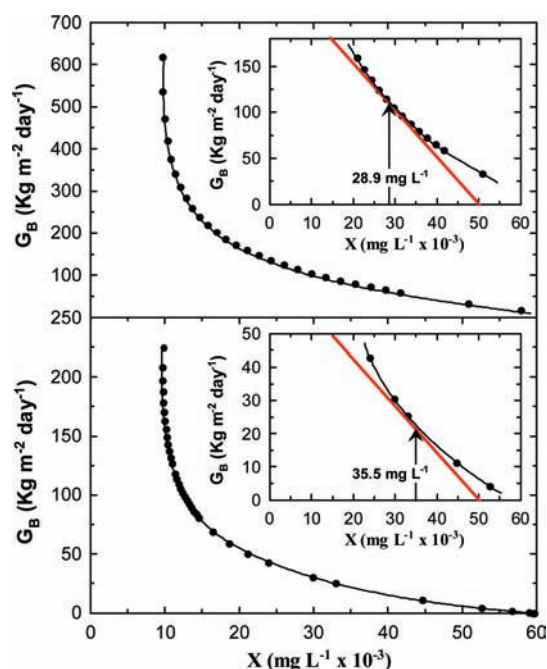
Figure 6. Coagulation−flocculation of wastewater from the production of "Serpa cheese". Solids flux (G_B). (Top) FeSO$_4$ (250 ppm). (Bottom) Al$_2$(SO$_4$)$_3$ (1000 ppm).

Figure 7. Aerobic biodegradation of wastewater from the production of "Serpa cheese".

13.0 m with an average height of 0.6 m (a 2.0 hydraulic retention time is considered). From the previous calculations, a clear advantage of using FeSO$_4$ instead of Al$_2$(SO$_4$)$_3$ is inferred.

Aerobic Biodegradation of Supernatants. The supernatants obtained in the coagulation−flocculation pre-stage were aerobically biodegraded by microorganisms typically found in a municipal wastewater plant. The results were compared to the biodegradation of raw wastewater.

Figure 7 shows the evolution profiles of COD and BOD for the aforementioned experiments. As observed, the pretreatment of CWW with Fe^{III} or Al^{III} involves a significant increase in the final biodegradation rate, halving the time needed to achieve almost complete elimination of COD or BOD. In contrast, when Fe^{II} was used, the biological process was slightly inhibited if compared to results obtained with raw wastewater. The reason is not clear and seems to relay on the properties of the supernatant. Thus, it can be hypothesized that the fraction of easily biodegradable material removed in the Fe^{II} coagulation−flocculation step was higher than that for the other two coagulants (lowest BOD/COD ratio

when using Fe^{II}). Phosphorus and oil and fat concentrations are the two parameters showing major differences after a comparison of supernatant quality between Fe^{II}-treated CW and Fe^{III}- or Al^{III}-treated CW.

An additional advantage of the biological process is that the formation of sludge excess is avoided. Thus, in all cases, volatile suspended solids (VSS) hardly varied at the end of the process. Hence, variations of 1, −25, and 19% in VSS were experienced after the aerobic biodegradation of effluents pretreated with Fe^{III}, Fe^{II}, and Al^{III}, respectively. This low microbial growth avoids the post-stage of sludge disposal and management.

Table 4 shows the reductions achieved in other parameters after application of the biological process. As depicted in this table, the biodegradation of CWW constitutes an attractive option in terms of contamination removal efficiency. Thus, parameters such as COD and BOD are reduced to values suitable for direct discharge. Application of a coagulation−flocculation pre-stage involves a significant decrease of the time required by the biological process.

A rigorous approach to process economy cannot be conducted because data on aeration costs, mechanical agitation, initial capital costs, etc. do depend upon plant size and regulatory limits to be fulfilled. However, it is worthy to say that, at lab scale, the costs associated with coagulation−flocculation reagents and pH modifiers are very low. Thus, in the case of using FeCl$_3$ to treat 1 L of raw wastewater, just 0.25 g of this reagent was used ($ 0.15/lb) plus 1.62 g of NaOH ($ 0.8/lb) to modify the pH previous to biodegradation (cheaper CaOH$_2$ can be used instead of NaOH).

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Table 4. Characterization of the Supernatant after the Combined Coagulation−Flocculation and Biodegradation of Wastewater from the Production of "Serpa Cheese"[a]

	FeSO$_4$	Al$_2$(SO$_4$)$_3$	FeCl$_3$	raw
process time (h)	175	80	80	190
pH	7.7 (−20%)	7.4 (−23%)	7.6 (−16%)	8.5 (−8%)
redox potential (mV)	21.3 (184%)	74.8 (−22%)	−430 (115%)	
conductivity (mS cm^{-1})	12.6 (−7.8%)	13.3 (4%)	12.5 (−3%)	11.3 (−11%)
COD (mg of O$_2$/L)	8213 (95%)	7463 (94%)	7713 (96%)	9525 (97%)
BOD at pH 7.0 (mg of O$_2$ L^{-1})	7900 (99%)	7400 (100%)	7900 (99%)	9400 (100%)
turbidity (NTU)	71 (79%)	43 (81%)	210 (99%)	824 (99%)
total suspended solids (mg L^{-1})	3184 (18%)	3090 (−9%)	5518 (−19%)	4400 (89%)
volatile dissolved solids (mg L^{-1})	2390 (25%)	2082 (−19%)	3410 (−2%)	3116 (93%)
sludge volume (mL L^{-1})[b]	40 (−25%)	40 (−25%)		20 (−100%)[b]
absorbance at 220 nm[c]	0.528−1.016	0.378−0.730	0.441−0.556	0.932−0.69
absorbance at 254 nm[c]	0.176−0.382	0.114−0.263	0.168−0.245	0.456−0.272
absorbance at 292 nm[c]	0.078−0.282	0.04−0.195	0.094−0.180	0.336−0.198
absorbance at 386 nm[c]	0.066−0.070	0.05−0.014	0.074−0.041	0.242−0.071
absorbance at 410 nm[c]	0.060−0.05	0.040−0.006	0.07−0.04	0.226−0.057

[a] Initial value and percentage removal in parentheses (regarding effluent after coagulation−flocculation). [b] After centrifugation. [c] Initial value (1:25 dilution) − final value (1:3 dilution).

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