Freeze concentration for the valorization of agro-industrial waste effluents

By

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The present thesis entitled *Freeze concentration for the valorization of agro-industrial waste effluents*, by Imane Uald lamkaddam, was carried out at the Technological Centre for the Biodiversity, Ecology, Environmental and Agri-food Technologies (BETA Tech. Centre) at the University of Vic – Central University of Catalonia (UVic-UCC), under the supervision of Dr. Mabel Mora Garrido and Dr. Esther Vega Martínez and tutored by Dr. Joan Colón Jordà.

Mabel Mora Garrido Esther Vega Martínez

Joan Colón Jordà

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“Nothing in this world can take the place of persistence. Talent will not: nothing is more common than unsuccessful men with talent. Genius will not; unrewarded genius is almost a proverb. Education will not: the world is full of educated derelicts. Persistence and determination alone are omnipotent.”

Calvin Coolidge

To mom, dad and my sisters,
for all their support during this journey.

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Acronyms and abbreviations

FC	Freeze concentration
PFC	Progressive freeze concentration
SFC	suspended freeze concentration
CW	cheese whey
PS	Pig slurry
FPS	Fattening pig slurry
SPS	shows pig slurry
PE	Process efficiency
N	nitrogen
P	phosphorus
K	potassium
Cu	copper
Zn	Zinc
TS	total solids
SC	solids concentration
SCcw	solid concentration of the cheese whey
SCc	solid concentration of concentrate
SCd	solid concentration of diluted fraction (melted ice)
TSc	total solids of concentrate
TSd	total solids of diluted fraction
TSin	initial total solids
RMS	root mean square
Wth	theoretical formed ice mass ratio
Wexp	experimental formed ice mass ratio
Bx	brix degree
WPC	whey protein concentrate
WPI	whey protein isolate
HWP	Hydrolyzed whey protein
CAGR	compound annual growth rate
CSW	Cheese salted whey
Y	yield
K	effective partition constant
CF	Concentration factor
Si	salt concentration in the ice fraction
Sc	salt concentration in the concentrated fraction
ZLD	Zero liquid discharge
SS	Suspended solids

Abstract

Despite the benefits of agro-industrial based aliments in our daily life in its different forms, we cannot neglect the backstage operations assuring the delivery of good quality products to consumer market. In the last decade, a sharp increase on the consumption of agro-industrial products is being reached caused by population growth and in consequence its food demand. On the other side, agro-industrial activities generate waste streams and managing them properly is considered one of the main challenges that nowadays producers face. Agro-industrial waste liquid effluents usually have a high-water content but also valuable compounds, such as nutrients, that must be valorized fostering the circular bioeconomy in the sector. To do so, many technologies are already deployed for concentrating the abovementioned waste streams aiming first to recover value-added compounds, in this case mainly nutrients, and take advantage of the recovered bio-products benefits, and secondly, resolve the high-water content side-effects for transporting the generated effluents besides enabling the possibility to depurate and reuse the extracted water on-site. Thermal-based technologies, membrane-based technologies and chemical separations are the main processes to concentrate nutrients in various sectors and wide variety of agro-industrial waste effluents. The available techniques are differing in terms of efficiencies, operational and investment costs, technical withdraws and selectivity for treating a given waste effluent or another.

In this thesis, the main purpose was to implement and demonstrate the technical feasibility of an innovative technology to concentrate and/or recover valuable compounds from agro-industrial waste effluents or by-products on one side, and to deliver a clean effluent that can be reused for agricultural purposes on the other. The freeze concentration of a selection of different raw materials was tested based on regional issues related to the sector in Catalunya: Cheese whey, pig slurry, concentrated liquid fraction of digestate and a hyper saline solution from meat processing industry. The abovementioned effluents are generated in substantial amounts and have high-water content which burden transportation cost to other regions.

As defined by its name “Freeze concentration” technology is a thermal process operating at sub-zero temperatures, where the treated solution is being frozen under specific conditions to generate a concentrated liquid fraction and a cleaner effluent (melted ice). Many types and configurations are available under the name of freeze concentration, however in this thesis, progressive and suspended freeze concentration were tested. Each chapter contains assays performed with one raw material selected under different freezing temperatures, agitation rates, freezing multi-stages and with two types of configurations to assess the influence of these parameters on the efficiency of the technology to reduce volume, allowing the recovery of either water or valuable compounds.

Overall, results obtained in this thesis demonstrated that freeze concentration is a potential, low energy consuming, alternative to existing technologies applied for waste liquid effluents concentration. Freeze concentration could be also considered as pre- or post- treatment concentration process to the conventional technologies due to its simple operation and configuration, low maintenance requirements and comparative investment costs together with its high efficiency to recover nutrients and water from selected waste liquid effluents. Finally, this thesis opens the path to continue testing and optimizing the application of freeze concentration to concentrate waste liquid effluents and by-products containing diluted valuable compounds from agro-industrial activities.

Resumen

A pesar de los beneficios de los alimentos de base agroindustrial en nuestra vida diaria en sus diferentes formas, no podemos descuidar las operaciones entre bastidores que aseguran la entrega de productos de buena calidad al mercado de consumo. En la última década se está alcanzando un fuerte incremento en el consumo de productos agroindustriales provocado por el crecimiento de la población y en consecuencia su demanda de alimentos. Por otro lado, las actividades agroindustriales generan flujos de residuos y gestionarlos adecuadamente se considera uno de los principales desafíos que enfrentan los productores en la actualidad. Los efluentes líquidos residuales agroindustriales suelen tener un alto contenido de agua, pero también compuestos valiosos, como los nutrientes, que deben valorizarse fomentando la bioeconomía circular en el sector. Para ello, ya se están desplegando muchas tecnologías para concentrar los flujos de residuos antes mencionados con el objetivo primero de recuperar compuestos de valor agregado, en este caso principalmente nutrientes, y aprovechar los beneficios de los bioproductos recuperados, y en segundo lugar, resolver el alto contenido de agua. efectos colaterales para el transporte de los efluentes generados además de permitir la posibilidad de depurar y reutilizar el agua extraída en sitio. Las tecnologías térmicas, las tecnologías basadas en membranas y las separaciones químicas son los principales procesos para concentrar nutrientes en diversos sectores y una gran variedad de efluentes residuales agroindustriales. Las técnicas disponibles se diferencian en cuanto a eficiencias, costos operativos y de inversión, retiros técnicos y selectividad para tratar un determinado efluente residual u otro.

En esta tesis, el objetivo principal fue implementar y demostrar la viabilidad técnica de una tecnología innovadora para concentrar y/o recuperar compuestos valiosos de efluentes o subproductos de desechos agroindustriales, por un lado, y entregar un efluente limpio que pueda ser reutilizados con fines agrícolas por el otro. Se probó la concentración por congelación de una selección de diferentes materias primas en base a problemas regionales relacionados con el sector en Catalunya: Suero de queso, purines de cerdo, fracción líquida concentrada de digestato y una solución hiper salina de la industria cárnica. Los efluentes antes mencionados se generan en cantidades sustanciales y tienen un alto contenido de agua que encarece el transporte a otras regiones.

Tal como lo define su nombre, la tecnología de “concentración por congelación” es un proceso térmico que opera a temperaturas bajo cero, donde la solución tratada se congela en condiciones específicas para generar una fracción líquida concentrada y un efluente más limpio (hielo derretido). Muchos tipos y configuraciones están disponibles bajo el nombre de concentración por congelación, sin embargo, en esta tesis, se probaron la concentración por congelación progresiva y suspendida. Cada capítulo contiene ensayos realizados con una materia prima seleccionada bajo diferentes temperaturas de congelación, velocidades de agitación, congelación multietapas y con dos tipos de configuraciones para evaluar la

influencia de estos parámetros en la eficiencia de la tecnología para reducir volumen, permitiendo la recuperación de cualquiera de los dos. agua o compuestos valiosos.

En general, los resultados obtenidos en esta tesis demostraron que la concentración por congelación es una alternativa potencial, de bajo consumo de energía, a las tecnologías existentes aplicadas para la concentración de efluentes líquidos residuales. La concentración por congelación también podría considerarse como un proceso de concentración previo o posterior al tratamiento de las tecnologías convencionales debido a su operación y configuración simples, bajos requisitos de mantenimiento y costos de inversión comparativos junto con su alta eficiencia para recuperar nutrientes y agua de efluentes líquidos residuales seleccionados. Finalmente, esta tesis abre el camino para continuar probando y optimizando la aplicación de la concentración por congelación para concentrar efluentes líquidos residuales y subproductos que contienen compuestos valiosos diluidos de actividades agroindustriales.

Resum

Malgrat els beneficis dels aliments de base agroindustrial en la nostra vida quotidiana en les seves diferents formes, no podem descuidar les operacions entre bastidors que garanteixen el lliurament de productes de bona qualitat al mercat de consum. En l'última dècada s'està aconseguint un fort augment del consum de productes agroindustrials a causa del creixement demogràfic i, en conseqüència, de la seva demanda d'aliments. D'altra banda, les activitats agroindustrials generen corrents de residus i la seva correcta gestió es considera un dels principals reptes als quals s'enfronten els productors en l'actualitat. Els efluents líquids de residus agroindustrials solen tenir un alt contingut en aigua però també compostos valuosos, com els nutrients, que cal valoritzar afavorint la bioeconomia circular del sector. Per fer-ho, ja s'han desplegat moltes tecnologies per concentrar els corrents de residus esmentats amb l'objectiu, en primer lloc, de recuperar compostos de valor afegit, en aquest cas principalment nutrients, i aprofitar els beneficis dels bioproductes recuperats, i en segon lloc, resoldre l'alt contingut en aigua. efectes secundaris per al transport dels efluents generats a més de permetre la possibilitat de depurar i reutilitzar l'aigua extreta in situ. Les tecnologies de base tèrmica, les tecnologies de membrana i les separacions químiques són els principals processos per concentrar nutrients en diversos sectors i gran varietat d'efluents de residus agroindustrials. Les tècniques disponibles són diferents en termes d'eficiència, costos operatius i d'inversió, retirades tècniques i selectivitat per tractar un efluent residual determinat o un altre.

En aquesta tesi, l'objectiu principal era implementar i demostrar la viabilitat tècnica d'una tecnologia innovadora per concentrar i/o recuperar compostos valuosos d'efluents o subproductes de residus agroindustrials d'una banda, i oferir un efluent net que es pugui reutilitzats per a finalitats agrícoles per l'altra. La concentració de congelació d'una selecció de diferents matèries primeres es va provar a partir de qüestions regionals relacionades amb el sector a Catalunya: sèrum de formatge, purins de porc, fracció líquida concentrada de digestat i una solució hipersalina de la indústria de processament de carn. Els esmentats efluents es generen en quantitats substancials i tenen un alt contingut en aigua que encareixen el transport a altres regions.

Tal com es defineix pel seu nom, la tecnologia "concentració de congelació" és un procés tèrmic que funciona a temperatures sota zero, on la solució tractada s'està congelant en condicions específiques per generar una fracció líquida concentrada i un efluent més net (gel fos). Hi ha molts tipus i configuracions disponibles sota el nom de concentració de congelació, però en aquesta tesi es van provar la concentració de congelació progressiva i suspesa. Cada capítol conté assajos realitzats amb una matèria primera seleccionada a diferents temperatures de congelació, velocitats d'agitació, congelació multietapa i amb dos tipus de configuracions per avaluar la influència d'aquests paràmetres en l'eficiència de la tecnologia per reduir el volum, permetent la recuperació de qualsevol dels dos capítols. aigua o compostos valuosos.

En conjunt, els resultats obtinguts en aquesta tesi van demostrar que la concentració de congelació és una alternativa potencial, de baix consum energètic, a les tecnologies existents aplicades per a la concentració d'efluents líquids residuals. La concentració de congelació també es pot considerar un procés de concentració pre o post-tractament a les tecnologies convencionals a causa del seu funcionament i configuració senzills, els baixos requisits de manteniment i els costos d'inversió comparatius juntament amb la seva alta eficiència per recuperar nutrients i aigua d'efluents líquids residuals seleccionats. Finalment, aquesta tesi obre el camí per continuar provant i optimitzant l'aplicació de la concentració de congelació per concentrar efluents líquids residuals i subproductes que contenen compostos valuosos diluïts d'activitats agroindustrials.

Chapter 1: Introduction

1.1 Agro-industrial waste

World population has doubled in the last 40 years and reached 7.7 billion in 2019; with a current growth rate of 1.08 % per year the population is estimated to reach 9 billion by 2037 (Max et al., 2019). Undoubtedly, this rapidly growing human population generates pressure on agricultural production and subsequent consumption to satisfy the demand for protein. The highest quality rating of proteins is attributed to animal sources (i.e. meat, dairy, eggs, fish and poultry) (Hoffman et al., 2004). Agricultural wastes are generally referring to unwanted products produced as a result of agricultural activities (i.e., manure, oil, silage plastics, fertilizer, pesticides and herbicides; wastes from farms, poultry houses and slaughterhouses; veterinary medicines, or horticultural plastics) (Ramírez-García et al., 2018). High consumption of meat and dairy products, leads to massive generation of agro-industrial wastes such as livestock manure, food processing wastes and wastewaters, making their disposal a serious challenge worldwide.

When talking about the generation of agro-industrial wastes effluents, the region of Catalunya is topping the list of Spain. The high density of the livestock farms makes the surrounding areas subjected to potential pollution of ground water and air quality due to the activities related to the inappropriate management of these effluents. The valorization of the abovementioned effluents is highly dependent ¡ on its nature and its chemical/physical characteristics.

A common factor that hinders the management of such type of effluents is its high-water content causing a serious transportation side-effect such as increased transportation costs. Thus, the separation of original effluent into a concentrate, which keeps the bulk of the nutrients/valuable material (facilitating its transportation) and a diluted fraction (that has the potential to be purified and recover water) can facilitate the management/valorization of these original effluents. The key goal would be to find an appropriate technology, or combination of technologies, to optimize the treatment of agro-industrial waste effluents and generate recycled value-added materials in a true circular economy approach. Regarding the investigated effluents in this thesis, the selection was made after talking to the surrounding farmer and manufactures that are main generators of these effluents who needed a solution for the current situation, namely, livestock waste, cheese whey and brines from meat industry. Below a brief description of each effluent separately and the conventional technologies that are being used to be valorized.

1.1.1 Livestock production and the resulting impacts

The development of intensive animal production following the high increase of world population leads to generating large quantities of livestock manure and turning the disposal of such waste into a serious worldwide environmental issue. Numerous national and international environmental control regulations have been developed to reduce the disposal of these wastes; however, large volumes of gas, organic materials, and other substances are still generated by manure, posing a significant risk factor for natural resources degradation (Van Dijk et al., 2016). A common example would be the ground or surface water pollution caused by the discharge of waste effluents on soils or into water bodies. The damage caused by various livestock wastes generation and unsuitable management have been frequently enormous and even tragic. In Europe, pollution cost derived from manure management is estimated to be over 12,300 M euros per year (Bernal et al., 2015; Leip et al., 2011). The high moisture content (around 95–98 %) associated with high nutrients content of these wastes negatively affects any strategy for direct application in the surrounding areas and negates any plan to export them to other regions with low-nutrient soils as a source of biofertilizers to boost soil fertility and quality. Therefore, the challenge for EU countries, and other areas, is to integrate manure management and treatment into overall farm management plans (IAEA, 2008). In 2011, the EU reported a total of 1,400 Mt of livestock waste production, out of this, 600 Mt are in the form of liquid manure from cattle and pig and about 300 Mt from solid cattle manure; the rest is produced by other livestock groups much of which is deposited on land by grazing animals (Buckwell and Nadeu, 2016). France, Germany, Spain, and the United Kingdom recorded the highest total numbers of livestock units with 22.1, 18.2, 14.4, and 13.3 M units/km^2 respectively.

According to Petit-Boix and Leipold (2018), the implementation of long term strategic environmental policies to base cities evolution on circular economy, which leads to the growth of a more efficient and innovative economy, may rely on the production of bio-products and other materials from renewable resources. The sustainable management of manure to recover nutrients is of paramount importance to create new, high-quality fertilizers and depends significantly on infrastructure and handling. Ammonia evaporation, nutrient leaching, and pathogen contamination are some of the major drawbacks of direct application of manure into the soil (Bernal et al., 2015). Therefore, before introduction of livestock manure as fertilizer into the market, it should be treated and undesirable compounds and minerals must be removed or recovered (Bernal et al., 2015). Different management strategies and treatment technologies have already been tested and scaled-up during recent times to optimize the volume reduction, nutrient concentration and final transportation or exportation of livestock wastes (Martinez et al., 2009). However, an overall nutrient recovery strategy is still required to meet environmental, economic and market needs. Operational problems, regulatory constraints, and the instability of market prices associated to the production of fertilizers, in terms of both quality and quantity, makes setting a global strategy difficult.

1.1.1.1 Valorization of livestock waste

The characterization of livestock manure would be advantageous to optimally select appropriate treatment or valorizing technologies (Malomo et al., 2018). Table 1.1 highlights the useful components of manure that can be obtained from animal wastes, that are mainly energy, fiber, organic matter, and nutrients. A wide range of technologies that are potentially available to treat livestock manure, depending on the desired benefit, the management could be via biological treatments, physicochemical treatment or what is called integrated systems. To take advantage of useful components in animal manure (Table 1.1), many case studies have been reported recently within the framework of encouraging renewable energies and sustainable circular economy. Synthesis of different biofuels from livestock as sustainable feedstocks has seen many interest (Jung et al., 2021), aside with the fertilizers are the largest piece of the agricultural market input and the consumption of fertilizers has increased remarkably over the last decades, driven by the need to feed a rapidly expanding global population (FAO, 2017).

Table 1.1. Useful components contained in manure (Manitoba, 2015).

Manure component	Use	Benefit
Energy	Bio oil and biogas	Supplementary source of energy; Significant reduction of relying on fossil fuels
Fiber	Building material and paper	AS an environmentally friendly source turned into lucrative goods
Organic matter	Soil relief	Reclaim of soil construction and improving water holding capacity
Nutrients	Compost, fertilizers, animal feed	Cost effectiveness strategy to replace chemical fertilizers and revenue output from sales of manure

1.1.2 Cheese whey as a dairy effluent

Dairy has become a top-ranking commodity all over the world, dairy industry producers are greatly challenged by the growing demand of increasing population throughout the world for milk and milk-related products. The global cheese market is witnessing progressive growth due to the rising demand for cheese in assorted types of food products, reaching a peak in 2018 (IndexBox 2019). Cheese industries produce about 9-10 L of cheese whey (CW) per kg of produced cheese (Eurostat, 2018). CW effluent is particularly characterized by a high organic and volumetric load making it the main polluting waste stream in the dairy industries (Ryan and Walsh, 2016; Slavov, 2017). The amount of CW produced is strongly related to the productivity of the cheese produced (Carvalho et al., 2013), accounting for 85-95 % of the milk volume; containing an average of 55 % of whole milk nutrient content; 20 % of it is protein and characterized by COD and BOD contents of 50–102 and 27–60 g/L, respectively, in which more than 90% is made up of lactose (Carvalho et al., 2013; Ryan and Walsh, 2016). Moreover, CW also contains sodium (0.045 %), chloride (0.09 %), potassium (0.14 %), calcium (0.035 %) and salts (0.46–10 %) (Prazeres et al., 2012). Part of the 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 (Carvalho et al., 2013). Figure 1.1, illustrate a comparison between CW and milk content on components.

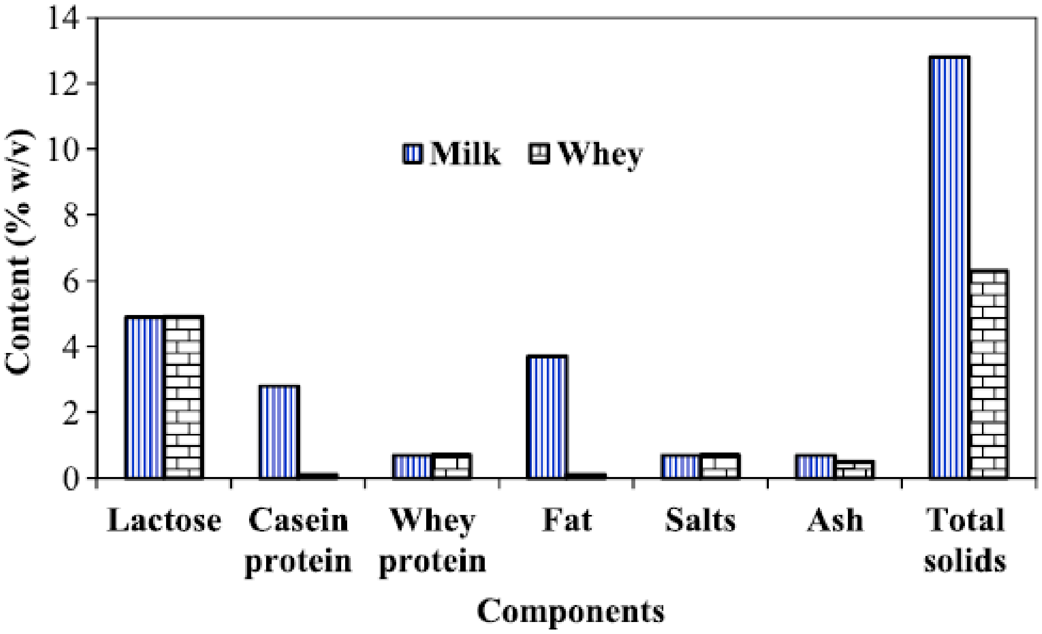

Figure 1.1. Comparison of the proximate analysis of bovine milk and its whey.

1.1.2.1 Valorization of the cheese whey:

Initially, whey was directly discharged into the environment or used as an animal feed. However, due to its high organic load, it is considered as a threat to the environment as well as to human health. On the contrary, whey, being the ample source of lactose, functional proteins, peptides, and other nutrients, is a promising source for the production of a variety of value-added products (Panesar and Kennedy, 2012). Due to the valuable characteristics of the CW several biotechnologies for bioenergy and biochemicals production have been used to valorize this nutrient and energy rich waste, namely the anaerobic digestion and fermentative processes (Figure 1.2).

Additionally, the nutritional content of CW is attracting much more interest resulting in the development and application of different physical, chemical and biological processes to recover value-added products from cheese whey, such as vitamins, proteins and sugars (Bald et al., 2015; Panesar et al., 2007; Mollea et al., 2012). In this regard, about 45 % of the CW is used directly in liquid form, 30 % in the form of powdered cheese whey, 15 % as lactose and by-products from its removal, and the rest as cheese whey protein concentrates (Marwaha and Kennedy, 1988; Panesar et al., 2007; Guimarães et al., 2010; Baldasso et al., 2011). However, since the CW is an unbalanced source of nutrients, due to the higher lactose content versus the protein, it results in fewer nutritional benefits of more typical protein sources (Baldasso et al., 2011). Thus, for better valorization and wide use of the protein and lactose from whey, the separation of the two components is a crucial step. Many techniques have been developed to concentrate whey proteins selectively, mainly the wider known physical processes to concentrate CW are temperature-based processes, membrane-based processes and demineralization (Kaur et al., 2020).

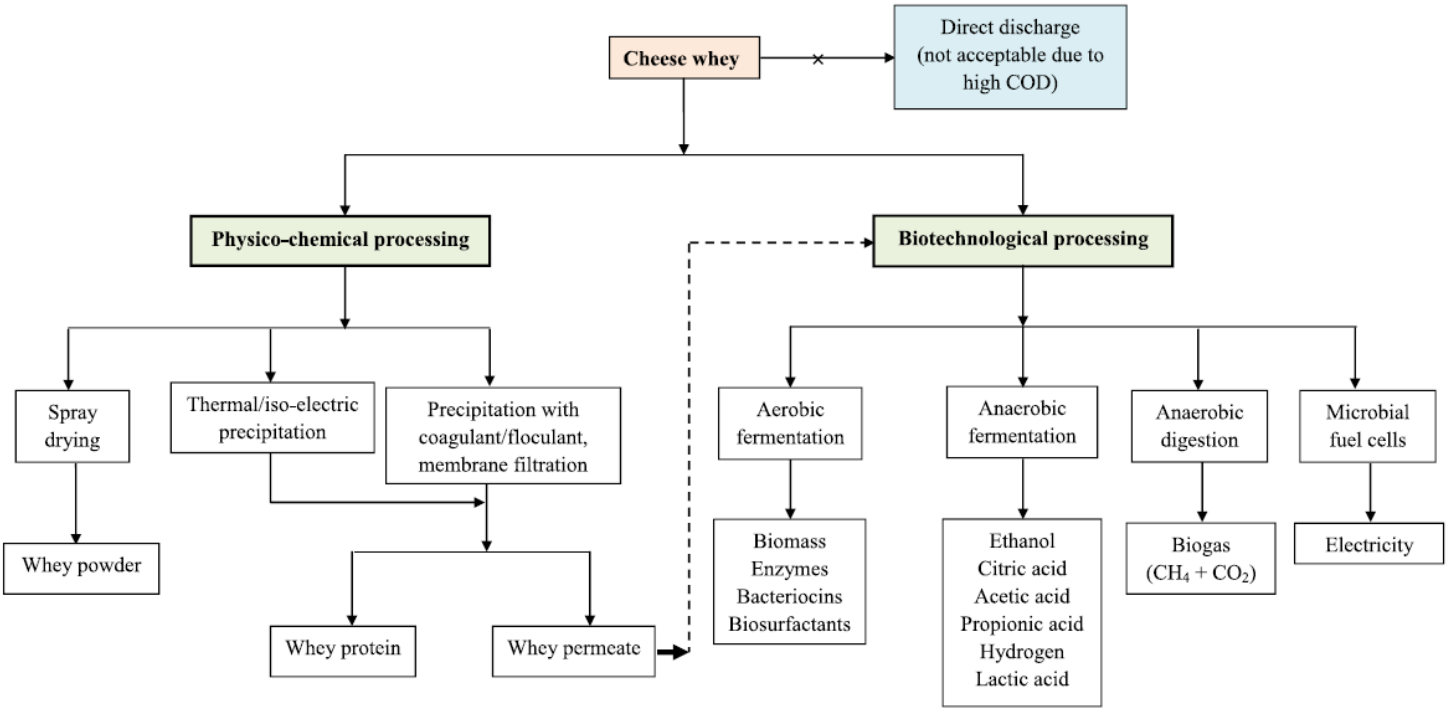

Figure 1.2. Processing of whey by physic-chemical and biotechnological methods.

1.1.3 Brines from meat industry

Brines is a solution of salt in water, where the salinity ranges from 3.5 % up to 26 % (from seawater to typical saturated solution, depending on the temperature). Specifically, brine solution also refers to the by-product stream generated throughout the process of desalination to recover fresh water (Panagopoulos et al., 2019). Besides sweater, industrial brines could be found as by-products generated in the production of some types of cheese, the processing and production of some products of meat, in the mining industry, chemical manufactures, etc. Depending on the total dissolved solids of each brine solution, the classification of the type of water was made and defined the industrial brines as Highly saline brine with total dissolved solids (TDS) level of 70,00 ppm up to full saturation (Ahmed and William, 2011).

There are many stages in meat processing such as canning, cooking among others that uses brines solution for the conservation of flavor and quality of the products (Vestergaard et al., 2005). Curing (salting, dry salting, vessel salting, injection) and pickling are the main operations engendering wastewaters containing brines and meat juice. The typical preparation of brines used in the meat industry is by dissolving solid salt (NaCl) to water, other salts may be added or used as substitute to the common table salt (NaCl). These salts are potassium nitrate (KNO_3), sodium nitrate ($NaNO_3$) and sodium nitrite (NaNO2). Pickling and curing brines contain also other additives with properties of enhancing flavor, prevention of discoloration, improvement of water-holding capacity of the meat. These additives may be sugars, ascorbic acid and polyphosphates. Considering the later, it is expected that wastewater from brining meat and sub-products will contain ions such as Na^+, Cl^-, K^+, NO_3^-, NO_2^-, phosphates (PO_4^{-3}) and is to be characterized with significant levels of COD and BOD (because of the presence of sugar and ascorbic acid). Additionally, the presence of COD, BOD, NH_4 and phosphorous is expected because of the meat components that are transferred to the brine. Many of the ingredients of brine solutions represent polluting material in high concentrations and add significantly to the raw waste load from the pickle operation (Johnson et al., 2004).

1.1.3.1 Brines disposal and treatment

Considering the significant amount of brines generated through desalination processes besides food processing industry, different methods of either disposal or treatment have been developed. The main methods include surface water discharge (Ziolkowska., 2014), sewer discharge (Chang, 2015), deep-well injection (Thomas and Benson, 2015) and evaporation ponds (Rodríguez et al., 2012). Each method is hindered by either its complexity or the operation cost. Also depending on the marine environment of the disposal one method could be more suitable than other in order to comply with regional environmental regulations and minimize environment hazards. In this note, the public awareness has increased in regard to the environmental impacts of brines, thus restricted regulations were adapted of the abovementioned disposal methods (Abualtayef et al., 2016), leaving no other choice than developing and optimizing desalination techniques that are known as Zero Liquid Discharge (ZLD). As its label indicates, ZLD can be described as a single or a combination of desalination techniques aiming to produce high-purity freshwater with the complete removal of liquid waste (Alnouri et al., 2017; Bazargan, 2018). Desalination technology can be defined as a treatment system that is capable of producing fresh potable water from a saline water supply at a reasonable cost and reasonable reliability (Hanbury et al, 1993). These technologies are divided into three main categories which include thermal, membrane, and chemical processes (Buros, 2000).

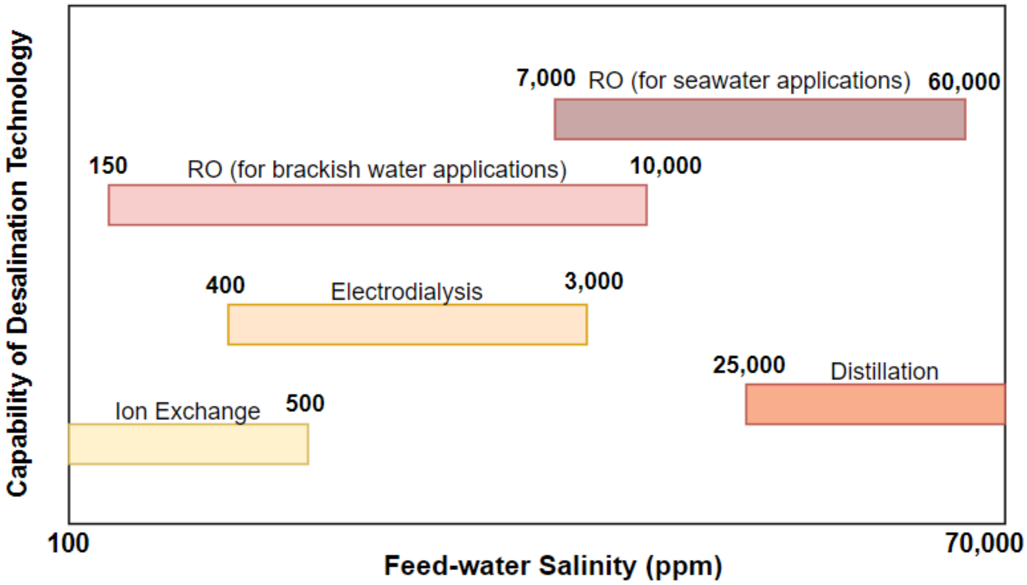

Figure 1.3. Desalination technologies as a function of feed water salinity adapted from (Ahmad, 2012).

1.2 Valorization of agro-industrial waste effluents for nutrient and water recovery

To recover either water or nutrients, the conventional technologies used follows the same principle, as in one hand the recovery of nutrient from a certain solution means concentration of a maximum amount in a smaller volume, which deliver a diluted fraction of the same solution at the same time. Thus, there are many common technologies and techniques that are used for either concentrating nutrients or water recovery.

1.2.1 Membrane filtration

1.2.1.1 Membrane filtration for nutrient recovery from livestock waste

Membrane technologies target treating those effluents containing compounds or elements that may be either retained or pass through a thin physical barrier depending on molecular or particle size, concentration of certain compounds, operational temperature and applied pressure (Logan and Visvanathan, 2019; Van-Beek et al., 2018). Many parameters should be considered to apply membrane filtration such as the chemical composition of the effluent to be treated and the interactions between membrane surface and components in the feed flow (Logan and Visvanathan, 2019). According to the literature, the utilization of membranes has been proven effective to concentrate and purify nutrients (Ainscough et al., 2017; Massias et al., 2015). Microfiltration and ultrafiltration membranes are basically aimed to remove particles, while reverse osmosis and nanofiltration membranes can be applied as nutrient recovery techniques (Shi et al., 2018). Nanofiltration membrane was used to recover phosphorous and ammonia from anaerobic digester effluent at pilot scale (Zacharof et al., 2019). The findings reported that the separation and filtration of P and N are correlated to pH, membrane electric charge, and ionic speciation. Besides that, the application of gas-permeable membrane to an extend to be coupled with anaerobic digesters, targeting the recovery of N from liquid manures in a concentrated stable ammonium solution; the final product could be used as a stable fertilizing salt solution (Molinuevo-Salces et al., 2018). The application of three bipolar membrane electro-dialysis (BMED) units configured for nutrient recovery from animal manure was also one of the recent applications of membrane filtration techniques (Shi et al., 2020). One major drawback associated with membrane separation technologies is membrane fouling, which negatively affects the process efficiency, application and durability due to the increasing hydraulic resistance (Fierascu et al., 2019). The fouling issue is a complex phenomenon which mainly depends on the feed stream composition and causes flux decline. Fouling reduces the membrane performance and productivity (regardless of its type) and requires additional costs for cleaning and maintenance. Membrane technology is the main separation technique used for industrial and for commercial applications as the technique provides high recovery rates of over 98 % with comparatively low capital cost (Komesu et al., 2017).

1.2.1.2 Membrane technology for protein and lactose recoveries from cheese whey

Separation, concentration and fractionation of total solids are processing alternatives used in the treatment of cheese whey for a valuable end product. Reverse osmosis, nanofiltration and their combination are generally used as a pre-concentration step before drying the cheese whey and evaporating it, as it is more economical to use evaporation with high dry matter content (Dairy processing handbook, 2006). Protein recoveries were originally isolated through precipitation techniques, however, nowadays membrane separation, chromatographic processes and crystallization are widely used for the recovery of whey protein concentrate and isolate (Brans et al., 2004) that allows obtaining concentrated solutions of both whey protein in a concentrated fraction and lactose in the permeate while removing fats and minerals leading to an optimal use of whey, resulting additionally in the development of newer product formulations (Ramhandran and Vasiljevic, 2012). Lactose, as the main constituent of CW (Ryan and Walsh, 2016), is being recovered by means of crystallization either of untreated CW or after the removal of protein (Dairy processing handbook, 2006).; depending on the application of lactose (pharmaceutical manufacturing processes, food compliments, etc.) a higher or moderate purity of lactose is required, thus further steps of purification must be considered for improving its quality (Souza et al., 2010).

1.2.1.3 Membrane filtration for desalinating brine solutions

The most commonly used membrane-based technology for desalination purposes is the pressure driven reverse osmosis, despite its unpromising efficiency for high-salinity brines which is mainly limited by the required pressure for such high salt composition. Specialized membranes were designed to handle very-high pressure allowing the treatments of High saline brine solutions (Davenport et al., 2018). Forward osmosis is differing from reverse osmosis in types of pressure used, as no external pressure is required for desalting brines, however, faces the fooling challenge (Bell et al., 2017). Osmotically assisted reverse osmosis, which combines the principle of reverse and forward osmosis membranes, is also a recent well-adapted technic for desalination of brine solution (Bartholomew et al., 2017), and that is expecting a potential advance in the coming years (Bartholomew et al., 2018; WDR, 2018). Besides that, membrane distillation and membrane crystallization are thermal-driven membrane-based technologies that have as a purpose desalination of brines with very high salinity. In one side, the brine is warmed before achieving the membrane to recovery pure evaporated water condensate whereas a concentrate is being retained in the hydrophobic membrane (Park et al., 2019). On the other side, membrane crystallization offers the option to recover freshwater and valuable crystal salts simultaneously (Quist-Jensen et al., 2015), following the principle of evaporation and condensation the volatile compounds together with water. Electrodialysis is voltage-driven membrane-based technology that has been commercially successful in desalination following the principle of selective transport of ions to obtain fresh water and a concentrated brine solution (Tado et al., 2016).

1.2.2 Chemical amendment and separation

1.2.2.1 Chemical separation for nutrient recovery

An alternative to recover target nutrients from digested manure is to form struvite (precipitation of substrates) in order to get a slow release of fertilizing compounds into the soil (Shi et al., 2018). Struvite formation is strongly affected by temperature, suspended solids, ion concentration and pH. For example, if magnesium ion concentration in the digestate is insufficient, magnesium chloride or magnesium sulphate must be supplemented to induce struvite formation. A high concentration of magnesium ions would negatively affect the calcium ion precipitation and would adversely impact the recovery yield of struvite (Tervahauta et al., 2014). Various pre-treatment methods have been applied to increase the concentration of target macro and micronutrients in their soluble form such as ultrasonic, microwave, acidification and heating; however, these chemical amendment techniques are costly, especially at large scale (Cerrillo et al., 2015; Kataki et al., 2016).

1.2.2.2 Biotechnological and chemical methods for protein and lactose recovery

Non-protein nitrogen products can be used as partial replacement for natural protein in ruminants because certain microbes in the cattle rumen can synthesize protein from urea and ammonia (Zadow, ,1984). However, in order to get a balanced feed of nitrogen and energy, urea and ammonia have to be transformed into more suitable forms, which slowly release nitrogen to the rumen for improved protein synthesis. Lactosyl urea and ammonium lactate are two such products based on whey. Lactosyl urea is a result of the chemical reaction between urea and lactose in the presence of sulphuric acid, meanwhile ammonium lactate is resulting from the fermentation of lactose into lactic acid maintaining the pH with ammonia (Dairy handbook, 2006).

1.2.2.3 Chemical methods for desalination of brine solutions

Ion exchange technologies are considered as chemical methods due to its principles of separation; the main purpose of ion exchange technologies is water softening among other applications (Younos et al., 2005). It follows the principle of interchange of ions between solid and liquid phases. Ion-Exchange technologies used for brine desalinations are known by its complexity, which was the main reason behind its lack of attraction recently (Arden 1997, Sengupta 1995).

1.2.3 Thermal-based and thermochemical technologies

1.2.3.1 For valorizing livestock waste

Thermochemical treatments such as incineration, gasification, hydrolysis, pyrolysis, and hydrothermal carbonization could convert biomass into gases and ash residues and reduce the bulk volume of wastes (Liu et al., 2018; Shi et al., 2018). Direct combustion of solid organic wastes in the presence of air have been performed at full scale as an energetic valorization process of municipal sludge in Europe (Vaneeckhaute et al., 2017). Incineration was reported as a potential treatment for the recovery of phosphorous from poultry litter (Lynch et al., 2013). Gasification and hydrolysis at reaction temperatures of 800 °C and 400 °C produce synthesis gases (Panigrahi et al., 2003), bio-oil, and biochar respectively (Jadhav et al., 2019). Hydrolysis is a promising technology to manage animal manure and add value by producing biochar as a fertilizer (Cantrell et al., 2012). Hydrothermal carbonization is a less energy intensive technology and has been applied to treat digested and fresh manure through a first hydrolysis of the biomaterial at 170 °C followed by carbonization at 250 °C. The final product is a valuable solid char (hydrochar) and is used as a sustainable sorbent for pollutants. As the evaporation of water is avoided, this technology requires less energy than other thermal treatments and the technology has received increasing attention in the last decade. Compared to pyrolysis method, the liquid fraction produced by hydrothermal carbonization process can be applied as a liquid fertilizer because of the high ammonium concentration, while in pyrolysis technique a pre-drying of materials to be hydrothermally carbonized is not required (Lucian and Fiori, 2017).

1.2.3.2 For treating brine solutions

Thermal-based technologies as described by its name, require thermal energy for operating the process and recover fresh water. In this sense, the most commonly used technologies in ZLD approach are brines concentrators and brine crystallizers that differs on the configuration and the by-product beside freshwater (Spellman, 2015). Multi-stage flash distillation and multi-effect distillation are the leading thermal-based desalination technologies, however, with material upgrade a potential has been detected for brine desalination (Mabrouk and Fath, 2015). Spray dryer and eutectic freeze concentration are two technologies that recover solid salts beside freshwater during the desalination process (Tillberg, 2014; Williams et al., 2015). Wind aided intensified evaporation id another thermal-based desalination technology, the main purpose with this technology is volume minimization- following the principal of evaporation using intense power wind (Basile et al., 2018).

1.2.4 Biological treatments for valorizing agro-industrial waste effluents

Anaerobic digestion (AD) is a common biological treatment technology for the hydrolysis of organic solids, pathogen reduction, stabilization of wastes and energy recovery through biogas generation from livestock manure (Logan and Visvanathan, 2019). At the end of the AD process, the released nutrients from digested wastes will turn into inorganic forms or get adsorbed onto the solid surface of digested materials (Nag et al., 2019). In AD process, phosphorus is mostly released in the organic form, however, less than 10 % of this organic form remains soluble after digestion (Hongjian et al., 2015). Reduction of solids handling costs for AD processes requires the solid digested parts to be dewatered to produce a by-product rich in nutrients (mainly K and N). This nutrient-rich by-product can be a substrate for nutrient recovery purposes and the remaining materials (particle bound nutrients), considered as bio-solids, have value as nutrient amendments for agricultural applications (Buckwell and Nadeu, 2016). The AD process is not a nutrient valorization technique, but a technology used to produce local energy for farms and agri-food industries.

Besides, AD and fermentation are the leading technologies when it comes to the production of biofuels from CW. The production of biogas (Comino et al., 2009; Ukpai and Nnabuchi, 2012), bioethanol (Balia et al., 2018, Zhou et al., 2019), biobutanol (Diez-Antolinez et al., 2016; Qureshi et al., 2014) and biodiesel (Girard et al., 2014) from CW and its permeate has gained interest because of their nontoxic, renewable, and biodegradable nature (Zhang et al., 2016) and to mitigate the issues of climate change and cost effects of fossils. Bioethanol production from whey is currently gaining attention where the lactose present can either be fermented or hydrolyzed for bioethanol production (Sansonetti et al., 2009). The tradition route for butanol production consists of anaerobic process known as acetone-butanol-ethanol fermentation generating acetone, butanol and ethanol as products (Zhang et al., 2016), which is an optimized and effective process where multiproduct are being produced at once. CW effluent composition has a 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 nitrogen components for aerobic or anaerobic processes (Prazeres et al., 2012).

1.3 Freeze concentration technology

1.3.1 Freeze concentration technique

Freeze concentration (FC) has become a technology of interest due to the low temperature of the process (Sánchez et al., 2009). The use of FC has been reported by many sectors including concentration of liquid foods, seawater desalination, purification of organic chemicals, and treatment of hazardous wastewater (Chen et al., 2019; Htira et al., 2018). Regardless of the application, the freezing temperature should be below the freezing point of the treated solution. The performance of newly developed FC methods is evaluated according to energy consumption and the feasibility of the method when compared to the existing in-place technologies. FC is advantageous as energy required to evaporate water is seven times greater than that to freeze it (2500 kJ/kg vs 335 kJ/kg) (Pazmiño et al., 2017). This does not take into account the possibility of energy recovery in both processes, where the economic potential benefits of using FC remain high. The experience with full-scale FC in a variety of industries shows that the process is superior in terms of efficiency to state-of-the-art mechanical vapor recompression and thermal vapor recompression evaporators (Pazmiño et al., 2017). Evaporation shows outstanding results in terms of concentration obtained compared to membrane technology which is limited by the osmotic pressure limit (Hubbe et al., 2018). Perhaps, the potent advantage of FC are the low energy and temperature requirements that will significantly reduce energy consumption when compared to other technologies. Similarly, low temperature operation leads to low-cost materials of construction for the process equipment, for example, the use of plastics rather than steels has a major improvement to the carbon footprint of the resulting equipment, and with the advent of bioplastics, this could improve even further with time. All of these aspects offer a potentially significant environmental improvement over other technology. Additionally, for desalination, crystallization, juice concentration and general water removal, the initial solution to be frozen does not need a pretreatment step, thus chemicals typically required for pre-treatment are avoided.

1.3.2 Principle and the general concept of freeze concentration

Crystallization processes can be divided into crystallization from melts and crystallization from solutions (Figure 1.4). In the case of melt crystallization, the crystallizing species are the main component (solvent) of a liquid mixture. Supersaturation in melt crystallization is mostly created by cooling or modifying the pressure, although a high-pressure difference is required. In the case of solution crystallization, the crystallizing species are one of the minor components of the liquid mixture (solute). For highly soluble substances, like sugars and highly soluble salts, the difference between solution crystallization and melt crystallization becomes unclear (Pronk, 2006). Some authors suggest that whenever heat transfer dominates the phase change process, this should be called melt crystallization, while in solution crystallization mass transfer dominates the process (Ulrich et al., 1988). Eutectic Freeze Crystallization (EFC) can be considered as a combination of both melt and solution crystallization since water and solute crystallize simultaneously (Williams et al., 2015).

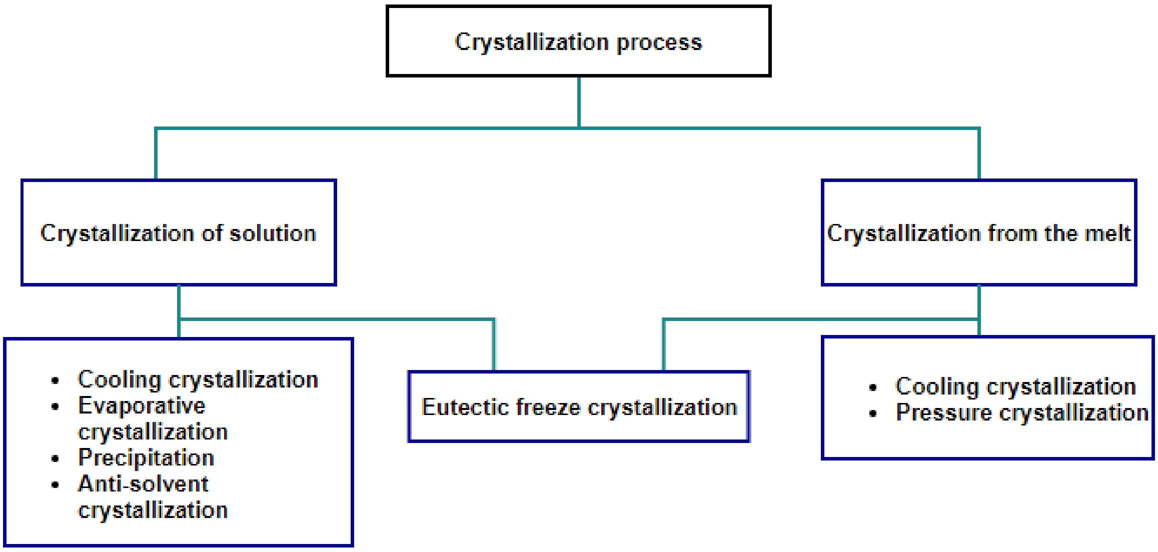

Figure 1.4. Overview of crystallization processes adapted from (Pronk, 2006).

The different types of crystallization can be seen in a typical binary phase diagram of water solution, as shown in Figure 1.5. Separation by freezing is based on solid-liquid phase equilibrium and depending on the initial concentration, different products can be obtained in a crystallization process by freezing. If the initial concentration of the solution is higher than the eutectic concentration, the solute will crystallize first. In contrast, if the initial concentration is lower than the eutectic concentration, ice will crystallize first. Finally, if the solution concentration is equal to the eutectic concentration, the crystallization of ice and solute occurs simultaneously. At the eutectic point an equilibrium exists between ice, salt and a solution with a given concentration. This concentration is called the eutectic concentration and the temperature at which this equilibrium is found is called eutectic temperature/point.

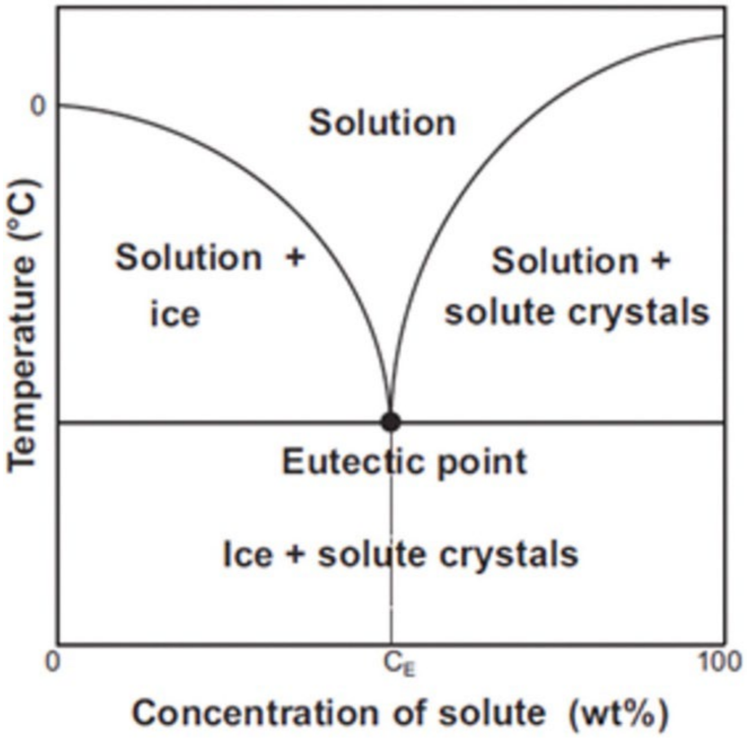

Figure 1.5. Binary phase diagram for a solute in water (Randall and Nathoo, 2015).

FC is a particular type of cooling crystallization from the melt, in which water is separated from the liquid through ice crystallization at low temperature, followed by a separation step to remove ice from the concentrate (Fig. 1.6) (Lu et al., 2017).

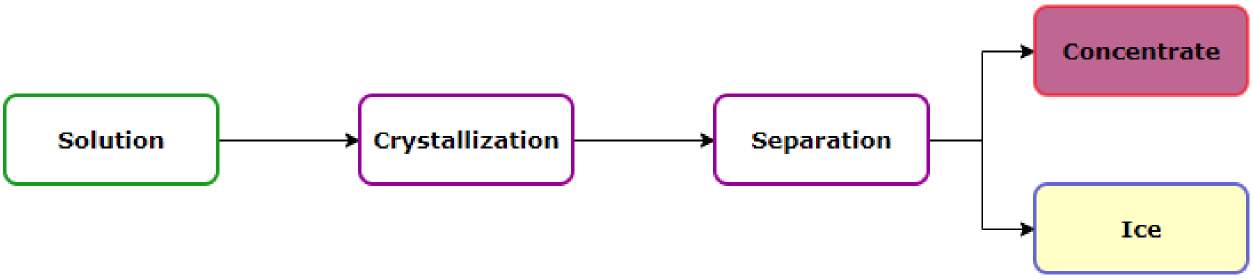

Figure 1.6. Schematic for a basic freeze concentration process adapted from (Berk, 2009).

This technology involves lowering the temperature of the product in a sufficiently controlled manner to partially freeze the product, resulting in the formation of ice crystals in a fluid concentrate. If formed under the appropriate conditions, these ice crystals will be very pure. This results in the formation of ice crystals with the lowest possible incorporation of product solute. The ice crystals are then removed whilst maintaining a minimum of liquid carryover, resulting in a concentrated product. The process of FC is dependent on two main characteristics of the concentrate product. The maximum concentration obtainable is determined by the viscosity of the concentrate and the freezing point (Ruemekorf, 2000). The maximum concentration is reached when the viscosity of the liquid prevents the growth of ice crystals (Van-Beek et al., 2018). The crystal growth rate decreases as viscosity increases and the system requires a longer residence time (and thus larger equipment) to reach a separable crystal size because the capacity of ice separator is inversely proportional to the viscosity (Petzold and Aguilera, 2009). The freezing point depression due to the solute concentration can be so great that the lower temperature limit for the refrigerant may be reached and results in the need for a multi-stage refrigeration system, which is usually too expensive to be feasible. Typically, commercial systems in the food industry operate with up to 45–55 % of total dissolved solids (Van Nistelrooij, 2013).

1.3.3 Classification of freeze concentration

1.3.3.1 Direct systems

FC processes can be classified by the contact mechanism between the refrigerant and the solution. In the direct freezing, the refrigerant used to cool the solution is mixed directly with the solution and promotes highly efficient heat transfer. Other advantages include the high production rate per unit volume at a low driving force, low power consumption, absence of moving parts, and a compact and efficient unit (Rahman and Al-Khusaibi, 2014). The major drawback is the refrigerant contamination besides the use of a flammable and potentially explosive refrigerant, such as butane, creates a major safety concern (Randall and Nathoo, 2015). There are three main direct FC methods, namely: direct contact or triple point, direct secondary and c) direct Clathrate (gas hydrate.

In contrast, indirect freezing is obtained without direct contact and occurs via some form of heat exchanger device. One of the advantages of this system is no interaction between solution and refrigerant, which allows the separation of ice crystals and concentrate solution in the same equipment. The main disadvantage is the large heat transfer resistance of the wall and ice layers, which result in the requirement for a large heat transfer area with low heat transfer rate and long crystallization time (Rahman et al., 2007). In this thesis, attentions were focused on the indirect FC.

1.3.3.2 Indirect systems

In the indirect process, there exists a wall separating the solution and refrigerant. The indirect-contact process can be subdivided into suspension freeze concentration (SFC), progressive or layer freeze concentration (PFC) and block freeze concentration (BFC).

SFC: in this process, small ice crystals grow large in suspension crystallizers and are purified by the Ostwald ripening mechanism (Figure 1.7). The effective ice removal and separation can be done in wash columns specifically developed for this purpose. Using this technique, the impurity of the ice crystals is <100 ppm (Van-Beek et al., 2018), which is highly attractive. Although SFC has been used industrially in liquid food applications as a key technology, in practice the Ostwald ripening process needs a long operation time.

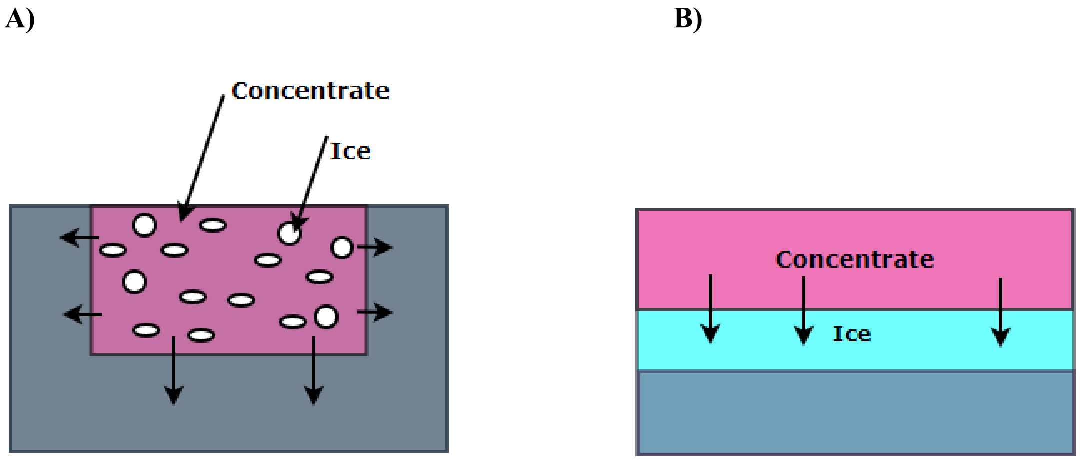

Figure 1.7. Freeze concentration methods. A) SFC B) PFC. The direction of arrows represented heat transfer adapted from (Petzold and Aguilera, 2009).

Thus, SFC is usually limited to large scale processes in continuous operation mode. For this reason, this technology requires a high initial investment with less operational flexibility, limiting the practical application of SFC.

PFC: unlike the suspension method, progressive FC consists of the formation of a single ice crystal, which is formed layer by layer on the heat exchange surface (instead of many ice crystals as in SFC) (Figure 1.7). The separation between the ice crystal and the concentrated solution is then easier and can be done in the same equipment, significantly reducing the cost of the operation. This process is used for purifying chemicals, but not at large scale. One reason for this is probably because solute inclusion or entrapment in the ice layer is hard to avoid during the growth process (Flesland, 1995). For PFC there exists a range of different equipment at various scales that have been applied to several food liquid applications (Sánchez et al., 2011). Figure 1.8 illustrate two different configurations of PFC, known as falling film-based reactor (A) and agitated vessel-based reactor (B).

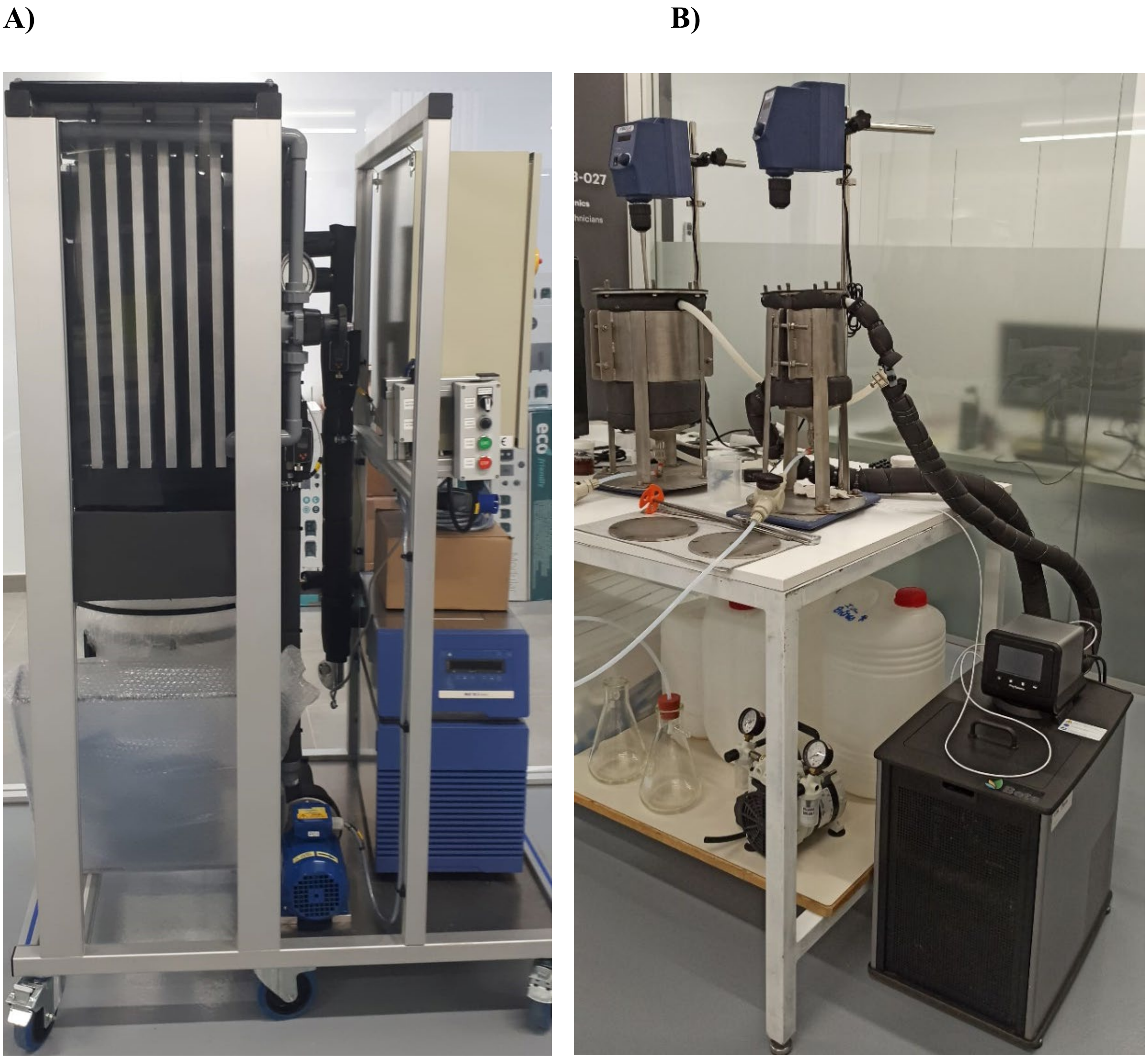

Figure 1.8. Progressive freeze concentration falling film-based plant (A) and agitated vessel-based plant (B).

BFC: in the case of the block system (BFC), also known as FC by freezing-thawing, the fluid is completely frozen and the temperature in the center of the product is below the freezing point (Aider and de Halleux, 2009). Subsequently, the block is thawed, and a concentration gradient is observed among the thawed fractions with a higher concentration in the initial fractions (Figure 1.9). The concentrated fraction is separated from the ice fraction by gravity, combined with techniques to improve solute performance through the application of centrifugal force, vacuum, microwave, annealing, ice nucleation protein (INP), among others. One of the main advantages of this technique is related to the absence of moving parts, like stirrers or pumps, which offers a reduction in production costs. The concentration efficiency of BFC is limited and multistage operations are inevitable (Aider and de Halleux, 2008) to obtain a high level of concentration, which requires high energy consumption. This technique is still at the laboratory stage of development.

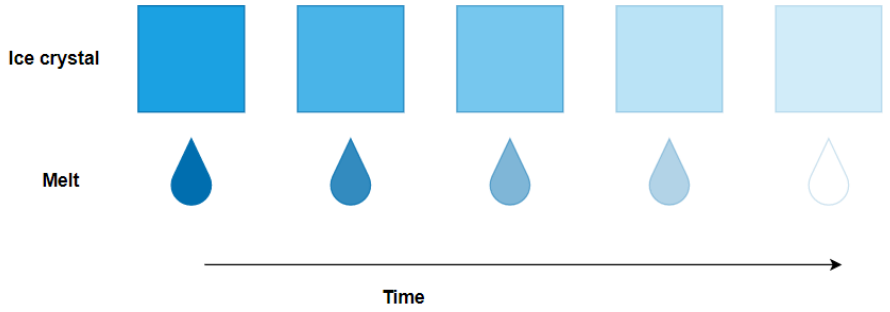

Figure 1.9. The principle of partial ice-melting for a frozen block (Miyawaki, 2018).

1.3.3.3 Eutectic freeze crystallization (EFC)

EFC has been examined to recover water and salts from solutions. The solution is cooled down to a eutectic temperature where both salt and ice simultaneously crystallize (Lu et al., 2017). The salt, being denser than the solution and ice, sinks to the bottom of the crystallizer while the ice, being less dense, floats to the top. Theoretically, the technique can handle all kinds of soluble contaminants with removal efficiency close to 100 %. The EFC process has used both direct and indirect freezing to reach eutectic conditions (Figure 1.10). In the case of food liquids, the FC process can only be applied to a concentration just below that of the eutectic point, this is because problems arise when separating ice from a very viscous liquid (both increased concentration and low temperature create difficulty) (Deshpande et al., 1984).

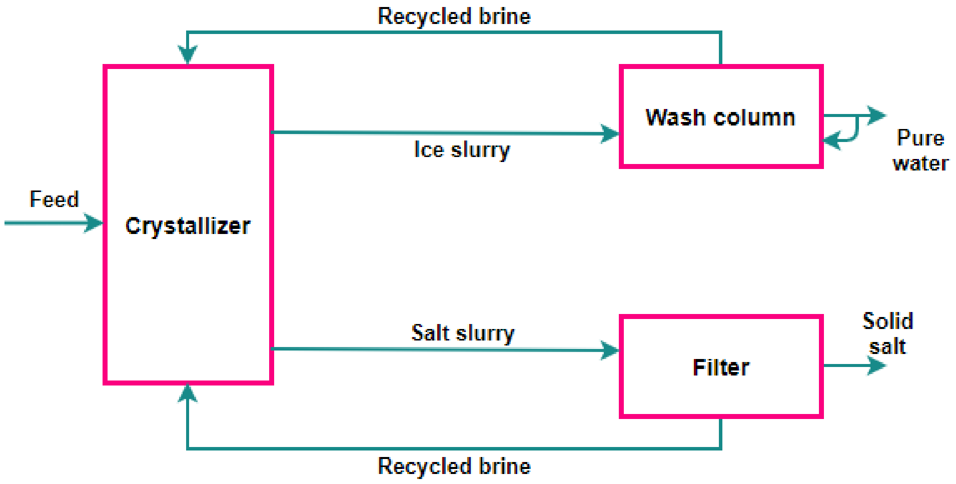

Figure 1.10. The basic process for eutectic freeze concentration (Frank et al., 2004).

1.3.4 Advantages and disadvantages of the freeze concentration technique

FC is of particular interest due to the sub-zero temperatures used in the process and has been explored industrially for food processing but has merit for various other sectors such as seawater desalination and wastewater treatment. The major advantage for FC is the relatively low energy consumption when compared to evaporative processes and could compete with membrane separations at large scale production volumes (Table 1.2). Throughout history, many methods have been developed to optimize the efficiency of the FC process and to improve the quality of the final product. Regardless the sector of application FC, also known as Cryo-concentration, the freezing temperature should always be below the freezing point of the treated solution. The performance of novel FC applications is normally evaluated according to the energy consumption and the feasibility of the method when compared to the existing technology in use (Raventós et al., 2012a). For example, evaporation shows outstanding results in terms of concentration achieved when compared to membrane technology. However, membrane technology will use far less energy as the requirement for a phase change is avoided. The lower energy requirement for freezing coupled to low temperature operation means that low-cost materials can be used for the process and the usual problems with corrosion and scaling disappear (Samsuri et al., 2016). For desalination, crystallization, juice concentration and water removal, the initial solution to be frozen does not need pretreatment. The chemicals required and costs associated with pretreatment are then avoided. Similarly, there is no fouling of surfaces, which would be the case with membrane separations and low ecological impact (Shi et al., 2018; Wang et al., 2015). Another major advantage of FC is the ease of hybridization, especially with membrane systems. The use of a hybrid process will be beneficial due to synergies between technologies. Membrane processes are often limited by the fouling potential of certain salts present in wastewater and also by the osmotic limit of the solution as concentration increases. In contrast, FC can operate at any salt concentration under the eutectic composition. Also, if EFC is adopted, then salts can be recovered from the wastewater and a hybrid process using membranes can then work at higher water recoveries. Similarly, the volumes of brine created are significantly reduced, which will aid in the unsustainable disposal problems currently faced. Hybrid FC processes are also suggested to have the lowest energy consumption when compared to conventional saline waste stream treatment options (Zikalalaa et al., 2017). Obviously, any technology cannot guaranty a complete and perfect solution without limitation (Table 1.3). The FC process, when compared to evaporation and membranes process, has a higher capital and operating cost. This is mostly related to the ice separation stage and is the most common problem among the various forms and methods of freezing technologies (Kalista et al., 2018). To optimize the separation step, the use of a compressor has been implemented, However, this also represents an expensive method of furnishing the energy requirements of the system (Sánchez et al., 2011). Quality improvement of solutions requires high quality energy, required for crystallization, when compared to low quality energy that can be used in many evaporation processes. The points raised in this section suggest that the FC technique has significant potential as a cleaner and more sustainable technology when directly compared to other technologies for the treatment of animal manures.

Table 1.2. Advantages and applications of freeze concentration reported in the literature.

Advantages	Method	Sector	References
1- Less energy consumption	Direct freezing with n-butane	Desalination	Madani (1992)
	FC system with two stage compression using tubular heat exchanger	Desalination	Rane and Padiya, (2011)
2-Atmospheric pressure operation	Direct freezing with air	Desalination	Cerci (2003)
	Indirect freezing with scrapped surface heat exchanger SSHE	Desalination	Habib and farid (2006)
	FC system with heat pump, FCSwHP	Food industry	Rane and Jabade (2005)
	Indirect freezing with fluidized bed Heat exchanger	Desalination	Cheng et al. (1987)
3- High mass transfer coefficient	Vacuum freezing multi-phase transformation	Desalination	Rane and Jabade (2005)
	Indirect freezing with fluidized bed Heat exchanger	Food industry	Habib and Farid (2006)
4- Eliminate difficulty of ice brine separation	FC system with two stage compression using tubular heat exchanger	Desalination	Rane and Jabade (2011)
5- Eliminates refrigerant and compressor	FC system with heat pump, FCSwHP	Desalination	Rane and Jabade (2005)
	FC system with two stage compression using tubular heat exchanger	Desalination	Rane and Padiya (2011)
6- 75% to 90% reduction of the energy required by conventional thermal process	Vacuum absorption vapour compression	Desalination	Cheng et al. (1987)
	Vacuum freezing ejector absorption	Desalination	El-Nashar (1984)
7- The advantage of a low operating temperature, which minimizes scaling and corrosion problems	Freezing melting separation	Desalination	Heist, 1979
	Freezing melting separation	Desalination	Rahman et al. (2007)
8- Heat transfer coefficient with phase change is about 3 to 5 times greater than that without phase change.	Scraped-surface heat exchanger SSHE	Food industry	Qin et al., 2006
9- Conservation of nutritional and organoleptic characteristics of fresh product	Cryoconcentration	Food industry	Qin et al., 2006
10- Minimal loss of volatile compounds	Cryoconcentration (Ruiz et al., 2001)	Food industry	Raventós et al., 2012

Table 1.3. Disadvantages of freeze concentration reported in the literature.

Disadvantages	Method	Sector	References
1- Difficult ice brine separation	Direct freezing with n-butane	Desalination	Madani (1992)
	Direct freezing with vapor compression	Desalination	Cheng et al. (1987)
	Direct freezing with air	Desalination	Cerci (2003)
	Indirect freezing with scrapped surface heat exchanger SSHE	Desalination	Habib and farid (2006)
	Vacuum absorption vapor compression	Desalination	
	Vacuum freezing ejector absorption	Desalination	Cheng et al. (1987)
	Vacuum freezing multi-phase transformation	Desalination	El-Nashar (1984) Cheng et al. (1987)
2- Batch process results in thermal cycling loss	FC system with heat pump, FCSwHP	Desalination	Rane and Jabade (2005)
	FC system with two stage compression using tubular heat exchanger	Desalination	Rane and Padiya (2011)
3- Higher capital costs and higher operating costs during the ice separation	Freezing melting process	Desalination	(Muller, 1967)
4- Retention of undesirable flavors	Freezing melting process	Food industry	(Braddock and Marcy, 1987)

1.4 Industrial applications of the freeze concentration process

The three applications where the FC process has gained popularity at industrial scale are the concentration of fruit juices, purification of organic chemicals and treatment of hazardous wastes (Rahman and Al-Khusaibi, 2014). The main reasons for these successes are due to the development of more efficient high-capacity processes and products of high purity or quality. The choice of a separation system depends upon the type of solution to be concentrated and several options may exist. The status and the prospects of these applications will now be presented.

1.4.1 Food industry

Several authors have published applications of FC in the food industry. From these works, the conclusions can be made that FC is highly effective to concentrate juices (Raventós et al., 2012a), wine, beer, milk (Sánchez et al., 2011), coffee, and tea; with all flavor and aromatic components retained (Miyawaki, 2018).

The SFC system is the only technique applied at a commercial level by the companies GEA Group and Sulzer Ltd. Both companies have created a mature and efficient technology to obtain clean ice (impurity

< 100 ppm) and highly concentrated effluents (45–55 % w/ w dissolved solids). Nevertheless, some disadvantages can be cited: technical complexity, high initial capital cost (€ 2 M for 10 m^3/h capacity), and high energy consumption (35–40 kWh/t) (Van-Beek et al., 2018). These drawbacks limit application of FC to products with high added value as these products are usually produced in much lower quantities. With the purpose to overcome these inconveniences, a new generation of equipment has been developed, namely the Icecon™ by GEA Group and Multiblok™ by Sulzer Ltd. The major difference between traditional design and latest Icecon™ technology is the production of ice crystals and ice crystal growth in the same vessel, avoiding the construction of an auxiliary vacuum vessel and significantly reducing the equipment footprint. This improvement reduces the capital cost of the system by around 35 % and reduces energy consumption by 20 % (Van Nistelrooij, 2013). The Multiblok™ system uses an increased crystallizer volume and simplifies the technology by combining two processes in one. Dividers were added to the crystallizer to enable effective radial and axial mixing, which increases average crystal size and prevents crystal agglomeration. Ding et al. (2019) considered that the future of FC in food industry applications will guide the development of new PFC equipment to replace the SFC system due to the simplicity of the separation process. The main challenges for the PFC technique to be commercialized are obtaining high purity ice, the implementation of a continuous process and optimizing the energy consumption. MEIWA CO. Ltd. Successfully applied PFC to brewing, winery, fragrance production, dairy applications and pharmaceutical manufacturing. The progress made is the result of more than 5 years of joint research between the Ishikawa Prefecture University and the Ishikawa Prefecture Industrial Research Institute. The equipment is available from a laboratory-scale of approximately 5 L, to a practical scale of approximately 50 L and higher capacity equipment at 250 L is under development. Apple juice was effectively concentrated from 12.8 to 21.0 °Brix with 79.0- % yield, which was improved to 90 % by recovering 30 % of the initially melted fractions using the ice partial melting system.

1.4.2 Chemical industry

FC processes in the chemical industry focus mainly on the organic melt crystallization technology (Wynn, 1992). The key advantage of melt crystallization over distillation is in the separation of substances with very close boiling points like isomers (Rahman et al., 2007). Crystallization is often the best alternative when distillation is difficult or even impossible. High purity products are manufactured from close boiling or azeotropic mixtures of components that are thermally unstable at their boiling point. The capital investment is high, but the process is affordable for a high-value product. Some typical applications include the purification of acetic acid, acetonitrile, adipic acid, benzene, caprolactam, durene, ethyl lactate, hexamethylenediamine, ionic liquids, lactic acid, methylene diphenyl isocyanate, methacrylic acid, o-phenyl phenol, p-diisopropylbenzene, p-dichlorobenzene, p-chlorotoluene, p-nitrochlorobenzene, p-xylene, phenol and trioxane (Ahmad et al., 2018; Rahman et al., 2007).

1.4.3 Industrial wastewater

Pre-concentration with FC is one possibility for hazardous wastewater treatment (Lemmer et al., 2001). This technique is applicable when incineration is required, and the hazardous material is a mix of non-volatile and volatile components (VOCs) (Van Nistelrooij, 2013). FC and incineration costs are likely to be of the same order of magnitude as the viable oxidation and bio-treatment alternative. FC has several advantages over bio-treatment such as the elimination of large vessels, higher flexibility and reliability relative to changes in both feed flow rate and composition and the avoidance of shutdowns caused by the presence of random toxins (Kalista et al., 2018). FC has a lower environmental impact and improved inherent safety. For this application, EFC may be suitable to reduce saline loads to bio-treatment. EFC is a sustainable and environmentally friendly technology offering zero waste potential and is capable of cleaning water while producing valuable products, leading to a low-cost process with realizable potential for a circular economy. Treatment of acetone containing industrial wastewater, by static progressive freezing on a cold wall, has also been studied. The lowest impurity concentration (3.92 g /L) was obtained by applying the lowest ice growth rate (0.1 mm/h) (Htira et al., 2018). However, this concentration was not in agreement with the standards set for direct discharge of the water into the natural environment of France. As a solution, the authors suggested adding a sweating step to drain out the liquid trapped in the ice and to improve the resulting ice purity. PFC may also provide an effective, economical, and feasible alternative for recovering Tetrahydrofuran from Grignard reagent wastewater (Chen et al., 2019). Results obtained from pilot-scale tests showed an optimal COD removal efficiency of 98.1 % and a COD as low as 680 mg/L in the melted ice solution. Similar results regarding COD removal have been reported (99.1 %) when the FC technique was applied to milking wastewater using a rotary ice-making machine (Dai et al., 2018). Ab Hamid and Jami (2019) also achieved high solute recovery (0.9 g of glucose obtained per 1 g of initial glucose). A prototype of indirect contact freezing was also developed to demonstrate the application of FC to purify landfill leachate (John et al., 2020). Average removal efficiencies over 95 % were achieved for both organic and inorganic matter including heavy metals (Szpaczynski et al., 2017). The first 30 % of the melted liquid volume contained over 90 % of all impurities and a significant agglomeration of solid particles was also noted. The results revealed that the application of this process at full scale is feasible.

1.4.4 Desalination

In this section, the term desalination should be understood in a broad sense, not only salt removal to obtain potable water, but also to treat brines from reverse osmosis processes or certain types of industrial wastewater. Technologically all the FC methods used in the food industry could be used for desalination purposes. The only real consideration needed is the economic analysis of the FC process for desalination since water is a low-value product compared to food (Rahman and Al-Khusaibi, 2014). To date, FC technology is mainly adopted when there are no other alternatives available for the desalination application. FC is gaining interest as a technological option to treat brine (Randall and Nathoo, 2015). In contrast to membrane systems, EFC does not have the feed composition limitations and produces high purity solid salts (>90 % purity). The general conclusion from previous studies is that the research and development of FC for desalination should focus principally on the following aspects (Randall and Nathoo, 2015): design of new equipment to reduce costs and improve the efficiency; reduction of energy consumption, use of low-grade energy and renewable energies for cooling and integration with existing technologies such as membrane systems (Kalista et al., 2018). Continuous efforts are being carried out for the reduction of energy consumption in FC processes. The freezing process was proposed as a method of seawater pre-treatment for reverse osmosis (RO) membranes (Baayyad et al., 2015). For seawater desalination, Chen et al. (2020) presented the SWDIM (super-cooled water dynamic ice making) with an energy consumption of 58 % when compared to the indirect progressive contact freezing (IPCF) system. Whereas Cao et al. (2015) presented a new suggestion to apply the liquefied natural gas (LNG) cold energy in the freezing desalination. Due to the low temperatures of the processes (-162 °C), the recommendation was made to use intermediate refrigerant to transfer energy to the process. The calculations show that the consumption of 1 kg equivalent of LNG cold energy can obtain about 2 kg of ice meltwater (Cao et al., 2015).

Lin et al. (2017) presented a seawater freeze desalination prototype system applying R410 as a secondary refrigerant. The prototype was able to reach the freshwater capacity of 150 L/h and the salt removal rate was around 50 %. Thus, more cycles of freeze desalination, or freeze desalination assisted with RO, are needed to produce drinking water. Likewise, membrane distillation (MD) and FC were evaluated as alternative RO concentrate treatment options (Naidu et al., 2018). A direct contact MD (DCMD) could obtain 60 % water recovery with chemically pre-treated RO concentrate. FC in the three-stage freeze/thaw approach was able to achieve 57 % water recovery with no scaling issues. The efficacy of DCMD was compromised by membrane scaling, which implies an additional cost due to pre-treatment for scale removal. The FC was advantageous as a non-scaling and chemical-free process. The FC could be coupled to the LNG refrigerant coolant source, given that most LNG plants are located in coastal areas. However, the practical industrial application of FC is inherently restricted due to the complexity of the operation that limits capabilities in large-scale configurations. Suspension crystallization has also been successfully demonstrated as a desalination technology (Ahmad et al., 2018). In the study of Lu et al. (2019) a novel freeze desalination and membrane distillation-crystallization (FD-MD-C) hybrid system has been developed at lab-scale and may provide valuable guidance for designing a low-cost desalination system with zero liquid discharge (ZLD). A hybrid RO-Freeze process has been proposed that increased water recovery by 400 %. On the other hand, the feasibility of a hybrid system of freeze desalination and vacuum membrane distillation powered by LNG regasification and solar energy for seawater desalination was demonstrated (Chang et al., 2019), with a high-water recovery of 74 %.

1.4.5 Applications of freeze concentration in animal manure

The application of FC in animal manure was testes purposing the elimination of impurities, few studies investigated the potential of the technology on that sense. One of the first works in this area was reported by Gao (1998). The “freezability” of the wastewater can be evaluated by quantitative determination of the ice nuclei concentrations. Pig slurry piggery wastewater had the lowest nuclei concentration and therefore the lowest “freezability”, compared to other types of waste effluents. The freezing temperature of piggery wastewater was sensitive to the change in the impurity concentration, volume drop, and pH. Different studies have been published regarding the application of PFC to treat animal manure. The performance of PFC to concentrate organic matter contained in liquid fraction of digested manure was evaluated using a batch freezing reactor with a working volume of 300 mL (Young et al., 2001). Dissolved organic matter and suspended solids (SS) were further concentrated to 98 % and 92 % respectively. Also, PFC (falling film type) on a semi-industrial scale has been used to treat different types of wastewaters (Rodriguez, 2015). The equipment used was an evolution of the design presented by Raventós et al. (2007). In the case of poultry manure, an 82 % reduction in TDS and conductivity was achieved in a single treatment stage and a TDS reduction of 94 % and conductivity diminishment were reported for a two-stage treatment processes. Rodriguez-Pascual (2016) suggested for the treatment of pig slurry, combining different separation techniques in a semi-commercial facility at 1 m^3/h. Reduction volumes greater than 80 % and energy consumption in FC of 25–40 kWh/m^3 water removed were reported (Rodriguez, 2015). In a recent work conducted by Cantero et al. (2019), FC is mentioned as an option for the physical pre-treatment of manure, to convert the raw material into a more efficient form in terms of storage, transport, and capability of being employed in further treatment. Moisture content contained in solid residues derived from livestock waste was reduced by 50 %. Since the management of the liquid fraction of animal manure has certain similarities with the management of human urine, some references in this area can also be cited. Gulyas et al. (2004) conducted laboratory-scale batch FC of yellow water with a stirred vessel and a falling film freeze concentrator. The results indicated that multistage processes are necessary, i.e. the melted ice phase must be purified (and the concentrates must be further enriched) in a second or even in a third stage to decrease the ice contamination observed. Ganrot et al. (2007) investigated a freezing methodology to recover nitrogen and phosphorus in a hybrid system that also included struvite precipitation and nitrogen adsorption on zeolite and activated carbon. The freezing-thawing method concentrated 60 % of the nutrients in 40 % of the initial volume and significantly improved the N reduction. The P recovery was 95–100 %, mainly as struvite. Recently, EFC was considered as means of volume reduction (Chipako and Randall, 2020). When applied to urine, up to 99 % of the nitrogen bound in urine could be recovered at a temperature of -30 °C. An estimated 95 % water recovery was possible when using EFC for urine treatment. However, due to the low-temperature requirements, and considering that most of the energy is required for ice formation, EFC works better when the stream is already significantly concentrated. As an alternative, the volume reduction of wastewaters could be achieved using RO as a pre-treatment step and followed by EFC. The information presented to this point highlights the possibilities and challenges for the FC process. Cost is the main limiting factor hindering application of the technology, requiring the development of new systems targeting a reduction in capital and energy cost of the process. The technology may potentially save 55–90 % of energy compared to the existing concentration technologies such as evaporation and regular FC.

1.5 Energy consumption of the freeze concentration process

Evaluating the economic aspects of emerging resource recovery processes is critical for uptake and establishment in the agricultural sector. The freeze concentration process is considered to have high energy consumption due to the nature of feed solutions that are being treated (Chourot et al., 2003). Typically, high moisture content (40–80 %) of raw materials would require significant energy usage in water solidification. Therefore, the energy demand would reduce significantly in processing systems with less water content to crystalize (Lopez-Quiroga et al., 2016). The capital and energy cost of the FC system might be the most concerning factor and a key challenge that will limit future applications. Recent studies are more focused on reducing the energy and capital cost of FC technology while maintaining the quality of the final product (Van Nistelrooij, 2013). Basically, the energy consumed in FC systems comes from the electrical energy required for the pump, engine, and refrigeration units. The refrigeration system removes heat or energy from the feed fluid; this is the inherent sensible and latent heat of the feed, penetration of heat into the equipment from ambient conditions (assuming ambient temperature is higher than that of the equipment) and energy derived from agitation and heat related with ice crystal formation. About 10 and 25 % of the total heat generated is estimated to come from mechanical sources and ambient conditions respectively (Hartel and Heldman, 1997). The energy consumption in the FC system is based on the heat used to convert one kg of the raw material into a concentrated solution and ice mixture. As a comparison to membrane technology, FC can be considered as requiring similar or even lower energy expenditure for processing in some cases. For instance, the energy required to recover freshwater from seawater using reverse osmosis technique is much higher than other alternative techniques for water treatment and nutrients recovery (Schunke et al., 2020). Conventional techniques consume much more energy, commonly extracted from fossil fuels, which contributes to global warming and greenhouse emissions (Schunke et al., 2020). Sustainable techniques for nutrient recovery from animal waste have become increasingly important. The negative environmental effects produced by some manufacturing processes undoubtedly contribute to this trend. For example, the Haber-Bosch process, by which most synthetic fertilizers are produced, contributes significantly to pollution and global energy consumption (Sutton et al., 2011). The typical energy consumption for the production of NH3 through the Haber-Bosch process is around 11, 000 kWh/m-3 (Rafiqul et al., 2005). To make a unit cost comparison among various technologies is difficult as many parameters must be considered, such as the type of technology in use, the type of feed solution, the ambient temperature, the targeted recovery rate, and the cost of electricity in each region. The required investment of each technique could be variable based on the construction cost and production capacity. Pazmiño et al. (2017) reported energy savings up to 30 % utilizing a continuous system of FC, treating sucrose solutions, and integrated with the falling film technique, compared to the energy consumption of other conventional methods. They obtained a high concentration index of 4.0 and a concentration efficiency of 98.5 % with energy consumption of 10.3 kWh/m^3. In a similar study, the energy usage of 23.3 kWh/m^3 was reported in the integrated system for treating orange juice and coffee (Rodriguez et al., 2011). Recent research are based on the improvement efficiency of FC in terms of energy consumption and operation. For instance, the operation of at least two FC units in a parallel mode, would be a good approach to reduce the total energy consumption of the process and consequently increase the economic feasibility of the FC process (Rane and Jabade, 2005). Theoretically, FC has a huge energy-saving potential compared to thermal and evaporating processes. FC uses 304 % less energy than evaporation to treat wastewater and consumes less than 62 % energy while combined with ice thermal storage technology and precooling method (Ling et al., 2012). Table 1.4 shows a cost comparison between the freezing, evaporation and membrane processes for various concentration purposes. The membrane processes have the lowest operating costs, although it must be considered that FC is an emerging technology with wide possibilities for improvement. For example, the study of He et al. (2018) reported the use of LNG to replace the external refrigeration cycle used in classical hydrate desalination plants. They found that this method could reduce energy consumption to 0.60 to 0.84 kWh/m-3, which is equivalent to only 25 % of the energy requirement for the RO process. Also, as indicated in previous sections, a good energy option and therefore cost-effective process is the combination of FC and membrane process. However, the freezing process is not fully commercially developed and requires further effort. Therefore, future research on FC systems for full-scale industrial applications is necessary to boost the economic argument for the technology when compared with conventional techniques. The studies to date would suggest that the key to achieving a more sustainable method to treat animal manure would be a hybrid process that can be optimized for improved recovery and sustainable operation.

Table 1.4. A comparison between the average operational cost (US $ per m3) for concentration processes.

Industrial application	Freezing	Evaporation	Membrane
Desalination seawater	0.8 (4)	1.8 (1)	1.5 (1)
Fruit juice concentration	2 (3)	5.4 (4)	1 (3)
Sugar product	1.3 (5)	8.4 (3)	-
Digested manure	-	-	2.4 (2)
Brine treatment	1.4 (6)	1.4 (1)	0.76 (6)

(1) Druetta et al. (2014) ; (2) Gerardo et al. (2015) ; (3) Moreno et al., 2014 ; (4) Panagopoulos et al. (2019) ;

(5) Rahman et al. (2006) ; (6) Williams et al. (2015)

Position of the current study

The structure of the present thesis was made with attentions focused on the potential of freeze concentration technology on resolving the abovementioned issues related to liquid livestock waste, dairy wastewater, and brine from meat industry. Up to today, no previous study was documented about the recovery of nutrient and water from agro-industrial waste effluents. Apart from the experiments carried out at laboratory scale, the obtained results allowed a scale-up of the freeze concentration technology with the purpose to be implemented industrially once the process is fully optimized and the operation cost are proven to be feasible. Freeze concentration technology is showing promising results to be an alternative for nutrient concentration and water recovery.

Chapter 2: Objectives

The primary objective of this thesis is to explore and seek potential methods of valorization technologies to fill some of the existing gaps in treating and valorizing effluents from agro-industrial wastes. This, through the investigation of the efficiency of freeze concentration as a sub-zero operating technology on the valorization of agro-industrial wastes effluents for the recovery of valuable bio-products and to assess its competitiveness with the existing techniques in the market in terms of efficiency and energy consumption. The attention was focused on two main themes:

1) Assessment of efficiency of freeze concentration technology on the recovery of nutrient-rich products from agro-industrial waste.
2) Performance assessment of freeze concentration on the purification of wastewater for water recovery.

Therefore, the main sub-objectives of this thesis are as follow:

- To investigate the applicability of freeze concentration technology on a livestock effluent for the recovery of nitrogen, phosphorus, and potassium, with the aim of delivering a nutrient-rich fertilizer.
- To investigate the influence of affecting parameters for the freeze concentration technology, namely: the agitation rate, the freezing temperature, and the initial concentration of the treated effluents in this thesis.
- To investigate the feasibility of recommending freeze concentration as emerging technology for the management of livestock waste with the aim of solving the transportation side-effect by reducing its volume meanwhile concentrating the nutrients.
- To examine and validate the efficiency of progressive freeze concentration on the management of cheese whey, while assessing the influence of freezing parameters of the concentration process. Then use the best tested freezing conditions for the recovery of protein and lactose from cheese whey in a reduced volume.
- To assess the efficiency of freeze concentration technology on the desalination and purification of brine solution of meat processed industry and implementing a combined system for optimizing the quality of obtained water.
- Propose a simple and low-maintenance technology to be attractive for farmers, so it can be readily deployed locally at farm level or small industrial scale.

Chapter 3: Materials and method

3.1 Introduction

In the present thesis, the Freeze concentration technology (FC) was the main technology studied. As mentioned in the introduction (Chapter 1) different streams of livestock waste effluents were studied. In this chapter, a general description of the progressive freeze concentration (PFC) and the suspended freeze concentration (SFC) as well as the physio-chemical analysis performed. A more elaborated section of the characterization and preparation of each studied raw material will be included in the corresponding chapter. The experiments performed throughout this thesis as well as the majority of physic-chemical analysis were carried out in BETA TC.

3.2 Materials:

As mentioned in Chapters 1 and 2, different waste effluents from agro-industrial activities were treated using FC technology along this thesis. In each of the results chapters, a detailed description of each feedstock treated through FC is provided, as well as the specific operating conditions (agitation, temperature, solids concentration, etc.). Meanwhile, in the present chapter the description of the FC technologies configuration, monitoring procedures and chemical analysis is provided.

Table 3.1. Studied raw materials and corresponding freeze concentration for each of them.

Raw material	Freeze concentration configuration
Cheese whey	Progressive freeze concentration
Concentrated of RO from digestate	Progressive freeze concentration Suspended freeze concentration
Pig slurry	Progressive freeze concentration
Brine from meat industry	Progressive freeze concentration

3.3 Experimental procedures and operation:

3.3.1 Freeze concentration configuration and operation

The FC performance was investigated under two methodological approaches, a progressive freeze concentration (PFC) and a suspension freeze concentration (SFC), set through the utilization of different lab-scale FC configurations described in detail in the following sections.

3.3.2 Progressive freezing and vacuum separation

The system consists of a tank with a capacity of 2 L (internal diameter of 110 mm and 257.5 mm of height), a refrigerant stream circulating through a thermally isolated outer jacket (15 mm thickness) of the tank, allowing heat transfer mainly towards the interior of the tank. An overhead stirring system (AM20-D ARGO Lab, IT) was providing a mechanical agitation to optimize the homogeneous distribution of the raw material inside the tank and in contact with its refrigerated walls. The cooling system consisted of a chiller (POLYSCIENCE AD20R, USA) with propylene glycol liquid refrigerant (cooling temperature up to -30 ºC) circulating externally (Figure 3.1).

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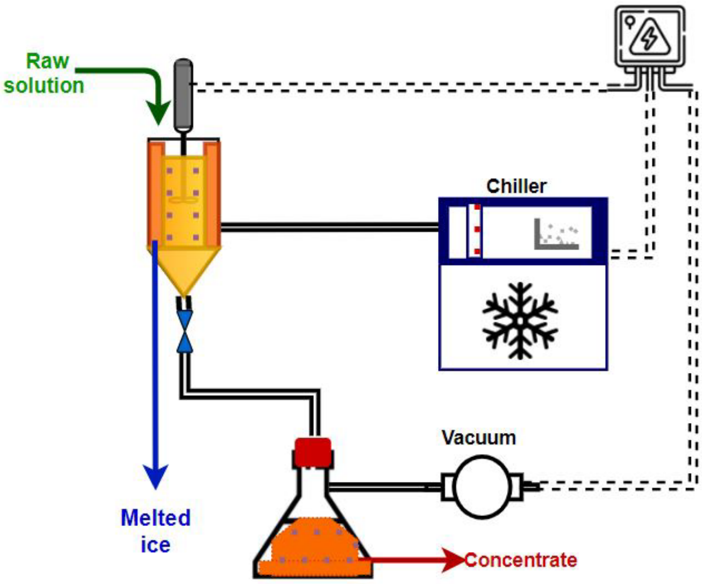


Figure 3.1. Principle and component of progressive freeze concentration configuration.

The PFC process was carried out as follows: the tank was filled with a volume of 1.8 L of sample once the refrigerant achieved the setpoint temperature selected to perform the test (from -5 ºC to -15 ºC). The agitation of the sample was activated, and the temperature began to decrease until reaching the cooling temperature of the sample. A temperature probe connected to the chiller was incorporated at the center of the tank to record and display the temperature of the sample along time. A single large ice layer was formed through the progressive accumulation of ice on the cooling surface of the tank creating two different samples (diluted and concentrated) from the initial one with two different states (ice and liquid) (Figure 3.2).

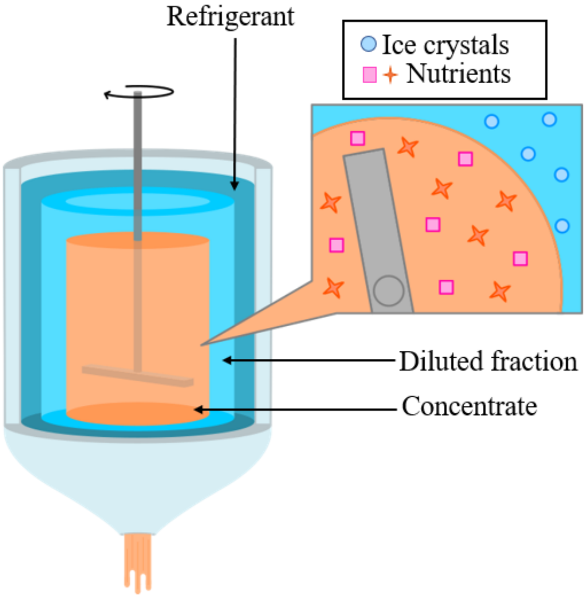


Figure 3.2. Ice formation during the progressive freeze concentration.

In each new application of the PFC, a screening of conditions was always performed to select the optimal performance based on the % of nutrient recovery and the ice quality. To this aim, three temperatures of refrigerant (-5, -10 and -15 ºC) were combined with different agitation rates (150, 300 and 600 rpm), fixing the volume reduction at around 50%. Once the optimal conditions were set, a sequence of two PFC cycles was performed and assessed under the same terms mentioned above. In the first stage (PFC-S1), the raw sample was freeze concentrated; afterwards, the concentrated effluent obtained from PFC-S1 was used as the input material for the second stage of PFC (PFC-S2). This procedure could be performed similarly with the ice fraction, once melted, to obtain a cleaner water stream. The application of sequenced stages theoretically allows obtaining higher % of nutrients recovered and cleaner ice fractions.

Once the 50% of the volume was reduced in each cycle, the refrigerating stream and agitation were stopped, and the concentrated solution was discharge from the bottom of the tank (Figure

3.1). To extract the remaining concentrated solids trapped in the ice matrix, a suction step was performed right after the PFC process was finished. The suction was performed connecting a vacuum pump (WELCH model 2545c-02 B, USA) to the outlet of the reactor (Figure 3.1). The length of the experiment was set to 2 h for 50 % of volume reduction. The suction period lasted 30 min using a vacuum pressure of 50 kPa. Once the FC process was finished, the melted ice fraction was referred as the diluted fraction and the concentrate liquid as concentrated fraction.

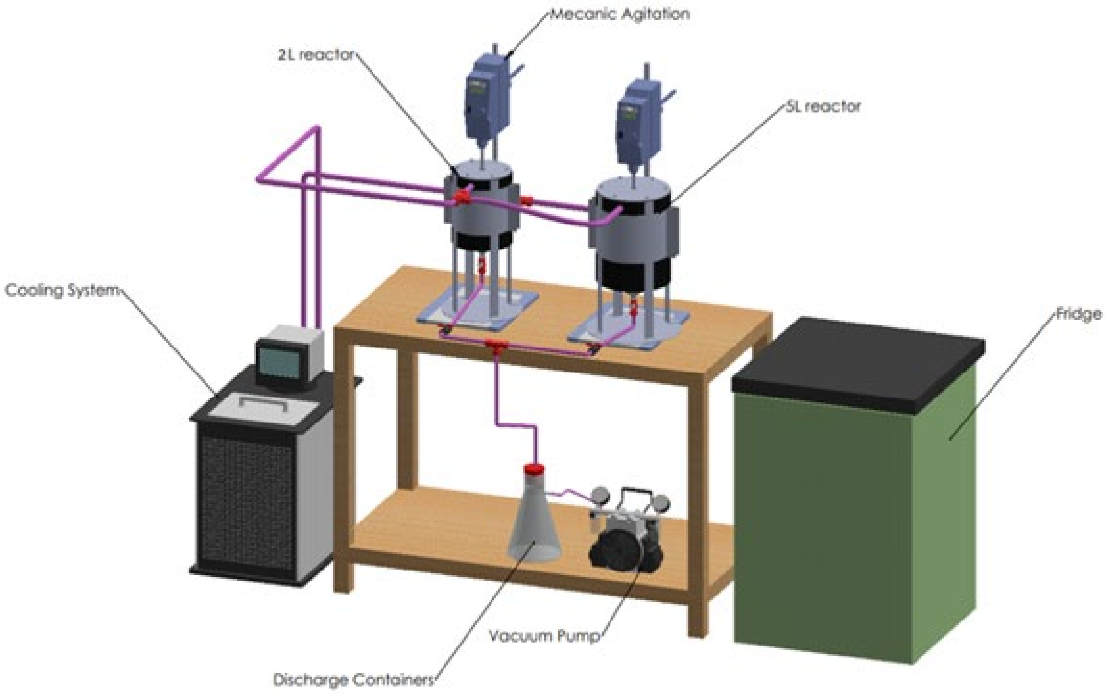


Figure 3.3. Experimental setup of progressive freeze concentration used in this thesis.

3.3.3 Suspended freeze concentration for ice granulation

The SFC or granulation test was assessed in a 3-chamber lab-scale experimental setup (FROSTY DREAM 3, AU). Each chamber was independently working and was provided with a double mixing system to form the ice granulation thus obtaining an optimum product consistency. Both the cooling temperature and the agitation/mixing rate were set by default in the granulation device. The cooling temperature was limited to -2 ºC and the agitation rate was fixed to 45 rpm. The sample was poured into the FC chamber at room temperature which leaded to the formation of bigger nucleation of ice (Figure 3.5) and improve the vacuum performance due to the granulated structure of the frozen bulk. A sample volume of 5 L was required for each granulation test or cycle, which lasted 2.5 h to ensure a homogeneous granulation of the ice. Once the process was completed, the granulated sample was discharged towards an enclosure to apply vacuum pressure and extract the concentrated solution (Figure 3.4), similarly to the previous method (PFC). The pressure used for the vacuum suction was between 50 and 90 kPa for a period of 30 min. Analogously to the PFC, two stages were also performed for SFC, namely SFC-S1 and SFC-S2 for the first stage of SFC and the second stage of SFC, respectively.

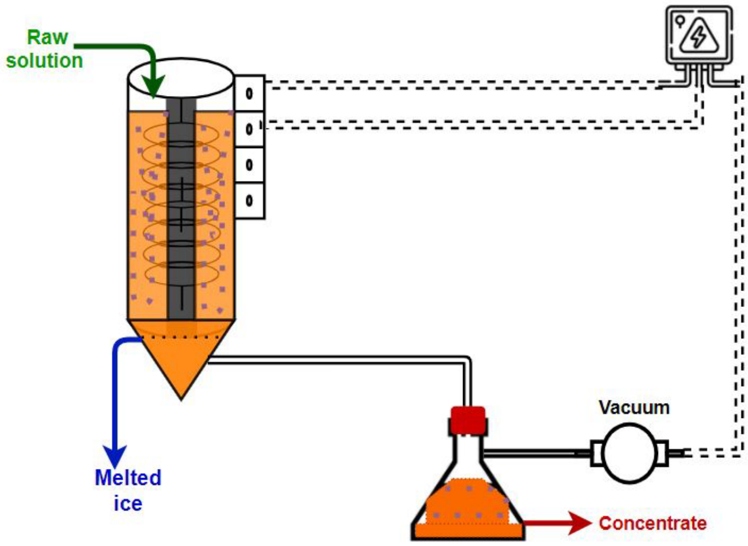


Figure 3.4. Principle and component of suspended freeze concentration.

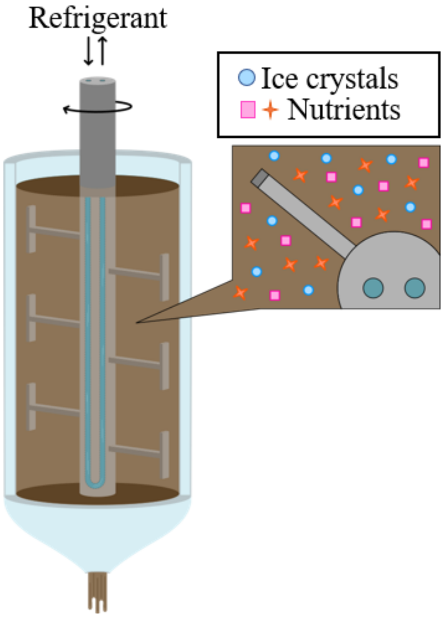


Figure 3.5. Ice formation during suspension freeze concentration process.

In case of SFC, the experimental setup that was available at the time of performing the experiment was basic (Figure 3.6), and neither the freezing temperature, agitation rate or the frozen volume could be controlled, Thus, the only way to adjust the concentrated volume was when applying the vacuum, as we complete a cycle when a recovery of half initial volume in form of concentrate (liquid fraction) was achieved.

Figure 3.6. Experimental setup of suspended freeze concentration used in this thesis.

3.3.4 Multi-stage freeze concentration:

The multi-stage FC is the process of refreezing the concentrated and/or diluted fractions produced in a freeze concentration cycle in order to obtain a more concentrated liquid fraction or a cleaner ice, respectively. Figure 3.7 illustrates the multi-stage process aiming to further concentrate the liquid fraction (Figure 3.7A) or clean the ice fraction (Figure 3.7B). In this thesis, both types of multi-stages were performed, as for the aim of concentrating the nutrients from cheese whey, pig slurry and reverse osmosis concentrate while cleaning the ice formed from the FC of meat industry brines.

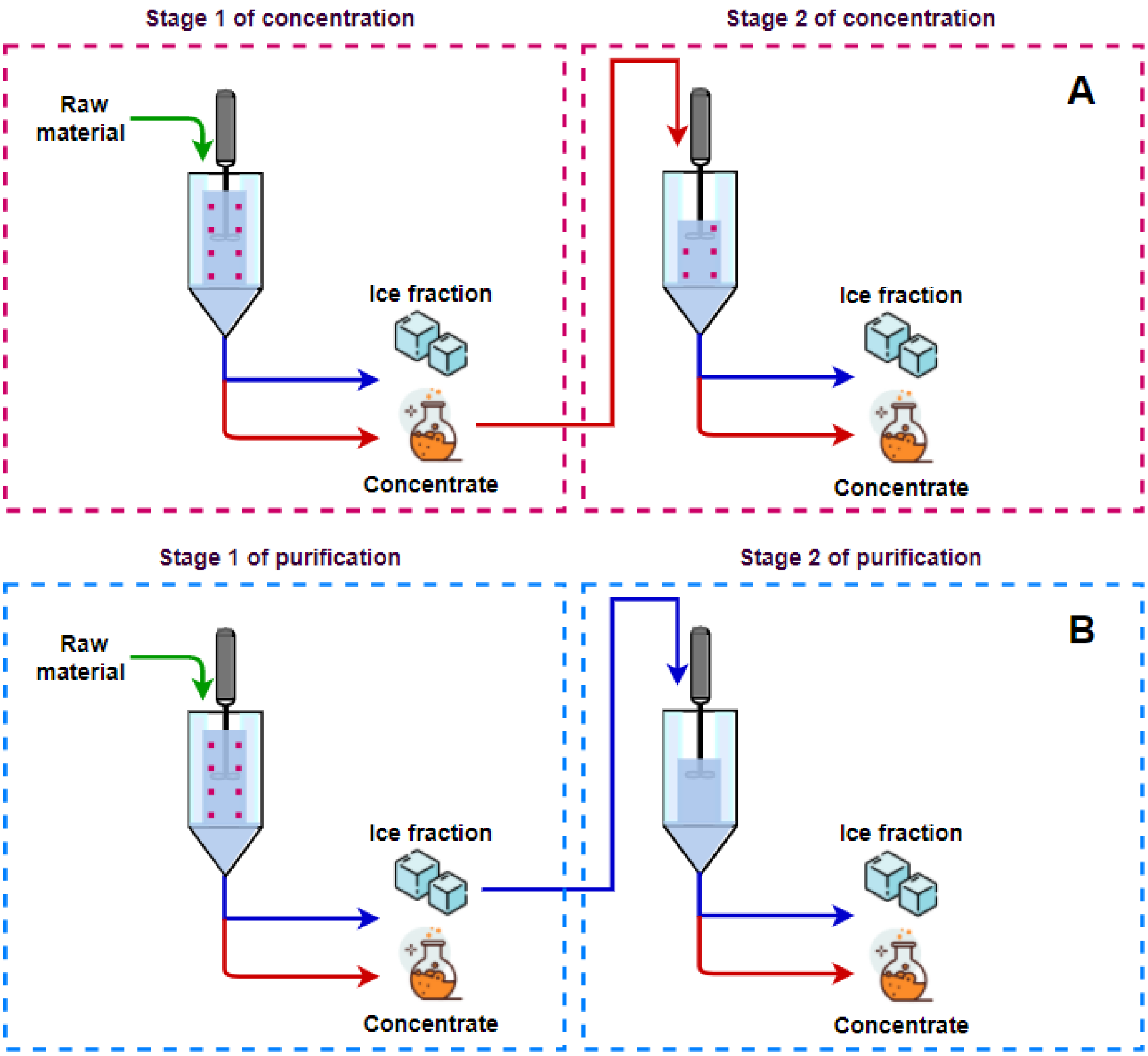


Figure 3.7. Multi-stage freeze concentration steps for the purpose of concentrating a solution (A) or cleaning an ice fraction (B).

3.4 Physical-chemical analysis

3.4.1 Nitrogen, Phosphorous, Potassium content

N content in the samples was determined according to the Kjeldhal method (Kjeldahl Method, 2008). A volume of 20 mL of sulfuric acid (96 %) was added to the samples (15 mL) and digested for 3 hours at 350 ºC. The digested samples were then distilled, and the ammonia volatilized was retained in a boric acid solution (3 %). The absorbed nitrogen in the boric acid solution is determined by titration using 0.1 N hydrochloric acid. The extracts for P and K content were prepared by digesting the samples at 100 ºC with the addition of nitric acid (65%) and sulfuric acid (96%), then going through a filtration and diluted to be adjusted to the measuring range of the used equipment for the analysis (APHA, 2005). P and K content in the extracts were determined using a spectrophotometer (HACH DR 3900, USA). The K content was measured using a commercial kit (Hach LCK 228) with a range of 5-50 mg L-1, meanwhile the P content using the Watanabe-Olsen method (Watanabe and Olsen, 1965). The wavelength for the reading was 695 nm for K and 882 nm for P.

3.4.2 Protein and lactose content

Protein content in the cheese whey (CW) was determined by the intermediate of N content. Nitrogen concentration in the CW (N, g/L) was determined according to the Standard Methods (APHA, 2005) and to obtain the protein content (g/L) this value was multiplied by a conversion factor (f) of 6.38 (Barbano et al., 1991). Lactose content was determined by HPLC according to the method presented by AOAC (2005).

3.4.3 Chemical oxygen demand content

Chemical oxygen content was determined using commercial kits (Hanna instrument, HI94754B-25, USA) with a range detection of 15 to 1500 ppm. The measuring tubes were digested at 120 ºC for 2h, and afterwards cooled at room temperature. The content on COD was obtained using a spectrophotometer (HACH, DR/2010, USA).

3.4.4 Heavy metals content

The extracts for metals analysis, namely the zinc (Zn), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni) and chrome (Cr) were prepared according to the Standard Methods (APHA, 2005). A volume of 15 mL of sample was digested for two hours with 5 mL of sulfuric acid (96 %) and 15 mL of nitric acid (65 %) for the preparation of 100 mL of extracts. The metals analysis was carried out through Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) by an external certified laboratory.

3.4.5 Electrical conductivity pH, turbidity and solid content

The pH, the electrical conductivity (EC) and the total and volatile solids were only measured for the characterization of the raw material. The pH was measured with a pH sensor (CYBERSCAN ion 510, Eutech Instruments, SG). The EC was determined with conductivity meter (COND 510, XS Instruments, IT) using temperature compensation. The total solids (TS) are determined according to the Standard Methods (APHA, 2005).

The turbidity of a solution was measured using a portable turbidimeter (Hanna Instrument, HI98713, USA).

3.4.6 Salinity and Brix content

Brix degree (ºBx) represent the percentage of dissolved solids in a solution and was used as an indicator to follow the FC process of the CW concentration. The ºBx of the solution was determined using a portable refractometer (HHTEC, RHB-50). The salinity content was determined using a portable refractometer (‰) for an instant value allowing a more precise follow up of the FC process throughout the performance of the freezing cycles.

3.4.7. Ions and cations content

A characterization of brines was performed by measuring the ions and cations content. The ions, namely, chloride (Cl^-), nitrate ($NO3^-$), nitrite ($NO2^-$), sulfate (SO_4^{2-}) and phosphate (PO_4^{3-}) were analyzed using ionic chromatographer (Thermo scientific Dionex AS-AP, USA) by diluting the corresponding samples with Milli-Q water to fit in the detection and quantification range of the equipment. The sodium content (Na^+) was determined using atomic absorption spectroscopy by diluting the corresponding samples with Nitric acid (2 %) and 10 % of selenium acid to fit in the detecting and quantification range of sodium lamp (Varian, AA240FS, USA).

3.5 Process monitoring

3.5.1 Nutrient recovery

Considering the concentrate, the nitrogen, phosphorus, and potassium recoveries were calculated as follows.

$$R_i(\%) = \frac{\mathrm{V_f} \cdot \mathrm{C_{f_{(i)}}}}{\mathrm{V_{in}} \cdot \mathrm{C_{in_{(i)}}}} \tag{3.1}$$

Where i= [N; P; K] representing nitrogen, phosphorus or potassium, or any other compound recovered through FC; V_f (L) is the final volume of the concentrate, V_{in} (L) is the initial volume of the raw material, $C_{f\ (i)}$ (g/L) is the concentration of nitrogen, phosphorus or potassium in the concentrated fraction and, $C_{in\ (i)}$ (g/L) is the initial concentration of nitrogen, phosphorus or potassium in the raw material.

3.5.2 Mass balance

In order to validate the obtained experimental results, a mass balance was made in each test, and for each of the nutrients (N, P and K) or compounds studied. The mass balance was calculated as follows.

$$MB(i) = \frac{\mathrm{C}_{\mathrm{in}_{(\mathrm{i})}} * \mathrm{V}_{\mathrm{in}} - \left[\left(\mathrm{C}_{\mathrm{f}_{(\mathrm{i})}} * \mathrm{V}_{\mathrm{f}}\right) + \left(\mathrm{C}_{\mathrm{d}_{(\mathrm{i})}} * \mathrm{V}_{\mathrm{d}}\right)\right]}{\mathrm{C}_{\mathrm{in}_{(\mathrm{i})}} * \mathrm{V}_{\mathrm{in}}} \ (\%) \tag{3.2}$$

Where i= [N; P; K] representing nitrogen, phosphorus or potassium, or any other compound recovered through FC; V_f (L) is the final volume of the concentrated solution, V_{in} (L) is the initial volume of the raw material, $C_{f\,(i)}$ (g/L) is the concentration of the recovered compound in the concentrated solution, $C_{in\,(i)}$ (g/L) is the initial concentration the compound to be recovered in the raw material, V_d (L) is the volume of melted ice (diluted fraction or solution), $C_{d\,(i)}$ (g/L) is the concentration of the recovered compound in the diluted fraction.

3.5.3 Process efficiency (PE)

The efficiency of each concentration stage reflects the increase in concentration of the compounds of interest in the raw material in relation to the concentration remaining in the ice. The efficiencies are calculated by Eq. (3.3):

$$PE(\%) = \frac{\mathrm{C}_{\mathrm{f}_{(\mathrm{i})}} - \mathrm{C}_{\mathrm{d}_{(\mathrm{i})}}}{\mathrm{C}_{\mathrm{f}_{(\mathrm{i})}}} \tag{3.3}$$

Where i= [N; P; K] representing nitrogen, phosphorus or potassium, or any other compound recovered through FC; Cf (i) (g/L) is the concentration of the recovered compound in the concentrated solution, Cd (i) (g/L) is the concentration of the recovered compound in the diluted fraction.

3.5.4 Yield (Y)

The concentrating yield was defined as the ratio of the mass of solute present in the separated liquid to the mass of solute present in the original solution.

$$Y\ (\%) = \frac{\mathrm{C}_{\mathrm{f}_{(\mathrm{i})}} * \mathrm{V}_{\mathrm{f}}}{\mathrm{C}_{\mathrm{f}_{(\mathrm{i})}} * \mathrm{V}_{\mathrm{f}} + \mathrm{C}_{\mathrm{d}_{(\mathrm{i})}} * \mathrm{V}_{\mathrm{d}}} \tag{3.4}$$

Where V_f (L) is the final volume of the concentrated solution, $C_{f\ (i)}$ (g/L) is the concentration of the recovered compound in the concentrated solution, V_d (L) is the volume of melted ice (diluted fraction or solution) and $C_{d\ (i)}$ (g/L) is the concentration of the recovered compound in the diluted fraction.

3.5.5 Concentration increase

The increase (I) of a given concentration was defined as the growth of the concentration in relation to the original one.

$$I\,(\%) = \frac{Cf-Ci}{Ci} \tag{3.5}$$

Where C_f (g/L) is the concentration of the recovered compound in the final product and C_i (g/L) is the concentration of compound under study in the raw material.

3.5.6 Salt rejection

Salt rejection or the salt removal efficiency, in the chapter where brines from meat industry were treated through FC, was calculated as follows:

$$SR\,(\%) = \frac{So-Si}{So}.100 \tag{3.6}$$

Where S_0 is the initial salt concentration, and S_i is the salt concentration in the ice fraction.

3.5.7 Ice recovery

Ice recovery (as water once melted) efficiency was evaluated using the percentage of ice recovered. IR is known also as degree of crystallization and is defined as:

$$IR\,(\%) = \frac{Vd}{Vin}.100 \tag{3.7}$$

Vin (L) is the initial volume of the raw material (brines) and Vd (L) is the volume of melted ice.

Volumes were measured at room temperature.

3.5.8 Effective partition constant

The effective partition constant, an important function in the operation of the separation process when treating brines, is defined as:

$$K = \frac{Si}{Sc} \tag{3.8}$$

where S_c is the salt concentration in the concentrated fraction and S_i is the salt concentration in the ice fraction. K has a value between 0 and 1. A value of $K = 0$ indicates that the ice formed is completely pure, and there are no salts trapped inside the ice. A value of $K = 1$ indicates the salt concentrations of the ice and final brine solution are the same, and no separation occurred during the process.

3.5.9 Concentration factor

The concentration factor (CF) is defined as a function of the increment of the ºBx concentration of the concentrated fraction of the solution in relation to the total solids content of the initial CW as described in Eq. 3.9.

$$\mathrm{CF}\ (\%) = \frac{\mathrm{TSn}}{\mathrm{TS0}} \tag{3.9}$$

Where TS_n is the concentration of total solids at a given stage of FC in the concentrated fraction and TS_0 is the concentration of total solids in the initial solution.

3.5.10 Energy consumption

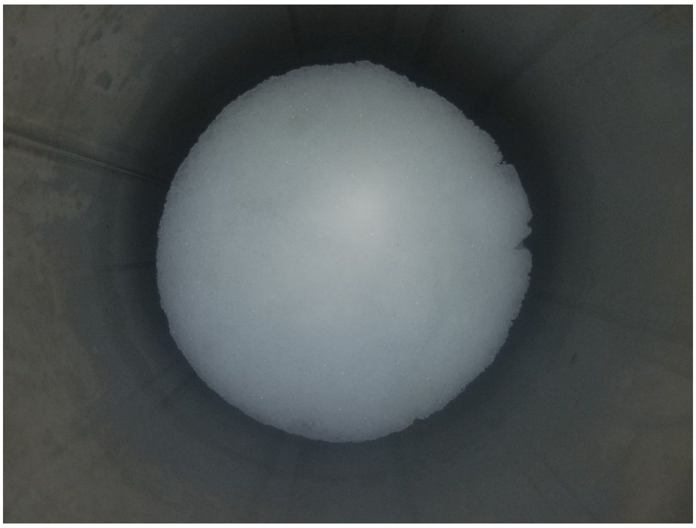
The energy consumed in each FC stage was measured considering the pre-cooling of the reactors and the time set to achieve the cooling temperature and finally the experimental time of the freezing process. The suction of the solids from the ice structure while applying the vacuum was not assessed in terms of energy consumption, since the application of the vacuum was identical in terms of duration and pressure for both PFC and SFC. The energy consumption was calculated by the mean of the power measured with an energy meter (ZHURUI TEC-PR10, CH).

3.6 The optimum operation conditions

As explained in section 3.2, for each type of raw material treated through FC, a screening experiments were performed combining different operation parameters. The freezing temperature and the agitation rate were the main parameters influencing the efficiency of the FC. An additional parameter considered was the initial solid content of the solution, as in the PFC configuration it was concluded to be a major factor for the recovery of different nutrients. Combining the freezing temperature with the agitation rate and the initial solids content, the optimal conditions were defined for each raw material. The concept of optimal conditions in this thesis refers to the point (freezing temperature, the agitation rate, initial solids content) where the maximum PE of the FC cycle was obtained. Then, the optimal conditions do not refer to statistically proven numbers or modeled numbers, however it defines the optimal conditions in terms of PE among the tested conditions in each study separately.

3.7 Volume reduction

The notion of volume reduction refers in the present study to the volume obtained in the concentrated fraction and that represents the fraction with major total solids content from the raw solution. One of the crucial parameters that serves for monitoring the efficiency is the volume reduction. In this thesis, the volume reduction is defined as the percentage of the concentrated solution in relation to the volume of the raw solution. As an example, when it is mentioned that the volume reduction is 50 %, it means that the volume of the concentrate (concentrated fraction) and the ice (once melted, the ice corresponds to the diluted fraction) are equal and represent the half of the initial volume. For some chapters of this thesis, the volume reduction was a fixed parameters for the purpose of comparing the efficiencies, other chapters aimed to freeze the maximum fraction possible by letting the formation of the ice ongoing until chemical composition of the solution cannot be frozen anymore. A more elaborated section about the volume reduction will be provided in each chapter.



Chapter 4: Progressive freeze concentration of cheese whey: performance of the process for protein and lactose recovery

4.1 Introduction

Despite the beneficial nutrient content in the cheese whey (CW), its water content makes the valorization and management of such effluent costly due to the transportation costs to treat it off-site. Then it is essential to remove a significant fraction of the CW water content and concentrate its nutrient content and minerals while conserving the nutritional characteristics of this valuable stream (proteins, sugars, vitamins, etc.).

The aim of the present study was to assess the overall progressive freeze concentration (PFC) efficiency of the CW under a multiple combination of operating conditions (freezing temperature, agitation rate and initial concentration of dissolved solids), and to identify the influence of the freezing process on the distribution of the CW components (protein and lactose) into the concentrated and the ice (or diluted) fractions through a multi-stage FC sequence.

4.2 Material and methods

4.2.1 The raw material

The CW was supplied from a cheese factory in Catalunya, Spain. Fresh samples were preserved at low temperature (0 – 1 °C) and replaced frequently to ensure its freshness during the experiment performance. The CW used in the present study was generated during the production of cow cheese and had an initial concentration of 7 °Brix. The characterizations of the CW are given in Table 4.1.

Table 4.1. Characterization of the raw cheese whey.

TS (% w/w)	pH	EC (mS/cm)	Concentration (ºBx)	Protein (% wt)	Lactose (%wt)
6.66 ± 0.02	4.5 ± 0.01	6.87 ± 0.38	7	0.89 ± 0.06	5.9 ± 0.02

4.2.2 Screening experiments

Setting a volume reduction to 50 %, a preliminary screening of operating conditions was performed combining three cooling temperatures (-5, -10 and -15 °C) with three agitation rates (150, 300 and 600 rpm) and three initial concentrations of the CW (3, 5 and 7 °Brix) in order to define the optimal operating conditions in terms of protein and lactose recovery.

To extract the remaining concentrated solids trapped in the ice matrix after the PFC cycle, a suction step was performed right after the process was completed and the concentrated fraction discharged. The suction was performed connecting a vacuum pump (WELCH model 2545c-02 B, USA) to the outlet of the reactor tightly closed with a rubber cover.

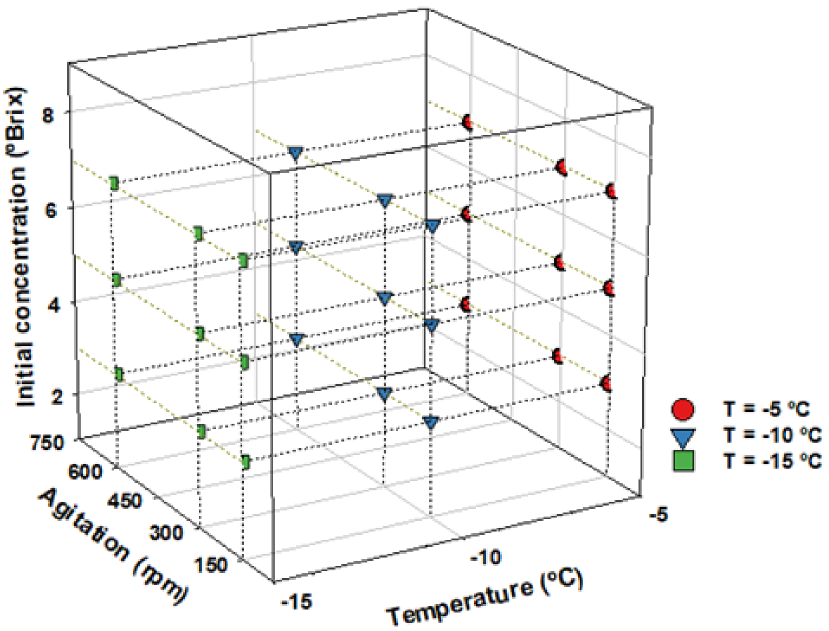


Figure 4.1. Screening experiments performed for the freeze concentration of cheese whey.

The length of the experiment was set to 3, 2 and 1h for the cooling temperatures -5, -10 and -15 °C, respectively, verifying that the volume reduction was around 50 %. The suction period lasted 30 min using a vacuum pressure of 50 kPa. Once the FC process ended, the melted ice was referred as the diluted fraction and the liquid as the concentrated fraction.

4.2.3 Multi-stage progressive freeze concentration

A multi-stage PFC was carried out in a sequence of four stages performed under the optimal conditions defined through the screening cycles (section 4.2.2). Figure 4.2 illustrates the performed stages and the volume used in each of them. Setting the volume reduction to around 50 %, the concentrated fraction obtained in one stage was used as a feed solution for the following one. A CW volume of 1.8 L was poured into the PFC tank in the first stage (S1) and second stage (S2), 1.6 L in the third stage (S3) and 0.6 L in the fourth stage (S4) of the experimental assay. Several replicates were performed in each stage to ensure an enough volume for the upcoming stages as shown in Figure 4.2. The concentrated fractions in the mentioned stages are marked as C1, C2, C3 and C4, meanwhile the ice fractions are mentioned as I1, I2, I3 and I4 for the stage S1, S2, S3 and S4, respectively.

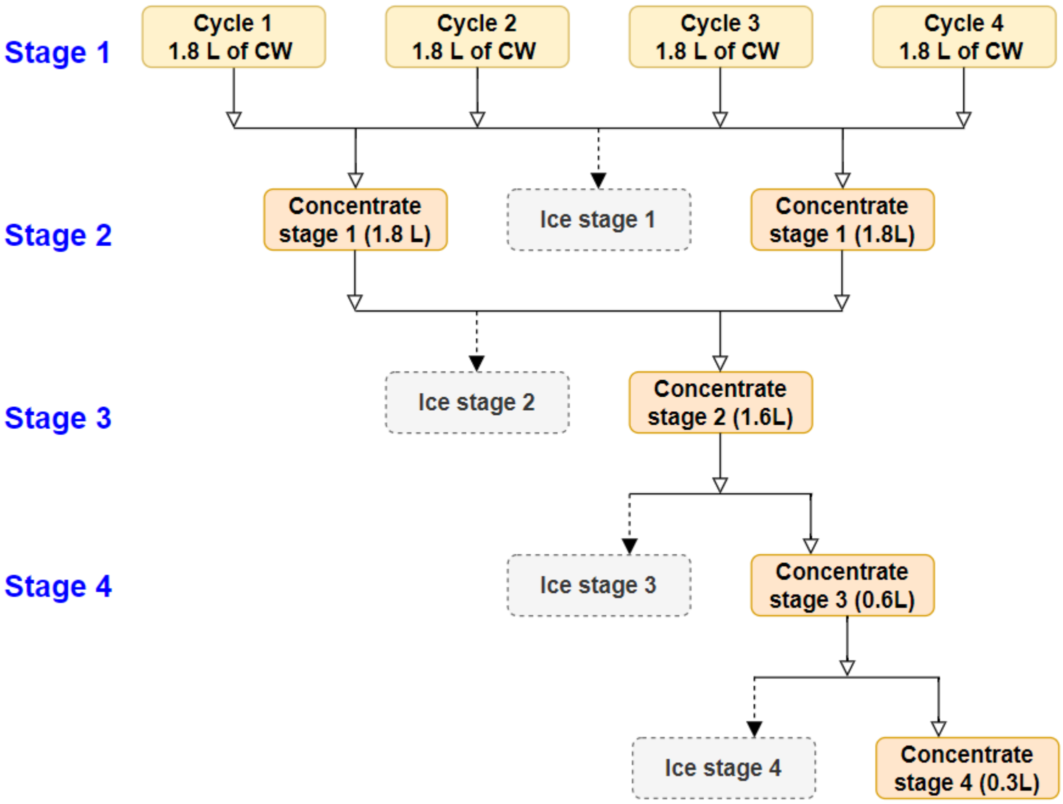


Figure 4.2. Flowchart of the PFC multi-stage assay to concentrate cheese whey.

4.2.4 Validation of experimental results

A comparison between the mass balance and theoretical data was performed by calculation of the theoretical formed ice mass ratio (Wth) (kg of ice per kg of cheese whey), as defined in Equation 4.1.

$$\mathrm{Wth} = \frac{\mathrm{TSin - TSc}}{\mathrm{TSd - TSc}} \tag{4.1}$$

where TS_{in} is the initial total solids content (g Kg^{-1}) of the cheese whey, TS_c is the total solids content (g Kg^{-1}) of the concentrated fraction, and TS_d is the total solids content (g Kg^{-1}) of the ice (I) fraction of the CW.

The deviation between experimental and theoretical data was expressed as root mean square (RMS) deviation, as described in the equation 4.2 below.

$$\mathrm{RSM}\ (\%) = \sqrt{\frac{\Sigma(Wexp - \frac{Wpred}{Wexp})^2}{\mathrm{N}}} * 100 \tag{4.2}$$

where Wexp and Wth correspond to the experimental and the predicted ice mass ratio, respectively, while N is the number of repetitions performed.

4.2.5 Physical and chemical analysis

Analyses of samples were performed per triplicate. The volume of the concentrated solution was measured along each PFC cycle (every 30 minutes) by discharging the liquid from the bottom of the tank into a graduated cylinder.

The content of solids in the cheese whey and the concentrated and diluted fractions was measured on one hand by applying the Standard Method (APHA, 2005) for total solids (TS) determination. On the other hand, a hand-held refractometer (ATC RHB-50, CH) was used to estimate the solids content in °Brix (°Bx) with an accuracy of 0.1 °Bx and a measurement range from 0 to 50 °Bx. The refractometer was used during the freezing process to follow up the evolution of the dissolved solids content in the concentrated fraction along the PFC cycles. The sampling and measurement of the °Bx in the concentrated fraction were performed every 30 minutes.

The different solids and total solids concentrations for the CW, concentrated and diluted fractions will be mentioned throughout the manuscript as follows: solid concentration in °Bx of the CW (SCcw), of the concentrated fraction (SCc), of the diluted fraction (melted ice) (SCd), the total solids of the CW (TScw), the total solids of the concentrated fraction (TSc) and the total solids of the diluted fraction (TSd).

4.3 Results and discussion

4.3.1 Freeze concentration screening tests

The initial SCcw used in this study was 7 °Bx. To perform PFC cycles at different initial concentrations, derived samples of CW were prepared by diluting the raw CW with deionized water to achieve initial solids contents of 5 and 3 °Bx. The length of the operation time was different depending on the cooling temperatures. Then, to achieve around 50 % reduction of the volume, PFC cycles of 3, 2 and 1.5 hours for the cooling temperatures -5, -10 and -15 °C, respectively, were performed. After each cycle the volumes of each fraction were measured, considering the temperature and density of the solutions and integrating the real volume reduction in the corresponding calculations.

Table 4.2 shows the results obtained from the screening tests. °A similar trend was observed for the three initial concentrations of the CW and under the effect of the cooling temperatures -5 °C and -10 °C, as the final °Bx concentration of the obtained concentrated fraction was equal for almost all the agitation rates. However, a slight decrease in the °Bx was observed in few assays operating at -15 °C for the three tested initial °Bx of the CW. Aider et al. (2007) also stated similar results for the cooling temperatures -10, -20 and -40 °C while cryoconcentrating CW, as no significant influence on the composition of the concentrated and ice fractions. In a similar experimental device, Muñoz et al. (2019) concentrated skimmed milk. The finding stated that the highest solid recovery (SR) was obtained at the lowest cooling temperature (-15°C) and highest agitation rate tested (1000 rpm). Even though the experimental device was similar to the one used in the present study, the recovery of solids was found to be a function of the agitation rate only.

Table 4.2. Solids content at the end of the screening experiments.

		Solids content in the concentrated fraction of CW at 50 % volume reduction		
Cooling temperature		**-5 °C**	**-10 °C**	**-15 °C**
Initial concentration	**Agitation rate**			
3 °Bx	**150**	4.5	4.5	4
	300	5	5	5
	600	5	5	5
5 °Bx	**150**	6.5	6.5	6
	300	7	8	6
	600	8	8	7
7 °Bx	**150**	10	10	8.5
	300	10	10	10
	600	11	11	11

Also, an increase of the agitation rate induces a higher contact between the reactor wall and the treated CW during the FC process, allowing greater concentration rate of the solids in the concentrated fraction, which is important to optimize and enhance the FC process. This result was also obtained in this work, not only through the solids content in the concentrated fraction but also through the process efficiency of each of the assays). Figure 4.3 shows the process efficiency (PE) (Eq. 3.3) of the performed screening experiment as a function of the agitation rates for the three initial concentrations (3 °Bx, 5 °Bx and 7 °Bx). As can be observed, the higher the agitation the higher the PE, achieving PE values, at 600rpm, of 82 %, 88 % and 80

% for the initial concentrations of 7, 5 and 3 °Bx respectively. The increase in the PE with the increase of the agitation rate reflects the low concentration of solids retained in the ice fraction compared to the solids content in the concentrate, as the higher the speed of the solid particles in the CW during the process, the less they are captured inside the ice structure (Figure 4.3). This behavior was stated for the first time by Shirai et al. (1998), as the finding demonstrated that the decrease in the concentration of the ice fraction is due to the combination between the high agitation rate and the slow formation of the ice.

The PE was also influenced by the cooling temperature, as a proportional increase was obtained in the sense of lower temperatures (from -15 °C to -5 °C) for the three initials SC tested and for all the agitation rates. Consequently, the reported results indicated that the PFC efficiency in a stirred tank is responding analogously regardless the initial CW concentration (Figure 4.3).

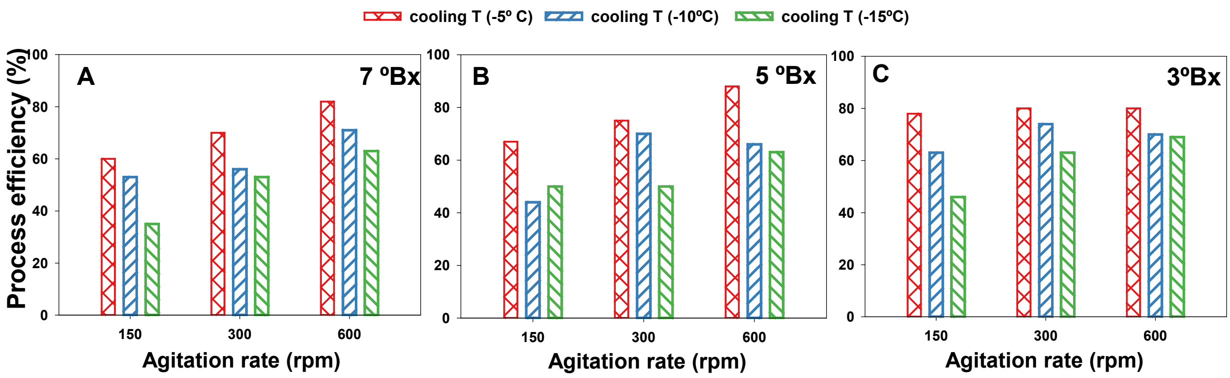


Figure 4.3. Process efficiency of the screening experiments versus the agitation rate for the initial concentrations 7°Bx (A), 5°Bx (B), 3°Bx (C).

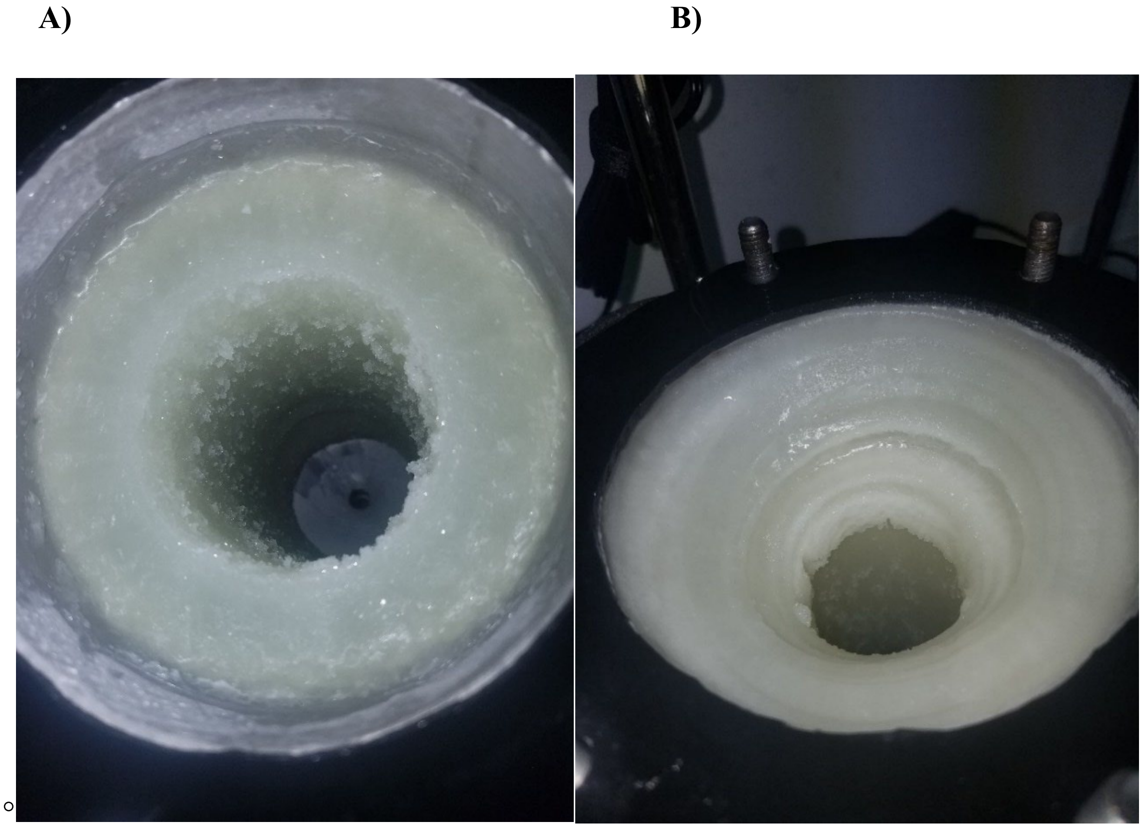


Figure 4.4. Pictures of the formed ice after completing the FC process at different agitation rates, low (A) and High (B).

Through all the screening experiments performed, it was possible to distinguish the influence of the freezing parameters on the process efficiency of the FC of CW in a stirred tank. The highest efficiencies were obtained at -5 °C and 600 rpm.

4.3.2 Multi-stage PFC

4.3.2.1 Total solids content

The total solid content (TS) in the concentrated and diluted (melted ice) fractions of the CW (TSc and TSd), per each FC stage (S1 to S4), are illustrated in Figure 4.5. A drastic increase of the TSc was observed between S1 and S3, while slight increases were observed from S3 to S4. Starting with a TScw of 6.66 ± 0.02 % (w/w), an average value of 10.18 ± 0.06 % (w/w) and 14.81 ± 0.02 % (w/w) of TSc were reached after completing S1 and S2 of the PFC, respectively. The maximum TSc content was achieved in S3 and S4, as the average values obtained were 20.34 ± 0.02 % (w/w) and 20.52 ± 0.13 % (w/w), respectively. A similar TS increase was observed in (Belén et al. (2018) and Sánchez et al. (2011). The increase of the TS in each stage decreased in each FC stage, counting for 52.8 %, 45.4 %, and 37.3 % increase of the TS content in S1 and S2 and S3, respectively. The weakest increase was measured in S4 corresponding to 0.88 %. After each completed FC stage, the CW was losing an important fraction of its free water in form of ice which leads to the increase of the viscosity. Sánchez et al. (2011) reported that the concentrated fraction of the CW is behaving as a Newtonian fluid near the freezing point temperature and that the total solids are in ranged from 10 to 20 % (w/w). As during the four stages, the SR of TS achieved 76.4 %, 72.7 %, 68.6 % and 50 % in S1, S2, S3 and S4, respectively. A Newtonian fluid is a solution whose viscosity is not being affected by any flow speed or shear rates, it remains unchangeable.

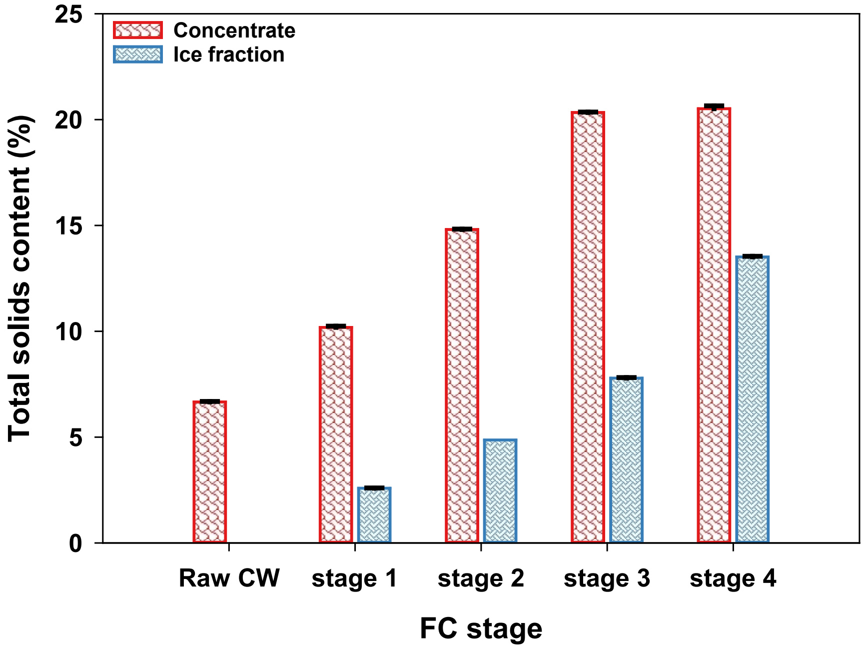


Figure 4.5. Solids content in the concentrate and ice fractions obtained in each PFC stage.

Likewise, the TS in the ice fraction proportionally increased in each PFC stage. Starting from an average TS of 2.58 ± 0.02 % (w/w) in S1, 4.86 % (w/w) in S2, 7.78 ± 0.03 % (w/w) in S3 and 13.52 ± 0.03 % (w/w) in S4. The given pattern could be due to the lack of free water in the treated CW, which allow merging the formed ice and thus the purity of the ice decreases in each stage. The increase of TS in the ice fraction was also stated by other authors for CW, for FC of sugar solutions, for tofu whey and for cheese salted whey (CSW) (Aider et al., 2007, Belén et al., 2018, Belén et al., 2012, Sánchez et al., 2011) .

4.3.2.2 Process efficiency, concentration factor and yield

Table 4.3 shows the process efficiency (PE, Eq. 3.3), yield (Y, Eq. 3.4, and concentration factor (CF, Eq. 3.9) of each PFC stage. PE average values of 74.9 %, 68.0 %, 62.8 % and 39.6 % were obtained in S1, S2, S3 and S4, respectively. Sanchez et al. (2011) also reported PE values ranging between 53.67 % and 73.33% for the FC process in an agitated vessel of CW and CSW, respectively. Belén et al. (2018) reported an average PE of 63% in a falling film-based FC treating CW, which agrees with the obtained efficiencies in the present study. In this study, the highest PE was measured in stages S1 and S2 of the PFC. A drastic decrease from S3 to S4 was detected regarding the PE as the efficiency of the process dropped to less than 40 %. Based on the results obtained for the TS content, the last stage (S4) could be considered as the TS saturation point since the recovery of solids from S3 to S4 was insignificant in the concentrated fraction. Aider et al. (2007) also obtained a PE decrease (from 93.12 % to 38.95 %) concentrating CW in block and stated that it was caused by the sharp decrease of the water content in the last stages of FC.

Table 4.3. Process efficiency, concentration factor and yield obtained from the multi-stage freeze concentration of cheese whey.

FC stage	Process efficiency (%)	Concentration factor	Yield (%)
Stage 1	74.9	1.57	79.3
Stage 2	68.0	2.23	73.9
Stage 3	62.8	3.07	71.4
Stage 4	39.6	3.42	58.8

Regarding the concentration factor (CF), the untreated CW (Stage 0) is conventionally representing a CF of 0. The CF increases in each FC stage and, specifically in this study, it ranged from 1.57 in S1 to achieve 3.42 in the last stage (S4) (Table 4.3). Higher concentration factor was obtained by (Aider et al., 2007) in four stages (4.82) operating under a cooling temperature of -20 °C while freeze concentrating CW in block. In terms of yield, the results follow the same trend obtained for the CF. The highest yield (79%) was obtained in S1, followed by an average yield of 74 %, 71% and 59% in stages S2, S3 and S4, respectively (Table 4.3). Since the yield also depends on the TS content of the concentrated fraction compared to the one of the feed CW in each stage, a drastic drop in the last PFC stage (S4) was observed as a consequence of the almost negligible TS increase compared to S3 (from 20,34 ± 0.02 % (w/w) in S3 to 20.52 ± 0.13 % (w/w) in S4).

4.3.2.3 Electrical conductivity

Figure 4.6 shows the increase of the electrical conductivity (EC) of the concentrated and diluted fractions of CW obtained in each PFC stage. The EC of the concentrated fractions increased from 6.78 mS cm^{-1} (S1) to 13.76 mS cm^{-1} (S4). The EC of the ice fractions, I0, I1, I2, I3 and I4, was 3.05, 5.33, 7.63 and 11.01 mS cm^{-1} respectively. Regarding dairy products, an increase of the EC is due to a rise of the concentration of charged compounds and in this case mineral salts of the CW. Mineral salts content plays an important role in the quality of the whey protein, as salt content affects the solubility of the whey on water. The increase of the EC in the concentrated and diluted fractions of the CW showed similar trend to the one of TS content. These EC increasing trends were also observed by other authors concentrating CSW and CW in FC systems (Freddy Belén et al., 2018; Sánchez et al., 2011). Additionally, FC was used as desalination technique by removing the salt while concentrating it in the concentrated fraction resulting in the cleaning of the ice fraction (Williams et al., 2015), which justify the increase of the EC in the concentrated fraction. If considering that the EC of CW represents the amount of mineral salts, then most of the salt is being retained in the concentrate, which could be beneficial for the following application of whey as human dietary supplement, as calcium and magnesium content is always favorable for losing weight and blood pressure adjustment.

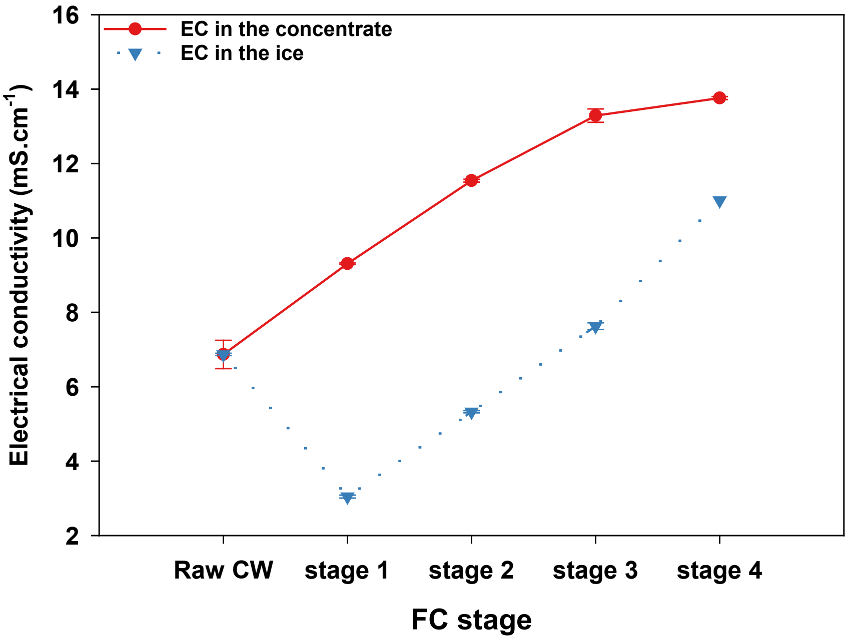


Figure 4.6. Evolution of the electrical conductivity of both the concentrated and diluted fractions of CW obtained in each PFC stage.

4.3.2.4 Protein content

Figure 4.7 illustrates the protein content of the raw CW and the concentrated and ice fractions in each stage of the PFC. The protein content in the raw CW was 0.90 % (w/w), then it increased in the concentrated fraction from 1.36 % (w/w) in S1 to 2.85 % (w/w) in the last stage (S4). It is important to mention that the protein content at S4 was close to the previous one (Table 4.4), presenting a similar behavior to the one showed by the TS content in the concentrated fraction. The protein content in the dry matter of the concentrated CW was 13.4 %, 13.9 %, 13.7 % and 14.0 % for C1, C2, C3 and C4, respectively, being the increase of protein content proportional to the TS increase in the concentrated fraction. In a similar study, Aider et al., (2007) concentrated CW in five FC stages and stated that after the fourth FC stage the protein content reaches a plateau, contrarily to the present study that was reached at the third stage. In other studies, a protein concentration of 3.82 % (wt) was obtained from CW and CSW in four FC stages performed in a falling-film based FC system (Belén et al., 2018; Sánchez et al., 2011).

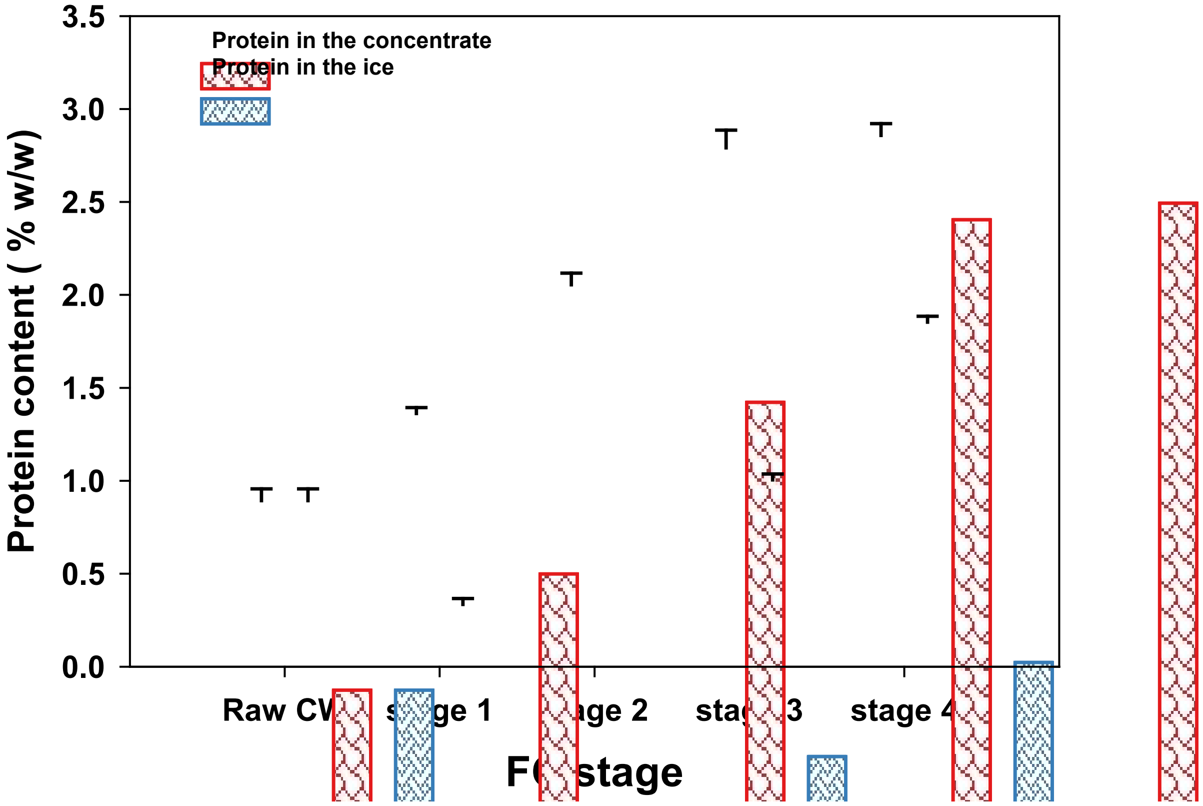


Figure 4.7. Protein content in the concentrated and ice fractions of each freeze concentration stage.

Although the PFC allowed achieving high efficiencies to concentrate the protein from CW in the concentrated fraction, yet an important fraction of the protein is remaining in the ice fraction. As previously mentioned, the concentration of TS and protein achieve a limit for the recovery in the concentrated fraction, and the available free water in the CW is the reason behind it. Following the increase of protein in the CW, the free water in the solution was becoming less available in each stage, which justify the retention of protein fraction into the ice structure resulting in the decrease of recovery in the concentrated fraction (Aider et al., 2007; Sánchez et al., 2010). A partial melting of the ice could be a considerable step to enhance the efficiency of the concentration process. In fact, the application of vacuum pressure after softening the ice structure by the increase of temperature, would allow higher recovery of TS and thus protein in the concentrated fraction. The thawing method was also proposed to avoid the decrease of the effectiveness of the multi-stages FC by Moreno et al. (2013).

Table 4.4. Protein content during the multi-stage freeze concentration of CW.

Sample	Protein content (% w/w)
CW	0.90 ± 0.06
C1	1.36 ± 0.03
C2	2.05 ± 0.06
C3	2.80 ± 0.09
C4	2.85 ± 0.06
I1	0.33 ± 0.03
I2	0.62 ± 0.00
I3	1.00 ± 0.03
I4	1.85 ± 0.03

4.3.2.5 Lactose content

Figure 4.8 shows the evolution of the lactose content in concentrated and ice fractions in each FC stage. The concentrations of lactose in the CW, concentrate, ice fractions, as well as the mass balance are given in Table 4.5 for each stage of FC performed. Initially, the CW had a lactose content of 4.26 % (w/w), then an increase in lactose content was observed in the concentrated fractions in each stage of FC. Around 6.50 and 9.97 % (w/w) of lactose content was measured in the concentrate after completing S1 and S2, respectively. The highest lactose content in the concentrate was obtained after completing S3 (13.7 %) and exhibit a plateau in S4 reaching the same value, similarly with the behavior previously observed with the protein content. In terms of lactose content in the concentrate, Aider et al., (2007), stated results from the FC of CW (operating at -10 °C, -20 °C and -40 °C), where the increase of lactose content in the concentrated fractions were not significant and showing an oscillation around the initial content of the untreated CW. Likewise, Sánchez et al., (2010) found similar results in a falling-film based FC system for the concentration of whey, where the an increase of lactose content was observed in the concentrate. Lactose from CW is known to be retained in the ice fraction according to previous studies (Belén et al., 2018), as by the fourth stage of FC, the lactose content in ice fraction exceeds the one in the concentrate. The distribution of the protein and lactose into the concentrated and diluted fractions was first explained by Aider et al., (2007), and it was justified by the molar concentration of the two components, as at equal molar concentrations, lactose solution is characterized by a higher freezing point than the freezing point of the protein solution. This means that the phase transition of lactose solution (from liquid to solids state) will happen before that of the protein solution. The retention of lactose in the ice fraction, which represent the diluted fraction in the FC process, is not only exclusive for FC methods. Bosco et al. (2018) used an ultrafiltration process to treat CW and found that the permeate retains about 80% of the lactose contained in the original CW, has a high salinity and low concentration of proteins and fats.

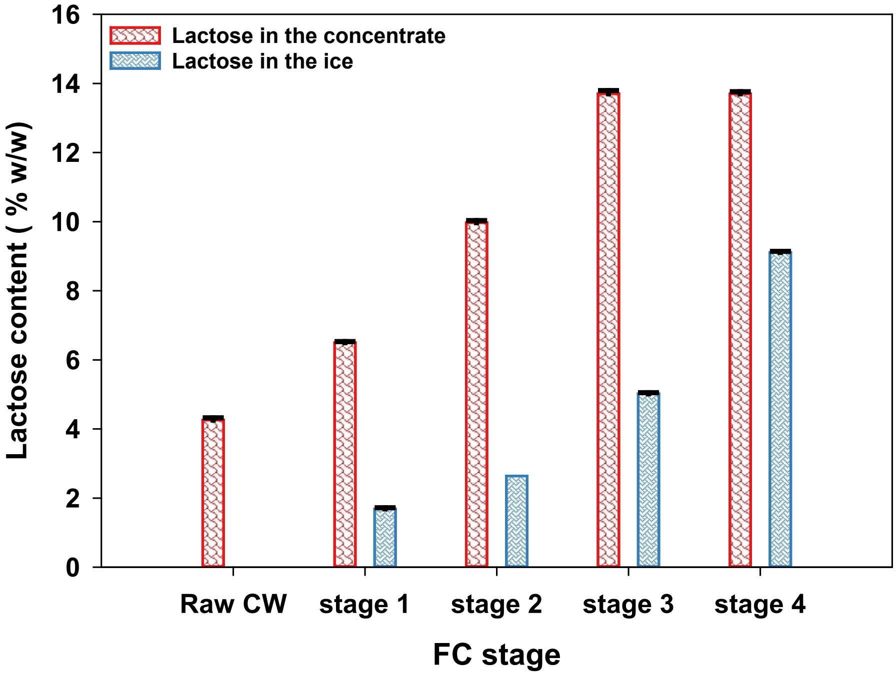


Figure 4.8. Lactose content in the concentrated and the ice fractions of CW obtained in each PFC stage.

Regarding the ice fraction (mentioned in Table 4.5 as I1, I2, I3 and I4), a sharp increase was observed from S1 to S4 counting a content of 1.69 and 9.11% (w/w), respectively, reaching the highest lactose content in the ice fraction in S4. The increase of lactose content in the ice fraction depends highly on the retention of the TS in the fraction. As the concentrate is becoming more charged in terms of protein, lactose and TS, the availability of the free water becomes lower. Which the main reason behind the formation of an ice with low purity caused by the retention of TS in the ice fraction during the process of FC.

Table 4.5. Lactose content in the concentrate and ice fraction during the multistage of CW.

Sample	Lactose content (% w/w)
CW	4.26 ± 0.06
C1	6.50 ± 0.03
C2	9.97 ± 0.06
C3	13.7 ± 0.09
C4	13.7 ± 0.06
I1	1.69 ± 0.03
I2	2.64 ± 0.00
I3	5.02 ± 0.03
I4	9.11 ± 0.03

As illustrated in Figure 4.8, the lactose content in the present study was more retained in the concentrate than in the ice fraction, following the same pattern of protein and TS contents. The uncommon behavior of the lactose retention in the concentrate obtained in the present study, could be justified by the assumption that the agitated vessel FC configuration hinder the optimum crystallization of lactose inside the ice fraction. As from one hand, the performed multi-stage FC experiments were carried out at higher freezing temperature (-5 °C) compared to documented ones (-15.01 °C (Belén et al., 2018) and -10, -20 and – 40 °C (Aider et al., 2007)); and from the other hand, the first formed ice layers against the freezing surface of the FC vessel could give the same results as previous studies, however, once the growth of ice increases, the thermal exchange between the CW solution in the center of the vessel and freezing refrigerant is getting higher, thus the crystallization conditions of lactose are not achieved.

4.3.2.6 Validation of experimental results

The validation of the experimental results is calculated by the mean of the mass balance. The predicted mass of the formed ice of the CW was calculated in each stage and for all the screening experiments. The comparison of the predicted mass ratio and the experimental mass ratio of the ice allowed the calculation of the root mean square error (RMSE) to determine the deviation between the obtained data and the estimated ones. For the screening experiments, the RMSE ranged between 0.011 to 0.24. The obtained values are in an acceptable range when below 25 % according to (Lewicki., 2000). For the four stage FC, the RMSE obtained for the overall experiment was 0.17. The obtained value validates the obtained results for the screening experiment in the studied reactor and the multi-stages freezing of the CW.

Table 4.6. Protein and lactose mass balance during the four stages of FC.

FC stage	Protein mass balance (%)	Lactose mass balance (%)
Stage 1	5	4
Stage 2	2	3
Stage 3	8	6
Stage 4	16	17

4.4 Market analysis of the concentrated solution of cheese whey:

Table 4.7 gives the amount of protein, lactose and TS content obtained in the first stage of FC, in the raw CW, concentrated and diluted fractions. Depending on the application and the purpose of considering the concentration of the CW, the multistage FC may be a beneficial option instead of a single stage FC. The multistage FC allows a further concentration step of the CW in a reduced volume, however, fixing the target amount of the value-added products (protein and lactose in this case) is curtail for defining the steps for its extraction. FC is shown to be a good pre-concentration step (results of Table 4.7) to other costly existing technologies, by reducing the water content in a more economical way, since during the freezing concentration process is considered relatively low, around 335 kJ/kg water (Jusoh et al., 2008). In this process, the latent heat of fusion is lower than the latent heat of vaporization of the evaporation process (Hunter and Hayslet, 2002; Qin et al., 2006).

Table 4.7. Protein, lactose, TS contents and EC in a single stage of PFC (S1), in the raw CW, the concentrated and diluted (melted ice) fractions.

	Raw CW	Concentrated CW	Diluted CW
Protein content (g)	64.3	49	12
Lactose content (g)	306.7	234	60.8
Total solids (g)	480	366	92.9
EC (mS/cm)	6.78	9.39	3.05
Brix (°Bx)	7	11	3

4.4.1 Commercialization of value-added products obtained from concentrated cheese whey

In general, the market existing for concentrated cheese whey will be that available near the producing industries. Based on all the above-mentioned nutritional benefits of the CW from one hand, and the potential to concentrate protein and lactose as value-added products, the is an interesting opportunity in the market for the concentrated whey as a rich source of protein, lactose, and minerals to many sectors. A major challenge can hinder the valorization of CW consist of its high-water content, and since generally the farms are located in rural areas, the transportation of the CW to valorization centers would be costly and not beneficial economically. For these reasons, farmers are seeking for technologies that are economically feasible and sustainable at ones. The implementation of FC technology in-situ may be a potent alternative to concentrate value-added products from CW, meanwhile reducing the volume of to be transported volume by eliminating a fraction of water ion form of ice that can be discharged. Once a concentrated volume is rich in most of the nutrient, its transportation to the destined valorization center no longer would be an issue.

In the last years, the interest on CW valorization has increased significantly. Nowadays, the industrial activities that consume higher amounts of CW, and therefore would consume concentrated CW, are principally whey protein, demineralized whey powder, and lactose powder manufacturing activities.

- **Whey protein**

Whey protein concentrates (WPC) or isolates (WPI) and hydrolyzed whey protein (HWP) are three available forms of whey in the market. These ingredients are widely used in the food industry in a variety of formulated products, such as dairy, bakery, meat, beverage, and infant formula products due to the excellent functional properties of their proteins and they are also gaining more a more importance in the protein rich supplements sports market. In these products, whey is almost exclusively used in powder form.

Global production of whey protein amounted to 240 million MT in 2014 and is expected to increase 3.5% annually. The global whey protein market is enormously growing. The market size is projected to reach US$ 25.7 billion by 2031 at a registering a compound annual growth rate CAGR 7.39 % from 2022. Factor such as, rising applications of whey in food and beverage products is anticipated to drive the growth of the global whey protein market over the forecast period. Particularly in Europe the whey protein market is projected to exhibit a CAGR of 7.5% during the forecast period 2018-2023 due to the robust demand for whey protein based functional foods. The whey protein market in Europe is mainly driven by highly matured sports nutrition and functional beverages ingredients. The geriatric population in Europe, health-conscious consumers, and increasing number of health & fitness clubs/centers facilitate the growth of whey protein market in Europe. These clubs and health centers are a key distribution channels for dairy ingredients/whey protein products in Europe.

- **Lactose powder**

Lactose is the most abundant carbohydrate in cheese whey and represents around 65% of the total dry matter content. Lactose is a disaccharide composed of the monosaccharides D-glucose and D-galactose, which are the source of biological instant energy. The commercial formulation of lactose is as powder. Lactose powder has wide applications in chocolate, confectionery, dairy and soft drinks, diet and sports nutrition and pharmaceutical industry. Owing to the use of lactose in medical and pharmaceutical applications the market for lactose is anticipated to witness significant growth over the forecast period. Lactose is widely used as a filler-binder in capsules, tablets and lyophilized items. Lactose is also used as a diluent in animal feed and infant food products as it is cost effective, has a bland taste and is compatible with active ingredients and other excipients.

According to the report "Lactose Powder Market: Global Industry Trends, Share, Size, Growth, Opportunity and Forecast 2018-2023" published by IMARC Services Private Limited, the global lactose powder market grew at a CAGR of around 1.4% during 2010-2017 reaching a volume of almost 800 thousand tonnes in 2017. Specifically, in 2015 the US was the country that exported more lactose powder to the ROW (360 thousand tonnes) followed by the EU (66278 tonnes) and New Zealand (23590 tonnes). The global lactose market is expected to reach a market value of US$ 2697.3 million by the end of 2029 at a CAGR of 4.4% over the period 2019-2029.

- **Demineralized whey powder**

Demineralized whey powder is a dried whey with a low content of minerals. It contains 65-75 percent of lactose and 11-12 percent of protein. Demineralized whey powder is increasingly being used in various dairy products such as sweets, pastry products, infant food and sports nutrition products as a high-protein healthier additive.

In terms of numbers, the global demineralized whey powder ingredient market is projected to reach nearly US$ 805 million by the end of 2027, registering a compound annual growth rate (CAGR) of 5.1% over the forecast period 2017-2027. Nowadays, the US and EU account with more than 65% of the demineralized CW powder market.

- **Preliminary assessment of the global market available for concentrated cheese whey**

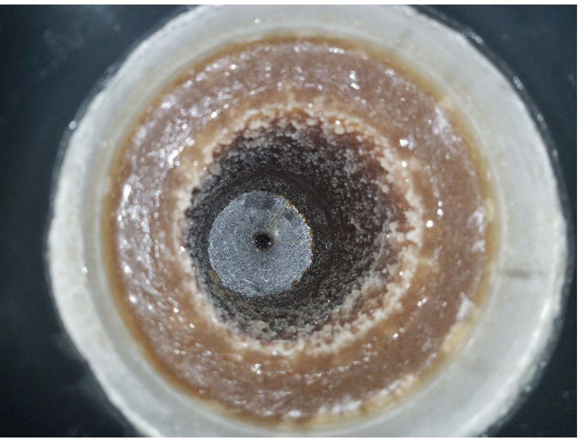
To sum up, cheese whey is currently a value-added product, which can be transported economically to numerous processing industries after the application of pre-concentration stage such as freeze concentration. Freeze concentration preserves the nutritional potential of cheese whey, and this is why the market for this product is promising and even wider than for raw cheese whey, not only to produce whey powder, lactose or whey proteins but also to manufacture new products still under development.

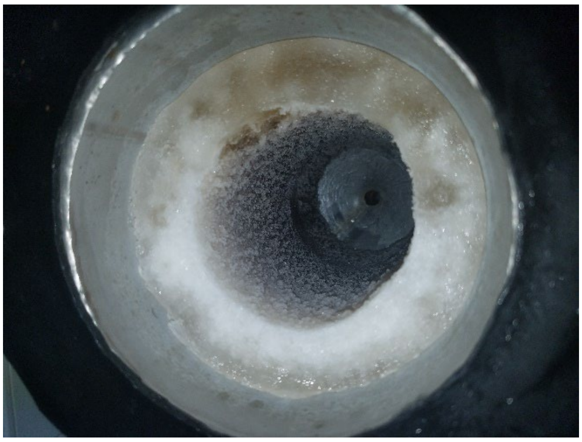
4.5 Conclusion

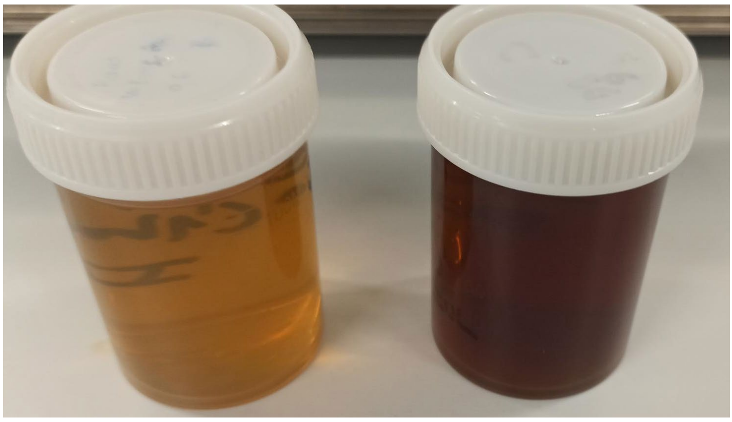
Overall, the application of PFC for concentrating protein and lactose has shown promising results. Regarding the operating conditions, the cooling temperature and the agitation rates showed a positive influence on the process efficiency to concentrate cheese whey. Setting the volume reduction to 50 %, the four stages of FC allowed a recovery up to 20.52 % (w/w) of total solids, up to 13.93 % (w/w) of total protein of total solids and 6.24 % (w/w) of lactose in the diluted fraction. The protein and lactose were concentrated in the concentrate meanwhile some traces are being trapped in the ice fraction if we are talking about g of lactose/g of TS, delivering by the end of the process. The process efficiency, the yield of the system decreased as the freezing level increases.

The multi-stage freeze concentration also showed promising results in terms of PE, recovery, and yield, however, once achieved the 20% of total solids dissolved in the cheese whey no effect was observed in further freezing stages.

The application of progressive freeze concentration in a stirred tank to recover value-added products contained in cow cheese whey, while significantly reducing its water content, showed an important potential. Due to the freeze concentration technique, it is possible to preserve the nutritional and biological properties of the cheese whey, the concentrate, and diluted fractions, maintaining adding value to the final product, the concentrated cheese whey.







Chapter 5: Nutrient recovery using freeze concentration technology from livestock waste

5.1 Introduction

To reduce adverse effects of nutrient losses in high-density livestock areas, a considerable amount of manure could be moved off by transporting it to nutrient-deficit croplands. However, the farther the destination from the production region is, the more expensive and less energy effective is the transportation. Therefore, it is important to continue developing suitable and innovative cost-effective technologies and management strategies to optimize the concentration of livestock manures and/or their valorization before their transportation to nutrient-deficit croplands and utilization for agricultural purposes. FC process allows removing solutes from water by freezing the last one until achieving a high purity of crystallized water and separate the concentrated solution from the ice formed. Less energy requirement, high separation factor, and easy availability of the equipment required for this technology are the main advantages of the FC process compared to other conventional techniques, such as evaporation of filtration, since the proposed technology offers significant advantages over the other nutrient concentration processes in respect to the technical, economic, and environmental aspects.

Thereby, the aim of the present study is to assess the efficiency of FC technology on the recovery of nitrogen, phosphorus, and potassium from a digestate from food-processing industry waste streams combined with pig slurry to deliver a nutrient-rich solution that could be used as a biofertilizer for agricultural purposes. The preliminary results obtained in this study pave the way for a wide research area concerning the employment of FC technology on other livestock effluents for nutrient recovery and as an environmentally friendly and cost-effective alternative to the existing concentration techniques.

5.2 Materials and methods

5.2.1 Raw material

Samples were obtained from an anaerobic digestion (AD) plant located in Catalonia (Spain), treating pig slurry and waste organic effluents from food processing industries. After the AD process, the digestate goes to a post-treatment step consisting in a solid/liquid separation (centrifugation), the liquid fraction is subjected to an extra step consisting in membrane technologies (ultrafiltration and Reverse Osmosis), as illustrated in Figure 5.1, to obtain a clean effluent that can be directly discharged to water bodies and a concentrated fraction that currently is being dried and used as fertilizer, however the effluent remains with high content in water making its transportation to be applied to croplands is costly. The concentrated fraction is the one used in the FC studies to evaluate the feasibility to upcycle this effluent into a nutrient-rich concentrate.

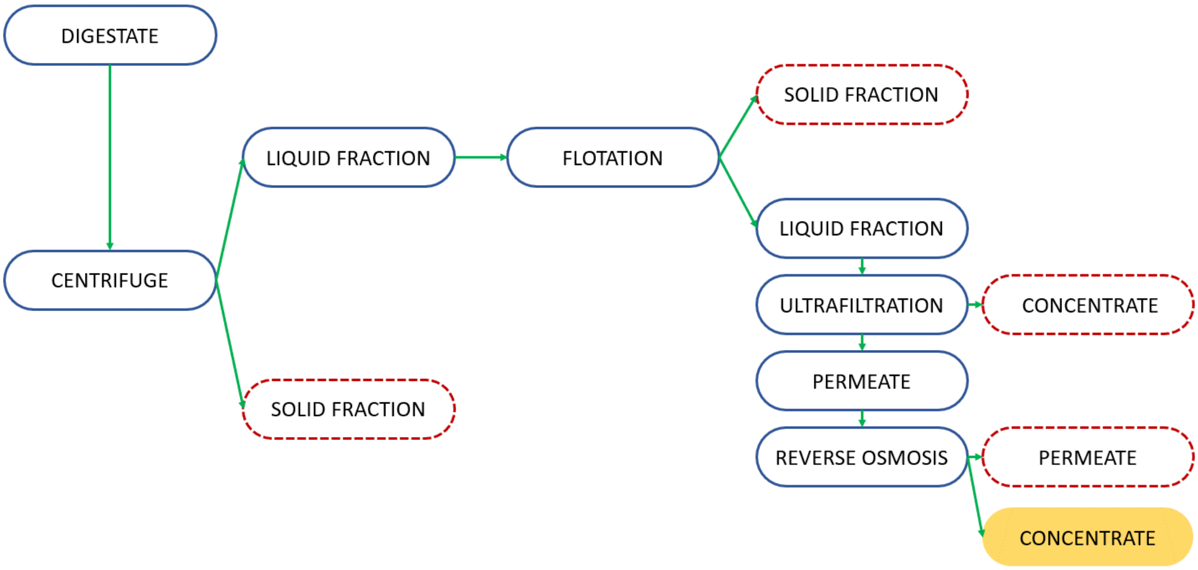


Figure 5.1. Origin of the effluent treated through freeze concentration in this work: the concentrated solution obtained from a reverse osmosis unit treating the liquid fraction of a digestate.

The concentrate from the reverse osmosis (RO concentrate) was sampled and stored at 5°C until processing. The characterization of the sample is presented in Table (5.1).

Table 5.1. Characterization of the RO concentrate used as the raw material for the FC tests.

Total Solids (g/kg)	pH	Conductivity (mS/cm)	P (g/L)	N (g/L)	K (g/L)
18.1±0.6	8.04±0.00	48.95±0.64	0.0207±0.001	12.8±0.1	1.97±0.19

5.2.2 Freeze concentration tests and multi-stage

For the RO concentrate, the FC performance was investigated under two methodological approaches, a progressive freeze concentration (PFC) and a suspension freeze concentration (SFC). Regarding the PFC a screening experiments were carried out at -5, -10 and -15 °C under an agitation rate of 150 rpm, once the highest efficiency was obtained, its freezing conditions were used to perform the multi-stage FC (Figure 5.2). Meanwhile, as for SFC, the freezing conditions cannot be modified, a multi-stage procedure was carried out without any screening.

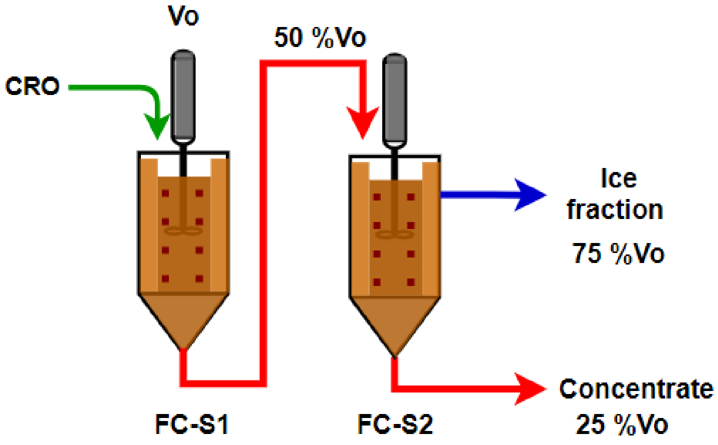


Figure 5.2. Scheme of the experimental design for the multistage FC treating the RO concentrate.

5.3 Results and discussion

5.3.1 Screening experiments

The very first trials of FC applied to this particular raw material were basic with the purpose of understanding the freezing phenomenon. In this regard, the experiments given in Table 5.2 were performed. The screening experiments were carried out performing PFC cycles under three freezing temperatures and an agitation rate of 150 rpm. The obtained results besides the visual behavior, ruled out the freezing temperature -5 °C, as the formation of ice achieved a limit state where no more ice was being formed. The temperature of the liquid fraction (the concentrate) inside the freezing vessel was -4.3 °C, and with the formed ice layers against the vessel made the freezing of the sample under -5 °C unachievable. Table 5.2 provides N concentration of the raw material, the concentrate and ice fraction of screening experiments. Taking the results into account, the highest efficiency (74 %) was obtained at -10 °C, which is the temperature used for the multi-stage, combined with an agitation rate of 600 rpm.

Table 5.2. Nitrogen concentration in the screening experiments.

Temperature (°C)	Nitrogen content (g/L)			Process Efficiency (%)
	Raw material	Concentrated fraction	Diluted fraction	
-5	**12.76**	**10.81**	**2.3**	**79%**
-10	**12.76**	**16.05**	**4.14**	**74%**
-15	**11.12**	**19.16**	**6.66**	**65%**

5.3.2 Multi-stage freeze concentration

5.3.2.1 Total solids concentration

The distribution of the total solids in the concentrated and diluted fractions of both freezing techniques (PFC and SFC) are presented in Figure (5.3). Results obtained indicated a significant impact of the freezing process on the TS recovery. The PFC results show that 2.88 ± 0.02 wt. % and 4.02 ± 0.01 wt. % of TS were obtained in the concentrate after completing S1 and S2, in comparison to the feed solution (1.84 ± 0.04 wt. %), corresponding to an increase of 56.5 in S1 and of 39.5 %, respectively, and a total increase of 118.5 % (from feed solution to S2). Regarding SFC, a TS content of 2.53 ± 0. 1 wt. % and 3.49 ± 0.01 wt. % were obtained in the concentrate at the end of S1 and S2, corresponding to 37 % increase in both stages and a total increase of 89.6 %.

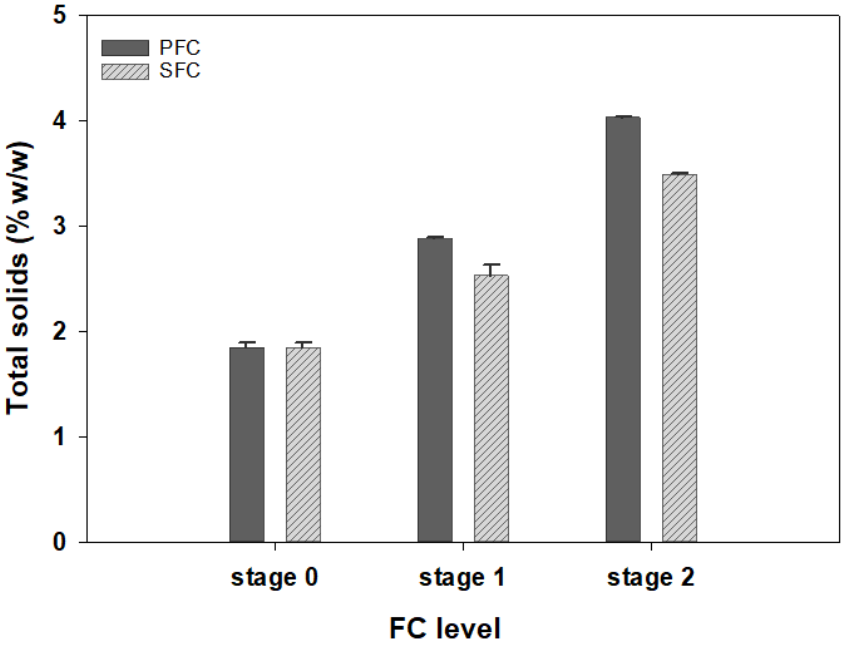


Figure 5.5. Total solids evolution in the concentrated fractions of PFC and SFC.

The high concentration efficiency obtained in the present work was achieved combining freeze concentration with a vacuum separation post-processing (Figures 5.4 and 5.5). Jusoh et al. (2009) stated that the formed ice in the cooling surface of the PFC reactor separated from the centric concentrated solution makes the separation more efficient and easier. In another study, it was reported that the major disadvantage of the SFC is the difficulty of separating the formed ice in suspension of the mother solution (Samsuri et al., 2016). Thus, the application of vacuum, as an external force, is an advantage to intensify the concentrated solution by releasing impurities from the ice surface and consequently increasing the % of TS recovered and enhancing the separation step.

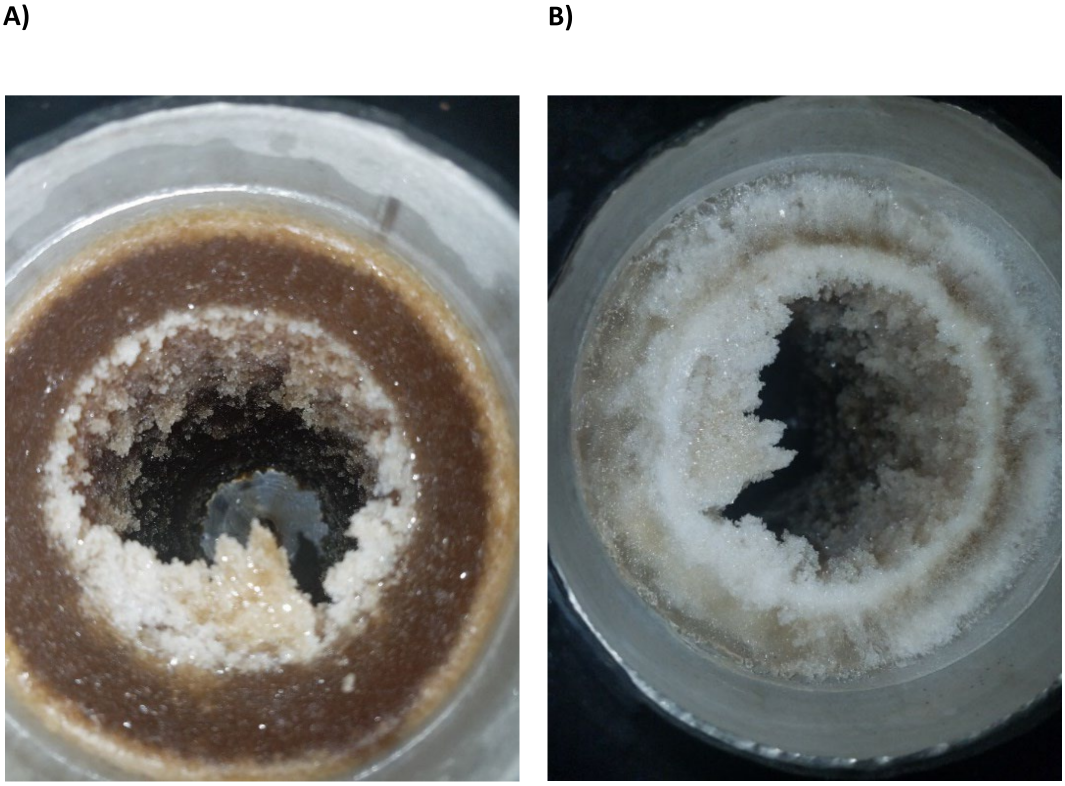


Figure 5.4. Formed ice in the PFC of the RO concentrate, A) before and B) after vacuum application.

Figure 5.5. Concentrated and ice fractions obtained from the SFC of the RO concentrate separated through a vacuum suction stage.

Due to the novelty of the present study, there is no previous works reporting results about FC technology for the purpose of concentrating nutrients from livestock waste (e.g., raw manure, digestate or digestate concentrates). Nevertheless, the FC showed similar behavior for the recovery of TS from fruit juices, namely, orange and pineapple with an increase of 61 % and 4.5 times more than the fresh samples, respectively (Orellana-Palma et al., 2017; Pierucci et al., 2017).

5.3.2.2 Nutrient recovery

The results obtained from the application of FC in terms of nutrient (N, P, K) recovery (Eq. 3.1), using SFC and PFC, is given in Table 5.3. The concentrations of N, P and K in the raw material, concentrate and ice fractions are given is Figure 5.6.

Table 5.3. Nutrient recovery and mass balance in S1, S2 and the total multi-stage process of PFC and SFC.

FC Level	Nutrient recovery (%)			Mass balance (%)		
	N	P	K	N	P	K
PFC-S1	56 ± 3.0	90 ± 7.2	63 ± 5.3	25 ± 0.7	-5 ± 0.02	3 ± 0.02
PFC-S2	71 ± 3.0	59 ± 1.6	52 ± 2.2	17 ± 0.17	30 ± 0.71	29 ± 0.33
2-Stages PFC*	40 ± 0.09	53 ± 0.11	33 ± 0.11	4.2 ± 0.03	-1.5 ± 0.2	0.87 ± 0.17
SFC-S1	62 ± 1.8	88 ± 13.0	60 ± 3.33	9 ± 1.7	-27 ± 6.3	19 ± 2.8
SFC-S2	69 ± 3.3	53 ± 1.5	48 ± 2.1	8 ± 0.3	16 ± 1.5	21 ± 2
2-Stages SFC*	42 ± 0.5	46 ± 0.19	29 ± 0.6	0.72± 0.2	-4.32 ±0.09	4 ± 0.05

* *From feed solution to S2*

In all performed FC cycles, N and P exhibited the same pattern of recovery in the concentrated fraction for both PFC and SFC. Regarding PFC, N concentration increased in the concentrate from 11.20 g L^{-1} (feed solution) to 14.75 g L^{-1} in S1 (50 % of V_i) and 22.66 g/L in S2 (25 % of V_i) representing a recovery of 56 and 71 %, respectively counting a recovery of 40 % in 25 % of V_i (two stages). P concentration increased in the concentrate from 20.66 mg/L to 38.5 mg L^{-1} in S1 and 49.93 mg/L in S2 representing a recovery of 90 and 59 %, respectively and counting a total recovery of 53 % in 25 % of V_i. Likewise, K concentration increased in the concentrate from 1974 mg/L to 2530 mg/L in S1 and 2908 mg/L in S2, respectively representing a total recovery of 33 % in 25 % of V_i. Meanwhile in SFC, the concentrations of N and P showed the same pattern (Figure 5.6) and similar recoveries (Table 5.3), counting 62 and 69 % of N recovery, 88 and 53 % of P recovery recorded at the end of S1and S2, respectively.

K content showed an unexpected behavior in S2 of both PFC and SFC since the concentration of K slightly increased (<100 mg L) in PFC-S2, meanwhile in SFC-S2, K was not concentrated but rather distributed equally between the concentrated and diluted fractions. A possible explanation of this behavior is the precipitation of K during both PFC-S2 and SFC-S2.

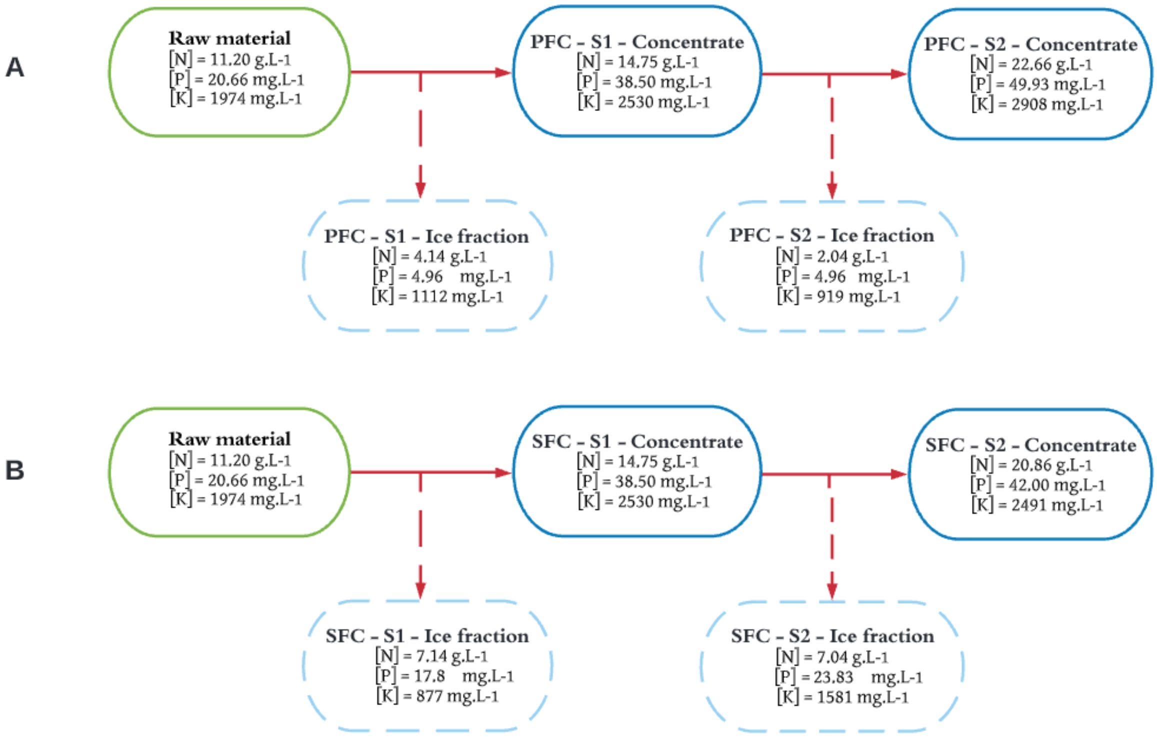


Figure 5.6. Nitrogen, phosphorus, and potassium concentrations in the raw material, concentrated and diluted fractions for the PFC (A) and SFC (B).

Quantitatively, it is noticeable that higher P could be recovered by FC process than N and K (Table 5.3). An explanation of this behavior is in the difference between molecular weight, structure, and size of nutrient. P has larger molecular weight than N which makes it easy to separate and concentrate (Gu, 2016). The result of this work was similar to that reported by

Jiang et al. (2015) achieving a removal of 80 % of ammonia from wastewater in 50 % of formed ice. A typical P recovery technique applied in livestock manure/slurry treatment processes is struvite precipitation through the addition of magnesium salts (mainly magnesium hydroxide and magnesium chloride), which allows recovering at least 80 % of inorganic P from pig slurry (Schoumans et al., 2014), and reduce 72 % of P from swine slurries (Burns et al., 2001). However, up today there is not additional comparable studies reporting the nutrient recovery from livestock slurry or manure using FC technology, in which the initial TS is generally high, and the matrix is complex.

The purity of formed ice during the FC process is the main parameter affecting the yield of nutrient in the concentrate, which is directly associated to the separation capacity of the two methods (PFC and SFC). Samsuri et al. (2016) reported that the difficulty of ice crystals separation in the SFC method is due to its big surface area which makes it a complicate and expensive process than other concentration technologies. Thus, it is less attractive to be applied in the market.

The second stage of FC was performed using the concentrated fractions of the first stage to achieve higher concentration of nutrients in the fraction. N showed a reverse pattern of recovery compared to P and K, since the recovery of N increased from S1 to S2, meanwhile the P and K recoveries decreased using both PFC and SFC (Table 5.3). Finally, it must be highlighted that the second stage of PFC require two identical stages with a reduction of 50 % to achieve 1.8 ± 0.1 L of concentrate. However, despite the use of the same freezing parameters, the concentration of nutrients was never identical. The differences on the concentrations were not significant ($p<0.05$) but the mass balance (Eq. 3.2) was influenced and was ranged between -27 and 30 % for N, P and K (Table 5.3).

From the promising results obtained, it could be concluded that low cost and highly efficient FC processes could be applied to recover significant amounts of nutrient from an RO concentrate treating digestate or other livestock effluents and can be an alternative to existing technologies for nutrient recovery. Figure 5.7 illustrate visual concentration efficiency of FC on the treated raw material, on top samples obtained from SFC and bottom samples obtained from PFC.

Figure 5.7. Raw RO concentrate of reverse osmosis, the concentrated and the ice fractions generated through the PFC and SFC in two stages.

5.3.2.3 Process Efficiency and yield

The efficiency of each concentration stage was calculated and expressed as the increase in N, P, and K concentration in the final concentrated sample (Eq. 3.3). Table (5.4) shows the process efficiency (PE), and the yield (Y) for both FC technologies in two stages of FC. The PE of PFC in terms of N reached 74 and 91 % in PFC-S1 and PFC-S2, respectively. The PE of PFC in terms of P reached 88 and 90 % in PFC-S1 and PFC-S2, respectively. Likewise, the PE of PFC in terms of K reached 60 and 68 % in PFC-S1 and PFC-S2, respectively. As observed, the PE increased from PFC-S1 to PFC-S2 for N, P and K, this means that an important fraction of free water was remaining in the concentrate of S1 to be used in S2, and that the purity of the formed ice in PFC-S2 was relatively high related to the concentrated fraction. Regarding the SFC, quantitatively lower PE were obtained in S1 and S2 (Table 5.4) and this is due to the low operating parameters used for the technique (-2 °C and 45 rpm). Additionally, the PE dropped in S2 compared to S1 is SFC, in terms of P and K contrary to N that increased. Several parameters could be the reason behind the obtained behavior, as the high operating temperature (-2 °C), the low agitation rate (45 rpm) and the configuration of the SFC. Generally, the volume of ice produced by PFC process is relatively low with high purity, but lower productivity compared to the SFC (Samsuri et al., 2016).

Moreover, the mechanical stirring (150 rpm) presented in the PFC system improves the heat transfer and the water flow and mass transfer (from concentrated fraction towards the ice fraction), thus a significant efficiency was observed in PFC system. An increase of the stirring rate in future studies should be considered in order to allow greater PE in both PFC and SFC, as it is allowing a better homogeneity of the solution in terms of TS inside the FC vessel. Osorio et al. (2018) also indicated this phenomenon in the FC system, their finding agrees that there is a significant correlation between higher stirring rate and increasing the mass transfer at the interface. It is well documented that increasing the heat transfer will enhance the ice growth rate and creating ice layer with higher purity and consequently lead to high system efficiency (Jusoh et al., 2008). In another study conducted to remove nutrients from synthetic municipal wastewater effluent, authors also reported 99.9 and 96.5 % removal efficiencies of P and N in a single freezing test at -15 °C in the ice fraction (Gu, 2016). Song et al. (2001) evaluated the performance of a batch freezing apparatus for separation of organic matter from livestock wastewater and demonstrated a high-quality effluent and PE of over 98% at -3 °C and 300 rpm. The difference in efficiency of a system results from the selectivity of growing ice crystal based on the recovery of different resources. It is important to emphasize that even the complex matrix of the concentrated liquid fraction of digestate challenges the PE of the FC, the results obtained in this work are promising and competes with the existing technologies.

Regarding the yield, this parameter reflects the ratio of the mass of solute present in the separated liquid to the mass of solute present in the original solution (Eq. 3.4). A total yield of 90 %, 90 % and 73 % of N, P and K, respectively, was reached in two stages of PFC. A total yield of 75 %, 64 % and 62 % of N, P and K, respectively, was reached in two stages of SFC. The yield obtained in PFC and SFC are relatively high (Table 5.4), this means that the mass of N, P and K in the concentrate and ice fraction is remarkable compared to the feed solution and that the operating conditions are steadily a major influence. Among the aims of the present study, the use of concentrated fraction as an organic nutrient-rich fertilizer for agricultural region with a nutrient deficiency issue, and ice fractions as irrigation water targeted for areas with high livestock density. The FC allowed an optimal distribution of nutrients into 50 % of the initial volume of the feed solution, meanwhile reserving the quality of the obtained fractions in terms of nutrient content. Thus, delivering two potential customized fertilizers in terms of N, P and K content.

The Yield during the FC process reflect the ratio of the mass of solute present in the separated liquid to the mass of solute present in the original solution (Eq. 3.4). A total yield of 74 %, 82 % and 55 % of N, P and K, respectively was reached in two stages of PFC (75 % of V_i). A total yield of 75 %, 64 % and 62 % of N, P and K, respectively was reached in two stages of SFC. The yield obtained in PFC and SFC are relatively high (Table 5.4), this means that the mass of N, P and K in the concentrate and ice fraction is remarkable compared to the feed solution and that the operating conditions are steadily a major influence. Among the aims of the present study, the use of concentrated fraction as an organic nutrient-rich fertilizer for agricultural region with a nutrient deficiency issue, and ice fractions as irrigation water targeted for areas with high livestock density. The FC allowed an optimal distribution of nutrients into 50 % of the initial volume of the feed solution, meanwhile reserving the quality of the obtained fractions in terms of nutrient content. Thus, delivering two potential customized fertilizers in terms of N, P and K content.

Table 5.4. Nitrogen, phosphorus, and potassium process efficiency and yield during the PFC and SFC multi-stages.

FC method	FC stage	Process efficiency (%)			Yield (%)		
		N	P	K	N	P	K
PFC	Raw-S1	74 ± 2	88 ± 4	60 ± 1	81 ± 3	90 ± 6	73 ± 2
	S1-S2	91 ± 4	90 ± 4	68 ± 3	92 ± 3	91 ± 7	76 ± 2
	Raw-S2	67 ± 0.08	79 ± 0.16	41 ± 0.03	74 ± 0.09	82 ± 0.42	55 ± 0.04
SFC	Raw-S1	52 ± 1	54 ± 1	65 ± 3	68 ± 2	69 ± 2	75 ± 3
	S1-S2	66 ± 2	43 ± 3	37 ± 1	74 ± 1	63 ± 3	61 ± 1
	Raw-S2	34 ± 0.02	23 ± 0.03	24 ± 0.03	50 ± 0.02	43 ± 0.06	45 ± 0.03

5.3.2.4 Heavy metals content

To be used as an organic fertilizer for the soil, the concentrated and diluted fractions obtained from the FC were characterized also in terms of heavy metals content. Among the seven metals analyzed (Cr, Ni, Hg, Pb, Cd, Cu and Zn), some of them were not detected in any of the fractions, namely, the Cr (< 0.01 mg/L), the Hg (<0.004 mg/L) and the Cd (<0.0005 mg/L).

Lead was not detected in the raw material, however, it appeared in the diluted fractions of the SFC-S1 and PFC-S1 only, with a concentration of 0.067 mg/L and 0.207 mg/L which are equivalent to 9.311 mg/kg TS and 18.973 mg/kg TS, respectively. The obtained concentrations of the Pb, although there are retained in the diluted fractions, are below 120 mg/kg TS, which is the maximum permitted concentration fixed by the regulation (EU) 2019/1009 for organic fertilizers (EU, 2019).

The Ni concentration in the raw material was 0.520 mg/L, to be distributed after the first stage into 0.340 mg/L in the concentrate and 0.220 mg/L in diluted fraction of PFC-S1. The results obtained after PFC-S2 showed a similar distribution of the Ni in the two fractions, a concentration of 0.167 mg/L was obtained in the concentrated fraction and 0.120 mg/L in the diluted fraction of PFC-S2. The Ni content in the raw material was not concentrated as expected, however it was decreasing as the FC level increased, which means that the Ni content in the final concentrate (S2) was lower than in the raw material. The concentrated and diluted fractions of the SFC showed a similar distribution of the Ni in the two fractions, however, the concentration of the concentrate in the SFC-S2 was 0.313 mg/L and was higher than the concentrate of the PFC-S2. This could be justified by the formation of the ice in both methods, as the principle of the SFC require a formation of the ice nucleation inside the mother solution (Petzold and Aguilera, 2009), which facilitates the migration of the ions of the heavy metals from the formed ice to concentrate during the separation. The Ni content in the concentrates of the second stage of PFC and SFC are equivalent to 4.138 mg/Kg 8.972 mg/Kg TS in the PFC-S2 and SFC-S2, respectively. The Ni concentrations of the concentrates obtained in two stages and for the two methods were below the maximum allowed concentration for Ni by the regulation (EU) 2019/1009 for organic fertilizers which fixed at 50 mg/kg of dry matter. The concentration of Ni in relation to the nitrogen content in the concentrate is valued of 0.466 mg Ni/kg N which is much lower than the equivalent value for pig slurries in Spain, 22.94 g Ni/Kg N (Antezana et al., 2016).

Regarding the Cu content, the concentration increased with the increase of the level of freezing. Starting from a concentration of 1.535 mg/L in the raw material to achieve 1.980 mg/L and 6.050 mg/L in the concentrate from S1 and S2 of PFC, respectively. Unlike the behavior of the Ni content that was higher in the SFC, the Cu exhibited an opposite pattern, as the concentration in the concentrate of the SFC was lower than the one in PFC. The Cu content was 1.660 mg/L and 1.460 mg/L in the concentrate of SFC-S1 and SFC-S2, respectively. The final concentrations are equivalent to 150.208 mg/kg TS in the PFC-S2 and 41.806 mg/kg TS in the SFC-S2. The concentrations of Cu obtained in two stages of FC were below the limits stated in the regulation (EU) 2019/1009 for organic fertilizers which is fixed to 300 mg/kg of dry matter. The concentrate of PFC-S2 achieved a Cu content per kg of nitrogen of 84.507 mg Cu/kg N. The obtained value is lower than the average Cu content per nitrogen content of pig slurries in Spain corresponding to 2650 mg Cu/kg N (Antezana et al., 2016).

Likewise, the Zn showed a similar pattern of the concentration to the Cu. Starting from an initial concentration of 1.508 mg/L in the raw material, to achieve a concentration of 2.200 mg/L in PFC-S1 and 4.750 mg/L in SFC-S1 concentrated fractions. Analogously to the Cu, the concentration was less efficient in the case of the SFC, as the concentrated fractions ended up with a concentration of 1.480 mg/L and a 1.620 mg/L in the SFC-S1 and SFC-S2, respectively. The given final concentrations are equivalent to 117.93 mg/kg TS and 46.389 mg/kg TS respectively in the PFC-S2 and SFC-S2. Thus, the concentration obtained with the raw material under study for the Zn are also below the established limit by the regulation (EU) 2019/1009 for organic fertilizers corresponding to 800 mg/kg of dry matter. Similar to the interpretations for Ni and Cu contents, the equivalence of the Zn in relation to the N content is lower than the Zn to N ratio in pig slurries, respectively, 209.620 mg Zn/kg N and 900 mg Zn/kg N (Antezana et al., 2016).

The quality of the studied raw material as well as the products of the FC to be used as an organic fertilizer is completely guarantied with the two evaluated methods of FC. Hence, the use of either the diluted or concentrated fractions is safe for their application to the soil, as the concentrations of all the heavy metals are below the range on the regulation (EU) 2019/1009 for organic fertilizers and the limits values for concentration of heavy metals in the soil.

5.3.3 Quality assessment of FC products from the concentrated digestate

Generally, pig slurry, digestate and concentrated digestate fractions are being used as nutrient-rich fertilizers. However, high-density livestock areas are subjected to nitrate contamination of ground water, thus, there is a limitation of N_{org} content that can be applied to each hectare of agricultural lands in Nitrate Vulnerable Zones, this limitation is currently 170 Kg N_{org}/ha annually (council of European communities 91/676/EEC). The implementation of FC can have a strong impact in how this manure nutrient-rich fractions could be managed, facilitating the use of diluted fractions near the production site (reducing the total amount of ha needed) and facilitating the nutrient exports to other agricultural areas with nutrient deficits.

An example, and considering the results obtained in the PFC trials, starting with a total amount of 22.96 g of N in the feed solution, about 12.84 g of N is being concentrated in the concentrate of PFC-S1, from which 10.19 g of N ends up in in the concentrate of PFC-S2, reflecting a two-stage recovery of 44.3 % of the total initial N in only 25 % of the initial volume (V_i) (Figure 5.8). The 75 % of the remaining volume represent the sum of the ice fraction of PFC-S1 and PFC-S2 (diluted fractions). Considering the diluted fraction, 4.47 g of N was retained in the 50 % of Vi and 5.38 g of N in 75 % of Vi. of PFC-S1 and PFC-S2, respectively. Assuming that the N unbalance in PFC-S1 (5.65 g of N) and PFC-S2 (2.28 g of N) is being equally distributed into the concentrate and the ice fractions in the two stages the total N distribution is as follows: 12.47 g of N in 25% V_i and 10.52 g of N in the remaining 75%.

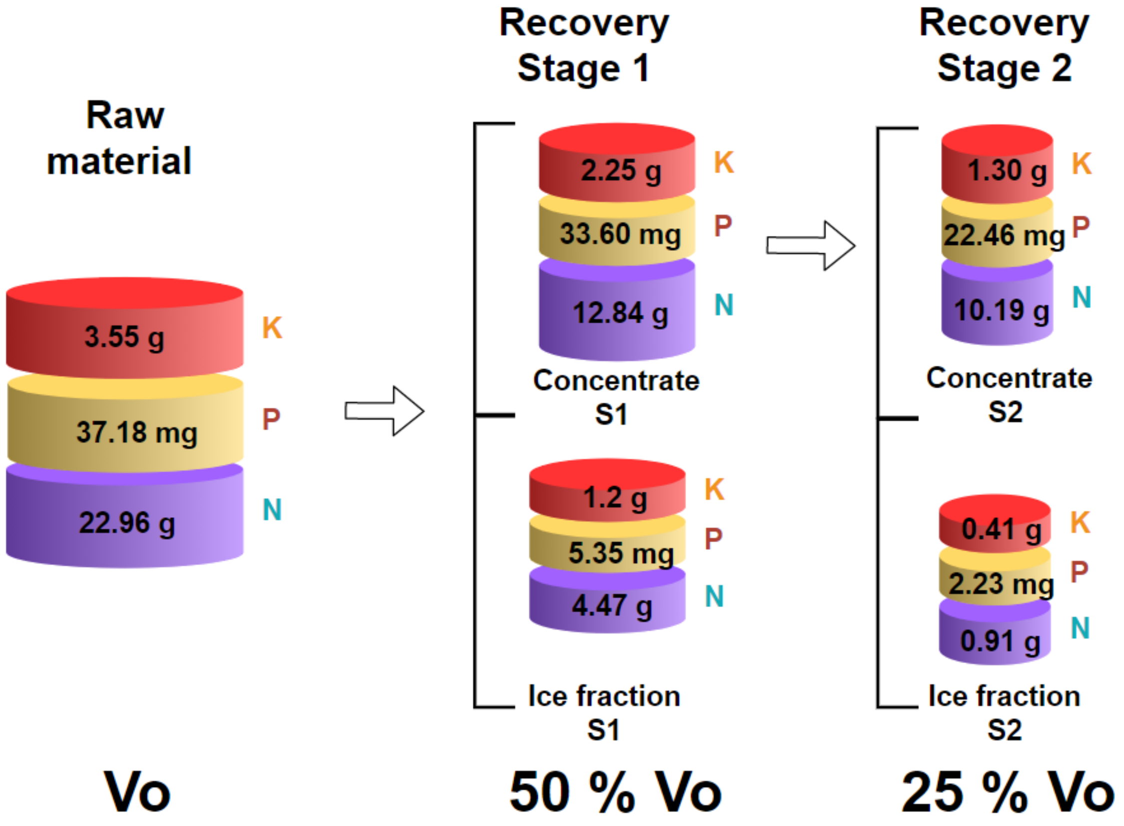


Figure 5.8. Summary of nitrogen, phosphorus and potassium distribution into the concentrate and ice fractions for PFC in two-stages.

Scaling up the obtained results for the application of FC on a volume of 1000 m^3 of concentrated digestate, around 75.03 ha of agricultural lands shall be needed for the application of 1000 m^3 of the raw concentrated digestate. However, if treating the same volume using FC, only 34.37 ha of lands is needed to the application of the diluted fractions of PFC-S1 and PFC-S2 (75 % of Vi), which represent only 45.8 % of the lands required using the raw material. Applying FC can help to solve one of the major issues in manure management which is the lack of Useful Agricultural Surface Area in highly dense livestock populated areas. The remaining 25 % of Vi, could be transported to the nutrient deficit lands saving 75 % of the original transportation cost.

Besides, the quality of the concentrate, and ice fractions (diluted fraction) were guaranteed in terms of heavy metals content (above section). Thus, the FC technology application to concentrate nutrients from any type of livestock waste could have double-effect consisting in the concentration of nutrient in a reduced volume and reduction the transportation cost from one side and reducing the need of nearby agricultural lands to manage the remaining diluted fractions reducing at the same water pollution from agricultural source and prevent further pollution from other hands.

5.3.4 Energy balance

Evaluating the economic aspects of emerging resource recovery processes is critical for their uptake and establishment in the agricultural sector. Therefore, the energy consumption of the whole process was measured in the present study as an additional parameter to assess the performance of PFC and SFC methods to recover nutrients from the raw material (concentrated digestate of pig slurry and food processing wastes). Figure (5.9) represents the profile of energy power used by the experimental PFC and SFC sets. Basically, the energy consumed in FC systems comes from the electrical energy required for the refrigerant recirculating pump, mixing engine, and refrigeration units. The power in the case of the SFC was constant during the whole process, since the operation consist of mixing and freezing automatically without any additional modification. Meanwhile, the PFC requires a cooling period of approximately 1 h followed by a concomitant freezing and mixing during the process which justifies the power jump in the profile of the power during the performed cycle (Figure 5.9). Although the power used for SFC was higher than PFC, the process length was shorter for SFC. The energy consumed was calculated by the mean of the power used and the total duration of a single cycle and marked 2230 Wh in case of PFC and 1530 Wh in case of SFC. Compared to membrane-based technologies (one of the most implemented to concentrate effluents and recover specific compounds), FC requires similar or even lower operational energy consumption. Theoretically, FC also has a huge energy-saving potential compared to thermal and evaporating processes. It has been reported that FC uses 30.4 % less energy than evaporation to treat wastewater and consumes less than 62 % energy while combined with ice thermal storage technology and precooling method (Ling et al., 2012). Generally, the energy usage depends on many parameters such as the type of technology in use, the type of feed solution, the ambient temperature, the targeted recovery rate, and the cost of electricity in each region. The required investment of each technique could also be variable based on the construction cost and production capacity. Pazmiño et al. (2017) reported energy savings up to 30% utilizing a continuous system of FC, treating sucrose solutions, and integrated with the falling film technique, compared to the energy consumption of the most efficient evaporation systems. According to Attia (2010), FC only requires 114 Wh of energy to produce 1 kg fresh water and to remove salt. Mtombeni et al. (2013) also reported the lowest energy consumption (0.39 kWh) using freezing desalination technology to remove salts from wastewater. The result of this research shows 111.5 and 122.5 Wh of energy consumption to recover nutrients from 1 kg of a concentrated digestate of pig slurry and food waste mixture using PFC and SFC systems, respectively. However, the capital and operation costs are one of the main factors that needs to be considered in separation and concentration technologies. Other separation technologies such as ammonia stripping, thermal treatment, ion exchange, and adsorption may require higher energy input and influence by pH and aeration, while FC technology is identified as an environmentally friendly separation process with easy operation and low energy consumption, and high rejection rate (Shi et al., 2018).

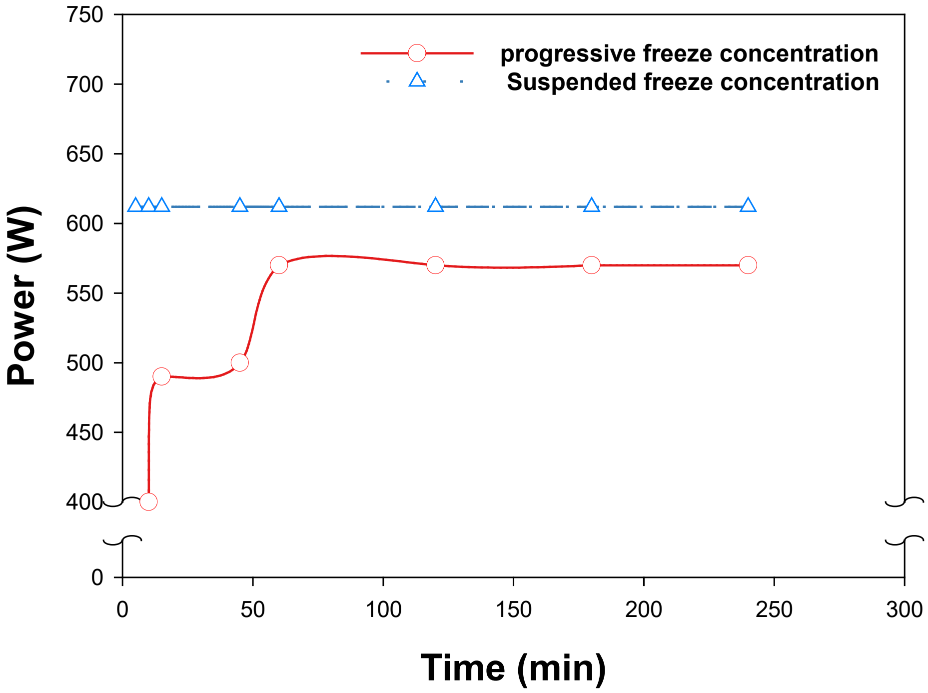
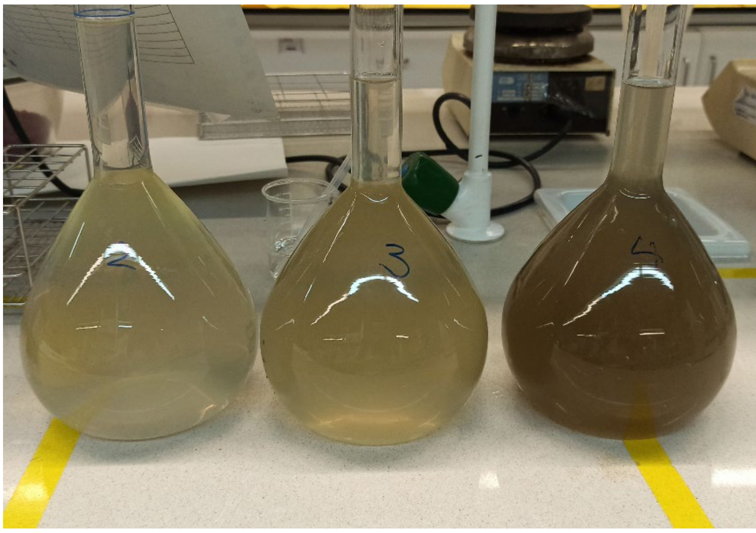


Figure 5.9. Energy consumed in PFC and SFC systems.

5.4 Conclusion

The implementation of the freeze concentration technology as an alternative to recover nutrients, such as nitrogen, phosphorous and potassium, from digestate of organic waste effluents has shown promising results. The volume reduction resulting from this low temperature concentration process improves the management of the transportation side-effect generated by the massive volumes of generated waste. The concentration of nutrients was achieved using two different freeze concentration technologies, and in both cases the concentrated fraction obtained can be delivered as a nutrient-rich fertilizer that agrees with the regulations in terms of nutrients and metals content. The diluted fraction of the FC process can be ideally introduced to irrigate soils in nutrient-rich regions or vulnerable areas due to the excess of nitrates in soil or underground water. The investigation of freeze concentration technology will allow a wide application of the technique in waste effluents derived from agro-industrial activities for agriculture purposes.



Chapter 6: Influence of freezing parameters on the efficiency of nutrient concentration from fattening pigs and sows slurries using FC technology

6.1 Introduction

Nutrient redistribution between areas with surpluses and those with shortages is limited by transportation and spreading costs, caused by the high-water content of the slurries and their relatively low nutrients concentration. Pig slurry is one of the most problematic types of livestock waste. The large volume generated, its high polluting potential, and its high-water content often limit its correct management. If appropriately administered, this could substitute significant amounts of fertilizer. The concentration of pig slurry (PS) at sub-zero temperatures is worth to be investigated for resolving the mentioned issues. Suggesting FC as a concentration method with the purpose of nutrient recovery from PS could be a potent alternative to the abovementioned methods, and which also guarantee an odorless, corrosion-free, and basic technique.

The aim of this study was to concentrate the nutrients contained in fattening pigs and sows slurries in 50 and 25 % of the initial treated volume to generate a nutrient-rich and a diluted fraction of PS through freeze concentration, an innovative technological application in the field of agro-industrial waste treatment and management. Based on chapter V findings, the study presented in this chapter pursued to assess the influence of refrigerant temperature and agitation rate as well as initial TS content on the recovery of nitrogen, phosphorus, and potassium. In this way, the efficiency of FC treating two types of pig slurries, with different solids content and different textures were calculated and compared to the efficiencies obtained in other studies.

6.2 Material and methods

6.2.1 Fattening and sows pig slurries

Two types of pig slurry were selected to be treated through FC, namely, fattening pig slurry (FPS) and sows pig slurry (SPS) provided from two different farms in Catalonia (Spain). Previous to FC process, pig slurry was sieved (0.5 mm) to remove any intruder that was accidently dripped in the slurry pit and stored at 5°C until processing. Nitrogen (N), phosphorus (P), potassium (K) and total solids (TS) contents are given in Table 6.1 for the two types of pig slurry.

Table 6.1. Nutrient and total solids content of the fattening and sows slurries.

Parameter	N (g/L)	P (mg/L)	K (g/L)	TS (g/Kg)
Fattening pig slurry	3.28 ± 0.35	787.5 ± 1.05	1.36 ± 0.07	24.39 ± 0.5
Sows slurry	3.2 ± 0.07	700 ± 0.14	1.43 ± 0.02	20.14 ± 0.27

6.2.2 Freeze concentration tests and multi-stage

The first part of this study consists of a screening experiment following the methodology described in Chapter 3. In this case, the freezing temperatures -10 and -15 °C were combined with the agitation rates of 150, 300 and 600 rpm in order to assess the distribution of the nutrient concentration into the concentrated and the diluted (melted ice) fractions influenced by PFC operating parameters. Once selected those parameters leading to the highest efficiency, the corresponding freezing T and the agitation rates were set as the optimal conditions and used to perform the multi-stage PFC experiments. A two-stage FC was carried out for each type of PS setting the volume of the concentrated fraction at the end of each cycle around 50 % of the initial volume as illustrated in Figure 6.1.

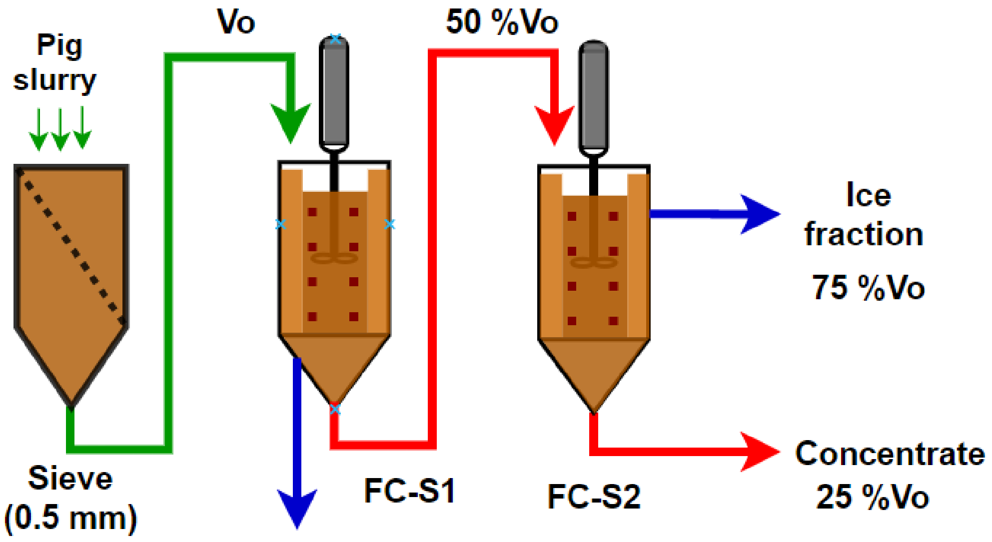


Figure 6.1. Experimental design for the multi-stage FC treating pig slurries (fattening pigs and sows).

6.3 Results and discussion

Once the efficiency of the FC technology to recover nutrients from a concentrated liquid fraction of digestate was proven (Chapter 5), the next step was to determine the influence of the freezing operational parameters on this efficiency, namely, freezing temperature and agitation rate. In this context, the following sections aim to assess the behavior of the efficiency influence of the freezing parameters, namely, the agitation rate and the freezing temperature, on the concentration growth of each nutrient and TS separately (the PE of N, P, K and TS) for the two types of PS. Same experimental procedure as the prior chapters, after completing each FC cycle, a vacuum separation was performed to extract the remaining solid in the ice fraction. Figure 6.2 illustrate the ice fraction before vacuum application (A) and after vacuum application (B).

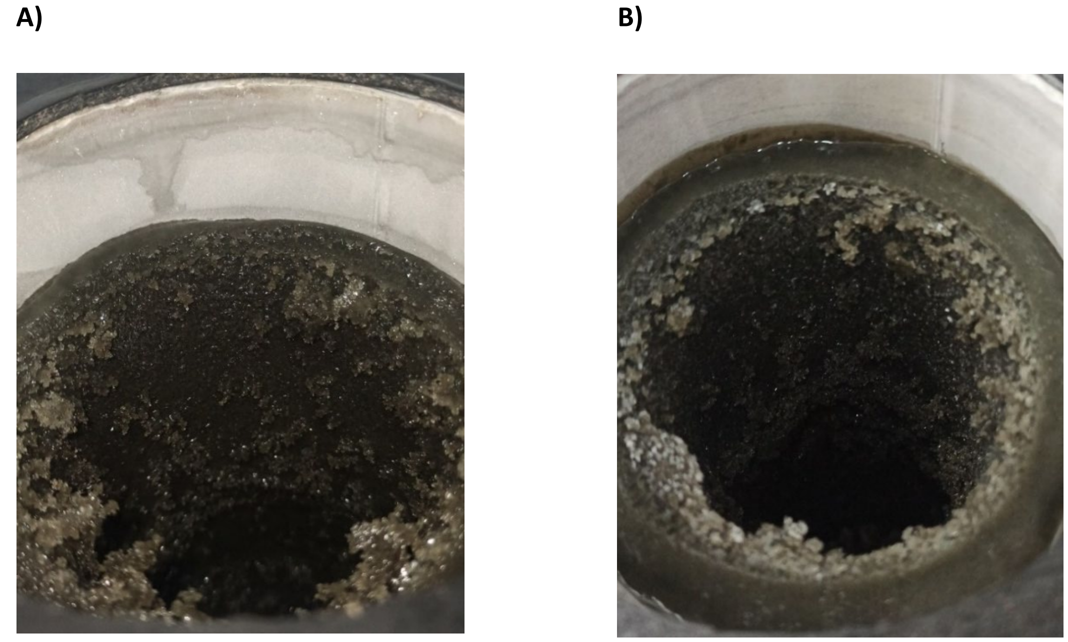


Figure 6.2. Formed ice during the PFC of PS before (A) and after vacuum application (B).

6.3.1 Freeze concentration efficiency

The process efficiency (PE) (Eq. 3.3) was calculated for N, P, K and TS in each PFC experiment. Figure 6.3 illustrates the evolution of the PE in terms of TS and nutrient content (N, P, K) for both types of PS tested, as a function of the agitation rate and the freezing temperature (-10 and -15 °C). Table 6.2 shows the overall PE for each operating condition set. Pig slurries tested had a different TS content (TS content of FPS is 21.1 % higher than SPS after sieving), allowing also to assess the performance of FC technology under the influence of TS mainly in terms of process efficiency.

Table 6.2. Process efficiency of N, P, K and TS as a function of the agitation rate and freezing temperature for the SPS and FPS in the screening experiments.

Operating conditions		Process efficiency of SPS				Process efficiency of FPS			
T	**Agitation (rpm)**	**N (%)**	**P (%)**	**K (%)**	**TS (%)**	**N (%)**	**P (%)**	**K (%)**	**TS (%)**
-15 °C	**150**	30 ± 1	26 ± 1	38 ± 0	23 ± 2	33 ± 0	26 ± 2	28 ± 1	34 ± 2
	300	57 ± 1	59 ± 2	54 ± 1	58 ± 2	56 ± 1	62 ± 1	57 ± 2	58 ± 2
	600	68 ± 2	78 ± 1	74 ± 1	77 ± 2	69 ± 0	78 ± 3	65 ± 2	74 ± 3
-10 °C	**150**	33 ± 0	28 ± 1	46 ± 1	33 ± 2	33 ± 1	41 ± 2	47 ± 1	45 ± 3
	300	66 ± 1	64 ± 3	55 ± 2	66 ± 2	65 ± 1	72 ± 2	48 ± 0	66 ± 1
	600	71 ± 3	79 ± 1	72 ± 2	73 ± 3	70 ±0	92 ± 1	69 ± 1	75 ± 1

Generally, the PE of all nutrient and TS showed the same trend following the agitation rate for the FPS and SPS with some exceptions that will be elaborated in the following sections. In the following sections, the influence of each operational freezing parameter will be elaborated in terms of the efficiency of PFC applied to FPS and SPS. Due to the pigmented color of pig slurry, no visual difference was spotted at the end of the freezing process. Figure 6.3 illustrate a diluted fraction (1/100) of raw PS, concentrated and ice fraction after completing a PFC cycle, where clearly see the color degradation of PS fractions.

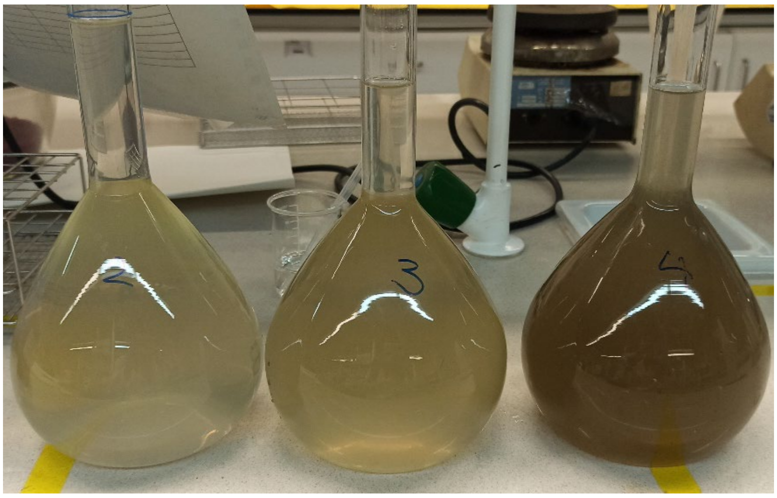


Figure 6.3. Dilution 1/100 of raw pig slurry (n° 3), concentrate (n° 4) and ice fraction (n° 2).

6.3.1.1 Influence of the freezing Temperature

The freezing temperature is one of the main parameters controlling the FC process, as the crystallization of a solution occurs when the freezing temperature during the process is below the freezing point of the treated solution. A freezing temperature of -5 °C was tested besides -10 and -15 °C, although the freezing process could not be completed under the high freezing temperature tested, thus it was ruled out.

The PE of N did not show a difference following the influence of the freezing temperatures -10 and -15 °C ($p<0.001$) obtaining same values of PE for the two types of PS. Regarding P, the freezing temperature -15 °C did not show any influence on the PE, as the FPS and SPS showed the same pattern ($p<0.001$) regardless also the agitation rate. However, while operating at -10 °C, the PE was higher for SPS compared to FPS; this trend could be due to the influence of the TS content in each type of PS, which is more noticeable in higher freezing temperatures, in this case -10 °C. The lowest the freezing temperature, the highest the freezing rate of a solution, which means that at high freezing rate. Regarding K, the PE obtained at -15 and -10 °C of FPS were quantitatively higher than SPS, however no significant difference was found ($p<0.001$).

6.3.1.2 Influence of agitation rate

From Figure 6.4 it is apparent that can be observed that e PE for (N, P, K) and TS is greater in the case of higher agitation rates increase with the agitation rate. Regarding N, the increase of the PE was similar for the two types of PS tested at constant freezing temperature ($p<0.001$). Among the followed nutrient the nutrients monitored in this study, only some of N forms only are soluble in water and bonds more than P and K and the size of its molecule is small compared to P and K. Hence, the distribution of N molecules into the ice and concentrate fractions is less affected by TS content of the solution; thus, only the increase of PE as function of agitation was observed without a, no significant difference measured between the two types of PS or within the same type of PS operating at different temperatures. Regarding P, the increase of the PE with increase of agitation rate was identical operating at -15 °C for the FPS and SPS. However, operating at -10 °C, different values of PE for the two types of PS were observed, as it was higher for SPS than FPS ($p=0.686$). Regarding K, the PE of FPS and SPS increased with the increase of the agitation rate, however, operating at -10 °C, the increase between 150 and 300 rpm was negligible where similar results were obtained for the two types of PS in the two agitation rates (identical PE ($p<0.001$)), meanwhile, a significant increase ($p=0.293$) was observed at 600 rpm for both SPS and FPS. The molecular size (Van der Waals radius) of K is about 280 pm, which is superior to the one of P (195 pm) and N (155 pm). The big size of K rises its chances to remain in the concentrated fraction instead of being entrapped within the ice matrix, while N and P molecules have more chances to be retained in the ice fraction. Concerning the TS distribution into the concentrate and ice fraction, it was most influenced by low agitation rates, as operation a. At 150 rpm and regardless the freezing temperature, the PE in terms of TS concentration was higher for SPS than for FPS ($p=0.477$) for the reasons abovementioned.

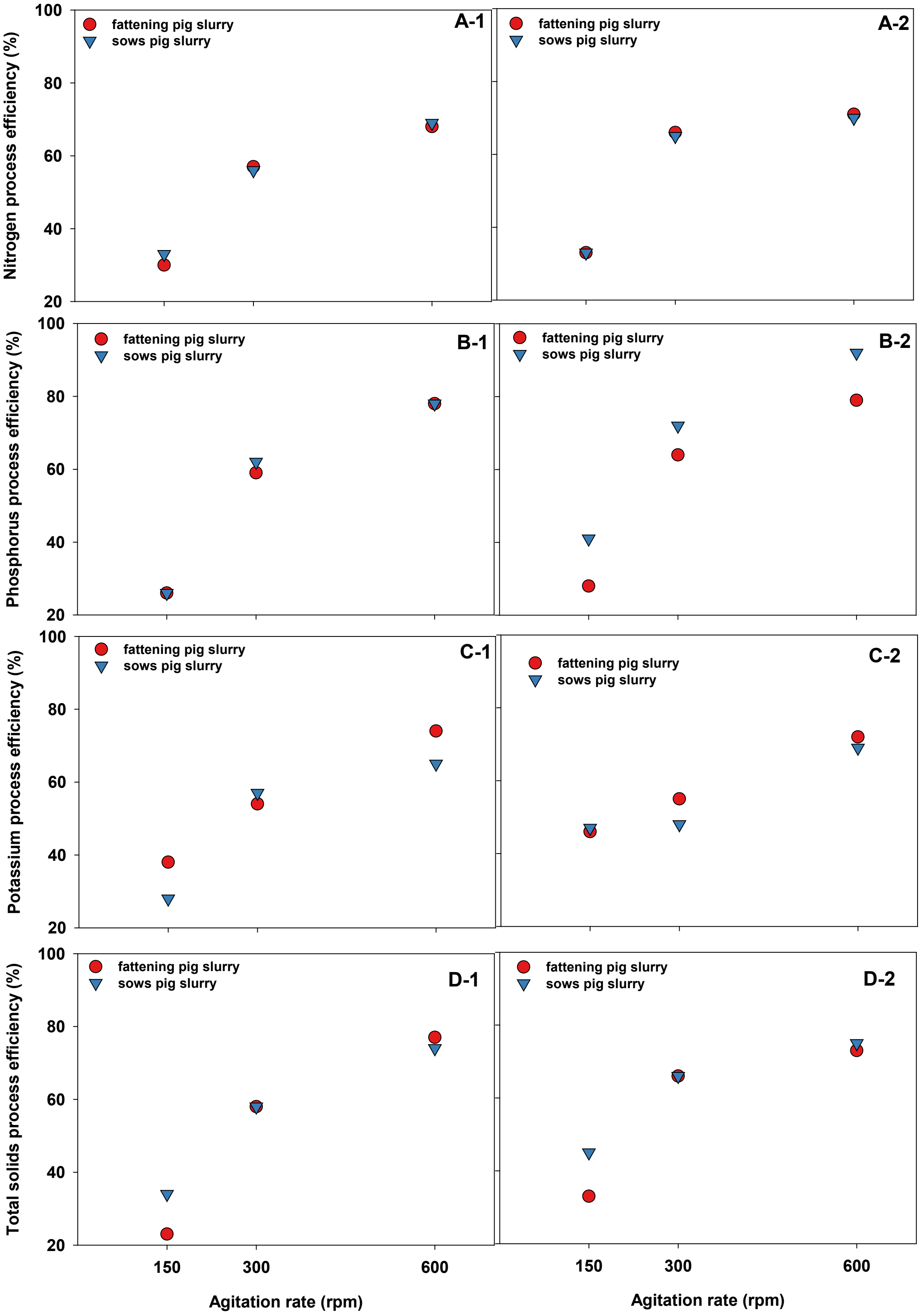


Figure 6.4. Evolution of N, P, K and TS process efficiencies as a function of the agitation rate of the FPS and SPS operating under the freezing temperatures of -15 °C (A-1, B-1, C-1, D-1) and -10 °C (A-2, B-2, C-2, D-2).

6.3.2 Nutrient and total solids recovery

The recovery of N, P, K and TS for FPS and SPS defines the amount of nutrient recovered in the concentrated fraction from the raw PS (Eq. 3.1) and is given in Table 6.3 for the screening experiments. The mass balance for the measured concentrations of N, P, K and TS is given in Table 6.3. Figure 6.5 illustrates N, P, K and TS recoveries (A-1-D-1, respectively) in FPS and SPS (A-2 to D-2, respectively)) for the freezing temperatures -10 and -15 °C.

The recovery of N, P, K and TS for the two types of PS correlates well with the results obtained in the PE section, in terms of PE, where an increase was observed with higher agitation rates. The recovery of N, P, K and TS was higher in the concentrate of FPS than of SPS at -15°C.

The recovery of nutrients and TS at -15 °C exhibited the same pattern within the same type of PS, as a noticeable increase of recovery with the agitation rate was observed for the FPS meanwhile minimal increase was observed for the SPS. The superior results obtained in the recoveries of nutrients in FPS were the reason behind the prementioned gap, and that is due to the initial TS content in the two types of PS. The PFC of FPS delivers significantly better results than of SPS in terms of N, P, K and TS recoveries regardless the agitation rate (Figure 6.5). When comparing the results obtained for the PE at -10 °C and the recoveries at -10°C, the corresponding behaviors can be seen in Figures 6.5 and Figure 6.6, respectively. Regarding N recovery, no significant difference was detected between FPS and SPS and increased slightly with agitation rate. Regarding the P recovery, quantitively superior results were seen for SPS than FPS. Likewise, regarding K recovery, higher values were obtained for FPS compared to SPS. For the recovery of TS, no significant differences between the FPS and SPS regardless the agitation rate.

Table 6.3. Nutrient and total solids recovery for the fattening pigs and sow slurries.

Freezing parameters		**Nutrient recovery in SPS**				**Nutrient recovery in FPS**			
Temperature (°C)	**Agitation rate (rpm)**	**N (%)**	**P (%)**	**K (%)**	**TS (%)**	**N (%)**	**P (%)**	**K (%)**	**TS (%)**
-15 °C	**150**	51 ± 0	50 ± 1	55 ± 0	46 ± 0	52 ± 0	51 ± 1	58 ± 1	50 ± 0
	300	52 ± 1	56 ± 2	64 ± 2	57 ± 0	58 ± 0	59 ± 1	65 ± 1	63 ± 2
	600	53 ± 1	64 ± 1	60 ± 2	61 ± 1	77 ± 0	72 ± 0	67 ± 1	78 ± 1
-10 °C	**150**	59 ± 0	58 ± 0	62 ± 0	58 ± 2	57 ± 0	42 ± 0	65 ± 1	55 ± 0
	300	71 ± 0	79 ± 2	53 ± 0	72 ± 0	65 ± 1	69 ± 0	70 ± 0	62 ± 0
	600	65 ± 1	84 ± 2	59 ± 1	74 ± 0	67 ± 1	68 ± 0	69 ± 0	78 ± 1

It is worth discussing this interesting behavior revealed by the abovementioned results of recoveries. As demonstrated previously, the PE of N, P, K and TS was higher for SPS than for FPS contrarily to what was found in section (6.3.1) related to recovery in the concentrate. This implies that the PE of PFC process for the recovery of nutrient is associated with the level of purity of the formed ice, meanwhile the recovery of nutrient only considers the amount of nutrient recovered in the concentrate.

The obtained results lead to the conclusion that the recovery of nutrient at -10 °C was relatively higher that at -15 °C for both FPS and SPS and the highest the agitation rate, the highest recovery (values given in Table 6.3). A low freezing temperature associated with a low agitation rate, induce a quick-freezing rate resulting in the capture of the solids inside the ice structure due to the lack inefficient of continuous homogenization during the FC process. The high agitation rate helps the continuous homogenization of the PS inside the FC reactor. Once the ice started to form, the mixing rate of the solids helps to avoid the capture of an important fraction of the solids inside the ice structure.

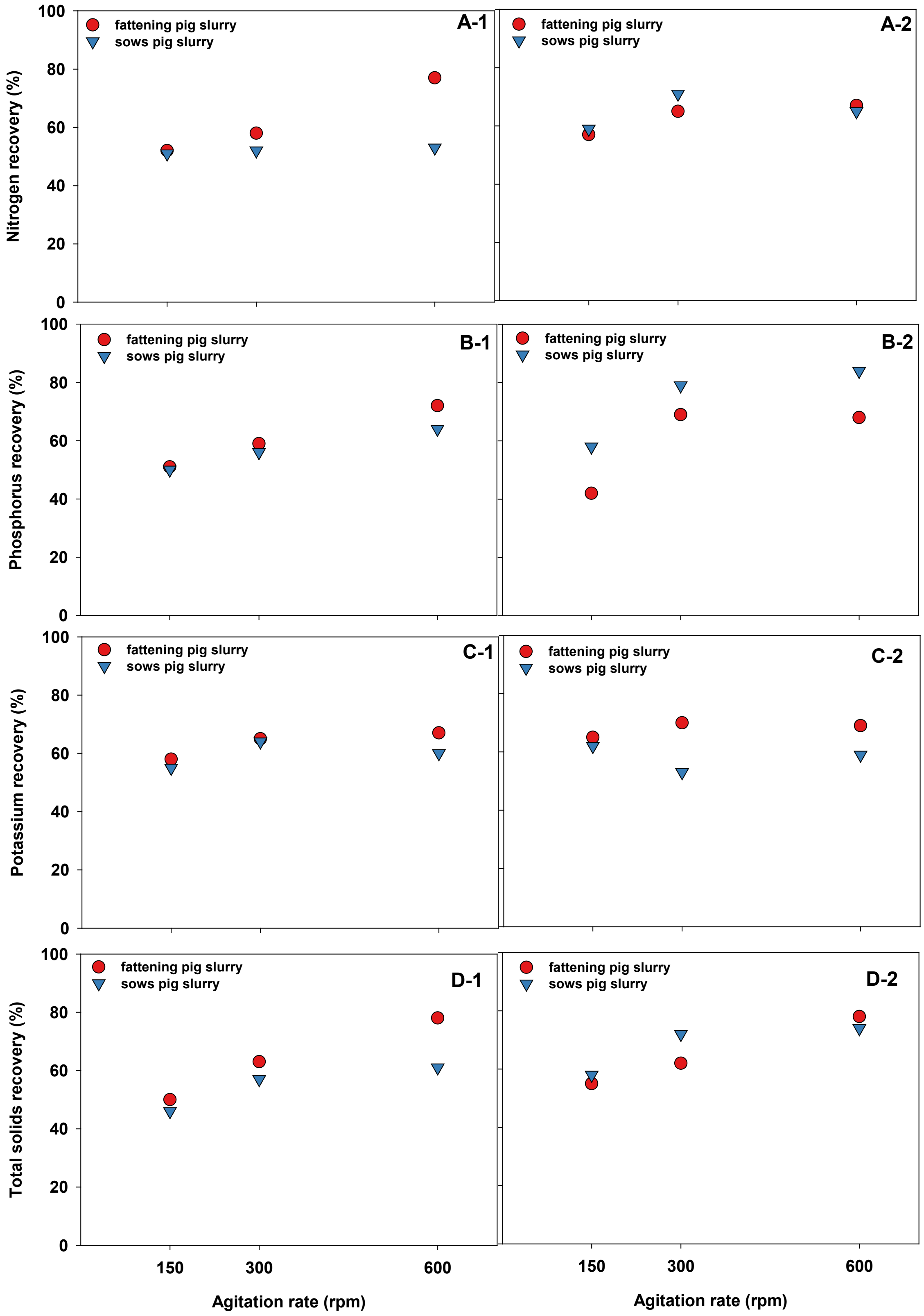


Figure 6.5. The evolution of N, P, K and TS recoveries as a function of the agitation rate of the FPS and SPS operating under the freezing temperatures of -15 °C (A1, B1, C1, D1) and -10 °C (A2, B2, C2, D2).

In line with the previous paragraph, the slightly better results (in terms of nutrient recovery) obtained for the FPS compared to SPS is mainly due to the initial TS content of the two types of PS. Since the experiments were tested under the same operating conditions, the high TS content is presenting a resistance to the bulk mixture stirring leading to a remanence of an important fraction of TS in the concentrated fraction and, consequently a higher recovery of nutrient in FPS than in SPS. The recovery of nutrient in the concentrate obtained in the present work can be compared to the conventional methods for concentrating nutrients from PS. Either aiming to concentrate PS to reduce the transportation cost, or remove nutrients to recover and reuse water, the results obtained in the present study are in the range of the documented results. (Astals et al., 2021) investigated struvite precipitation using a low-cost magnesium oxide to recover N from PS and achieved a 26 to 73 % removal of TAN using different stabilizing agents which agrees with the obtained recoveries in the present study, 71 % and 77 % as highest N recoveries in SPS and FPS, respectively. (Pantelopoulos and Aronsson, 2021) reported a recovery of 73.8 % of the PS P content, 52.6 % of TS and 14.4 % of N to the solid fraction from PS using a two-stage separation and acidification system. The finding in terms of N, P, and TS are the same range of the obtained recoveries in the present study displayed in Table 6.3.

6.3.3 Mass balance

The mass balance of N, P, K and TS is given is Table 6.4, for all the performed experiments. An imbalance up to ± 25 % due to the nature of PS and its high content in TS.

Table 6.4. Mass balance of N, P, K and TS in each stage of the performed screening experiment of FC applied to SPS and FPS.

Freezing parameters		**Sows slurry mass balance**				**Fattening slurry mass balance**			
T	**Agitation**	**N (%)**	**P (%)**	**K (%)**	**TS (%)**	**N (%)**	**P (%)**	**K (%)**	**TS (%)**
-15 °C	**150**	**12**	**10**	**1**	**21**	**-6**	**2**	**-2**	**2**
	300	**20**	**18**	**2**	**13**	**11**	**11**	**-2**	**4**
	600	**22**	**14**	**8**	**14**	**-2**	**13**	**16**	**4**
-10 °C	**150**	**-5**	**3**	**1**	**6**	**-1**	**23**	**-4**	**2**
	300	**3**	**-1**	**18**	**3**	**1**	**6**	**-1**	**17**
	600	**-2**	**-5**	**18**	**3**	**13**	**12**	**12**	**1**

6.3.4 Two-stage FC: Nutrient recovery in the concentrate and ice fractions of pig slurry

Multi-stage FC was performed under the conditions -10 °C and 600 rpm, Table 6.5 represents the recoveries of nutrients in the first and second stages of FC for the FPS and SPS. As previously observed in Chapter 5, freeze concentrate the concentrated fraction of the previous stage leads to have a more viscose and dense solution as a raw material (due to the high content of solids and the lower content of available free water). Thus, the second stage of FC in a multi-stage process highly depends on the TS content recovered in S1 besides the lower content in nutrient (in g) compared to the raw material as a fraction remained in the ice fraction of S1. The behavior of N, P and TS recoveries in FPS and SPS showed similar pattern of decrease from S1 to S2, however, the recovery of K was different in a sense that an increase was observed in FPS (from 65 % to 87 %) and a maintenance in SPS (from 54 % to 56 %).

Table 6.5. Recoveries of N, P, K and TS in the multi-stage FC of FPS and SPS.

Feed slurry	Nutrient	First stage recovery (%)	Second stage recovery (%)	Two-stages (%)
FPS	N	68 ± 0	57 ± 1	38 ± 1
	P	56 ± 2	52 ± 1	29 ± 2
	K	65 ± 0	87 ± 2	56 ± 2
SPS	N	69 ± 1	68 ± 0	47 ± 1
	P	78 ± 1	63 ± 2	50 ±01
	K	54 ± 0	56 ± 1	30 ± 0

Figures 6.6 and Figure 6.7 illustrate the content on nutrients in the raw PS, concentrate and ice fractions of the two performed stages of FC applied to FPS and SPS, respectively. Once the first stage of FC process is completed, the volume of the generated concentrate and ice is 50 % of the initial treated volume, afterwards in the second stage, the volume of the concentrate represent 25 % of the initial volume (of the raw material) and the ice fraction (diluted fraction) represent 75 % of the initial volume.

Regarding FPS, after completing two stages of PFC, 44.4 % of N, 33.8 % of P and 66.2 % of K remained in the concentrate of FPS (25 % Vo), meanwhile the remaining percentage was being accumulated in the ice fraction after each stage of FC. Regarding SPS, after completing two stages of PFC, 50,1 % of N, 54,5 % of P and 31.6 % of K remained the concentrate of SPS, meanwhile the remaining percentage was accumulating in the ice fraction after each stage of PFC. The recovery of N and P was higher in the concentrate of SPS than in FPS, contrarily to the recovery of K that was two-fold in FPS than in SPS.

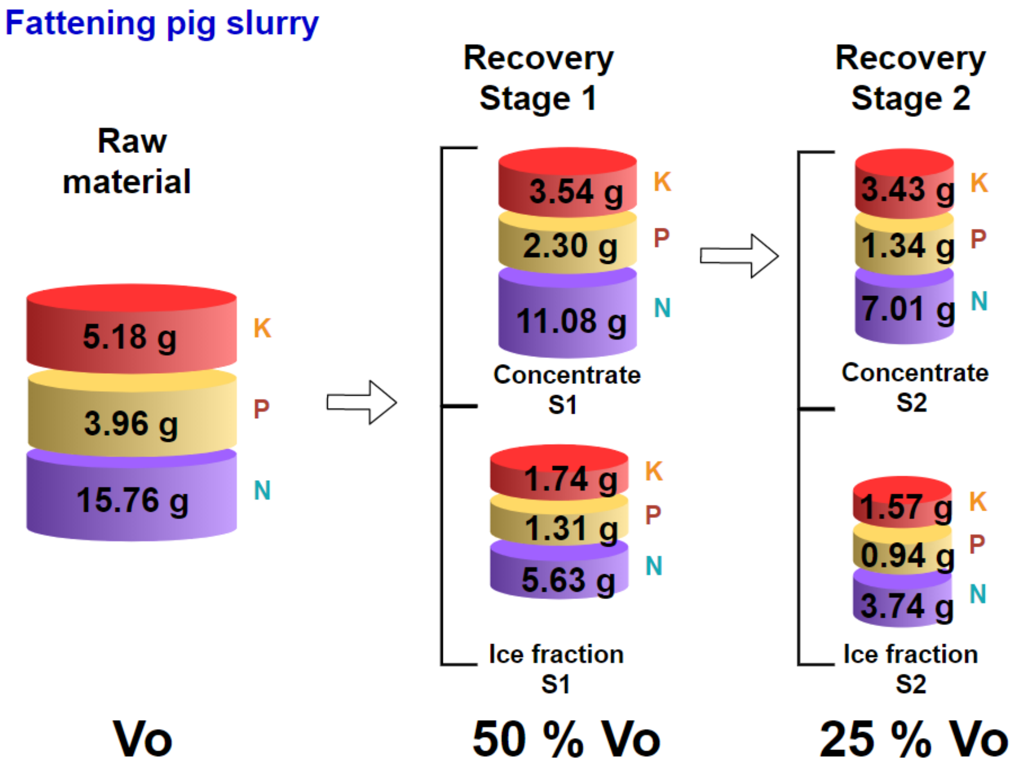


Figure 6.6. Nutrient mass distribution in the concentrate and ice fraction in two-stages of PFC applied to FPS.

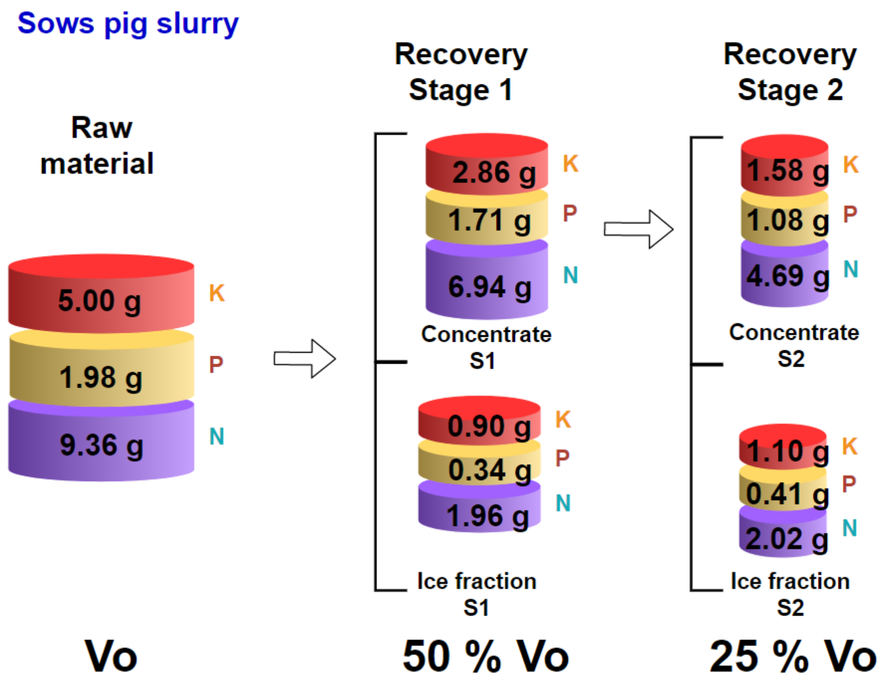


Figure 6.7. Nutrient mass distribution in the concentrate and ice fraction in two-stages of PFC applied to SPS.

As a starting point, the K content in FPS is higher than in SPS due to the diet and the metabolism of the two types of pigs. During the FC process, the crystallization of K is typical, however, the formed crystals maybe be coherent to the ice structure or remained with the solid particles in the concentrate. The K crystals formation and distribution is mainly related to the Eutectic point of PS which is mainly influenced by its composition. As the FPS has a more complex matrix than the SPS, containing more minerals and TS, the Eutectic point would be lower and harder to achieve for the FPS. For this reason, the retention of K in FPS is due to the low crystallization of the K in the ice matrix, remaining in the liquid concentrated fraction.

6.3.5 Metal content

Copper (Cu) and Zinc (Zn) are common heavy metals in raw PS that are expectedly to exceed the limits recommended by the regulations (Xiong et al., 2010). The high concentration of Zn and Cu in PS is generally related to animal feed, as they are usually added for their antimicrobial, antidiarrheic and growth-stimulating effects (Lu et al., 2014). As the daily intake of Zn and Cu cannot be completely absorbed by animals, thus most of the Zn and Cu are excreted by metabolism and remain in feces (Leclerc and Laurent 2017). Therefore, the investigation of their evolution after FC has an important reference value if the purpose of its application is delivering potential organic fertilizers.

Copper (Cu) and Zinc (Zn), being the most abundant metals in PS, were measured in each obtained fraction of the FC process and their concentration growth is given in Table 6.6. Initially, the concentration of Cu was around 201.25 and 234.71 mg/Kg TS in FPS and SPS, respectively. Likewise, the concentration of Zn was around 1336.94 and 1416.46 mg/Kg TS in FPS and SPS, respectively. As shown in Table 6.6, a noticeable increase of the concentration increase with the agitation rate was observed in the concentrated fractions of FPS and SPS. Same tendency observed for N, P and K, which is mainly related to the TS and the solids particles present in the PS. Cu and Zn analysis were carried out to guaranty the proper use of both concentrate and diluted fractions of freeze concentration as a customized fertilizer one for cropland regions in need of nutrients and the later can be used in contaminated regions without harming the soil. Following the regulations (EU) 2019/1009, the metal contents are in (g of metal/Kg of TS), this allows a better distribution of the metals content in the concentrate and ice fractions. The increase of TS content in the concentrate and its decrease in the ice fraction from one hand, associated with the increase of Cu and Zn content in the concentrate and its decrease in the ice fraction, induce a moderate content in (g of metal/Kg of TS) for both fractions. Table 6.7 shows the Cu and Zn content in the concentrate and ice fractions of the FC experiments for FPS and SPS. The limitation of Cu and Zn set by the regulation for organic fertilizers is also given in Table 6.7.

Table 6.6. Cu and Zn growth during progressive freeze concentration screening experiments of FPS and SPS.

Freezing parameters		**Heavy metal increase in SPS**		**Heavy metal increase in FPS**	
T (°C)	**Agitation rate (rpm)**	**Cu (%)**	**Zn (%)**	**Cu (%)**	**Zn (%)**
-15 °C	**150**	37	36	33	20
	300	42	54	57	50
	600	69	71	68	73
-10 °C	**150**	41	39	33	20
	300	65	61	58	51
	600	75	76	64	70

An et al. (2020) reported five forms of Cu and Zn in PS investigated in thirty freeze-thaw cycles, namely, the exchangeable form (EXCH-X), Carbonate bound form (CARB-X), Fe/Mn oxide form (Fe/Mn-X), organic and sulfide bound form (ORG-X) and residual form (RES-X). The finding stated that after freezing-thawing cycles a sharp increase in EXCH-Cu/Zn was observed (from 2 to 53 % for EXCH-Cu and from 19 to 25 % for EXCH-Zn) versus a nonsignificant difference on ORG-Cu/Zn and RES-Cu/Zn and a decrease on CARB-Cu/Zn and Fe/Mn-Cu/Zn. Regarding FPS and SPS studied in this thesis, the content of Cu did not exceed the value limited by the regulation (EU) 2019/1009 in none of the raw PS, concentrate and ice fractions. However, in regard to Zn content, the concentration in the raw FPS and SPS exceeded the limit value by the regulation abovementioned. Before freeze-thaw treatment, Zn in the pig manure might be mainly combined with iron/manganese oxides because the surfaces of Fe/Mn oxides have strong adsorption of Zn (Cestonaro do Amaral et al. 2014).

Throughout the FC process, and due to the change of the structure of PS in an ice form, the PS is subjected to a breakage of particles while the formation and the melting ice fraction due to the change of the structure of PS in an ice form. Thus, an accumulation of small particles of Cu and Zn into the ice fraction is expected to be observed.

As a summary, in order to apply PS as a fertilizer the Zn content should be reduced, either by reducing its content in the pigs diet, if possible, otherwise as pre-treatment or a post-treatment is required for concentrate and ice fractions after FC, we can cite bioleaching or biochar application (Jiang et al., 2018; Wei et al., 2018). Nevertheless, the objectives for the up-coming rules stated in legislations are following the approach of reducing Cu and Zn from swine diet, which means, in the future, the application of pig slurry hopefully will not be burdened by its content of heavy metals.

Table 6.7. Cu and Zn content in the concentrate and ice fractions of the FPS and SPS under the influence of the agitation rate and the freezing temperature.

Slurry type			Cu content (mg/Kg TS)			Limitation for Cu (mg/Kg TS)	Zn content (mg/Kg TS)			limitation for Zn (mg/Kg TS)
	Freezing T (°C)	Agitation (rpm)	Raw PS	Concentrate	Diluted		Raw PS	Concentrate	Diluted	
SPS	-10	150	234.71 ± 2.82	222.07	279.23	300	1416.46 ± 17.07	1357.85	1246.53	800
		300		276.02	266.13			1522.54	1746.81	
		600		264.49	295.12			1546.68	1377.52	
	-15	150		337.71	197.92			2091.84	1757.89	
		300		193.35	287.86			1122.17	1217.86	
		600		219.93	240.42			1214.04	1513.43	
FPS	-10	150	201.25 ±3.44	208.19	208.33		1336.94 ± 29.31	1249.13	1496.53	
		300		247.08	307.49			1444.63	2087.01	
		600		206.69	272.90			1336.49	1500.97	
	-15	150		216.23	199.90			1273.08	1339.04	
		300		214.20	221.02			1262.44	1506.54	
		600		181.23	249.72			1192.93	1392.36	

6.4 Techno-economic assessment of the FC technology applied in a fattening pig farm

After demonstrating the technical feasibility of the FC application to concentrate pig slurry, a simple techno-economic assessment model was performed considering a specific case study. To this aim, the implementation of a FC system on-farm, with a capacity of 100 L and 1,200 heads of pigs fattened per year, was considered. A volume reduction of 50 % was also set to transport uniquely the concentrated fraction of fattening pig slurry. The techno-economic assessment also considered 2 scenarios, a first one with a unique FC stage (FC-S1) and a second one with two FC stages (FC-S2). The model also compared the results obtained with fattening pig slurry and digestate since the concentration of both effluents have been tested in previous chapters besides being organic and rich in nutrients.

Annual savings, internal rate of return and time to recover costs are given as a function of the transported distance of the concentrate of FC. It has been considered that the treatment of livestock slurries in Catalonia with anaerobic digestion costs up to 15 €/m^3 (Prenafeta-Boldú, F.X. i Parera, 2020). The installation cost of the FC reactor with a treatment capacity of 0.2 m^3/day is 50,000 € including the chiller, the housing of the system, the agitator, the liquid refrigerant, and the control panel. The energy consumption by the FC system varies depending on the operational cooling temperature and the length of the freezing cycle. The freezing system uses a three-phase current (8 A) at 400 V tension resulting in the maximum power around 5.5 kW. Operating the FC system at -10 °C requires a power of 1.5 kW for a single FC cycle, which is the freezing temperature used for the two-stages FC. Based on the tests experiments performed in the abovementioned FC system, the length of the experiments to concentrate 50 % of the initial PS is about 3h. The price of electricity in Spain for business adapted in the model is 0.103 €/kwh (https://www.globalpetrolprices.com/Spain/electricity_prices/).

The techno-economic assessment model allowed determining the extent in which the application of FC technology is worth to solve the expensive side-effect of the transportation of livestock slurries to croplands located far away from the farm. By way of illustration, a volume of 160 m3 of pig slurry is being generated in a fattening cycle of 400 heads (Uald Lamkaddam et al., 2021).Table 6.8 summarizes the g of N, P and K contained in the raw PS, in the concentrate and in the ice fraction of FPS and SPS, as well as the number of hectares required for the application of raw PS, the concentrate, and the ice fraction before and after use of FC as well as the amount of nutrient remained in each fraction.

Table 6.8. Nutrient content in the raw, concentrate and diluted fraction of FPS and SPS generated in a fattening or sow cycle of 3 months.

Feed solution	Nutrient content in FPS			Required hectares	Nutrient content in SPS			Available hectares
	N (kg)	P (kg)	K (kg)		N (kg)	P (kg)	K (kg)	
Raw PS	541.2	128.7	224.4	3.18	528	115.5	236	3.10
Concentrated PS	238.12	43.5	148.55	1.40	269.28	62.94	74.57	1.58
Diluted PS	303.07	85.19	75.84	1.78	258.72	52.55	161.42	1.52

6.4.1 Annual savings using FC for concentrating pig slurry

The annual savings using FC technology, is defined as the subtraction of the yearly operation cost from the external management cost that is considered in the model as baseline cost. Figure 6.8 illustrates the annual savings as a function of the transported distance of the concentrate. The annual savings obtained by modelling the operation and the installation costs was getting higher as the transport distance increased, making the implementation of FC more adequate for disposal destinations at long distances. The increase was minimal for small distances to become sharp at a transportation distance over 20 km (Figure 6.8). The energy required to perform a two-stage FC (FC-S2) in kwh was twice the energy required performing a single cycle (FC-S1). This led to a higher annual saving using a single stage FC instead of a two-stage FC, counting 103360 and 9376 €/year while transporting the concentrate of FC-S1 and FC-S2, respectively. Seemingly, for transporting the concentrate to distances above 100 km, the application of either one stage or two-stages of FC will lead to the same annual saving values, and this is observed by the narrow gap between the two corresponding plots of the two scenarios at high transported distances compared to low ones.

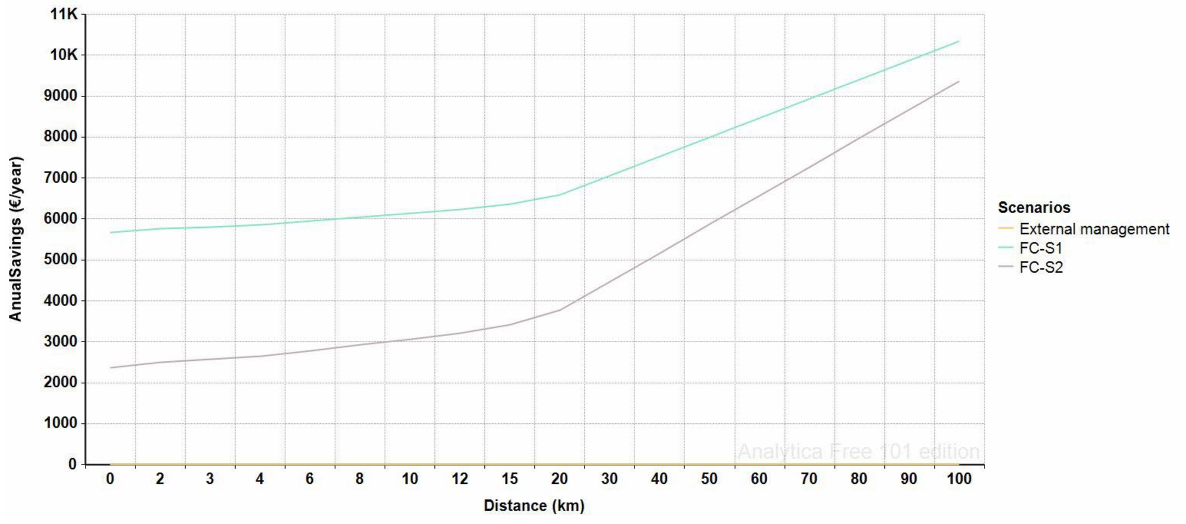


Figure 6.8. Evolution of annual savings in the case of performing a single stage of FC, two-stage or to be sent to an external management plant applied to pig slurry.

6.4.2 Pay-back of the installation

The estimation of the necessary period to recover the investment on the installation is a main index for the efficiency of the technology or the proposed solution. Figure 6.9 represent the calculated time in years to recover the costs of installation of the FC technology under the two proposed scenarios as a function of the transported distances. The farther the destination the quickest the recovery time is being achieved for the two FC scenarios. At the greatest distance in the model (100 km), 5 years recovery was necessary to recover the costs by application a single stage of FC, meanwhile 6 years were needed to recover the cost of applying two-stage FC.

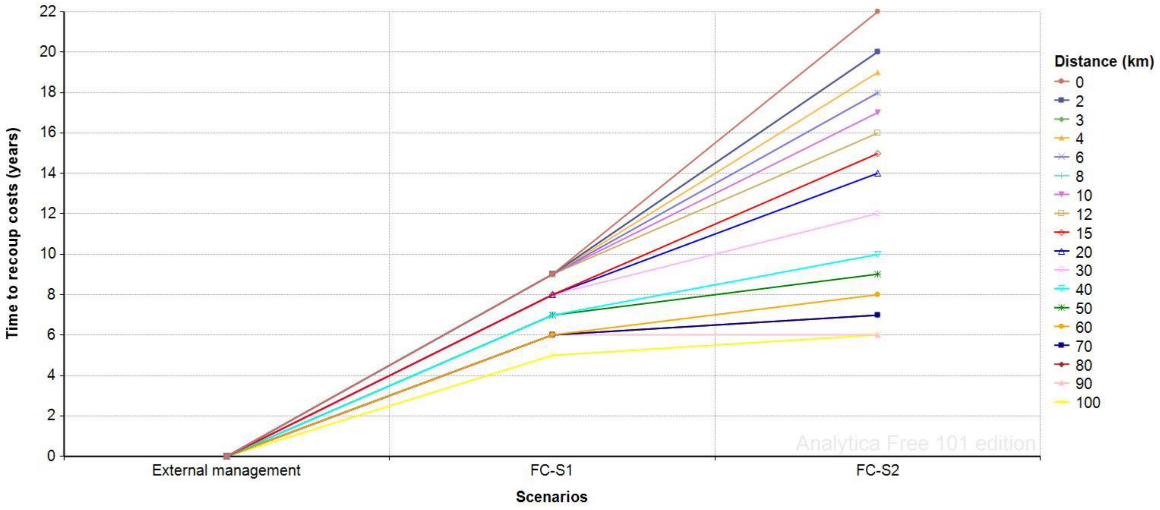


Figure 6.9. Time of installation cost recovery of each scenario: external management, single and two stages of FC applied to pig slurry as function of transported distance.

6.4.3 Internal rate of return

The internal rate of return (IRR) of the investment was calculated also to assess the benefits of integrating FC as an alternative to the existing pig slurry management technologies. Figure 6.10 represents the internal rate of return of the external management and the two scenarios of FC. The application of a single stage of FC reaches IRR values over 20.48 % if the transported distance is 100 km and above; meanwhile an IRR of 18.48 % is being reached applying two-stages of FC. The IRR trend for both scenarios (applying one stage or two stages of FC) as a function of the transported distances is similar to the one obtained for the annual savings.

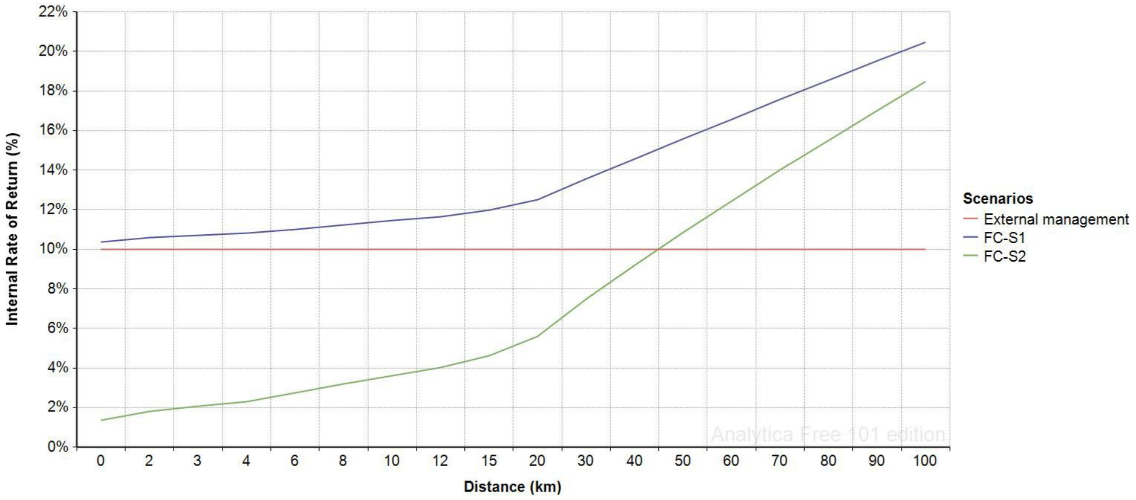
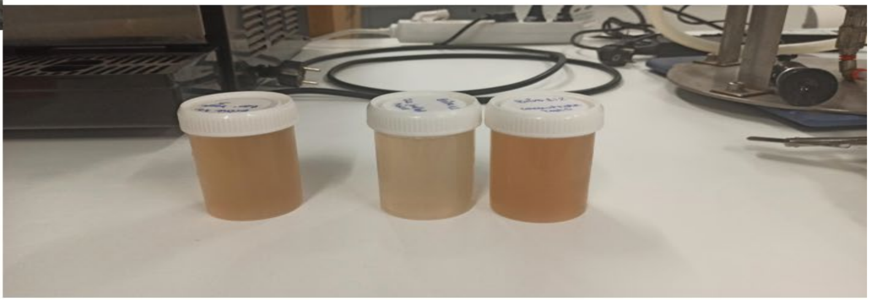


Figure 6.10. Time of installation cost recovery of each scenario: external management, single and two stages of FC applied to pig slurry as function of transported distance.

6.5 Conclusion

Applying freeze concentration to reduce the volume of pig slurries showed promising and interesting results in terms of nutrient recovery and process efficiency. The freezing conditions plays a crucial role on the efficiency of the process; the highest efficiencies were obtained at higher agitation rates and lower temperatures. The initial total solids content in pig slurry also affected the efficiency of the nutrient recovery into the concentrated fraction. The use of FC to concentrate PS is not only beneficial for the recovery of nutrient in a smaller volume, but also showed potential benefits on resolving the transportation of livestock slurries to farther destinations. The results showed that as far as the transporting distance after the application of FC, as the savings increase, which makes it a feasible and potent alternative to be installed in-situ for concentrating livestock waste effluents.



Chapter 7: Assessment of freeze concentration technology as a solution for salt removal and water recovery from brines generated in meat processing industry

7.1 Introduction

The production of processed meat requires massive volumes of brines on a daily basis because of its properties as a taste enhancer and as a preservative agent. Brine solutions from meat industry contain multiple compounds that makes it unique and different from other conventional brines like seawater, synthetized brines, cheese brines, etc. Since it contains high concentration on COD, protein, sugar and NaCl and other residues from each meat processing step. Due to the complexity of this type of effluents (high salt content, high COD, meat traces), manufacturers are facing problems related to its disposal or management for environmental or economic reasons.

In this line, the objective of this chapter was to assess the feasibility of applying progressive freeze concentration to treat brine solutions from meat processing industry, combined with additional technologies or processes such as coagulation and electrodialysis, to obtain a clean effluent with water quality.

7.2 Methodology

7.2.1 Raw material

The feed solution for the experiments carried out in this study was a hypersaline waste effluent, namely brines, generated in a meat processing company in Catalunya that produces cured ham. The generation ratio of the brines is 0.035-0.101 L/kg of processed meat. The composition of the brines is variable and depends on the sampling period (during, before or after the campaign curing campaign). In Table 7.1 average ranges of Cl^-, Na^+, COD and protein contents are given based on preliminary studies (Justificativa & Espec, 2012).

Brines were preserved at 5 °C prior to freeze concentration (FC) assays. To assess the efficiency of the FC on salt rejection and recovery of water from brines, several experiments were performed. At first, the freezing temperature set to perform the experiments was -26 °C, based on the phase diagram of NaCl (Farnam et al., 2014) (Figure 7.1).

Table 7.1. Maximum, minimum and case study values of relevant parameters describing the type of brine solution to be treated in this chapter.

Parameter	Unit	Minimum value	Maximum value	Case study value
Cl^-	mg /L	87,738.5	180,795.0	98,300 ± 186
Na^+	mg /L	40,178.5	86,352.2	552,900 ± 570
COD	mg /L	26,167.0	161,833.5	5,300 ± 20
Protein	g/L	9.6	27.4	8.5 ± 0.2

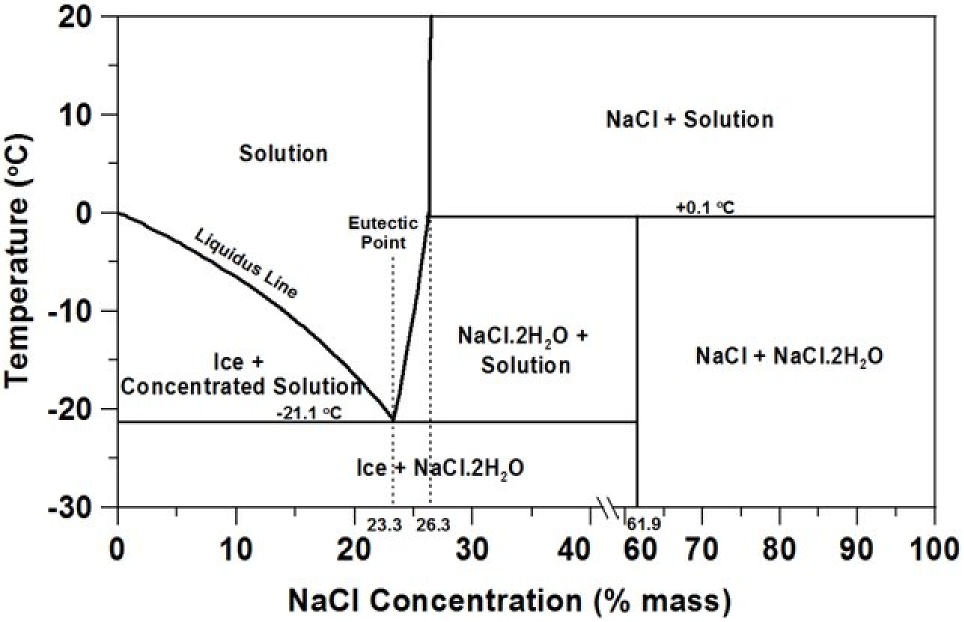


Figure 7.1. Phase diagram of NaCl solution illustrating the physical status versus the composition and temperature.

7.2.2 Progressive freeze concentration test

To assess the efficiency of the PFC technology on salt rejection and water recovery from brines generated in the meat industry, various experiments were carried out. Figure 7.2 illustrate A terminated PFC process of frozen brine solutions from meat industry after vacuum separation.

Figure 7.2. Ice fraction of the tested brines after vacuum application.

The experiments were performed in two parts. In the first part of this study, batch tests of progressive freeze concentration (PFC) were conducted to investigate the effect of two different parameters: agitation rate (rpm) and initial volume (L) treated, as shown in Figure 7.3.

The second part consists of a multi-stage purification (5 stages) of PFC, where in the first stage the raw brine solution was used as a raw material, afterward, the recovered ice of each stage was used as a raw material for the following one.

7.2.2.1 Influence of agitation rate

To investigate the effect of the agitation rate on the salt rejection and water recovery from brines, experiments were carried out at a fixed freezing temperature and volume of -26 °C (to operate near the eutectic point of NaCl) and 1.8 L, respectively. Agitation rates of 100, 300 and 600 rpm were tested to assess the performance of the process, at the lowest agitation rate of the equipment, medium, and highest agitation possible to stir 1.8 L without loss of the brines during the PFC process.

7.2.2.2 Influence of initial volume

To investigate the effect of the initial volume of brines on salt rejection and water recovery, experiments using 0.6, 0.9 and 1.8 L of sample were carried out a freezing temperature and agitation rate of -25 °C and 600 rpm, respectively.

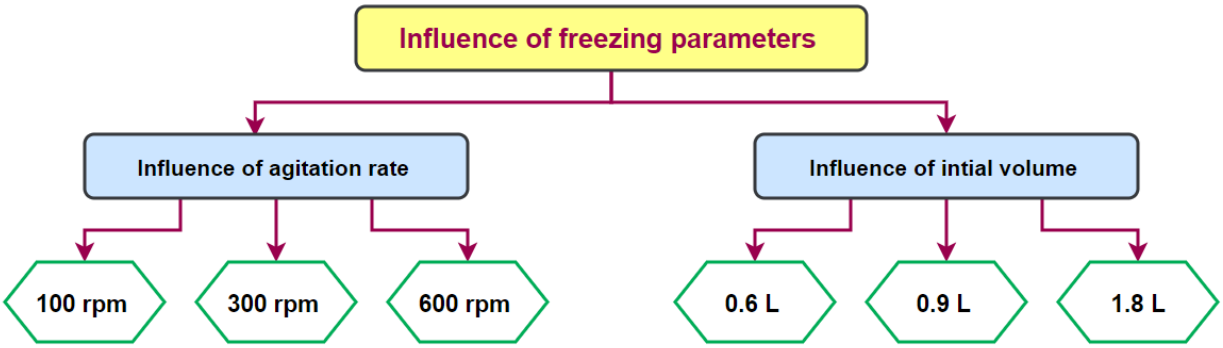


Figure 7.3. Investigated influences of the agitation rate and initial volume parameter.

7.2.2.3 Multi-stage freeze concentration

Multi-stage PFC was composed of 5 freezing stages, operating at -25 °C and 600 rpm. The initial volume of brines introduced to the PFC in the first stage was 1.8 L. After each PFC, a vacuum step was performed in order to clean the ice from the residues of the concentrated brine. The melted ice of each stage was used as a raw material for the following one, repeating the same steps for all the multi-stage process (Figure 7.4).

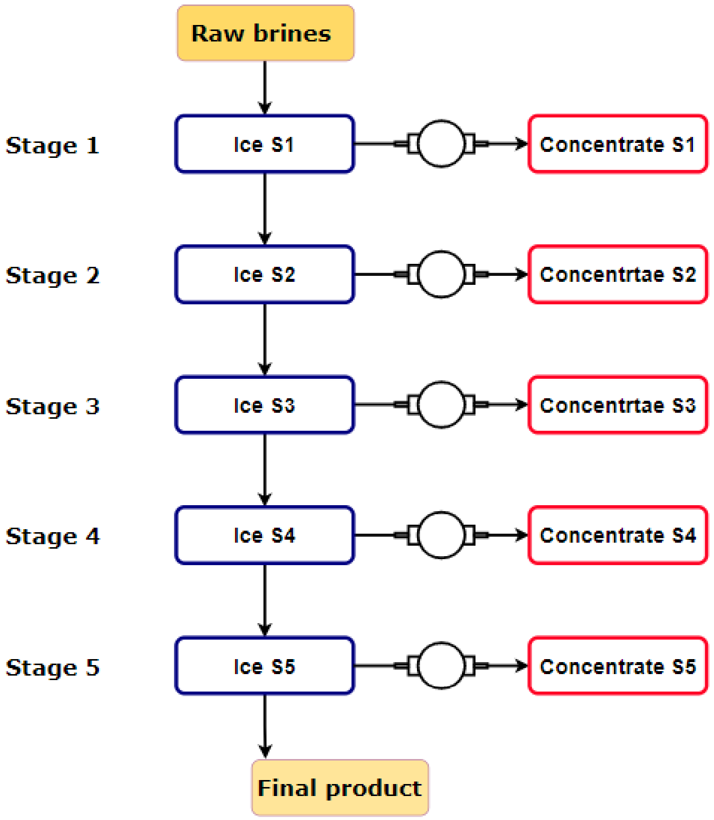


Figure 7.4. Multi-stage PFC scheme of the performed cycles treating brine solutions from meat industry.

7.2.3 Optimization of ice fraction: post-treatment

7.2.3.1 Coagulation test

To optimize the quality of the recovered ice after completing stage 5 of PFC, a coagulation step was carried out to remove the impurities remained in the ice. Different doses of a commercial coagulant were added to the melted ice solution to achieve the optimum concentration to be added. The turbidity of the initial solution and the final products was measured to assess the efficiency of the coagulation process and to determine the optimum coagulant dose to be added. A dose of 0.1 %, 0.195 %, 0.394 % and 0.63 % of coagulant was added to 200 mL of melted ice of stage 5 of PFC.

7.2.3.2 Electrodialysis test

Electrodialysis cell is a technology widely used for water desalination, the method is based on transporting salt ions from one solution through ion-exchange membranes (as known as electric membrane) under the influence of an applied electric potential difference. After the coagulation test, a bench scale laboratory electrodialysis (ED) system (PCCell BED 1-2) developed at GmbH (Heusweiler, Germany) was used for improving the quality of the obtained effluent (Figure 7.5). The limiting current density for the given solution was determined and set at 15V and the flow used in the ED test was 25 L/h. The volume of the solution to be treated in the ED was 2.2 L which was equally distributed in the two cylinders of the ED system. The final solution obtained through ED desalination step was then characterized in terms of reusable water limiting parameters.

Figure 7.5. Electrodialysis equipment used as last step of water recovery system.

7.2.4 Physical-chemical analysis

To examine the quality of the final product of the system consisting on a multi-stage FC, followed by a coagulation, filtration and ED processes, the characterization of samples was performed according to the methodology described in Chapter 3.

7.3 Results and discussion

7.3.1 Influence of the agitation rate on salt rejection

Figure 7.6 shows the results obtained from the assays performed at different agitation rates (section 7.2.2). Salt rejection, ice recovery and chloride and sodium concentrations in the ice were the main parameters monitored. Differences noticed in ice recovery and salt rejection, operating at the three agitation rates, were not significant ($p<0.001$). Likewise, the retention of Na and Cl in the ice fraction allowed assessing the quality of the ice fraction obtained compared to its initial composition (Table 7.2).

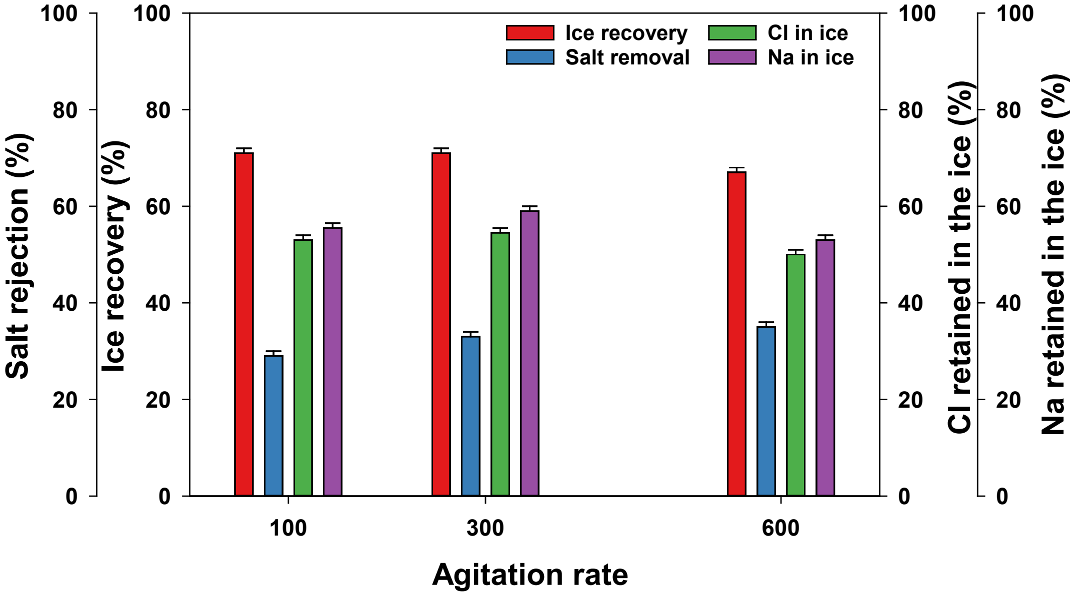


Figure 7.6. Percentage of salt rejection, ice recovery, and the retention of Na and Cl in the ice fraction for different agitation rates (150, 300 and 60 rpm).

The results obtained in this study confirmed that the agitation rate did not have any effect, under 600 rpm, on the abovementioned monitored parameters (Figure 7.6) although a visible effect would be expected at higher agitation rates as other authors have previously observed. Fujioka et al. (2013) investigated the influence of relevant parameters of PFC on the desalination process of seawater and found that higher stirring (agitation rates) induces cleaner ice from a mother solution of an initial concentration of 3.5 (wt) %. Bearing in mind the initial salt concentration and complex composition of the treated solution in the present study, the results cannot be fully comparable, as many influencing parameters are playing a major role on the efficiency of the desalination process using PFC. (Moharramzadeh et al. (2021) in the same topic reported that an increase of the agitation rate lower the percent recovery of ice however favorize the removal of the salt significantly. The documented studies were more focused on desalination processes of seawater or synthetized brine solutions, which are by nature different than the brines treated in the present study.

Table 7.2. Performance of PFC efficiency as a function of agitation rate and initial volume.

	Influence of agitation rate			**Influence of initial volume**		
	100	**300**	**600**	**0.6**	**0.9**	**1.8**
Ice recovery (%)	70 ± 2	71 ± 2	67 ± 0	72 ± 12	63 ± 2	67 ± 0
Salt rejection (%)	29 ± 6	33 ± 18	36 ± 4	31 ± 4	31 ± 9	36 ± 4
Cl remained in the ice (%)	53 ± 3	55 ± 5	50 ± 2	55 ± 7	46 ± 5	50 ± 2
Na recovered in the ice (%)	55 ± 3	59 ± 4	53 ± 1	53 ± 9	42 ± 5	53 ± 1
TDS recovered in the ice (%)	55 ± 2	57 ± 6	52 ± 1	58 ± 9	46 ± 2	52 ± 1

7.3.2 Influence of the initial volume on salt rejection

The influence of the initial volume on the performance of the FC was studied to assess if it was significant to be considered as part of the multi-stage PFC assays results. As a clarification, each further stage performed in the multi-stage PFC assays was decreasing due to the volume reduction in previous stages. Then, the energy provided by the cooling system and the surface available for the brines to freeze was higher for lower volumes affecting the overall performance. Generally, treating smaller volume of solution under same operating conditions will allow faster growth of the ice, which was not followed in the present study, however it is well documented that higher "advance speed of ice front" results on more impurities in the ice fraction (Fujioka et al., 2013; Moharramzadeh et al., 2021). For this reason, it was essential to study this effect before conducting the multi-stage assays.

Figure 7.7 illustrates the results obtained when the initial volume was 0.6, 0.9 and 1.8 L. Table 7.2 provides the percentage of ice recovery, salt rejection and the content on salts ions for each initial volume added to the PFC system. In this case, also not significant differences were found between the conditions tested. The reason behind this behavior remained in the hyper salinity of the brines under study. Such a high concentration of salts caused a decoupling between the agitation rate and initial volume set in the system and its performance. Then, it was expected to get a noticeable behavior treating diluted brine solutions.

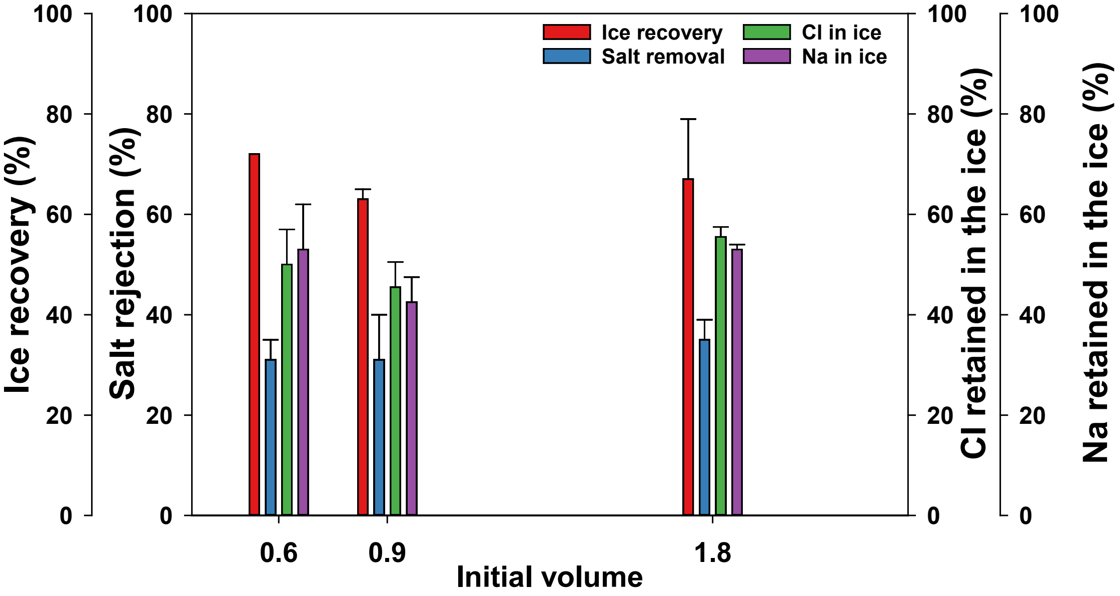


Figure 7.7. Percentage of salt rejection, ice recovery, and the retention of Na and Cl in the ice fraction for different initial volumes (0.6, 0.9 and 1.8 L).

7.3.3 Multi-stage freeze concentration for ice cleaning

Based on the previous findings in this chapter, a 5-stage PFC was performed using the recovered ice from each stage as a raw material for the following one as shown if Figure 7.3.

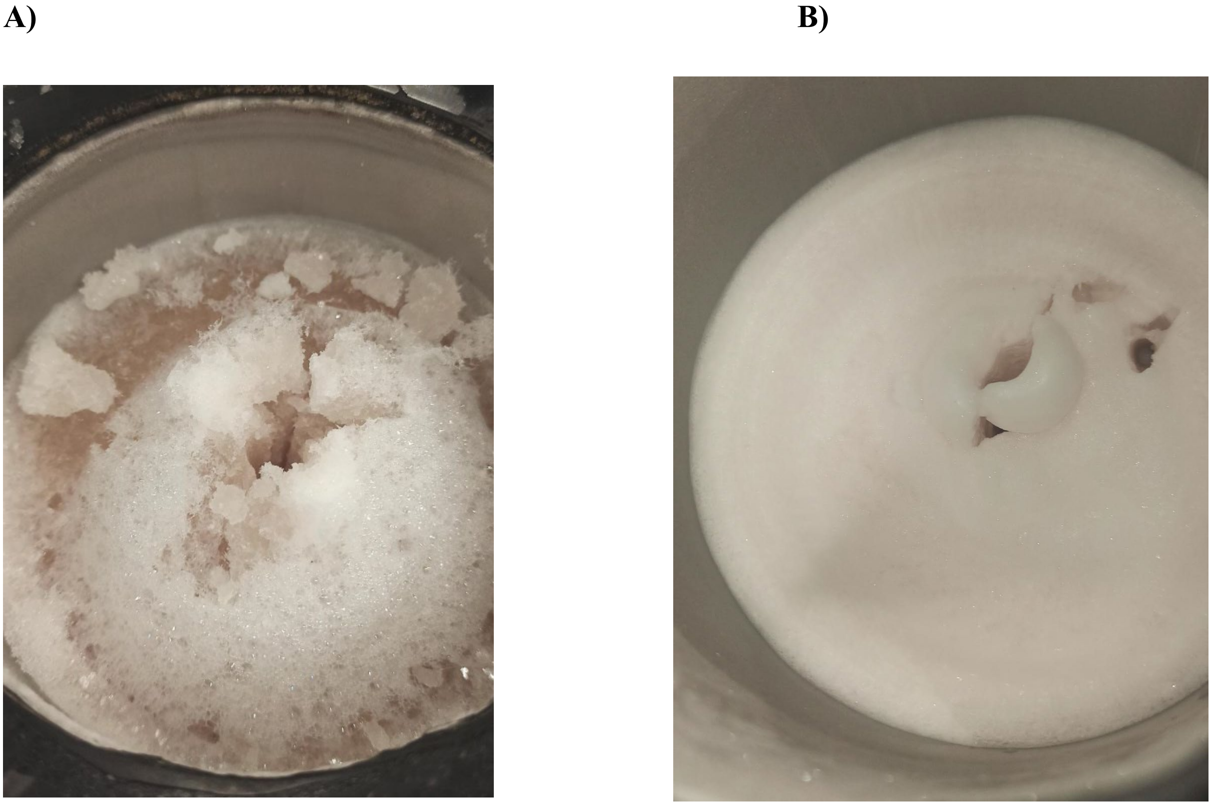


Figure 7.8. Structure of formed ice from studied brine solution when the salt concentration is low in S5 (A), and when the concentration of ice is high in S1 (B).

Figure 7.9 shows the concentration of Cl and Na, EC and salinity profiles obtained from the multi-stage FC assays. Additional data is given in Annex A of this thesis. The sample of brines was poured into the PFC vessel when the freezing temperature achieved -26 °C, then it took approximately one hour for the sample to reach the conditions where the supercooling happens. The supercooling phenomenon occurs when a solution is cooled under its freezing temperature to promote the formation of ice nucleation. The first stage of PFC was the one receiving the raw brine solution characterized by its hyper salinity. Once the freezing occurs, the concentrated fraction became more saline reaching a point where no more ice is formed. In that case the concentration of NaCl in the concentrate is exceeding the eutectic point and the formation of more ice is thermodynamically impossible (Figure 7.1). However, the composition of ice from S1 allowed obtaining higher amounts of ice in S2 with improved removal of salts and impurities. From S2 to S5, the removal of Na and the drop of EC and salinity were oscillating and did not show a uniform trend in the ice fraction. The reason behind it remains unknown however the assumption of the high salinity of the solution may be the explanation.

Regarding the removal of Cl and Na from the ice, total removals of 88 % and 87%, respectively, were achieved in five stages of FC. The results are in correlation with the EC of the final ice fraction (ice of S5) as it dropped by 85 % in 5 stages. Regarding the total salinity of the ice fraction, after completing five stages it dropped by 88%, and that can be an indicator that NaCl salt is the main salt component in the studied brine solution.

From the results obtained in this section, it was stated that the influence of the high salt concentration showed a resistance on salt removal percent, as it was seen as well in the retention of Cl and Na in the ice fraction in S1 compared to S2 where a fraction of the salt was lost in the concentrate of the first stage. As mentioned before, there is a lack of information regarding the conventional methods of management of brines from meat industry, however, a study was conducted to recover salt and water that can be sent to WWTP from concentrated brines from meat industry of 20 %, using a system of flocculation, membrane and vacuum evaporation (Justificativa & Espec, 2012). Whereas using FC technology, various studies were reported regarding the desalination of seawater and other types of brine solutions.

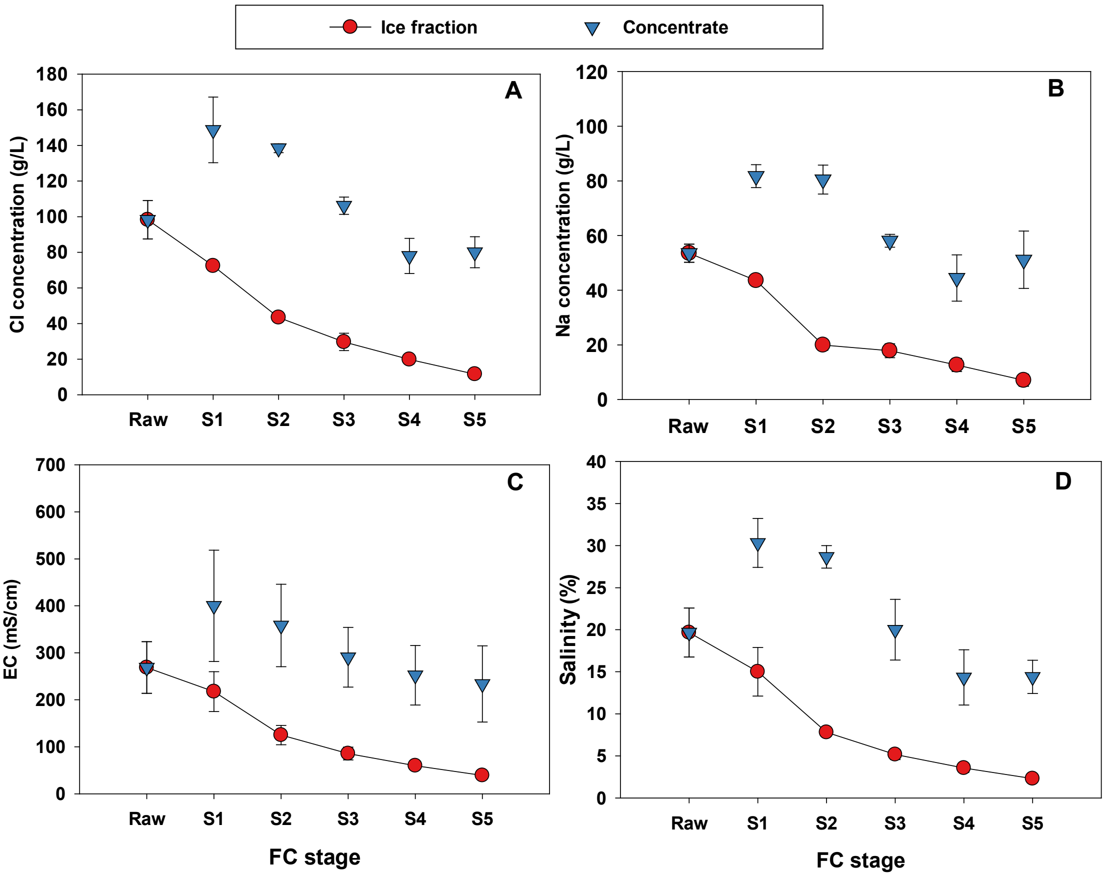


Figure 7.9. Evolution of Cl and Na concentrations (A, B respectively), EC (C) and salinity (D) of the concentrate and ice fractions in each stage of PFC.

Figure 7.17 illustrate in order from left to right the raw brine solution, a sequence of concentrate and ice fractions of each stage of PFC performed.

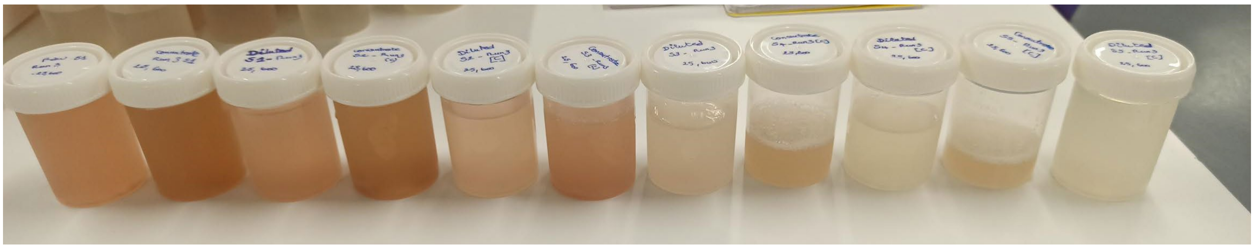


Figure 7.10. Picture of raw brine solution (extreme left), a sequence of concentrate and melted ice of each stage of FC.

7.3.4 Protein and COD removal

Brines solution used in the meat industry contains traces of protein and fat released from the meat during the process which makes it unique compared to conventional brines. Besides, COD as well is present due to the addition of sugar during the preparation of brine solution and releasing some component from the meat. Figure 7.11 illustrates the concentration of protein and COD in the concentrate and ice fraction in each stage of PFC. The concentrations of this section can be found in the Annex A of this manuscript. After completing 5 stages, the total removal of the protein was 83% from the ice fraction, meanwhile around 81 % of COD was removed. The removal pattern of protein and COD was similar for both parameters as well as the parameters in the previous section. The FC performance was not sensitive to the fluctuation of COD, as the removal or the loss of COD in the ice fraction occurred in the first stage of PFC reaching a 72 % removal, then it sharply decreased to 8, 6 and 7 % in the following stages (Table 7.3). The COD findings demonstrates that in this type of solution, the high concentration of salt has no significant effect on the removal of COD, which can be considered as an advantage in case the objective was eliminating the COD while using PFC as a pre-treatment of other technologies that require low COD in a given solution.

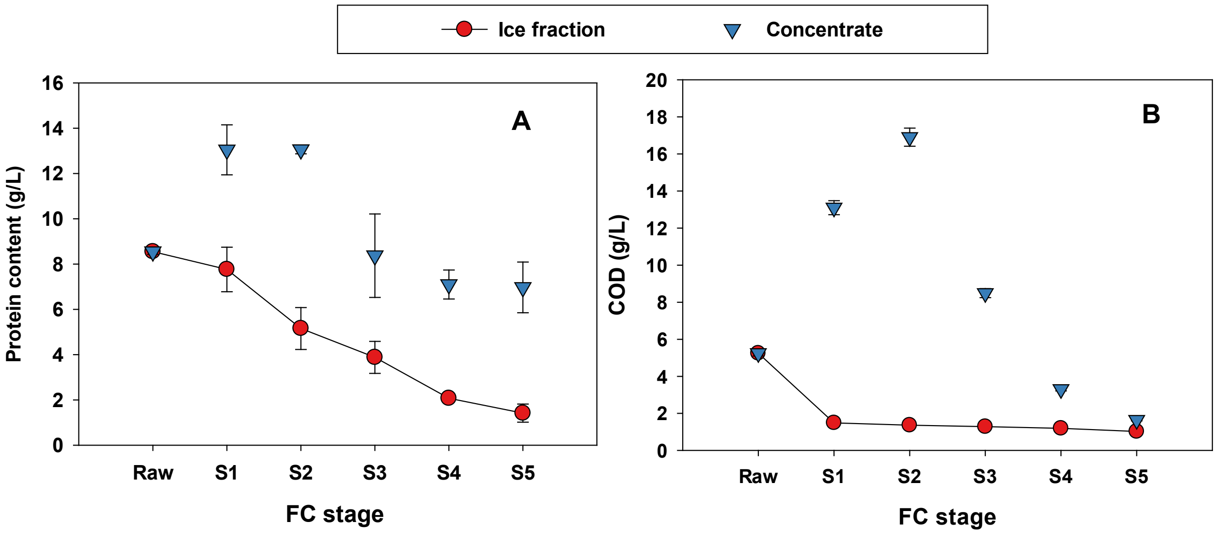


Figure 7.11. Evolution of protein concentration (A) and COD content (B) in the concentrate and ice fraction of each performed stage of PFC.

Table 7.3. Multi-stage assays monitoring.

Experiment		Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Total
Volume reduction	%	75	71	82	86	90	83
Volume balance	%	1	3	0	1	3	
Ice recovery	%	74	68	82	85	88	17
Salt removal	%	24	48	34	31	36	88
EC drop	%	19	43	31	83	34	85
Cl recovery in D	%	55	41	56	57	51	
Na recovery in D	%	60	31	73	60	49	
Cl removal	%	26	40	32	33	42	88
Na removal	%	19	54	10	29	44	87
Protein loss	%	9	34	25	46	33	83
TDS loss	%	15	35	30	31	46	86
COD loss	%	72	8	6	7	14	81

7.3.5 Optimization of the ice fraction

7.3.5.1 Coagulation tests

A coagulation step was performed on the ice fraction of S5 to remove the remaining impurities and to decrease its turbidity to be adequate for an ED application. Table 7.4 shows the turbidity results obtained after the separation of the supernatant from the original solution. The optimum tested dose resulted in a supernatant turbidity of 4.07 FNU, corresponding to the lowest dose of coagulant (0.195 mL), and achieving a turbidity reduction of 96.8 %. After the separation of the two phases in the solution, a filtration through a 0.21µm was performed to obtain an effluent suitable to be treated in the ED unit.

Table 7.4. Coagulation tests to treat the S5 melted ice (diluted fraction).

Coagulant concentration in the ice fraction (mL)	Turbidity before coagulation of the ice	Turbidity after coagulation of the ice
0.195	124 ± 2	4.07 ± 0.01
0.39		19.3 ± 0.5
0.629		106 ± 0
0.1		12.5 ± 0.07

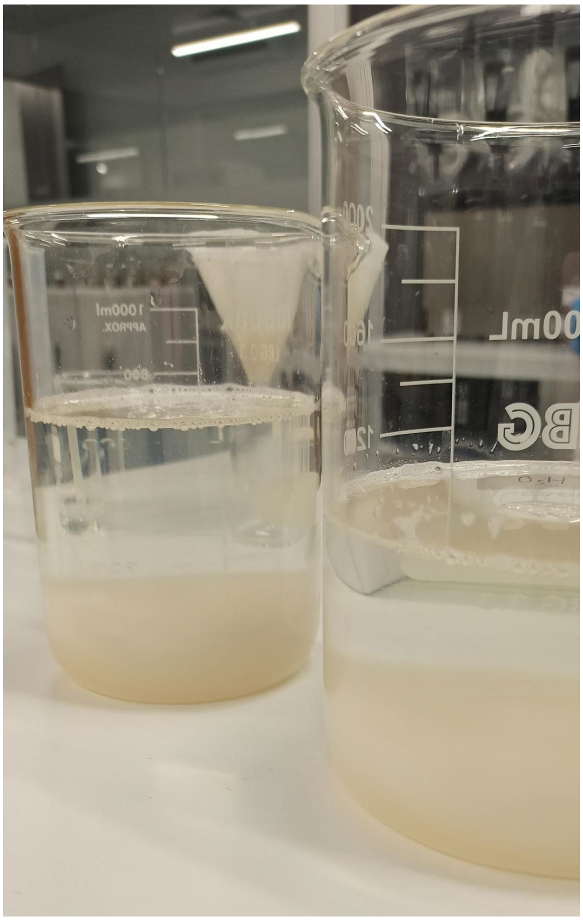
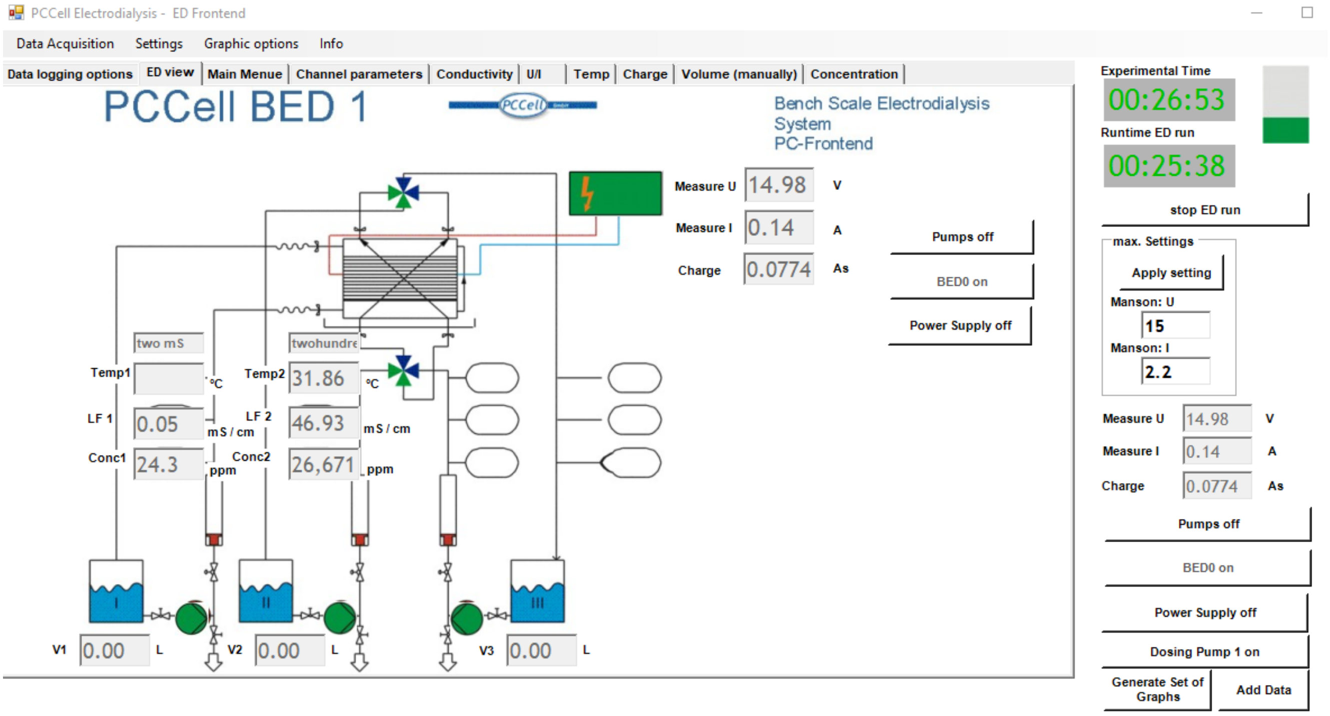


Figure 7.12. Diluted fraction (melted ice from stage 5) treated with coagulant.

7.3.5.2 Electrodialysis test of the ice solution after coagulation

The solution obtained after the coagulation, separation and filtration processes were treated in an ED unit to mainly remove salts (Figure 7.13). The desalination process performed in the ED unit lasted until the EC of the treated effluent was below 0.05 mS/cm and its salt concentration around 24 ppm. Then, starting with an EC of 25 mS/cm, a salt content of 13309 ppm and turbidity of 4.07 FNU in the treated solution, to achieve an EC of 0.05 mS/cm, a salt concentration of 24.3 ppm and a turbidity of 2.99 FNU. EC, salt content and turbidity decreased by 99.8 %, 99.8 % and 26.53 %, respectively, through the ED application. Table 7.5 provides the characterization of the water obtained by the end of the ED cycle. After the ED, 0.82 L of water was recovered from the 1.1 L of treated effluent.



Experimental Time 00:26:53
Runtime ED run 00:25:38

Measure U 14.98 V
Measure I 0.14 A
Charge 0.0774 As

Manson: U 15
Manson: I 2.2

Measure U 14.98 V
Measure I 0.14 A
Charge 0.0774 As

two mS
twohundre
Temp1 °C
Temp2 31.86 °C
LF 1 0.05 mS / cm
LF 2 46.93 mS / cm
Conc1 24.3 ppm
Conc2 26,671 ppm
V1 0.00 L
V2 0.00 L
V3 0.00 L

Figure 7.13. Screenshot of the relevant parameters set in the ED unit to treat the water obtained from the multi-stage FC plus a coagulation, separation and filtration step.

Table 7.5. Characterization of the clean water obtained after treating brines from meat processing through FC, coagulation, separation, filtration and ED.

Salinity (ppm)	Turbidity (FNU)	TDS (mg/L)	BOD_5 (mg/L)	E.Coli	EC (µS/cm)
24.3	2.99 ± 0.17	32.5 ± 1.3	8.427 ± 0.20	0	50 2

7.4 Alternative treatments to obtain reclaimed water from meat processing brines

Despite that the origin of the investigated brine solution in this chapter is not from a desalination process, however, the high content on salt it requires a similar treatment that can be either a disposal or recovering recourses to achieve a Zero Liquid Discharge (ZLD) approach. Comparing with the treatment techniques reported in Chapter 1, the finding cannot be compared to the results obtained in this study. The water solution obtained from the adapted system in this chapter (Figure 7.11) has indeed similar EC, turbidity, BOD and TDS of water, nevertheless, a ZLD goal was not accomplished and that because we have a concentrate and ice fraction in each cycle of PFC from one hand and from ED from another hand.

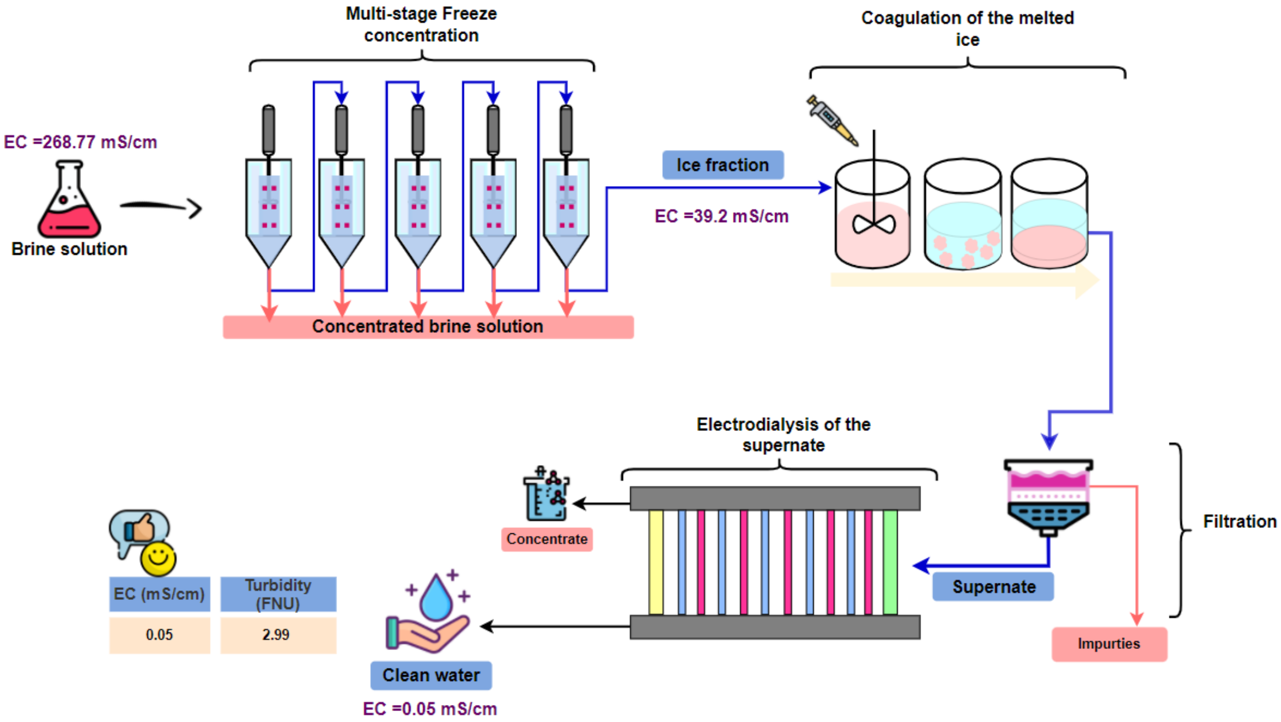


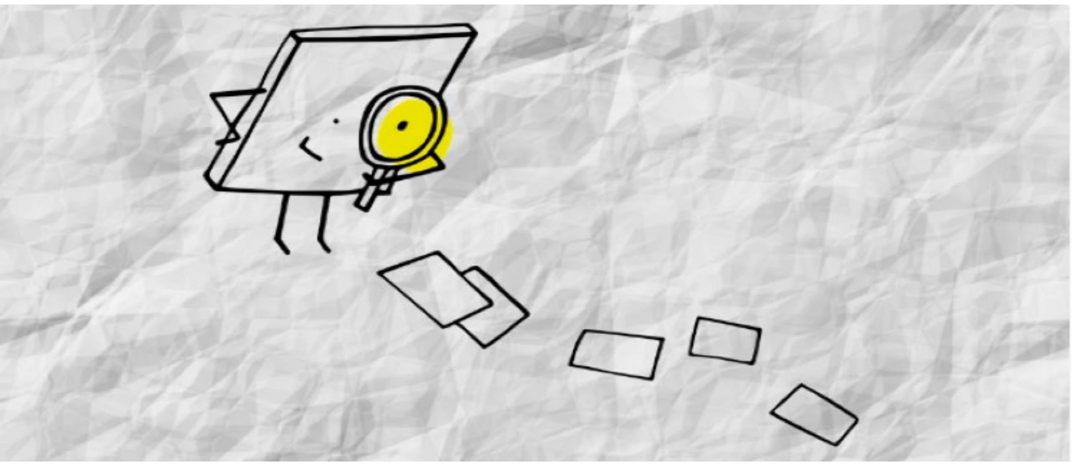
Figure 7.12. Summary of the desalination system used in this chapter for water recovery and salt rejection.

By implementing a pre-treatment system prior to PFC could solve this issue and achieve the goal. Crystallization of only a half of salt content will allow a complete freezing of the solution and then separating the suspended solids by partial melting coupled with vacuum. Thus, crystallizing salts from brine solutions using EFC is one of the ways that can make the PFC work to achieve a ZLD. Preliminary assays were made in this sense (Figure 7.12), however, the topic worth deep investigation and trials. Regarding disposal techniques, since the brines solution is generated in a meat processing industry, its disposal is not the best approach to be adapted, a purification step is mandatory in case one of the disposal methods are being considered.

Figure 7.12. First trials of salt crystallization using PFC on brine solutions from meat processing industry.

7.4 Conclusion

Results obtained from the present study show that the combination of multi-stage FC with coagulation and electrodialysis allowed obtaining clean water with high quality. However, the obtained volume of clean water was low compared to the amount of brines that were still remaining as an environmental and economic issue. The proposed treatment train could not be currently declared as economically and environmentally feasible to obtain clean water from brines, although a techno-economical assessment is necessary to finally confirm this perception. From the present study, another alternative has been proposed to treat brines from meat processing industry based on the precipitation of salts prior to desalination with FC, and that can be performed as well using a more specific configuration like Eutectic Freeze Concentration, which would operate near the eutectic point of the solution to precipitate the maximum amount of salt and obtain a diluted solution to be treated with other configurations of FC.



Chapter 8: General conclusions and outlook

8.1 General conclusions

This thesis has delivered a brand-new application of the freeze concentration technology in the agro-industrial sector aimed to recover valuable compounds and clean water from waste streams. Results obtained in each chapter have been the starting point of many other up-scaled studies that are currently ongoing at BETA Technological Center, part of competitive projects or that have been and continue being transferred to the industry. This thesis has paved the way to potential opportunities specially aiming to use the freeze concentration technology as an innovative technique for either its high efficiency on the concentration of nutrient from livestock slurries, digestates or dairy industry by-products, or desalination and purification of concentrated solutions for water recovery purposes.

Overall, the conclusions can be summed up on the high concentration efficiency of nutrient from agro-industrial waste effluents (digestate, pig slurry, cheese whey), and a potent salt rejection factor while treating hyper saline brine solutions. In the following section, exclusive conclusions drawn from each chapter/study carried out in this thesis are provided and segmented depending on each raw material treated.

Protein and lactose recovery from cheese whey

An assessment of the influence of agitation rate (150; 300 and 600 rpm), initial concentration of the cheese whey (3; 5 and 7 ºBx) and the freezing temperature (-5; -10 and -15 ºC) was investigated setting 50% of the volume reduction in each FC cycle. Once the most favorable operating conditions were selected (in terms of solids recovery in the concentrated fraction), an FC multistage of 4 levels was performed. The main findings are listed below:

1- In terms of process efficiency, the optimum result was obtained at the highest freezing temperature and highest agitation rate.
2- Higher process efficiencies were obtained at initial concentration of 3º Bx compared to 5 and 7 ºBx. Higher solids concentrations in the cheese whey led to an inefficient FC process where the concentration remained almost the same in the concentrated fraction generating worst ice quality. This phenomenon was caused by the low availability of free water in the solution and the Newtonian behavior of the concentrated cheese whey.

3- Contrarily to other research studies, in this research work lactose was not retained in the diluted fraction but in the concentrated fraction together with the protein. The finding is worth further investigation due to its particularity, and the only fact stated at the moment is related to the configuration of the PFC stirred tank and the range of conditions tested.

Nutrient recovery from livestock waste effluents

Part of this thesis was dedicated to assess for the first time the efficiency of freeze concentration on the recovery of nutrient from pig slurry and concentrated digestate. The performance of the technology was investigated considering the FC operating conditions, namely the freezing temperature (-5, -10 and -15 ºC) and the agitation rates (150, 300 and 600 rpm). The conditions that engendered a higher efficiency were used to perform a two-stage PFC for further concentration of the effluents. The relevant outcomes regarding this research are cited below:

1- The application of PFC to recover nutrients from the abovementioned effluents showed a huge potential, in terms of efficiency, and advantages compared to conventional technologies such as filtration or evaporation processes: less energy consumption and operating costs, no pre-treatment required and minimum maintenance, less odors emissions, preservation of valuable compounds, etc.

2- PFC of livestock slurries and digestate (concentrated liquid fraction) delivers 2 products to be used as fertilizers without harming the surrounding soil and polluting the environment. First, a concentrated fraction suitable to be used as a fertilizer, characterized by its reduced volume and richness in nutrients allowing a feasible transportation to nutrient scarce areas. Second, a diluted fraction of the initial raw waste effluent, with a low concentration of nutrients that can be used in contaminated regions to avoid excess application of nitrogen.

3- A recovery range of around 33 to 67 % of N, P and K were concentrated in 25 % of the initial volume of livestock waste effluent using PFC (mass of nutrient in concentrate in comparison to mass of nutrient in raw material).

4- The influence of the freezing parameters is similar to the ones obtained in the case of the cheese whey. Higher agitations lead to higher process efficiencies. The freezing temperature -5 ºC was discarded due to its insufficiency in completing the freezing process, meanwhile higher freezing temperatures seemed to be more effective in the concentration process.

Water recovery from brines from meat industry

FC of liquid brines from meat processing industry was investigated in this thesis to assess the feasibility of recovering clean water. The solution in question is known by its high concentration on salt NaCl among other components that are not found in conventional brines like seawater and synthetized brines. Fixing the freezing temperature at -26 ºC, the influence of three agitation rates (150, 300 and 600 rpm) and three initial volumes (0.6, 0.9 and 1.8 L) was tested to assess the efficiency of the process as a function of the freezing parameters. The main conclusions arising from this study were:

1- The agitation rate and treated initial volume did not show any significant influence neither on the salt rejection nor the ice recovery since the treated solution is classified as hyper saline brine solution and the effect of this parameters was not as visible as that probably observed with more diluted brines, where the amount of salt distributed between both fractions could be noticed quantitatively.

2- Results obtained from the influence of the agitation rate and initial treated volume allowed better discussion the multi-stage progressive freeze concentration of the treated brin solutions, as only the influence of salt content was observed.

3- The multi-stage PFC allowed reducing more than 80 % in salt rejection, protein and COD removals in 5 stages treating the diluted fraction of hyper saline brines.

4- Ice formation inside the freezing vessel of PFC is strongly dependent on the salt content of the bulk mixture (which mainly corresponds to that in the concentrated fraction). The more the formed ice, the more salt concentration increases in the liquid fraction, making the freezing process terminated before with remaining liquid fraction, as no more ice can be formed.

5- Water recovered from hypersaline brines through 5 stages of PFC, post-treated through a coagulation-sedimentation (turbidity removal) and electrodyalisis filtration (salinity removal) processes, had similar quality to clean water characterization.

6- FC has proven to deliver water solution which the characterizations are similar to clean water in term of electrical conductivity, turbidity, and biological oxygen demand, from brine solutions from meat processing industry, which is a first to be investigated so far. Whereas the water obtained clean, the adaptation of such system needs intensive optimization in terms of volume of water recovered from one hand, besides the possibility of reusing water originated from meat processing industry that may cause conflictions due to its origin.

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Annexes

Annex - A

A-1: Concentrations and monitoring parameters of freeze concentration applied to brine solution from meat processing industry

Table A1. Measured values in the multi-stage of brine solution from meat processing industry

	Experiment		Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
Condition	Temperature	(ºC)	-25	-25	-25	-25	-25
	Agitation	rpm	600	600	600	600	600
Volume	Initial volume	L	1.8	1.2	0.8	0.5	0.4
	Volume concentrate	L	0.4	0.4	0.1	0.1	0.0
	Volume ice	L	1.3	0.8	0.6	0.5	0.3
Salinity	Initial salinity	%	19.7	15.0	7.8	5.2	3.6
	Concentrate salinity	%	30.3	28.7	20.0	14.3	14.4
	Ice salinity	%	15.0	7.8	5.2	3.6	2.3
EC	Initial EC	mS/cm	268.7	217.4	125.0	342.3	59.9
	Concentrate EC	mS/cm	400.1	358.3	290.6	252.3	233.7
	Ice EC	mS/cm	217.4	125.0	85.7	59.9	39.2
Cl	Initial Cl	(g/L)	98.3	72.4	43.4	29.7	19.9
	Concentrate Cl	(g/L)	148.7	138.5	106.2	78.0	80.1
	Ice Cl	(g/L)	72.4	43.4	29.7	19.9	11.6
PO4	Initial PO4	(mg/L)	833.3	716.7	666.7	550.0	466.7
	concentrate PO4	(mg/L)	833.3	916.7	1083.3	1041.7	1500.0
	Ice PO4	(mg/L)	716.7	666.7	550.0	466.7	316.7
SO4	Initial SO4	(mg/L)	1375.0	1283.3	966.7	700.0	700.0
	concentrate SO4	(mg/L)	1500.0	1625.0	1791.7	1625.0	1541.7
	Ice SO4	(mg/L)	1300.0	966.7	700.0	700.0	400.0
Turbidity	Initial turbidity	FNU	489.7	513.1	676.2	333.4	204.0
	Concentrate turbidity	FNU	613.6	619.1	804.7	430.7	353.7
	Ice turbidity	FNU	513.1	676.2	333.4	380.0	93.9
TDS	Initial TDS	(mg/L)	16.3	13.8	9.0	6.3	4.3
	Concentrate TDS	(mg/L)	24.7	23.5	18.5	14.7	14.2
	Ice TDS	(mg/L)	13.8	9.0	6.3	4.3	2.3
Na	Initial Na	(g/L)	53.5	43.6	20.0	17.9	12.7
	Concentrate Na	(g/L)	81.8	80.5	58.1	44.5	51.2
	Ice Na	(g/L)	43.6	20.0	17.9	12.7	7.1
COD	Initial COD	(mg/L)	5.3				
	Concentrate COD	(mg/L)					
	Ice COD	(mg/L)					1.0
Protein	Initial Protein	(g/L)	8.5	7.8	5.2	3.9	2.1
	Concentrate protein	(g/L)	13.0	13.1	8.4	7.1	6.0
	Ice protein	(g/L)	7.8	5.2	3.9	2.1	1.4

Table A2. Followed parameters during the multi-stage of brine solution from meat processing industry

	Experiment		Stage 1	Stage 2	Stage 3	Stage 4	Stage 5
	Volume reduction	%	75%	71%	82%	86%	90%
Mass balance	Volume balance	%	1%	3%	0%	1%	3%
	Salinity balance	%	5%	10%	0%	4%	5%
	EC balance	%	3%	13%	2%	75%	5%
	Cl balance	%	7.88%	4.15%	0.01%	7.36%	9.91%
	PO4 balance	%	11%	0%	3%	2%	10%
	SO4 balance	%	3%	12%	7%	-17%	29%
	Turbidity balance	%	-9%	-24%	38%	-14%	43%
	TDS balance	%	0%	7%	6%	9%	21%
	Na balance	%	2%	16%	-26%	6%	12%
	Protein balance	%	-5%	7%	9%	29%	13%
Ice quality	Ice recovery	%	74%	68%	82%	85%	88%
	Salt removal	%	24%	48%	34%	31%	36%
	Partition constant		49%	27%	26%	25%	16%
	EC drop	%	19%	43%	31%	83%	34%
Recovery in	Cl recovery in C	%	38%	55%	44%	36%	39%
	Na recovery in C	%	38%	53%	52%	34%	39%
	PO4 recovery in C	%	25%	37%	29%	26%	31%
	SO4 recovery in C	%	27%	37%	33%	32%	21%
	Protein recovery in C	%	38%	49%	29%	25%	28%
	TDS recocvery in C	%	37%	49%	37%	32%	31%
Recovery in Ice	Cl recovery in D	%	55%	41%	56%	57%	51%
	Na recovery in D	%	60%	31%	73%	60%	49%
	PO4 recovery in D	%	64%	63%	67%	72%	60%
	SO4 recovery in D	%	70%	51%	59%	85%	
	Protein recovery in D	%	67%	45%	62%	46%	59%
	TDS recovery in D	%	63%	44%	57%	59%	47%
Removal	Cl removal	%	26%	40%	32%	33%	42%
	Na removal	%	19%	54%	10%	29%	44%
	Cl loss factor	%	40%	61%	44%	85%	43%
	degree of crystallization	%	74%	68%	82%	85%	88%
	Protein loss	%	9%	34%	25%	46%	33%
	TDS loss	%					
	COD loss	%					