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# MANAGEMENT OF CHEESE WHEY BY FILM FREEZE CONCENTRATION

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## Abstract

This study evaluates the behavior of freeze concentration of cheese whey (CW). Parameters studied were: Chemical Oxygen Demand (COD), Total Dissolved Solids (TDS), Suspended Solids (SS), Total Settleable Solids (TSS), pH and electrical conductivity (EC) in the concentrated cheese whey and in the ice. The final concentration of TDS reached was 25 ± 0.16 %wt for the liquid phase, which corresponds to a reduction of 83% of the initial volume. The COD in the ice fractions had lower values than the COD in the original cheese whey. The mean energy consumption was of 0.25 kWh/kg of ice. The results indicate that low levels of fat and low levels of salt in cheese whey improve the efficiency of the process of freeze concentration and reduce the environmental impact.

*Key words:* freeze concentration, fresh cheese production, organic matter, solids percent, volume reduction

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## 1. Introduction

The dairy industry generates large volumes of waste water, with a high contamination in organic matter, composed mainly of lactose and proteins, and other contamination parameters, namely, suspended solids, nitrogen, phosphorus, fat etc. An example of this is the by-product from the manufacture of cheese (cheese whey). Whey exhibits a biochemical oxygen demand (BOD) of 30-50 $g \cdot L^{-1}$, and a chemical oxygen demand (COD) of 60-80 $g \cdot L^{-1}$. Lactose is largely responsible for the high BOD and COD (Guimarães et al. 2010). The dumping of cheese whey increases the presence of organic matter in wastewater considerably (Arrojo et al., 2003). According to Morales and Prieto (1992), a concentration between 1 and 2% of cheese whey in the water of the rivers rapidly produces acidic aerobic fermentation, which hinders the biological activity of the rivers, due to the high value of biological oxygen demand (BOD). A typical small or medium size industry in North Spain generates about 1500 L/day of whey (Bonet et al., 2006). Each 1000 L of cheese whey generates about 35 kg of biological oxygen demand (BOD) and 68 kg of chemical oxygen demand (COD). This pollutant force is equivalent to the domestic wastewater produced in a day by 450 people. Dumping cheese whey increases the cost of wastewater treatment considerably (Koutinas et al., 2009).

Dairy wastewater are characterized by large fluctuations in the flow, which are correlated with the discontinuity of the production cycle, as well as a high electrical conductivity and pH variations, which affect the efficiency and performance of biological treatment. Some possibilities for the use of this by-product have been proposed by supplying proteins and lactose for feeding farm animals, protein source of WPC (whey protein concentrate) or SCP (single cell protein) as food additive and ingredients, lactose as culture medium ingredient for fermentation or fermentation for ethanol, and edible films (Guimarães et al., 2010; Spálátelu, 2012), but statistics indicate

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that the major portion of this fluid is discarded as effluent, without respecting the current regulations (in Spain R.D.L. (2001)) creating a serious environmental problem. This effluent can cause physical and chemical effects on the soil structure which causes a decrease in the yield of agricultural crops and can cause effects on aquatic life by the depleting off dissolved oxygen (Arrojo et al., 2003). Each day the environmental regulations are more rigorous and the cost per discharge increases, thus creating the need to optimize the processes in the industry.

Therefore, it is increasingly attractive to consider the possibilities of treating and using these by-products. This not only facilitates the protection of water resources, but it also leads to economic savings. In some countries, such as Spain, the environmental legislation does not allow the discharge of cheese whey to the environment. For this reason, the manufacturer of cheese needs to manage the volume of cheese whey produced, either by treating it or providing it to a third party for its valorization or transformation. In Mediterranean countries where the dairy sector, cheese making-oriented, has a marked traditional character, constraints in the utilization of fresh liquid whey are linked to high transportation costs of the bulky liquid and the low productivity of drying facilities (Lustrato et al., 2013; Tian et al., 2016). By reducing the volume of this by-product, a reduction in operation costs will be obtained. There are three main methods available for concentration of solutions: membrane processes, evaporation, and freeze concentration. Each of these three processes has its specific energy consumption: the energy costs are highest for evaporation, intermediate for freeze concentration and lowest for membranes, because no phase transition is needed (Miyawaki et al., 2005). According to Bonet et al. (2006), Sarkar et al. (2006), and Mawson (1994), these concentration processes are relatively expensive for their use in small-scale industries. Fig. 1 shows typical concentration values costs. In the current study the application of falling-film freeze concentration was investigated as a means to concentrate cheese whey and thus reduce the costs of transportation in its waste management and valorization. Freeze concentration is based on a solid–liquid phase separation (freezing). Process temperatures are low, which favors a good retention of flavors and thermally fragile components (Miyawaki, 2003). Another advantage of freeze concentration is that it can be used as a preconcentration step for wastewater which contains toxic compounds, heavy metals (Lemmer et al., 2000), and organic matter at high levels. Freeze concentration has already been applied to the concentration of dairy products (Sánchez et al., 2011). Recent research has focused on freeze concentration of dairy products by crystallization in suspension (Habib and Farid, 2007; Park et al., 2006). This process comprises a first phase of formation of ice nuclei (nucleation) followed by a second phase of growth of ice nuclei in the solution. There have also been studies on the concentration of dairy products by layer crystallization (Chen and Chen, 2000).

Falling-film freeze concentration is based on the principle known as layer freeze concentration or progressive freeze concentration. In this process the fluid to be concentrated flows down over a chilled surface (Sánchez et al., 2009). The system has successfully been used to concentrate sugar solutions (Raventós et al., 2007), apple and pear juices (Hernández et al., 2009), and must (Hernández et al., 2010). So far no tests have been reported on freeze concentration of cheese whey without added salt in similar equipment, which may show the behavior of organic matter as a potential force of pollution. Sánchez et al. (2011) studied the falling-film freeze concentration of salty cheese whey, which will be used to compare some of the results obtained in the current study. The current paper aims to evaluate experimentally the behavior of organic matter, soluble solids, settleable solids and total solids content during falling-film freeze concentration of cheese whey without added salt and to investigate the purity of the ice obtained (retention of organic matter, settleable solids, suspended solids and total solids). The freeze-concentrated cheese whey was characterized based on its content of nitrogen, lactose, protein and fat, and its electrical conductivity, pH and freezing point.

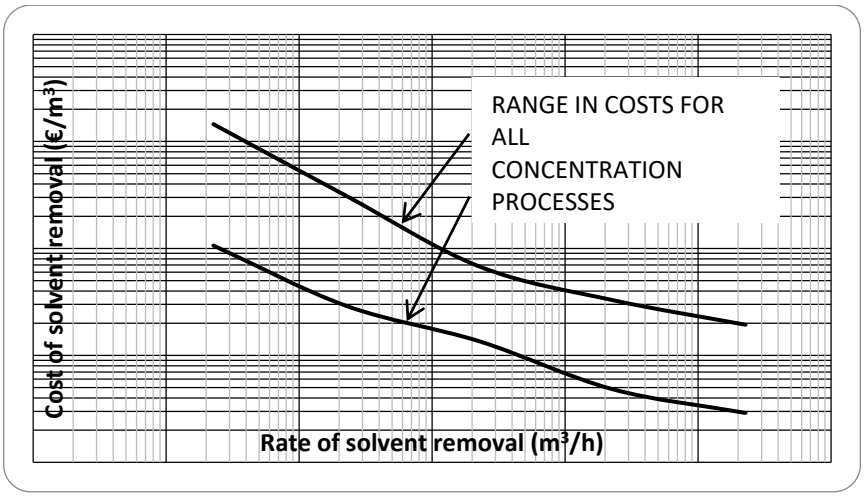


**Fig. 1.** Total cost of concentration (adapted from Barron and Wrobel (1985))

## 2. Experimental

### *2.1. Cheese whey*

Two hundred and twenty kg of cheese whey without added salt (CW) were supplied by ‘‘CAN CORDER” (Vallès Oriental, Barcelona, Spain). The CW resulted from the production of fresh cheese without salt, using enzymatic clot, based on Friesian cow’s milk. The CW was stored at -20ºC. Cheese whey characterization is included in a Table 1.

### *2.2. Freeze concentration test*

The freeze concentration test (FCT) was carried out using pilot scale equipment based on falling-film freeze concentration. The test was carried out in three stages and for each stage the average flow rate was maintained at $1 \pm 0.2$ L·s$^{-1}$ to ensure good contact between the evaporator plates and the fluid being concentrated. The equipment used in this study was described in detail by Sánchez et al. (2010). The freezer unit consisted of evaporator plates laid out vertically. The temperature of the CW at the entry and exit of the plate, the ambient temperature around the plate, and the temperature of the cooled plate were monitored using a Testo datalogger, model 177-T4 (Barcelona, Spain) with 4 type K probes (NiCr-NiAl sensors), connected to a computer. The concentration stage was stopped when it was impossible to maintain the flow rate at the required level ($1 \pm 0.2$ L·s$^{-1}$). Stage one was repeated four times and stage two was repeated twice so that enough volume of concentrated CW was obtained to guarantee the desired average flow rate in the third stage of the experiment. During each of the stages samples were taken of both the concentrate and the ice obtained (the ice formed was melted for analysis). Each batch processed at the start of the test contained an average of 55 kg of CW at 0ºC. Freeze concentrated samples of CW and ice were obtained according to Fig. 2. The samples analyzed were: CW before concentration (in stage 0), the concentrated CW (CW1, CW2, and CW3) and ice fractions (I1, I2, and I3) for stages 1, 2 and 3 respectively. The weight and the solids concentration of the separated ice were measured at the end of each stage.

#### *2.2.1. Freezing point depression*

The freezing point depression was determined for fresh CW, and for the samples CW1, CW2 and CW3, using the method described earlier (Belén et al., 2013). The temperature of the samples was controlled with a Data Logger (Testo 177-T4; Barcelona-Spain) connected to 4 sensors with type K probes (and NiCr-NiAl sensors). Data analysis was performed using “Testo Comfort Software”. The cryostat used was a HAAKE DC10-K10 (Thermo Electron GmbH, Karlsruhe, Germany), with a mixture of ethylene glycol and water.

**Table 1.** Cheese whey characterization

| *SS (mg·L$^{-1}$)* | *TSS (mL·L$^{-1}$)* | *TS (mg·L$^{-1}$)* | *SVI (mL·g$^{-1}$)* | *TDS (% wt)* | *pH* | *EC (dS·m$^{-1}$)* | *COD (mg·L$^{-1}$)* | *Protein (% wt)* | *Lactose (g·L$^{-1}$)* | *Fat (% wt)* |
|---|---|---|---|---|---|---|---|---|---|---|
| 7,100 | 20 | 63,500 | 2.82 | 7.7 | 6.00 | 13.89 | 96,083 | 0.938 | 11.22 | 0.35 |

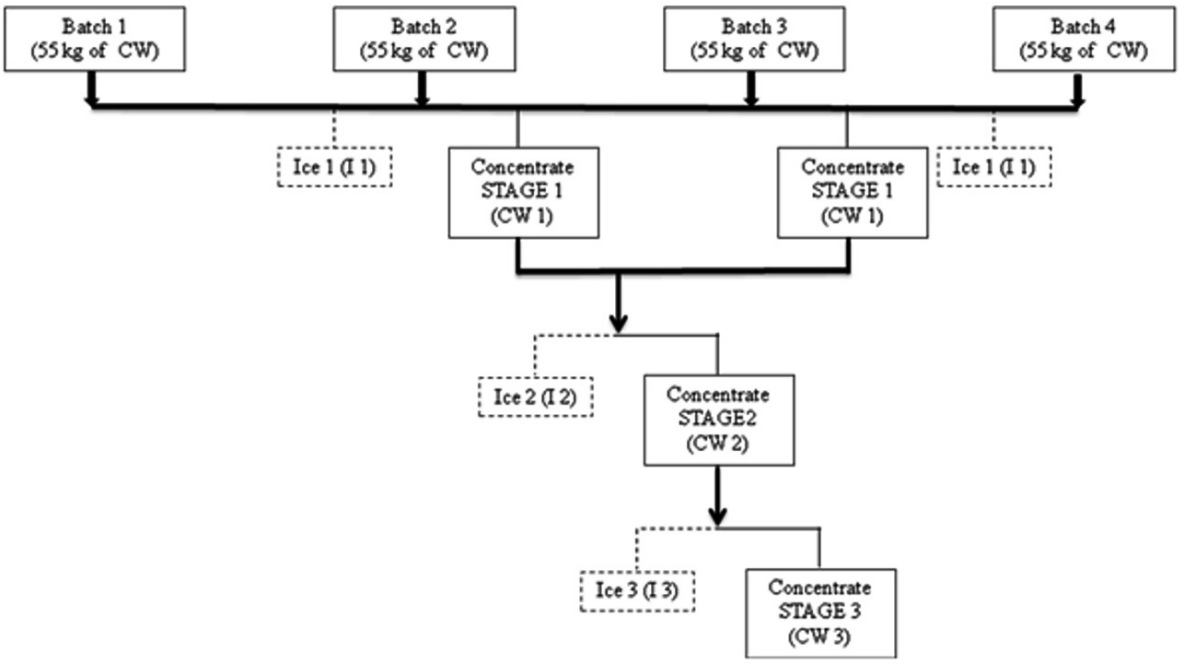


**Fig. 2.** Flowchart of the three concentration stages of CW

*2.2.2. Mass balance*

As has been done in previous studies with this equipment (Belén et al., 2012; Hernández et al., 2010), in order to validate the obtained experimental results, a mass balance of each stage is made, which is compared with theory (Eq. 1) (Burdo et al., 2008).

$$L = G_{in} (C_{in} - C_f) / (C_{ice} - C_f) \quad (1)$$

where: $L$ is the theoretical mass of ice formed (kg), $G_{in}$ is the initial mass of (concentrated) *CW* (kg), $C_{in}$ is the initial solids concentration of the (concentrated) *CW* (%wt), $C_f$ is the final solids concentration of the concentrated *CW* (%wt) and $C_{ice}$ is the solids concentration of the ice formed (%wt).

*2.2.3. Process efficiency*

The efficiency of each concentration stage reflects the increase in concentration of the CW in relation to the concentration of solids remaining in the ice. In theory, the lower the amount of solids present in the ice, the more concentrated the solution will be. The efficiency is calculated by Eq. (2):

$$Efficiency\ (\%) = [(C_f - C_{ice}) / C_f]\ 100 \quad (2)$$

In this study, the concentration of solids in the liquid phase and in ice (TDS, TSS, SS, TS and COD) at the end of each step is measured.

*2.3. Physicochemical analysis*

Analyses of samples were performed in triplicate and the physicochemical characteristics evaluated were the ones presented in the next sections.

*2.3.1. Solids content*

Various parameters were analyzed that reflect the amount of solids in the samples. The total dissolved solids (TDS), expressed in %wt, were determined using an Atago refractometer (model DBX-55; Barcelona, Spain). The concentration of suspended solids (SS), expressed in $mg \cdot L^{-1}$, total settleable solids (TSS), expressed in $mL \cdot L^{-1}$, total solids (TS), expressed in $mg \cdot L^{-1}$, and the sludge volumetric index (SVI), expressed in $mL \cdot g^{-1}$, were determined according to their Standard Methods (APHA-AWWA-WPCF, 1995)

*2.3.2. Chemical Oxygen Demand (COD)*

The analysis of Chemical Oxygen Demand (COD) of the samples was performed using a commercial kit for photometric determination of COD (DINKO®, DINTER S.A., Barcelona, Spain), with a measuring range of 1000-20000 ppm, This kit is based on the standard method according to APHA-AWWA-WPCF (1995). It consisted of closed reaction tubes containing sulfuric acid and potassium dichromate in the presence of a silver sulphate catalyst. Digestion of the samples (2.0 mL) was conducted during 2.00 hours at 350°C using a heating block (Hach®) (Loveland, Colorado, USA). The determination of the COD (mg $O_2 \cdot L^{-1}$) was performed directly with a portable photometer model YSI3900 (Yellow Springs, Ohio, USA), at a wavelength of 580 nm.

*2.3.3. Electrical conductivity and pH*

The pH was measured with a pH sensor (Micro pH 2001, CRISON-Barcelona, Spain). The electrical conductivity (EC) was determined with conductivitymeter (GLP31, CRISON-Barcelona, Spain) using temperature compensation. The conductivity of CW is mainly determined by the presence of organic and inorganic salts originating from the milk, including chlorides, phosphates, citrates and bicarbonates of sodium, potassium, calcium and magnesium, which remain in the CW after milk coagulation and cheese production. Multivalent ions $Ca^{+2}$ and $Mg^{+2}$ are in the form of complexes such as Ca-citrates, Mg-citrate and $PO_4H_2Ca$ (Hansen, 1974), which generally contribute less to the EC. Lactose, an uncharged sugar, does not conduct current. The contribution of proteins to the EC is of minor importance and fat is a nonconductor and hinders the conduction of electricity by occupying volume and by impeding the mobility of ions (Zhuang et al., 1997).

*2.3.4. Nitrogen, protein, lactose and fat content.*

Nitrogen content in the samples (N, % wt) was determined according to AENOR (2002). The protein content (% wt) was then calculated as N*f, where f is a constant factor, in this case 6.38. Lactose content was determined by HPLC according to the method presented by AOAC (2005). This test was carried out in a Shimadzu high-performance liquid chromatograph equipped with a LC-10AD double pump, a 77725 Rheodyne manual injector (Cotati CA, USA) with a 20 µL loop, a RID_6A Shimadzu refractive index detector and a C-R6A Chromatopac integrator. Chromatographic separation was achieved with a tracer carbohydrates column (5µm particle size; 250 mm x 4.6 mm i.d.) and an $NH_2$ precolumn (13mm x 3 mm i.d.), both from Tracer (Teknokroma. Barcelona, Spain). Fat content (%) was measured by the method of Gerber, based on the separation and quantification of the fat through a sample treatment with sulfuric acid and isoamyl alcohol. A Gerber centrifuge (Astor 16, Italy) was used, with capacity for 16 butyrometers.

*2.4. Statistical analysis*

Statistical data analysis was carried out using the multivariate statistical software package STATGRAPHICS PLUS 7, of Statpoint Technologies (Warrenton, Virginia-USA). The correlation coefficient ($R^2$) was used to determine the best fit for the curves. Analysis of variance was performed using the test of Kruskall-Wallis to confirm the level of significance between the simple repetitions performed ($p < 0.05$).

## 3. Results and discussion

### *3.1. Freeze concentration test*

The CW was freeze concentrated from 7.7% to 25.0% (wt% of TDS) in three stages. The TDS concentration shows a linear increase in time during the CW freeze-concentration process (Fig. 3), and is very well described with the linear regression equation CW = 1.20 t + 8.60 ($R^2$ =0.99). In the equation obtained, CW represents the concentration of TDS (%wt) in the concentrate and *t* (h) is the time elapsed since starting the process. A similar linear behaviour was observed in others studies using the same experimental equipment with tofu whey, pear and apple juices, must, and solutions of sugars (Belén et al., 2012; Hernández et al., 2009, 2010; Raventós et al., 2007).

For the specific case of salty cheese whey (CSW), Sánchez et al. (2011) reported a similar study and their results are shown in Fig. 2, together with the fit equation ($R^2$= 0.98) for CSW. It can be observed that during freeze-concentration of CW the solids are more quickly concentrated than during freeze concentration of CSW, mainly because CW doesn´t contain salt. The concentration speed of CW (1.2 %wt·$h^{-1}$) is 30% higher than the concentration speed of CSW (0.9%wt·$h^{-1}$). The intersection of the straight lines for the CW freeze concentration and the CSW freeze concentration indicates the point where the numerical values of CW and CSW concentrations are equal (0.37h). The accumulated ice during the CW freeze-concentration process was 55kg more than that obtained for CSW at the end of the three stages. The total weight of ice produced during the CW freeze-concentration (183kg) and the CSW freeze-concentration (128kg) represents the amount of water removed during the process, including the solutes retained in the ice. The temperature of the evaporator and the temperatures of the CW at the entrance and exit of the evaporator were registered.

The average temperature difference of the CW between the entrance and the exit of the evaporator was 1.0 ± 0.1ºC for all stages, once the equilibrium conditions were reached. The average temperature of the CW in the tank decreased progressively from -0.1 ± 0.02 ºC in the first stage to -1.5 ± 0.04 ºC in the last stage. Once the equilibrium conditions were reached in the system, the temperature of the evaporator plates remained constant throughout the process with an average value of -15.10 ± 0.12 ºC.

Ice was obtained as a porous ice layer on the heat exchanger plates. In the first concentration stage the thickness of the ice layer was 30 ± 1.5 mm. In the last concentration stage this value decreased to 20 ± 1.2 mm. In a similar device Chabarov and Aider (2014) cryoconcentrated skim milk from 8.50 % w/w to approximately 18 % w/w and indicate the highest process efficiency has been obtained up to 20-30 mm of ice thickness. The porosity of the ice layer is probably due to a slight sub-cooling of the liquid film that descends over the chilled plates (Belén et al., 2012; Flesland, 1995; Sánchez et al., 2010). This is possibly due to the decrease of the ice-layer thickness in each progressive stage, which allows an increase of heat transfer from the CW.

### *3.2. Solids content*

The TS, SS, TSS, TDS and COD content in the concentrated CW were fitted to linear equations. The fit equations obtained are shown in Table 2. The TS, SS, TSS, TDS and COD content in the ice fraction were fitted to an exponential trend (Table 1).

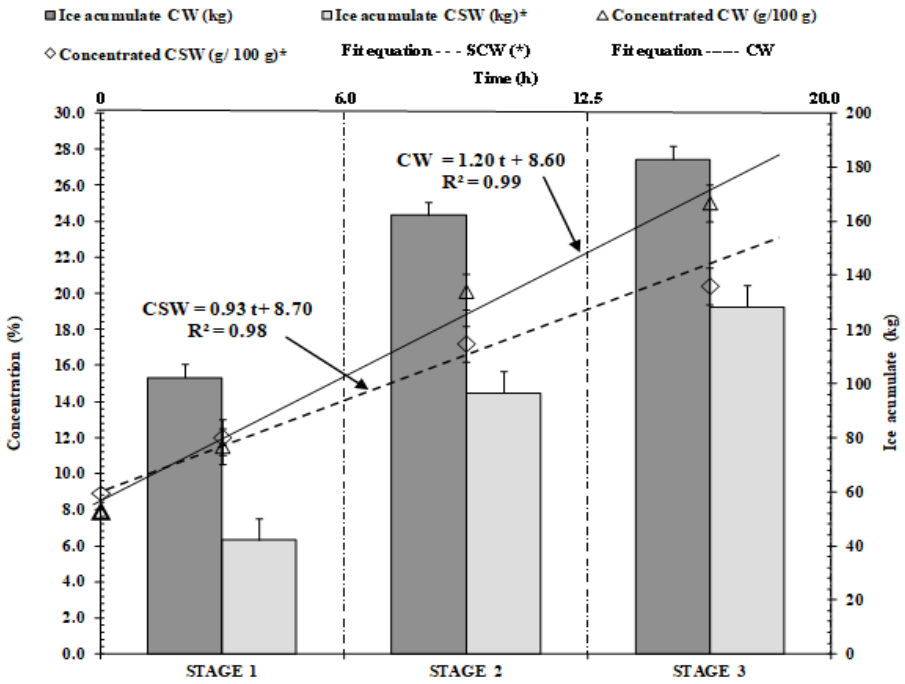


**Fig. 3.** Behavior of the CW and CSW concentration and quantity of ice formed as a function of time

Similar fitting equations have been reported by Belén et al. (2012) for tofu whey, by Sánchez et al. (2011) for CSW, by Hernández et al. (2009) for most, and by Raventós et al. (2007) for sugar solutions. The differences observed between the various fitting equations are due to the type and quantity of solids present in each of the liquids.

In this study the increase in concentration of solids content in the ice shows an exponential trend (Fig. 4). The exponential trend for the solute retention in the ice for the freeze concentration of liquid food stuffs in a falling-film based equipment has been observed in earlier studies with solutions of sugars (Raventós et al., 2007) and must (Hernández et al., 2010) using the same experimental equipment.

**Table 2.** Linear and exponential fit equations for various parameters during freeze concentration of CW

| *CW solids content* | *CW concentration* | | *Ice fraction* | |
|---|---|---|---|---|
| | *Fit equation* | $R^2$ | *Fit equation* | $R^2$ |
| **SS** | 5,654.9 t + 7,100 | 0.96 | 560.2 $e^{0.80\ t}$ | 0.99 |
| **TSS** | 8.5 t + 20 | 0.97 | 2.01 $e^{0.44\ t}$ | 0.98 |
| **TS** | 40,933 t + 51,333 | 0.96 | 4,057.2 $e^{0.77\ t}$ | 0.99 |
| **TDS** | 1.20 t + 8.60 | 0.99 | 1.5.8 $e^{0.11\ t}$ | 0.99 |
| **COD** | 29,730 t + 96,083 | 0.99 | 12,813 $e^{0.44\ t}$ | 0.96 |

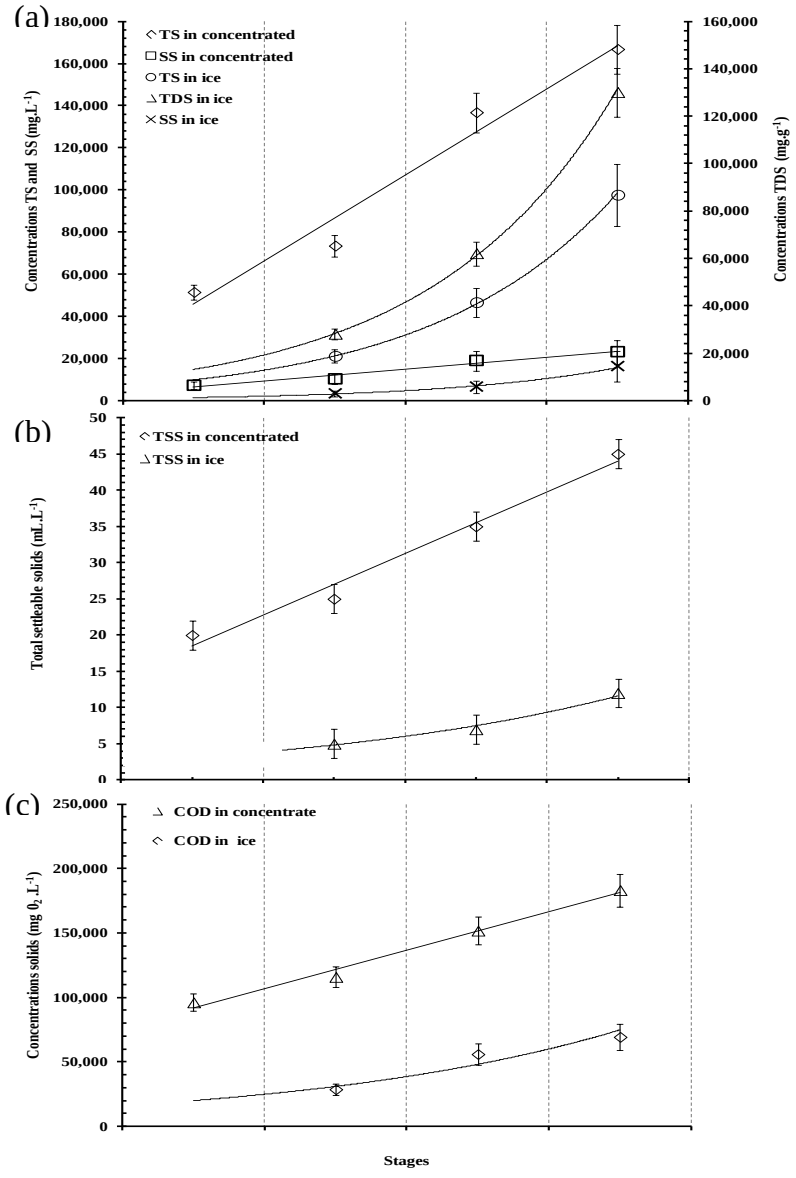


**Fig. 4.** (a) Behavior of TS, SS,TDS, (b) Behavior of TSS and (c) Behavior of COD content in the CW in stage 0, concentrated CW (CW1, CW2, and CW3) and ice fractions (I1, I2, and I3) for stages 1, 2 and 3 respectively

According to Sanchez et al. 2011 freeze-concentrated whey behaves as a Newtonian fluid at temperatures near to freezing point, and TS in the range 10 to 20 % TS. On the other hand it is believed that the exponential trend in the purity of the ice formed is closely related to viscosity, since in Newtonian liquids viscosity shows an exponential trend with concentration (Sanchez et al. 2010).

The sludge volumetric index (SVI) is the volume (mL) occupied by 1 g of SS. With this index it is possible to determine parameters of silting up by zone, such as the settling velocity (Härtel and Pöpel, 1992; Gernaey et al., 2001). This information is important for calculations and/or simulations used for the design of a settling tank (Gernaey et al., 2001). The SVI during freeze concentration for the CW and for the ice fraction (after melting) (Fig. 5) as a function of TS. It is seen that the SVI of the concentrated CW decreases during the later stages of the freeze concentration process (i.e. at higher values of TS).

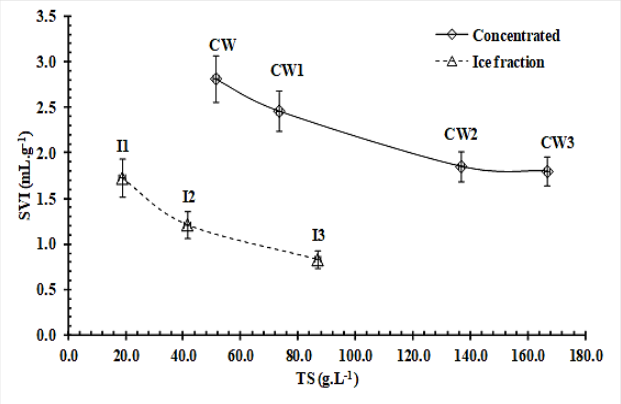


**Fig. 5.** Comparison between the SVI for CW in stage 0, concentrated CW (CW1, CW2, and CW3), and melted ice fractions (I1, I2, and I3), for stages 1, 2 and 3 respectively

### *3.3. Nitrogen, protein, lactose and fat content*

The nitrogen content in the CW increased significantly ($p<0.05$; Table 3) during freeze concentration. In the ice fraction the nitrogen content shows lower levels. The observed increase in nitrogen concentration is equivalent to an increase in protein concentration (N*6.38).

The observed nitrogen in the ice fraction is due to retention of protein in the ice (0.79%; Table 3). This result is similar to that reported by Sánchez et al. (2011) for CSW freeze concentration, where the ice obtained shows a relatively high protein content. The ice obtained has an average relative impurity of 53% at the last stage, showing a fat content equal to that of the original CW used (0.35%), and contents of nitrogen (0.13%), protein (0.79%), and lactose (8.21 $g \cdot L^{-1}$) slightly lower than that of the original CW used.

It is observed that there is a significant difference in lactose content ($p<0.05$; Table 3) between the concentrated CW and the ice fraction in each stage. It is observed that the lactose concentration in the concentrated CW decreases during the third stage.–This result could be due to that part of the lactose crystallizes during the third stage of the process; there is also a greater retention of lactose into the layer of ice, probably induced by the relatively high level of fat in ice during this third phase of the process. The observed behavior also corresponds to the correlation presented by Aider et al., (2009).

According to Gulfo et al. (2013) it was found that fractionated thawing can recover most of the solute content in the ice in a falling-film freeze concentrator (multi-plate freeze-concentrator). The recovery of these solutes during thawing can increase overall system efficiency.

A process to concentrate aqueous coffee extract by freeze concentration is proposed to achieve a continuous system industrially viable. The ice from each stage was fractionally thawed to recover the coffee solids retained in the ice (Moreno et al., 2014).

### *3.4. Electrical conductivity and pH*

The increase of EC for the concentrated CW (CW1, CW2, and CW3) and for the ice fractions (I1, I2, and I3) for stages 1, 2 and 3 respectively (Fig. 6.). The EC of the concentrates, CW1, CW2, and CW3, was 14.23; 15.83 and 17.02 dS/m respectively. The EC of the ice fractions, I1, I2, and I3, was 5.98; 8.65 and 9.35 mS/cm respectively. In the study reported by Sánchez et al. (2011), the EC of the concentrated CSW and the ice fraction at the end of the process was 53.5 mS/cm and 29.4 dS/m, respectively.

**Table 3** Average values ± (SD) of physicochemical characteristics of CW in stage 0, concentrated CW (CW1, CW2, and CW3) and ice fractions (I1, I2, and I3) for stages 1, 2 and 3 respectively

| ***Samples*** [(a)] | ***Physicochemical characteristics*** | | | |
|---|---|---|---|---|
| | ***Protein (% wt)*** | ***Nitrogen (% wt)*** | ***Lactose ($g \cdot L^{-1}$)*** | ***Fat (% wt)*** |
| **CW** | 0.94±(0.099) | 0.15±(0.089) | 11.22±(0.166) | 0.35±(0.073) |
| **CW1** | 1.02±(0.078) | 0.16±(0.068) | 12.34±(0.079) | 0.55±(0.054) |
| **CW2** | 1.98±(0.071) | 0.31±(0.081) | 15.43±(0.326) | 0.60±(0.087) |
| **CW3** | 3.82±(0.044) | 0.60±(0.054) | 10.56±(0.067) | 0.70±(0.274) |
| **I1** | 0.59±(0.115) | 0.09±(0.125) | 5.16±(0.063) | 0.10±(0.082) |
| **I2** | 0.66±(0.048) | 0.10±(0.068) | 6.89±(0.039) | 0.25±(0.050) |
| **I3** | 0.79±(0.050) | 0.13±(0.040) | 8.21±(0.322) | 0.35±(0.063) |

*SD: Standard deviation; (a) Significance differences ($p < 0.05$) were observed between CW1, CW2 and CW3; between I1, I2, and I3; and between CW1, CW2, CW3, I1, I2, and I3 respectively for all physicochemical characteristics*

These relatively high values of EC were obtained because the salt (NaCl) added during the cheese manufacturing increases the EC both in the concentrate and in the ice fraction for CSW. The measurement of electrical conductivity is an indicator of salt content. A high salt content is undesirable since it increases the corrosion and lowers the freezing point making the transfer of heat and the efficiency of the process.

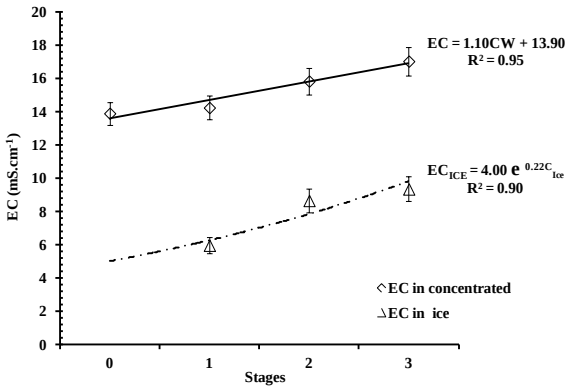


**Fig. 6**. Behavior of EC in the CW in stage 0, freeze concentrated CW (CW1, CW2, and CW3) and melted ice fractions (I1, I2, and I3) for stages 1, 2 and 3 respectively

The pH obtained during the freeze concentration process was in the range of 6.00 to 5.50 for the CW and its concentrates while it was in the range of 5.45 to 5.37 for the ice fractions. In both phases, the change of pH, does not present a significant difference ($p < 0.05$).

### *3.5. Freezing point depression*

The freezing point of a liquid depends on the concentration and type of solutes present in solution (Hernández et al., 2009), the higher the level of dissolved solids, the lower the freezing point (Gabas et al., 2003). For CW the freezing point is influenced by the concentration of lactose, chlorides and other salts and is lower than that of pure water (273ºK) (Bakshi and Johnson, 1983). The freezing point depression ($\Delta t$) was determined for CW and its concentrates CW1, CW2 and CW3 and was plotted versus solids concentration (Fig. 7). The experimentally determined freezing point depression increased with increasing concentration of solids, as expected. Similar results were obtained by Sánchez et al. (2011), shown in the Fig. 7. For comparison, Fig. 7 also includes results for rehydrated spray-dried cheese whey (CWRSD), obtained by Bakshi and Johnson (1983), which are actually in between the results for cheese whey without added salt (CW) and salty cheese whey (CSW).

Combining the graph of freezing point versus concentration (Fig. 7) with the correlation of Choi and Okos (1986), estimates can be obtained for the values of physico-chemical properties such as thermal conductivity, specific heat, thermal diffusivity and density (Ibarz and Barbosa, 2005). Once these properties have been determined, simulations and/or calculations can be made of the process of falling-film freeze concentration, which include the estimation of energy consumption, as suggested by Auleda et al., (2011a) and Auleda et al., (2011b). Moreover, obtaining the values of these properties is of great importance for process design in the industry.

### *3.6. Mass balance*

A mass-balance calculation was performed for each of the concentration stages. This was done by calculating the theoretical mass of ice (kg) that would be produced per kg of freeze-concentrated CW (L), according to equation (1). The predicted ice mass ratio ($W_{Pred}$) was calculated as $L/G_{in}$ for each stage. The experimental ice mass ratio ($W_{Exp}$) was determined as the quantity of ice formed, determined experimentally by weighing ($L_r$), divided by the amount of CW entering in each stage. The comparison of the theoretical result with the experimental value is shown in Fig. 8 for each stage.

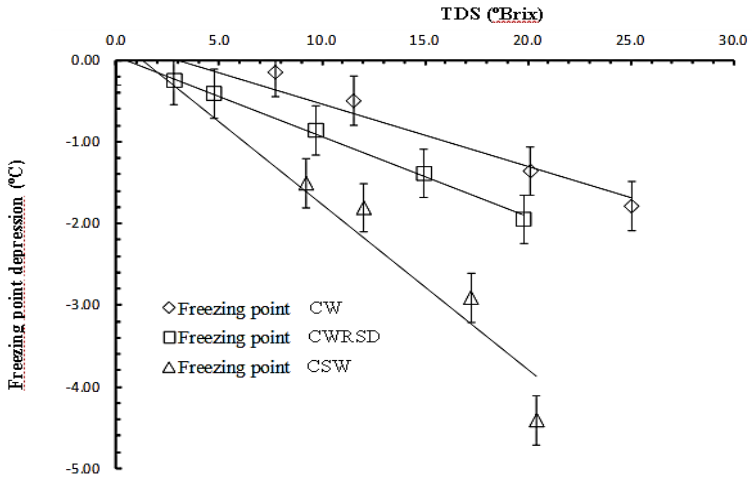


**Fig. 7.** Freezing point depression (ºC) for concentrated cheese whey of various types, versus TDS (ºBrix)

The fit equation between $W_{Exp}$ and $W_{Pred}$ was calculated ($R^2$ = 0.97). The fact that there is a slight difference between $W_{Exp}$ and $W_{Pred}$ ($R^2$ = 0.97 instead of 1.00) is mainly due to product losses during freeze concentration that generally are below 10%, as also shown by Belén et al. (2012), Hernández et al. (2010), and Sánchez et al. (2010 and 2011).

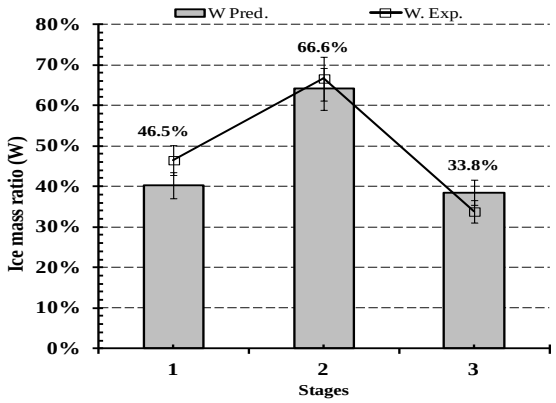


**Fig. 8.** Experimental and predicted ice mass ratio

*3.7. Process efficiency*

This was calculated for each type of solids content analyzed. Results are shown in Fig. 9, which compares the decrease in efficiency during the process with the increase in TS concentration in the CW. The efficiency of the process has average values of 70%, 67% and 53% for stage 1, 2 and 3 respectively. It is observed that efficiency decreases mainly for SS (37%) and TDS (48%) in the final stage. For COD, the efficiency is 70%, 42% and 28% for stage 1, 2 and 3 respectively.

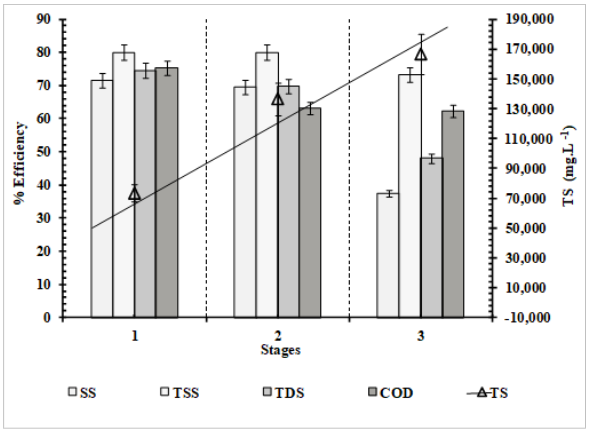


**Fig. 9.** Efficiency process Vs. CW freeze-concentration

The average value for efficiency of the freeze-concentration process is 63%. Sanchez et al. (2011) reported TDS efficiency between 73.33 % at the first stage and 53.67 % at the end stage for salty cheese whey. In whey freeze concentration using a block system Aider et al. (2007) reported that the efficiency of dry mater concentration varies between 93 to 32 % for the first and last level respectively. The observed decrease in efficiency of the process is the result of the increase in retention of solids in the ice. It is believed that due to the increased viscosity of the solution with increasing concentration, the solids accumulate in the ice-liquid interface (concentration polarization) as the diffusion of these solids away from the interface is slower. Therefore these solids are more easily retained in the ice formed (Belén et al., 2012; Bhatnagar et al., 2005; Hernández et al., 2010).

The porosity of ice obtained during freeze concentration of CW could also contribute to the retention of solutes in the frozen phase (Botsaris and Qian, 1999). This causes an increase in the partition coefficient of solids in the ice phase and thus increases the solids loss during the process (Miyawaki, 2003). The results obtained show an increase in concentration of solids in the ice with an exponential trend. This behavior in the ice is similar to that observed during the freeze concentration of sugar solutions (glucose, fructose and sucrose) (Raventós et al., 2007), tofu whey (Belén et al., 2012), salty whey (Sánchez et al., 2011) and must (Hernández et al., 2010) using the same experimental equipment. The ice fraction obtained in each stage presents retention of solids that can possibly be recovered by fractional thawing (Yee et al., 2003). Miyawaki, et al. (2012) also suggested the use of partial melting of ice to improve the yield for freeze concentration.

However, the obtained ice fractions, possessing less COD than the initial fluid (CW), have the advantage that they can be treated easily using biological processes. According to Arvanitoyannis and Kassaveti (2008), biological treatment can reduce the COD level by 82% (aerobic treatment) or even by 96% (anaerobic treatment) at different operation times. For anaerobic treatment it has been reported that it is possible to obtain a 100% reduction of COD, if a pretreatment is used, such as centrifugation or silting up. The efficient removal of settleable solids directly influences the subsequent biological and sludge treatment units (Lindeborg et al., 1996).

*3.8. Energy consumption of freeze concentration*

Theoretically, when comparing the heat of evaporation (2260 $kJ \cdot kg^{-1}$) at a pressure of 0.1MPa) with the enthalpy of freezing (335$kJ \cdot kg^{-1}$), the process of freeze concentration seems to be cheaper than evaporation from an energy point of view. But due to the combination of the different forms of energy used, it is appropriate to consider energy consumption expressed as primary energy (Sánchez et al., 2009). The energy consumption per kg during the freeze concentration of CW was estimated, taking into account the power rating of the equipment, reported by Hernández et al. (2010) and Sánchez et al. (2010) and the duration of the three stages of freeze concentration. The mean energy consumption for concentration from 7.7 to 25.0 %wt was 0.25 $kWh \cdot kg^{-1}$ of ice. In the study of Sánchez et al. (2011) with CSW, a total energy consumption was obtained of 0.28 $kWh \cdot kg^{1}$ (for concentration from 9.2 to 20.0

%wt). The main energy consumption was during the final stage, possibly due to the fat content that obstructed the heat transfer.

## 4. Conclusions

Freeze concentration of cheese whey increases the solids concentration from 7.7 to 25 % wt, which correspond to an 83% reduction of the initial volume processed and can optimize the management and use, since the process is performed at low temperatures. With a biological treatment it's not possible to concentrate the components of interest for use as a byproduct.

The increase in concentration of solids in the concentrated CW shows a linear trend in time for parameters studied. The increase in concentration of solids in the ice fraction followed an exponential trend. The fat content in the ice fraction reduces the efficiency of the last stage of the freeze concentration process. The mean energy consumption for concentration from 7.7 to 25.0 %wt was 0.25 kWh·kg$^{-1}$ of ice.

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