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Desempenho do leite de cabra submetido aos processos de nanofiltração e crioconcentração em blocos com descongelamento gravitacional e a vácuo

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O presente trabalho em nível de doutorado foi avaliado e aprovado por banca examinadora composta pelos seguintes membros:

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Certificamos que esta é a **versão original e final** do trabalho de conclusão que foi julgado adequado para obtenção do título de doutor em Ciência dos Alimentos.

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Profª. Elane Schwinden Prudêncio, Dra.
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Este trabalho é dedicado a minha família.

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"Desistir? Eu já pensei seriamente nisso, mas nunca me levei realmente a sério. É que tem mais chão nos meus olhos do que cansaço nas minhas pernas, mais esperança nos meus passos do que tristeza nos meus ombros, mais estrada no meu coração do que medo na minha cabeça." Cora Coralina

RESUMO

O aumento da produção de leite de cabra está associado à incorporação de novas tecnologias ao seu processamento, como a crioconcentração e a nanofiltração. A parir destas tecnologias é possível obter concentrados do leite com alta qualidade nutricional, sem alterações químicas e bioquímicas indesejáveis. Desta forma, este trabalho de tese de doutorado avaliou duas técnicas de concentração de leite de cabra, a crioconcentração em blocos e a nanofiltração. O leite de cabra desnatado foi concentrado primeiramente pela técnica de crioconcentração em blocos até o terceiro estágio de processo e as frações de concentrado e gelo obtidas foram avaliadas em relação as suas propriedades físicas, químicas e reológicas e perfil mineral. Ao submeter o leite de cabra desnatado ao processo de nanofiltração foram avaliados o desempenho do processo pelo declínio do fluxo de permeado, resistência à incrustação e, composição e propriedades reológicas do retentado. Posteriorment, foi avaliado o desempenho do processo de concentração de congelamento em blocos assistido a vácuo no leite de cabra semidesnatado, utilizando a metodologia de superfície de resposta para otimizar os parâmetros de tempo de congelamento (1, 7 e 14 dias), condições de vácuo (10 kPa, 40 kPa e 70 kPa) e tempo sob vácuo (20 min, 40 min e 60 min) em relação à resposta de rendimento do concentrado e após, a influência do NaCl no processo. Na primeira etapa deste estudo, em geral, com o aumento dos estágios de crioconcentração em blocos, a densidade, o teor total de sólidos, o teor total de proteínas, caseína e proteína de soro de leite aumentaram nas frações de concentrado e gelo. Além disso, em todas as etapas, foi possível notar que o conteúdo de lactose mostrou um equilíbrio entre as duas frações. Ao avaliar as propriedades de cor, foi observado que os concentrados apresentaram índice de brancura semelhante ao leite integral e tendência à coloração esverdeada e amarelada. Modelos de Power Law e Herschel-Buckley ajustaram-se para descrever o comportamento do fluxo de todas as frações de concentrado e gelo. Como esperado, observou-se um aumento no teor de minerais avaliado com o aumento dos estágios de concentração de congelamento do leite de cabra desnatado. Entretanto, as maiores eficiências ($P < 0,05$) do processo foram observadas no primeiro e segundo estágio. Assim, os concentrados dos estágios 1 e 2 demonstraram ser um produto promissor a ser utilizado pelas indústrias de laticínios. Quando o leite de cabra desnatado foi submetido ao processo de nanofiltração até um fator de redução de volume (VRF) igual a 2, verificou-se uma rápida diminuição do fluxo de permeado em um curto período de tempo, apresentando fluxo contínuo, causado pela resistência reversível, que é caracterizado pelo bloqueio padrão e completo. O modelo combinado de incrustação forneceu uma descrição realista do comportamento da nanofiltração no leite de cabra desnatado. Além disso, o retentado apresentou maiores valores de sólidos totais, proteínas, lactose, cinzas, fração mineral, bem como, uma maior luminosidade e tendência à cor esverdeada e amarelada em relação ao leite de cabra inicial e ao permeado. Os modelos de Power Law e Herschel-Buckley foram adequados para descrever o comportamento do fluxo do retentado, o qual apresentou a maior viscosidade aparente. Finalmente, os parâmetros ótimos do processo de crioconcentração em blocos assistido por vácuo de leite de cabra semidesnatado foram de um tempo de congelamento de 1 dia, condições de vácuo iguais a 10 kPa e tempo de vácuo de 60 min. Quando verificada a influência do NaCl utilizando diferentes teores de sal (0,5, 1, 1,5 e 2%), o concentrado com adição de 1,5 e 2% de NaCl apresentou os maiores valores para os teores totais de sólidos e proteínas e parâmetros de processo mais satisfatório. Desta forma, o melhor desempenho foi observado quando se utilizou adição de NaCl a 1,5 e 2% no leite de cabra submetido ao processo de concentração de congelamento assistido a vácuo. Por fim, vale ressaltar o potencial inovador que este trabalho representa através do estudo de dois diferentes tipos de processo de concentração, a fim de obter leites de cabra concentrados que possam ser utilizados pelas indústrias alimentícias.

Palavras-chave: Leite de cabra; Crioconcentração; Nanofiltração; Eficiência de processo; Fluxo de permeado.

ABSTRACT

The increase in the production of goat milk is associated with the incorporation of new technologies to its processing, such as freeze concentration and nanofiltration. From these technologies it is possible to obtain milk concentrates with high nutritional quality, without being observed undesirable chemical and biochemical changes. In this case, this thesis work evaluated two techniques for the concentration of goat's milk, block freeze concentration and nanofiltration. The skimmed goat milk was concentrated first by the block freeze concentration technique until the third stage of the process and the concentrate and ice fractions obtained were evaluated in relation to their physical, chemical and rheological properties and mineral profile. When submitting skimmed goat milk to the nanofiltration process, the performance of the process was evaluated by the decline in permeate flow, resistance to fouling, and composition and rheological properties of the retentate. Subsequently, the performance of the vacuum assisted block freezing concentration process in semi-skimmed goat milk was evaluated, using the response surface methodology to optimize the freezing time parameters (1, 7 and 14 days), vacuum conditions (10 kPa, 40 kPa and 70 kPa) and time under vacuum (20 min, 40 min and 60 min) in relation to the yield response of the concentrate and afterwards, the influence of addition of NaCl in the process. In the first stage of this study, in general, with the increase of freeze concentration stages, the density, the total content of solids, the total content of proteins, casein and whey protein increased in the concentrate and ice fractions. In addition, at all stages, it was possible to notice that the lactose content showed a balance between the two fractions. When evaluating the color properties, it was observed that the concentrates showed a whiteness index similar to whole milk and a tendency to greenish and yellowish color. Power Law and Herschel-Buckley models adjusted to describe the flow behavior of all concentrate and ice fractions. As expected, an increase in the mineral content was observed with the increase in the freezing concentration stages of skimmed goat milk. However, the highest efficiency ($P < 0.05$) of the process were observed in the first and second stage. Thus, the concentrates from stages 1 and 2 proved to be a promising product to be used by the dairy industries. When skimmed goat milk was submitted to the nanofiltration process up to a volume reduction factor (VRF) of 2, there was a rapid decrease in the permeate flow in a short period of time, showing continuous flow, caused by resistance reversible, which was characterized by standard and complete blocking. The combined scale model provided a realistic description of the nanofiltration behavior in skimmed goat milk. In addition, the retentate showed higher values of total solids, proteins, lactose, ash, mineral fraction, as well as, a greater luminosity and tendency to greenish and yellowish color in relation to the initial goat milk and permeate. The Power Law and Herschel-Buckley models were adequate to describe the behavior of the retentate flow, which presented the highest apparent viscosity. Finally, the optimum parameters of the vacuum-assisted block freeze concentration process applied to semi-skimmed goat milk were a freezing time of 1 day, vacuum conditions equal to 10 kPa and a vacuum time of 60 min. When evaluated the influence of NaCl using different concentrations of salt (0.5, 1, 1.5 and 2%), the concentrate with the addition of 1.5 and 2% NaCl showed the highest values for total solids and proteins and more satisfactory process parameters. Thus, the best performance was observed when the addition of 1.5 and 2% NaCl was used in goat milk submitted to the vacuum assisted freezing concentration process. It is worth highlighting the innovative potential that this work represents through the study of two different types of concentration process, in order to obtain concentrated goat milk that can be used by the food industries.

Keywords: Goat milk. Freeze concentration. Nanofiltration; Process efficiency; Permeate flux.

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INTRODUÇÃO

O Brasil é o maior produtor de leite de cabra da América do Sul, com produção de 135.000 toneladas/ano (FAOSTAT, 2018). A caprinocultura cumpre importante papel socioeconômico nas diversas regiões brasileiras, por gerar renda direta e representar uma excelente fonte alimentar. No nordeste, a maior parte da produção tem como destino os programas governamentais de merenda escolar e de combate à desnutrição infantil na população carente. Segundo Silanikove *et al.* (2010), o aumento do consumo de leite de cabra em todo o mundo contribui para que os derivados caprinos, se tornem mais popular, demonstrando assim a sua capacidade em oferecer produtos de alta qualidade.

De acordo com Clark e García (2017), o crescente interesse do consumidor pelo leite de cabra e seus derivados está relacionado aos benefícios nutricionais oferecidos por esses produtos. Estes autores ainda afirmam que as diferenças entre a composição de aminoácidos, a estrutura secundária das proteínas do leite e as propriedades químicas do leite de cabra ajudam a reduzir seu potencial alergênico quando comparado ao leite de vaca. Silanikove *et al.* (2010) relataram que seria necessário utilizar em média 5 vezes mais leite de cabra do que o leite de vaca para desencadear uma reação adversa. Sua composição é semelhante ao leite de vaca, no entanto, a proporção de micelas de caseína de menor tamanho é maior no leite de cabra do que no leite de vaca, o que explica a melhor digestibilidade do leite de cabra e de seus derivados (HAENLEIN, 2004; CEBALLO *et al.*, 2009).

No Brasil, há uma crescente demanda por novos produtos lácteos com alto valor agregado em sofisticados nichos de mercado, o que estimula a produção e comércio do leite de cabra (FONSECA *et al.*, 2013). Para aumentar a qualidade do leite de cabra em relação a suas propriedades nutricionais e tecnológicas para a produção de derivados, métodos de concentração podem ser aplicados. Uma tecnologia amplamente utilizada em processos lácteos é a concentração de leite por evaporação (LIU; DUNSTAN; MARTIN, 2012). Entretanto, sabe-se que o uso da evaporação para reduzir o volume de leite pode danificar as proteínas do leite e acelerar a reação de Maillard. Ainda assim, é importante ressaltar que a estabilidade do leite de cabra durante os tratamentos térmicos na produção de derivados é menor que a de leite de vaca (MONTILLA; CALVO, 1997). Neste contexto, os processos de crioconcentração e separação por membranas se destacam, devido ao uso de baixas temperaturas, preservando os componentes termicamente sensíveis e as propriedades sensoriais.

O processo de crioconcentração tem como objetivo promover a concentração de produtos alimentares líquidos, pelo congelamento e subsequente separação de uma parte da água congelada (BELÉN *et al.*, 2012) removendo a água de maneira mais seletiva do que a evaporação (YEE; WILEY; BAO, 2007) e, além disso, com custos menores (SÁNCHEZ *et al.*, 2011). Para melhorar a eficiência do processo, Aider e Halleux (2009) e Chabarov e Aider (2014) indicam que é necessário conhecer o comportamento da matéria prima a ser submetida a esta tecnologia, prevendo assim as condições necessárias para o seu emprego. Atualmente a crioconcentração vem sendo associada a sistemas *one-step*, uma vez que é caracterizada pela separação de compostos em apenas uma etapa e pela simplicidade do equipamento, como a crioconcentração em blocos (ORELLANA-PALMA *et al.* 2017). No processo de crioconcentração em blocos, um alimento líquido é completamente congelado e posteriormente descongelado em temperatura controlada visando a recuperação de uma porção de alimento com uma concentração mais alta, a fração concentrada, e a fração do gelo. O processo consiste em três etapas: congelamento, degelo e separação (PETZOLD *et al.*, 2016). A etapa de separação é realizada por um método gravitacional, mas para aumentar a eficiência do processo, técnicas assistidas ou chamadas forças externas, como ultrassom, centrifugação ou vácuo podem ser utilizadas (PETZOLD; NIRANJAN, K; AGUILERA, 2013). Nessa condição, o vácuo como técnica assistida aplicada à crioconcentração é semelhante ao princípio usado pelas crianças para sugar a solução de açúcar dos picolés e aproveitando o sistema hidráulico existente na matriz congelada formada por canais entre os cristais de gelo que contêm a solução concentrada, aumentando a extração de concentrado e melhorando parâmetros do processo, como eficiência e recuperação de solutos (PETZOLD *et al.*, 2016).

Outro processo promissor para concentração de compostos termossensíveis em alimentos é o processo de separação por membrana. Os processos de separação por membranas possuem uma barreira seletiva, representada por uma membrana semipermeável, permitindo a permeação preferencial de um ou mais componentes, levando à sua separação, purificação ou concentração (NATH; DAVE; PATEL, 2018). Dentre os métodos de separação por membranas, destaca-se a nanofiltração que permite uma variação na concentração de vários componentes do leite, devido a retenção seletiva das proteínas e da permeação de sais minerais, água e compostos de baixa massa molar. Isto ocorre devido o limite de peso molecular da nanofiltração que está na faixa de 150 a 1000 Da (QIAN; MALMAMLI; WICKRAMASINGHE, 2016). Não apenas como um sistema independente, a nanofiltração é aplicada integrada com outros

processos de membrana em todas as etapas do processamento de leite e laticínios - fabricação de queijos, concentração de proteínas de soro de leite, fracionamento de hidrolisados de proteínas, purificação de efluentes e recuperação de efluentes (NATH; DAVE; PATEL, 2018). Embora os processos de membrana apresentem várias vantagens, o declínio do fluxo durante a filtração e a resistência a incrustações ainda representam um fator limitante para o processo industrial, exigindo pesquisa (NG, DUNSTAN; MARTIN, 2018).

Considerando que o leite é constituído por aproximadamente 88 g 100 g^{-1} de água, muitos processos envolvidos na transformação do leite em seus derivados poderiam ser otimizados, caso o mesmo esteja concentrado, aumentando, por exemplo, as propriedades nutricionais e tecnológicas do concentrado obtido. Portanto, este estudo foi conduzido para explorar o potencial dos métodos de crioconcentração e nanofiltração na concentração dos componentes do leite de cabra desnatado, bem como otimização destes processos. Assim, esta tese é apresentada em capítulos, sendo o primeiro referente à revisão bibliográfica e os demais referentes aos resultados experimentais obtidos, os quais estão expostos na forma de artigos científicos.

Capítulo 1 – Revisão Bibliográfica abordando os principais temas envolvidos no trabalho: leite de cabra, os processos de crioconcentração e os processos de separação por membranas.

Capítulo 2 – Block freeze concentration of skimmed goat milk: Effect of process on physical, chemical and rheological properties, cujo objetivo foi concentrar o leite de cabra desnatado empregando o método de crioconcentração em blocos, bem como caracterizar as propriedades físico-químicas e reológicas dos concentrados e gelos obtidos.

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Capítulo 5 – Optimization of the vacuum-assisted block freeze concentration process in goat milk concentration, cujo objetivo foi a otimização do processo crioconcentração em

blocos assistida por vácuo na concentração de leite de cabra semi desnatado pela metodologia de superfície de resposta. Os fatores otimizados foram o tempo de congelamento da amostra, a pressão utilizada durante o vácuo, e o tempo de vácuo durante o processo para obter os melhores resultados na recuperação dos sólidos totais.

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CAPÍTULO 1

1 REVISÃO BIBLIOGRÁFICA

1.1 LEITE DE CABRA

A caprinocultura é uma atividade explorada em todos os continentes, devido à capacidade de habituação dos caprinos às condições ambientais diversas e qualidade nutricional do seu leite e subprodutos. De acordo com a Organização das Nações Unidas para Agricultura e Alimentação, a produção mundial de leite de cabra aumentou cerca de 17% nos últimos 5 anos (FAOSTAT, 2017). O leite de cabra é o terceiro tipo de leite mais produzido no mundo, perdendo apenas para o leite de vaca e de búfala (Tabela 1.1). Sua produção faz parte da economia local de muitos países, principalmente nas regiões do Mediterrâneo, Oriente Médio, Europa Oriental e América do Sul (RIBEIRO; RIBEIRO, 2010; SILANIKOVE *et al.*, 2010).

Tabela 1.1 - Produção mundial de leite de diferentes espécies.

Espécie	**Toneladas**
Vaca	659.150.049
Búfala	111.000.836
Cabra	15.262.116
Ovelha	10.366.980
Camela	2.696.337
Total	798.476.317

Fonte: FAOSTAT (2017).

O Brasil é o maior produtor de leite de cabra da América e contribui com 80,47% da produção de leite de cabra sul americana (FAOSTAT, 2017). Com o incentivo de ações conjuntas de governos estaduais, instituições de pesquisa e criadores, o Brasil atingiu em 2016 uma produção estimada de 253.133 toneladas de leite de cabra, envolvendo, em grande parte, empresas de pequeno porte (FAOSTAT, 2017). No entanto, de acordo com Haenlein (2004), a produção de leite de cabra é maior do que observado nos dados oficiais, devido a produção familiar para consumo próprio em países em desenvolvimento não ser reportada. A região Nordeste concentra a maior parte da produção de leite de cabra, seguida das regiões Sudeste e Sul (IBGE, 2017). Em regiões áridas e semiáridas, especialmente para pessoas de baixa renda ou mal nutridas, o leite de cabra tem constituído um alimento essencial como fonte de proteína

de alta qualidade e cálcio, já que nessas regiões as vacas têm dificuldades para serem mantidas (HAENLEIN, 2004; RANI *et al.*, 2017).

O leite pode ser considerado uma fonte de macro e micronutrientes, além de conter vários compostos ativos que desempenham um papel significativo tanto na nutrição quanto na manutenção da saúde (BOZA; SANZ SAMPELAYO, 1997; CEBALLOS *et al.*, 2009). O leite de cabra é um alimento de alto valor nutritivo, com elementos necessários à nutrição humana, como açúcar (lactose), proteínas, gorduras, vitaminas, cálcio, fósforo e outros minerais (COSTA, 2008). Ocupa lugar de destaque dentre os alimentos de origem animal utilizados na alimentação humana, uma vez que fornece também calorias e aminoácidos essenciais em proporções iguais ou superiores aos recomendados pela Organização Mundial de Saúde (OMS) (GOMES *et al.*, 2004).

O Departamento de Inspeção de Produtos de Origem Animal (BRASIL, 2000) denomina leite de cabra como produto oriundo da ordenha completa, ininterrupta, em condições de higiene, de animais da espécie caprina sadios, bem alimentados e descansados. A Instrução Normativa nº 37 (IN37/2000) (BRASIL, 2000) regulamenta as condições de produção e identidade, além dos requisitos mínimos de qualidade do leite de cabra destinado ao consumo humano. Foram estabelecidos como padrões mínimos 2,8 g 100 g^{-1} de proteína bruta, 4,3 g 100 g^{-1} de lactose, 8,2 g 100 g^{-1} de sólidos não gordurosos e 0,7 g 100 g^{-1} de cinzas. Existem grandes variações entre leites de diferentes espécies de mamíferos e entre as diferentes raças de uma mesma espécie. Porém, todas as espécies apresentam os mesmos componentes gerais em diferentes proporções. O leite de cabra é semelhante ao leite de vaca em composição (Tabela 1.2), porém possui propriedades únicas que o distinguem do leite de vaca.

Tabela 1.2 - Composições físico-químicas e valor calórico dos leites de cabra, ovelha e vaca.

Componentes	**Cabra**	**Vaca**
Gordura (g 100 g^{-1})	3,8	3,6
Sólidos não gordurosos (g 100 g^{-1})	8,9	9,0
Lactose (g 100 g^{-1})	4,1	4,7
Sais Minerais (g 100 g^{-1})	0,8	0,7
Proteína (g 100 g^{-1})	3,4	3,2
Caseína (g 100 g^{-1})	2,4	2,6
Valor calórico (Kcal)	70,0	69,0

Fonte: Park *et al.* (2007).

As proteínas do leite de cabra são semelhantes às principais proteínas do leite de vaca em suas classificações gerais, mas diferem em polimorfismos genéticos, frequências e teores (MOATSOU *et al.*, 2005; RAYNAL-LJUTOVAC *et al*., 2008). Como no leite de vaca, as caseínas do leite de cabra são classificadas como κ-, β-, αs1-, αs2- e γ-caseínas e as proteínas do soro do leite como β-lactoglobulina, α-lactalbumina, albumina sérica e imunoglobulinas. O conteúdo de caseína no leite de cabra representa 74% do total de proteínas do leite, as proteínas do soro do leite chegam a quase 17% e a proporção de compostos nitrogenados não protéicos é de 9% (AL-SAADI; SHAKER; USTUNOL, 2014; VERRUCK; DANTAS; PRUDENCIO, 2019). Comparado com o leite de vaca, o leite de cabra possui teor mais alto de β –caseína e um teor mais baixo de αs1-caseína (AMIGO; FONTECHA, 2011). Chatchatee *et al.*, 2001, Ruiter *et al.*, 2006 relataram que as principais proteínas responsáveis pela alergia às proteínas do leite de vaca são a caseína αS1 e β-lactoglobulina. Por essa razão, na maioria dos casos, pessoas alérgicas ao leite bovino respondem bem ao leite caprino (HAENLEIN, 2004; CHACÓN VILLALOBOS, 2005).

A ação da protease estomacal no leite de cabra é mais rápida, devido ao menor tamanho das micelas de caseína no leite de cabra quando comparadas ao leite de vaca (CLARK; GARCÍA, 2017). Por suas proteínas serem mais facilmente digeríveis, os aminoácidos são absorvidos de forma mais eficiente do que os do leite de vaca (PARK, 2009). Além disso, durante as últimas décadas, as proteínas do leite de cabra ganharam cada vez mais atenção especialmente os peptídeos bioativos liberados das proteínas parentais por enzimas digestivas. Estes peptídeos demonstraram exercer atividades biológicas, incluindo imunomoduladores, antibacterianos e atividades antioxidantes (CORREA *et al.*, 2011; AHMED *et al.*, 2015; VERRUCK; DANTAS; PRUDENCIO, 2019). Outra característica relacionada aos menores tamanhos das micelas de caseína é a produção de coalhos mais fracos e menos compactos que os do leite de vaca. (BRANDAO *et al.*, 2017).

A Instrução Normativa nº 37 (BRASIL, 2000) estabelece que o leite de cabra deve apresentar teor de gordura de acordo com sua classificação, sendo: leite de cabra integral, quando não houver qualquer alteração do teor de gordura contido na matéria-prima; leite de cabra padronizado, quando o teor de gordura for acertado para 3%; leite de cabra semidesnatado, quando o teor de gordura for acertado para o intervalo entre 0,6 e 2,9 % e leite de cabra desnatado, quando o teor de gordura não for superior ao limite máximo de 0,5% (BRASIL, 2000). O diâmetro médio dos glóbulos de gordura individuais no leite de cabra é de

2,76 mm e é menor que o diâmetro médio de 3,51 mm do leite de vaca (AMIGO; FONTECHA, 2011). Além do seu menor diâmetro, os glóbulos de gordura no leite caprino são melhores distribuídos na emulsão de lipídios lácteos, em comparação com os glóbulos de gordura no leite bovino (ATTAIE; RICHTER, 2000; HAENLEIN, 2004). Além disso, a gordura pode ser considerada uma excelente fonte de energia para uso em vários processos metabólicos (SANZ CEBALLOS, 2007; CEBALLOS *et al.*, 2009)

O leite de cabra apresenta maiores concentrações de ácidos graxos de cadeia curta e média, devido às diferenças na polimerização do acetato produzido pelas bactérias do rúmen em caprinos (AMIGO; FONTECHA, 2011). A maior proporção de glóbulos de gordura de tamanho pequeno no leite de cabra aumenta a superfície de exposição à ação das lipases, o que proporciona melhor digestibilidade ao leite de cabra em relação ao leite bovino. Além disso, as enzimas lipases são mais efetivas em ácidos graxos de cadeia curta que aos de cadeia longa. (GOLINELLI *et al.*, 2014; DI PINTO *et al.*, 2017). Outra característica da gordura do leite de cabra é que estas não agregam naturalmente após o resfriamento pois não possuem aglutinina, responsável pela agregação de glóbulos de gordura no leite de vaca (AMIGO; FONTECHA, 2011). O leite de cabra geralmente possui mais gordura que o leite bovino e esta diferença tem forte influência no sabor do produto, sendo os ácidos graxos capróico (C6:0), caprílico (C8:0) e cáprico (C10:0) os responsáveis pelo *flavor* característico do leite de cabra e seus derivados (AHMED *et al.*, 2015).

Com relação à sua composição mineral, o leite de cabra contém de 0,70 a 0,85% de minerais. Comparado ao de vaca, o leite de cabra apresenta um nível mais alto de cálcio, fósforo, potássio, magnésio e cloro, e um nível mais baixo de sódio (SILANIKOVE *et al.*, 2010; AMIGO; FONTECHA, 2011). No entanto, a repartição de cálcio, fósforo e magnésio entre as fases solúvel e coloidal do leite é semelhante para ambas espécies. Mais de 50% do magnésio é encontrado na fase solúvel. A concentração de alguns elementos, como zinco, molibdênio e estrôncio, varia muito com a concentração na dieta. O zinco e o manganês são encontrados em grande parte na fase micelar, enquanto que o cobre e o ferro são mais abundantes na fase solúvel do leite (AMIGO; FONTECHA, 2011). Em geral, os níveis dos principais elementos, e o uso nutricional dos mesmos, mostram que o leite de cabra é de qualidade superior ao leite de vaca (MORENO, 1995; HAENLEIN, 2001; CAMPOS *et al.*, 2003; CEBALLOS *et al.*, 2009).

A lactose é o principal carboidrato no leite de cabra, mas é aproximadamente 0,2 a 0,5% menor do que no leite de vaca. Sua concentração pode variar em função do estágio de

lactação, de 4,4 a 4,7%. Outros carboidratos encontrados no leite de cabra incluem oligossacarídeos, glicopeptídeos, glicoproteínas e açúcares nucleotídicos (AMIGO; FONTECHA, 2011). Conforme relatado por Park *et al.* (2007), os oligossacarídeos do leite de cabra têm propriedades antigênicas consideráveis e são valiosos na promoção do crescimento da microbiota em recém-nascidos. A concentração de oligossacarídeos do leite de cabra também é maior do que a do leite de vaca e ovelha (KISKINI; DIFILIPPO, 2013).

O teor vitamínico do leite de cabra é semelhante ao da vaca e leite humano (SILANIKOVE *et al.*, 2010). No entanto, o leite de cabra contém um nível mais alto de vitamina A, o que proporciona ao leite uma cor esbranquiçada. Em contraste, é pobre em ácido fólico e vitamina E (AMIGO; FONTECHA, 2011).

As características especiais relativas à composição do leite de cabra, em termos de seus principais nutrientes, significam que a utilização nutricional é marcadamente maior do que no caso do leite de vaca (CEBALLOS *et al.*, 2009). O uso de leite de cabra e subprodutos tem efeitos benéficos na manutenção da saúde, nas funções fisiológicas e na nutrição de crianças, idosos e pessoas com necessidades médicas específicas, além de pode ser um substituto do leite de vaca por apresentar menor capacidade alergênica (RIBEIRO; RIBEIRO, 2010; SILANIKOVE *et al.*, 2010; DI PINTO *et al.*, 2017; VERRUCK; DANTAS; PRUDENCIO, 2019).

As características físico-químicas e tecnológicas do leite de cabra permitem a sua utilização em uma ampla gama de produtos além do leite fluido, que pode ser consumido cru, pasteurizado ou UHT, ou como na forma de leite em pó e outros produtos industrializados como queijo, leites fermentados, sorvetes e cosméticos (SILVA *et al.*, 2016). Para aumentar qualidade dos derivados de leite de cabra em relação a suas propriedades nutricionais e tecnológicas, métodos de concentração podem ser aplicados. O processamento térmico continua sendo o método mais empregado para a concentração de alimentos. No entanto, a estabilidade do leite de cabra durante os tratamentos térmicos é baixa (AL-SAADI; SHAKER; USTUNOL, 2014). Neste contexto, os processos de concentração que não utilizam calor, preservando os componentes termicamente sensíveis e as propriedades sensoriais do leite, são altamente recomendados.

1.2 CRIOCONCENTRAÇÃO

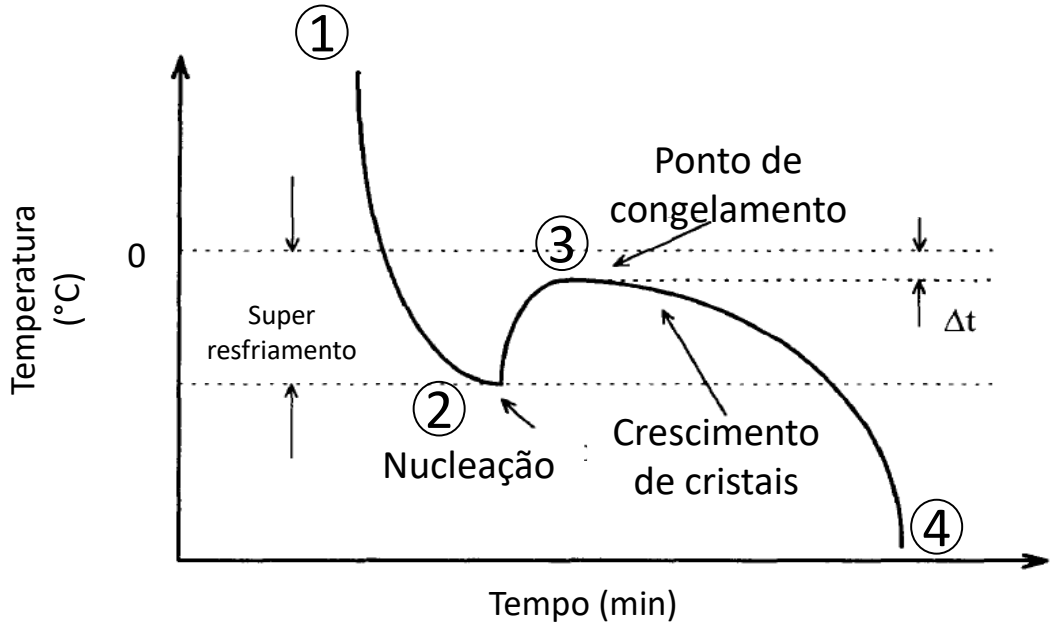
O processo de crioconcentração é uma tecnologia usada para remover parcialmente a água dos alimentos líquidos. Tem como objetivo promover a concentração de produtos alimentares líquidos pelo congelamento e subsequente separação de uma parte da água congelada (BELÉN *et al.*, 2012). A crioconcentração de alimentos líquidos minimiza a perdas de compostos voláteis e termolábeis, sendo possível a obtenção de um produto final com uma qualidade que não pode ser obtida por processos convencionais de concentração utilizados na indústria de processamento de alimentos (SÁNCHEZ *et al.*, 2010; MORENO *et al.*, 2015; ROBLES *et al.*, 2016). Possui algumas vantagens para ser realizada com alimentos, como a baixa deterioração química pela diminuição da atividade enzimática e microbiológica (YEE *et al.*, 2003). Esta tecnologia assegura maior qualidade do produto concentrado (AIDER; DE HALLEUX, 2009), proporcionando a remoção de água mais seletiva do que a evaporação (YEE; WILEY; BAO, 2007). Sánchez *et al.* (2011) afirmam que o processo de crioconcentração permite maior qualidade do produto concentrado e redução de três a quatro vezes nos custos totais (incluindo capital, limpeza e energia) quando comparado aos processos de evaporação. Além disso, o uso da crioconcentração é energeticamente interessante, devido ao baixo calor latente do congelamento da água em comparação com o calor latente da evaporação da água (80 kcal/kg versus 540 kcal/kg) (BALDE; AIDER, 2017).

Um processo de crioconcentração básico compreende duas etapas fundamentais: congelamento da solução, através da cristalização da água e separação de uma fração liquida concentrada e outra de gelo. Com a redução da temperatura da solução, inicia-se o processo nucleação e de cristalização da água. A partir desta etapa, cristais de gelo são formados e separados da solução concentrada (BELÉN *et al.*, 2012). O processo envolve a redução controlada da temperatura da solução abaixo do seu ponto de congelamento, a fim de evitar a temperatura eutética, na qual todos os componentes do produto se solidificam de uma só vez (RAVENTÓS *et al.*, 2007; SÁNCHEZ *et al.*, 2010). No crescimento de cristais ocorre o alargamento dos núcleos formados na fase de nucleação, promovido pela adição de moléculas de água ao núcleo de cristalização. A formação de cristais pode ocorrer de diferentes formas, dependendo do meio. Na presença de solutos em solução, as moléculas de água cristalizam junto ao sólido, levando à formação de cristais irregulares, nos quais várias colunas são formadas a partir do centro de cristalização (COLLA; PRENTICE-HERNANDEZ, 2003). O crescimento destes cristais pode ser controlado pela velocidade de congelamento de um sistema de crioconcentração e pela taxa de calor liberada durante a mudança de fase da solução (líquido-

sólido) e também pela velocidade de transferência de massa (PETZOLD; AGUILERA, 2013). A etapa de cristalização entende-se também como um processo de transferência de calor e massa que ocorre devido a diferença de temperatura entre o fluído e o sistema de resfriamento. Observa-se uma transferência de calor entre o fluído a ser concentrado e a placa refrigerante, ao mesmo tempo que ocorre a transferência de solutos entre a fração de gelo e a solução a ser concentrada. Por fim, os cristais de gelo formados se reorganizam em número, tamanho, forma e orientação (SÁNCHEZ et al., 2009). De acordo com Hartel e Espinel (1993), se cristais de gelo crescem muito rapidamente, cristais irregulares podem ser formados, os quais são difíceis de separar da solução concentrada. Portanto, um equilíbrio entre a taxa de crescimento e a morfologia do cristal pode ser necessário. Segundo Chabarov e Aider (2014), a eficiência de concentração das soluções por crioconcentração depende da pureza do cristal formado, que por sua vez depende da cinética de formação do gelo (núcleos).

A Figura 1.1 apresenta as etapas de resfriamento de uma alimento líquido que ocorrem durante os processos de concentração (SÁNCHEZ, 2011).

Figura 1.1 - Curva adaptada de resfriamento de um alimento líquido.



Fonte: Adaptado de Chen, Chen e Free (1996).

O ponto 1 representa a temperatura inicial do líquido. O intervalo entre os pontos 1 e 2 é onde a temperatura cai abaixo do seu ponto de congelamento sem a formação de cristais de

gelo, chamado de sub resfriamento. O ponto 3 corresponde o início da cristalização e o ponto de congelamento do líquido, onde se observa um aumento da temperatura associado ao calor latente gerado para formar os primeiros cristais de gelo. Quanto maior for a concentração de solutos de um alimento, menor será a temperatura do ponto 3. Após atingir a temperatura no ponto 3 os cristais de gelo começam a crescer, a solução começa a ser concentrada e a temperatura do sistema começa a cair novamente até chegar ao ponto 4 que corresponde a temperatura eutética do sistema. No ponto 4 os solutos e a água cristalizam simultaneamente não havendo mais aumento da concentração ou seja, não ocorre a separação de uma fase concentrada. Este comportamento de resfriamento é observado para todos os alimentos líquidos, no entanto o ponto de congelamento e a temperatura eutética são diferentes para cada alimento.

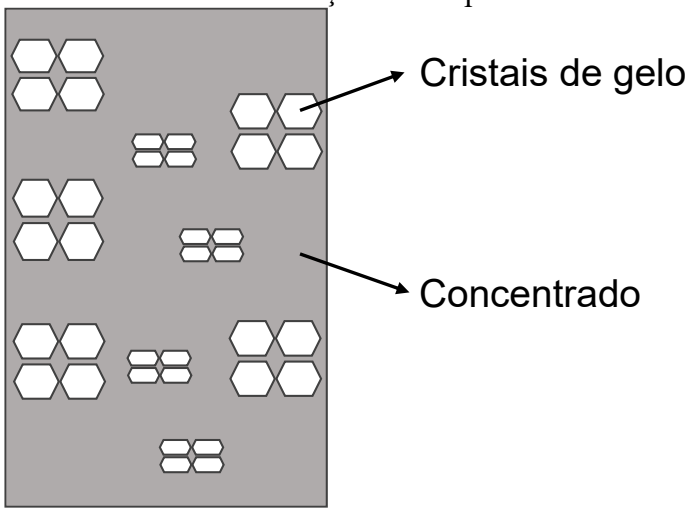
Existem diferentes métodos para a aplicação da tecnologia de crioconcentração, porém, são três os mecanismos básicos de formação dos cristais de gelo: crioconcentração em suspensão, crioconcentração em filme, e crioconcentração em blocos.

1.2.1 Crioconcentração em suspensão

O processo de crioconcentração em suspensão é o processo mais utilizado na indústria (ROBLES *et al.*, 2016). Este método envolve a formação de cristais de gelo em um trocador de calor de superfície raspada. Em um tanque cristalizador agitado, os cristais de gelo crescem até que eles atinjam um tamanho apropriado para que possam então ser separados do líquido concentrado através de colunas de filtragem e lavagem, no entanto o tamanho dos cristais de gelo formados é limitado (Figura 1.2) (MIYAWAKI *et al.*, 2005; SÁNCHEZ *et al.*, 2009).

A crioconcentração em suspensão é uma técnica eficiente em termos de pureza do gelo e aumento da concentração de uma solução (QIN *et al*., 2006; VAN DER HAM; SECKLER; WITKAMP, 2004). No entanto, requer sistemas complexos para separação de gelo e muitas partes móveis, o que aumenta os custos iniciais e operacionais (AIDER; HALLEUX, 2009; MIYAWAKI *et al*., 2005; SÁNCHEZ *et al*., 2009). Desenvolvimentos recentes têm se concentrado em minimizar as peças móveis, substituir o trocador de calor de superfície e melhorar as colunas de lavagem (PETZOLD; AGUILERA, 2013; SÁNCHEZ *et al*., 2009; VAN DER HAM; SECKLER; WITKAMP, 2004).

Figura 1.2 - Processo de cristalização em suspensão.



Fonte: Adaptado de Miyawaki *et al.* (2005).

1.2.2 Crioconcentração em filme

A crioconcentração em filme consiste na formação de um único filme/camada de gelo em uma superfície resfriada (Figura 1.3). A separação do gelo é mais fácil em relação a técnica de suspensão, pois, o filme permanece aderido à superfície e as etapas de crescimento e separação de gelo são realizadas usando o mesmo equipamento. Neste processo a transferência de calor é afetada através da camada de gelo (MIYAWAKI *et al*., 2005). Dois processos diferentes foram desenvolvidas para a crioconcentração em filme: crioconcentração progressiva e crioconcentração de filme descendente.

Figura 1.3 - Processo de cristalização em filme.

Fonte: Adaptado de Miyawaki *et al.* (2005).

1.2.2.1 Crioconcentração progressiva

Na crioconcentração progressiva ocorre a formação de um único cristal de gelo sob uma superfície refrigerada, a qual fica em contato direto com a solução a ser concentrada (AIDER; HALLEUX, 2009; GULFO *et al.*, 2013). A separação de gelo e solução concentrada ocorre porque o gelo adere à superfície, enquanto o líquido concentrado flui ao longo da superfície (SÁNCHEZ *et al.*, 2009). O emprego de agitação mecânica neste processo auxilia na diminuição da retenção de sólidos na fração de gelo. Parâmetros como fluxo da solução, concentração da solução inicial e temperatura de resfriamento são primordiais para reduzir a retenção de sólidos na camada de gelo (MIYAWAKI *et al.*, 2005; OJEDA *et al.*, 2017).

1.2.2.2 Crioconcentração de filme descendente

Nesta técnica de crioconcentração de filme descendente a solução a ser concentrada recircula em uma placa vertical resfriada. Nesse processo, o fluido a ser concentrado flui para baixo sobre uma superfície gelada, o que causa a cristalização do gelo e o crescimento adicional dos cristais de gelo na superfície (SÁNCHEZ *et al*., 2009). A separação do gelo e da solução concentrada ocorre porque o gelo adere à superfície, enquanto o líquido concentrado flui ao longo da superfície (SÁNCHEZ *et al*., 2011). A simplicidade da separação do gelo é uma vantagem dessa técnica.

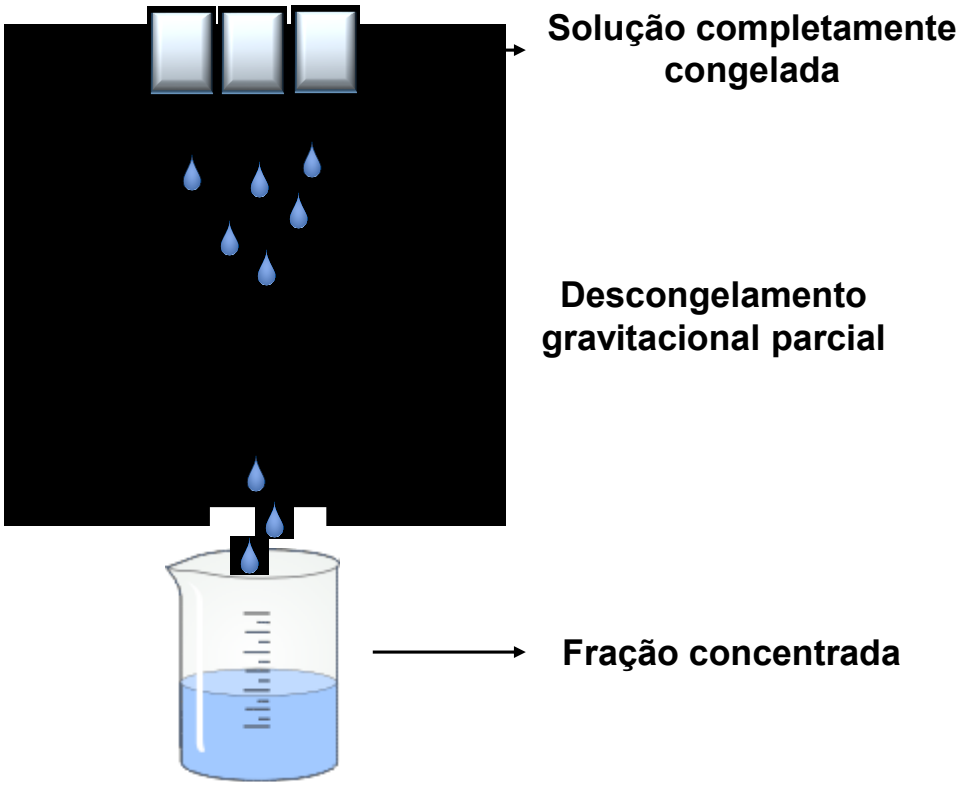
1.2.3 Crioconcentração em blocos

A crioconcentração em blocos tem como base o completo congelamento de uma solução líquida. Esta solução congelada é então descongelada parcialmente e a fração concentrada é separada da fração de gelo por descongelamento gravitacional assistida ou não por outras técnicas para melhorar a eficiência da separação (AIDER; HALLEUX, 2008). Sob essas condições, o bloco de gelo atua como uma carcaça sólida através da qual a fração concentrada passa (AIDER; HALLEUX, 2009). A eficiência desse processo é dependente da taxa de impurezas no gelo (AIDER; HALLEUX; AKBACHE, 2007). Além disso, o processo pode ser repetido em ciclos sucessivos para aumentar a eficiência da concentração (AIDER; OUNIS, 2012). No entanto, sua principal limitação é a quantidade relativamente alta de solutos

aprisionados na fase de gelo nos terceiro e quarto estágios de crioconcentração (CHABAROV; AIDER, 2014). Neste processo o controle da temperatura de descongelamento é importante, para que a quantidade de sólidos retidos no gelo seja minimizada (AIDER; HALLEUX, 2009). A Figura 1.4 apresenta um esquema básico de crioconcentração em blocos.

Na indústria alimentícia, a crioconcentração em bloco já foi utilizada para concentração de extrato de café (MORENO *et al.*, 2015; ROBLES *et al.*, 2016), sucos de frutas (AIDER; HALLEUX, 2008; PETZOLD *et al.*, 2015), açúcares (PETZOLD; NIRANJAN; AGUILERA, 2013), extrato de erva mate (BOAVENTURA *et al.*, 2013), soro de tofu (BENEDETTI *et al.*, 2015). Em relação aos derivados lácteos vem sendo utilizada na concentração de soro de leite (AIDER; HALLEUX; AKBACHE, 2007; AIDER; HALLEUX; MELNIKOVA, 2009; SÁNCHEZ *et al.*, 2011; CANELLA *et al.*, 2018) e leite de vaca (BALDE; AIDER, 2016; MUÑOZ *et al.*, 2017). A eficiência desta técnica é determinada por estes autores em função da pureza do gelo obtido e também da quantidade de solutos recuperados.

Figura 1.4 - Esquema básico do processo de crioconcentração em blocos.



1.2.3.1 Crioconcentração em blocos assistida por vácuo

Recentes inovações da crioconcentração têm sido associadas com processos de apenas uma etapa (crioconcentração em blocos e progressiva), uma vez que se caracteriza pela simplicidade de separação em apenas uma etapa e a simplicidade do equipamento (PETZOLD; AGUILERA, 2009; MIYAWAKI; KATO; WATABE, 2012). Especificamente, na crioconcentração em blocos, a etapa de separação é realizada gravitacionalmente, mas para aumentar a eficiência do processo técnicas assistidas ou denominadas forças externas como ultrassom, centrifugação ou vácuo podem ser utilizadas. Petzold *et al.* (2016) mencionaram que o processo de vácuo é semelhante ao movimento quando crianças removem o açúcar de picolés por sucção, ou seja, o processo de sucção aumenta a extração do concentrado pelos canais entre os cristais de gelo, melhorando os parâmetros do processo, como eficiência e recuperação de solutos (PETZOLD; NIRANJAN; AGUILERA, 2013). O uso do vácuo como técnica assistida na crioconcentração em blocos vem sendo estudado em soluções salinas (HSIEH, 2008), sacarose (PETZOLD; NIRANJAN; AGUILERA, 2013; PARDO; SÁNCHEZ, 2015), extratos de café (MORENO *et al.*, 2014), vinho tinto (PETZOLD *et al.*, 2016), suco de laranja (ORELLANA-PALMA *et al.* 2017a) e suco de mirtilo (ORELLANA-PALMA *et al.* 2017b). O leite pode ser facilmente concentrado através da técnica de evaporação, contudo, Aider e Ounis (2012) confirmaram que a sua estabilidade é afetada em temperaturas acima de 70°C podendo causar a agregação irreversível de proteínas sensíveis ao calor. Ao utilizar o método de crioconcentração em substituição às técnicas que empregam calor para concentrar, seria possível diminuir os danos aos compostos termo sensíveis presentes no leite e ainda promover o aumento do teor de proteínas e lactose, agregando valor à matéria prima e diversificando a produção no setor lácteo (AIDER; OUNIS, 2012).

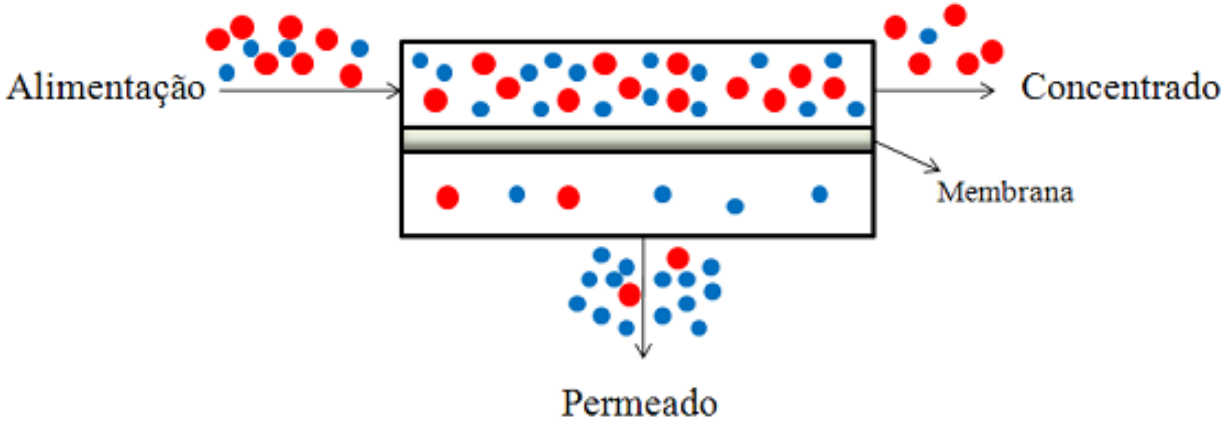
1.3 PROCESSO DE SEPARAÇÃO POR MEMBRANAS (PSM)

A crescente preocupação com a busca de produtos alimentícios de melhor qualidade e a valorização de seus subprodutos, vêm privilegiando o surgimento de processos alternativos de separação e concentração não convencionais. Os processos de separação por membrana surgiram como uma tecnologia convencional desde o início dos anos 90. Por apresentar inúmeras vantagens, como alta eficiência, design compacto e modular, operação fácil e menor consumo de energia, a tecnologia de membranas tornou-se uma das técnicas de separação industrial mais importantes a serem aplicadas de forma expansiva em vários setores, como

indústrias químicas, farmacêuticas e biotecnológicas (ADAMS; HURT; BARBANO, 2015; LIU, et al., 2016), incluindo a recuperação de componentes valiosos de produtos agrícolas e alimentares (ECHAVARRÍA *et al*., 2011; NATH; DAVE; PATEL, 2018). De modo geral, as separações por membrana são realizadas sob condições físico-químicas leves de temperatura, pressão e tensão de cisalhamento, mantendo assim a atividade biológica máxima dos compostos a serem recuperados e as propriedades inerentes ao produto original (CASSINI *et al.*, 2010). Além disso, trabalham sem nenhum agente de massa de extração, como solventes ou aditivos químicos, evitando a contaminação do produto e a necessidade de purificação subsequente (PATEL; NATH, 2013).

Os processos de separação por membrana representam uma classe de processos que utilizam membranas sintéticas para a separação de substâncias dos mais variados tipos e tamanhos. As membranas artificiais servem como uma barreira seletiva para uma filtração em escala molecular de uma solução, quando aplicada alguma força motriz (STRATHMANN, 1990) visando à concentração e/ou fracionamento de componentes de uma mistura (HABERT; BORGES; NÓBREGA, 2006). Nos PSM a alimentação é dividida em duas correntes distintas, o concentrado ou retentado, constituído pelos solutos que não ultrapassam a membrana por apresentarem partículas maiores do que o tamanho médio dos poros e o permeado, que é o fluido que atravessa a membrana (Figura 1.5) (ORDÓÑEZ, 2005; CHEN *et al.*, 2008).

Figura 1.5 - Esquema do processo de separação por membranas.



Fonte: Silva (2010).

Dois tipos de parâmetros são normalmente empregados para caracterizar membranas: parâmetros de natureza morfológica e parâmetros relativos à suas propriedades. No caso de membranas porosas, características como a distribuição de tamanho de poros, porosidade

superficial e espessura representam parâmetros morfológicos relevantes. Para membranas densas, as características físico-químicas envolvendo o polímero usado e as substâncias a serem separadas, bem como a espessura do filme polimérico, são parâmetros importantes. Entretanto, parâmetros como permeabilidade e capacidade seletiva são adotados como parâmetros característicos do processo, independentemente do tipo de membrana (PESSOA JR, KILIKIAN, 2005).

As membranas podem ser fabricadas a partir de diversos materiais, sendo as membranas orgânicas (poliméricas) e as inorgânicas (cerâmica) as mais utilizadas. As membranas orgânicas podem ser fabricadas com acetato de celulose, poliamida, polisulfona, polietersulfona, polifluoreto de vinilideno, dentre outros (HABERT; BORGES; NÓBREGA, 2006; HE *et al.*, 2008). Essas membranas apresentam altos fluxos, boa rejeição a sais, tolerância a altas temperaturas e variações de pH, boa resistência ao cloro e à compactação, variando de acordo com o tipo de membranas que são constituídas. Com relação ao transporte de moléculas, este ocorre em etapas através da membrana: sorção das moléculas na superfície da membrana, difusão através da membrana e dessorção das moléculas no lado do permeado (MULDER, 2000; HABERT; BORGES; NÓBREGA, 2006). Em função disso, a retenção é expressa como razão nominal que se refere a um diâmetro de corte (*cut off*), definido como o valor da massa molar das moléculas para o qual a membrana apresenta coeficiente de rejeição de 95% (CHERYAN, 1998). Na indústria de laticínios, as membranas orgânicas são comumente usadas para processos de concentração devido seus baixos custos de investimento e de substituição (MEYER; MAYER; KULOZIK, 2015).

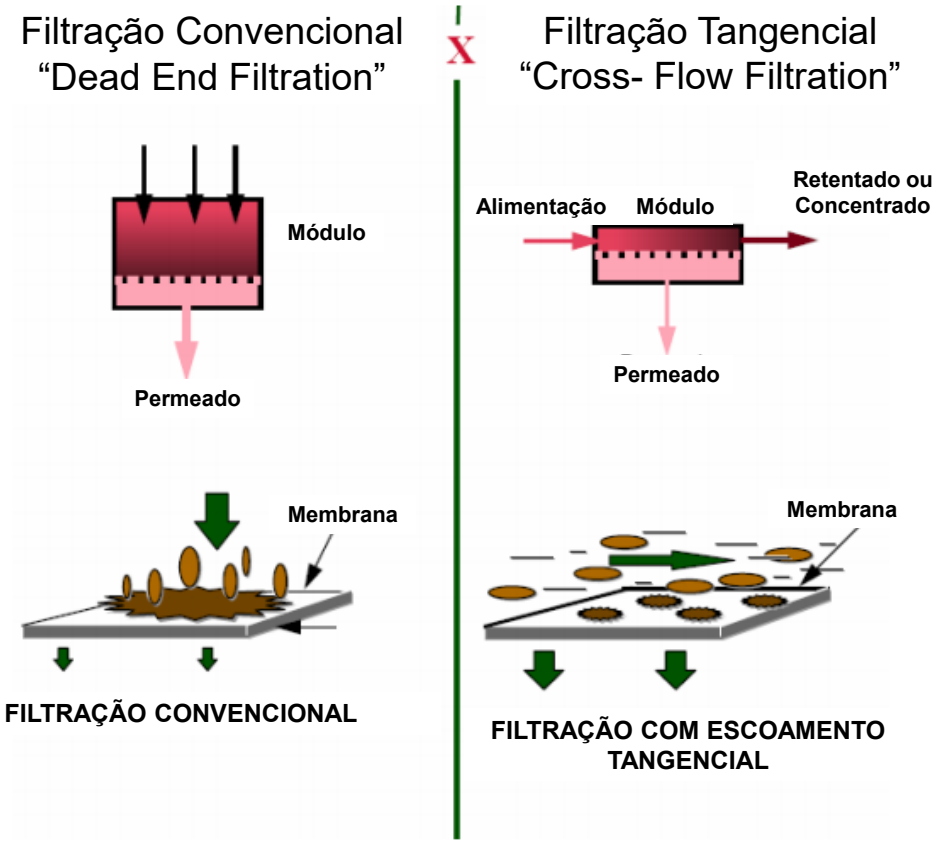
1.3.1 Configuração de filtração

Diferentes configurações hidrodinâmicas podem ser utilizados no processo de separação por membranas; o método de filtração convencional, denominado “dead-end”, e a filtração tangencial “crossflow” (Figura 1.6) (HABERT; BORGES; NOBREGA, 2006).

Na filtração convencional, a solução passa perpendicularmente ao filtro, gerando uma única corrente, denominada permeado ou filtrado. As partículas retidas no filtro formam rapidamente uma “torta” na sua superfície, o que resulta numa diminuição considerável do fluxo de permeado e exige frequentes paradas no processamento para limpeza ou troca do filtro. Assim, esta configuração é viável somente para trabalhar com suspensões que contêm baixo

teor de sólidos (DZIEZAK, 1990). Na filtração tangencial o fluido escoa paralelamente à superfície da membrana, possibilitando que a maior parte dos solutos depositados na membrana seja arrastada continuamente com a corrente de alimentação. Desta forma, é possível utilizá-la para soluções cuja concentração de solutos é mais alta, trabalhar com maior volume de matéria-prima e operar em sistemas contínuos. Constitui a configuração mais utilizada industrialmente, pois permite a manutenção do fluxo e a maior eficiência do processo de separação (HABERT; BORGES; NÓBREGA, 2006). A filtração tangencial permite a separação de compostos nas escalas de micro, molecular e iônica (SONDHI; BHAVE; JUNG, 2003).

Figura 1.6 - Filtração convencional (dead-end filtration) e filtração tangencial (crossflow filtration).



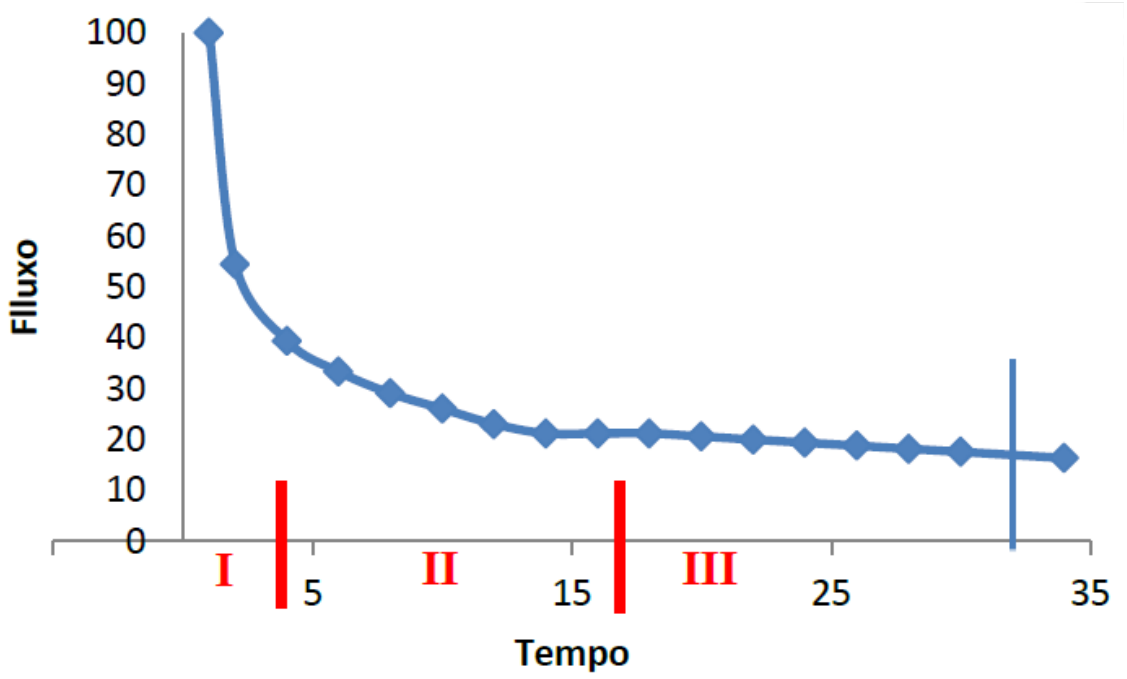
Fonte: Adapatado de Habert, Borges e Nóbrega (2006).

1.3.2 Declínio do fluxo

Durante o PSM, normalmente ocorre um declínio do fluxo do permeado com o tempo. Esse declínio geralmente é resultado de alguns fenômenos decorrentes do processo, tais como

a formação da camada gel polarizada, polarização por concentração e efeito *fouling* (MIRANDA, 2005). A formação de uma camada de gel ocorre quando na superfície da membrana há uma precipitação de macromoléculas. Esta camada ocasiona um prejuízo no funcionamento hidrodinâmico do sistema, pois constitui em mais uma barreira para o fluxo de permeação (DAUFIN *et al.*, 2001; ALICIEO *et al.*, 2007). Já a polarização por concentração ocorre pelo acúmulo de solutos próximo à superfície da membrana, por transporte convectivo, onde parte do solvente é removido do fluido, o que ocasiona uma maior concentração de solutos na superfície da membrana em relação à da solução. Esse aumento da concentração de solutos na superfície da membrana é responsável pela diferença observada entre o fluxo de permeado final e inicial, comparando-se com o fluxo de água pura (SCHÄFER; FANE; WAITE, 2006). O *fouling* é caracterizado pela deposição e acúmulo de solutos na superfície e dentro dos poros da membrana, por adsorção ou bloqueio físico dos poros (AL-AMOUDI; LOVITT, 2007). A intensidade do *fouling* depende do tipo da membrana, da concentração e solutos presentes na solução, bem como da temperatura, pH e tempo de operação. A redução no fluxo permeado é representada por uma curva, como ilustrada na Figura 1.7, composta por três estágios. No primeiro estágio tem-se uma rápida redução do fluxo permeado devido à polarização por concentração, sendo a redução do fluxo permeado reversível neste estágio. Em um segundo estágio, o fluxo permeado continua decaindo em função do *fouling* ocasionado pelo bloqueio dos poros e adsorção de componentes na membrana. No segundo estágio a redução de fluxo permeado é irreversível. Por fim, no terceiro estágio ocorre a consolidação do *fouling* em um estágio quase estacionário, ou também denominado de estágio pseudo-estacionário, pois o fluxo permeado passa a cair mais lentamente. (MARSHALL; DAUFIN, 1955; GIRARD; FUKUMOTO, 2000).

Figura 1.7 - Estágios do declínio do fluxo permeado com o tempo.



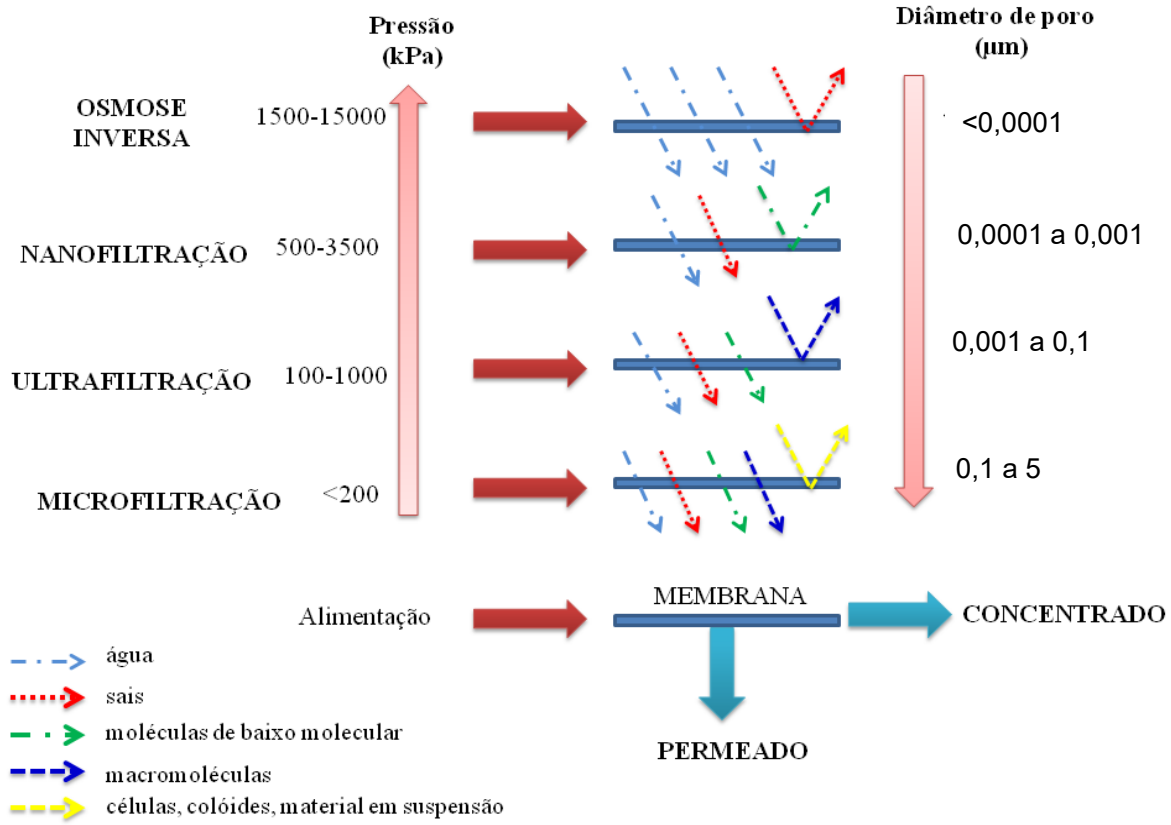
Fonte: Adaptado de Marshall e Daufin (1995).

Devido à acumulação de substâncias na superfície da membrana, obstruindo seus poros e fazendo com que haja uma redução do fluxo de permeado, os sistemas com membranas requerem limpezas periódicas. Esses sistemas possibilitam a limpeza química periódica, denominado CIP (clean in place), e a periodicidade irá depender do *fouling* que se formará durante o processo de filtração. Os ciclos de limpeza química podem variar de 45 minutos a 24 horas e são capazes de restaurar o fluxo das membranas para valores próximos aos iniciais (SCHNEIDER; TSUTIYA, 2001). No entanto, a substituição das membranas pode ser recomendada dependendo do *fouling* formado (PETRUS, 1997; RODRIGUES, 2002).

1.3.3 Tipos de processos de separação por membrana

Dentre os PSM, destacam-se a microfiltração, ultrafiltração, nanofiltração e osmose inversa, que utilizam pressão como força motriz de acordo com o tamanho dos poros das membranas, permitindo ou não a passagem de determinados componentes (MIERZWA *et al.*, 2008) (Figura 1.8).

Figura 1.8 - Classificação dos processos de separação por membranas quanto à sua seletividade.



Fonte: Adaptado de Mierzwa *et al.* (2008).

Os PSM, especialmente a microfiltração (MF) vem sendo utilizada em processos de clarificação de bebidas, como substituto às técnicas convencionais de centrifugação e filtração a vácuo para remoção de sólidos em suspensão; e também para estabilização microbiológica de bebidas (pasteurização a frio) (CARNEIRO *et al.*, 2002; SALAZAR *et al.*, 2007).

A ultrafiltração (UF), que compreende membranas com tamanho de poro de 0,001 a 0,1 µm, vem sendo utilizada na purificação e fracionamento de soluções (HABERT; BORGES; NOBREGA, 2006). Na indústria de alimentos é utilizada para a filtração de suco, para separar ou concentrar componentes de uma solução ou mistura, tais como açúcares, biomoléculas, polímeros e partículas coloidais. Além disso, vem sendo empregada na separação e concentração de componentes do leite, soro de leite e derivados (CUARTAS-URIBE *et al.*, 2009; BERGILLOS-MECA *et al.*, 2015; MORENO-MONTORO *et al.*, 2015; LIU *et al.*, 2017; NG; DUNSTAN; MARTIN, 2018).

Nanofiltração é um processo de separação com membranas capaz de efetuar separações de moléculas com massa molar média entre o limite superior da ultrafiltração e o

limite inferior da osmose inversa, combinando os mecanismos de convecção da ultrafiltração com aqueles tipicamente característicos de transporte através de membranas densas de osmose reversa (OTERO *et al.*, 2006; NATH; DAVE; PATEL, 2018). As primeiras membranas de nanofiltração foram projetadas pela Filmtec Corporation® por volta de 1983 com o objetivo de remover compostos iônicos em sistemas de tratamento de água do mar em indústrias de petróleo (CRITTENDEN *et al.*, 2012). Na indústria de alimentos já vem sendo utilizada para recuperação de água, fracionamento de lactose, concentração de extratos de frutas e plantas, desmineralização de leite e soro de leite, dentre outros (BALYAN; SARKAR, 2018; SANTIBÁÑEZ *et al*. 2019; SUÁREZ *et al.* 2009; ZHAO *et al.*2019) Sua principal característica é a capacidade de separação de íons mono e divalentes, bem como alta rejeição para os compostos orgânicos com massa molar entre 100-500 g mol^{-1} (HE *et al.*, 2008). Além disso, a tecnologia de nanofiltração pode ser aplicada para separar materiais anfotéricos (aminoácidos, proteínas, etc.), visto que a maioria das membranas de nanofiltração comerciais mostraram desempenho de rejeição diverso para solutos a diferentes valores de pH (WANG *et al.*, 2009). A nanofiltração se distingue dos demais processos, pois tem a capacidade de rejeição de íons negativos multivalentes, rejeição de até 70% de cloreto de sódio (NaCl) e a rejeição de partículas sem cargas, materiais dissolvidos e íons positivos sendo dependentes do tamanho e do formato dos mesmos. Ou seja, a eficiência de um processo de NF não é somente dependente do tamanho das partículas presentes na solução, mas também das cargas moleculares (SCHÄFER; FANE; WAITE, 2006). Devido às suas características, associadas ao baixo consumo de energia e aos altos fluxos obtidos, as membranas de nanofiltração tornam-se úteis para fracionamento e remoção seletiva de solutos a partir da filtração de soluções complexas (OTERO *et al.*, 2006) como o leite.

A pesquisa e o interesse nas membranas de nanofiltração abriram portas para novas oportunidades na indústria láctea. Desde então, várias aplicações foram desenvolvidas utilizando membranas de nanofilatração em soro de leite e leite (REKTOR; VATAI, 2004; ATRA *et al.*, 2005; SUAREZ *et al.*, 2006; PRUDÊNCIO *et al.*, 2014; PINTO *et al.*, 2015; CHANDRAPALA *et al.*, 2016). No entanto, não há relatos na literatura em relação a utilização da nanofiltração em leite de cabra.

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CAPÍTULO 2

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Block freeze concentration as a technique aiming the goat milk concentration: fate of physical, chemical, and rheological properties

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ABSTRACT

In the face of the results scarcity for the goat milk processing using emerging and innovative technologies, the results obtained in the present study are relevant, and may in the future be extremely important for goat milk industry. Therefore, block freeze concentration technique was used to concentrate skim goat milk until three stages. The effects of freeze concentration on skim goat milk properties were evaluated by the analysis of total solids content, lactose content, total protein content, casein content, whey protein content, mineral content, and density. The color parameters of concentrate and ice fractions were also evaluated according to the CIELab color scale, and according to the rheological parameters. As the freeze concentration stages progressed, the total solids content, total protein, casein, and whey protein contents increased in both concentrate and ice fractions. In all stages, it was possible to note that the lactose content showed an equilibrium between both fractions. The densities values of both fractions also increased by increasing of the freeze concentration stages. Block freeze concentration obtained concentrates from skim goat milk with a whiteness index similar to whole milk. Overall, all concentrate and ice fractions showed tendency a greenish and yellowish color. The transition from Newtonian to non-Newtonian behavior was observed for concentrates and ices from second and third stages, respectively. Power Law and Herschel-Buckley models fitted to describe the behavior of the flow of all concentrate and ice fractions. The results generated in this study showed that concentrates from stage 1 and 2 demonstrated a promising product to be used by dairy industries.

Keywords: Skim goat milk; block freeze concentration; goat milk concentrate; physical-chemical properties; rheological properties.

1 INTRODUCTION

The production of goat milk and its processing constitutes an economic activity of increasing importance due to the high nutritional interest of goat milk. Although goat milk production has been relatively minor compared to bovine milk, the world production of goat milk increased 17% between the years 2000 and 2016 (FAOSTAT, 2017). Goat milk and its products are important in human nutrition and have become a part of the current trend of healthy eating around the world (HASSAN *et al.*, 2014; SOSNOWSKI *et al.*, 2016; YANGILAR, 2013). Besides that, the increase in demand for new dairy products with high added value in sophisticated market niches has stimulated goat milk production and trade (FONSECA *et al.*, 2013). The goat milk has high added value because it is a source of proteins of excellent quality, due to the proportion of essential amino acids (OLALLA *et al.*, 2009; YANGILAR, 2013). The importance of this milk is also intensifying because utilization of bovine milk had become a common cause of human food allergy (RANI *et al.*, 2017). The difference in protein composition of the goat milk in relation to cow milk, particularly regarding the casein fractions, made the goat milk be considered less allergenic (ALBENZIO; SANTILLO, 2011; BRANDÃO *et al.*, 2017) and more digestible (BRUZANTIN *et al.*, 2016; IBRAHIM *et al.*, 2017; RANI *et al.*, 2017) in comparison with the cow milk. The goat milk has some particular properties that confer technological advantages with others species. The lower content of αs_1-casein in the goat milk results in softer gel products, with a higher water holding capacity and with a lower viscosity (YADAV *et al.*, 2016).

The high nutritional value of goat milk throughout the world, including Brazil, has generated a need for a variety of techniques to preserve or increase these properties. According to Clark and Garcia (2017) these studies have increased because of interest in intensive dairy goat production and value-added goat milk. However, emerging technologies, such as the freeze concentration process, is still innovative for goat milk. Even though that this process has the advantage of low energy usage with an effective concentration, for the goat milk industry, application of this process has been limited due to the dominance of more traditional technologies. However, it is known that industrial processes, such as heat treatment, homogenization, concentrating and spray drying, applied to goat milk can also affect their properties. However, the submission of goat milk to the freeze concentration process, in order to evaluate its effect on the properties of this milk specie, is innovative.

In the case of the block freeze concentration technique, the whole sample is frozen once as an ice block and then thawed slowly by gravity. One of the main advantages of this technique is related to the absence of moving parts (stirrers, pumps), which makes it a promising technology in relation to their operating costs. This technique is highlighted studies focusing on improving the performance in solutes recovery but not for goat milk. According to Petzold *et al.* (2015) this process makes it possible to produce food concentrates with high quality by recovering a food solute based on the separation of pure ice crystals from a freeze-concentrate aqueous phase. When compared with traditional concentration processes, such as evaporation, the freeze concentration not only shows some significant potential advantages for the production of a concentrate where no vapor/liquid interface exists, but also can protect thermally fragile food compounds (PETZOLD *et al.*, 2015). According to Sánchez *et al.* (2011), the freeze concentration reduces around three times the total cost off the process (including capital, cleaning and energy), when compared to the evaporation or reverse osmosis processes. The concentration of solutes retained in the ice formed determines the efficiency of this process (AIDER; HALLEUX, 2009). The freeze concentration process has already been used successfully by our research group for other products such as whey (CANELLA *et al.*, 2018), milk (MUÑOZ *et al.*, 2017), yerba mate extract (BOAVENTURA *et al.*, 2013), and tofu whey (BENEDETTI *et al.*, 2015). But additional research into methods to generate new products from goat milk will be essential in management of the global dairy industry. In this sense, the purpose of the present study was to evaluate the physicochemical and rheological properties of skim goat milk submitted to the block freeze concentration process.

2 MATERIAL AND METHODS

2.1 MATERIAL

Skim goat milk (Caprilat®, CCA Laticínios, Rio de Janeiro, Brazil) (8.46 ± 0.01 g total solids 100 g^{-1}, 2.91 ± 0.05 g total protein 100 g^{-1}, 3.93 ± 0.05 g lactose 100 g^{-1} and 0.89 ± 0.03 g ash 100 g-1) was used as feed material. All reagents were of analytical grade.

2.2 PROTOCOL OF THE SKIM GOAT MILK FREEZE CONCENTRATION PROCEDURE

The freeze concentration procedure used to concentrate the skim goat milk was carried out by applying the block freeze concentration technique, according to the process proposed by Canella *et al.* (2018). An initial volume of 5 L of skim goat milk was separated into five batches of 1 L. Each batch of skim goat milk was fractionated in plastic containers and they were frozen at - 20 ± 2 °C in a freezer unit (Consul, Biplex CRD41D, São Bernardo do Campo, Brazil). After the skim goat milk has been completely frozen, 50 % of the initial volume was defrosted at room temperature (20 ± 2 °C), obtaining two fractions, the concentrate goat milk (CG1) and the ice (I1). The defrosted liquid that is the concentrate goat milk (CG1) was frozen again at - 20 ± 2 °C, and used as feed solution in the second stage. This procedure was repeated until the third stage. After each stage, a portion of concentrate (CG1, CG2, and CG3), and ice fractions (I1, I2 and I3) was collected and stored at - 20 ± 2 °C until physical, chemical and rheological analysis.

2.3 PHYSICOCHEMICAL ANALYSIS

The skim goat milk, concentrates (CG1, CG2, and CG3), and ice (I1, I2 and I3) fractions were analyzed in relation to the following physicochemical analysis: pH measurement; total solids content; lactose content; protein content (total protein, true protein, casein and whey protein content); and ash and mineral fractions.

The measurements of pH were obtained using a pH meter (PHS-3 BW, BEL, Piracicaba, São Paulo, Brazil). The total solids content (g 100 g^{-1}) were analyzed through the drying of the samples until reaching a constant weight at 103 ± 2°C (IAL, 2008). The ash content (g 100 g^{-1}) were analyzed through a gravimetric method (IAL, 2008).

The lactose content (g 100 g^{-1}) were obtained using a spectrophotometer FT-NIR model MPA (Multi Purpose Analyzer) (Bruker Optik, Ettlingen, Germany) operating with a spectral acquisition program OPUS version 7.0 (Bruker Optik, Ettlingen, Germany). The measurements were made by near-infrared Fourier transform (FTNIR) spectra of diffuse reflectance. Each vial containing the samples was positioned in the diffuse reflectance accessory and the NIR spectra

were collected in the spectral range of 9.000 to 4.000 cm^{-1} at a nominal resolution of 16 cm^{-1} in transmission mode. Each spectrum was the average of 500 scans.

The total protein, true protein, casein and whey protein content (g 100 g^{-1}) were analyzed by the Kjeldahl method (N x 6.38) (AOAC, 2005). The determination of true protein was performed by Kjeldahl method, after previous preparation of samples, using the trichloroacetic acid at 15% for coagulation of all milk proteins that were removed by filtration, and the filter paper with the proteins coagulated was submitted to analyses.The fractions of milk casein were determined by the precipitation of milk casein of the samples in pH = 4.6 using acetic acid and sodium acetate solution. After precipitation, casein was separated by filtration and determined by Kjeldahl method. The whey protein was determined through the subtraction of casein content from the true protein.

2.4 DENSITY

The density of skim goat milk, concentrates (CG1, CG2, and CG3), and ice (I1, I2 and I3) fractions was determinate by methodology described by AOAC (2005). A glass pycnometer (Gay-Lussac's pycnometer) (previously equilibrated to constant weight at 25 °C) was used. The density (g mL^{-1}) realized in triplicate was calculated using the following Equation 1:

$$\rho_S = \frac{(m3-m1)}{(m2-m1)x\rho H_2O} \quad (1)$$

where ρ_S is the density of solutions (g mL^{-1}), m1 is the mass of empty pycnometer (g), m2 is the mass of pycnometer with water (g), m3 is the mass of pycnometer with samples (g), and ρH_2O is the density of water.

2.5 COLOR ANALYSIS

The color of the skim goat milk, and all fractions obtained by the freeze concentration process (CG1, CG2, CG3, I1, I2, and I3) were determined using a colorimeter Minolta Chroma Meter CR-400 (Konica Minolta, Osaka, Japan). The colorimeter was calibrated with a white standard plate and adjusted to operate with D65 lightning and 10º of observation angle. The CIELab color scale was used to measure the L^*, b^* and a^* parameters, that indicates the

luminosity (variation from black to white), variation from yellow (+ b^*) to blue (- b^*) and variation from red (+ a^*) to green (- a^*), respectively. The total difference of color (ΔE) between the measured values of skim goat milk and each concentrates (CG1, CG2, and CG3), and ice (I1, I2 and I3) fractions was calculated according to Okpala *et al.* (2010), as described in Equation 2,

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (2)$$

where ΔL^* is the difference of luminosity between the measured values of skim goat milk and each concentrates (CG1, CG2, and CG3), and ice (I1, I2 and I3) fractions, while Δa^* represents the intensity of the red color and Δb^* the intensity of the yellow color. The value of Hue angle (h^o) and Chroma (C^*) were determined using Equation 3 and 4, respectively. Five replicates were performed for each sample, and the mean values were reported.

$$h^* = tan^{-1}(b^*/a^*) \quad (3)$$

$$C^* = \sqrt{(a^*)^2 + (b^*)^2} \quad (4)$$

2.6 FREEZE CONCENTRATION PARAMETERS CALCULUS

The freeze concentration parameters calculus was evaluated by concentration factor (CF), process efficiency (*eff*), and validations of results. CF was calculated in agreement with the method suggested by Aider and Ounis (2012). The CF of each freeze concentration stage was determinate as a function of the increase of total solids content, using the following Equation 5:

$$CF(\%) = \frac{TS_n}{TS_0}\ x\ 100 \quad (5)$$

where TS_n is the total solids (g 100 g^{-1}) content of the concentrate goat milk from each freeze concentration stage and TS_0 is the total solids (g 100 g^{-1}) content of the initial goat milk.

The process efficiency (*eff*) was calculated based on the increase of total solids (TS) in the concentrate goat milk (g 100 g^{-1}) relative to the TS remaining in the ice (g 100 g^{-1}) from each freeze concentration stage (n), as described in the Equation 6:

$$PE\ (\%) = \frac{\text{TS in the CG}_n - TS \text{ in the I}_n}{\text{TS in the CG}_n}\ x\ 100 \qquad (6)$$

To validate the experimental results obtained, the experimental mass balance of each stage was calculated and compared to the theoretical value (BELÉN *et al.*, 2012; BURDO *et al.*, 2008; SÁNCHEZ *et al.*, 2011) using the following Equation 7:

$$w_{pred} = \frac{\text{Ci} - \text{Cc}}{\text{Cg} - \text{Cc}} \qquad (7)$$

where *Wpred* is the predicted ice mass ratio (kg ice/kg skim goat milk), Ci is the total solids content of initial skim goat milk (g 100 g^{-1}), Cc is the total solids content of the concentrate fraction (g 100 g^{-1}) and Cg is the total solids content of the ice fraction (g 100 g^{-1}).

The root mean square deviation was calculated from Equation 8 to determine the deviation between experimental and theoretical data.

$$RSM\ (\%) = 100\sqrt{\frac{\Sigma\left(\frac{w_{exp} - w_{pred}}{w_{exp}}\right)^2}{N}} \qquad (8)$$

where Wexp and Wpred are the ratio of experimental and predicted ice mass, respectively, and N is the number of test repetitions.

2.7 RHEOLOGICAL ANALYSIS

The measurements of rheological properties of skim goat milk, concentrates (CG1, CG2, and CG3), and ice (I1, I2 and I3) fractions were carried out using a Thermo Haake DC 10 rotational viscosimeter (model VT 550, Thermo Haake, Karlsruhe, Germany), with concentric cylinders (NV ST 807-0713 CE and NV 807-0702), and collected using the software program Pro Rheowin® (version 2.93, Haake). Experimental studies were conducted on skim

goat milk, concentrate (CG1, CG2, and CG3), and ice fraction (I1, I2, and I3) under controlled temperature at 5 °C. The control of temperature was realized through water circulation in a temperature controlled bath (Phoenix P1, Thermo Haake, Karlsruhe, Germany) and coupled to the equipment. An aliquot volume of 10 mL of samples was loaded into the cup of viscometer and the data were obtained. The flow curves were generated by a linearly increased shear rate of 0 s^{-1} to 2000 s^{-1} (upward curve) and 2000 s^{-1} to 0 s^{-1} (downward curve) during 3 minutes. To accurately evaluate the most adapted flow behavior, the models most frequently employed in food characterization (VÉLEZ-RUIZ *et al.*, 1997) were used to describe the shear rate–shear stress data expressed by Equations 9 and 10.

$$\text{Power} - \text{law:} \quad \sigma = K(\dot{\gamma})^n \tag{9}$$

$$\text{Herschel} - \text{Bulkley:} \quad \sigma = \sigma_0 + K\dot{\gamma}^n \tag{10}$$

where σ is shear stress (Pa), $\dot{\gamma}$ is shear rate (s^{-1}), K is consistency index (Pa s^{-1}), n is flow behavior index, and σ_0 is yield stress (Pa).

2.8 STATISTICAL ANALYSIS

The data were expressed as means and standard deviations. One-way analyses of variance (ANOVA) and Tukey's studentized range (5 % significance) were carried out to test for any significant differences between the results. The validity of the results was evaluated based on the coefficient of determination (R^2). The data also were submitted to linear correlation (R) from regression analysis. All statistical analyses were performed using the software STATISTICA 13.3 software (TIBCO Software Inc., Palo Alto, CA).

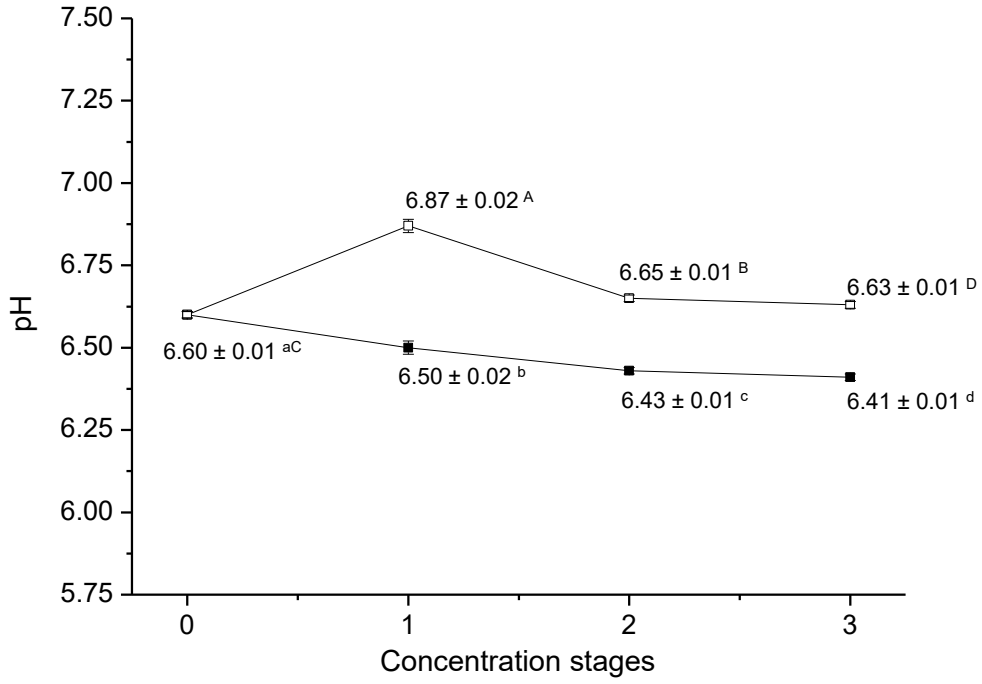
3 RESULTS AND DISCUSSION

3.1 PHYSICAL AND CHEMICAL PARAMETERS

The freeze concentration of skim goat milk resulted in a change of pH (Fig. 3.1). The concentrate fractions (CG1, CG2, and CG3) showed lower pH values ($P < 0.05$) than initial

skim goat milk. In addition, with the evolution of the stages the pH values decreased ($P < 0.05$) in both fractions. Balde and Aider (2016) noted the freeze concentration process of skim milk resulted in a slightly lower pH in concentrate fractions compared to pH of the fractions non-concentrate.

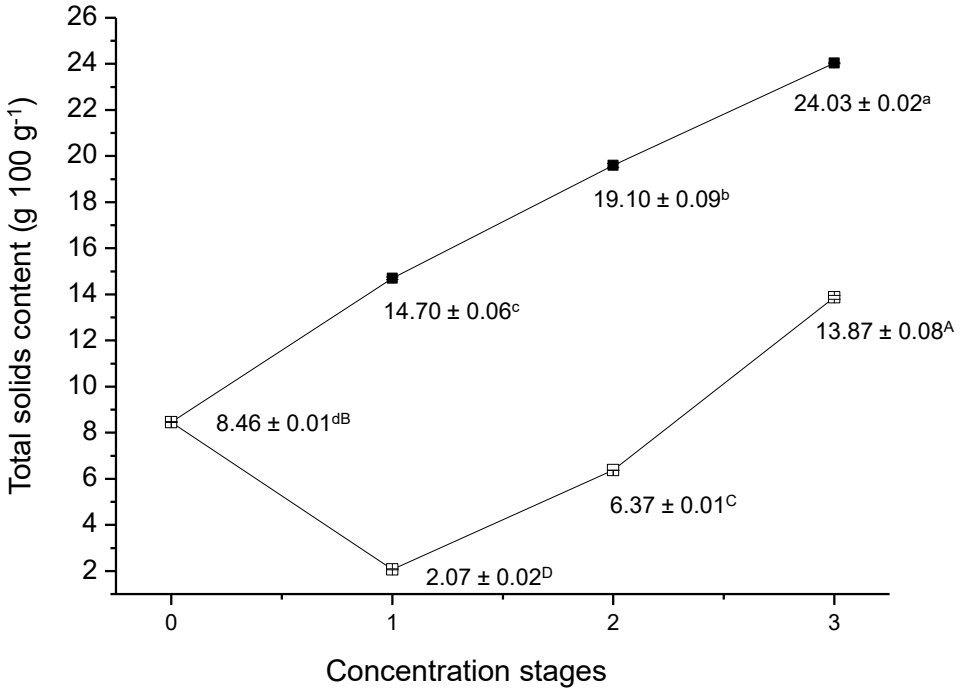
Figure 3.1 - Evolution of the pH in the concentrated (■) and ice (□) fraction as function of the freeze concentration stage from skim goat milk.



The total solids contents of the initial skim goat milk, concentrates (CG1, CG2, and CG3), and ice fractions (I1, I2, I3) are showed in Figure 3.2. By increasing the freeze concentration stages, the total solids content in the concentrates fractions increased ($P < 0.05$) almost linearly presenting a correlation coefficient of $R^2 = 0.9936$. The concentrate goat milk reached values observed represent an increase of total solids content of 174, 226, and 284% at the first, second, and third freeze concentration stages, respectively, compared with the initial total solids content. These results are in agreement with those reported by Aider and Ounis (2012) and Balde and Aider (2016) during freeze concentration of skim cow milk. During the freeze concentration process, the total solids content of I1 and I2 decreased ($P < 0.05$) in comparison with initial skim goat milk. However, in the third stage, the total solids content in I3 increased significantly ($P < 0.05$). According to Aider and Ounis (2012), this behavior is

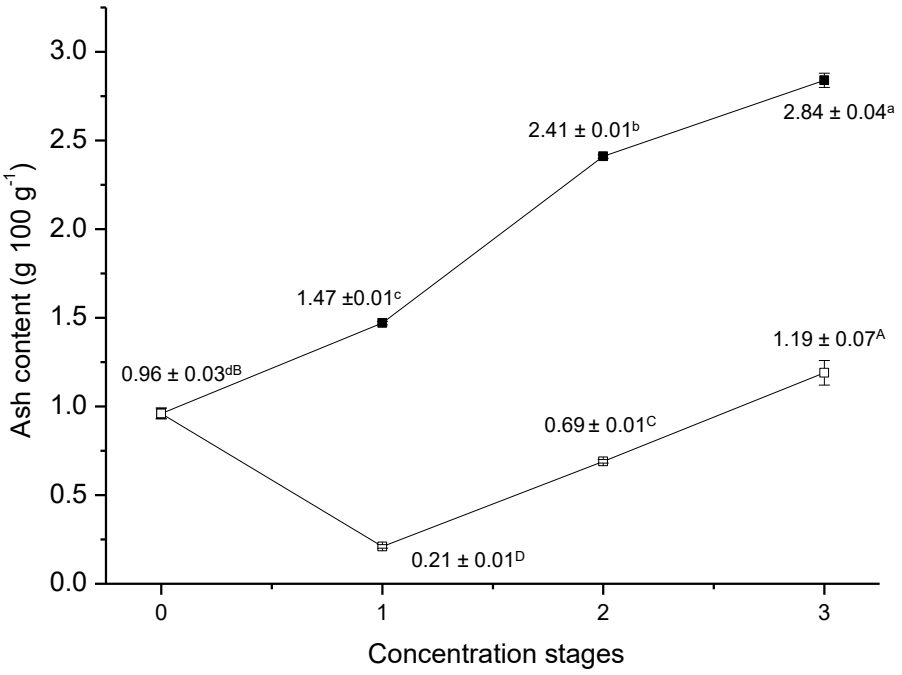
common, and could be associated to the presence of high total solids content. This is because when ice crystals are formed according to a hexagonal structure, the concentration of solution total solids is increased in the interstitial region between the growing ice crystals, which difficult the elimination of solids from the ice fraction (AIDER; OUNIS, 2012; OKAWA *et al.*, 2009).

Figure 3.2 - Evolution of the total solids content (g 100 g^{-1}) in the concentrated (■) and ice (□) fraction as function of the freeze concentration stages of skim goat milk.



The ash content and the mineral fractions of skim goat milk, concentrate (CG1, CG2, and CG3), and ice fractions (I1, I2, I3) are shown in Figure 3.3. In both concentrate and ice fraction, the ash content evolution showed similar behavior to that observed in the total solids content (Fig. 2). The values founded to ash content in concentrate fraction were higher than the ash content reported by Balde and Aider (2016) during freeze concentration of skim cow milk. Ceballos *et al.* (2009), Raynal-Ljutovac *et al.* (2008), and Yadav *et al.* (2016) credit this behavior to the fact that the goat milk contains mineral contents, as for example, such as Ca, P, K, Mg, at higher levels than the cow milk.

Figure 3.3 - Evolution of the ash content (g 100 g^{-1}) in the concentrated (■) and ice (□) fraction as function of the freeze concentration stages of skim goat milk.



Lactose content of skim goat milk, concentrate (CG1, CG2, and CG3), and ice fractions (I1, I2, and I3) are shown in Figure 3.4. In the concentrate fractions, it was observed that the lactose content presented a slight increase ($P < 0.05$) in CG1 and CG2. At the third freeze concentration stage, lactose content of CG3 not showed ($P > 0.05$) difference with the CG2. In the ice fraction, lactose content followed different behaviors depending on the freeze concentration stage. The lactose content of I1 increased ($P < 0.05$) compared to its content in the initial skim goat milk. At the second freeze concentration stage, lactose content decreased ($P < 0.05$) presenting similar values to the initial skim goat milk. However, at the third stage of freeze concentration, lactose content in the I3 increased slightly ($P < 0.05$) again. Aider and Ounis (2012) reported that when freeze concentration is used, the increase of the total solids content in the concentrate phase is accompanied by an increase in the amount of lactose entrapped in the ice crystals. Although the total solids content increased with the increase of freeze concentration stages, the lactose content was not accumulated in the only one fraction, once it is water soluble. Indeed, there were variations of the lactose content in the concentrate and ice fractions of skim goat milk, however, the values remained close to the lactose content of the initial skim goat milk. These results suggest that the concentrate fractions of skim milk

goat, can be used in the manufacture of lactose intolerant products without increasing their costs with the extra addition of lactase enzymes.

Figure 3.4 - Evolution of the lactose content (g 100 g^{-1}) in the concentrated (■) and ice (□) fraction as function of the freeze concentration stages of skim goat milk.

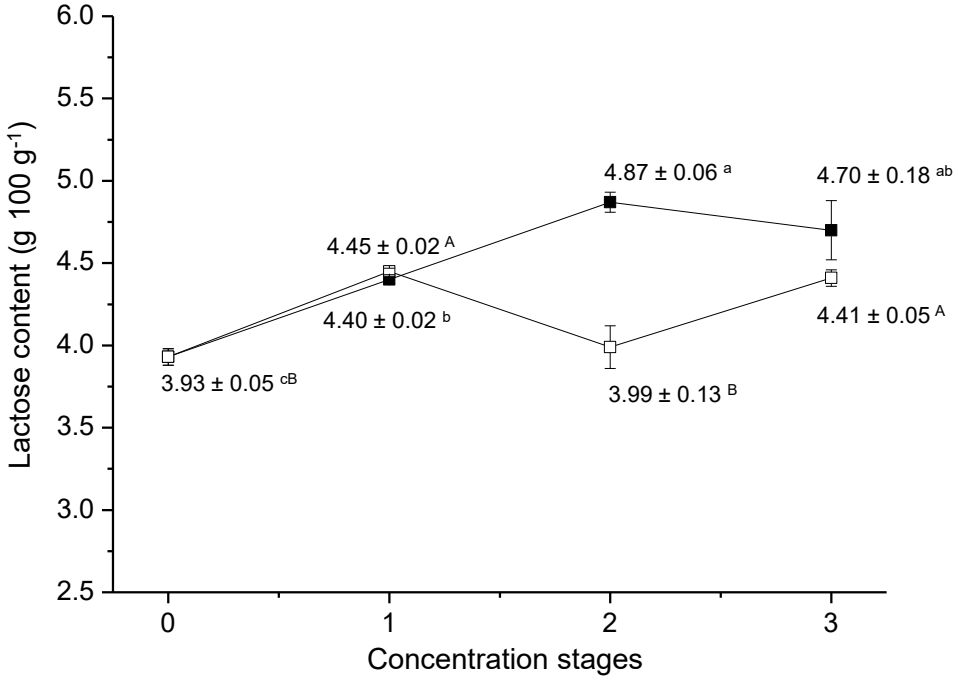


Table 3.1 exhibits the total protein, casein, and whey protein content of skim goat milk, concentrate (CG1, CG2, and CG3), and ice fractions (I1, I2, I3). The results obtained showed the freeze concentration stages had a significant effect on total protein, casein, and whey protein content in the concentrate and ice fractions ($P < 0.05$). The increase of the total proteins content in the concentrate fraction followed a quasilinear kinetics (R^2=0,994). The results obtained in the present study are also in agreement to the results observed by Aider and Ounis (2012) and Balde and Aider (2016), in skim cow milk freeze concentrate. However, the total protein content of CG2 and CG3 was higher than total protein content observed by Moreno-Montoro *et al.* (2015) and Domagala and Kupiec (2003) in skim goat milk and raw goat milk concentrate by ultrafiltration, respectively. In the ice fractions, total protein content decreased ($P < 0.05$) in the I1 and I2 when compared with the total protein content of initial skim goat milk. Thereafter, an increase ($P < 0.05$) in total protein content was observed in I3. The high concentration of total solids in this fraction (Fig. 2) was favorable to high protein inclusion in the I3.

Table 3.1- Total protein, casein and whey protein content of skim goat milk, concentrated (CG1, CG2, and CG3), and ice (I1, I2, and I3) fractions.

	Samples	Total protein (g 100 g^{-1})	Casein (g 100 g^{-1})	Whey protein (g 100 g^{-1})
	Skim goat milk	2.91 ± 0.05^{dB}	1.98 ± 0.01^{dB}	0.63 ± 0.10^{dB}
Stage 1	CG1	5.14 ± 0.02^{c}	3.18 ± 0.05^{c}	1.11 ± 0.05^{c}
	I1	0.72 ± 0.01^{D}	0.49 ± 0.01^{D}	0.17 ± 0.01^{C}
Stage 2	CG2	6.93 ± 0.01^{b}	4.47 ± 0.05^{b}	1.88 ± 0.17^{b}
	I2	2.20 ± 0.03^{C}	1.35 ± 0.01^{C}	0.54 ± 0.01^{B}
Stage 3	CG3	8.53 ± 0.02^{a}	5.32 ± 0.22^{a}	2.43 ± 0.18^{a}
	I3	5.02 ± 0.01^{A}	2.72 ± 0.03^{A}	1.03 ± 0.09^{A}

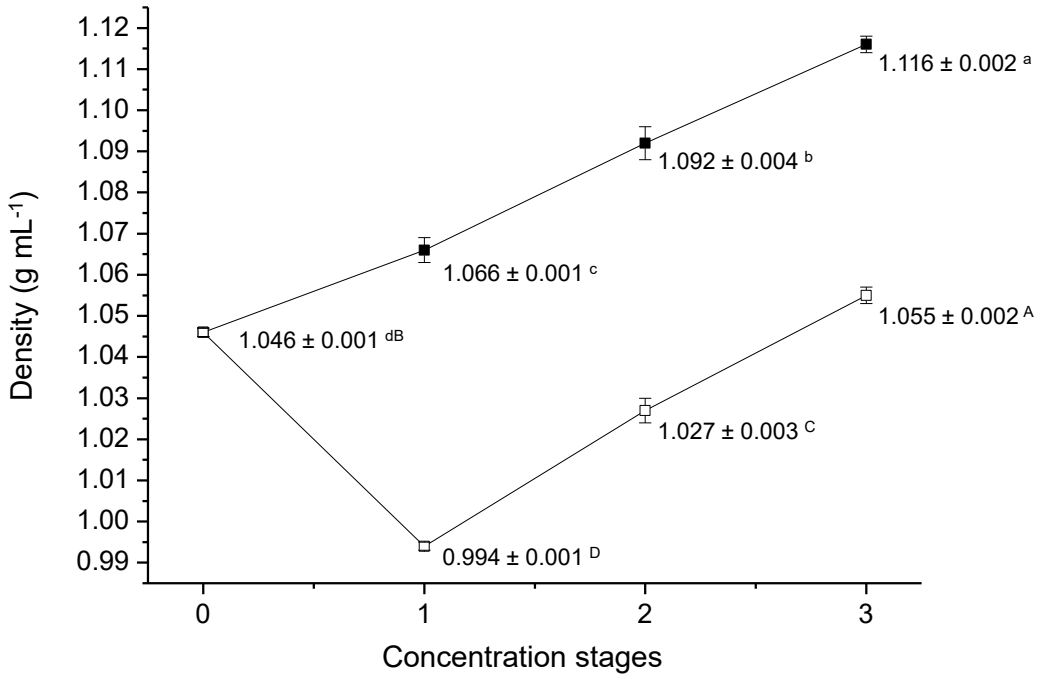
[a,b,c] Within a column, means ± standard deviations with different superscript lowercase letters denote significant differences ($P < 0.05$) between the skim goat milk and the concentrated fraction of each freeze concentration stage. [A,B,C] Within a column, means ± standard deviations with different superscript uppercase letters denote significant differences ($P < 0.05$) between the skim goat milk and the ice fraction of each freeze concentration stage. CG1: concentrated fraction of first freeze concentration stage. I1: ice fraction of first freeze concentration stage. CG2: concentrated fraction of second freeze concentration stage. I2: ice fraction of second freeze concentration stage. CG3: concentrated fraction of third freeze concentration stage. I3: ice fraction of third freeze concentration stage.

Casein and whey protein content showed the same behavior of protein content, presenting an increase ($P < 0.05$) in the concentrate fractions (CG1, CG2, and CG3) with the increase of freeze concentration stages. As observed in total protein data, the casein and whey protein content decreased in the I1 and I3, when compared with the casein and whey protein content of initial skim goat milk, and only I3 presented casein and whey protein content higher than initial skim goat milk. According to Anema (2008) and Balde and Aider (2016), the volumetric fraction of the suspended material is determined mainly by proteins such as casein micelles, dissociated caseins, native whey proteins and denatured whey proteins.

3.2 DENSITY

As observed in total solids content, by increasing the freeze concentration stages, the densities of concentrate (CG1, CG2 and CG3) increased ($P < 0.05$), since the total solids content are directly related to the density of a solution (Fig. 3.5). The densities of I1 and I2 also decreased ($P < 0.05$) in relation to density of initial skim goat milk (1.046 ± 0.001 g mL^{-1}). With the concentration change of the ice fraction, the milk density decreases as the amount of solvent increases and the amount of solute (milk components) remains constant or decreases. In addition, the increase of density in I3 ($P < 0.05$) corroborated with the increase of total solids content of this ice fraction. These results are in good agreement with those reported by Aider *et al.* (2007) from studies with the freeze concentration of milk whey.

Figure 3.5 - Evolution of the density (g mL^{-1}) in the concentrated (■) and ice (□) fraction as function of the freeze concentration stages of skim goat milk.



3.3 COLOR MEASUREMENTS

The Table 3.2 shows the color parameters of the initial skim goat milk, concentrate goat milk (CG1, CG2, and CG3), and ice fractions (I1, I2, and I3). As it can be observed on the data, the whiteness (L^*) increased ($P < 0.05$) until the second stage, with a small decrease at the third stage. Only the I3 showed higher ($P < 0.05$) whiteness than the initial skim goat milk. This behavior could be due to the total solids content in the final ice fraction. The values of L* determined in this study for concentrate fraction was higher than observed by Balde and Aider (2016) for skim cow milk freeze concentrate. The reason for goat milk to be whiter than bovine milk is that goats convert all β-carotene into Vitamin A. According to Bermúdez-Aguirre *et al.* (2009), in addition to nutritional properties, sensorial characteristics in milk, such as color, are very important for consumer acceptance. The whiteness (L^*) of milk has been shown to have a positive influence on consumer preference, which is why consumers have the more attractive for blades with visual properties close to the whole milk (BERMÚDEZ-AGUIRRE *et al.*, 2009; OWENS *et al.*, 2001).

All concentrate and ice fractions presented negative values for the *a** parameter, indicating a tendency to greenish color. However, this tendency was higher for CG3 and I3. According to Nozière *et al.*, (2006) *a** color parameter of the milk could be influenced by the natural pigment concentration presented in milk, such as the riboflavin. This pigment was a green compound present in the aqueous phase which is found in significant quantities in goat milk (PARK *et al.*, 2007).

The initial skim goat milk and the concentrate fractions showed increase ($P < 0.05$) of *b** parameter, indicating a tendency for yellowish color with the increase of freeze concentration stages. According to Quiñones *et al.* (1997) and Balde and Aider (2016), the increase of the yellowness of milk is associated with the increase of protein content. This trend was confirmed by the protein determination presented in Table 3.1, where only the I1 showed negative values for *b**, and a tendency to the bluish color, due to the low protein content in this fraction. This parameter behavior also confirm the fact verified for the angle hue behavior.

As the Chroma C* parameter indicates the degree of saturation, purity or intensity of the color, it was observed that the C* of CG3 and I3 showed higher values ($P < 0.05$) than all the others fractions. Therefore, it was possible to note that, as the stages increased, the color intensified. The same behavior was observed to the ΔE^* value of concentration fractions, which increased ($P < 0.05$) with de increase of freeze concentration stages. At the same time, with the evolution of stages de total difference of color between ice fractions and skim goat milk decreased ($P < 0.05$), probably due to the total solids content in this fractions.

Table 3.2 - Color parameters of skim goat milk, concentrated (CG1, CG2, and CG3), and ice (I1, I2, and I3) fractions.

Samples		Color parameters					
		*L**	*a**	*b**	*C**	*h**	Δ*E*
Skim goat milk		73.5 ± 0.25^{cB}	-3.22 ± 0.03^{bB}	4.19 ± 0.01^{dB}	5.28 ± 0.02^{dB}	127.55 ± 0.28^{aC}	-
Stage 1	CG1	77.89 ± 0.25^{b}	-3.23 ± 0.01^{b}	7.64 ± 0.01^{c}	8.30 ± 0.02^{c}	112.88 ± 0.04^{b}	5.54 ± 0.10^{c}
	I1	56.27 ± 0.06^{D}	-2.11 ± 0.02^{A}	-3.20 ± 0.01^{D}	3.84 ± 0.01^{C}	236.63 ± 0.23^{A}	18.71 ± 0.05^{A}
Stage 2	CG2	78.66 ± 0.07^{a}	-3.02 ± 0.01^{a}	10.27 ± 0.01^{b}	10.71 ± 0.01^{b}	106.41 ± 0.05^{c}	8.03 ± 0.05^{b}
	I2	68.26 ± 0.10^{C}	-3.54 ± 0.03^{C}	1.02 ± 0.03^{C}	3.69 ± 0.02^{D}	164.28 ± 0.14^{B}	6.06 ± 0.08^{B}
Stage 3	CG3	77.85 ± 0.12^{b}	-3.37 ± 0.05^{c}	11.42 ± 0.03^{a}	11.91 ± 0.04^{a}	106.47 ± 0.19^{c}	8.46 ± 0.07^{a}
	I3	74.53 ± 0.13^{A}	-3.51 ± 0.03^{C}	6.20 ± 0.03^{A}	7.12 ± 0.03^{A}	119.55 ± 0.24^{D}	2.31 ± 0.08^{C}

^{a,b,c} Within a column, means ± standard deviations with different superscript lowercase letters denote significant differences ($P < 0.05$) between the skim goat milk and the concentrated fraction of each freeze concentration stage.

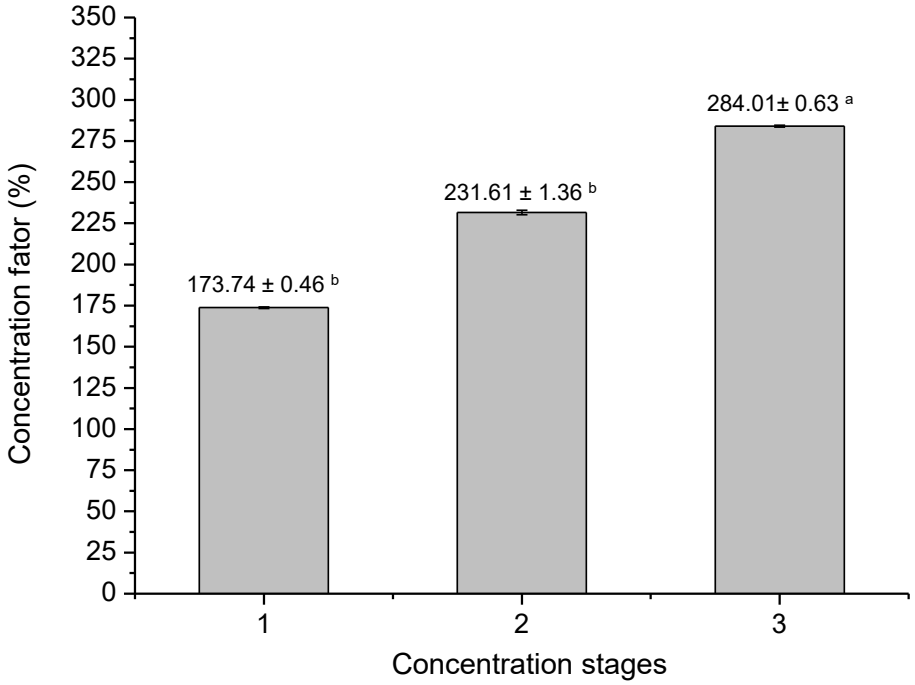
^{A,B,C} Within a column, means ± standard deviations with different superscript uppercase letters denote significant differences ($P < 0.05$) between the skim goat milk and the ice fraction of each freeze concentration stage.

CG1: concentrated fraction of first freeze concentration stage. I1: ice fraction of first freeze concentration stage. CG2: concentrated fraction of second freeze concentration stage. I2: ice fraction of second freeze concentration stage. CG3: concentrated fraction of third freeze concentration stage. I3: ice fraction of third freeze concentration stage.

3.4 BLOCK FREEZE CONCENTRATION PERFORMANCE

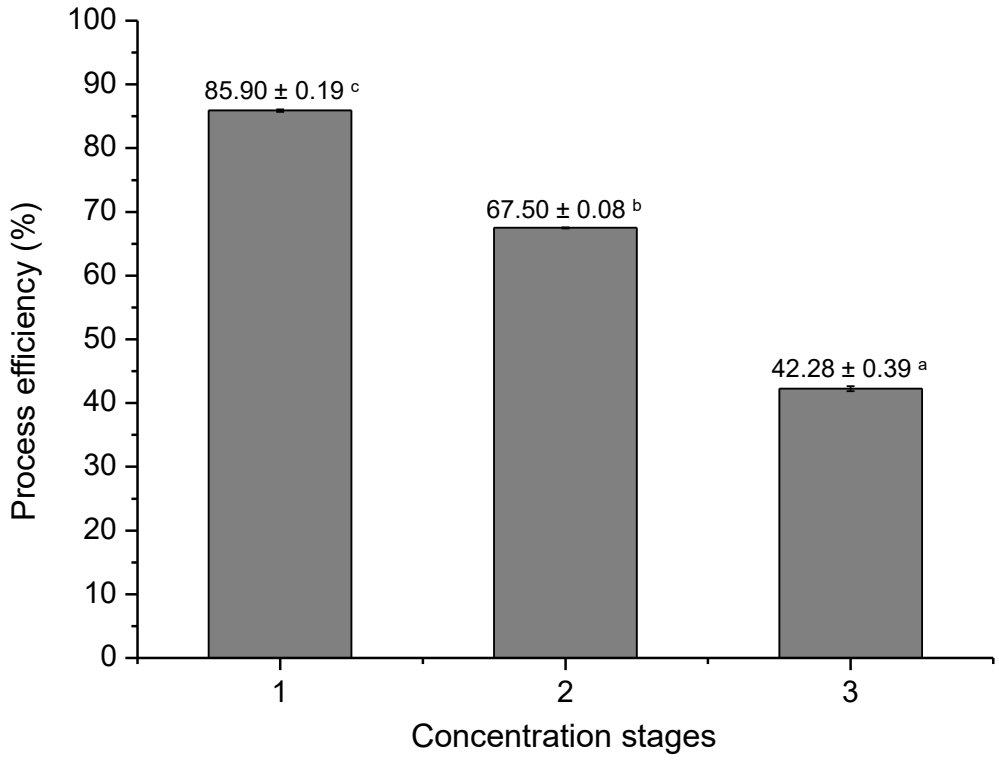
The performance of block freeze concentration procedure was determined from the total solids content obtained in concentrates and ice fractions. A progressive increase in concentration factor (CF) ($P < 0.05$) was observed with the increase of freeze concentration stages (Fig. 3.6). This behavior is expected once the CF is directly related with the total solids, increasing its value with the increase of the total solids content. A similar performance was observed by Aider *et al.* (2007), Aider and Ounis (2012), and Muñoz *et al.* (2017) in freeze concentration of cheese whey, skim milk, and whole milk, respectively.

Figure 3.6 - Evolution of concentration factor (CF) as function of the freeze concentration stages of skim goat milk.



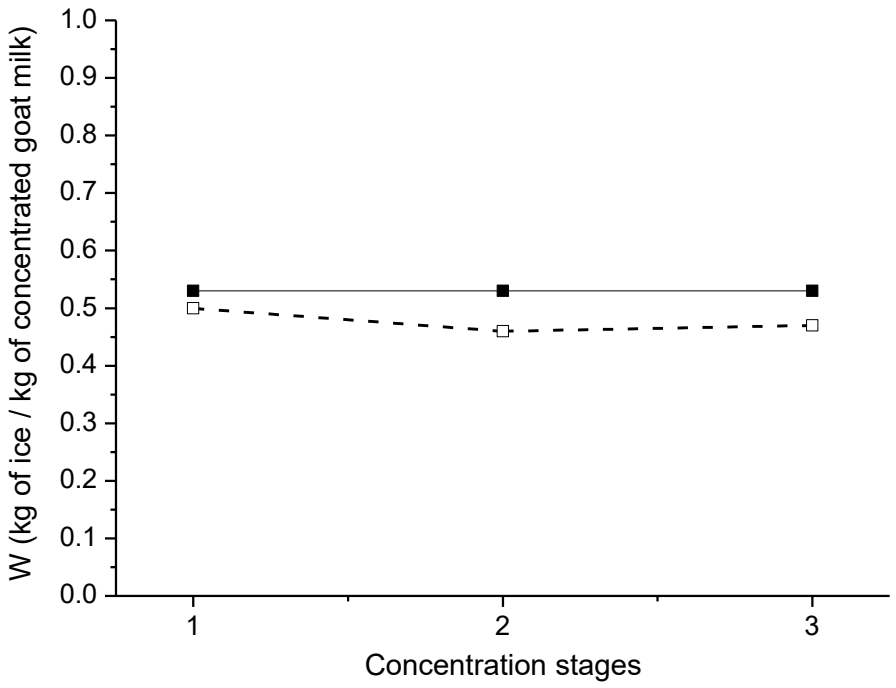
On the other hand, it was observed that the efficiency of the process (*eff*) decreases throughout the freeze concentration stages (Fig. 3.7). The same performance was noted by Aider *et al.* (2009) and Balde and Aider (2016) during freeze concentration of cheese whey and skim milk, where it was noted that *eff* is directly dependent on the total solids content in the ice fraction. Likewise, the density increase of I3 contributed to decrease of *eff* due to more solutes included in this fraction.

Figure 3.7 - Evolution of process efficiency (*eff*) as function of the freeze concentration stages of skim goat milk.



When compared mass balance theorical data of each one freeze concentration stage with experimentally determined mass of the ice formed a good agreement is observed (Fig. 3.8). The root mean square deviation was calculated to determine the deviation between the experimental data and the theoretical estimates. It was observed a good adjustment of the process since the RSM values obtained in this study in the first (6.9%), second (12.0%), and third (12.2%) stage of concentration were lower than 25%, which is considered an acceptable fit, according to Lewicki (2000). These values were close to the values of 7.3%, 6.5%, 9.5%, and 10.8% reported by Hernández *et al.* (2010), Petzold *et al.* (2016, 2015), and Belén *et al.* (2012), respectively, in the freeze concentration process.

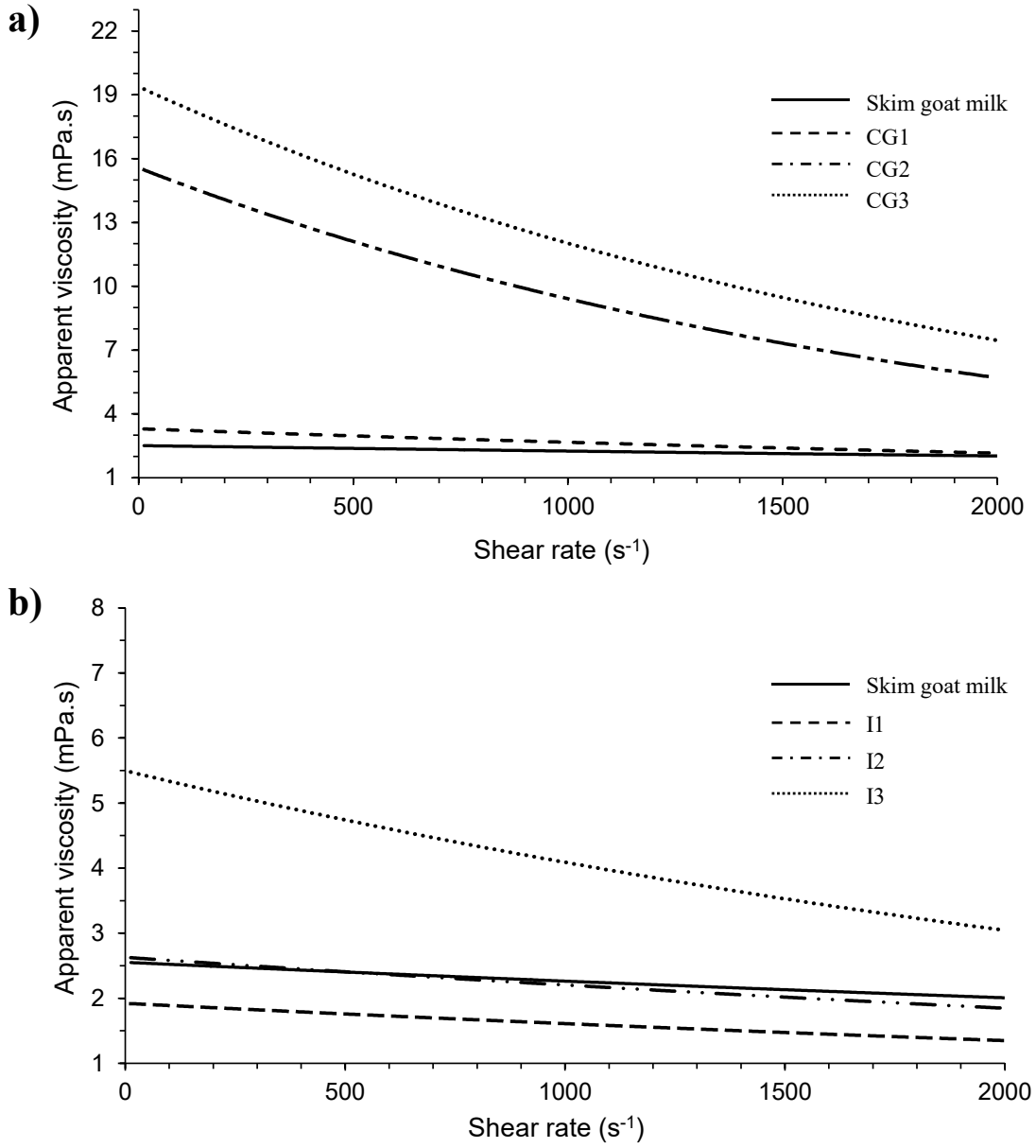
Figure 3.8 - Experimental (■) and predicted (- □ -) ice mass ratios as a function of freeze concentration stages of skim goat milk.



3.5 RHEOLOGICAL ANALISIS

In relation to the rheological parameters, as a function of shear rate profiles, the Figure 3.9 (a, b) shows relevant differences between the viscosity values of skim goat milk, concentrates (CG1, CG2, and CG3), and ice fractions (I1, I2, and I3). CG2, CG3, and I3 fractions showed a small decrease in apparent viscosity with increasing the shear rate, whereas the initial skim goat milk, CG1, I1, and I2 exhibited a Newtonian behavior. However, the apparent viscosity decreased in the CG2, CG3 and I3 fractions indicated that these fluids had shear thinning characteristics (non-Newtonian behavior). These results are in agreement with Vélez-Ruiz *et al.* (1997) and Bienvenue *et al.* (2003) who mentionated that the milk is a Newtonian fluid. According to Vélez-Ruiz and Barbosa-Cánovas (1998), when a Newtonian nature is detected, this behavior is related to low solids concentrations, such as observed in this study in the fractions CG1, I1, and I2 (Figure 3.2).

Figure 3.9 - Apparent viscosity versus shear rate of (a) skim goat milk and concentrated fraction (CG1, CG2, CG3), and (b) skim goat milk and ice fraction (I1, I2, I3).



It was also possible to note that the viscosity of all samples increases when concentration stages increased, which is also credited to increases in the total solids and in the protein content (Table 3.1). The same behavior was observed by Aider and Ounis (2012) in skim milk freeze concentrate. According to Anema *et al.* (2004), the viscosity of a system is dependent on the volume fraction occupied by the contributing particles in combination with the inherent viscosity of the continuous phase. In skim milk systems, the proteins determine the volume fraction of the suspended material. This increased of viscosity occurs because the removal of water causes an increase in volume fraction of dispersed particles and increases the

micelle-micelle interactions as the distance between the micelles becomes smaller (BIENVENUE *et al.*, 2003). Also, it was reported that the ability to separate ice of high purity from the concentrate is dependent and inversely proportional to the solution viscosity (RAVENTÓS *et al.*, 2007; SÁNCHEZ *et al.*, 2011; PETZOLD *et al.*, 2015), explaining the decrease in *eff* of this study (Fig. 3.7).

The rheological behavior of a fluid can be described with two values: the "consistency coefficient" K, and the "flow behavior index" *n*. The flow behavior index describes the shear behavior of the fluid and is a measure of the departure from Newtonian behavior. If the *n* value is close to 1, the sample is Newtonian. If *n* is less than 1, the sample shear thins with increasing shear rate, whereas if *n* is higher than 1, the sample shear thickens (ANEMA *et al.*, 2014). There are various models to describe the dependence of viscosity from shear rate and to determinate the consistency coefficient and the flow behavior index (HOLDSWORTH, 1971; RAO, 2007). In our study, different models were tested; however, the best adjustments were founded with the Power law and Herschel-Bulkley models. In accordance with Balde and Aider (2016), Chang and Hartel (1997), and Vélez-Ruiz and Barbosa-Cánovas, (1998) the milk concentrates behaved as non-Newtonian fluids, with flow curves well fitted by the Power law and/or Herschel-Bulkley models. Therefore, the fit for all data sets was good in both models, with a coefficient of determination between 0.93 and 0.97 (Table 3.3).

The flow parameters of the initial skim goat milk, concentrates goat milk (CG1, CG2, and CG3), and ice fractions (I1, I2, and I3) are in the Table 3.3. Although the Herschel-Bulkley model presented a good fit, the yield stress were of the samples were very small, close to 0. These results are in agreement with those obtained by Balde and Aider (2016). These authors affirmed that when the total solid content is lower than 30 g 100 g^{-1} the yield stress decrease. The initial skim goat milk, CG1, I1, and I2 exhibited a Newtonian behavior because *n* values were very close to 1, whereas the fractions CG2, CG3, and I3 showed *n* lower than 1, and therefore a shear thinning behavior. From the results obtained for the parameter *n* of both models it was possible to confirm the behavior of samples observed previously in Figure 3.9.

According to Power law and Herschel-Bulkley models it was noted that the consistency index was higher ($P < 0.05$) in the final fractions of freeze concentration process (CG3 and I3). As expected, the consistency of concentrate goat milk increased with its total solids content (Fig. 3.2), and this behavior is in accordance with the results observed for other food concentrates such as skim cow milk (BALDE; AIDER, 2016), grape juice (CASTILHOS

et al., 2017) and orange juice (QUEK *et al.*, 2013). The increase in the consistency index of concentrates is justified by the sum of the interaction effects caused by each of the individual milk particles suspended in a medium with less water content (CHANG; HARTEL, 1997). The values of consistency index of skim goat milk founded in this study were higher than consistency index of freeze concentrate skim cow milk observed by Balde and Aider (2016). According to Park *et al.* (2007), the viscosity of goat milk is slightly higher than in cow milk. Thereby, with these results we can highlight that the freeze concentration was an efficient technique for the skim goat milk concentration. We also recommend that the concentrates obtained up to the second stage can be used in the development of news goat milk products, which will contain even more valuable nutritional properties. It is hoped that the results of this study will allow a better understanding of the performance of skim goat milk freeze concentration, because the development of alternative technologies to protect and retain nutritional quality of goat milk are extremely relevant for use industrial.

Table 3.3 - Rheological parameters obtained using Power Law and Herschell-Buckley model of skim goat milk, concentrated (CG1, CG2, and CG3), and ice (I1, I2, and I3) fractions at 5.0 ± 0.1°C.

	Samples	Power Law model			Herschell-Buckley model			
		K (Pa.s^n)	*n*	R^2	σ_0	K (Pa.s^n)	*n*	R^2
	Skim goat milk	0.003 ± 0.001^{cB}	0.970 ± 0.021^{aA}	0.97^{aAB}	0.051 ± 0.018^{cA}	0.002 ± 0.001^{bB}	0.990 ± 0.030^{aAB}	0.97^{aA}
Stage 1	CG1	0.003 ± 0.001^{cB}	0.957 ± 0.035^{a}	0.96^{abC}	0.089 ± 0.034^{bc}	0.002 ± 0.001^{b}	1.013 ± 0.031^{a}	0.96^{ab}
	I1	0.002 ± 0.001^{D}	0.973 ± 0.021^{A}	0.95^{B}	0.024 ± 0.008^{A}	0.001 ± 0.001^{B}	1.043 ± 0.029^{A}	0.93^{B}
Stage 2	CG2	0.024 ± 0.003^{b}	0.833 ± 0.021^{b}	0.95^{b}	0.334 ± 0.021^{ab}	0.015 ± 0.001^{a}	0.891 ± 0.004^{b}	0.95^{b}
	I2	0.002 ± 0.001^{B}	0.968 ± 0.008^{A}	0.96^{B}	0.044 ± 0.053^{A}	0.002 ± 0.001^{B}	0.996 ± 0.027^{AB}	0.96^{A}
Stage 3	CG3	0.032 ± 0.002^{a}	0.831 ± 0.007^{b}	0.96^{a}	0.564 ± 0.212^{a}	0.019 ± 0.004^{a}	0.892 ± 0.018^{b}	0.96^{a}
	I3	0.006 ± 0.001^{A}	0.929 ± 0.017^{A}	0.97^{A}	0.110 ± 0.049^{A}	0.004 ± 0.001^{A}	0.963 ± 0.023^{B}	0.97^{A}

[a,b,c] Within a column, means ± standard deviations with different superscript lowercase letters denote significant differences ($P < 0.05$) between the skim goat milk and the concentrated fraction of each freeze concentration stage. [A,B,C] Within a column, means ± standard deviations with different superscript uppercase letters denote significant differences ($P < 0.05$) between the skim goat milk and the ice fraction of each freeze concentration stage. *K*, Consistency index; *n*, flow behavior index; R^2, determination coefficient; σ_0, yield stress. CG1: concentrated fraction of first freeze concentration stage. I1: ice fraction of first freeze concentration stage. CG2: concentrated fraction of second freeze concentration stage. I2: ice fraction of second freeze concentration stage. CG3: concentrated fraction of third freeze concentration stage. I3: ice fraction of third freeze concentration stage.

CONCLUSION

Skim goat milk was successfully concentrate by applying the block freeze concentration procedure. The high total solids content presented by I3 explains the higher efficiency of the process achieved by the first and second stages. While de total solids content increased in both concentrated and ice fractions, the pH values reduced. The values of lactose content showed no difference at the end of second and third concentrate stage. The total proteins were also concentrate and their content reached up reached almost 3 times more than the initial total protein value of skim goat milk. As the total protein content, the casein and whey protein content increased with increasing freeze concentrate stages, in both concentrate and ice fractions. The concentrate and ice of third stage (CG3 and I3) presented the higher densities. In addition, it was also possible to obtain concentrates skim goat milk with a whiteness index similar to that of whole milk, as observed by L* value. In general, all the concentrates and ice fractions presented tendency a greenish and yellowish color. The Power Law and Herschel-Buckley models were fitting to describe the flow behavior for all concentrate and ice fractions. The transition from a Newtonian to a non-Newtonian behavior was observed for the second stage to concentrate fractions, and for the ice from third stage. The results obtained applying the block freeze concentration suggests that freeze concentration stages positively affected the skim goat milk. Finally, both concentrates from the first and from the second stages would be used for the manufacture of goat's milk products.

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CAPÍTULO 3

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Performance of Skim Goat Milk Mineral Content Subjected to the Block Freeze Concentration Process

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ABSCTRACT

The aim of this study was to evaluate the goat milk mineral performance concentrated by block freeze concentration process. Twenty batches of skim goat milk, each one with one liter, were subjected until the third stage of the freeze concentration process. The initial skim goat milk, concentrated, and ice fractions obtained were analyzed by calcium, magnesium, zinc, phosphorus, sodium and potassium content. Results showed that phosphorus content not increased ($P < 0.05$) with the increase of freeze concentration stages, for concentrated and ice fractions. In the first stage of freeze concentration process, the magnesium element showed the higher ($P < 0.05$) efficiency (95 %). However, the higher ($P < 0.05$) concentration factor was determinate to calcium element in the third stage of the process. Also, it was observed an increase in the minerals contents evaluated with the increasing of freeze concentration stages of skim goat milk. Based on results obtained in the present study, the skim goat milk concentrated obtained in the first stage showed the best performance of skim goat milk mineral content concentration.

Keywords: Goat milk concentrated; concentration process; main mineral elements; efficiency of process; concentration factor.

1 INTRODUCTION

Goat milk and its products are important in human nutrition and have become a part of the current trend of healthy eating around the world (HASSAN *et al*., 2014; SOSNOWSKI; ROLA; OSEK, 2016). Goat milk has high added value because it is a source of nutritional compositional of excellent quality, including the quantity of minerals (OLALLA *et al*.,2009; YANGILAR, 2013). Goat milk present some major and minority minerals in larger amounts than cow milk (CEBALLOS *et al.,* 2009; RAYNAL-LJUTOVAC *et al.,* 2008; YADAV; SINGH; YADAV, 2016). Minerals are fundamental for human health, as they are required for many physiological functions such as tissue growth, regulation of enzyme activities, blood clotting, and to facility of membrane transport of essential nutrients (STOCCO *et al.,* 2016; LOMBARDI *et al.,* 2018). Besides their effects on health, minerals influence milk technological traits, casein micelle structure and aggregation, rennet coagulation time, curd structure, and cheese yield (STOCCO *et al.,* 2016; FRANZOI *et al.,* 2018; MORENO-MONTORO *et al.,* 2015).

It is known that most people consume foods that have less than two-thirds of one or more essential minerals (ACHANTA; ARYANA; BOENEKE, 2007). In addition, because of that, the production of mineral-supplemented foods is growing as an important strategy to prevent mineral deficiencies. Milk and milk based products are good materials for mineral fortification due to their worldwide consumption by all groups at risk of deficiency (LOMBARDI *et al.,* 2018). The concentration of milk may be an alternative to supplementation of these products. New methods are developed to increase goat milk and its derivate quality. Also, the development of new added value products has led to increased interest in specific studies focused on the suitable ways of improve goat milk nutrition, quality, and consumption.

The block freeze concentration technology makes it possible to produce concentrated food with high quality by recovering a food solute based on the separation of pure ice crystals from a freeze-concentrated aqueous phase. When compared with traditional concentration processes, such as evaporation, freeze concentration shows some significant potential advantages because can protect thermally fragile food compounds (PETZOLD *et al.,* 2015). According to Sánchez *et al.* (2011), the freeze concentration reduces about three times the total cost of the process (including capital, cleaning and energy), when compared to the evaporation or reverse osmosis processes.

The freeze concentration has highly promising applications, especially, in the production of foods and ingredients that have high nutritive value (AIDER; HALLEUX, 2009). In this technology, a food liquid solution is completely frozen and then, the whole frozen solution is thawed, with separation of concentrated fraction from ice fraction by gravitational thawing. The separation may be carried out assisted by other techniques to enhance separation efficiency (ORELLANA-PALMA *et al.,* 2017; PETZOLD *et al.,* 2016). The concentration of solutes retained in the ice formed determines the efficiency of this process (AIDER; HALLEUX, 2009). This technique has been used in concentration of different foods, such as cheese whey (SÁNCHEZ *et al.*, 2011; CANELLA *et al.,* 2018), milk (MUÑOZ *et al.,* 2017), skim milk (BALDE; AIDER, 2016), wine (PETZOLD *et al.,* 2016), fruit juices (PETZOLD *et al.,* 2015; HERNÁNDEZ *et al.,* 2009; MIYAWAKI *et al.,* 2016), coffee extract (MORENO *et al.,* 2015), and tofu whey (BELÉN *et al.,* 2013).

Studies have been conducted on the properties of concentrated skim goat milk prepared by ultrafiltration (MORENO-MONTORO *et al.,* 2015). However, in the light of our knowledge, there are no reports in the literature on how mineral performance of skim goat milk is affected by the block freeze concentration technology. A better understanding of this behavior is necessary to further understand the use of freeze concentrated milk in production and processing of new dairy products. Therefore, the aim of the present study was to concentrate skim goat milk by block freeze concentration process and to evaluate the impact of the process on mineral performance of the concentrated and the ice fractions.

2 MATERIALS AND METHODS

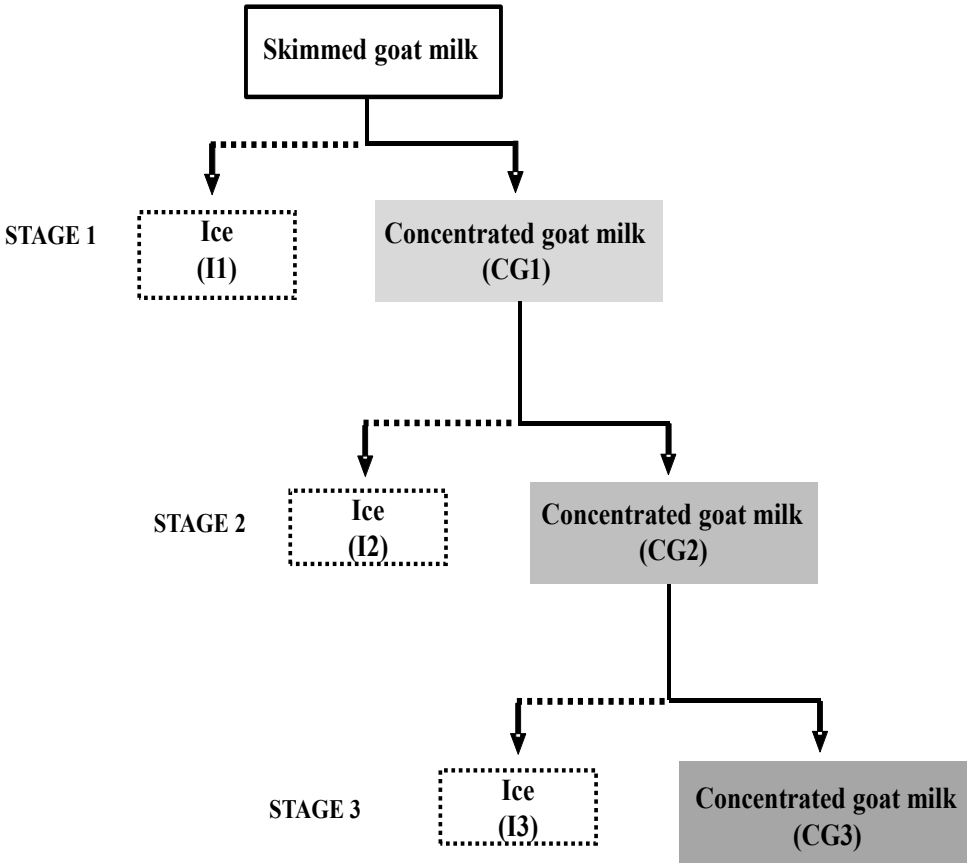
2.1 MATERIALS

Commercial skim UHT goat milk (Caprilat®, CCA Laticínios, Rio de Janeiro, Brazil) was used as the start material. The skim goat milk composition was 8.46 ± 0.01 g total solids 100 g-1, 2.91 ± 0.05 g total protein 100 g-1, 3.93 ± 0.05 g lactose 100 g-1 and 0.89 ± 0.03 g ash 100 g-1. All reagents were of analytical grade.

2.2 PROTOCOL OF THE SKIM GOAT MILK FREEZE CONCENTRATION PROCEDURE

The freeze concentration procedure used to concentrate the skim goat milk was carried out by applying the block freeze concentration technique, according to the process proposed by (AIDER; HALLEUX; AKBACHE, 2007). An initial volume of 20 L of skim goat milk was separated into twenty batches of 1 L. Each 1L of skim goat milk was fractionated in plastic containers and were frozen at - 20 ± 2 °C in a freezer unit (Consul, Biplex CRD41D, São Bernardo do Campo, Brazil). After the skim goat milk has been completely frozen, 50 % of the initial volume was defrosted at room temperature (20 ± 2 °C), obtaining two fractions, the concentrated goat milk (CG1) and the ice (I1). The defrosted liquid (CG1) was frozen at - 20 ± 2 °C and used as feed solution in the second stage. This procedure was repeated until the third stage (Fig. 2.1). After each stage, a portion of concentrated (CG1, CG2, and CG3), and ice fractions (I1, I2 and I3) was collected and stored at - 20 ± 2 °C until the analysis.

1.
2. Figure 2.1- Diagram of the skim goat milk block freeze concentration process.



2.3 MINERAL CONTENT ANALYSIS

2.3.1 Calcium, magnesium and zinc content

The determination of mineral elements Ca, Mg, and Zn content (mg kg-1) were carried out by flame atomic absorption spectrometry (F-AAS) according to Navarro-Alarcón *et al.* (2011), with modifications. The spectrometer used was the AAnalyst 200 model (PerkinElmer, Inc., Waltham, MA, EUA) equipped with the background corrector, and the deuterium arc illumination, using the Echelle resolution system. Acetylene (purity 99.7 %) was employed as fuel gas to heat the atomization system and as compressed gas was used as the compressed air. Before the measurement, all samples were calcined at 520 °C, and the ash obtained were treated with hydrochloric acid 8 mol L^{-1}. The analytical and instrumental parameters were adjusted to obtain the best sensitivity for each element (Table 2.1). For this, the samples were diluted with Milli-Q water for interpolation in the linear range of each mineral element. Cathode lamps (PerkinElmer, Inc., Waltham, MA, USA) were employed to determinate minerals elements. All analyses were carried out in triplicate and blanks were prepared with bidistilled deionized water.

Table 2.1 - Flame atomic absorption spectrometry (F-AAS) instrumental parameters.

Minerals	Wavelengths (nm)	Linear range (mg kg^{-1})
Ca	422.67	1.00 - 5.00
Mg	285.21	0.10 - 0.30
Zn	213.86	0.10 - 1.50

2.3.2 Phosphorus content

Phosphorus content (mg kg^{-1}) was measured by molecular spectrometry at 420 nm in a spectrophotometer UV-Vis, with deuterium lamp (Thermo Fisher Scientific Inc., Waltham, MA, USA). The samples were initially calcined (520 °C), and complexed with molybdenum phosphoric acid. Samples results were interpolated in calibration curves constructed with diacid phosphate of potassium, in the range of 1 to 20 mg L^{-1}. All analyses were carried out in triplicate and blanks were prepared with bidistilled deionized water.

2.3.3 Sodium and potassium content

The sodium and potassium content (mg kg^{-1}) were determined through the technique of atomic emission spectrometry (F-AES), with a flame photometer 910M (Analyser Comércio e Indústria Ltda., São Paulo, Brazil) at 589.0 e 710 nm, respectively. For the evaluation of these minerals, the samples were calcined at 520 ° C, and treated with nitric acid 4 mol L^{-1}. Sample results were interpolated in calibration curves constructed in the range of 1 to 10 mg L^{-1}. All analyses were carried out in triplicate, and blanks were prepared with bidistilled deionized water.

2.4 FREEZE CONCENTRATION PARAMETERS

2.4.1 Concentration factor

The concentration factor (CF) was calculated in agreement with the method proposed by Aider and Ounis (2012). The CF of each freeze concentration stage was determinate as a function of the increase of mineral content, using the following Equation 1:

$$CF\ (\%) = \frac{MC_n}{MC_0}\ x\ 100 \qquad (1)$$

where MC_n is the mineral (mg kg^{-1}) content of the concentrated goat milk from each freeze concentration stage and MC_0 is the mineral (mg kg^{-1}) content of the initial skim goat milk.

2.4.2 Process efficiency

The process efficiency (*eff*) was calculated based on the increase of mineral content (mg kg^{-1}) in the concentrated goat milk (MC_n) in relation to the mineral content (mg kg^{-1}) remaining in the ice (MC_i) from each freeze concentration stage (n), as described in the Equation 2:

$$eff\ (\%) = \frac{\mathrm{MC}_n - MC_i}{\mathrm{MC}_n}\ x\ 100 \qquad (2)$$

2.5 STATISTICAL ANALYSIS

Data were expressed as means and standard deviations. Statistical analysis of data was performed using the software STATISTICA 13.3 software (TIBCO Software Inc., Palo Alto, CA). One-way analyses of variance (ANOVA) and Tukey's range test (5 % significance) were carried out to test significant differences between the results.

3 RESULTS AND DISCUSSION

Goat milk is considered an exceptionally important food because is rich in mineral content. The mineral fractions of skim goat milk, concentrated (CG1, CG2, and CG3), and ice fractions (I1, I2, I3) are shown in Table 3.1. Generally, the mineral content in the concentrated and ice fraction increased with increase in freeze concentration stages. When verified the concentration of major elements such as Ca, Mg, Na, K and P, it was possible to note that the values of Ca, Mg, Na, K were higher ($P < 0.05$) in all concentrated fractions (CG1, CG2, and CG3), when compared with the initial skim goat milk. Besides that, these minerals contents in CG1, CG2, and CG3 increased ($P < 0.05$) with the increase of the freeze concentration stages. This performance was expected, because similar behavior was reported in block freeze concentration process of the skim cow milk (BALDE; AIDER, 2016). The concentration of Ca and Mg were higher than those reported by Moreno-Montoro *et al.* (2015) during the ultrafiltration of skimmed goat milk. Ca and Mg contents are related to casein structure, which is primarily involved in the coagulation process and curd formation and a higher concentration of Ca in the milk could decrease the rennet clotting time and increase the curd firmness (FRANZOI *et al.,* 2018; LANDFELD; NOVOTNÁ; HOUŠKA, 2002; VISENTIN *et al.,* 2016). The P content showed no difference ($P > 0.05$) between the initial skim goat milk and concentrated fraction (CG1, CG2, and CG3). It was noted a slight progressive increase in relation to Ca, Mg, Na, K, and P contents for the ice fractions of freeze concentration stages. However, I1 and I2 fractions showed lower values ($P < 0.05$) of these minerals when compared with the initial skim goat milk.

Table 3.1 - Mineral contents of skim goat milk, concentrated (CG1, CG2, and CG3) and ice (I1, I2, and I3) fractions during block freeze concentration stages.

Samples	Ca (mg kg^{-1})	Mg (mg kg^{-1})	Na (mg kg^{-1})	K (mg kg^{-1})	P (mg kg^{-1})	Zn (mg kg^{-1})
Skim goat milk	987.48 ± 3.38^{dB}	82.52 ± 1.21^{dB}	676.59 ± 0.32^{dB}	1429.89 ± 108.48^{dB}	476.74 ± 35.62^{aB}	6.97 ± 0.02^{dA}
CG1	1720.38 ± 3.31^{c}	147.36 ± 0.01^{c}	1004.86 ± 1.19^{c}	1842.38 ± 239.03^{c}	508.25 ± 4.55^{a}	10.71 ± 0.01^{b}
I1	122.30 ± 0.01^{D}	7.11 ± 0.12^{D}	316.00 ± 6.00^{D}	316.02 ± 6.50^{D}	242.52 ± 5.96^{D}	0.93 ± 0.01^{D}
CG2	2307.57 ± 666^{b}	235.97 ± 1.20^{b}	1258.26 ± 0.56^{b}	2831.08 ± 1.26^{b}	503.99 ± 0.22^{a}	7.94 ± 0.03^{c}
I2	707.34 ± 6.52^{C}	13.97 ± 0.01^{C}	608.27 ± 0.52^{C}	1216.55 ± 1.05^{C}	420.83 ± 0.11^{C}	2.55 ± 0.01^{C}
CG3	10388.28 ± 213.62^{a}	458.99 ± 9.44^{a}	1652.70 ± 33.99^{a}	3305.39 ± 67.97^{a}	522.40 ± 10.74^{a}	17.36 ± 0.36^{a}
I3	1494.75 ± 6.67^{A}	136.45 ± 1.20^{A}	880.67 ± 1.28^{A}	1907.97 ± 204.80^{A}	529.81 ± 0.17^{A}	5.26 ± 0.01^{B}

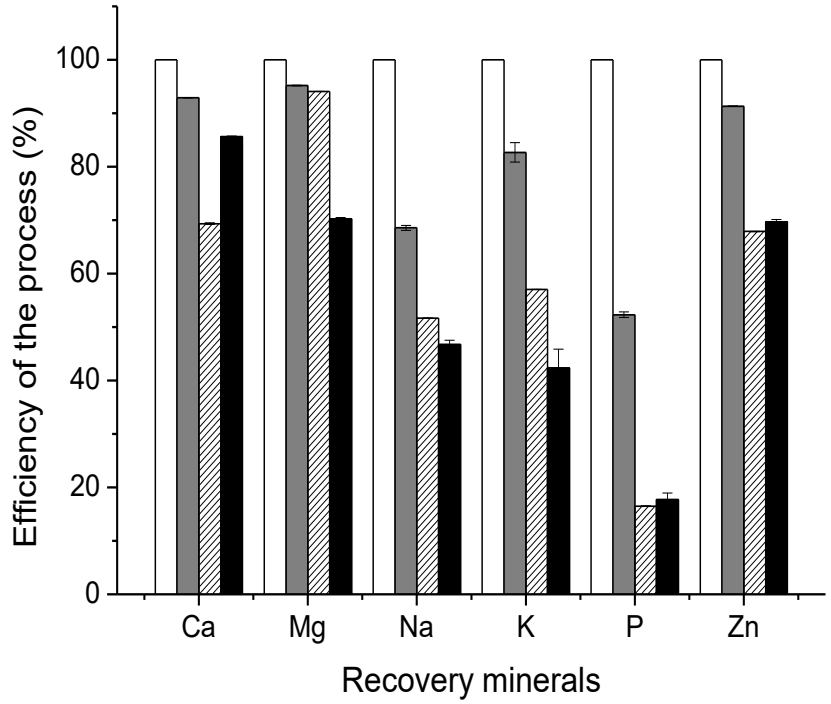
^{a,b,c} Within a column, means ± standard deviations with different superscript lowercase letters denote significant differences ($P < 0.05$) between the skim goat milk and the concentrated fraction of each freeze concentration stage. ^{A,B,C} Within a column, means ± standard deviations with different superscript uppercase letters denote significant differences ($P < 0.05$) between the skim goat milk and the ice fraction of each freeze concentration stage. CG1: concentrated fraction of first freeze concentration stage. I1: ice fraction of first freeze concentration stage. CG2: concentrated fraction of second freeze concentration stage. I2: ice fraction of second freeze concentration stage. CG3: concentrated fraction of third freeze concentration stage. I3: ice fraction of third freeze concentration stage.

The Zn content decreased ($P < 0.05$) for the CG2 in comparison with the CG1, and with the skim goat milk. At the third stage, the Zn content increased ($P < 0.05$), showing higher values for the CG3. The initial skim goat milk showed higher ($P < 0.05$) Zn content than all ice fractions. According to Gao *et al.* (2004), and Aider and Ounis (2012), freezing of salt solution above its eutectic temperature causes rejection of salt (poorly soluble in ice) to the surrounding medium, creating water with very high salt content brine.

Minerals content of Ca, P, K, Na and Mg were higher than those reported by Balde and Aider (2016) during the block freeze concentration of skim cow milk. This behavior could be related to the fact the goat milk present some mineral contents in larger amounts than cow milk (CEBALLOS *et al.,* 2009; RAYNAL-LJUTOVAC *et al.,* 2008; YADAV; SINGH; YADAV, 2016).

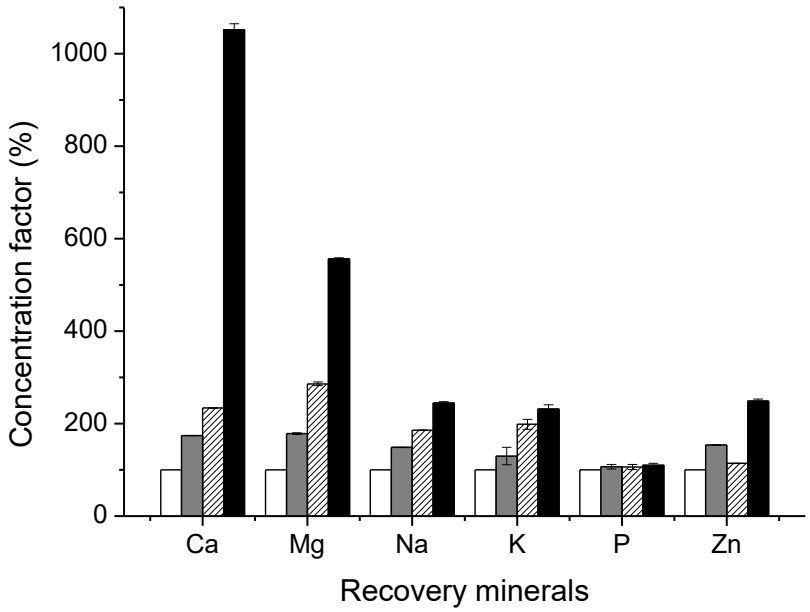
Regarding mineral efficiency concentration (Fig. 3.1), overall notable values were achieved. However, the best value was obtained at concentration of Mg with an efficiency of approximately 95 % in the first stage and around 70 % at the third stage. The lowest efficiency was to P concentration with an efficiency of 52 %, 16 %, and 17 % at the first, second and third stages, respectively. Predominantly, the highest process efficiencies were recorded at the end of the first freeze concentration stages. These results indicate that more minerals were entrapped in the ice fraction at the final stages of freeze concentration process (I2 and I3). This performance was also stated by Aider, de Halleux, and Melnikova (2009) for the freeze concentration of skim acidic milk.

Figure 3.1 - Performance of freeze concentration process on the efficiency (*eff*) of goat milk minerals concentration as a function of freeze concentration stages (□ initial skim goat milk, ▨ stage 1, ▨ stage 2, and ■ stage 3).



In the present study, for all mineral content evaluated, the concentration factor (CF) (Fig. 3.2) showed an opposite performance than those observed by the mineral efficiency concentration. An increase ($P < 0.05$) of the concentration factor was observed over the freeze concentration stages, reaching a CF of 10000 % for the Ca content in the third freeze concentration stage.

Figure 3.2 - Performance of freeze concentration process on the concentration factor (CF) of goat milk minerals concentration as a function of freeze concentration stages (☐ initial skim goat milk, ▒ stage 1, ▨ stage 2, and ■ stage 3)



As observed by Ceballos *et al.* (2009), Yadav, Singh, and Yadav (2016), and Campos *et al.* (2003) in the present work it is possible to note that main elements contents of skim goat milk are higher than cow milk. Finally, in a near future, the results obtained from the block freeze concentration process of skim goat milk mineral content performance could be used by dairy industries to produce nutritive products with high mineral contents without mineral supplementation, which would affect positively the economic and the nutritive value of milk products.

CONCLUSION

The mineral content of skim goat milk was successfully freeze concentrated by applying the block freeze concentration. As the freeze concentration stages increased, Ca, Mg, Na, K, and Zn contents increased in both concentrated and ice fractions. It was possible to concentrated Ca and Mg after three stages, around 10 and 6 times more than the initial skim goat milk, respectively. Indeed, the K, Na and Zn elements were concentrated after three stages, almost 3 times more than initial skim goat milk, respectively. However, the phosphorus showed no difference of concentrated fraction in

the three stages compared with the initial skim goat milk. All mineral content showed high efficiency and concentration factor during the freeze concentration process. The skim goat milk concentrated obtained in the first stage showed the best performance of skim goat milk mineral content concentration, because higher efficiencies results were obtained in this stage.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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CAPÍTULO 4

Flow decline modelling and characterization of skimmed goat milk concentrated by nanofiltration

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ABSTRACT

The skimmed goat milk was submitted to the nanofiltration process using volume reduction factor (VRF) equal to 2. It was verified a rapid decrease of the permeate flux at a low time, with a continuous flux, caused by the reversible resistance, which is characterized by the standard and complete blocking. The combined fouling model was evaluated, including both complete pore blocking and cake filtration mechanism, which provided a realistic description of the skimmed goat milk nanofiltration behavior. For the VRF equal to 2 was determined the total solids, protein, lactose, ash, mineral fraction content, which increased successfully with the nanofiltration process. The nanofiltration of skimmed goat milk improve the tendency to whiteness, greenish and yellowish color of the retentate. The Power Law and Herschel-Buckley models were fitting to describe the flow behavior for retentate, wich presented the higher apparent viscosity.

Keywords: Skimmed goat milk; concentration; permeate flux; physicochemical properties; rheological properties.

1 INTRODUCTION

Goat milk has become popular with consumers because of its high protein content, high calcium content, and high proportion of more digestible fatty acids compared with cow milk (HAENLEIN, 2004; CHEN *et al.*, 2018). Therefore, is widely used in dairy products because it is highly digestible, is hypoallergenic, and has high nutritional value (CHEN *et al.*, 2019). Many types of research were involved in studying the concentration of goat milk. According to Depping et al. (2017) the concentration of milk representing an intermediate processing step in production of milk products or concentrated milk products, which can be used in several food formulations, such as yoghurts, ice cream, bakery products or some meals, by replacing the use of milk powder, since this material is expensive and requires intensive energy for drying.

Among the concentration, processes highlight the membrane process, which has been successfully investigated for the concentration of milk components. Therefore, the membrane process could be a promising technology for recovery fragile compounds in comparison with others concentration processes which employ higher temperature. Ng *et al.* (2017) emphasized that the membrane processes have been demonstrated to be advantageous over the conventional process for the recovery of thermosensitive compounds from milk and cheese whey using the methodologies such as the nanofiltration, retaining protein, lactose, and minerals. However, the nanofiltration of skim milk is particularly susceptible to poor operational efficiency due to flux decline resulting form concentration polarization and fouling. For Ng, Dunstan and Martin (2018), the membrane fouling is due to several possible causes, such as adsorption and blocking of solute on the membrane, formation of a deposited layer on the membrane surface, and also to the milk composition. Ferrer, Alexander and Corredig (2014) cited that during the process, concentration polarization at the membrane surface can rise to a point where the concentrated solutes form a gel layer on the membrane, and this irreversibly decreases the permeation flux and process performance, ultimately causing fouling of the membrane, which is associated with a decline in the permeate flux with operation time. As the concentration increases, the permeate fluxes decline (FERRER; ALEXANDER; CORREDIG, 2014).

In this sense, modeling is warranted to quantify the flux decline during concentration that allows the prediction of process behavior (BALYAN; SARKAR,

2018). Membrane fouling in the dairy industry has generally been attributed to adsorption of proteins and precipitation of calcium phosphate (NG; DUNSTAN; MARTIN, 2018), but the exact nature of fouling is difficult to ascertain, as this would require some form of in situ and in real time observation and measurement. Some of the best models known are described by Hermia and Ho and Zydney, which can quite helpful in understanding the main reasons for flux decline. Hou, Wang, and Song (2017) cited that Ho and Zydney developed a combined fouling model considering both pore blocking and the filtration layer to describe flux decline. However, the performance of nanofiltration process it should not only be evaluated regarding the permeate flux and the flux decline but also about the physical, chemical and rheological properties of the fractions obtained. Thereby, the present study aimed to characterize the performance of the nanofiltration process of skimmed goat milk by evaluating permeate flux decline, fouling resistance, and retentate composition and rhelogical properties.

2 MATERIAL AND METHODS

2.1 MATERIAL

Commercial skim UHT goat milk (Caprilat®, CCA Laticínios, Rio de Janeiro, Brazil) was used as the start material. The skim goat milk composition was 8.46 ± 0.01 g total solids 100 g^{-1}, 2.91 ± 0.05 g total protein 100 g^{-1}, 3.93 ± 0.05 g lactose 100 g^{-1} and 0.89 ± 0.03 g ash 100 $g^{-}1$. The initial pH value and titratable acidity was 6.60 ± 0.01 and 0.12 ± 0.01 g 100 g^{-1} lactic acid, respectively. All reagents were of analytical grade.

2.2 NANOFILTRATION PROCEDURE

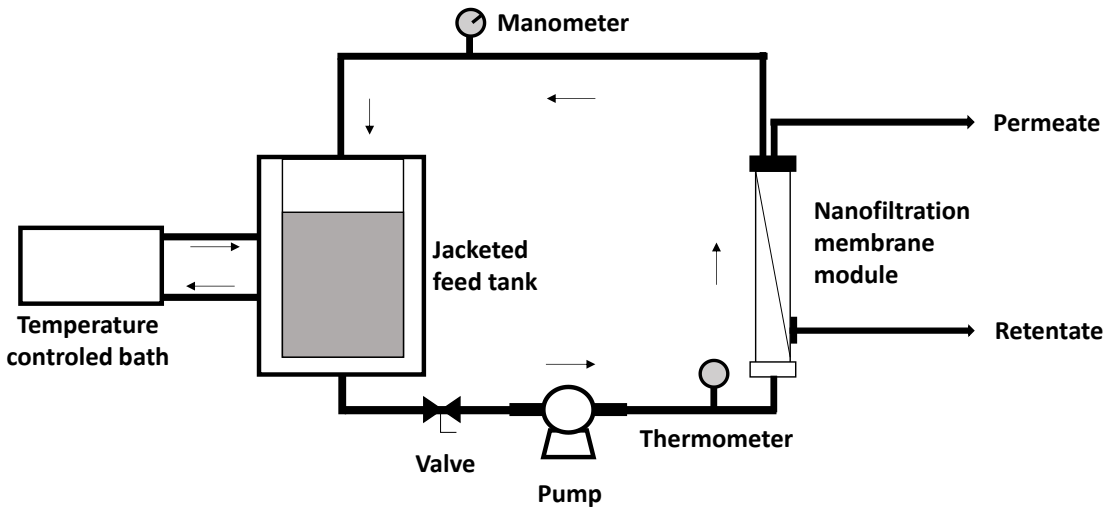
The skimmed goat milk was submmited to the nanofiltration process in a pilot filtration unit (Figure 2.1), using a tangential filtration system and a polyvinylidene fluoride (PVDF) spiral nanofiltration membrane (Osmonics, Minnetonka, MN), with an approximate a molar mass cut-off ranging between 150 - 300 Da, and a filtration area of 1.2 m^2. The operating parameters controlled during the nanofiltration process were a temperature of 25 ± 1 °C and pressure of 700 kPa, up to the volume reduction factor (VRF) of 2 as the end point of the process. The VRF was calculated as the ratio between

the initial volume (L) of skimmed goat milk used in the feed and the final volume (L) of the concentrate after nanofiltration process. The permeate flux (J) ($L.h^{-1}.m^{-2}$) was measured at 5 min and removed in order to obtain the skimmed goat milk concentrate, according to Equation (1):

$$J = \frac{V_p}{t \times A_p} \quad (1)$$

where Vp (L) is the amount of permeate collected during the period of time t (h) and Ap (m^2) is the permeation surface area of the membrane.

Figure 2.1- Schematic diagram of the nanofiltration unit.



In order to assess the fouling mechanism during the nanofiltration process, the model of flow decline during filtration can be selected (HERMIA, 1982) (Eq. 2).

$$d^2/dV^2 = \beta(\frac{dt}{dV})^n \quad (2)$$

where *V* is the cumulative volume of filtrate, *t* the time of operation, and *n* is a constant. Field *et al.* (1995) modified classical constant pressure dead end filtration equation (HÉRMIA, 1982) which expressed as

$$-dJ/dt\ (J^{n-2}) = K(J - J^*) \quad (3)$$

where *j** is the steady state flux, *t* is time and *K* is a constant whose dimension depends on the values of *n*. *n* in both two models is general index which depending on fouling mechanism (TODISCO *et al.*, 1996) assumes different values (BOWEN *et al.*, 1995).

When n corresponds to 2, the complete blocking model is assumed, that is, each particle when arriving at the membrane surface blocks some membrane pores such that no superposition happens and the blocked surface area is proportional to the permeate volume. In this case, the size of the solute particles is similar to the pore size of the membrane, forming a monomolecular layer on the membrane surface (Eq. 4).

$$Ln(J) = LnJ_0 - K_b t \quad (4)$$

In standard pore blocking, n value is equal to 1.5, and the solute particles with a smaller size than the pores of the membranes can pass through the membrane pores, reducing the pore size effectiveness (Eq. 5).

$$\frac{1}{J^{1/2}} = \frac{1}{J_0^{1/2}} + K_s t \quad (5)$$

When n is 1, the fouling mechanism represents the incomplete or intermediate blocking model in which the solute particles cannot penetrate completely inside the porous structure, and they can settle on other particles deposited before, forming multilayers (Eq. 6).

$$\frac{1}{J} = \frac{1}{J_0} + K_j A t \quad (6)$$

Finally, when the value of n is 0, the pore blocking is neglected, and it is related to the formation of a cake layer by the accumulation of solute particles onto the membrane surface with a thickness proportional to the permeate volume (GARCIA-IVARS *et al.*, 2017) (Eq. 7).

$$\frac{1}{J^2} = \frac{1}{J_0^2} + K_c t \quad (7)$$

Furthermore, to evaluate the combined effect of the different pore blocking and the filtration layer was used a model suggested by Ho and Zydney (2000) (Equation 8).

$$Q = Q_0 \left[exp\left(-\frac{\alpha \Delta PC}{\mu R_m} t\right) + \frac{R_m}{R_m + R_p} X \left(1 - \exp\left(-\frac{\alpha \Delta PC}{\mu R_m} t\right)\right)\right] \quad (8)$$

where Q_0 is the initial flow rate ($m^3.s^{-1}$), α is the pore blockage parameter ($m^2.kg^{-1}$), ΔP is the transmembrane pressure (Pa), C is the bulk concentration s, μ is the permeate viscosity (Pa.s), R_m is the membrane resistance (m^{-1}), and *t* is the filtration time (s).

Different resistances can appear throughout the process when a complex solution is used as the feed solution (LEU *et al.* 2017). The sum of these resistances is represented by a total resistance Rt (m^{-1}) (Equation 9).

$$R_t = R_m + R_r + R_{ir} \quad (9)$$

The Rt was calculated according to Equation 10:

$$R_t = \frac{P}{\mu_w J_f} \quad (10)$$

Where, Jf ($L.h^{-1}.m^{-2}$) is the final permeate flow, the permeate viscosity was considered to be similar to that of water μw ($mPa.s^{-1}$) and the experimental pressure P (Pa) was controlled. The membrane resistance R_m (m^{-1}) was obtained from Equation 11 by permeating pure water through the nanofiltration membrane. The viscosity of water μ_W ($mPa.s^{-1}$) and the permeate flow J_W ($L.h^{-1}.m^{-2}$) were considered before the process with the skim milk.

$$R_m = \frac{P}{\mu_W J_W} \quad (11)$$

The irreversible fouling resistance R_{ir} (m^{-1}) was obtained after filtration of the skimmed goat milk by the Equation 12. The skimmed goat milk was removed, and pure water was fed into the system to obtain the water permeate flow J_{Wf} ($L.h^{-1}.m^{-2}$).

$$R_{ir} = \frac{P}{\mu_W J_{Wf}} \quad (12)$$

The reversible resistance *Rr* (m^{-1}) was obtained by difference, as shown in Equation 13.

$$R_i = R_t - R_m - R_{ir} \quad (13)$$

For adjusting all the equations, a computer routine for Matlab (R2013a, MathWorks Inc, MA, USA) was developed, using the nlinfit function.

2.3 PHYSICALCHEMICAL ANALYSIS

All the physicalchemical analysis were realized in the initial skimmed goat milk, retentate e permeate from the nanofiltration process and were carried out in triplicate. The total solids content (g 100 g^{-1}) were determined through the drying of the samples until reaching a constant weight at 105 °C (IAL, 2008) and the total protein, by the Kjeldahl method (N x 6.38) (AOAC, 2005). The lactose content (g 100 g^{-1}) were obtained using a spectrophotometer FT-NIR model MPA (Multi Purpose Analyzer) (Bruker Optik, Ettlingen, Germany) operating with a spectral acquisition program OPUS version 7.0 (Bruker Optik, Ettlingen, Germany). The measurements were made by near-infrared Fourier transform (FTNIR) spectra of diffuse reflectance. Each vial containing the samples was positioned in the diffuse reflectance accessory and the NIR spectra were collected in the spectral range of 9.000 to 4.000 cm^{-1} at a nominal resolution of 16 cm^{-1} in transmission mode. Each spectrum was the average of 500 scans.

The ash content (g 100 g^{-1}) were analyzed through a gravimetric method (IAL, 2008). Mineral content of Ca, Mg, Zn, Mn, Cu, and Co (mg 100g^{-1}) were determined by flame atomic absorption spectrometry (F-AAS) according to Navarro-Alarcón *et al.* (2011), with modifications. The spectrometer used was the AAnalyst 200 model (PerkinElmer, Inc., Waltham, MA, EUA) equipped with the background corrector with the deuterium arc illumination and the Echelle resolution system. Acetylene (purity 99.7%) was used as fuel gas to heat the atomization system and as compressed gas, compressed air was used. Before de measurement, all samples were calcined at 520 ° C and the ash treated using hydrochloric acid 8 mol L^{-1}. The analytical and instrumental parameters were adjusted to obtain the best sensitivity for each element. For this, the

samples were diluted with Milli-Q water for interpolation in the linear range of each element. The wavelengths used to determinate the elements were of 422.67 nm for Ca, 285.21 nm for Mg, 213.86 nm for Zn, 279.50 nm for Mn, 324.80 nm for Cu, and 240.73 nm for Co using cathode lamps (PerkinElmer, Inc., Waltham, MA, USA).

The color of the skimmed goat milk, retentate and permeate were determined using a colorimeter Minolta Chroma Meter CR-400 (Konica Minolta, Osaka, Japan). The colorimeter was calibrated with a white standard plate and adjusted to operate with D65 lightning and 10º of observation angle. The CIELab color scale was used to measure the L^*, b^* and a^* parameters, that indicates the luminosity (variation from black to white), variation from yellow (+ b^*) to blue (- b^*) and variation from red (+ a^*) to green (- a^*), respectively. The total difference of color (ΔE) between the measured values of skimmed goat milk and retentate and permeate were calculated as described in Equation 14,

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (14)$$

where ΔL^* is the difference of luminosity between the measured values of skimmed goat milk and retentate and permeate, while Δa^* represents the intensity of the red color and Δb^* the intensity of the yellow color. Five replicates were performed for each sample, and the mean values were reported.

2.4 RHEOLOGICAL PROPERTIES

The measurements of rheological properties of skimmed goat milk, retentate and permeate were carried out using a Thermo Haake DC 10 rotational viscosimeter (model VT 550, Thermo Haake, Karlsruhe, Germany), with concentric cylinders (NV ST 807-0713 CE and NV 807-0702), and collected using the software program Pro Rheowin® (version 2.93, Haake). The control of temperature (5 ºC) was realized through water circulation in a temperature controlled bath (Phoenix P1, Thermo Haake, Karlsruhe, German) and coupled to the equipment. An aliquot volume of 10 mL of samples was loaded into the cup of viscometer and the data were obtained. The flow curves were generated by a linearly increased shear rate of 0 s^{-1} to 2000 s^{-1} (upward curve) and 2000 s^{-1} to 0 s^{-1} (downward curve) during 3 minutes. To accurately evaluate the most adapted

flow behavior, the models most frequently employed in food characterization (Vélez-Ruiz; Cánovas; Peleg, 1997) were used to describe the shear rate-shear stress data expressed by Equations 15 and 16.

$$\text{Power} - \text{law:} \quad \sigma = K(\dot{\gamma})^n \tag{15}$$

$$\text{Herschel} - \text{Bulkley:} \quad \sigma = \sigma_0 + K\dot{\gamma}^n \tag{16}$$

where σ is shear stress (Pa), $\dot{\gamma}$ is shear rate (s^{-1}), K is consistency index (Pa s^{-1}), n is flow behavior index, and σ_0 is yield stress (Pa).

2.5 STATISTICAL ANALYSIS

The results were expressed as means ± standard deviations and were evaluated using the software STATISTICA version 13.3 (TIBCO Software Inc., Palo Alto, CA). One-way analysis of variance (ANOVA) and Tukey's studentized range ($P < 0.05$) were carried out to test for any significant differences between the results. R^2 values were calculated for the fit of the model's data.

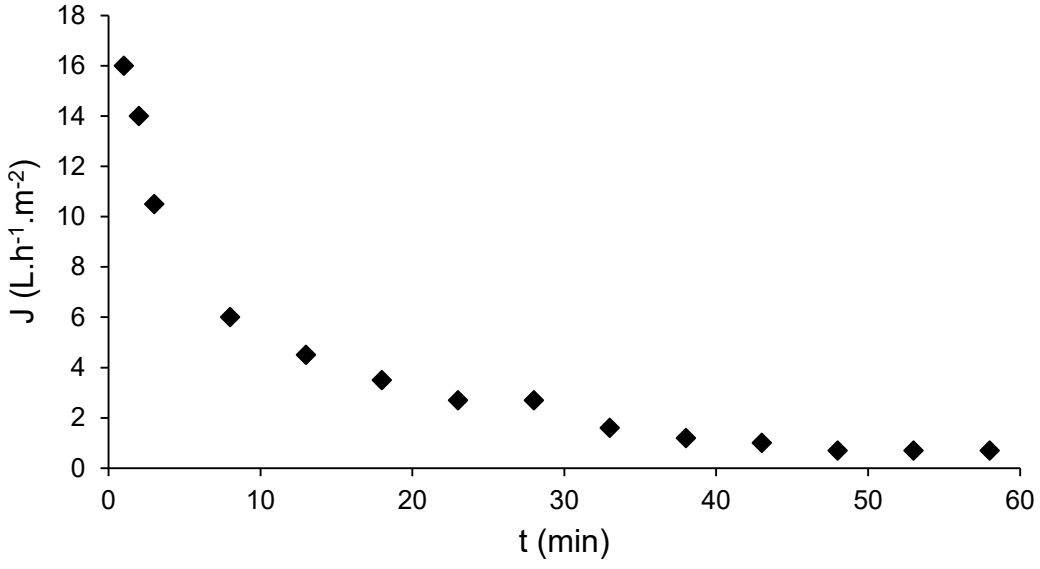
3 RESULTS AND DISCUSSION

3.1 NANOFILTRATION PROCESS

Figure 3.1 shows the permeate flux as a function of operating time, for the nanofiltration process using skimmed goat as feed solutions. Two stages can be distinguished, evidencing the membrane fouling during nanofiltration processes of the skimmed goat milk. The initial decline of permeate flux values visualizes on the first minutes of the process is related to the solute particles accumulated and adsorbed onto the surface and inside the pore walls, known as concentration by polarization. According to Ng *et al.* (2017), the concentration polarization occurs, in the case of skimmed milk, due to the presence of proteins and mineral. Milk proteins foul the membrane by adsorbing to and depositing onto the membrane surface and creating a flux resistance in the form of a gelatinous cake layer (RICE *et al.* 2009). This protein adsorption has been shown to be influenced by electrostatic effects between the charged protein and charged

membrane, and also by the hydrophobicity of the membrane. Rice *et al.* (2009) stated that calcium is able to contribute to this protein cake by forming protein–protein and protein–membrane bridges. Meanwhile, soluble ions can precipitate once their solubility is exceeded, potentially forming a scale within the pores or on the surface of the membrane. Calcium phosphate salts are of particular concern in the dairy industry due to their supersaturation in the aqueous phase of milk. This phenomenon results in an increase in the osmotic pressure of the solution, resulting in a significant decrease in flow, so that the system must be stopped, as observed in the second stage of permeate flux in Figure 3.1, where a gradual flux decline at more extended periods, up to VRF equal to 2. In this VRF the equilibrium between the attachment and detachment of skimmed goat milk particles on the membrane was reached, achieving an almost constant value of the permeate flux. The mechanisms involved in this process can promote higher concentrations of some constituents next to the membrane surface and, consequently, adhere to the surface and creating a resistance to fluid flow.

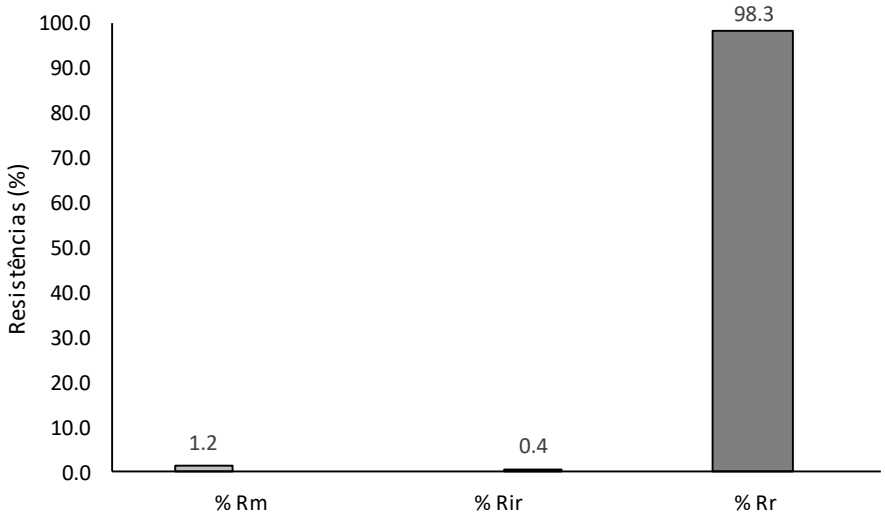
Figure 3.1 - Permeate flux curve (J) for nanofiltration of skimmed goat milk processes up to volume reduction factor (VRF) equal to 2 at 700kPa and 25 ± 1 °C.



During a fouling experiment, the resistance to the fluid flow increases due to various mechanisms, such as pore plugging, cake layer formation, concentration polarization, and osmotic pressure. Skimmed milk filtration is particularly susceptible to poor operational efficiency due to flux decline resulting from concentration polarization

and fouling. The resistance by concentration polarization is the accumulation of retained particles at the membrane surface, and is responsible for the most of reversible resistances. While resistance by fouling, occurs due to adsorption or deposition of colloidal particles on the membrane surface and in the membrane pores and is responsible for the irreversible resistance (NG *et al.*, 2017). In the present study, the reversible resistance contributed over 90% of total resistance, while membrane and irreversible resistance contributed to 1.2 and 0.4%, respectively (Fig. 3.2). Rezzadori *et al.* (2014) cited that processes operating at pressures above 3 bar are more susceptible to the deposition of solutes on the membrane surface, this deposition being related to the concentration by polarization layer, corroborating with the results described in this study. The reversible resistance is a direct result of flux and is usually reversible in the sense that it will quickly diffuse if flux across the membrane is halted. However, if the reversible resistance be high, as observed in this study, a gel layer may be formed by particle-particle interactions and such layer dissipates slowly, if at all, when the flux is interrupted (NG *et al.* 2018). From an operational perspective, the reversible resistance is unavoidable but it can be minimized by improving particle convection away from the membrane (BRANS *et al.*, 2004). On the other hand, irreversible resistance fouling is irreversible (upon cessation of flux), and its removal requires back washing or often even chemical cleaning. This interrupts operation, lowers productivity, consumes large amounts of water and chemicals, and decreases membrane life (BRANS *et al.*, 2004). Baudry *et al.* (2002) identified that after the membrane rinsing, lactose and salts of milk were removed, but proteins remained adhered to the membrane. Therefore, lactose and salts play a role in reversible resistance, whereas proteins take part in both resistances (reversible and irreversible).

Figure 3.2 - Membrane (Rm), irreversible (Rir), and reversible (Rr) resistance of skimmed goat milk nanofiltration process up to volume reduction factor (VRF) equal to 2.



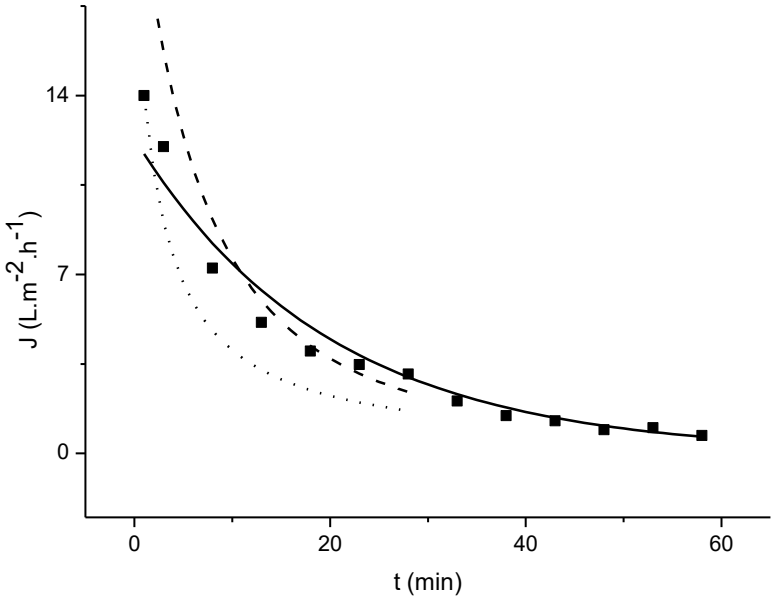
The membrane fouling mechanism during nanofiltration process of the skimmed goat milk up to VRF of 2 was estimated by Hermia's model, and the fitting of the models was evaluated in the light of the R^2. The results of the sample calculations for the studied model with the experimental results are shown in Table 3.1 and Figure 3.3. According to De Bruijn *et al.* (2002) and Razi *et al.* (2012) the resistance coefficient (K) is dependent on the resistance and concentration of filter cake layer and blocked surface, mostly being influenced by the system pressure. The highest resistance coefficient was obtained for the complete pore blocking models, while the the best fit (R^2) were obtained for the standard and complete pore blocking models, with $R^2 \geq 0.97$. Vela *et al.* (2008) stated that adsorptive fouling of membranes by particles smaller than the membrane pore sizes is incorporated in the standard blocking model. Therefore, particles may deposit inside the membrane pore walls, leading to the reduction of cross-sectional area of membrane pores and consequent increase in membrane resistance. This fouling phenomenon always operates in non-steady-state condition and it is independent of the crossflow rate (ALMANDOZ *et al.* 2010). In the nanofiltration process of skimmed goat milk, this behavior could occurring by the deposit of whey protein and some mineral that have lower size then the membrane pore.

Table 3.1- Phenomenological constant (K) and R^2 values from the fouling mechanism of the skimmed goat milk nanofiltration up to volume reduction factor (VRF) equal to 2.

Fouling mechanism	**K**	**R^2**
Complete blocking (n = 2) (s^{-1})	0.051	0.98
Standard blocking (n = 1.5) ($m^{-0.5}$ $s^{-0.5}$)	0.016	0.97
Incomplete blocking (n = 1) (m^{-1})	0.015	0.86

K = resistance coefficient; R^2 = determination coefficient.

Figure 3.3 - Permeate flux experimental (■) by the complete pore blocking model (——), standard pore blocking (– – –), and intermediate pore blocking (- - - -) from skimmed goat milk nanofiltration process up to volume reduction factor (VRF) equal to 2.

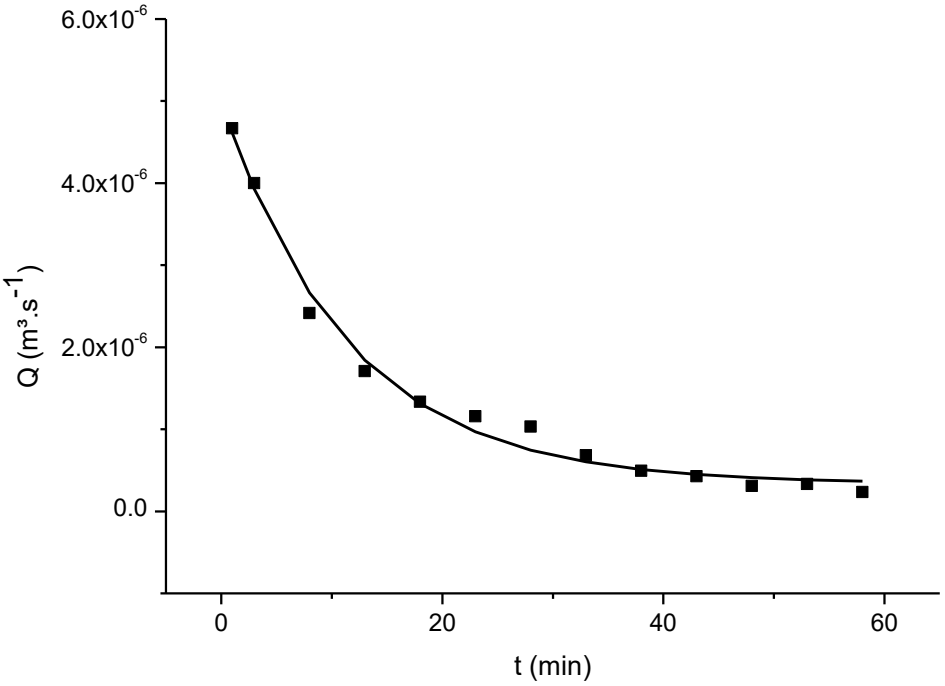


According to Corbatón-Báguena, Álvarez-Blanco, and Vincent-Vela (2015), it is important to note that one of the hypotheses of the Hermia's complete blocking model is that the pore entrance is completely blocked or sealed when one solute molecule arrives at the membrane surface. Therefore, complete blocking consider membrane fouling mechanisms that are external and occur on the membrane surface. These external membrane fouling mechanisms are related to the difference between the solute molecule size and the membrane pore size. Consequently, particles/solutes do not permeate through the membrane, such as casein, lactose, phosphate minerals, and minerals bound to casein micelles. By the obtained results, it was established that in the early stage the rapid

permeate flux decline of the nanofiltration process was characterized initially by standard blocking model and subsequently, by complete blocking model.

NG *et al.* (2017), affirm that a single fouling model did not provide a good description of the entire filtration process. A combined fouling model which take into account both pore blocking and cake formation may be more appropriate, such as the transient area-averaged protein filtration model developed by Ho and Zydney (2000). The data and model predictions are shown in Figure 3.4. The model calculations were in good agreement with the experimental data over the entire nanofiltration period, showing an $R^2 > 0.97$. Corbatón-Báguena, Álvarez-Blanco, and Vincent-Vela (2015), stated that in this model are considered the two stages in the decrease in permeate flux with time: a rapid flux decline due to a pore blocking phenomena and, after that, a slow decrease until the steady-state is achieved due to the formation of a cake layer. According Torkamanzadeh *et al.* (2016), the hypothesis assumed in this model is that by deposition of the first protein aggregates on the membrane surface, the blocked pores will still be partially permeable to the fluid flow. The model also accounts for the nonuniform character of foulant particle deposition over the surface of the membrane. Li *et al.* (2017) suggest that the fouling mechanism in a filtration of concentrated milk is not purely cake formation or protein deposition, but a combination of both, influenced by operating conditions and evolution of the feed composition. Besides the protein deposition, mineral fouling by dairy streams is attributed to the precipitation of calcium phosphate as it is sparingly soluble. Skim milk is supersaturated with respect to calcium phosphate, but precipitation of calcium phosphate does not occur naturally. This is mainly due to associations with casein micelles, which provide a sufficient buffering capacity for calcium phosphate (NG *et al.* 2018). In addition, the nanofiltration membrane cut-off used in this study are smaller than molecular mass of some mineral ions, thus fouling by calcium phosphate precipitation in the bulk fluid could occur during skimmed milk nanofiltration.

Figure 3.4 - Permeate flux experimental (■) by (−) by the combined model from skimmed goat milk nanofiltration process up to volume reduction factor (VRF) equal to 2.



3.2 PHYSICAL AND CHEMICAL PROPERTIES

The total solids, protein and lactose content of skimmed goat milk, retentate and permeate are shown in Table 3.2. It was possible to note that the nanofiltration process was successfully employed for concentrating on total solids, protein and lactose content ($P < 0.05$) from skimmed goat milk indicated that the skimmed goat milk molecular size in the great majority is larger than nanofiltration membrane pore size. The total solids content determined to retentate in this study was higher than that found by Moreno-Montoro *et al.* (2015), in the ultrafiltration of skimmed goat milk. Indeed, the total solids and protein content were higher than the determined by Magenis *et al.* 2006 in ultrafitrated role milk. However, in the present study, some protein molecules do pass through the membrane due to dehydration. The concentration of protein is important, which is advantageous for dairy production given that they are the most important proteins for curd formation in the fermentation process. Casein and whey protein are valuable food ingredients because of their nutritive value and physicochemical and

functional properties. Due to their water-binding, emulsifying, whipping, foaming, and texturizing properties, they are used in a range of commercial applications, including protein fortification of dairy foods, and ingredients for beverages, bakery, and meat (SAUER; DOEHNER; MORARU, 2012). The nanofiltration process was also efficient in the concentration of lactose content, once cannot be quantified in permeate, been predominantly in the retentate.

Table 3.2 - Total solids, protein, and lactose content (g 100 g-1) of skimmed goat milk, retentate and permeate from nanofiltration up to volume reduction factor (VRF) equal to 2.

Samples	Total solids (g 100 g^{-1})	Total protein (g 100 g^{-1})	Lactose (g 100 g^{-1})
Skimmed goat milk	8.46 ± 0.01^{b}	2.91 ± 0.05^{b}	3.93 ± 0.05^{b}
Retentate	13.46 ± 0.08^{a}	4.41 ± 0.02^{a}	8.10 ± 0.32^{a}
Permeate	1.00 ± 0.01^{c}	0.24 ± 0.01^{c}	ND

[a-e] Within a column, means ± standard deviations with different superscript lowercase letters denote significant differences ($P < 0.05$) between the skimmed goat milk and retentate and permeate from nanofiltration (NF). VRF: volume reduction factor.

The nanofiltration process contributed to the increase ($P < 0.05$) of the ash and mineral fractions of retentate (Table 3.3). In relation to mineral fraction, Ca, Mg, and Mn showed the highest ($P < 0.05$) values in the retentate. However, Zn content was presented in the retentate and permeate with similar values. Cu showed higher ($P < 0.05$) values in the permeate, while the Co was lower ($P < 0.05$) in the retentate and permeate in relation to skimmed goat milk. This behavior was related to mineral molecules accumulated and adsorbed onto the surface and inside the pore walls. For this reason, the retentate and permeate showed lower Co content in relation to skimmed goat milk.

Table 3.3 - Ash content and mineral fractions of skimmed goat milk, retentate and permeate from nanofiltration up to volume reduction factor (VRF) equal to 2.

	Skimmed goat milk	Retentate	Permeate
Ash (g $100g^{-1}$)	0.96 ± 0.03^{b}	1.22 ± 0.01^{a}	0.45 ± 0.01^{c}
Ca (mg $100g^{-1}$)	9874.80 ± 3.38^{b}	19266.85 ± 34.77^{a}	848.45 ± 0.36^{c}
Mg (mg $100g^{-1}$)	825.16 ± 1.21^{b}	1801.00 ± 0.15^{a}	99.94 ± 0.01^{c}
Zn (mg $100g^{-1}$)	69.71 ± 0.03^{a}	41.91 ± 0.01^{c}	42.12 ± 0.03^{b}
Cu (mg $100g^{-1}$)	2.99 ± 0.01^{c}	3.80 ± 0.01^{b}	10.10 ± 0.01^{a}
Mn (mg $100g^{-1}$)	0.21 ± 0.01^{c}	2.05 ± 0.01^{a}	0.62 ± 0.01^{b}
Co (mg $100g^{-1}$)	0.869 ± 0.01^{a}	0.665 ± 0.01^{b}	0.276 ± 0.01^{c}

[a-e] Within a row, means ± standard deviations with different superscript lowercase letters denote significant differences ($P < 0.05$) between the skimmed goat milk and retentates and permeates from nanofiltration (NF). VRF: volume reduction factor.

Table 3.4 shows the color parameters of the skimmed goat milk, retentate and permeate. As it can be observed on the data, the whiteness (L^*) was higher ($P < 0.05$) in the retentate and lower ($P < 0.05$) in permeate. The whiteness (L^*) of milk has been shown to have a positive influence on consumer preference, which is why consumers have the more attractive for blades with visual properties close to the whole milk (BERMÚDEZ-AGUIRRE *et al.*, 2009; OWENS; BREWER; RANKIN, 2001). Although retentate presented lower a* values ($P < 0.05$) than skimmed goat milk, it still presented higher ($P < 0.05$) values than permeate. This tendency to a greenish color of the goat milk occurs due to the natural pigment concentration presented in milk, such as the riboflavin. Park *et al.* (2007) cited that this pigment was a green compound present in the aqueous phase which is found in significant quantities in goat milk. The tendency for yellowish color (b*) was observed in skimmed goat milk, retentate and permeate, however showed higher values in retentate. This tendency is associated with the increase of protein content. This behavior was confirmed by the protein content presented in Table 3.2. The combination of these color parameters (L^*, a^*, b^*) are relevant, once that result in the total difference of color (ΔE^*) values. The largest global color difference was verified for the nanofiltration permeate when compared to the skimmed goat milk. Mokrzycki and Tatol (2011) reported that when the ΔE^* values are between 2 and 3.5, the color difference can be detected by human eye, while when the ΔE^* values are higher than 5 the human eye can differentiate two distinct colors. Although the Global color difference of permeate

are 3.16, this value is relatively low, which indicates that the color is similar to skimmed goat milk. Permeate presented ΔE* values of 18. This values show high global color variation in relation to the skimmed goat milk. This behavior observed in permeates can be attributed to the retention of color compounds in the retentate. The maintenance of the color during the process is an important parameter. Conventional processes of concentration can cause change in the color of the milk, perceived as low quality by consumers.

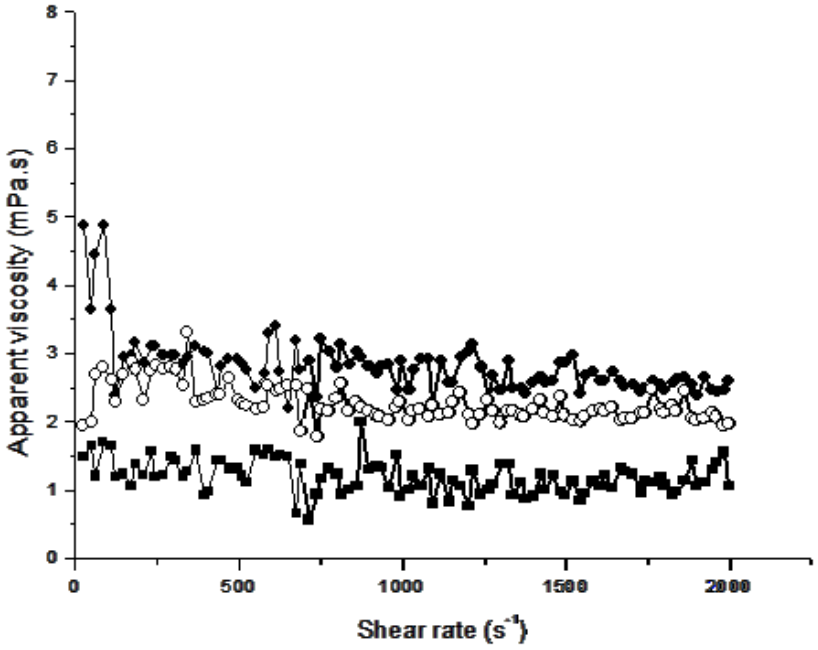
Table 3.4 - Color parameters of skimmed goat milk, retentate and permeate from nanofiltration up to volume reduction factor (VRF) equal to 2.

Color parameters	Skimmed goat milk	Retentate	Permeate
*L**	73.40 ± 0.10[b]	75.45 ± 0.09[a]	55.10 ± 0.22[c]
*a**	-3.22 ± 0.03[a]	-2.51 ± 0.01[b]	-0.62 ± 0.03[c]
*b**	4.19 ± 0.01[b]	6.49 ± 0.01[a]	2.58 ± 0.02[c]
ΔE		3.16	18.51

[a-c] Within a column, means ± standard deviations with different superscript lowercase letters denote significant differences ($P < 0.05$) between the skimmed goat milk and retentates and permeates from nanofiltration (NF). VRF: volume reduction factor.

In relation to the rheological properties, the Figure 3.5 shows the differences between the apparent viscosity behaviors of skimmed goat milk, retentate and permeate. The skimmed goat milk and retentate showed a slight decrease in apparent viscosity with increasing the shear rate, indicated that these fluids had shear thinning characteristics (non-Newtonian behavior). Showing a different behavior, the permeate exhibited a Newtonian behavior. Vélez-Ruiz and Barbosa-Cánovas (1998) related the Newtonian behavior of permeate to the low solids concentrations of these samples (Table 3.2). It was also possible to observe that the apparent viscosity was higher ($P < 0.05$) for retentate. In the concentration of skimmed milk, the increase of viscosity occurs because the removal of water causes an increase in volume fraction of dispersed particles and increases the micelle-micelle interactions as the distance between the micelles becomes smaller (BIENVENUE *et al.*, 2003).

Figure 3.5 - Apparent viscosity versus shear rate of (○)skimmed goat milk (●) retentate and (■) permeate from nanofiltration up to volume reduction factor (VRF) equal to 2.



According to Balde and Aider (2016), Chang and Hartel (1997), and Vélez-Ruiz and Barbosa-Cánovas, (1998) the milk concentrates behaved as non-Newtonian fluids, with flow curves well fitted by the Power law and/or Herschel-Bulkley models as observed in the present study for the skimmed goat milk and retentate, with showed a coefficient of determination (R^2) higher than 0.95 (Table 3.5). The rheological behavior of a fluid can also be described by the consistency coefficient (K), and the flow behavior index (*n)*. When e *n* value is close to 1, the sample shown Newtonian behavior and *n* is less than 1, the sample shear thins with increasing shear rate, whereas if *n* is higher than 1, the sample shear thickens (ANEMA *et al.*, 2014). Both models used showed the higher flow behavior index (*n),* confirming the Newtonian behavior presented in the Figure 3.5. The yield stress (σ_0) were of the samples were close to 0. According Balde and Aider (2016) and Canella *et al.* (2019), when the total solid content of the skimmed milk is lower than 30 g 100 g^{-1} the yield stress presented lower values.

The above experimental results and analysis suggest that the nanofiltration is an interesting technology for skimmed milk concentration. Moreover, it is important to determine the flow decline behaviour since the resistances visualized throughout the

process had a direct influence on the retention of the constituents and the process performance.

Table 3.5 - Rheological parameters obtained using Power Law and Herschell-Buckley model of skimmed goat milk and retentate from nanofiltration up to volume reduction factor (VRF) equal to 2 at 5.0 ± 0.1°C.

Samples	Power Law model			Herschell-Buckley model			
	K (Pa.s^n)	*n*	R^2	σ_0	K (Pa.s^n)	*n*	R^2
Skimmed goat milk	0.003 ± 0.003^{ab}	0.920 ± 0.029^{b}	0.955	0.012 ± 0.002^{c}	0.003 ± 0.001^{ab}	0.927 ± 0.031^{b}	0.955
Retentate	0.005 ± 0.001^{a}	0.922 ± 0.002^{b}	0.968	0.047 ± 0.001^{b}	0.004 ± 0.001^{a}	0.946 ± 0.015^{b}	0.965
Permeate	0.002 ± 0.001^{b}	0.976 ± 0.003^{a}	0.850	0.092 ± 0.001^{a}	0.001 ± 0.001^{b}	1.006 ± 0.012^{a}	0.851

$^{a-e}$ Within a column, means ± standard deviations with different superscript lowercase letters denote significant differences ($P < 0.05$) between the skimmed goat milk and retentates and permeates from nanofiltration (NF). VRF: volume reduction factor; *K*, Consistency index; *n*, flow behavior index; R^2, determination coefficient; σ_0, yield stress.

CONCLUSION

During the nanofiltration process of the skimmed goat milk was observed at the low time a rapid decrease of the permeate flux. At a long time of the nanofiltration process, it was verified a continuous flux, which was characterized by an additional resistance to the permeate flux caused by concentration polarization. For the VRF value equal to 2, the standard and complete blocking was the best fitting modes. The conclusions obtained from a combined model based on the crossflow of the permeate flux decline along the whole filtration curve were that the reversible resistance was the main responsible by the flux decline and the rapid permeate flux decline in the early stage of the nanofiltration process was characterized by standard and complete blocking. The combined model calculations were in good agreement with the experimental data over the entire nanofiltration period. It was determined that the nanofiltration process be successfully employed to concentrate total solids, protein, lactose, ash, and mineral fractions and improve the tendency to whiteness, greenish and yellowish color. The Power Law and Herschel-Buckley models were fitting to describe the flow behavior for retentate, wich presented the higher apparante viscosity. Finally, these findings not only clarify the fouling mechanism involved during the nanofiltration process of the skimmed goat milk but also provide valuable knowledge about the concentration of its components that can be used by dairy industry. These high values prove the potential of this technology for use as a pre-concentration step, aiming to obtain a product with the sensory and nutritional qualities preserved with lower production costs.

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CAPÍTULO 5

*** Artigo submetido para a Revista LWT- Food Science and Technology.**

CANELLA, M. H. M.; DANTAS, A.; BLANCO, M.; RAVENTÓS, M.; HERNANDEZ, E.; PRUDENCIO, E. S. Optimization of goat milk vacuum-assisted block freeze concentration using response surface methodology and NaCl addition influence.

Optimization of goat milk vacuum-assisted block freeze concentration using response surface methodology and NaCl addition influence

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ABSTRACT

Response Surface Methodology was applied to optimize the effects of freezing time (1, 7, and 14 days), vacuum conditions (10 kPa, 40 kPa, and 70 kPa), and time under vacuum (20 min, 40 min, and 60 min) regarding concentrated yield response, resulting from optimal parameters of the milk vacuum-assisted block freeze concentration process. Additionally, it was verified the NaCl influence, using different salt contents (0.5, 1, 1.5, and 2 %) addition and freezing time of 1 day, vacuum equal to 10 kPa, and time under vacuum 60 min, in goat milk vacuum-assisted freeze concentration performance. The concentrate with 1.5 and 2 % of NaCl addition showed the highest values for the total solids (35.06 and 36.21 g 100 g^{-1}) and protein contents (10.43 and 10.70 g 100 g^{-1}), while the concentrate without NaCl addition concentrated more lactose content (17.42 g 100 g^{-1}). The samples with 1.5 and 2% of NaCl addition reached parameters of the process more satisfactory with a concentrate yield of 85.79 and 92.14 %, concentration percentage of 28 and 32 %, and efficiency of process approximately of 90 %. Finally, the best performance was observed when used 1.5 and 2 % NaCl addition in the goat milk submitted to the vacuum-assisted freeze concentration process.

Keywords: Concentration, caprine milk, optimization, sodium chloride, vacuum thawed.

1 INTRODUCTION

Verruck, Dantas, and Prudencio (2019) highlighted that goat milk has attracted huge amounts of attention in the dairy industry and by the researchers in the elaboration because it can be considered a reliable alternative/if not a replacement to cow milk. The increased rates of cow protein allergies of children, credited to the αs1-casein (Albenzio et al., 2012), has encouraged goat product development, such as goat's milk yogurt (Beltrán, Morari-Pirlog, Quintanilla, Escriche, & Molina, 2018) and probiotic fermented goat milk beverages (Mituniewicz-Małek, Zielin´ska, & Ziarno, 2019). However, the scarcity of scientific information on new technologies concentration use, such as the freeze concentration process, and their effects on composition effects is still evident for goat milk.

The freeze concentration process involves a controlled decrease in temperature of the liquid food below the freezing point, with the purpose to avoid the eutectic temperature where the components of the product frozen (Raventós, Hernández, Auleda, & Ibarz, 2007). The block freeze concentration is one type of freeze concentration processes able to result in a concentrated and an ice fraction separated, which can be separated by the use of external forces, such as the vacuum (Aider & Halleux, 2008). Petzold, Orellana, Moreno, Cerda, and Parra (2016) mentioned that the suction by the use of vacuum as an assisted technique in freezing concentration focuses on improving concentration performance. However, according to the author's knowledge, the goat milk vacuum-assisted freeze concentration has not been pursued before in literature, including the addition of salts in this milk as a step before the freeze concentration process.

The addition of NaCl, in milk in the production of dairy products has a preservative effect, extending shelf life. On the other hand, the NaCl addition into the milk prior to the preparation of a dairy product results, for example, in greater salt homogeneity in the matrix and in a reduction in the salting step during cheese making (Yanachkina, McCarthy, Guinee, & Wilkinson, 2016). It knows the presence of sodium chloride changed the mechanism of freezing and thawing in milk solution by lowering their freezing point. The ice crystal grows in the form of dendritic instead of a planar form. As the ice crystal grew, both sodium chloride and other solutes were concentrated. These concentrated salt solutes were released through the channel formed during the melting of these dendritic ice crystals. However, according to Yee,

Wakisaka, Shirai, and Hassan (2004), the concentration index varies according to the amount of sodium chloride added in the milk, which could or not increase the recovered solutes of milk.

Whilst the results of this approach highlight the acceptability of this process for goat milk, they also suggest a potential alternative to the current concentration methods adopted by goat dairy industries. This process, due to its cheaper capital and operating costs, could be an attractive alternative for dairy industries to pursue. Bearing this in mind, firstly was investigated the optimal operating parameters of the goat milk vacuum-assisted freeze concentration process by Response Surface Methodology. In the sequence, the best parameters, founded previously, were used to evaluate the NaCl addition influence about goat milk vacuum-assisted freeze concentration process performance.

2 MATERIAL AND METHODS

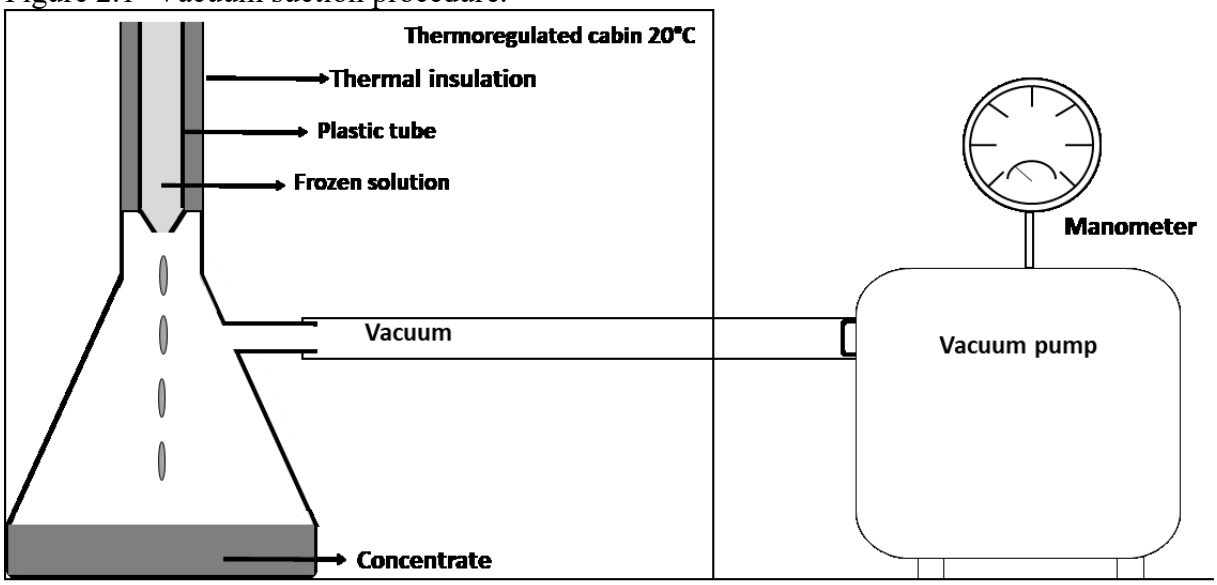
2.1 MATERIAL

Semi-skimmed UHT goat milk (COVAP®, Córdoba, Spain), used as the start material, was obtained from a local supermarket in the area of Barcelona (Spain). The goat milk composition was 9.93 ± 0.01 g total solids 100 g-1, 3.53 ± 0.07 g total protein 100 g-1, 5.08 ± 0.22 g lactose 100 g-1 and 1.60 ± 0.03 g fat 100 g-1. All reagents were of analytical grade.

2.2 GOAT MILK VACUUM-ASSISTED BLOCK FREEZE CONCENTRATION PERFORMANCE

The goat milk (45 mL) placed in plastic tubes was frozen in a static freezer at - 20 ± 1°C. During the freezing process, the external surface of the plastic tubes was covered with thermal insulation made of foamed polystyrene for that the heat transfer mainly occurred unidirectional form. After the freezing process, vacuum goat milk was performed according to the procedure described by Petzold, Niranjan, and Aguilera (2013), to achieve the separation of the most concentrated ice solution. The suction was generated by connecting a vacuum pump to the bottom of the frozen sample at ambient temperature (Fig. 2.1).

Figure 2.1- Vacuum suction procedure.



2.2.1 Experimental design

The response surface methodology (RSM) was used to determine the optimum condition for goat milk vacuum-assisted block freeze concentration. It was used a central composite design (CCD) with the following three independent factors: vacuum (V) (10, 40 and 70 kPa), time under vacuum (T) (20, 40 and 60 min), and freezing time (F) (1, 7 and 14 days). The variation of independent factors values was obtained by preliminary tests. Based on Park and Drake (2016) and Sharma, Patel, and Patel (2016) were done a preliminary test with this pressure value equal to 74.5 kPa and between 14.6–8.0 kPa, respectively. However, the separation of the concentrated from the ice fraction was observed when the vacuum pump reached 70 kPa until 10 kPa. After these steps, new tests were realized to decide the time under vacuum variation. Therefore, in the pressure equal to 70 kPa the separation of both fractions (concentrated and ice) was only noted after the time under pressure of 20 min. On the other hand, at a pressure equal to 10 kPa with a time under vacuum above 60 min was not possible to continue the vacuum-assisted freeze concentration process due to cracks formation in the ice structure, resulting in absence of vacuum in the freeze concentration process. For this reason, the variation of the independent factor for the times under vacuum choice ranged from 20 to 60 min. It is also pointed out that for economic reasons; the small and medium goat dairy industry stored the goat milk for a minimum of 1 and a maximum of 14 days. Because of this was used freezing time range from 1 to 14 days. For better understanding, were also evaluated the average

of these three independent factors, such as vacuum, time under vacuum and freezing time of 40 kPa, 40 min and 7 days, respectively.

The experimental design was composed of seventeen combinations of the independent variables (-1 and 1); eight factorials; six axial; and three repetitions in the central point, as shown in Table 2.1. All tests are performed in triplicate. In order to avoid systematic errors, all the experiments were carried out at random in order to minimize the effect of unexplained variability on the responses obtained. The response variable was the concentrate yield (Y) using total solids contents. After assessing the fit of the initial regression model, the number of variables was reduced according to stepwise methods. Stepwise selection is an algorithmic procedure used to simplify the initial model and to find a reduced model that best explains the data. The Central Composite Design (CCD) for the two-level and three-factor scheme used is described in Table 2.1. The optimal condition was chosen by higher concentrate yield (Y). It is important to note that the pressures indicated in this study (10, 40 and 70 kPa) are absolute pressures (the absolute atmospheric pressure is 101 kPa) and corresponding approximately to 90, 60 and 30 kPa of vacuum.

Table 2.1- Central Composite Design (CCD) for three variables levels, and responses of concentrate yield (%) based on vacuum (kPa), time under vacuum (min), and freezing time (days).

		Variables levels[b]			Response
Assay[a]	Type	Vacuum (kPa)	Time under vacuum (min)	Freezing time (days)	Concentrate yield (%)
1	Factorial	10 (-1)	20(-1)	1(-1)	10.02 ± 2.34
2	Factorial	10(-1)	60(1)	1(-1)	77.97 ± 5.48
3	Factorial	10(-1)	20(-1)	14(1)	12.32 ± 0.37
4	Factorial	10(-1)	60(1)	14(1)	74.13 ± 1.04
5	Factorial	70(1)	20(-1)	1(-1)	3.95 ± 0.44
6	Factorial	70(1)	60(1)	1(-1)	73.35 ± 3.56
7	Factorial	70(1)	20(-1)	14(1)	1.16 ± 0.35
8	Factorial	70(1)	60(1)	14(1)	62.54 ± 5.08
9	Axial	40(0)	20(-1)	7(0)	6.81 ± 1.74
10	Axial	40(0)	60(1)	7(0)	79.70 ± 4.65
11	Axial	40(0)	40(0)	1(-1)	22.74 ± 3.94
12	Axial	40(0)	40(0)	14(1)	21.37 ± 4.27
13	Axial	10(-1)	40(0)	7(0)	27.46 ± 0.96
14	Axial	70(1)	40(0)	7(0)	12.07 ± 0.51
15	Center	40(0)	40(0)	7(0)	19.74 ± 0.75
16	Center	40(0)	40(0)	7(0)	15.35± 1.76
17	Center	40(0)	40(0)	7(0)	14.24 ± 1.79

[a]Experiments were conducted randomly.
[b]Coded levels are within brackets

2.2.2 Influence of NaCl content

Optimal conditions previously determined, such as vacuum, time under vacuum, and freezing time, were employed to evaluate the influence of NaCl in the goat milk vacuum-assisted block freeze concentration performance. Based on the results obtained by Yee,

Wakisaka, Shirai, and Hassan (2004), different NaCl content (0.5 g 100g-1, 1 g 100g-1, 1.5 g 100g-1, and 2 g 100g-1) were added to initial goat milk, which was frozen, and submitted in triplicate to the freeze concentration procedure. In this procedure, the goat milk without NaCl additions was used as a control sample. In this step were obtained from the goat milk with 0 (control), 0.5, 1, 1.5, and 2 g of NaCl addition per 100 g of milk, their concentrate and ice fractions. Therefore, the concentrate and the ice fractions were denoted as follows: concentrate control and ice control; concentrate 0.5 and ice 0.5; concentrate 1 and ice 1; concentrate 1.5 and ice 1.5; concentrate 2 and ice 2, respectively. The total solids, protein, and lactose contents were determined for initial goat milk, and for all concentrate and ice fractions.

2.3 PHYSICOCHEMICAL ANALYSIS

The total solids content was estimated by °Brix using an Atago refractometer (DBX-55, Japan) with an accuracy of 0.1 and measurement range of 0 to 55 °Brix a temperature of 20 ± 5 °C, according to Muñoz et al. (2018) and Floren, Sischo, Crudo, and Moore (2016), with some modifications. Firstly, a standard curve of total solids content (g 100 g-1) against °Brix readings was plotted using different concentrations of semi-skimmed goat milk. The curve points were constructed from samples consisting of freeze-dried semi-skimmed goat milk by applying different dilutions (5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, and 50%). Through a linear regression ($y = 0.9285x + 0.2764$, $R^2 = 0.999$) the °Brix results of the tests were converted and expressed as total solids content (g 100 g^{-1}).

Protein contents (g 100 g^{-1}) were carried out by the Kjeldahl method, converting the sample nitrogen content to protein content by a factor equal to 6.38 (AOAC, 2005). The lactose content procedure was realized according to Schuster-Wolff-Bühring, Michael, and Hinrichs (2010), with modifications. Hewlett Packard 1100 Series HPLC System (Agilent Technologies, Waldbronn, Germany) with tracer carbohydrate (250 × 4.6 mm, 5 μm) column (Teknokroma, Sant Cugat del Vallès, Barcelona, Spain) and C-8 column and refraction index as detector was used for determination. The mobile phase was a mixture of acetonitrile (Panreac Química SLU, Castellar del Vallès, Spain) and distilled water (75:25). The flow rate and column temperature were maintained as 1.3 mL min-1 and 28 °C, respectively. Before the determinations, a portion of 1 mL samples was diluted with 8 mL of distilled water and mixed. Thus, 0.5 mL of Carrez Reagent 1 and 2 were added and mixed for 1 min. The mixture was allowed to settle for 15 min,

and subsequently, filtered by a nylon syringe filter (0.45 μm of diameter pore) (Agilent, Santa Clara, California, United States). Each sample was prepared and injected in triplicate.

2.4 CONCENTRATE YIELD (Y)

Goat milk vacuum-assisted block freeze concentration performance and influence of NaCl content were evaluated by the concentrate yields (Y), which were calculated in accordance with Miyawaki, Liu, Shirai, Sakashita, and Kagitani, (2005), and Moreno, Hernández, Raventós, Robles, and Ruiz (2013), using the Equation 1.

$$Y\ (\%) = \left(\frac{concentrate\ fraction\ total\ solids\ (\mathrm{g\ 100\ g^{-1}})\ x\ concentrate\ fraction\ mass\ (g)}{initial\ goat\ milk\ \ total\ solids\ (\mathrm{g\ 100\ g^{-1}})\ x\ initial\ goat\ milk\ mass\ (g)}\right)\ x\ 100 \qquad (1)$$

2.5 CONCENTRATION PERCENTAGE (CP) AND EFFICIENCY OF PROCESS (*EFF*)

In order to elucidate the influence of different NaCl contents about goat milk, the concentration percentage (CP) and the efficiency of the process (*eff*) were calculated using Equation 2 and 3, respectively.

$$CP\ (\%) = \left(\frac{initial\ mass\ of\ frozen\ fraction\ (g) - final\ mass\ of\ ice\ fraction\ (g)}{initial\ mass\ of\ frozen\ fraction\ (g)}\right)\ x\ 100 \qquad (2)$$

$$eff\ (\%) = \left(\frac{concentrate\ fraction\ total\ solids\ (\mathrm{g\ 100\ g^{-1}}) - ice\ fraction\ total\ solids\ (\mathrm{g\ 100\ g^{-1}})}{concentrate\ fraction\ total\ solids\ (\mathrm{g\ 100\ g^{-1}})}\right)\ x\ 100 \qquad (3)$$

2.6 RESULTS VALIDATION

According to Belén, Sánchez, Hernández, Auleda, and Raventós (2012), Burdo, Kovalenko, and Kharenko (2008), and Sánchez, Hernández, Auleda, and Raventós (2011), the experimental results were validated by the experimental mass balance of each sample calculation. The experimental results were compared with the theoretical value from NaCl content influence, using Equation 4, where Wpred is the predicted ice fraction mass ratio (kg ice/kg goat milk). To determine the deviation between experimental and theoretical data was calculated the root mean square deviation (RMS) (Equation 5), where Wexp and Wpred are the

ratios of experimental and predicted ice mass, respectively, and N is the number of test repetitions.

$$w_{pred} = \frac{initial\ goat\ milk\ tatal\ solids\ (\mathrm{g\ 100\ g^{-1}}) - \ concentrate\ fraction\ total\ solids\ (\mathrm{g\ 100\ g^{-1}})}{ice\ fraction\ total\ solids\ (\mathrm{g\ 100\ g^{-1}}) - concentrate\ fraction\ total\ solids\ (\mathrm{g\ 100\ g^{-1}})} \quad (4)$$

$$RMS\ (\%) = 100\sqrt{\frac{\sum\left(\frac{w_{exp}-w_{pred}}{w_{exp}}\right)^2}{N}} \quad (5)$$

2.7 STATISTICAL ANALYSIS

The regression coefficients for linear, quadratic, and interaction terms were determined by using multiple linear regressions. The significance of each regression coefficient was judged statistically by computing the t-value from pure error obtained from the replicates at the central point of this experiment. The regression coefficients were then used to generate response surfaces. Results were expressed as a mean ± standard deviation. To determine significant differences ($P < 0.05$) between results of NaCl content influence, it was used one-way analysis of variance (ANOVA), and Tukey studentized range test. All statistical analyses were performed using Minitab 18 for Windows (Minitab Inc. State College, PA, USA).

3 RESULTS AND DISCUSSION

3.1 EXPERIMENTAL DESIGN

The responses obtained for concentrate yield (Y) from the seventeen experiments are shown in Table 2.1. The P-values of the reduced model are shown in Table 3.1, which shows that all the individual effects in the reduced model were significant ($P < 0.05$). Regarding the quadratic terms, the time under vacuum had an effect ($P < 0.05$). It was also possible to observe that an interaction between the vacuum and freezing time ($P < 0.05$), and between time under vacuum and freezing time ($P < 0.05$) had on effect on the concentrate yield (Y).

Table 3.1 - Analysis of variance of the values of concentrated yield of semi-skimmed goat milk vacuum-assisted block freeze concentration.

Source	*P* Value
Linear	
Vacuum	0.000*
Time under vacuum	0.000*
Freezing time	0.013*
Quadratic	
Time under vacuum * Time under vacuum	0.000*
Interaction	
Vacuum * Freezing time	0.038*
Time under vacuum * Freezing time	0.016*

*Values significantly different ($P < 0.05$).

The reduced model was obtained in order to eliminate the redundant information by means of the method of variable selection step-by-step (α to enter 0.15, α to remove 0.15). The regression equation of the reduced model is presented in Equation 6, being its R^2 value equal to 0.99. In this equation V is the vacuum (kPa), T is the time under vacuum (min), and F is the freezing time (days).

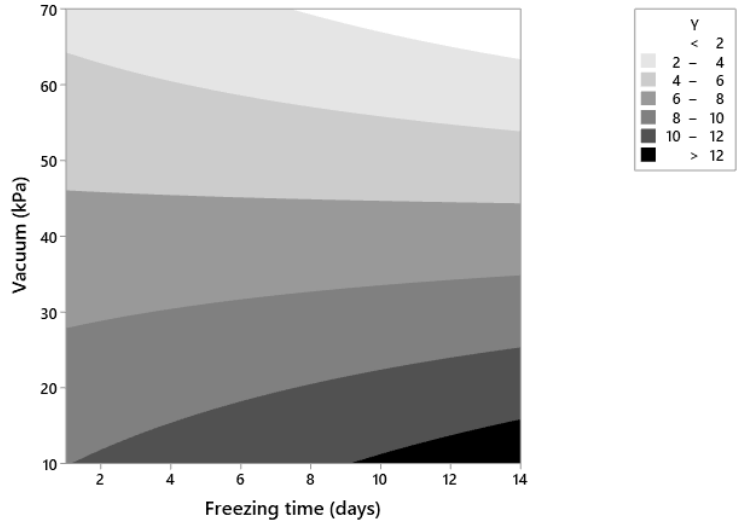
$$Y = 40.66 - 0.1024\,V - 2.579\,T + 0.601\,F + 0.05415\,T \times T - 0.00774\,V \times F\ 0.01361\,T \times F \qquad (6)$$

Fig. 3.1 (a,b,c) and 3.2 (a,b) show the contour and surface plot, respectively, elaborated from the regression model, which represents the trend of factor selection for better concentrate yield (Y). These contour and surface plots showed that there was an increase for Y value when time under vacuum was equal to 60 min (Fig. 2c and 3a,b). In Fig. 2 c also was noted that the best concentrate yield was determined when used a vacuum and freezing time equal to 10 kPa and 1 day, respectively, reaching values higher than 77.5 %. A close result for Y (between 76 to 83%) was obtained by Muñoz et al. (2018), after the progressive freeze concentration of skimmed cow milk with an agitated vessel. Tribst et al. (2020) verified that the goat milk freezing time was affected by the milk particle size distribution. According to

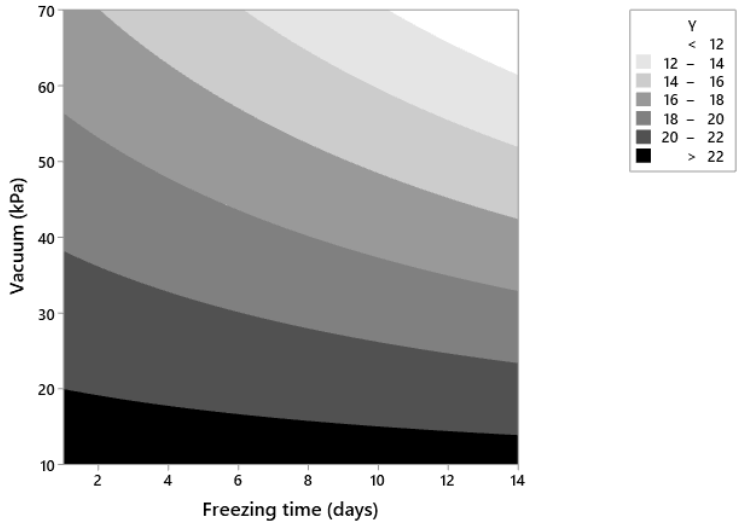
these authors, the interaction/adsorption of casein micelles with fat globules is responsible for the higher volume of larger particles, indicating that part of the fat globules was clumped or part of proteins were aggregated. Therefore, these clumped/aggregated can compromise the separation of total solids between concentrate and ice fractions. Park, Kim, Hong, Kwak, and Min (2006), evaluating the effect of ice recrystallization on freeze concentration of milk solutes, highlighted that the ice morphology changed during a long freezing time, affecting the solute recovery. These authors affirmed that ice crystal size increased with the freezing time, because most of the ice crystals exhibited an agglomerated and compacted form, reducing the dendritic form crystal, which is founded in shorter freezing times. Therefore, the compacted form may have caused a decrease in the ice channels, reducing the total solids of milk output from the ice fraction. This behavior leads us to believe that the crystal geometry obtained in a long freezing time, is not adequate for the scape of concentrate solution from the ice fraction, resulting in a decrease of the concentrate yield.

Figure 3.1- Contour plot of the concentrated yield (Y) at 20 (a), 40 (b), and 60 (c) minutes of time under vacuum.

a)



b)



c)

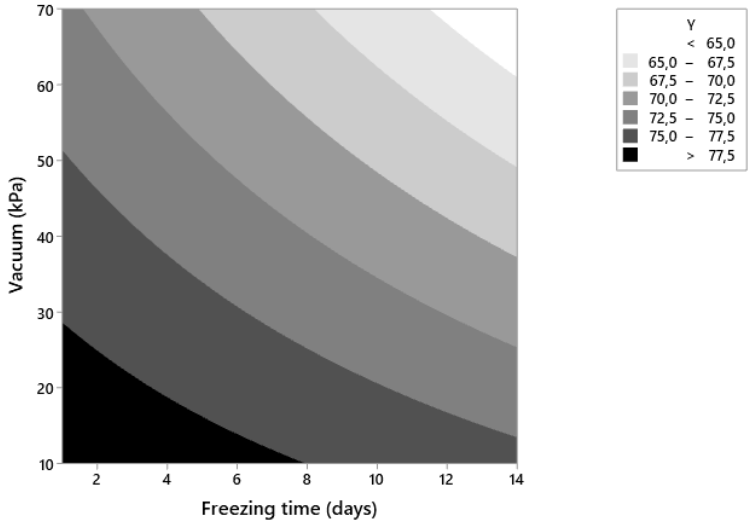
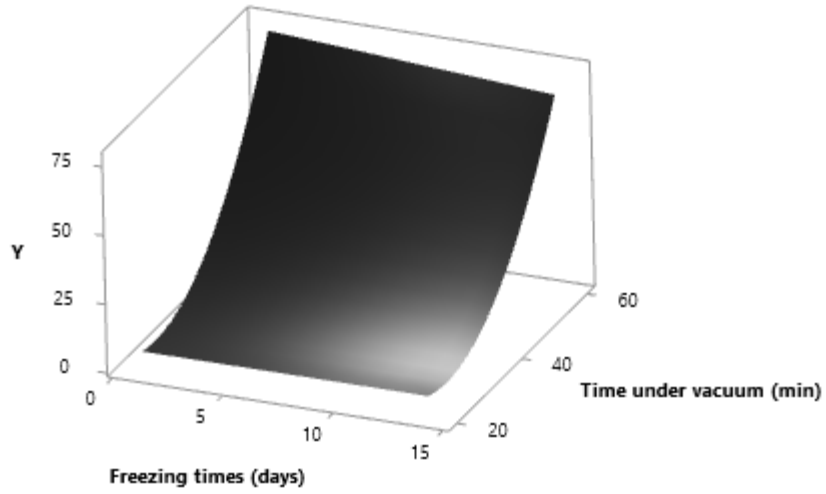
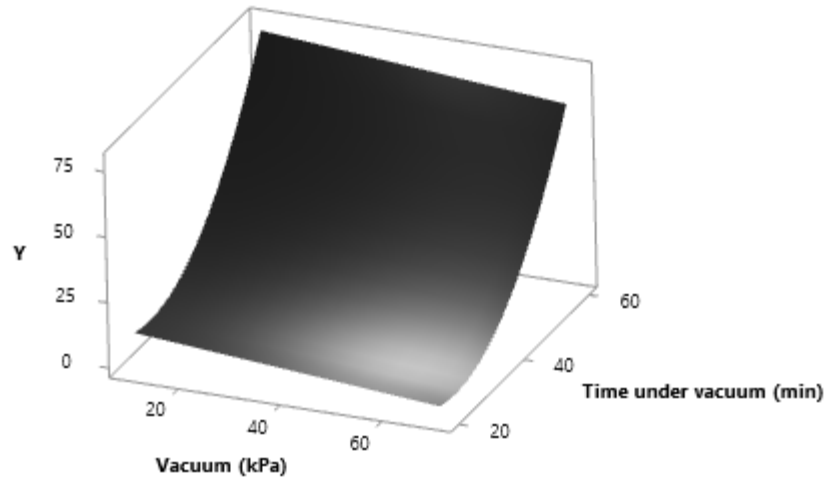


Figure 3.2 - Surface plot of the interaction effect of (a) time under vacuum (min) and freezing times (days); (b) time under vacuum (min) and vacuum (kPa) on concentrate yield (Y).

a)



b)



3.2 INFLUENCE OF NaCl CONTENT

Under optimal conditions (vacuum equal to 10 kPa, time under vacuum of 60 min, and freezing time of 1 day), the vacuum-assisted block freeze concentration was applied in the goat milk samples without (control) and with different NaCl contents additions. The total solids, protein and lactose contents determined in the concentrate (control, 0.5, 1, 1.5, and 2) and ice fractions (control, 0.5, 1, 1.5, and 2) are shown in Table 3.2. All concentrates fractions showed higher total solids content than the initial goat milk. However, in relation to the total solids and

protein contents, the best freeze concentration performance was observed when added 1.5 and 2%, and 1 to 2 % of NaCl, respectively. These concentrates showed approximately 4 times more ($P < 0.05$) for total solids content and 3 times more ($P < 0.05$) for protein contents, than the initial goat milk. However, in the present study, all total solids contents of concentrates were higher than those determined by Muñoz et al. (2018) and Balde and Aider (2016), for skimmed cow milk, using the progressive freeze concentration and the block freeze concentration, respectively. This behavior is expected because, in accordance with Petzold et al. (2013), the high separation of solids and protein contents obtained by vacuum-assisted freeze concentration is a consequence of using an external driving force (vacuum) that improves the natural separation of gravitational thawing. Between the concentrate fractions, the lower ($P < 0.05$) total solids content was found for the concentrate 0.5. As expected, all ice fractions showed lower ($P < 0.05$) total solids content than goat milk.

Table 3.2 - Total solids, protein and lactose content (g 100 g-1) of initial semi-skimmed goat milk, concentrates, and ice fractions obtained by vacuum-assisted block freeze concentration.

Samples	Total solids (g $100g^{-1}$)	Protein (g $100g^{-1}$)	Lactose (g $100g^{-1}$)
Semi-skimmed goat milk	9.94 ± 0.01^{eA}	3.53 ± 0.07^{cA}	5.08 ± 0.22^{fA}
Concentrate control	32.87 ± 1.31^{bc}	9.43 ± 0.11^{b}	17.42 ± 0.12^{a}
Ice control	3.71 ± 0.53^{F}	1.14 ± 0.08^{D}	1.53 ± 0.08^{D}
Concentrate 0.5	28.07 ± 1.18^{d}	9.31 ± 0.22^{b}	12.45 ± 0.08^{e}
Ice 0.5	9.72 ± 0.04^{B}	3.46 ± 0.16^{A}	2.77 ± 0.09^{B}
Concentrate 1	30.57 ± 1.34^{c}	10.45 ± 0.03^{a}	14.40 ± 0.09^{c}
Ice 1	6.18 ± 1.03^{C}	2.17 ± 0.01^{B}	2.42 ± 0.13^{C}
Concentrate 1.5	35.06 ± 2.76^{ab}	10.70 ± 0.39^{a}	15.63 ± 0.12^{b}
Ice 1.5	5.07 ± 0.20^{D}	1.71 ± 0.04^{C}	1.61 ± 0.14^{D}
Concentrate 2	36.21 ± 1.21^{a}	10.43 ± 0.01^{a}	14.06 ± 0.09^{d}
Ice 2	3.90 ± 0.01^{E}	0.96 ± 0.25^{E}	1.01 ± 0.10^{E}

[a,b,c] Within a column, means ± standard deviations with different superscript lowercase letters denote significant differences ($P < 0.05$) between the semi-skimmed goat milk and the concentrated fraction of each mixture of milk and NaCl content (g 100 g^{-1}). [A,B,C] Within a column, means ± standard deviations with different superscript uppercase letters denote significant differences ($P < 0.05$) between the semi-skimmed goat milk and the ice fraction of each mixture of milk and NaCl content (g 100 g^{-1}). Concentrate control and ice control, Concentrate 0.5, Ice 0.5, Concentrate 1, Ice 1, Concentrate 1.5, Ice 1.5, Concentrate 2, and Ice 2 were the concentrates and ice fractions obtained by vacuum-assited block freeze concentration of semi-skimmed goat milk without and with the addition of 0.5, 1, 1.5, and 2 g of NaCl per 100 g of milk, respectively.

Overall, our results indicated in the concentrates fractions that the increase of salt addition resulted in an increase of total solids and protein contents. Yee et al. (2003) stated that the sodium chloride addition, a monovalent salt, influenced the mechanism of freezing and thawing by lowering the freezing point of a protein solution. In this case, this behavior made us believe that the greatest concentration of sodium chloride transition changes the form of ice crystal from planar to dendritic. According to Yee et al. (2003) is expected the growth of dendritic ice crystal during the freezing of solutions with sodium chloride addition, as well as the freezing point becomes lower. Therefore, these dendritic ice crystals melted upon thawing, to form channels that allow the concentrate to be drained out, resulting in the increase of total solids and protein contents.

The lactose content was higher ($P < 0.05$) for the concentrate control, without NaCl addition, when compared with the others concentrates from goat milk with different NaCl additions. Bhargava and Jelen (1996) concluded that salt addition decreases the lactose solubility. Allan, Gruch, and Mauer (2020) related that the form in which lactose crystallizes into ice crystal is dependent on the water activity, temperature conditions during crystallization, among other factors. Chandrapala, Wijayasinghi, and Vasiljevic (2016) also observed that salts may change the solubility of lactose which leads to supersaturation, thereby affecting the growth of lactose ice crystal. Thus, this fact could have affected the output of lactose from the ice fraction.

The concentrate yield (Y) from the total solids contents is shown in Fig. 3.3. Concentrate yield highest values ($P < 0.05$) were obtained when used 1.5 % (85.79 %) and 2 % (92.14 %) of NaCl. Similar values were founded using vacuum-assisted block freeze concentration for wine by Petzold et al. (2016) and, for blueberry juice by Orellana-Palma, Petzold, Pierre, and Pensaben (2017b). Similar behavior was also observed for the concentration percentage (CP) values, whose concentrate 1.5 and 2 showed the highest values, is equal to 28 % and 32 %, respectively (Fig. 3.4). As cited before, these facts are related to the higher content of total solids present in concentrates (Table 3.2).

Figure 3.3 - Concentrate yield (Y) as function of NaCl content added to samples (0%, 0.5%, 1%, 1.5%, and 2%) of semi-skimmed goat milk.

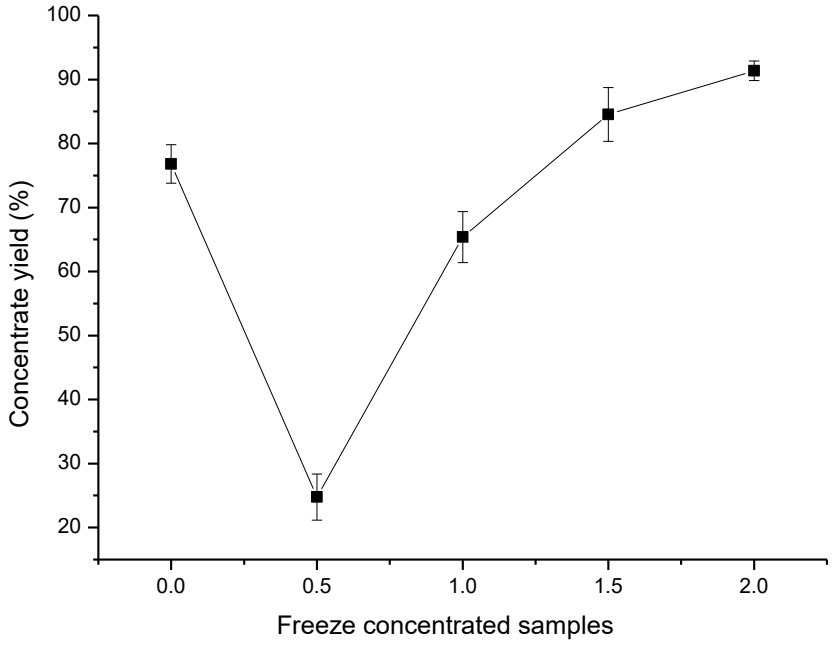
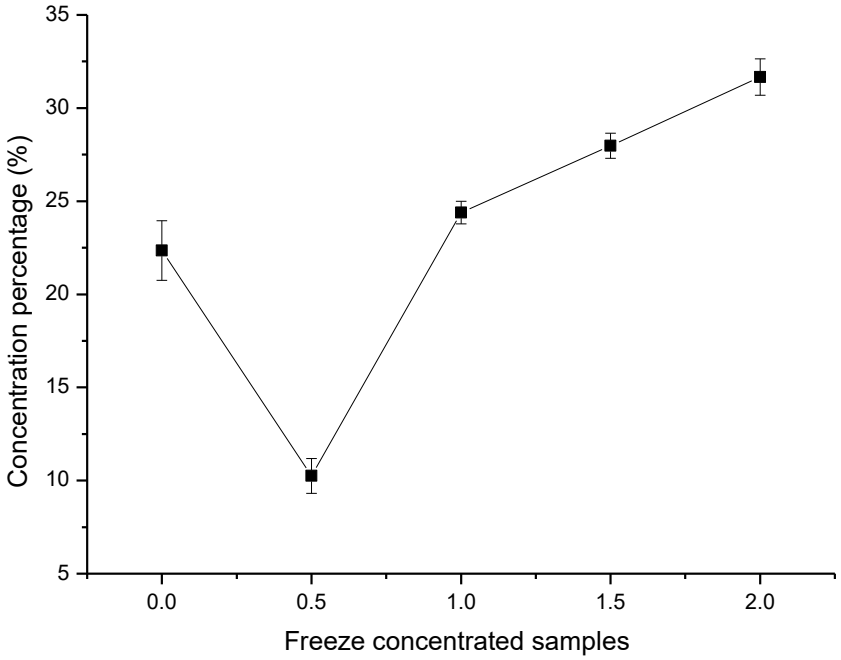
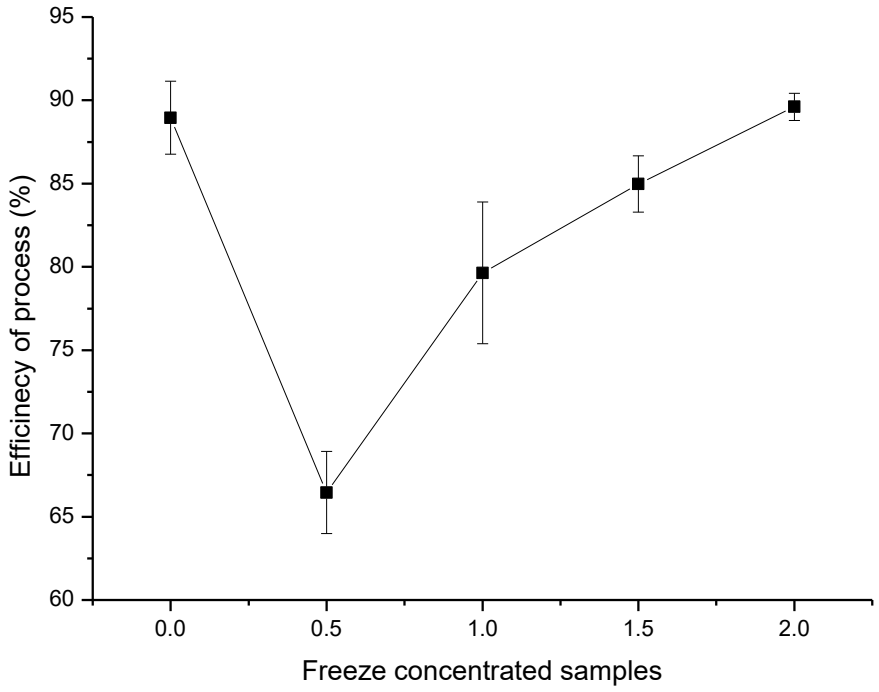


Figure 3.4 - Concentration percentage (CP) as function of NaCl content added to samples (0%, 0.5%, 1%, 1.5%, and 2%) of semi-skimmed goat milk.



The efficiency of the process (*eff*) had a progressive increase (P <0.05) with the increase of the NaCl content (Fig. 3.5). However, the best *eff* was noted for the process with the control and goat milk with 1.5 and 2 % of NaCl content, which achieved values approximately 90 %. Similar values were reached for the freeze concentration of whey by Aider, Halleux, and Melnikova (2009), and for the skim milk by Balde and Aider (2016) and Canella et al. (2019). These studies credited the highest eff from freeze concentration fractions to their dependence on the total solids contents. The vacuum improved the efficiency over atmospheric conditions in freeze concentration due to the positive effect of pressure difference on the movement of the concentrated liquid fraction in block freeze-concentration, showing conform Pardo and Sánchez (2015) higher efficiency than those in similar processing conditions that used gravity as the separation method.

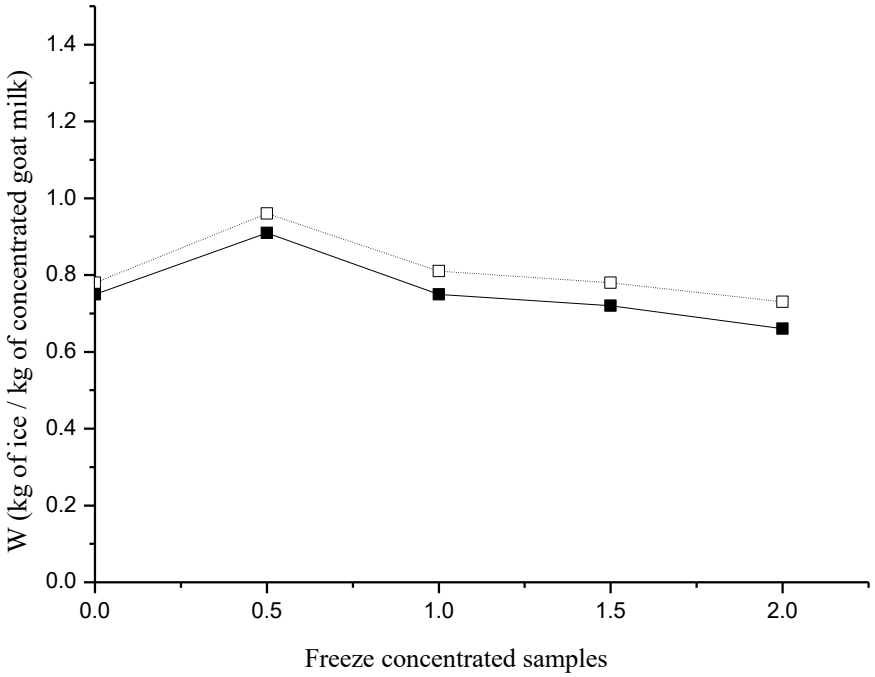
Figure 3.5 - Efficiency of process (*eff*) as function of NaCl content added to samples (0%, 0.5%, 1%, 1.5%, and 2%) of semi-skimmed goat milk.



To validate the experimental results, the mass balance was calculated and compared with the theoretical value from NaCl content influence. The ice mass ratio had an expected downward trend with NaCl addition (Fig. 3.6), which can be attributed to the NaCl addition. Besides, an agreement was observed between the experimental (Wexp) and predicted (Wpred) ice mass ratios over the NaCl content. With the root mean square (RMS) values were observed

a good adjustment of the process since these values were equal to 4.14%, 5.71%, 7.84%, 9%, and 10.52% for the vacuum-assisted block freeze concentration, goat milk without and with 0.5 %, 1%, 1.5 % and 2% of NaCl addition. Lewicki (2000) highlighted that a freeze concentration process is considered an acceptable fit when RMS value was lower than 25 %. Comparing with tests using vacuum-assisted freeze concentration process, Petzold et al. (2013); Petzold et al. (2016); Orellana-Palma, Petzold, Torres, and Aguilera (2017a); and Orellana-Palma et al. (2017b) achieved RMS values of 4.9 % for sucrose solutions; 6.8 % and 9.5 % for wine; 5.1 % and 8.7 % for orange juice; and 3.1 % and 9.6 % for blueberry juice, respectively. Comparing these literature results with our study, we confirm that the goat milk could be submitted to the vacuum-assisted block freeze concentration, considered a recent innovation of food concentration. The results of this approach highlight the acceptability of this process for goat milk is a potential alternative to the current concentration methods adopted by dairy industries. The vacuum-assisted freeze concentration process, due to its cheaper capital, operating costs, and energy consumed, in comparison with the traditional concentration process, such as the vacuum evaporation, is an attractive alternative for goat dairy industries. Balde and Aider (2017) emphasized that the use of freeze concentration is energetically highly interesting, because of the low water latent heat of freezing in comparison with the water latent heat of vaporization (80 kcal/kg versus 540 kcal/kg). Moreover, the concentration of goat milk frozen is also important, because of the seasonality of milk production, of the low animal productivity and of the short periods of lactation. Therefore, frozen goat milk is commonly used to overcome these limitations, allowing its storage for days, reaching a compatible volume with dairy production, mainly when the objective is the use of one concentration process. Goat milk concentration shows advantages in terms of processing, packaging, transportation, and handling. Since most changes occur in an aqueous environment, the removal of some part of goat milk water results in milk preservation. It is noteworthy that dairy industries are concerned principally with food preservation and the production of high-quality products.

Figura 3.6 - Experimental (■) and predicted (- □ -) ice mass ratios as a function as function of NaCl content added to samples (0%, 0.5%, 1%, 1.5%, and 2%) of semi-skimmed goat milk.



The results about the influence of NaCl content on the goat milk freeze concentration performance encourage us to recommend the use of concentrates 1.5 and 2 as an ingredient in dairy products development. Therefore, the vacuum-assisted freeze concentration process associated with NaCl addition could have a detrimental effect on the physical and chemical properties of skimmed goat milk, as well as consumer acceptance, which could affect the commercialization potential of these new products.

Sun and Zheng (2006) noted that the flavor and taste of the food products had been substantially increased, after the use of unitary operations which used low temperatures associated with the vacuum. Therefore, it is expected that skimmed goat milk submitted to the vacuum-assisted freeze concentration process could have different sensorial properties. Ranadheera et al. (2019) cited that, for the monitoring and adjustment of sensory characteristics to optimize the acceptability of goat milk products, descriptive tests present great applicability, such as descriptive analysis. This analysis is recognized as an adequate technique to determine the sensory profile of processed foods, thus providing detailed, robust, and reproducible results (Esmerino et al., 2017). In addition, to information on the sensory characteristics of the product, methods that take into account the needs, beliefs, feelings and motivations of consumers are also important for the elaboration of a food product. According to Gambaro (2018), the

projective techniques lies in the fact that they lead consumers to express themselves beyond the rational, and allow access to underlying or deep attitudes and emotions, revealing non-conscious or not openly accepted motivations in their buying behavior. These methods do not require training, have a low financial impact, optimize time and resources in dairy industries, and provide information highly correlated with traditional methods (Varela & Ares, 2012), providing a total assessment of products and take all sensory traits into account (Esmerino et al., 2017).

CONCLUSION

Applying the Response Surface Methodology to optimize and evaluate the effects of freezing time, vacuum, and time under vacuum to a frozen goat milk sample it was noted that all factors presented effect in the concentrate yield of the sample. To obtain the higher value of concentrate yield the optimal conditions of vacuum-assisted freeze concentration process are vacuum, time under vacuum, and freezing time equal to 10 kPa, 60 min, and 1 day, respectively. The concentrates fractions from goat milk with 1.5 % and 2 % of NaCl addition are recommended because they showed the best characteristics in relation to total solids and protein contents, which increased 4 and 3 times, respectively, when compared with initial goat milk. The recommendation of both concentrates is also based on their best results obtained to concentrate yield (> 85 %), concentration percentage (≥ 28 %), and efficiency of the process (approx. 90 %) values, as well as a good adjustment of the process, resulting in RMS values less than 11 %.

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Declaration of competing interest

The authors declare that they have no conflict of interest.

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CONSIDERAÇÕES FINAIS

A crioconcentração em blocos e a nanofiltração mostraram-se técnicas promissoras para a concentração de leite de cabra desnatado, visando a recuperação dos sólidos totais. Em ambos os processos, observou-se um aumento gradual no conteúdo de sólidos totais ao longo das etapas de concentração. Além disso, a crioconcentração apresentou alta eficiência de concentração nas duas primeiras etapas do processo em relação a concentração dos sólidos totais e minerais.

Os processos de crioconcentração em blocos e nanofiltração também possibilitaram o aumento do teor de proteínas e minerais do leite, estando positivamente correlacionado com o aumento do teor de sólidos totais. Foi possível detectar uma tendência à coloração amarelo-esverdeada em todas as amostras concentradas. Além disso, os modelos de Lei da Potência e Herschel-Buckley foram os mais adequados para descrever o comportamento do fluxo dos concentrados e retentado.

Na nanofiltração, o processo de concentração ocorreu até atingir um fator de redução volumétrica igual a 2. Através da avaliação do comportamento do processo de nanofiltração foi possível observar um declínio de fluxo do permeado e as resistências características deste processo no leite de cabra desnatado. Para fator de redução volumétrica igual a 2, os modelos de bloqueio padrão e completo foram os que apresentaram melhores ajustes. A resistência reversível foi a principal responsável pelo declínio rápido declínio de fluxo do permeado na fase inicial do processo de nanofiltração, enquanto que o posterior fluxo contínuo foi causado pela polarização da concentração.

No processo de crioconcentração em blocos assistido por vácuo, aplicando a metodologia de superfície de resposta para otimizar e avaliar os efeitos do tempo de congelamento, vácuo e tempo sob vácuo em uma amostra de leite semidesnatado de cabra, observou-se que todos os fatores apresentaram efeito no rendimento de concentrado da amostra. Para obter um maior rendimento do concentrado, as condições ideais do processo de crioconcentração assistido por vácuo foram de um vácuo a 10 kPa, tempo de vácuo igual a 60 min e tempo de congelamento de 1 dia. Quando adicionado NaCl nas amostras de leite, as frações concentradas do leite de cabra com adição de 1,5% e 2% de NaCl são recomendadas, pois apresentam as melhores características em relação ao teor total de sólidos e proteínas, que aumentaram 4 e 3 vezes, respectivamente, quando comparadas ao leite de cabra inicial. A

recomendação de ambos os concentrados também se baseia nos melhores resultados obtidos para o rendimento do concentrado, a porcentagem de concentração e a eficiência do processo. Assim, o conhecimento gerado neste estudo pode ser facilmente utilizado pela indústria de processamento de leite de cabra, a fim de obter um concentrado com alto teor de sólidos totais, com maior qualidade nutricional, sem alterações químicas e bioquímicas indesejáveis.

Sugere-se como trabalhos futuros a otimização das condições operacionais da crioconcentração em blocos e nanofiltração para os ensaios de concentração do leite de cabra e a realização da crioconcentração assistida por vácuo no leite de cabra adicionando diferentes sais, visando uma melhor recuperação de sólidos totais. Além de propor a aplicação dos leites de cabra concentrados por nanofiltração e crioconcentração em blocos assistido ou não por vácuo na elaboração de diferentes alimentos e a avaliação deste produtos por métodos sensoriais.

ANEXO A – Carta de aceite do artigo "Block freeze concentration as a technique aiming the goat milk concentration: fate of physical, chemical, and rheological properties" para a revista International Journal of Engineering Sciences & Research Technology.

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Sincerely
Prof. Jitendra Singh Chouhan,
Editor, IJESRT

ANEXO B – Primeira página da publicação do artigo "Block freeze concentration as a technique aiming the goat milk concentration: fate of physical, chemical, and rheological properties".

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BLOCK FREEZE CONCENTRATION AS A TECHNIQUE AIMING THE GOAT MILK CONCENTRATION: FATE OF PHYSICAL, CHEMICAL, AND RHEOLOGICAL PROPERTIES

Maria Helena Machado Canella*[1], Isabella de Bona Muñoz[1], Eulália Lopes da Silva Barros[2], Callebe Camelo Silva[2], Leandro Antunes de Sá Ploêncio[3], Heitor Daguer[3] & ElaneSchwinden Prudencio[1]*

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[3]Ministério da Agricultura, Pecuária e Abastecimento, Laboratório Nacional Agropecuário, Seção Laboratorial Avançada de São José (SLAV/SC/LANAGRO/RS), São José, SC 88102-600, Brazil

DOI: 10.5281/zenodo.2836603

ABSTRACT

In the face of the results scarcity for the goat milk processing using emerging and innovative technologies, the results obtained in the present study are relevant, and may in the future be extremely important for goat milk industry. Therefore, block freeze concentration technique was used to concentrate skim goat milk until three stages. The effects of freeze concentration on skim goat milk properties were evaluated by the analysis of total solids content, lactose content, total protein content, casein content, whey protein content, mineral content, and density. The color parameters of concentrate and ice fractions were also evaluated according to the CIELab color scale, and according to the rheological parameters. As the freeze concentration stages progressed, the total solids content, total protein, casein, and whey protein contents increased in both concentrate and ice fractions. In all stages, it was possible to note that the lactose content showed an equilibrium between both fractions. The densities values of both fractions also increased by increasing of the freeze concentration stages. Block freeze concentration obtained concentrates from skim goat milk with a whiteness index similar to whole milk. Overall, all concentrate and ice fractions showed tendency a greenish and yellowish color. The transition from Newtonian to non-Newtonian behavior was observed for concentrates and ices from second and third stages, respectively. Power Law and Herschel-Buckley models fitted to describe the behavior of the flow of all concentrate and ice fractions. The results generated in this study showed that concentrates from stage 1 and 2 demonstrated a promising product to be used by dairy industries.

KEYWORDS: Skim goat milk; block freeze concentration; goat milk concentrate; physical-chemical properties; rheological properties.

1. INTRODUCTION

The production of goat milk and its processing constitutes an economic activity of increasing importance due to the high nutritional interest of goat milk. Although goat milk production has been relatively minor compared to bovine milk, the world production of goat milk increased 17% between the years 2000 and 2016 [1]. Goat milk and its products are important in human nutrition and have become a part of the current trend of healthy eating around the world [2, 3, 4]. Besides that, the increase in demand for new dairy products with high added value in sophisticated market niches has stimulated goat milk production and trade [5]. The goat milk has high added value because it is a source of proteins of excellent quality, due to the proportion of essential amino acids [4, 6]. The importance of this milk is also intensifying because utilization of bovine milk had become a common cause of human food allergy [7]. The difference in protein composition of the goat milk in relation to cow milk, particularly regarding the casein fractions, made the goat milk be considered less allergenic [8, 9] and more

ANEXO C – Carta de aceite do artigo "Performance of Skim Goat Milk Mineral Content Subjected to the Block Freeze Concentration Process" para a revista Asian Journal of Advances in Agricultural Research.

Gmail **Maria Helena Canella <helenacanella@gmail.com>**

Fwd: Minor review comments for manuscript number: 2019/AJAAR/49102

1 mensagem

elane.prudencio@ufsc.br <elane.prudencio@ufsc.br> 8 de maio de 2019 12:01
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ANEXO D – Primeira página da publicação do artigo "Performance of Skim Goat Milk Mineral Content Subjected to the Block Freeze Concentration Process".

Asian Journal of Advances in Agricultural Research

9(4): 1-9, 2019; Article no.AJAAR.49102
ISSN: 2456-8864

Performance of Skim Goat Milk Mineral Content Subjected to the Block Freeze Concentration Process

Maria Helena Machado Canella[1], Eulália Lopes da Silva Barros[2], Callebe Camelo-Silva[2], Silvani Verruck[1], Heitor Daguer[3], Luciano Molognoni[3] and Elane Schwinden Prudencio[1*]

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Authors' contributions

This work was carried out in collaboration among all authors. Authors MHMC and ESP designed this study, reviewed all steps and the data analysis. Authors MHMC, LM and ESP wrote the protocol of the analysis and the first draft. Authors MHMC, ELSB and CCS realized the statistical analysis and managed the literature searches. Authors SV and HD reviewed all steps of this work. All authors read and approved the final manuscript.

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ABSTRACT

The aim of this study was to evaluate the goat milk mineral performance concentrated by block freeze concentration process. Twenty batches of skim goat milk, each one with one liter, were subjected until the third stage of the freeze concentration process. The initial skim goat milk, concentrated, and ice fractions obtained were analyzed by calcium, magnesium, zinc, phosphorus, sodium and potassium content. Results showed that phosphorus content not increased ($P < 0.05$)

**Corresponding author: Email: elane.prudencio@ufsc.br;*

ANEXO E – Carta de submissão do artigo "Optimization of goat milk vacuum-assisted block freeze concentration using response surface methodology and NaCl addition influence " para a revista LWT-Food Science & Technology.

Gmail **Maria Helena Canella <helenacanella@gmail.com>**

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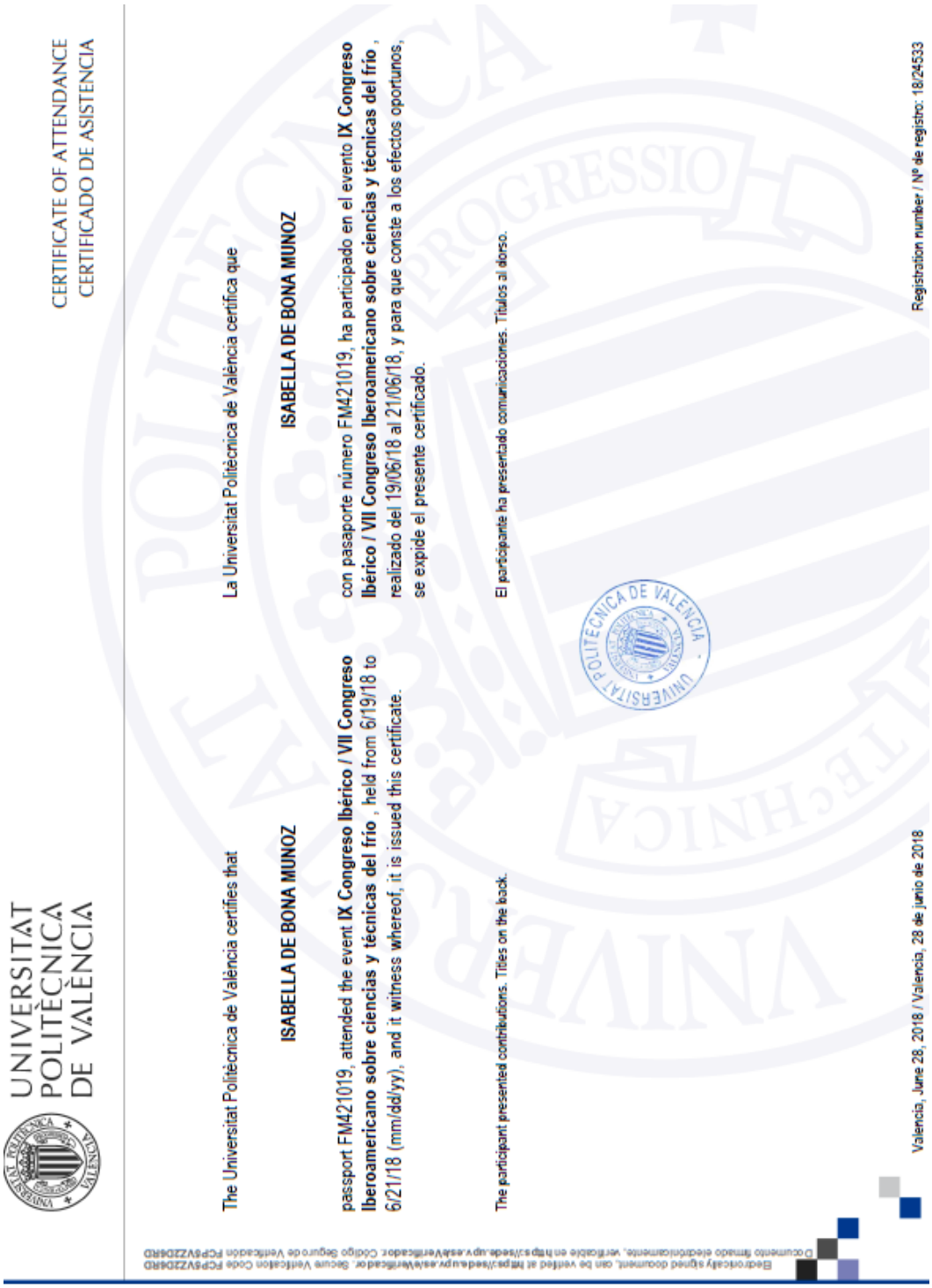
ANEXO F – Certificado de apresentação oral do trabalho "Processo de crioconcentração em blocos: efeito dos estágios de congelamento e descongelamento no teor de cálcio do leite de cabra desnatado" na VII Semana Acadêmica de Ciência e Tecnologia de Alimentos – 2018.

ANEXO G – Certificado de apresentação do trabalho “Effect of block freeze concentration process in the casein contente of skimmed goat milk” no IX Congreso Ibérico / Congreso Iberoamericano sobre ciencias y técnicas del frio – 2018.



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The participant presented contributions. Titles on the back.

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El participante ha presentado comunicaciones. Títulos al dorso.

Valencia, June 28, 2018 / Valencia, 28 de junio de 2018

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EFFECT OF THE BLOCK FREEZE CONCENTRATION PROCESS IN THE CASEIN CONTENT OF SKIMMED GOAT MILK

PROGRESSIVE FREEZE CONCENTRATION OF WHEY IN A PILOT PLANT: PROCESS PERFORMANCE

ANEXO H – Certificado de apresentação do trabalho "Efecto del cloruro de sódio y de la crioconcentración assistida por vacío en la concentración de proteínas en la leche de cabra" no X Congreso Nacional CyTA – CESIA.

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EFECTO DEL CLORURO DE SODIO Y DE LA CRIOCONCENTRACIÓN ASISTIDA POR VACÍO EN LA CONCENTRACIÓN DE PROTEÍNAS EN LA LECHE DE CABRA

M. H. M. Canella[2], E. Hernández[1], M. Raventós[1], E. S. Prudêncio[2]
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Breve descripción de la comunicación:
En este trabajo se evaluó el efecto del NaCl y de la crioconcentración asistida por vacío en la concentración de proteínas en la leche de cabra semidesnatada. Los resultados muestran que la adición de NaCl afectó significativamen-te la concentración de proteína de la leche de cabra.

Palabras clave – crioconcentración, cloruro de sodio, vacío, leche de cabra, proteína.

INTRODUCCIÓN

La crioconcentración es considerada una tecnología emergente en la que la solución alimenticia puede ser concentrada mediante la congelación parcial o total del agua con pos-terior separación de la fracción de hielo de la solución no congelada, asistida o no por fuer-zas externas como el vacío. Entre las ventajas de utilizar la crioconcentración en alimentos como la leche de cabra está la utilización de bajas temperaturas donde no hay pérdida de compuestos volátiles y termosensibles [1]. Se sabe que la cantidad de proteína en la leche es crítica para su valor comercial, tecnológico y biológico. Una alta cantidad de proteína en la leche mejoraría el rendimiento en la transfor-mación tecnológica requerida para preparar derivados, como la leche fermentada o los quesos. En este trabajo se estudia el efecto del cloruro de sodio y de la crioconcentración a-sistida por vacío en la concentración de pro-teína de leche de cabra.

MATERIALES Y MÉTODOS

Porciones de 45 ml de leche de cabra semidesnatada (COVAP®, Córdoba, España) fueron mezcladas con diferentes concentra-ciones de NaCl (0,5%, 1%, 1,5% y 2%) y sus puntos de congelación fueron determinados. Las condiciones de congelación y el proceso de concentración de las muestras se realizaron de acuerdo con el procedimiento descrito por Petzold et al. [1], con modificaciones. Las con-diciones de vacío fueron de 10 kPa de presión absoluta durante 60 minutos. Después de los ensayos, se recogió la solución concentrada y la fracción congelada restante para determinar las proteínas (AOAC, 2008) de ambas frac-ciones. Todos los análisis fueron realizados por triplicado. Se realizó el análisis estadístico de los datos utilizando el software Minitab 17.

RESULTADOS Y DISCUSIÓN

La leche de cabra inicial presentó una concentración de proteínas de 3,53 g 100g^{-1}. Con la adición de NaCl en las muestras de leche fue posible concentrar la proteína hasta 10,70 g 100 g^{-1} con 1,5% de NaCl. La cantidad de NaCl en la leche presentó efecto significativo ($p < 0,05$) en la concentración de proteínas hasta la concentración de 1% de NaCl. Los concen-trados obtenidos de las muestras con mayores cantidades de NaCl no presentaron diferencias significativas ($p > 0,05$) en la concentración de proteínas. Sin embargo, las fracciones de hielo presentaron una disminución significativa ($p < 0,05$) de la concentración de proteína retenida con el aumento de NaCl añadido. Con la adi-ción de NaCl el punto de congelación disminu-yó, como era de esperar, en todas las mues-tras de leche. De acuerdo con Yee *et al.* [2], la alta concentración de sal también puede me-jorar el efecto *salting out* de las proteínas de la leche, o sea, la concentración elevada de la sal puede eliminar el agua de hidratación de las moléculas de proteína, lo que ayudaría al pro-ceso de crioconcentración de las mismas.

CONCLUSIONES

Ha sido posible triplicar la concentración de proteína de los concentrados obtenidos a tra-vés de la crioconcentración asistida por vacío mediante la adición de NaCl y la consecuente disminución del punto de congelación. El tra-bajo muestra gran interés para el desarrollo de nuevos productos lácteos a partir de estos concentrados.

AGRADECIMIENTOS

Este trabajo ha sido apoyado por el Consejo Nacional de Desarrollo Científico y Tecnológico (CNPq, 405965 / 2016-8), por la Coordinación de Perfeccionamiento de Personal de Nivel Superior (CAPES, beca), por la Universidad Federal de Santa Catarina y por la Universidad Politécnica de Catalunya.

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[1] Petzold, G. et al. (2013). J. Food Eng. *115*(3), 357-361.
[2] Yee, P. L. et al. (2004). Japan J. Food Eng. 5(2), 97-103.

ANEXO I – Certificado de apresentação do trabalho “Influência do processo de nanofiltração no aumento do teor de cálcio do leite de cabra” no XXI Encontro Nacional e VII Congresso Latino Americano de Analistas De Alimentos – 2019.

ANEXO J – Certificado de apresentação do trabalho "Avaliação da concentração de proteínas no leite de cabra desnatado através dos processos de crioconcentração em blocos e nanofiltração" no XV ERSCTA - Encontro Regional Sul de Ciência e Tecnologia de Alimentos – 2019.

CERTIFICADO

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Na qualidade de autor(es) do Trabalho Científico: AVALIAÇÃO DA CONCENTRAÇÃO DE PROTEÍNAS NO LEITE DE CABRA DESNATADO ATRAVÉS DOS PROCESSOS DE CRIOCONCENTRAÇÃO EM BLOCOS E NANOFILTRAÇÃO

Curitiba, 29 de Novembro de 2019.

Leomara Floriano Ribeiro
Coordenadora da Comissão Científica do XV ERSCTA

Agnes de Paula Scheer
Presidente do XV ERSCTA

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ANEXO K – Certificado de apresentação do trabalho "Avaliação dos parâmetros de cor do leite de cabra concentrado através do processo de crioconcentração em bloco" no XV ERSCTA - Encontro Regional Sul de Ciência e Tecnologia de Alimentos – 2019.

XV Encontro Regional Sul de Ciência e Tecnologia de Alimentos

"Caminhos da produção de alimentos: Biodiversidade e Inovação"

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