Sustainable treatment of different high-strength cheese whey wastewaters: an innovative approach for atmospheric CO_2 mitigation and fertilizer production

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Abstract: Raw cheese whey wastewater (CWW) has been treated by means of $FeCl_3$ coagulation-flocculation, NaOH precipitation, and $Ca(OH)_2$ precipitation. Three different types of CWW were considered: without cheese whey recovery (CWW0), 60 % cheese whey recovery (CWW60), and 80 % cheese whey recovery (CWW80). Cheese whey recovery significantly influenced the characteristics of the wastewater to be treated: organic matter, solids, turbidity, conductivity, sodium, chloride, calcium, nitrogen, potassium, and phosphorus. Initial organic load was reduced to values in the interval of 60-70 %. Application of FeCl3, NaOH, or Ca(OH)2 involved additional chemical oxygen demand (COD) depletions regardless of the CWW used. Under optimum conditions, the combination of 80 % cheese whey recovery and lime application led to 90 % reduction in COD. Turbidity (99.8%), total suspended solids (TSS) (98-99 %), oils and fats (82-96 %), phosphorus (98-99 %), potassium (96-97 %), and total coli- forms (100 %) were also reduced. Sludge generated in the latter process showed excellent settling properties. This solid after filtration and natural evaporation can be used as fertilizer with limitations due to its saline nature. In an innovative, low- cost, and environmentally friendly technology, supernatant coming from the $Ca(OH)_2$ addition was naturally neutralized in 4-6 days by atmospheric CO_2 absorption without reagent addition. Consequently, a final aerobic biodegradation step can be applied for effluent polishing. This technology also allows for some atmospheric CO_2 mitigation. Time requirement for the natural carbonation depends on the effluent characteristics. A precipitate rich in organic matter and nutrients and depletions of solids, sodium, phosphorus, magnesium, Kjeldahl, and ammoniacal nitrogen were also achieved during the natural carbonation.

Keywords: Cheese whey recovery · Biodegradability · Physicochemical processes · Atmospheric CO_2 mitigation · Sludge characterization · Sludge filterability

Introduction

Wastewater coming from the cheese industry constitutes a contamination source of organic matter, mineral salts, total suspended solids (TSS), nutrients, oils and fats, acidity, salinity, etc. Direct release of these effluents into natural receiving waters can generate an unlimited number of environmental and public health impacts. High content of biodegradable organic matter and fats floatation have been linked to the rapid oxygen consumption and anaerobic conditions in aquatic eco- systems, endangering, therefore, the species survival. The presence of lactose, nitrogen, and phosphorus can lead to the development and growth of fungi and algae, with water quality degradation. Acid pH and high salinity are contamination indicators that must be also considered. Sodium and chloride are responsible for the high salinity level in cheese whey wastewater (CWW) (Prazeres et al. 2013a). Accordingly, suit- able treatment processes are required.

Several technologies have been proposed to deal with this challenging environmental problem. Traditionally, the direct application on land of the effluent for irrigation has been considered. In this case, TSS and fats can accumulate on soil surface, causing a negative impact on soil structure. Nevertheless, some beneficial effects can also be mentioned, based on the potential nutritional value of the cheese effluents, which are rich in biodegradable organic matter and nutrients (Prazeres et al. 2012; Prazeres et al. 2013b). Cheese whey, the major component of the CWW, has been used on sodic soils (Jones et al. 1993), degraded calcareous soil in irrigation fur- rows (Lehrsch et al. 2008), acid soils in high to moderate rainfall areas, and calcareous soils with neutral to alkaline properties under irrigation in an arid climate (Robbins and Lehrsch 1998). In those studies, the consequences revealed depletions of pH, sodium adsorption ratio, exchangeable sodium percentage, and sediment losses. Increases of soil flocculation, crop production, and soil aggregation stability have also been identified. Additionally, in a previous work, the potential agricultural reuse of pretreated CWW at different salinity levels in tomato production, with improving of the soluble solids content and epidermis firmness of tomato fruits was demonstrated (Prazeres et al. 2014).

Conventional treatments are based on the implementation of anaerobic or aerobic degradation processes to reduce the organic contamination. In this sense, many studies have been focused in biological treatments (Fang 1991; Gavala et al. 1999; Gutiérrez et al. 1991; Kalyuzhnyi et al. 1997; Martins and Quinta-Ferreira 2010; Rivas et al. 2010; Rivas et al. 2011). However, some drawbacks have been mentioned in the literature, such as the need of long hydraulic retention times, development of bulking phenomena, specific microorganism requirement, fats floatation, odor release, unstable operation, and excessive sludge formation. Additionally, in most cases, the effluent coming from the biological treatment is not appropriate to be discharged into the environment. Other options have been studied which can minimize the drawbacks of the biological processes. Thus, the integration of physicochemical processes before or after biological treatments has also been evaluated. Broadly speaking, physicochemical processes such as coagulation-flocculation, precipitation, and/or oxidation technologies are economically viable alternatives to small and medium-scale factories. Nevertheless, only a few studies were found treating raw CWW by coagulation- flocculation (Rivas et al. 2010) or precipitation (Rivas et al. 2011), biotreated CWW (activated sludge) by ozonation (Martins and Quinta-Ferreira 2010) or Fenton processes (Martins et al. 2010), and precoagulated CWW ($FeCl_3$) and pretreated CWW (Ca(OH)2 precipitation plus activated sludge) by Fenton-like system (Prazeres et al. 2013b). Thus, studies on the effect of different operating variables in physicochemical processes are also limited. Additionally, the effect of cheese whey recovery on the physicochemical processes used for the CWW treatment has not yet been considered.

Chemical precipitation processes are able to roughly re- duce 50 % of the organic matter (Prazeres et al. 2013c; Prazeres et al. 2014; Prazeres et al. 2016; Rivas et al. 2011). However, these processes require a pH neutralization step, increasing the costs of the treatment line. For that reason, the use of atmospheric CO_2 to neutralize the alkalinity of the effluent coming from the basic precipitation is a promising non-biological process. This sustainable alternative enables not only the wastewater neutralization and treatment but also the mitigation of the environmental problems associated with the increase of atmospheric greenhouse gases (Kumar et al. 2010). A comparable process was investigated by Xie et al. (2009) for alkaline soil, which absorbed CO_2 at a rate of 0.33.0 (imol m^{-2} s^{-1}, depending on the soil salinity, alkalinity, temperature, and water content. Regarding the wastewater, the effective carbonation is also influenced by several factors, such as temperature, pH, permeability, anions, and cations (Pan et al. 2012). Another alternative for the wastewater treatment and CO_2 fixation has been reported using microalgae (Kumar et al. 2010), since the wastewater offers the nutrients and organic matter required in the microorganism development. Contrary to the CO_2 sequestration by biological processes, CO2 absorption by the chemical process proposed in this work is easier to control than plants and microorganisms, which are responsible for the CO_2 fixation in the biological processes. Additionally, CO2 absorption by pretreated and basic wastewater is an economical technology that produces a byproduct (precipitate) rich in organic matter and nutrients. Despite the several advantages, carbonation of wastewater has been rarely investigated (Lim et al. 2010).

The present work aims at studying the effect of the cheese whey recovery on the CWW characterization and treatment by coagulation-flocculation and basic precipitation processes.

Three different CWW were assayed, for instance, without cheese whey recovery, with 60 % of cheese whey recovery, and with 80 % of cheese whey recovery. Sludge sedimentation, characteristics, and filterability were also investigated. Moreover, an innovative process of atmospheric CO_2 carbonation without chemical addition was developed in order to treat and neutralize the pretreated CWW coming from the basic precipitation with $Ca(OH)_2$ addition.

Materials and methods

Cheese whey wastewater characterization

Raw CWW was collected from a small industry located in the "Serpa Cheese" region of Alentejo, Portugal. This cheese factory produces cheese from goat and sheep milk. Three types of cheese effluents were collected from the storage la- goons at three different stages of cheese whey management, namely without cheese whey recovery (CWW0) and with cheese whey recoveries of 60 % (CWW60) and 80 % (CWW80). The generated wastewater volume varies according to the different situations, i.e., 4.3 (80 % cheese whey recovery), 4.5 (60 % cheese whey recovery), and 5.0 (without cheese whey recovery) L of CWW L^{-1} of milk (Carvalho et al. 2013). Raw and treated CWW characterization was accomplished by using the main contamination indicators. Additional analytical procedures can be found elsewhere (Prazeres et al. 2013c; Prazeres et al. 2014; Rivas et al. 2010). Absorbances at different wavelengths were investigated: 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), 410 nm (color) (Kasprzyk-Hordern et al. 2006; Pacheco and Peralta-Zamora 2004; Peuravuori et al. 2002; Rivas et al. 2005).

Experimental procedure

Wastewater treatment

Precipitation experiments were conducted in 1-L glass recipients by using a wastewater volume of 800 mL. To initiate an experiment, NaOH or Ca(OH)2 was added to the raw CWW0 (or CWW with previous cheese whey recovery) under vigorous agitation. When the predetermined precipitation pH was obtained, the agitation system was switched off. Coagulation- flocculation tests were carried out in a Qlabo ISCO Jar Test. In a typical run, 800 mL of CWW was placed in 1-L recipients. A rapid stirring (150 rpm) was applied in the first 2 min; thereafter, a slow stirring (20 rpm) was applied for 20 min. In the particular case of 80 % cheese whey recovery, experiments were conducted with the effluent immediately collected after generated (fresh) or with the effluent stored in a pond in the factory (stored).

Atmospheric CO_2 carbonation

The supernatants of the precipitation process with $Ca(OH)_2$ addition were maintained with no atmospheric CO_2 contact until the carbonation process started. Carbonation of pretreated CWW, after sludge separation, was conducted by using a volume of 3.5 L in bottles of 0.0162-m^2 sectional area without stirring. Temperature, conductivity, pH, chemical oxygen demand (COD), calcium, magnesium, and alkalinity were measured at dif- ferent reaction times.

Sludge sedimentation and filterability

Sludge sedimentation assays were completed in a normalized glass graduated cylinder (1 L, 34 cm height). After the sludge sedimentation, samples were collected and analyzed to determine the main contamination indicators. Filtration experiments were accomplished according to Prazeres et al. (2016) by means of columns with a height of 42 cm. Filtration columns had external and internal diameters of 6.8 and 6.1 cm, respectively. Sand filters were composed of a false fund covered with 2.1 cm of coarse gravel. This false fund was perforated to allow the drainage and collection of filtrated water. The filtration medium consisted of gravel (16 cm, whose diameter decreased from 4 in 4 cm); coarse sand (2 cm), intermediate sand (4 cm), and fine sand (2 cm). Filtration tests were carried out in triplicate. In the experiments, 500 mL (height of 15.7-16.2 cm) of sludge was filtrated. During the draining process, the volume of filtrated water (drainage water) and the height of wet sludge remaining in the column were monitored. Water drained from the filters was thereafter analyzed. When the drainage of water was completed, the sludge was removed from the column and placed in an open dish, starting the evaporation process at 23.7 ± 0.4 °C.

Results and discussion

Effect of the cheese whey recovery

Cheese whey wastewater characterization

The characteristics of CWW may widely differ, according to the final products, washing water volume, cleaning agent type, and valued cheese whey volume (Prazeres et al. 2013c). The milk type used in the cheese manufacturing process also plays an important role in the contamination level of the wastewater (Prazeres et al. 2013b). Similarly to the milk type, the recovered cheese whey volume has a significant role on the contamination level of CWW, as well as on the produced waste- water volume. Small and medium-scale factories usually have no technical and economic capacity to valorize their own cheese whey. However, these factories give the cheese whey to other companies interested in the cheese whey valorization. Thus, in the cheese factories, there is a great variability in the recovered cheese whey amount, volume, and composition of produced wastewater, depending on the season, production method, size, and location of the cheese factory, etc. Table 1 depicts the main properties of this effluent without and with cheese whey recovery. CWW presented a greenish white color and a disagreeable odor, presumably of butyric acid that causes discomfort and attracts insects such as flies and mosquitoes. CWW_0 displayed high contents of TSS (1.6-4.8 g L^{-1}) and fats (1.8-3.8 g L^{-1}), forming surface layers in the Springer

Table 1 CWW characterization without and with cheese whey recovery

Parameter	Units	Without cheese whey recovery[d]	60 % cheese whey recovery	80 % cheese whey recovery	
				Fresh	Stored
pH	-	4.23 ±0.11	4.28±0.20	4.62±0.20	5.74 ± 0.37
Redox potential	mV	5.8±169.1	175.3 ± 32.0	156.6 ± 11.6	103.9±13.2
Temperature	°C	1 2.0 ± 1.0	17.8±1.5	22.0±0.6	21.9±0.2
Conductivity	dS m^{-1}	12.39±1.11	5.71 ±1.20	2.41 ± 0.27	2.15 ± 0.03
COD	mg L^{-1}	13494± 4270	4700±1534	4340±829	4151 ±619

BOD5	mg L^{-1}	11686±962	4700±986	3233±1159	3983±208
BOD5/COD	-	1.05±0.16	1.00 ± 0.03	0.73±0.15	0.97±0.10
Total alkalinity	mg L^{-1} $CaCO_3$	-	-	279.6 ± 79.2	360.1 ±1.8
Turbidity	NTU	1557±219	336±4	-	191 ± 17
TS	mg L^{-1}	7910±613	-	3936±285	5067±1566
TSS	mg L^{-1}	3317±1269	-	1267±350	2922±2741
TVS	mg L^{-1}	-	-	2373±192	3918±1584
Oils and fats	mg L^{-1}	2489±711	-	989±433	4372 ± 2874
Kjeldahl-N	mg L^{-1}	323.7±18.4	-	93.5±0.15	78.4± 10.9
NH3-N	mg L^{-1}	62.9±7.3	-	9.9±0.9	56.2±0.8
P	mgL^{-1}	103.0±14.3	-	11.6±1.8	6.4±1.6
Cl	mg L^{-1}	2706 ± 929	-	988± 140	733±112
Na	mg L^{-1}	1345±418	-	684±433	510±337
K	mgL^{-1}	228.2 ± 139.9	-	54.4±3.4	25.3±10.9
Ca	mg L^{-1}	117.2±6.2	-	64.1 ±17.8	46.2±20.4
Mg	mg L^{-1}	49.2±25.8	-	44.3 ± 26.3	53.7±26.3
Total proteins	kgL^{-1}	943 ± 6	-	-	-
Lactose	mg L^{-1}	180 ± 3	-	-	-
Absorbance at 220 nm	cm^{-1}	0.736±0.105^{a}	0.548^{b}	0.325±0.017^{c}	0.341 ± 0.008^{c}
Absorbance at 254 nm	cm^{-1}	0.370 ± 0.045^{a}	0.170^{b}	0.125 ± 0.002^{c}	0.181 ± 0.005^{c}
Absorbance at 292 nm	cm^{-1}	0.285 ± 0.035^{a}	0.124^{b}	0.055 ± 0.002^{c}	0.134 ± 0.004^{c}
Absorbance at 386 nm	cm^{-1}	0.186±0.011^{a}	0.069^{b}	0.020±0.004^{c}	0.071 ± 0.004^{c}
Absorbance at 385 nm	cm^{-1}	0.172±0.016^{a}	0.071^{b}	-	-
Absorbance at 410 nm	cm^{-1}	0.158±0.016^{a}	0.066^{b}	0.033 ± 0.004^{c}	0.075 ± 0.002^{c}

COD chemical oxygen demand, BOD biological oxygen demand, TS total solids, TSS total suspended solids, TVS total volatile solids ^{a} 1 :50 dilution ^{b}1:25 dilution ^{c} 1 :20 dilution
^{d} Some parameters are from Rivas et al. (2010)

storage ponds. Thus, it creates anaerobic conditions with negative redox potential values (-436.5 to 148.6 mV). The key parameter of the CWW_0 is its relative high organic load, monitored by biological oxygen demand (BOD_5) and COD in the range of 10.0-12.5 and 8.8-25.6 g L^{-1}, respectively. The bio- degradability index (BOD_5/COD) was located in the interval of 0.79-1.17.

When a fraction of cheese whey was recovered in the factory, the contamination level of the CWW was reduced (aver- aging 70 % COD reduction). Hence, the initial COD values decreased to values in the interval 4.0-5.0 g L^{-1} while maintaining a high biodegradability index. Moreover, due to TSS depletion, turbidity was reduced at approximately 78 and 88 % when the cheese whey recovery was 60 and 80 %, respectively. Regarding the conductivity reduction, values of approximately 54 % (corresponding to 60 % cheese whey recovery) and 81-83 % (corresponding to 80 % cheese whey recovery) were obtained if compared to CWW0. This finding is mainly attributed to the sodium and chloride depletion. Finally, calcium, nitrogen, and potassium concentrations were also influenced by recovered cheese whey volume. These parameters presented diminutions in the ranges of 45-61, 71-76, and 76-89 %, respectively, when the maximum amount of cheese whey was recovered. In the case of stored CWW0, the nitrogen was essentially present in the form of organic and ammoniacal nitrogen in a percentage of approximately 80 and 19 %, respectively. Stored CWW80 showed just 28 % in the organic form.

Cheese whey wastewater treatment

Coagulation-flocculation or precipitation processes are effective technologies capable ofacceptably reducing the nutrients and organic load of CWW. These treatments render a biodegradable effluent that can be ultimately polished by a simple activated sludge process. The removal efficiency is influenced by reagent dose, temperature, operating pH, and, to a significant extent, by the fraction of recovered cheese whey.

Optimal operating conditions when using Ca(OH)2, NaOH, or FeCl3 (without cheese whey recovery) have been determined in preliminary works (Rivas et al. 2010, 2011). Given the complexity and variability of this effluent, a first sequence of experiments was conducted with CWW0. Figure 1a depicts the main results obtained in terms of COD, BOD_5, and turbidity elimination after chemical precipitation with $Ca(OH)_2$ or NaOH or alternatively after coagulation-flocculation with $FeCl_3$. The chemical precipitation with $Ca(OH)_2$ addition at pH 11.5 led to the best results. Other pHs in the interval 8.6-12.4 have also been tested in this work (Table 2). Under optimum pH conditions, COD, BOD5, and turbidity maximum removals close to 51, 47, and 99 % were found, respectively (Fig. 1a). Biodegradable organic matter was mainly removed. Table 3 shows the final values of additional parameters after treatment with $Ca(OH)_2$ addition. Significant reduction values after the precipitation stage were obtained in parameters such as TSS (90 %), oils and fats (88 %), total nitrogen (53 %), and phosphorus(97 %), as well as total coliform elimination (results not shown). Contrarily, total solids (TS) increased from 7.9 to 11.2 g L^{-1}, undoubtedly due to total dissolved solid increase as a result of lime addition. These findings may be caused by the reactions taking place when lime is added to the wastewater, with formation of insoluble species, such as calcium carbonate (reactions 14), magnesium carbonate, and magnesium hydroxide (reactions 3 and 4), and phosphates (reactions 5 and 6):

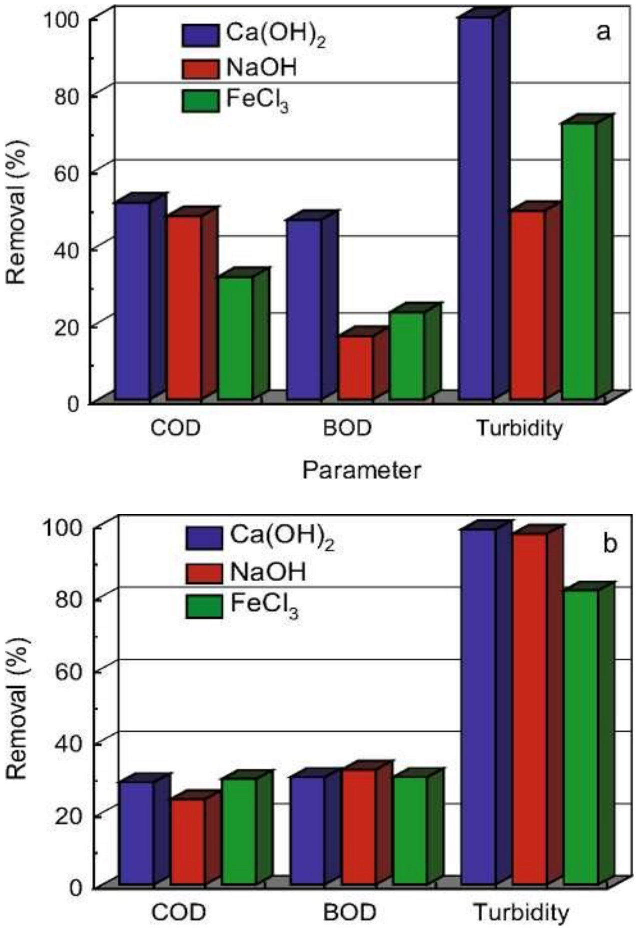
$$Ca(OH)_2 + H_2CO_3 \rightleftarrows CaCO_3\downarrow + 2\,H_2O \qquad (1)$$

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightleftarrows 2\,CaCO_3\downarrow + 2\,H_2O \qquad (2)$$

$$Ca(OH)_2 + Mg(HCO_3)_2 \rightleftarrows MgCO_3\downarrow + CaCO_3\downarrow + 2\,H_2O \qquad (3)$$

$$Ca(OH)_2 + MgCO_3 \rightleftarrows Mg(OH)_2\downarrow + CaCO_3\downarrow \qquad (4)$$

$$3\,Ca(OH)_2 + 2\,PO_4^{3-} \rightleftarrows Ca_3(PO_4)_2\downarrow + 6\,OH^- \qquad (5)$$



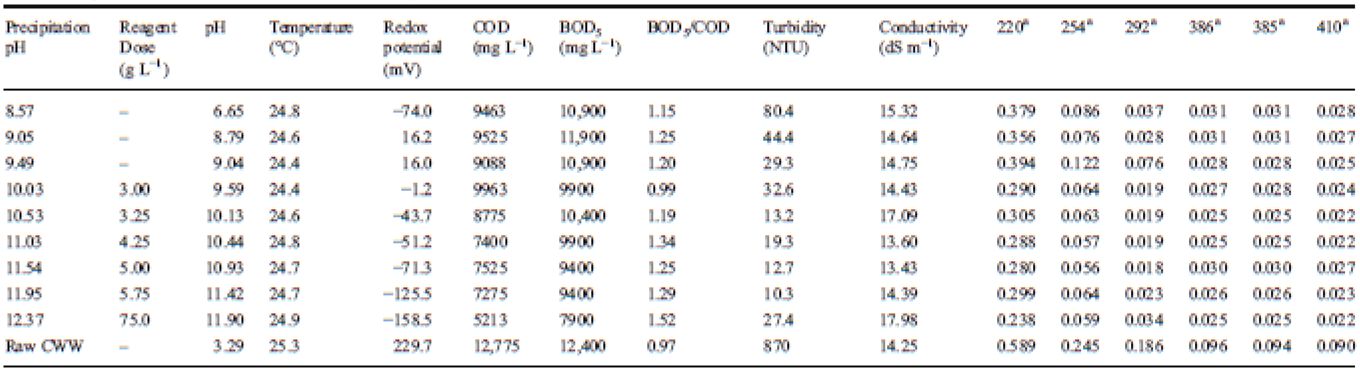
Parameter

Fig.1 Treatment by $Ca(OH)_2$, NaOH, and $FeCl_3$ processes of raw CWW without cheese whey recovery (a) and with 60 % cheese whey recovery (b). a Chemical precipitation experimental conditions: pH=4.24, temperature=12.0 °C, COD = 1 8,5 3 1 mg L^{-1}, BOD5=12,500 mgL^{-1}, turbidity = 1 33 1 .0 NTU. Coagulation-flocculation experimental conditions: pH=4.25, temperature = 1 2.0 °C, COD=13,900 mg L^{-1}, BOD_5 =11,000 mg L^{-1}, turbidity=1714.7 NTU. b Experimental conditions: pH=4.28, temperature = 17.8 °C, COD = 470 0 mg L^{-1}, BOD5=4700mgL^{-1},turbidity=336.3 NTU

$$4\,Ca(OH)_2 + 3\,PO_4^{3-} + H_2O \rightleftarrows Ca_4H(PO_4)_3\downarrow + 9\,OH^- \quad (6)$$

Chemical precipitation with NaOH led to a higher removal of organic content (BOD_5 17 % and COD 48 %) than did coagulation-flocculation with $FeCl_3$ (BOD5 23 % and COD 32 %), removing biodegradable and non-biodegradable organic matter. However, the last process was more efficient in turbidity depletion (72 against 49 % corresponding to NaOH precipitation). Regarding the precipitation with NaOH addition, the reactions that can occur are mainly responsible for the formation of magnesium and calcium hydroxides (reactions 7 and 8) (Prazeres et al. 2016). Finally, with

Table 2 Optimization of the treatment of CWW_0 with $Ca(OH)_2$ addition



Precipitation pH	Reagent Dose ($g\ L^{-1}$)	pH	Temperature (°C)	Redox potential (mV)	COD ($mg\ L^{-1}$)	BOD_5 ($mg\ L^{-1}$)	BOD_5/COD	Turbidity (NTU)	Conductivity ($dS\ m^{-1}$)	220[a]	254[a]	292[a]	386[a]	385[a]	410[a]
8.57	–	6.65	24.8	−74.0	9463	10,900	1.15	80.4	15.32	0.379	0.086	0.037	0.031	0.031	0.028
9.05	–	8.79	24.6	16.2	9525	11,900	1.25	44.4	14.64	0.356	0.076	0.028	0.031	0.031	0.027
9.49	–	9.04	24.4	16.0	9088	10,900	1.20	29.3	14.75	0.394	0.122	0.076	0.028	0.028	0.025
10.03	3.00	9.59	24.4	−1.2	9963	9900	0.99	32.6	14.43	0.290	0.064	0.019	0.027	0.028	0.024
10.53	3.25	10.13	24.6	−43.7	8775	10,400	1.19	13.2	17.09	0.305	0.063	0.019	0.025	0.025	0.022
11.03	4.25	10.44	24.8	−51.2	7400	9900	1.34	19.3	13.60	0.288	0.057	0.019	0.025	0.025	0.022
11.54	5.00	10.93	24.7	−71.3	7525	9400	1.25	12.7	13.43	0.280	0.056	0.018	0.030	0.030	0.027
11.95	5.75	11.42	24.7	−125.5	7275	9400	1.29	10.3	14.39	0.299	0.064	0.023	0.026	0.026	0.023
12.37	75.0	11.90	24.9	−158.5	5213	7900	1.52	27.4	17.98	0.238	0.059	0.034	0.025	0.025	0.022
Raw CWW	–	3.29	25.3	229.7	12,775	12,400	0.97	870	14.25	0.589	0.245	0.186	0.096	0.094	0.090

COD chemical oxygen demand, *BOD* biological oxygen demand

[a] 1:50 dilution; absorbance at 220, 254, 292, 386, 385, and 410 nm (cm^{-1})

respect to $FeCl_3$ coagulation-flocculation, the precipitate formation is related to the ferric hydroxide (reaction 9):

$$2\ NaOH + Mg(HCO_3)_2 \rightleftarrows Mg(OH)_2\downarrow + 2\ NaHCO_3 \qquad (7)$$

$$2\ NaOH + Ca(HCO_3)_2 \rightleftarrows Ca(OH)_2\downarrow + 2\ NaHCO_3 \qquad (8)$$

$$2\ FeCl_3 + 3\ Ca(OH)_2 \rightarrow 2\ Fe(OH)_3\downarrow + 3\ CaCl_2 \qquad (9)$$

Ca(OH)2 addition to CWW0 generated the largest amount of sludge (=12 % of the wastewater total volume), followed by $FeCl_3$ coagulation-flocculation (=9 % of the wastewater total volume) and NaOH precipitation (=6 % of the wastewater total volume). A second sequence of experiments was con- ducted by using CWW with previous partial recovery of cheese whey. The main results achieved for COD, BOD5, and turbidity removals when CWW60 was treated are presented in Fig. 1b. The effects on the supernatant characterization after the different processes are shown in Table 3. Thus, when CWW60 was processed, approximately an additional 30 % of COD was eliminated (75 % COD reduction if summing up the effects of cheese whey recovery and process efficiency). When CWW80 was considered, COD removals in the range of 50-60 % were obtained (COD reduction close to 90 % if considering the raw CWW_0). No significant differences were found when processing either the fresh or the stored CWW80. High reductions were also obtained for turbidity (98-99 %), TSS (94-99 %), oils and fats (90 %), phosphorus (80-86 %), and potassium (6385 %) when applying Ca(OH)2 in CWW80 treatment.

Besides the reduction of the produced wastewater volume, cheese whey recovery also reduces the costs associated to wastewater treatment due to the lower initial contamination level. Hence, by taking into account efficiency values and economic aspects, treatment with the less expensive process studied, Ca(OH)2 addition to CWW80, is recommended (70-80 % reduction in precipitant needs). In this situation, an amount of 1.071.21 g L^{-1} was consumed in the Ca(OH)2 process. The only drawback that could be mentioned is the lower value of the BOD_5/COD ratio in the proximity of 0.5; however, this value is still considered suitable to apply a final biodegradation step. In any case, higher values of BOD5/ COD ratio (close to 0.9) could be obtained when the precipitation with Ca(OH)2 was carried out at pH 11 in- stead of 11.5 with significant differences in some parameters, for example, final pH, phenolphthalein and total alkalinity, BOD_5, Kjeldahl and ammoniacal nitrogen, phosphorus, and potassium (results not shown). This effect is difficult to explain taking into account the small change in the precipitation pH; however, the results were confirmed after several replications.

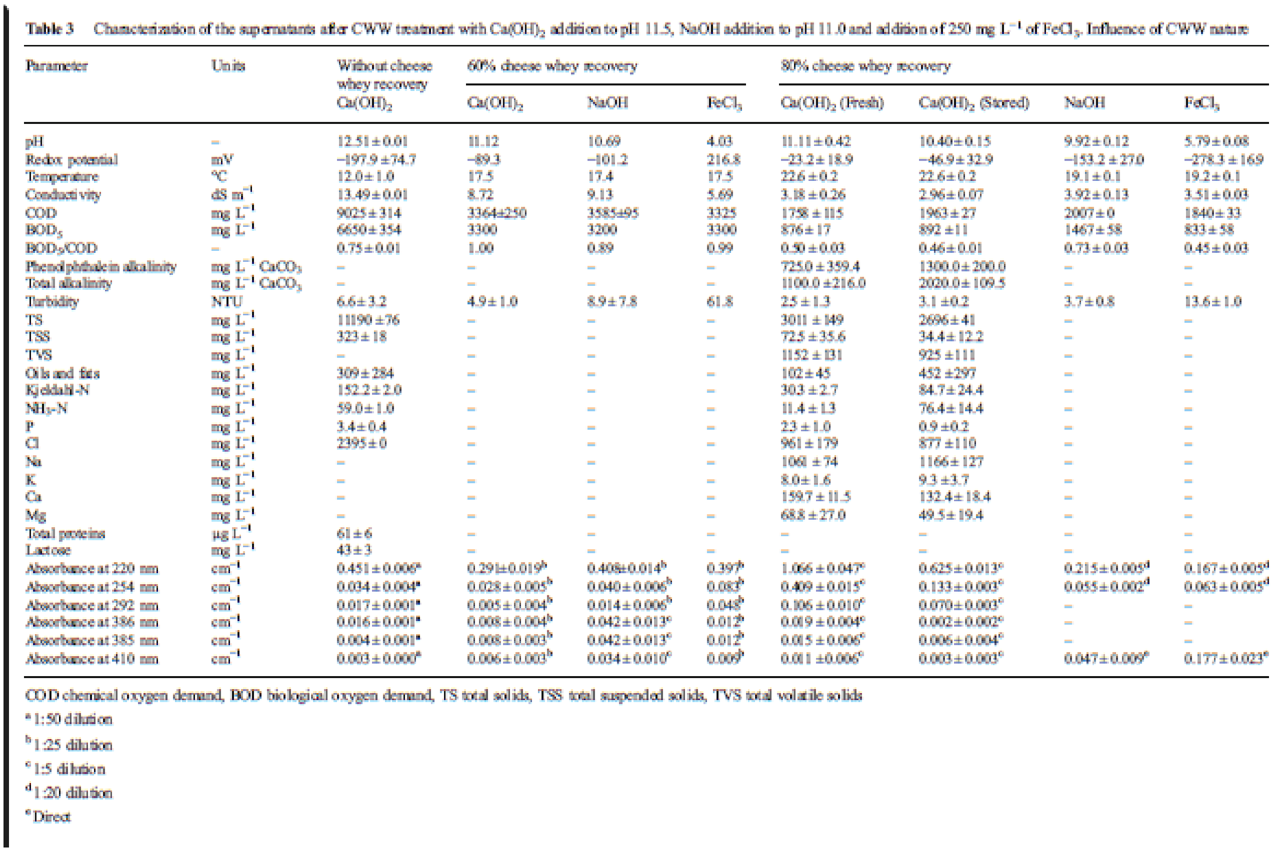


Table 3 Characterization of the supernatants after CWW treatment with $Ca(OH)_2$ addition to pH 11.5, NaOH addition to pH 11.0 and addition of 250 mg L^{-1} of $FeCl_3$. Influence of CWW nature

Parameter	Units	Without cheese whey recovery $Ca(OH)_2$	60% cheese whey recovery $Ca(OH)_2$	60% cheese whey recovery NaOH	60% cheese whey recovery $FeCl_3$	80% cheese whey recovery $Ca(OH)_2$ (Fresh)	80% cheese whey recovery $Ca(OH)_2$ (Stored)	80% cheese whey recovery NaOH	80% cheese whey recovery $FeCl_3$
pH	–	12.51 ± 0.01	11.12	10.69	4.03	11.11 ± 0.42	10.40 ± 0.15	9.92 ± 0.12	5.79 ± 0.08
Redox potential	mV	−197.9 ± 74.7	−89.3	−101.2	216.8	−23.2 ± 18.9	−46.9 ± 32.9	−153.2 ± 27.0	−278.3 ± 169
Temperature	°C	12.0 ± 1.0	17.5	17.4	17.5	22.6 ± 0.2	22.6 ± 0.2	19.1 ± 0.1	19.2 ± 0.1
Conductivity	dS m^{-1}	13.49 ± 0.01	8.72	9.13	5.69	3.18 ± 0.26	2.96 ± 0.07	3.92 ± 0.13	3.51 ± 0.03
COD	mg L^{-1}	9025 ± 314	3364±250	3585±95	3325	1758 ± 115	1963 ± 27	2007 ± 0	1840 ± 33
BOD_5	mg L^{-1}	6650 ± 354	3300	3200	3300	876 ± 17	892 ± 11	1467 ± 58	833 ± 58
BOD_5/COD	–	0.75 ± 0.01	1.00	0.89	0.99	0.50 ± 0.03	0.46 ± 0.01	0.73 ± 0.03	0.45 ± 0.03
Phenolphthalein alkalinity	mg L^{-1} $CaCO_3$	–	–	–	–	725.0 ± 359.4	1300.0 ± 200.0	–	–
Total alkalinity	mg L^{-1} $CaCO_3$	–	–	–	–	1100.0 ± 216.0	2020.0 ± 109.5	–	–
Turbidity	NTU	6.6 ± 3.2	4.9 ± 1.0	8.9 ± 7.8	61.8	2.5 ± 1.3	3.1 ± 0.2	3.7 ± 0.8	13.6 ± 1.0
TS	mg L^{-1}	11190 ± 76	–	–	–	3011 ± 149	2696 ± 41	–	–
TSS	mg L^{-1}	323 ± 18	–	–	–	72.5 ± 35.6	34.4 ± 12.2	–	–
TVS	mg L^{-1}	–	–	–	–	1152 ± 131	925 ± 111	–	–
Oils and fats	mg L^{-1}	309 ± 284	–	–	–	102 ± 45	452 ± 297	–	–
Kjeldahl-N	mg L^{-1}	152.2 ± 2.0	–	–	–	30.3 ± 2.7	84.7 ± 24.4	–	–
NH_3-N	mg L^{-1}	59.0 ± 1.0	–	–	–	11.4 ± 1.3	76.4 ± 14.4	–	–
P	mg L^{-1}	3.4 ± 0.4	–	–	–	2.3 ± 1.0	0.9 ± 0.2	–	–
Cl	mg L^{-1}	2395 ± 0	–	–	–	961 ± 179	877 ± 110	–	–
Na	mg L^{-1}	–	–	–	–	1061 ± 74	1166 ± 127	–	–
K	mg L^{-1}	–	–	–	–	8.0 ± 1.6	9.3 ± 3.7	–	–
Ca	mg L^{-1}	–	–	–	–	159.7 ± 11.5	132.4 ± 18.4	–	–
Mg	mg L^{-1}	–	–	–	–	68.8 ± 27.0	49.5 ± 19.4	–	–
Total proteins	μg L^{-1}	61 ± 6	–	–	–	–	–	–	–
Lactose	mg L^{-1}	43 ± 3	–	–	–	–	–	–	–
Absorbance at 220 nm	cm^{-1}	0.451 ± 0.006^a	0.291±0.019^b	0.408±0.014^b	0.397^b	1.066 ± 0.047^c	0.625 ± 0.013^c	0.215 ± 0.005^d	0.167 ± 0.005^d
Absorbance at 254 nm	cm^{-1}	0.034 ± 0.004^a	0.028 ± 0.005^b	0.040 ± 0.006^b	0.083^b	0.409 ± 0.015^c	0.133 ± 0.003^c	0.055 ± 0.002^d	0.063 ± 0.005^d
Absorbance at 292 nm	cm^{-1}	0.017 ± 0.001^a	0.005 ± 0.004^b	0.014 ± 0.006^b	0.048^b	0.106 ± 0.010^c	0.070 ± 0.003^c	–	–
Absorbance at 386 nm	cm^{-1}	0.016 ± 0.001^a	0.008 ± 0.004^b	0.042 ± 0.013^c	0.012^b	0.019 ± 0.004^c	0.002 ± 0.002^c	–	–
Absorbance at 385 nm	cm^{-1}	0.004 ± 0.001^a	0.008 ± 0.003^b	0.042 ± 0.013^c	0.012^b	0.015 ± 0.006^c	0.006 ± 0.004^c	–	–
Absorbance at 410 nm	cm^{-1}	0.003 ± 0.000^a	0.006 ± 0.003^b	0.034 ± 0.010^c	0.009^b	0.011 ± 0.006^c	0.003 ± 0.003^c	0.047 ± 0.009^e	0.177 ± 0.023^e

COD chemical oxygen demand, BOD biological oxygen demand, TS total solids, TSS total suspended solids, TVS total volatile solids

[a] 1:50 dilution

[b] 1:25 dilution

[c] 1:5 dilution

[d] 1:20 dilution

[e] Direct

Atmospheric CO_2 carbonation of the supernatant coming from the $Ca(OH)_2$ precipitation

As stated previously, regardless of the CWW considered (with or without whey recovery), once the physicochemical process is applied, a final aerobic biodegradation can be implemented. As a consequence, the pretreated effluent needs the corresponding pH amendment to neutral conditions, so the biodegradation can take place. In order to save in chemicals, the natural pH modification due to the atmospheric CO_2 absorption is suggested. The following reactions should be considered:

$$CO_2(air) + OH^- \rightarrow HCO_3^- \qquad (10a)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \qquad (10b)$$

$$CO_3^{2-} + Ca^{2+} \rightarrow \downarrow CaCO_3 \qquad (11a)$$

$$CO_3^{2-} + Mg^{2+} \rightarrow \downarrow MgCO_3 \qquad (11b)$$

$$2\,OH^- + Ca^{2+} \rightarrow \downarrow Ca(OH)_2 \qquad (11c)$$

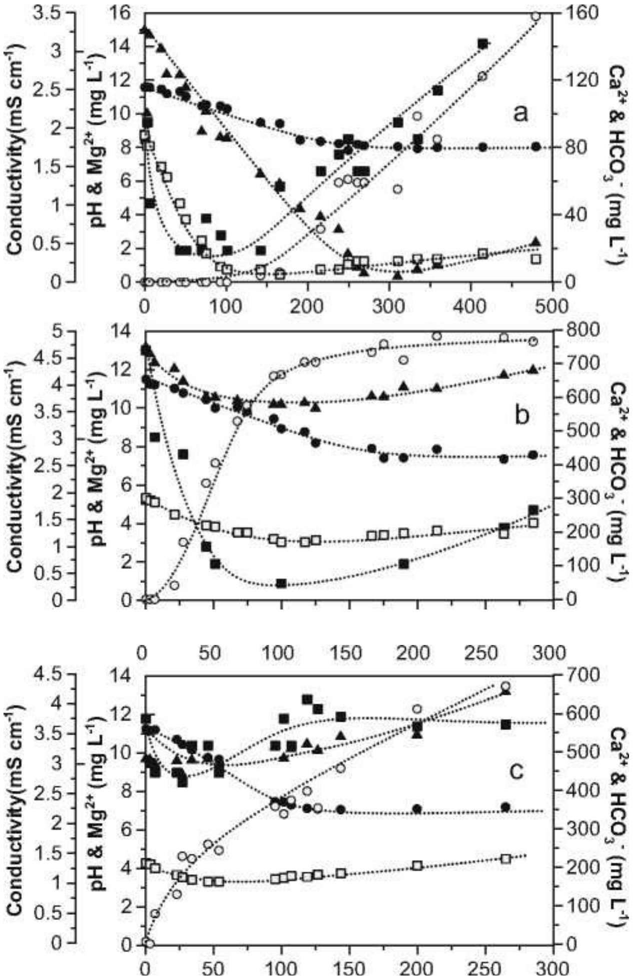
$$2\,OH^- + Mg^{2+} \rightarrow \downarrow Mg(OH)_2 \qquad (11d)$$

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2\,HCO_3^- \qquad (12a)$$

$$MgCO_3 + CO_2 + H_2O \rightarrow Mg^{2+} + 2\,HCO_3^- \qquad (12b)$$

The rate constant k_{10a} is 8500 M^{-1} s^{-1} at 25 °C while the reaction 10b is instantaneous (http://pac.iupac.org).

According to the solubility product constants (6.8 x 10 ^{9} and 3-6x10 ^{6} M^2 for Mg and Ca, respectively), the precipitation of carbonates is favored. For comparison purposes, a control run using distilled water was carried out with an initial pH of 1 1 .5. Figure 2a shows the results obtained. As observed, when considering distilled water, approximately 10 days were required to lower the pH to suitable values to consider a biological post-treatment (pH ~ 8). pH evolution was accompanied by a fast decrease of the conductivity and divalent cations content in the first 4 days. Reaction 10a was responsible for the pH decrease. When $HCO3^-$ was formed, this species was immediately transformed to carbonate due to the existing alkaline conditions. Calcium and magnesium carbonates and/or hydroxides precipitated and a whitish solid was experimentally observed. Characterization of the solid is presented in Table 4. This precipitate is rich in calcium and magnesium. Once the pH was naturally lowered, reaction 12 occurred increasing the concentration of Mg^{2+}, HCO_3^-, and Ca^{2+} (see Fig. 2a), and consequently the conductivity values. By considering all the equilibrium reactions taking place and the CO_2 partial pressure under normal room conditions (P_{CO2}=3.5x10^{-4} atm, Henry's constant=29. 8 atm M^{-1}), the theoretical values of pH and Ca^{2+} should be8.27and18mgL^{-1}, respectively, close to the experimental values of 8.06 and 17.2 mg L^{-1}.



Time, h

Fig. 2 Atmospheric CO_2 carbonation process: natural evolution of different parameters in Distilled water after addition of $Ca(OH)_2$ to pH
11.5 a, Stored CWW_{80} after $Ca(OH)_2$ addition to pH12.0 b, and Fresh CWW80 after Ca(OH)2 addition to pH 11.5 c. Symbols: black circle, pH; black square, Mg^{2+}; black triangle, Conductivity; white circle, HCO_3^-; white square, Ca^{2+}

Similar neutralization experiments were conducted after the treatment of stored and fresh CWW_{80} with $Ca(OH)_2$ addition. Figure 2b, c shows the results obtained. One of the most interesting facts observed was the reduction of the time required for the neutralization, around 4-6 days, lower than the values (8-13 days) obtained using biological processes for CWW treatment (Gavala et al. 1999; Kalyuzhnyi et al. 1997; Rivas et al. 2010;Yangetal.2003).

Atmospheric CO2 was absorbed by pretreated wastewater surface, reacting with OH$^-$ and forming HCO3$^-$. The amount of accumulated HCO3$^-$ was however increased if compared to the blank run. HCO_3^- was transformed into CO_3^{2-}, which reacted with the ions existing in the pretreated wastewater to form calcium and magnesium carbonates. The formation of calcium and/or magnesium hydroxides can also take place. Consequently, decreases of the conductivity, calcium, and magnesium were also obtained in the first days. The divalent cation profiles also presented a concave shape; however, these profiles were less abrupt than those obtained in distilled water due to the faster neutralization of the media. After a certain time, an increase of the calcium and magnesium concentrations could be experienced, as well as a conductivity value rise. The obtained precipitates were also characterized (Table 4), containing principally sodium, calcium, potassium, and magnesium. As an average, total hardness of the final wastewater showed values in the proximity of 500 mg L^{-1} as $CaCO_3$, likely due to the stabilization of cations by complexation processes; however, the most important characteristics were the high biodegradability of the COD content and the pH value located around 8.0. Table 5 depicts the pretreated CWW characterization after atmospheric CO_2 carbonation (stored CWW80). In this atmospheric CO2 carbonation process, the concentrations of TS, sodium, phosphorus, and

Table 4 Characterization of the precipitates obtained in the atmospheric CO_2 carbonation process of pretreated CWW_{80} (dry matter = 94–100 %)

Parameter	Units	Control run (distilled water)		Stored CWW_{80}		Fresh CWW_{80}
		pH = 12.0	pH = 11.5	pH = 12.0	pH = 11.5	pH = 11.5
Dry weight	g L^{-1} of water	0.73	0.21	0.95–0.97	0.47	0.61
Organic matter	%	2.4	3.1	16.8–19.8	18.3	37.4
P	g kg^{-1}	–	–	–	0.304	0.814
Na	g kg^{-1}	0.841	2.641	166–178	355	178
K	g kg^{-1}	0.086	0.262	13.7–14.2	15.8	11.7
Ca	g kg^{-1}	355.8	339.6	90.5–120.9	66.3	37.2
Mg	g kg^{-1}	8.23	20.0	0.14–3.94	11.5	7.92

Table 5 Characterization of the pretreated CWW_{80} (stored) from basic precipitation with $Ca(OH)_2$ addition and atmospheric CO_2 carbonation

Parameter	Units	Interval	Average
pH	–	7.92–7.93	7.92 ± 0.01
Redox potential	mV	139.8–157.5	145.9 ± 10.0
Conductivity	dS m^{-1}	3.70–3.76	3.73 ± 0.03
COD	mg L^{-1}	767–1600	1044 ± 481
TS	g L^{-1}	2.4–2.5	2.5 ± 0.1
TVS	g L^{-1}	0.5–0.6	0.5 ± 0.1
TFS	g L^{-1}	1.9–2.0	1.9 ± 0.1
Total hardness	mg L^{-1} $CaCO_3$	405.2–442.0	429.7 ± 21.3
Kjeldahl-N	mg L^{-1}	3.4–8.4	6.6 ± 2.8
NH_3-N	mg L^{-1}	1.0–1.6	1.3 ± 0.3
P	mg L^{-1}	0.3–0.9	0.6 ± 0.3
Na	mg L^{-1}	1032–1060	1042 ± 16
K	mg L^{-1}	76.4–84.4	81.7 ± 4.6
Ca	mg L^{-1}	147.3–162.1	152.2 ± 8.5
Mg	mg L^{-1}	9.0–17.9	11.9 ± 5.2

Results after three replicates

COD chemical oxygen demand, *TS* total solids, *TVS* total volatile solids, *TFS* total fixed solids

magnesium decreased by 7, 11, 33, and 76 %. Another important finding was the successful reduction of Kjeldahl (92 %) and ammoniacal (98 %) nitrogen, as well as the mitigation of 53.24 and 146.42 mg of atmospheric CO_2 per liter of treated fresh and stored CWW80, respectively. Contrarily, the distilled water presented lower mitigation of atmospheric CO_2 (3.41 mg per liter of distilled water), since the HCO_3^- formation occurred for a reaction time greater than 100 h.

Sludge sedimentation

Precipitation with $Ca(OH)_2$ addition not only led to the best results in terms of organic removal but also in terms of sludge settling properties. The average settling velocity (VS)could be calculated by considering the slope of the sedimentation curve in the clarification zone, that is, the straight line at the beginning of the sludge sedimentation (Metcalf and Eddy 2003; Ramalho 1996). Hence, a settling velocity value of 5.2 cm min^{-1} was experienced for the sludge obtained in the precipitation with Ca(OH)2 addition of stored CWW80. Figure 3a depicts the sludge sedimentation curves as a function of time in triplicate experiments after $Ca(OH)_2$ addition to stored CWW80. At this point, it should be highlighted that the sludge formed when Ca(OH)2 was added to fresh CWW80 did show significantly poorer settling properties than those obtained with stored wastewater (about eight times lower average sedimentation velocity). However, in both cases, the final sludge volume was similar (results not shown).

Some preliminary calculations could be conducted to assess the sedimentation tank dimensions needed in continuous operation. Hence, the height-time curve (Fig. 3a) was fitted to an exponential expression given by Rivas et al. (2010):

$$h(t,h_o)=\frac{\alpha X_o h_o}{\beta}+\left[h_o-\frac{\alpha X_o h_o}{\beta}\right]\exp\left(-\frac{\beta}{X_o h_o}t\right) \qquad (13)$$

where t stands for the time; h(t, h_o) = sludge height at time t; h_o = initial sludge height; a and 3 = adjustable parameters for the sedimentation process, and X_o = initial total suspended solids concentration. The initial conditions were h_o=34cm

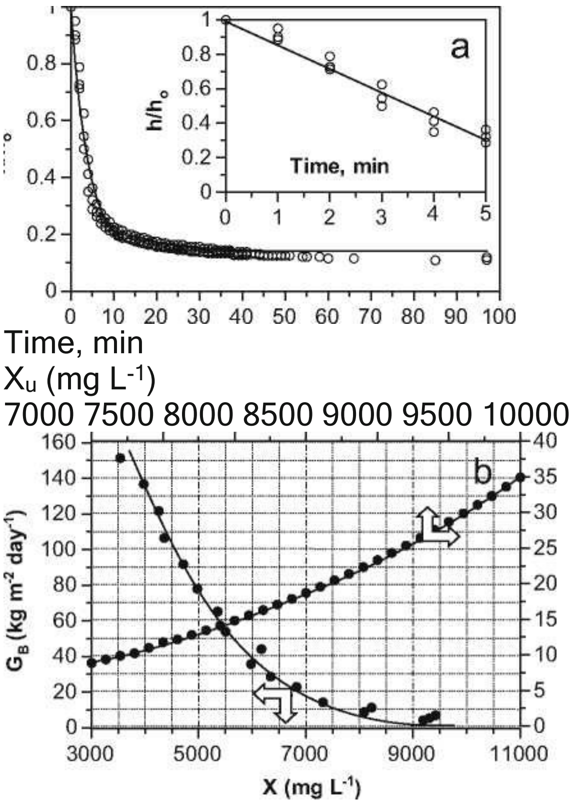


Fig.3 Settling profile of sludge after $Ca(OH)_2$ addition to stored CWW_{80} at pH 1 1.5 in a standard 1-L test tube (34 cm height) (a). Determination of settling tank area as a function of exit solids concentration (inlet solids concentration= 1937 mg L^{-1}) (b)

and X_o =1937mgL^{-1}. The following values for the adjustable parameters were achieved: a =1.22 cm min^{-1} and 3 = 16, 680 mg L^{-1} cm min^{-1} (R^2 ˜0.99). Solid concentration as a function of time and height could be determined by the following expression:

$$X(t,h)=\frac{X_o h_o}{h(t,h_o)-\left[\alpha-\frac{\beta}{X_o h_o}h(t,h_o)\right]t} \qquad (14)$$

The solids flow rate per surface unit in the settling tank (G_T, kg m^{-2} day^{-1}) should be considered for effluents with a high TSS content (>500 mg L^{-1}). The value of GT (global solid flow rate, GT=GB+GU) includes the solids flow rate due to gravity (GB) plus one due to the movement resulting from sludge outlet at the clarifier bottom (GU). GB, the solid flow rate in the clarifier due to gravity, was calculated by means of

$$G_B=X(t,h)\cdot v(t,h) \qquad (15)$$

where v(t, h) is the settling velocity corresponding to a sludge height of concentration X(t, h). The plot GB versus X(t, h) for stored CWW80 treated with Ca(OH)2 addition is displayed in Fig. 3b.

The design of a continuous clarifier is influenced by the compacting index, Y, a design variable set from the beginning. This parameter is defined as the ratio between the solid concentration in the concentrated sludge (X_u) withdrawn from the clarifier and the solid concentration fed (X_o), ($X_u = yX_o$) . The following step consists of plotting the tangent to the GB curve comprising the point (Xu, 0). The Y-axis intercept of this tan- gent provides G_T. The minimum tank sectional area was calculated by AT = QoXo/GT, being Qo, the volumetric CWW flow rate fed. Consequently, if Qo is supposed to be 1000 m^3 day^{-1}, a plot of A_T (m^2) versus X_u (mg L^{-1})is displayed in Fig. 3b. Depending on the compacting index, A_T values vary in the interval 8-35 m^2.

Sludge characterization and filterability

Once the sedimentation took place after $Ca(OH)_2$ addition to CWW, the sludge was collected and characterized. Table 6 shows the main properties of the solids obtained. As observed, the sludge presented an interval of 14-67 % (dry basis) of organic matter plus nutrients such as P, K, Mg, Ca, etc., suggesting the possibility of using this residue as a fertilizer.

In order to eliminate the water content of the sludge, some filtration experiments were conducted by using the experimental setup previously described. After filtration, natural evaporation of the remaining water at room temperature (20-25 °C) was applied. Figure 4a shows the evolution of the water volume collected in the filtration at the column bot- tom (base 1.0 L of sludge).

Pressure drop (AP_s) due to sludge accumulation on top of the filtration media is given by

$$-\frac{\Delta P_s}{L} = \frac{4.17\mu v(1-\varepsilon)^2 S_o^2}{\varepsilon^3} \qquad (16)$$

where (i is the viscosity of the filtrate, £ is the porosity of the accumulated sludge, So is the specific surface ofthe solid particles, v is the lineal velocity based on filtration sectional area, and L is the height ofthe accumulated sludge (cake). IfL is expressed as a function of filtration volume collected, the final expression is

$$\frac{dV}{Adt} = -\frac{\Delta P_s}{\psi \frac{\mu C_s V}{A}} \qquad (17)$$

where V is the volume of filtrate, A is the filter sectional area, C_s is the solids concentration in the media to be filtrated, and 4^1 stands for the specific resistance of the filtration cake. The resistance of the filtering material is located in series. As a

Table 6 Characterization of the sludge coming from CWW treatment with $Ca(OH)_2$ addition after sedimentation and after filtration and natural evaporation

Parameter	Units	After sedimentation						After filtration and natural evaporation	
		Without cheese whey recovery[b]		80 % cheese whey recovery[c]				80 % cheese whey recovery[c]	
		Stored		Fresh		Stored		Stored	
		Interval	Average	Interval	Average	Interval	Average	Interval	Average
pH	Sorensen scale (relation of sludge/water = 1:2.5)	12.64–12.73	12.69 ± 0.06	–	–	–	–	12.93–12.99	12.96 ± 0.03
Conductivity	dS m^{-1} (relation of sludge/water = 1:2.5)	11.62–11.99	11.81 ± 0.26	–	–	–	–	8.55–8.98	8.70 ± 0.24
Volume	mL L^{-1} of CWW	115.0–130.0	122.5 ± 10.6	62.5–75.0	68.8 ± 6.3	50.0–62.5	54.2 ± 7.2	–	–
Wet weight	g L^{-1} of sludge	–	–	948–994	977 ± 25	959–998	981 ± 20	–	–
Dry matter	%	10.7–11.5	11.1 ± 0.6	4.6–5.1	4.9 ± 0.3	7.7–12.3	9.4 ± 2.5	71.2–71.6	71.4 ± 0.2
Organic matter	% (wet basis)	1.2–1.9	1.6 ± 0.5	3.1–3.5	3.3 ± 0.2	1.4–2.3	1.7 ± 0.5	11.9–13.5	12.5 ± 0.9
Organic matter	% (dry basis)	11.0–16.7	13.9 ± 4.0	65.3-68.7	66.9 ± 1.7	17.7–18.7	18.1 ± 0.5	19.0–20.9	19.7 ± 1.0
Kjeldahl-N	g kg^{-1} (wet basis)	0.31–0.58[a]	0.44 ± 0.20[a]	–	–	0.13–0.61	0.45 ± 0.28	1.0–4.6	3.4 ± 2.1
P	g kg^{-1} (dry basis)	37.2–60.2	48.7 ± 16.3	10.0-10.6	10.4 ± 0.3	3.1–5.1	4.1 ± 1.0	2.7–2.9[d]	2.8 ± 0.1[d]
Cl	g kg^{-1} (dry basis)	–	–	–	–	–	–	6.0–6.5[d]	6.2 ± 0.2[d]
Na	g kg^{-1} (dry basis)	–	–	10.1–12.3	11.3 ± 1.1	4.4–7.2	5.9 ± 1.4	3.0–5.6[d]	4.4 ± 1.1[d]
K	g kg^{-1} (dry basis)	–	–	0.65–0.85	0.75 ± 0.10	0.33–0.41	0.36 ± 0.04	0.16–0.30[d]	0.21 ± 0.06[d]
Ca	g kg^{-1} (dry basis)	–	–	17.5–22.6	20.3 ± 2.6	32.4–58.8	46.7 ± 13.3	212.2–279.8[d]	245.3 ± 27.9[d]
Mg	g kg^{-1} (dry basis)	–	–	5.7–10.1	7.5 ± 2.3	1.2–4.5	2.5 ± 1.8	6.7–20.9[d]	13.6 ± 8.0[d]

[a] NH_3-N (wet basis), average = 0.017 ± 0.001 g kg^{-1}, range = 0.016–0.017 g kg^{-1}

[b] Results after two replicates

[c] Results after three replicates

[d] Results after four replicates

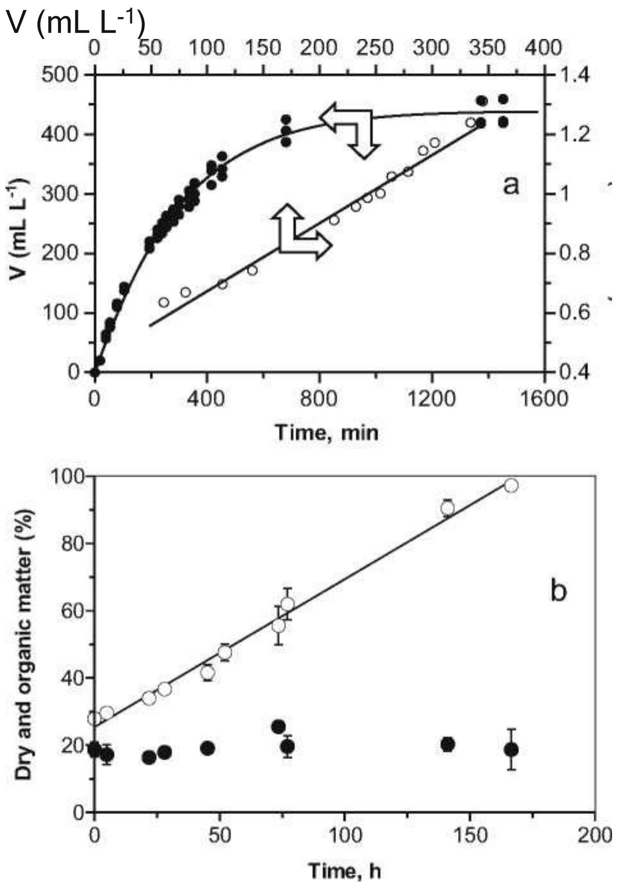


Fig. 4 Water volume collected during the filtration process—verification of Eq. 19 (a), dry and organic matter during the natural evaporation process (b) of the wet sludge formed in sedimentation experiments after

$Ca(OH)_2$ addition to stored CWW . a Symbols: black circle, Water volume collected from the filters; white circle, Verification of Eq. 19. b Symbols: black circle, Organic matter; white circle, Dry matter

consequence, the global resistance to filtration can be expressed as follows:

$$\frac{dV}{Adt} = -\frac{\Delta P}{\psi \frac{\mu C_s}{A}(V + V_e)} \tag{18}$$

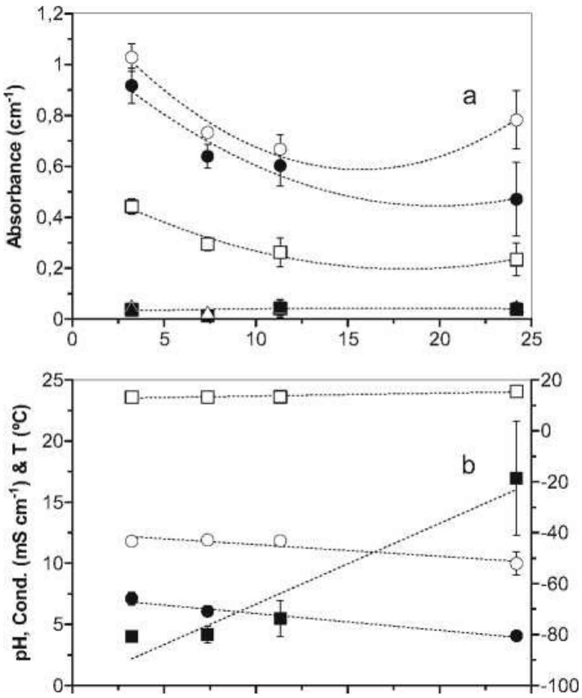
Now, AP is the total pressure drop and V_e is the volume of filtrated water to form a cake with resistance similar to the filtering media. After integration and mathematical manipulation, the following expressions can be deduced:

$$\frac{t}{V} = \frac{K_p V}{2} + B \tag{19}$$

$$K_p = \frac{\psi \mu C_s}{A^2(-\Delta P)} \tag{20}$$

$$B = \frac{\mu \psi C_s V_e}{A^2(-\Delta P)} \tag{21}$$

A plot of t/V versus V should lead to a straight line of slope $K_p/2$ and intercept B. Figure 4a illustrates this representation leading, after linear regression, to $K_p = 0.89$ min $(mL\ L^{-1})^{-2}$ and $B = 2.3 \times 10^{-3}$ min $(mL\ L^{-1})^{-1}$. Filtrated water showed an average COD value in the interval of 2.1-2.8gL^{-1} with a BOD_5/COD ratio always close to 1.0 (Fig. 5).



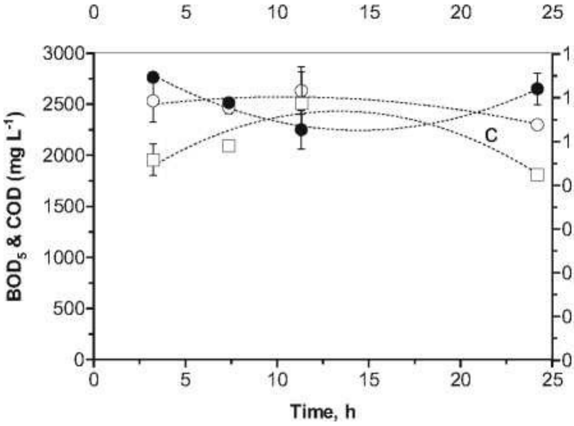


Fig. 5 Filtrated water characterization during the filtration process of the wet sludge formed in sedimentation experiments after Ca(OH)2 addition to stored CWW_{80}. a Absorbance values after 1 :20 dilution (Abs 220 nm) and 1:5 dilution (Abs 254, 292, 386, 385 and 410 nm). Symbols: white circle, Abs 220 nm; black circle, Abs 254 nm; white square, Abs 292 nm; black square, Abs 386 nm; white triangle, Abs 385 nm; black triangle, Abs 410 nm. b pH, conductivity, temperature, and redox potential. Symbols: white circle, pH; black circle, Conductivity; white square, Temperature; black square, Redox potential. c Organic matter (BOD_5 and COD) and biodegradability index. Symbols: white circle, BOD_5; black circle, COD; white square, BOD_5/COD

Natural evaporation of the filtration cake (evaporation for 1 week) led to a solid with only 2-4 % of humidity (see Fig. 4b). This sludge was characterized (Table 6) by a high content in organic matter (18-23 %, dry basis) and a N/P (as P_2O_5)/K(as K_2O) ratio of 14:27:1, similar to some salts based on different ammonium phosphates (with the logical exception of K). The Cl/Na ratio = 1.4 confirms that sodium chloride (Cl/Na = 1.5) is present in the sludge. As a consequence, if the sludge is to be used as fertilizer, cultivars resistant to saline conditions should be used (i.e., tomatoes).

Conclusions

CWW can be pretreated by simple precipitation and coagulation-flocculation processes rendering an effluent with an acceptable biodegradability character. If cheese whey is partially recovered before any treatment, the final COD (1.8-2.0 g L^{-1}) of the wastewater after the application of physicochemical processes is significantly reduced (up to 90 % COD removal if compared to raw CWW0). TSS, turbidity, conductivity, sodium, chloride, calcium, nitrogen, potassium, and phosphorus are also lowered when cheese whey is recovered. Among the processes studied, precipitation with $Ca(OH)_2$ addition offers some advantages, such as excellent settling properties of the generated sludge, low reagent costs, and good removal of COD, turbidity, TSS, oils and fats, phosphorus, nitrogen, potassium, and total coliforms. The sludge coming from the $Ca(OH)_2$ precipitation can be filtrated and dried. The characterization of this solid suggests the potential use as fertilizer with some restrictions due to the relatively high NaCl content. After the precipitation stage with $Ca(OH)_2$ addition, the supernatant naturally changes its pH to neutral conditions by atmospheric CO_2 absorption staying with a COD value in the range of 0.8-1.6 g L^{-1}, hence, no chemicals are required for the further biodegradation polishing stage. Furthermore, this carbonation process allows not only the wastewater treatment by reducing of TS, sodium, phosphorus, magnesium, Kjeldahl, and ammoniacal nitrogen, but also the sludge formation (precipitate) rich in organic matter and nutrients. Another important advantage of the natural carbonation of pretreated wastewater constitutes the atmospheric CO_2 mitigation.

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