CORVINUS
UNIVERSITY of
BUDAPEST

Faculty of Food Science

Investigation of nano- and diafiltration of whey

PhD thesis

András Román

Budapest

2010

PhD School/Program

Name: PhD School of Food Science

Field: Food Science

Head: Prof. Péter Fodor
Corvinus University of Budapest

Supervisor: Prof. Gyula Vatai
Department of Food Engineering
Faculty of Food Science
Corvinus University of Budapest

The applicant met the requirements of the PhD regulations of the Corvinus University of Budapest and the thesis is accepted for the defence process.

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Signature of Head of School Signature of Supervisor

INTRODUCTION

Whey is a by-product of cheese, curd and casein manufacture. The reason of necessity of whey treatment is the volume and the high dry matter content of the whey. 80-90 litres of whey are forming from 100 litres of milk during the cheese production. Annual volume of whey all over the world is 185-190 million tons and this volume probably will increase about 2 % next years. Dry matter content of whey is between 5.4 % and 6.6 % depending on the type of the product which is approximately 50 % of the dry matter content of milk. Main solute in whey is lactose.

One possibility of whey treatment is disposal without utilization. In this case, however, a large-scale reduction of biochemical oxygen demand of whey amounting to 35 000-50 000 mg O_2/litre is necessary to avoid overloading of sewage farms or environmental pollution caused by the significant organic matter content.

Revaluation of whey banished from the human diet for a long time has been getting under way by the development of food preservation processes and by the opportunity of investigation of whey constituents in molecular level. Nowadays, beneficial properties of components can be found in native form in whey are confirmed by researchers in numerous publications.

Wide spectrum of whey-derivatives can be produced through state-of-the-art separation techniques and chemical or biotechnological conversion of whey constituents. High value-added products are put into circulation by using these derivatives. Utilization of whey has not remained within the confines of the food industry, some derivatives can be used for production of medicines, cosmetics, ethyl alcohol, biogas or polymers.

Membrane operations can be used as separation techniques to separate whey and to concentrate several whey fractions. Separation can be carried out by using some driving force; particles can pass through the selective membrane layer form filtrate (permeate) and particles are retained by the membrane form concentrate (retentate). Membrane operations have a lot of advantages compared to conventional methods, e.g. separation can be carried out at low temperature in order to reduce operational cost and to avoid injuring of heat-sensitive components, additives are not required for the process and there is a good chance to create several hybrid technologies.

Applying nanofiltration membrane, only water molecules and partially monovalent ions can pass through the membrane under pressure difference so pre-concentration and demineralization (mainly refer to NaCl) of crude whey can be carried out at the same time. Products made from partially demineralized whey possess improved organoleptical properties and this kind of whey is a good raw material to produce infant food. Moreover, further processing of whey with high mineral content can caused difficulties.

Diafiltration is a process, which means that any amount of partially retained components can be removed from a multicomponent solution like whey, while other components will be enriched by adding deionized water to the retentate. Efficiency of mineral removal can be improved by using nanofiltration combined with diafiltration compared to nanofiltration without diafiltration.

OBJECTIVES

The aim of my work was the investigation of several nano- and diafiltration techniques which are suitable to produce such a concentrate as contains the valuable whey constituents and in the dry matter of it minerals (especially NaCl) represent lower proportion than in the dry matter of the crude whey. My research work can be divided into following parts:

- Investigation of the effect of operational parameters (such as transmembrane pressure, temperature, recirculation flow rate of the retentate) on the permeate flux.
- Batch concentration of sweet and acid whey without diafiltration using laboratory scale nanofiltration equipment. Following the concentration, the retention and the demineralization rate of whey components in both the permeate and the retentate in the function of volume concentration ratio based on samples have been taken during the experiment. Furthermore, the permeate flux and the specific conductivity in the function of volume concentration ratio has been followed.
- Concentration of sweet and acid whey by combination of nanofiltration and batch diafiltration: at first, concentration of whey to reach a certain volume concentration ratio using nanofiltration membrane than re-dilution to reach the initial volume of the feed using deionized water and after that, repeating former steps twice. The same parameters mentioned above in the previous paragraph in the function of volume of the permeate has been measured.
- Concentration of sweet and acid whey by combination of nanofiltration and variable volume diafiltration: keeping dialization solvent flow rate (deionised water) to the retentate tank lower than the flow rate of the permeate ($\alpha = V_D/V_P < 1$). Experiments has been carried out adjusting two different α-values, $\alpha = 0.5$ and $\alpha = 0.75$.
- Comparison of the behaviour of sweet whey with the behaviour of acid whey. Comparison of my results with results in the literature.
- Investigation of the effect of transmembrane pressure higher than 20 bar on the concentration of sweet whey without diafiltration using different type of equipment and membrane.
- Examination of adaptability of the resistance in series model for description of the permeate flux of sweet whey during the concentration.

- Mathematical modelling of the diafiltration experiments of acid whey based on the solute content by means of the method named response surface methodology.

MATERIALS AND METHODS

Acid whey and cheese whey were supplied by dairy companies of Sole-Mizo Zrt, from Szeged and from Bácsbokod, respectively. Two different lab-scale membrane filtration equipments were used for the experiments which can be found at the Department of Food Engineering, Corvinus University of Budapest. Lactose- and multivalent ion-retentions of applied polymeric nanofiltration membranes were at least 95 %.

Except of preliminary experiments, the experiments were carried out at batch concentration mode, which means that the permeate wasn't recirculated into the feed tank so retentate was concentrated continuously during the batch nanofiltration. Experiment was stopped when volume concentration ration reached a certain value. In case of batch diafiltration, about 10 litres of whey was concentrated to 3 litres. After that, deionized water was added to the retentate for reaching the initial volume of the feed. These two steps were repeated twice again. In case of variable volume diafiltration, two different α-ratios were used for experiments. α is the quotient of the flow rate of water used for diafiltration and of the flow rate of permeate so α = 0.75 means that 750 ml deionized water was poured into the feed tank in place of 1 litre of collected permeate and α = 0.5 means that 500 ml deionized water was poured into the feed tank during the process.

Specific conductivity of retentate- and permeate samples was measured by a hand-operated sension156 instrument equipped with a sensing head having type number of 51975. Total dry matter-, fat-, total protein-, true protein- and lactose content of the samples were determined by a Bentley 150 Infrared Milk Analyzer at the University of Szeged. Thermo Jarrell Ash ICAP 61 type ICP-OES instrument was used for the ion analysis (sodium, potassium, calcium, magnesium and phosphorus) at the Department of Applied Chemistry (CUB) except chloride for which an OP-211 type potentiometric pX/mV lab-scale instrument equipped with an OP-Cl-0711P type chloride ion-selective electrode and with a NOP-0871P type Ag/AgCl reference electrode was used.

Permeate flux which characterizes the permeability of the membrane, retention which is related to the selectivity of the membrane as well as degree of demineralization were calculated based on experimental data. Degree of demineralization is an index of the efficiency of mineral-removal that shows change in concentration of a certain component compared to change of the total solid content during the concentration. Adaptability of the resistance in series model was examined to describe concentration without diafiltration. Osmotic pressure of retentate was calculated based on the van't Hoff's law where total molar concentration was substituted for molar concentration of lactose. A method which has been already applied successfully for model solutions was also investigated to predict concentration of whey constituents in the function of process duration. Basis of this method is the numerical solution of differential equations that describe changes in volume and in composition of feed in the function of process duration. For solutions of them, it is required to know the concentration dependence of the permeate flux and of retentions of investigated components. Concentration dependences were determined by using response surface methodology.

NEW SCIENTIFIC RESULTS

1) It was experimentally demonstrated that the membrane retention of the investigated ions was lower – except chloride ion – during acid whey filtration than during sweet whey filtration at the same experimental conditions. The result of this phenomenon resulted in more efficient desalination in case of

acid whey. Using batch nanofiltration without diafiltration, degree of demineralization of potassium and sodium was 44 - 46 % in case of acid whey, while degree of demineralization of potassium and sodium was only 25-27 % in case of sweet whey at volume concentration ratio of 2.6. Degree of demineralization of chloride was 49 % and 55 %, respectively at the same volume concentration ratio.

2) Contrary to literature data it was verified experimentally, that by choosing suitable membrane, degree of demineralization of monovalent ions can be enhanced by even the third concentration-step of batch diafiltration while lactose was represented at the same proportion in dry matter of concentrate than in dry matter of crude whey. Until the end of the third concentration-step, degree of demineralization of sodium and potassium reached 64-66 % and of chloride reached 93 % in case of sweet whey while degree of demineralization was between 84 % and 86 % for all three components in case of acid whey.

3) There was also verified by my experiments that variable volume diafiltration – which hasn't been applied for reduction of mineral content of whey up to the present – is completely adequate to realize this purpose. Desalination can be enhanced by increasing the ratio of the flow rate of deionised water used for diafiltration and the flow rate of permeate. Taking VCR = 2.6 as a basis, degree of demineralization of sodium and potassium was increased 2.1-2.2-fold ($\alpha = 0.5$) and threefold ($\alpha = 0.75$) in case of sweet whey compared to values obtained by concentration without diafiltration. In case of acid whey, these values were 1.7-1.8-fold and 2.4-fold by taking VCR = 2.05 as a basis. Advantage of this technique is the lower lactose-loss compared to batch diafiltration because of the continuous concentration of retentate.

4) During whey concentration by nanofiltration, it was demonstrated experimentally, that permeate flux can be increased only up to a certain value with increase in driving force (transmembrane pressure), if the recirculation flow rate of the retentate is constant. This phenomenon can be explained by more and more considerably fouling of the membrane. Permeate flux was higher at 40 bar than at 20 bar during concentration of sweet whey but flux-curve obtained at 60 bar was practically the same as the curve obtained at 40 bar due to the increase of resistance caused by fouling.

5) There was verified by applying resistance in series model that osmotic pressure of retentate can be replaced with osmotic pressure of lactose in the model. Average value of concentration polarization index was determined for filtration of sweet whey. The value indicates that concentration of lactose was on average 1.66-times higher in the polarization boundary layer formed on the membrane surface than in the bulk of the retentate. Membrane resistance was less than a half of the average total resistance during the process.

6) There was proved by means of the mathematical model worked out by Kovács et al. that in case of acid whey, concentration change of whey components in the function of process duration can be predicted by means of only one basic experiment. Prediction is also valid for processes which differ from the type of the basic experiment. It is sufficient to know the lactose content and the specific conductivity of the retentate for the response surface methodology used for determination of concentration dependence of permeate flux and of retentions instead of the exact acquaintance with retentate composition.

CONCLUSIONS AND SUGGESTIONS

- XN45 (TriSep) nanofiltration membrane having 96 % lactose-retention and FILMTEC NF270 (Dow) nanofiltration membrane are both suitable to concentrate sweet and acid whey and reduce mineral content of them simultaneously, in addition, loss of lactose is minimal during the process.

- It isn't proposed to exceed value three of volume concentration ratio at 20 bar transmembrane pressure. If it is exceeded, dry matter content of permeate will increase by leaps and bounds due to the considerable decline of retention of whey constituents so loss of lactose will be significant as well.
- Value of volume concentration ratio proposed above can be extended by applying transmembrane pressure higher than 20 bar. However, increase of permeate flux has a limit in spite of increasing pressure due to the membrane fouling. The higher the pressure, the higher the retention of elements so this phenomenon exerts unfavourable influence on desalination. By reason of my results, concentration of whey isn't proposed at 60 bar. Below 60 bar, it is necessary to take retention of lactose and minerals, permeate flux and operational costs into consideration for choice of optimal transmembrane pressure.
- Degree of demineralization of monovalent ions (included sodium and chloride) can be enhanced considerably by using nanofiltration combined with multistage batch diafiltration or with variable volume diafiltration while the greatest part of multivalent ions remains in the concentrate and lactose represents at least proportion in dry matter of concentrate than in dry matter of crude whey. Variable volume diafiltration – which hasn't been applied for whey desalination up to the present – is a match for batch diafiltration at efficiency in terms of all of investigated parameters. Moreover, variable volume diafiltration is milder technique than batch diafiltration due to the continuous concentration of the retentate.
- Techniques were investigated in this work such as nanofiltration, batch diafiltration and variable volume diafiltration and even their hybrid processes can be alternatives of conventional processes since only one

equipment is enough for concentration and partially demineralization of whey and separation of monovalent ions from multivalent ions can be carried out efficiently contrary to electrodialysis and ion exchange. Whey concentrate having 18-20 % dry matter content can be utilized in whey-based beverages without further processing or after enzymatic hydrolysis of lactose, or it can be powdered after additional dehydration.

- Permeate of diafiltration can be utilized as rinsing water, CIP water or for diafiltration in an ultrafiltration equipment. It can be let also into the drainpipe after post-treatment.

PUBLICATIONS WITH IMPACT FACTOR

- **A. Román**, J. Wang, J. Csanádi, C. Hodúr, Gy. Vatai. (2009) Partial demineralization and concentration of acid whey by nanofiltration combined with diafiltration. Desalination, 241: 288-295 (ISSN: 0011-9164)

- **A. Román**, J. Wang, J. Csanádi, C. Hodúr, Gy. Vatai. (2010) Experimental investigation of the sweet whey concentration by nanofiltration. Food and Bioprocess Technology, accepted for publication, DOI 10.1007/s11947-009-0192-0 (ISSN: 1935-5149)

- **A. Román**, S. Popović, Gy. Vatai, M. Djurić, M. N. Tekić. (2010) Process duration and water consumption in a variable volume diafiltration for partial demineralization and concentration of acid whey. Separation Science and Technology, 45: 1347-1353 (ISSN: 0149-6395)

- **A. Román**, Gy. Vatai, A. Ittzés, Z. Kovács, P. Czermak (2010) Modeling of diafiltration processes for demineralization of acid whey: an empirical approach. Journal of Food Process Engineering (accepted for publication)