Review

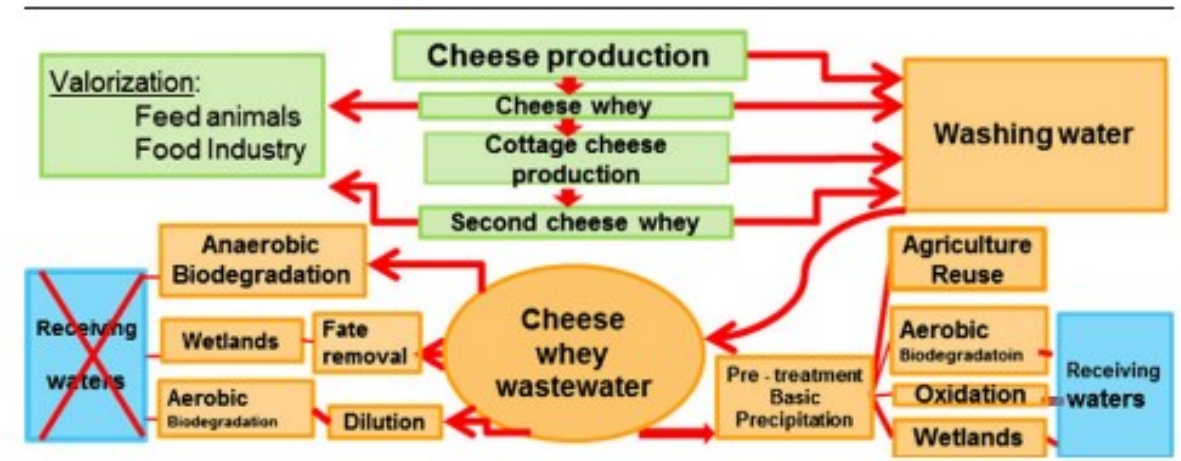
Cheese whey wastewater: Characterization and treatment

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HIGHLIGHTS

► This research presents an exhaustive characterization of cheese and other dairy effluents.
► We focus our attention on cheese whey wastewater as a strong biodegradable saline effluent.
► We report on the biological and physi- cochemical treatments of cheese whey wastewater.
► We show that a pre-treatment with chemical precipitation is a viable so- lution for these effluents.
► The implementation of zero discharge systems is possible for agricultural reuse.

GRAPHICAL ABSTRACT



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Abstract

Cheesewheywastewater(CWW)isastrongorganicandsalineeffluentwhosecharacterizationandtreatmenthave not been sufficiently addressed. CWW composition is highly variable due to raw milk used, the fraction of non val- orized cheese whey and the amount of cleaning water used. Cheese whey wastewater generation is roughly four times the volume of processed milk. This research tries to conduct an exhaustive compilation of CWW characteri- zation and a comparative study between the different features of CWW, cheese whey (CW), second cheese whey (SCW) and dairy industry effluents. Different CWW existing treatments have also been critically analyzed. The ad- vantages and drawbacks in aerobic/anaerobic processes have been evaluated. The benefits of physicochemical pre-stages (i.e. precipitation, coagulation-flocculation) in biological aerobic systems are assessed. Pre-treatments based on coagulation or basic precipitation might allow the application of aerobic biodegradation treatments with no dilution requirements. Chemical precipitation with lime or NaOH produces a clean wastewater and a sludge rich in organic matter, N and P. Their use in agriculture may lead to the implementation of Zero discharge systems.

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1. Introduction

The dairy industry is one of the main sources of industrial effluent generation in Europe (Demirel et al., 2005). This industry is based on the processing and manufacturing of raw milk into products such as yogurt, ice cream, butter, cheese and various types of desserts by means of different processes, such as pasteurization, coagulation, filtra- tion, centrifugation, chilling, etc. (Rivas et al., 2010). The characteristics of dairy effluents may vary significantly, depending on the final prod- ucts, system type and operation methods used in the manufacturing plant (Gutiérrez et al., 1991). These wastewaters are mainly composed by different dilutions of milk (or transformed products), and washing water containing alkaline and acidic chemicals after the cleaning of bot- tles, tanks, process equipment (tools, pumps).

From an environmental point of view, among the dairy effluent key parameters, a considerable high organic load should be highlighted. Dairy effluents, other than cheese effluents (see Table 1) are character- ized by an organic matter load below 15 g L^{-1} of COD and 5.0 g L^{-1} of BOD. Furthermore, typical intervals for fats and total suspended solids are 0.07-2.9 gL^{-1} and 0.2-5.1 g L^{-1}, respectively, also below the values reported for cheese effluents.

The generated volume of dairy wastewaters is quite variable depending on the different types of industry, techniques, processes and equipment. Table 2 summarizes the water consumption (L water per L of milk) in the manufacturing of different dairy products, include cheese products.

2. Characterization of cheese effluents

According to FAO (Food and Agricultural Organization) cheese is one of the main agricultural products worldwide. The European Union dominates its production and consumption, followed by the United States. Whatever type of cheese (Parmesan, Mozzarella, Gouda, Danish blue, Brie, Camembert, Feta, Serpa, etc.), the making factories generate effluents that represent a significant environmental impact (Ghaly and Singh, 1989; Comeau et al., 1996; Siso, 1996; Berruga et al., 1997; Lee et al., 2003). Cheese effluents exhibit COD values in the interval 0.8-102 g L^{-1} and BOD values in the range 0.6-60 g L^{-1} leading to a high consumption of dissolved oxygen in

Nomenclature

AS	Activated sludge
CSTR	Continuously stirred tank reactors
SBR	sequencing batch reactor
UASB	up flow anaerobic sludge blanket
VMBS	Vertically moving biofilm system

water bodies. The lactose and fat contents can be considered as the main responsible for COD and BOD.

With their very high concentra- tion of organic matter, these effluents may create serious problems of organic burden on the local municipal sewage treatment systems (Janczukowicz et al., 2008).

Normally, this effluent has a low pH, although basic pH's have also been reported in the wide interval 3.3-9.0. Suspended solids, TKN, and total phosphorus oscillate in the intervals (g L^{-1}) 0.1-22.0, 0.01 -1.7 and 0.006-0.5, respectively. Due to the total nitrogen and phosphorus contents, cheese effluents pose a considerable risk of eu- trophication in receiving waters (Prazeres et al., 2012) particularly in lakes and slow moving rivers. Eutrophication leads to many water quality problems including increased purification costs, interference with the recreational and conservation value of impoundments, loss of live-stock and the possible sublethal effects of algal toxins on ani- mals and humans. Furthermore, the ammonium nitrogen ($NH4^+$-N) value ranging from 60 to 270 mg L^{-1} can also cause toxic effects to aquatic life (Farizoglu et al., 2007).

In addition, cheese effluent composition can be approached to the following ratio for carbon, nitrogen and phosphorus C/N/ P«200/3.5/1 which may be considered as deficient in terms of ni- trogen components for aerobic or anaerobic processes (Prazeres et al., 2012).

Regardless ofthe cheese type, the making cheese process involves common general procedures that can be summarized as follows. The milk used in cheese manufacturing is stored at a low temperature in stainless steel tanks. Thereafter milk is sent to coagulation by the ad- dition of microbial or vegetable rennet. After the required time, the fermented milk produces the curds that are cut and converted to the commercial product. Part of the cheese whey (CW) resulting from hard cheese production is processed to obtain cottage cheese or curd cheese (Michaelis, 1995). The production of cottage cheese leads to the generation of the so called second cheese whey (SCW) or cottage cheese whey.

The cheese manufacturing industry is responsible for the three main types of effluents; cheese whey (resulting from cheese production), second cheese whey (resulting from cottage cheese production) and the washing water of pipelines, storage and tanks that generates a wastewater called cheese whey wastewater (CWW). This effluent also contains CW and SCW.

2.1. Cheese whey (CW)

The whey is a by-product from the cheese or casein manufacturing. This effluent is a greenish-yellow liquid and can be considered as milk free ofcasein and fat (Daufin et al., 1998).

Casein precipitation leads to the formation of two whey types. Acidic whey (pH b 5) is obtained after fermentation or addition of or- ganic or mineral acids. Sweet whey (pH = 6-7) is obtained by

Table 1
Physical and chemical characteristics of the dairy effluents.

Effluent type	pH/EC	BOD_5	COD	BOD_5/ COD	TS	TSS	VS	VSS	Fats	TN	TKN	$N\text{-}NH_4^+$	$N\text{-}NO_3^-$	Cl^-	TP	PO_4^{3-}	K	Reference
Butter	12.08	2.42	8.93	0.27	–	5.07	–	–	2.88	–	–	–	–	–	–	–	–	Janczukowicz et al. (2008)
Dairy	6.69	–	15	–	0.0065	–	–	–	–	–	–	–	–	–	–	–	–	Mendes and Castro (2005)
Dairy farm	6.8–7.4	–	2.20–10.45	–	0.23–1.32[b]	0.02–0.07[b]	–		–	0.054–0.899	–	–	–	–	0.015–0.041	–	0.338–0.805	Ali et al. (2007)
Ice–cream wastewater	5.2	2.45	5.2	0.47	3.9	3.1	2.6	2.1	–	–	0.05	0.015	–	–	–	0.014	–	Borja and Banks (1995)
Ice–cream wastewater	6.96 ± 0.33	–	4.94 ± 1.16	–	–	1.04 ± 0.40	–	0.99 ± 0.42	–	–	–	–	–	–	–	–	–	Hawkes et al. (1995)
Milking shed	6.5–8.1	–	1.65–4.0[a]	–	–	–	–		–	0.074–1.15	–	0.048–0.82	0–0.56	–	–	–	–	Williamson et al. (1998)
Milk factory	6.23 ± 0.54	0.104 ± 0.009	0.183 ± 0.022	0.57	0.101 ± 0.006	–	–	–	–	–	–	0.005 ± 0.0002	0.584 ± 0.19	–	–	–	–	Mishra et al. (2000)
Milk factory	4.0–7.0	3.0–5.0	5.0–10.0	0.53	3.0–7.0	–	–	–	0.07–0.50	–	0.05–0.15	–	–	–	0.05–0.07	–	–	Siriamuntapiboon et al. (2005)
Milk factory	–	–	–	–	1.31	0.7	–	–	–	–	–	–	–	–	–	–	–	Verheyen et al. (2011)
Milk reception point	7.18	0.80	2.54	0.31	–	0.65	–	–	1.06	–	–	–	–	–	–	–	–	Janczukowicz et al. (2008)
Mixtures of dairy and domestic wastewater (2.33:1)	7.9 ± 1.2	1.94 ± 0.86	3.38 ± 1.35	0.57	–	0.83 ± 0.39	–	0.75 ± 0.21	0.263 ± 0.023	–	0.051 ± 0.006	–	–	–	0.022 ± 0.005	–	–	Tawfik et al. (2008)
Pumping station	8.35	1.75	4.44	0.39	–	1.07	–	–	0.57	–	–	–	–	–	–	–	–	Janczukowicz et al. (2008)

Parameters expressed in g/L, with exceptions: EC (mS/cm); BOD_5/COD (adimensional); $N\text{-}NO_3^-$ (mg/L); [a] (as TOC); [b] (%).

addition of proteolytic enzymes like chymosin (Panesar et al., 2007). The milk type used in the cheese production (cow, goat, sheep, buffa- lo and other mammals) also influences the characteristics of the produced cheese whey. As an example, in a dry basis, bovine whey
contains 70-80% of lactose, 9% of proteins, 8-20% of minerais and other minor components, such as some hydrolyzed peptides of k-casein, lipids and bacteria (Daufin et al., 1998). Sheep whey has a ratio total nitrogen/dry matter much higher than the one existing in bovine whey, doubling the content in soluble proteins (Assenat, 1985).

From the valorization point of view, cheese whey has a high nutritional added value (Vasala et al., 2005; Prazeres et al., 2012). In addition, some authors have claimed that the processing ofwhey proteins can also be used for therapeutic purposes such as antioxidants and as antihypertensives (Macedo, 2010) because they release, by hydroly- sis, bioactive peptides witch can trigger physiological effects in the human body. Madureira et al. (2010) describe some of those effects, such as: on the nervous system; on the cardiovascular system via their antithrombotic and antihypertensive activities; on the immune system via their antimicrobial

and antiviral activities; and on the nutrition system via their digestibility and hypocholesterolemic effects.

As arule ofthumb, theacidicwheyhas ahigherashand lower protein content than sweet whey. Acid coagulation occurs close to the isoelectric pH of casein (pH 4.6), as a consequence, more milk protein precipitates. Acid whey has a limited use due to the acidic taste and high salt content (Weetal et al., 1974; Kosikowski, 1979; Mawson, 1994). Calcium (1.21.6 g L^{-1}) concentrations in acidic whey are approximately 2 times higher than the values observed in sweet whey. Thus, in the acidic coagulation, colloidal calcium contained in the casein micelles is solubilized and partitioned into the whey (Panesar et al., 2007). The lactose level is, however, higher in sweet whey than in acidic whey.

Cheese whey is considered the most important pollutant in dairy wastewaters, not only because of the high organic load, but also for the volume generated. The amount of whey produced is related to the productivity of cheese. This productivity is also related to the type of milk processed (Table 3).

The main physicochemical characteristics of CW are summarized in Table 4. Key parameters of cheese whey show a biological oxygen demand in the range 27-60 g L^{-1} and a chemical oxygen demand in the interval 50-102 g L^{-1}. Comparing the organic load of domestic wastewater (Metcalf and Eddy, 2003) with organic load of cheese whey, we can conclude that the load is equivalent to the pollution load of one hundred times the volume of common domestic waste- waters (Mockaitis et al., 2006). The BOD/COD ratio is normally above 0.5 constituting a substrate easily biodegradable by anaerobic or aerobic digestions (Prazeres et al., 2012). Total suspended solids have values within 1.3-22.0 g L^{-1}. The high CW salinity (conductivity in the proximity of 8 mS cm^{-1}) is the consequence of the type of whey produced in the process and NaCl addition during cheese production. Additionally, other minor components such as citric and lactic acids (0.02-0.05%), non-proteinic nitrogen compounds (urea and uric acid), and vitamins (B group), can also be found in CW (Kosikowski and Wierzbicki, 1973; Kosikowski, 1979; García Bilbao, 1981; Panesar et al., 2007).

Acidic pH favors the filamentous biomass growth (Ghaly, 1996). The low buffering capacity ofCW is responsible for the rapid acidification in biological treatments (Castelló et al., 2009). The main mineral components (>50%) are NaCl, KCl and calcium salts (Dragone et al., 2009; Venetsaneas et al., 2009). The high sodium content of CW can cause problems when operating biological digesters (Backus et al., 1988). Lactose is the main responsible of the organic load, (Kisaalita et al., 1990; Ghaly and Kamal, 2004) and an extensive number of microorganisms cannot directly use it as a carbon source (Siso, 1996). In addition, microorganisms may require tight conditions and addition of some supplementary Chemicals (Torija et al., 2003; Aktaç et al., 2006).

2.2. Second cheese whey (SCW)

As stated in Section 2, when cheese whey is used in cottage cheese production, it generates the second cheese whey (SCW).

Similarly to CW, this by-product is also a highly polluting effluent with a negative impact on aquatic environments. Second cheese whey has about 60% of the dry matter content of the original cheese whey (Pereira et al., 2002). Only few authors have reported studies featuring the second cheese whey. Table 5 depicts the main characteristics of SCW. This effluent maintains a significant organic matter content (COD values up to 80 g L^{-1}) and high salinity (7-23 mS cm^{-1}). This high sa- linity comes from the second addition of salts like calcium chloride in the cottage cheese production. Once more, lactose (around 50 g L^{-1}) is the principal constituent responsible of the high COD values (>70%).

The SCW has acidic characteristics with pH values within the range 3-6. A biodegradability value close to 0.5 makes these effluents suitable to undergo biological degradation. Protein («0.5-8 g L^{-1}), total solids (« 6.8 g L^{-1}) and total nitrogen (2 g L^{-1}) contents are similar to those reported for CW. The values of COD (60-80 g L^{-1}), BOD («30 g L^{-1}), fats (0.5-8 g L^{-1}) and total suspend solids («8.0 g L^{-1}) are normally below the maximum values observed in CW. These lower values are the consequence of the second flocculation carried out to obtain the cottage cheese. The second flocculation is accomplished by heating the CW at 100 °C. Formation of agglomerates that trap suspended solids, proteins and fats, occurs during the process. Inanycase, SCWstill keeps ahigh lactose concentration similar to that observed in CW. SCW is normally free of amino acids and vitamins (Minhalma et al., 2007).

Some researches designate the second cheese whey as deproteinized CW. However, this term can be confounded with the cheese whey permeate coming from membrane processes (Domingues et al., 2001; Sansonetti etal., 2009;Dragoneetal., 2009) orthe supernatant obtained by heating/autoclaving/precipitation followed by centrifugation/filtration, (Mostafa, 1996; Roukas and Kotzekidou, 1998; Lee et al., 2003; Mukhopadhyay et al., 2003; Silva et al., 2010; Dragone et al., 2011). The main goal to be achieved when deproteinizing these effluents should be the reduction of protein and fat contents, maintaining a high level of lactose within the range 34-50 g L^{-1}. A second step would in- volve a fermentation stage to produce lactic acid, ethanol or hydrogen.

2.3. Cheese whey wastewater (CWW)

Cheese whey wastewater presents characteristics similar to CW; however, the contamination level of CWW is usually lower than CW. The pollution level of CWW is variable and can be explained by considering that CWW can be generated after different procedures:

1. Cheese whey is not used in the cottage cheese production and is directly added to washing water.
2. Cheese whey is used in cottage production and second cheese whey is added to washing water.
3. CW and CCW are valorized and are not added to the washing water.

Additionally, the variability can also be attributed to the raw milk characteristics (see Table 3) and volume of the washing water used

Table 3
Production of whey volume, according to the yield of cheese, by type of milk labored.

Type of milklabored	average density milk (g cm^{-3})	Yield kg cheese/ 100 kg milk)	Volume of whey produced (L L^{-1})	Reference
cow	1.032	9.86	0.873	Fox *etal.*, 2000
		-	0.85-0.90	Mizubuti, 1994; Serpa *et al.*, 2009
sheep	1.036	14.78	0.822	Fox *et al.*, 2000
		-	0.85-0.90	Mizubuti, 1994 ; Serpa *et al.*, 2009
goat	1.034	9.84	0.872	Fox *et al.*, 2000
		-	0,85-0,90	Mizubuti, 1994; Serpa *et al.*, 2009

(see Table 1). The amount ofcheese whey wastewater varies according to the country, factory, methodologyapplied, type ofmilklabored orthe environmental conscience.

According to the considerations made earlier, the volume ofCWW (VCWW) generated during the production of cheese can be calculated by Eq. (1).

$$^{V}CWW = {}^{V}H2Oconsumed + {}^{n} * {}^{V}CW$$

In Eq. (1),VH2Oconsumed is the volume ofwater consumed in the pro- cess of cheese making and secondary activities (cleaning of facilities, equipment); VCW is the volume of CW produced in the factory and n represents the coefficient of CW not valorized. If CW is not valorized and is added to washing wasters, n=1.

Besides the dilution of CW and SCW components, cheese whey wastewater (CWW) still represents a negative environmental impact.

The main characteristics ofCWW are shown in Table 6. Due to the presence of CW and/or SCW, cheese whey wastewater generally pre- sents acidic characteristics; however basic pH's have also been reported. This parameter is logically affected by the volume of alkaline reagents used in washing stages. In general, CWW has an elevated concentration of organic matter, however values in a wide range from 0.8to77(COD)and0.6to16gL^{-1} (BOD) can be found in the literature (Fang, 1991; Gutiérrez et al., 1991; Kalyuzhnyi et al., 1997; Gavala et al., 1999; Yang et al., 2003; Lee et al., 2006; Janczukowicz et al., 2008; Martins etal., 2010; Rivas etal., 2010; Rivas et al., 2011). The high biode- gradability index (BOD/COD«0.46-0.80) suggests the suitability ofbio- logical process application. Lactose, protein and fat contents average concentrations of 45, 34 and 6 g L^{-1}, respectively (Yang et al., 2003; Kalyuzhnyi et al., 1997). The low values of lactose and protein observed by some authors can be explained by the tendency to acidification due to the fermentation of lactose to lactic acid. As a result, the lowering of the initial pH causes the casein precipitation (Nemerow and Dasgupta, 1991) and a disagreeable odor of butyric acid (see Fig. 1). Additionally, the CWW fat content can bring about sludge floatation (see Fig. 1.) and the washout ofactive microbial biomass in biological processes (Perle et al., 1995). The level of total suspended solids is reported to be in the range 0.1-5.0 g L^{-1} (Fang, 1991; Gutiérrez et al., 1991; Gavala et al., 1999; Lee et al., 2006; Janczukowicz et al., 2008; Rivas et al., 2010)

Table 2

Table 2
Bibliographic compilation:Water consumption (by milk received, LL^{-1}) for the manufacture of various dairy products.

Product	Australia	Belgium	Brazil	Finland	Denmark	Norway	New Zealand	Sweden	Portugal	Reference
butter	2.5	0.7-7.2	1.1	1.7-8.6	-	4.6-7	1.4-6.9	-	-	Saraiva et al., 2009
milkpowder	2.5	0.7-7.2	-	1.7-8.6	0.69-1.9	4.6-7	1.4-6.9	1.7-4.0	-	Saraiva et al., 2009
acid casein	-	-	-	-	-	-	1.7-3.2	-	-	Saraiva et al., 2009
yogurt	-	-	10	1.2-2.9	0.6-0.97	4.1	-	0.96-2.8	-	Saraiva et al., 2009
cheese	-	-	-	2.0-3.1	1.2-1.7	2.5-2.8	-	2.0-2.5	3.21	Djamila, 2011
	-	-	-	1.55	-	-	-	-	-	Saraiva et al., 2009
	-	-	-	-	-	-	-	-	5	Rivas *et al.*, 2010
Cottage cheese	-	-	1.4	-	-	-	-	-	-	Saraiva et al., 2009

Table 4

Table 4
Physical and chemical characteristics of cheese whey.

pH/EC	Lactose/ LA	Proteins	Fats and oils	Mineral salts	BOD_5	COD	BOD_5/ COD	TS	TSS	TVS	TN	TKN	$N\text{-}NH_4^+$	$N\text{-}NO_3^-$	TP	$P\text{-}PO_4^{3-}$	Reference
5	–	–	–	–	40–60	75.8	0.53–0.79	56.8	21.82	47.9	–	1.5	0.27	–	–	–	Ghaly and Singh (1989)
–	–	–	–	–	–	68.8 ± 11.5	–	3.19[b]	1.3 ± 1.14[b]	3.37[b]	–	1.46 ± 0.26	0.064	9.1	0.38 ± 0.05	–	Malaspina et al. (1996)
–	45–50/ 0.5	6–8	4–5[d]	8–10[a]	30–50	60–80	0.50–0.63	–	–	–		–	–	–	–	–	Siso (1996)
3.92	–	–	–	–	–	74.5 ± 0.4	–	–	9.4 ± 0.5	–	–	0.146	–	–	0.124	–	Ergüder et al. (2001)
4.9	50	–	–	–	–	74.2	–	66.83	22.15	–	–	1.49	0.17	–	–	–	Ghaly and Kamal (2004)
4.5–5.0	–	–	–	–	–	73–86	–	–	20–22	–	0.9–1.2	–	0.06–0.15	7–10	0.42–0.54	0.34–0.43	Farizoglu et al. (2004, 2007)
–	3.9[a]	0.72[a]	0.79[a]	0.46[a]	–	–	–	5.87[a]	–	–	–	–	–	–	–	–	Rektor and Vatai (2004)
4.2	49.2	–	–	–	–	102.1	–	70.9	–	–	1.76	–	–	–	–	–	Ferchichi et al. (2005)
3.8–6.3	–	–	–	–	35.5–46.0[c]	60.3–66.7	–	–	4.1–10.0	–	–	–	–	–	–	–	Blonskaja and Vaalu (2006)
4.9 ± 0.3	45.9 ± 0.88	2.71 ± 0.05	9.44 ± 1.14	–	37.7 ± 2.8	68.6 ± 3.3	0.55	5.93 ± 0.38[a]	1.35 ± 0.06	5.61 ± 0.36[a]	–	1.12 ± 0.01	–	–	0.5 ± 1.8×10^{-3}	–	Saddoud et al. (2007)
–	43.92	1.42	0[a]	6.1		100	–	–	–	–	–	–	–	–	–	–	Yorgun et al. (2008)
5.8	–	–	0.99	–	29.5	73.4	0.4	–	7.2	–	–	–	–	–	–	–	Janczukowicz et al. (2008)
4.46 ± 0.3/7.6 ± 0.15	–	125 ± 2[b]	0.9 ± 0.5[a]	–	40 ± 2.55	60 ± 10	0.67	59 ± 0.5	1.5 ± 0.23	–	–	–	–	–	–	–	Gannoun et al. (2008)
4.7	42.6	–	–	–	–	86.3	–	–	6.9	–	0.2	–	–	–	–	–	Azbar et al. (2009)
6.0–6.5	50–60	–	–	–	27–36	50–70	0.51–0.54	55–65	10–15	–	–	0.01–0.02	–	–	–	–	Ebrahimi et al. (2010)

Parameters expressed in g/L with exceptions: EC (mS/cm); BOD_5/COD (adimensional); $N\text{-}NO_3^-$ (mg/L); [a](%); [b](g/kg); [c](as BOD_7); [d](as lipids).

Table 5

Table 5
Physical and chemical characteristics of second cheese whey.

pH	EC	Lactose	Protein	Fats	TOC	COD	BOD_5	BOD_5/COD	TS	TSS	TN	TKN	NH_3-N	TP	Dry matter	Reference
4.5	–	45.0	8.2[c]	–	–	79.0	–	–	6.8[a]	–	2.0	–	0.7	–	–	Wildenauer and Winter (1985)
3.3	7.7	–	–	–	–	–	–	–	–	–		–	–	1.58	–	Robbins and Lehrsch (1992)
–	–	–	0.49 ± 0.09[a]	0.53 ± 0.28[a]	–	–	–	–	–	–		–	–	–	6.71 ± 0.64[a]	Pereira et al. (2002)
6.2	23.3	50.6	8.3[b]	–	31.2	–	–	–	–	–		1.74	–	–	–	Minhalma et al. (2007)
5.4	–	–	–	0.49	–	58.5	26.8	0.46	–	8.3		–	–	–	–	Janczukowicz et al. (2008)

Parameters expressed in g/L with exceptions: EC (mS/cm); BOD5/COD (adimensional); TP (g/kg); [a](%); [b]Protein and free amino acids; [c]Protein (g/l) = (total nitrogen − ammonia) × 6.25 (6.25 = factor for 16% N-content of protein).

while total solids average values of roughly 65 g L^{-1} (Yang et al., 2003; Janczukowicz et al., 2008).

The high salinity (11-14 mS cm^{-1}) is the result of previous salt addition in the cheese and cottage cheese production. As a result, sodium and chloride levels are extremely high (2.1-2.8 g L^{-1}). The values reported in total nitrogen (0.5-10.8 mg L^{-1}) and phosphorus (6-280 mg L^{-1}) indicate a serious risk of receiving water eutrophication.

3. Cheese whey wastewater treatments

3.1. Biological treatments

3.1.1. Anaerobic digestion

The conventional treatments ofCWW effluents are based on anaer- obic and aerobic digestion processes (see Table 7). A number of re- searchers have claimed that the anaerobic processes are essentially the only viable method of wastewater treatment with high organic load from cheese making-plants (Sayedm et al., 1988; Gutiérrez et al., 1991; Hawkes et al., 1995; Gavala et al., 1999). Accordingly, the major- ity of studies

have been conducted under anaerobic conditions using Upflow Anaerobic Sludge Blanket (UASB) reactors applied to raw CWW (Gutiérrez et al., 1991; Kalyuzhnyi et al., 1997; Gavala et al., 1999)anddilutedCWW(Gavala et al., 1999). COD removal values in the interval 81-99% (raw CWW) and 85-98% (diluted CWW) have been reported. Despite the significant COD removal obtained by the an- aerobic digestion of raw CWW, in some cases, the residual COD of the effluent still presents unacceptable values as high as 11.4 g L^{-1}. The effluent obtained after treatment of diluted CWW presents a residual COD in the range 00.74-5gL^{-1}. The required HRT seems to be highly de- pendent on initial COD concentration. Thus, COD values above 5 g L^{-1} require more than 2 days of digestion reaching up to 13 days.

Due to their highly flocculation capacity with elevated sludge settling and compaction, the use of the up flow anaerobic sludge blanket (UASB) reactors to treat CWW has been recommended. However, this reactor configuration is not the best option to deal with CWW with high initial COD>40-42 g L^{-1}. In the latter case the CSTR configuration is suggested (Gavala et al., 1999).

The continuously stirred tank reactors (CSTR) and vertically moving biofilm system (VMBS) configurations have been used to treat diluted (Yang et al., 2003) and synthetic (Rodgers et al., 2004) CWW, respectively. In the first case, a COD conversion in the range 94.6-96.4% could be achieved under thermophilic conditions and 10 days of hydrau- lic retention time. However the effluent presents residual COD values 4 times higher than the legal limit. Regarding the synthetic CWW treatment, 89% of COD elimination was obtained under mesophilic conditions and 1 day of Hydraulic retention time. The residual COD of the effluent obtained showed values close to 4 g L^{-1}. These authors achieved a 63-70% of methane in the biogas. The methane yield in the range 0.30-0.35 m^3 CH4 kg^{-1} COD was close to the theoretical methane pro- duction (0.35 m^3 m^3 CH4 kg^{-1} COD).

The biological degradation of CWW is characterized by unstable operation. Supplementation of alkalinity is necessary during the start-up period, (Gutiérrez et al., 1991; Kalyuzhnyi et al., 1997)or during the process (Gavala et al., 1999; Yang et al., 2003; Rodgers et al., 2004). Additionally, when the CWW has a high content of CW, the production of volatile acids by acetogenic bacteria is faster than the consumption by the methanogenic bacteria and VFA accumulates in the reaction media (Gutiérrez et al., 1991). This effect causes a re- duction of the pH and COD elimination extent (Rodgers et al., 2004). Another disadvantage of CWW anaerobic biodegradation is the diffi- culty of granular sludge formation when acidification occurs (Yang et al., 2003). The partial-acidification with formation of the best precursors of methane (acetate and butyrate) in a two-phase reactor decreases the reactor volume and the required HRT. The two-phase reactor increases the COD removal and the methane production com- pared to a single-phase reactor (Yang et al., 2003).

3.1.2. Aerobic digestion

Some studies have been carried out under aerobic conditions to treat raw CWW, mainly by activated sludge (Fang, 1991; Martins and Quinta-Ferreira, 2010; Rivas et al., 2010; Rivas et al., 2011)withhigh eliminations of the principal contaminant indicators (see Table 7). In the majority of cases the process has been conducted by using high HRTs(8 days). High HRTs sometimes involve limitations inoxygentrans- fer rates (Gutiérrez et al., 1991). The biodegraded effluent obtained presented a residual COD higher than the legal limit.

Fang (1991), reported a reduced HRT («19.8 h) by using a low initial COD cheese wastewater. This author completed some activated sludge experiments in three stages achieving a residual BOD lower than the value legally permitted for direct discharge. The aerobic di- gestion achieved an 89% of COD elimination. The consecutive anaerobic+aerobic digestions were tested thereafter. This sequence led to COD removals close to 99% and an effluent in accordance with the legal limit value. Similar results were reported by Frigon et al. (2009), when treating a reconstituted CW in a SBR system. The COD reduction was 98% and the residual COD was only 33 mg L^{-1}. However the initial COD of the reconstituted CW (2.0 g L^{-1}) does not approximate to the actual organic load of typical CWW.

Rivas et al. (2010, 2011), stated that when CWW was firstly pretreated by a coagulation-flocculation process (FeCl3 and Al2(SO4)3) or by alkaline precipitation (lime or NaOH), the HRT of an activated sludge system could be reduced 4-5 times if compared to raw CWW for similar COD removals (94-97%). The effluent obtained presented a residual COD value between 0.27 and 0.45 g L^{-1}.Normally, the aerobic biodegradation is limited by excessive sludge formation (Gutiérrez et al., 1991); however Rivas et al. (2010), minimized this effect when ap- plying the aerobic digestion to a precoagulated CWW.

3.2. Physicochemical treatment

3.2.1. Coagulation/flocculation and precipitation

Among the different physicochemical processes available (see Table 8), coagulation-flocculation is likely the most simple and eco- nomical system. The existence of proteins (mainly casein with an iso- electric point

of4.6) and further pH increase involve the precipitation of these species. In fact a higher COD removal has been reported by using FeSO4 at pH 8.5 than FeCl3 utilized at pH 4.5 (Rivas et al., 2010). Rivas et al. (2010), compared the performance of two

Table 6
Physical and chemical characteristics of cheese whey wastewater.

pH/EC	Lactose	Proteins	Fats and oils	BOD	COD	TOC	BOD_5/COD	TS	TSS/turbidity	VS	TN[a]	TKN	N-NH_4^+[a]	TP[a]	Cl	Reference
7.0±2.0	–	–	–	0.90±0.31	1.62±0.56	0.55±0.17	0.55±0.09	–	0.26±0.18	–	–	0.11±0.08	8.5±6.3	–	–	Fang (1991)
5.5–7.7	–	–	0.075–0.60	–	0.79–6.55	–	–	1.1–6.4	–	0.89–4.16	10.82	–	–	6–47	–	Gutiérrez et al. (1991)
4.3–8.7	–	2.3–33.5	0.4–5.7	–	5.4–77.3	–	–	3.9–58.9	–	3.1–48.7	0.5–5.6	–	–	–	–	Kalyuzhnyi et al. (1997)
4.7	–	–	–	–	40–60	–	–	–	1–5	–	–	0.83	–	280	–	Gavala et al. (1999)
5.92	44.37±0.88	9.06	–	–	71.41	35.4	–	62.44±2.9	–	–	–	1.61±0.11	161±1	–	–	Yang et al. (2003)
–	16.35±0.71	1.88±0.08	–	–	19.73±0.62	–	–	20.13±0.06	1.12±0.07	18.4±0.02	–	0.34±0.02	–	–	–	Lee et al. (2006)
7.83–7.90	–	–	0.33–0.95	2.6–3.5	11.8–17.6	–	0.15–0.29	–	0.94–3.38	–		–	–	–	–	Janczukowicz et al. (2008)
4.1		–	–	5.1±1	11.2±1.1	2.5±0.05	0.46	–	–	–		–	–	–	–	Martins et al. (2010); Martins and Quinta-Ferreira (2010)
4.0–4.6/11.3–13.5	0.178–0.182	(938–947)×10^{-6}	1.83–3.76	10–12.5	8.8–25.6	–	0.79–1.17	7.0–8.3	1.6–4.8/1331–2004	–	–	0.31–0.36	52–71	6.6–7.2	2.1–2.8	Rivas et al. (2010)
–	0.18±0.003	(943±6)x10^{-6}	–	14.8±1.5	18.5±1.4	–	0.8	7.7±0.6	–/1331±219	–	–	0.34±0.02	56.4±7.3	6.6±0.3	2.41±0.25	Rivas et al. (2011)

Parameters expressed in g/L with exceptions: EC (mS/cm); redox potential (mV); BOD5/COD (adimensional); turbidity (NTU); [a](mg/L).

coagulants based on ferrous and ferric iron. These authors found a similar optimum reagent dose in both systems (0.25 g L^{-1}). Howev- er a better BOD removal was obtained by using Fe (II) instead of Fe (III). Both systems showed acceptable phosphorus and turbidity re- movals. The supernatants still maintained a significant biodegradable character enabling a post-aerobic biodegradation with a short HRT.

Also Rivas et al. (2011), checked the viability of a precipitation process under alkaline conditions by using lime or NaOH. Almost 50% of COD was removed in the process. Similarly to the coagulation-flocculation stages with iron salts, the supernatant was highly biodegradable. Moreover, the pre-treated CWW presented an odorless and colorless aspect with low fat (0.2 g L^{-1}) and TSS (60-80 mg L^{-1}) contents (see Fig. 2). The high values of nutrients such as total nitrogen (=1804.4± 126.2 mg N L^{-1}), calcium (Ca^{2+}=402.2±0.9 mg L^{-1}), magne- sium (Mg^{2+}=14.0±1.6 mg L^{-1}), potassium (272.0 mg L^{-1}), phosphorus (49.7 mg L^{-1}) and organic matter (COD=1804.4± 126.2 mg L^{-1} O2), suggest its use in agriculture. The high salinity is the limiting factor for agricultural use. It can be used as fertilizer in fertigation, after the correct addition with irrigation water, according to crop tolerance and nutrient needs.

3.2.2. Oxidation processes

Oxidation processes are not recommended when dealing with raw CWW. Oxidation is suggested to perform better as a post-treatment process, after biodegradation (Martins and Quinta-Ferreira, 2010). Thus, the Fenton oxidation, as a post-treatment process presents leads to a significant COD removal (final COD=20 mg L^{-1}) using a high concentration of hydrogen peroxide, 0.5 M and 2 g/L of Fe^{3+} and a pretreated effluent with low COD, 00.5 g/L. This need for high reactants concentration leads to the high operational costs. The single ozonation and catalytic ozonation have also been tested, as pos-treatment, allowing a very good COD removal (Martins et al., 2010) using an ozone concentration of 10 mg/L.

3.3. Constructed wetlands

Typically the small and medium cheese factories are isolated from centralized wastewater treatment facilities, and in some cases, locat- ed next to ecologically sensitive areas, which exacerbates environ- mental risks. Land application is often the only viable option for wastewater disposal. The presence of suspended solids and high sa- linity content might affect the physical and chemical structures of soils (Dragone et al., 2009; Saddoud et al., 2007) and eventually pol- lute the groundwater.



Fig. 1. Cheese whey wastewater of the Guilherme “Serpa cheese” making plant.

Table 7

Table 7
Bibliographic compilation: biological treatment of CWW.

Experimental conditions							Results				Residual concentration (g/L)	Reference
Substrate	Reactor/process type	COD_i (g/L)	pH	T (°C)	HRT (day)	Loading ($kg/m^3 \cdot d$)	Gas production ($LCH_4/L/d$)	% CH_4	CH_4 yield ($m^3CH_4/KgCOD$)	% COD removal	COD	
CWW	UASB	2.05	7.2–7.3	35	0.071	31	0.32 m^3CH_4/kg COD	–	–	90	0.215	Gutiérrez et al. (1991)
CWW	Anaerobic Pilot plant	1.62 ± 0.56	7.0 ± 2.0	26	2	–	–	–	–	89[a]	0.141[a]	Fang (1991)
CWW	Anaerobic + aerobic	1.62 ± 0.56	7.0 ± 2.0	21	2.33	–	–	–	–	99[a]	0.012[a]	Fang (1991)
CWW	AS (three stage)	1.62 ± 0.56	7.0 ± 2.0	21–24	0.825	–	–	–	–	99[a]	0.009[a]	Fang (1991)
CWW	UASB	5–77	7–8	35	2.3–11.6	1–28.5	–	–	–	95–99	1–1.5	Kalyuzhnyi et al. (1997)
CWW	Laboratory UASB	47–55	6–7	22–30	5.4–6.8	7–9.5	–	–	–	90–94	3–4	Kalyuzhnyi et al. (1997)
CWW	Pilot UASB	16–50	6.8–7.0	20–29	3.3–12.8	1–6.7	–	–	–	90–95	4–6	Kalyuzhnyi et al. (1997)
Diluted CWW	UASB	37	7.0–7.3	35	6	6.2	–	–	–	98	0.74	Gavala et al. (1999)
Diluted CWW	UASB	42	7.0–7.3	35	6	7.5	–	–	–	85–90	5	Gavala et al. (1999)
CWW	UASB	57–60	6.6	35	10	1.5–1.9	–	–	–	81	11.4	Gavala et al. (1999)
Diluted CWW	CSTR single–phase	10	7	55	10	0.95	0.33	67.6	0.35	94.6	0.54	Yang et al. (2003)
Diluted CWW	CSTR two–phase	10	7	55	10	0.97	0.29	70.1	0.30	96.4	0.36	Yang et al. (2003)
Synthetic wastewater	VMBS	5.1–17.0	7.0–7.8	35	1	11.6	–	63	0.33	89	≤4.25	Rodgers et al. (2004)
Reconstituted CWW	SBR	2.0	7.3	20	4	0.78	–	–	–	98	0.033	Frigon et al. (2009)
CWW	AS	11.2	–	–	–	–	–	–	–	95.4	0.52	Martins and Quinta–Ferreira (2010)
CWW	AS	9.5	7.0	10–12	7.9	–	–	–	–	97	0.29	Rivas et al. (2010)
Pre-coagulated CWW with $FeSO_4$	AS	8.2	7.0	10–12	7.3	–	–	–	–	95	0.41	Rivas et al. (2010)
Pre-coagulated CWW with $FeCl_3$	AS	7.7	7.0	10–12	2.1	–	–	–	–	96	0.31	Rivas et al. (2010)
Pre-coagulated CWW with $AlAl2Al_2(SO_4)_3$	AS	7.5	7.0	10–12	2.1	–	–	–	–	94	0.45	Rivas et al. (2010)
Pre-precipited CWW with lime	AS	5.4	7.5	17	1.7	–	–	–	–	95	0.27	Rivas et al. (2011)
Pre-precipited CWW with NaOH	AS	6.4	–	–	2.0	–	–	–	–	96	0.29	Rivas et al. (2011)

UASB — upflow anaerobic sludge blanket; CSTR — continuously stirred tank reactors; VMBS — vertically moving biofilm system; AS — activated sludge.
[a] As BOD_5.

Table 8
Bibliographic compilation: physiochemical treatment of CWW.

Experimental conditions							Removal (%)					Residual concentration (g/L)	Reference
Effluent Type	Process type	COD_i (g/L)	Reagent Concentration (g/L)	pH	T (°C)	Time (h)	COD	BOD	Turbidity	TKN	P	COD	
Raw CWW	Coagulation–flocculation with $FeSO_4$	13.6–14.2	0.25	8.5	10–15	–	43	67	97	43	89	7.9	Rivas et al. (2010)
Raw CWW	Coagulation–flocculation with $FeCl_3$	13.6–14.2	0.25	4.4	10–15	–	32	23	72	19	14	9.5	Rivas et al. (2010)
Raw CWW	Coagulation–flocculation with $Al_2(SO_4)_3$	13.6–14.2	1.0	7.0	10–15	–	35	36	96	44	77	9.0	Rivas et al. (2010)
Pretreated with AS CWW	O_3	0.520	10 gO_3/Nm^3	10	Room	7	63	53	–	–	–	0.2	Martins and Quinta-Ferreira (2010)
Pretreated with AS CWW	$O_3 + H_2O_2$	0.520	$[H_2O_2] = 33.0$ mM; 10 gO_3/Nm^3	7.5	Room	7	100	100	–	–	–	0	Martins and Quinta-Ferreira (2010)
Pretreated with AS CWW	O_3 + N-150 (Fe_2O_3-MnOx)	0.520	Catalyst load = 10 g/dm^3; 10 gO_3/Nm^3	7.5	Room	1	66	21	–	–	–	0.18	Martins and Quinta-Ferreira (2010)
Pretreated with AS CWW	O_3 + Mn-Ce-O (70/30)	0.520	Catalyst load = 10 g/dm^3; 10 gO_3/Nm^3	7.5	Room	1	70	0.7	–	–	–	0.16	Martins and Quinta-Ferreira (2010)
Pretreated with AS CWW	Fenton	0.520	$[H_2O_2] = 0.5$ M; $[H_2O_2]$: $[Fe^{2+}] = 2$	3	–	3	96	100	–	–	–	0.02	Martins et al. (2010)
Raw CWW	Precipitation with lime	18.5	3.8–5.0	11.5	–	–	47	55	76	55	97	9.9	Rivas et al. (2011)
Raw CWW	Precipitation with NaOH	18.5	2.7	11.0	–	–	50	46	80	34	46	9.3	Rivas et al. (2011)

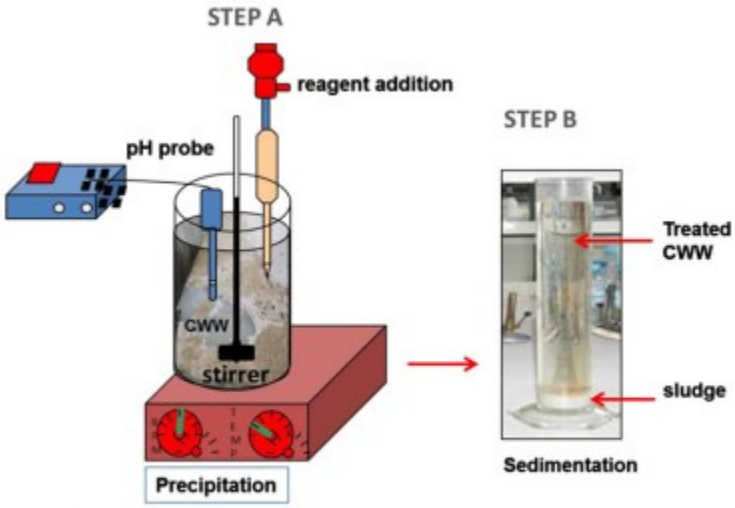


Fig. 2. Precipitation system: precipitation and sedimentation steps.

Constructed wetlands are an emerging technology which uses plants and microbial communities from the rhizosphere to eliminate various organic and/or inorganic chemical contaminants (see Table 9 and Fig. 3). Theoretically, this technology could be a good environmental-friendly solution. The technology does not need a full time monitoring strategy, presents low construction and operating costs with good ecological and landscape integration. Nevertheless, due to the especial characteristics of CWW, the use of constructed wetlands to treat CWW presents some limitations. Thus, this wastewater needs a pre-treatment for previous fat removal (Comino et al., 2011), or even fat removal plus dilution with domestic wastewater (Farnet et al., 2008).

The use of constructed wetlands to treat cheese effluents in com- bination with other wastewaters, like cheese-dairy farm effluents, can be possible depending on the volumes of domestic wastewater, washing water and cheese whey produced in the farm. Farnet et al. (2009), reported 76% of COD removal in the treatment of dairy farm wastewater without dilution.

The pretreatment of dairy farm wastewater by anaerobic bio- degradation may increase the COD removal to 94% (Travis et al., 2012).

In constructed wetland studies (Dragone et al., 2009; Saddoud et al., 2007; Farnet et al., 2009; Travis et al., 2012) the final effluent is not compatible with direct discharge, but can be used in the agricul- ture. From this point of view, constructed wetlands can be considered zero discharge systems.

Chemical pretreatment with lime (Rivas et al., 2010; Prazeres et al., 2012) can be a solution to allow the use of wetlands in the CWW treatment. This pretreatment can simultaneously reduce the fat and the organic load. Additionally, chemical precipitation is an easy and low cost technology adaptable to the small and medium cheese factories.

3.4. Agricultural reuse of pretreated CWW

The agricultural reuse of pretreated CWW and sludges, resulting in basic precipitation with lime, can be a management mechanism that

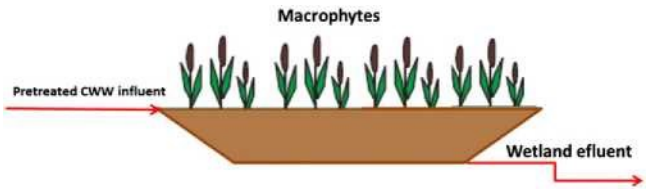


Fig. 3. Constructed wetland: macrophytes and wetland beds.

Table 9
Bibliographic compilation: Constructed wetland treatment of CWW.

Experimental conditions								Results (% removal)					Residual concentration (g/L)	Reference
Effluent type	Species	Reactor/ process type	Filling media	Surface area HF/SV (m^2)	Inflow m3/d	COD_i (g/L)	BOD_5 (g/L)	BOD_5	COD	Total phosphorus	TSS	Total nitrogen	COD	
Pretreated CWW for the reduction of the fat	–	Hybrid System	Gravel + sand	344/858	20	1.8	0.9	31–80	53-80	10–73	28–88	40–51	0.53 BOD_5 (mean value)	Comino et al. (2011)
Pretreated CWW for the reduction of the fat + domestic pretreated water in a septic tank	*Phragmites australis*	Surface horizontal flow	Calcareous gravel	169	–	–	–	84	–	–	75	–	–	Farnet et al. (2008)
Cheese-dairy farm wastewater	*P. australis*	Subsurface wetlands	–	160	–	–	–	–	91	–	–	76	–	Farnet et al. (2009)
Cheese-dairy farm wastewater, pretrated by anaerobic process	*Canna indica* and *Salvia arizonica*	Vertical flow	Crushed limestone sand and gravel	40	2.6	2.7± 0.14	0.84 ± 1.7	96	94	73	97	73	0.16	Travis et al. (2012)

presents several economic advantages and pollution control (Carvalho et al., 2012). The high content of biodegradable organic matter and nu- trients can be used as growth factors for plants. The high salinity is a limiting factor and the use of plants with moderate to elevated salinity tolerance is required. The reuse of this sludge and pretreated CWW can allow this system to be a zero discharge system. The tomato fruit fertigated with tap water and pretreated CWW by basic precipitation presents a viable culture to be developed (Carvalho et al., 2012). Six dif- ferent treatments were constituted: T0-drinking water was used as con- trol with average salinity level = 1.44 mS cm^{-1}. T1, T2, T3, T4 and T5-pretreated cheese whey wastewater and different portions of drink- ing water (average salinity level of 1.75, 2.22, 3.22, 5.02 and 10.02 mS cm^{-1}, respectively). Two cultivars of the tomato plant Lycopersicon esculentum Mill. (cv. Roma and cv. Rio Grande) were ex- posed to different salinity conditions for 72 days. The results show that the tomato irrigated with cheese whey wastewater is a sweet to- mato enriched with proteins, potassium and antioxidants (lycopene), with improved organoleptic and nutritional properties, thus benefiting consumers.

The evaluation of physical-chemical characteristics of the sludge resulting from basic chemical precipitation with lime, showed their high content in organic matter, nitrogen, phosphorus and pH (Rivas et al., 2010). These characteristics are compatible with agri- cultural use, especially for the correction of acid soils. This sludge was used on lettuce crop, since this is a very demanding and very sensitive to acidity organic material. The results showed that doses of sludge did not affect the chlorophyll content or leaf area of the lettuce. The levels of iron and potassium increased with the doses of sludge applied and the levels of sodium and nitrogen decreased (Carvalho et al., 2012).

4. Final considerations

Small and medium-scale cheese making plants are dispersed and have low daily CWW flow. The existing technologies are not appro- priate for these plants and, in most of cases; wastewaters are stored without any treatment. The development of easy and economic oper- ating technologies seems to be of paramount importance. The high content of salt and organic matter of the CWW is mainly due to the addition of whey or SCW to the washing waters. The salt content is a serious drawback at the time of CWW reclamation for agricultural purposes.

Fig. 4 shows a summarized and schematic overview ofthe produc- tion, treatment and reuse of cheese industry effluents. The current treatment systems show the impossibility ofdischarge into the receiv- ing waters. The physicochemical pre-treatments like chemical precipi- tation or coagulation/flocculation could be an alternative solution in the future of CWW management. These treatments are easy, cheap and adaptable to operating fluctuations. Physicochemical processes render an effluent suitable for a simple activated sludge biodegrada- tion. Additionally, under controlled conditions, the pre-treated efflu- ent and sludge can be used as fertilizer. The increase in nutrition properties of tomato and lettuce observed in agriculture farm trials, suggested that the use ofbasic precipitation to treat this effluent can transform a problem (CWW) in a solution with added value (sludge and fertilizer).

In the future, it will be necessary to widen these agricultural studies to other cultures to complete the studies about CWW effects.

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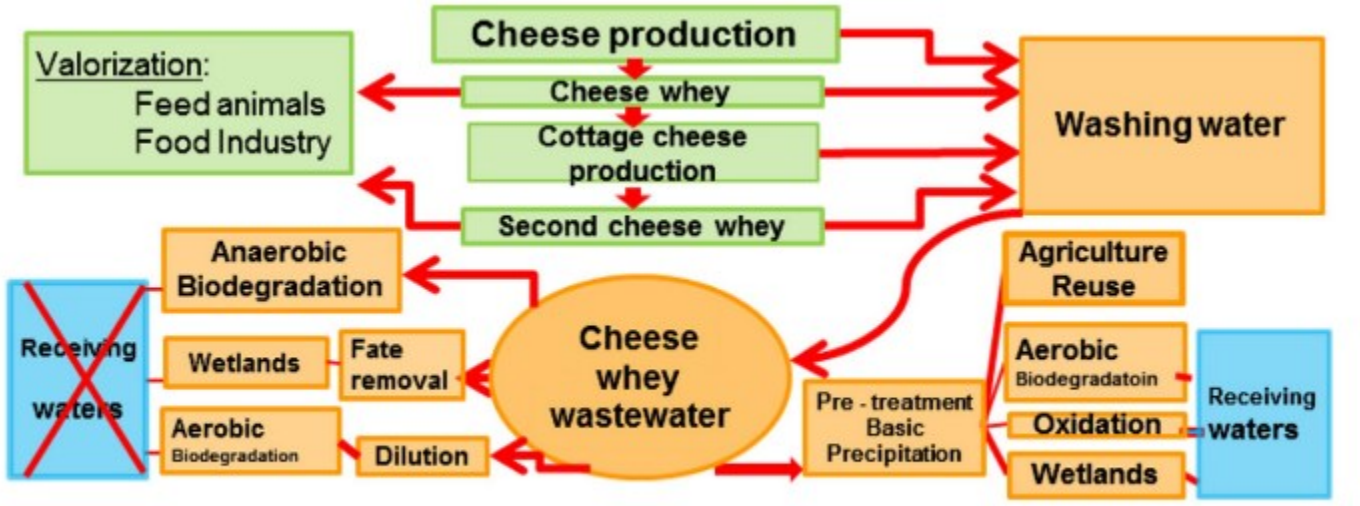


Fig. 4. Overview of the production of cheese industry effluents. Main forms of valorization. Resume of current treatment systems and future solutions.

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