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SCIENTIFIC PAPER

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EXPERIMENTAL AND NUMERICAL INVESTIGATIONS ON WHEY DESALINATION WITH NANOFILTRATION*

Whey is the by-product obtained when milk is transformed into cheese or casein. It is generated in large quantities world-wide: the annual volume of dairy whey produced globally exceeds 160 millions. Nanofiltration provides a demineralization performance that makes whey a suitable additive in human food formulas. This paper present robust and reliable simulation methods to predict the dynamics of batch membrane filtration processes dealing with multi-component systems such as whey. Experimental data was collected from lab nanofiltration investigations using sweet and acid whey. Our special interest is to employ data-driven models that minimize the necessary a-priori experiments and allow the conversion of raw data into useful information. We have integrated statistical tools and machine learning techniques in the proposed mathematical framework. We show that such techniques are capable to model multi-component systems where limited information on their true chemical composition is available.

Key words: desalination • diafiltration • nanofiltration • simulation • whey

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INTRODUCTION

Whey is the by-product obtained when milk is transformed into cheese or casein. This dairy stream represents an excellent source of functional proteins and peptides, lipids, vitamins, minerals, and lactose. It is produced in large quantities world-wide: the production of one ton of cheese generates approx. eight tons of liquid whey (Dec, 2007). The annual volume of dairy whey produced globally exceeds 160 millions of tons and it increases with an annual growth rate of 1-2% (Smithers, 2008). Depending on the type of cheese made and the corresponding casein precipitation procedure used, there are two main whey varieties: acid whey (pH <5) and sweet whey (pH 6−7). The acid type whey contains a higher amount of lactic acid and ash, calcium in particular. Table 1 shows the general composition of acid and sweet whey.

Nanofiltration membranes are a relatively recent development in the field of pressure-driven membrane separations, and their properties lie between ultrafiltration (UF) and reverse osmosis (RO). Due to its potential advantages, NF has gained a strong market position, brought about a number of patents, industrial research projects and commercial installations (Bessarabov and Twardowski, 2002). Starting in the late sixties, NF membrane processes have gradually found their way into industrial applications in various fields such as water softening, dye recovery, treatment of metal contained waste waters, oil-water separation, demineralization of whey, recycle of nutrients in fermentation processes, purification of landfill leachate, removal of sulfates from sea-water, bioproduct separation (Timmer, 2001).

NF systems are usually operated at medium pressures in the range of 10-50 bar, and have much higher water fluxes compared to RO membranes.

Nanofiltration can be applied for separation between ions with different valences and for separation of low- and high-molecular weight components. NF rejects uncharged, dissolved material and positively charged ions according to the size and shape of the molecule in question (Wagner, 2001). The degree of transportation of non-charged solutes through NF membranes is shown in Fig. 1.

NF membranes show diversity in separation behavior but they are common in rejecting multivalent ions (such as SO_2^{-4}, CO_2^{-3}, PO_3^{-4}, Mg^{2+}) in a higher degree, while in compari-

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Table 1. COMPOSITION OF SWEET-TYPE (CHEDAR CHEESE) AND ACID-TYPE WHEY (Sienkiewicz and Riedl, 1990)

Composition	Sweet whey	Acid whey
Water, %	93.3	95.6
Dry matter, %	6.70	6.42
Total protein, mg g^{-1}	0.60	0.53
Non-protein nitrogen, mg g^{-1}	0.34	0.34
Lactose, %	5.00	4.40
Ash, %	0.52	0.60
pH	6.10	4.70

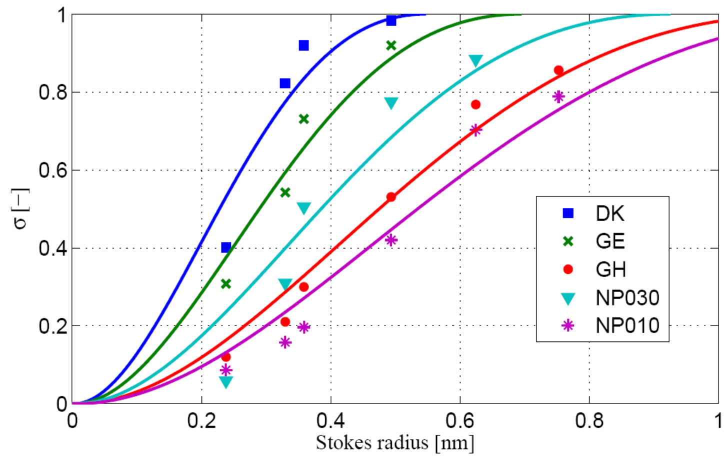

Figure 1. RELATIONSHIP BETWEEN REFLECTION COEFFICIENT Σ AND STOKES RADII OF DIFFERENT SOLUTES (BUTANOL, RIBOSE, GLUCOSE, LACTOSE, PEG, AND DEXTRAN) FOR SEVERAL NANOFILTRATION MEMBRANES (DK, GE, AND GH FROM GE W&P TECHNOLOGIES, US, AND NP030 AND NP010 FROM MICRODYN-NADIR GMBH, GERMANY) (Kovács and Samhaber, 2008)

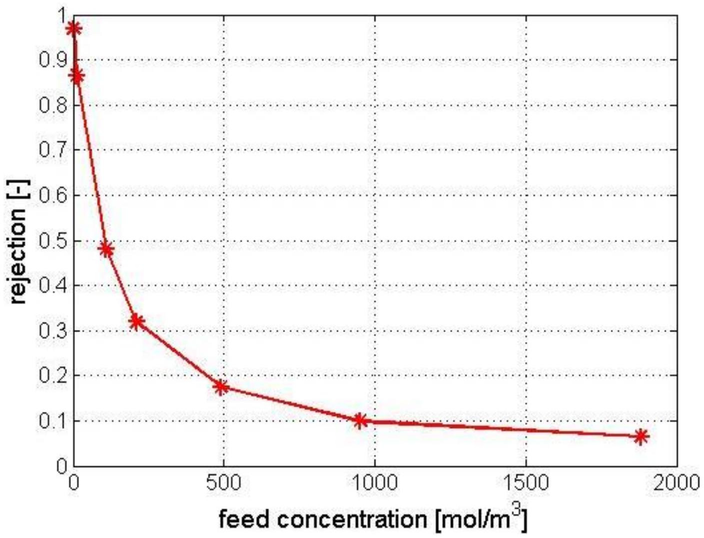

Figure 2. REJECTION OF THE MEMBRANE DESAL-DK5 (GE W&P TECHNOLOGIES, US) FOR NaCl AS A FUNCTION OF FEED CONCENTRATION (30 BAR, 25ºC, 0.55 M^2 SPIRAL-WOUND ELEMENT, 1 M^3H^{-1} RECIRCULATION FLOWRATE). SOLID LINE IS FOR EYE-GUIDANCE (Kovács et al., 2008)

son, rejection of monovalent ions (Cl^-, Na^+ K^+) is much less. As represented in Fig.2, rejection of ionic species is highly concentration-dependent.

Whey represents a complex multicomponent system. In processes of practical interest, the concentrations of both salts and organics present in whey are subject to change during operation, and a considerable interdependence in their permeation occurs. The modeling of nanofiltration of such a complex system is a difficult task.

Several physical models, such as the extended Nernst-Planck model (van der Horst et al., 1995), the Spiegler-Kedem model (Cuartas-Uribe et al., 2007), the solution-diffusion model (Minhalma et al., 2007), and the Donnan-steric-pore model (Cuartas-Uribe et al., 2007) have been employed to describe whey NF. However, these quantitative modeling techniques in their presented form can find only limited applications, because they are either restricted to model single components or simplified operation modes are considered (Román et al., 2011).

The most relevant factor that limits the applicability of physical models to filtration modeling is the available information on the solution itself. Due to costly chemical analysis of complex process streams, process engineers have often only limited information on several components. Moreover, many of the measured quantities are not solute-specific quantities; in fact, they represent certain collective features of a group of solutes of common types. Under such circumstances, the employment of empirical methods may be a reasonable alternative over physical models. This research work investigates robust data-driven modeling techniques to predict the dynamics of whey nanofiltration.

MATERIALS AND METHODS

Nanofiltration of both sweet whey and acid whey were experimentally investigated. In both cases, one-one single experiment was used to determine the parameters of the mathematical models. Then, two-two other experiments with different operational settings were conducted in order to validate the models.

A detailed description of the membrane filtration apparatus can be found in our previous work (Román et al., 2011). In brief, all experiments were carried out at constant trans-membrane pressure (20 bar), temperature (40°C), and cross-flow velocity (3.0 m s^{-1}) using a lab-scale apparatus equipped with a flat-sheet membrane module. The commercial polymeric membrane XN45 (TriSep Co., Goleta, CA, USA) was used for both sweet whey and acid whey NF. The schematic representation of batch membrane diafiltration setting is shown in Fig. 3.

Total soluble solid, lactose, protein, and fat content of both permeate and feed samples were analyzed. Determination of five major elements (Na, K, Ca, Mg, P) in milk was carried out by inductively coupled plasma mass spectrometry (ICP-MS). Conductivity of feed and permeate streams were also monitored.

Simulation procedure

A modular approach, shown in Fig. 4, is proposed to simulate desalination of whey.

In our previous work (Kovács et al., 2009) we have presented a general mathematical framework in a compact form to predict the dynamics of different configurations of batch membrane filtration processes. We have elaborated the common basis of the different operational modes, such as concentration, constant-volume dilution, or variable-volume dilution mode, and delivered a comprehensive model. The following initial-value problem can be formulated to represent the membrane system configuration:

$$\begin{cases} \frac{dV_f}{dt}(t) = u(t) - q(t) \\ V_f(0) = V_f^0 \end{cases} \quad (1)$$

and, for component *i*,

$$\begin{cases} V_f(t)\frac{dC_{f,i}(t)}{dt} = C_{f,i}(t)[q(t)R_i(t) - u(t)] \\ C_{f,i}(0) = C_{f,i}^0 \end{cases} \quad (2)$$

which describe the evolution in time of the volume in the feed tank V_f and of the feed concentration $C_{f,i}$ for *i=1,2...n.* V_f^0 and $C_{f,i}^0$ denote respectively the initial feed volume and the initial feed concentration of the solute *i.* The proportionality factor *α* (i.e. the ratio of diluant flow *u(t)* to permeate flow *q(t))* can be then adjusted to zero, unity, or a constant value between 0 and 1 in order to run the process in concentration mode, constant-volume dilution mode, or variable-volume dilution mode, respectively.

The estimation of flux *q* and rejections R_i presented in Eqs. (1) and (2) can be carried out separately using the most convenient method for the problem at hand. Thus, either mechanism-driven, or data-driven methods can be used without having to modify the proposed framework. We have investigated statistical tools, such as response surface methodology (RSM) and partial least-squares regression (PLSR), and machine learning techniques in order to estimate the dependence of flux and rejections on the feed composition such as

$$q = q(c_1, c_2 \ldots c_n) \quad (3)$$

$$R_i = R_i(c_1, c_2 \ldots c_n) \text{ for } i = 1, 2, \ldots n \quad (4)$$

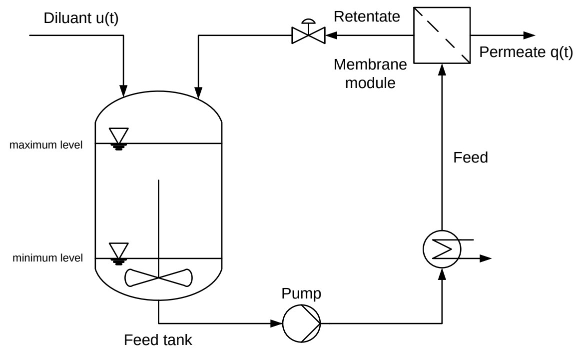

Figure 3. SCHEMATIC REPRESENTATION OF BATCH DIAFILTRATION SETTINGS

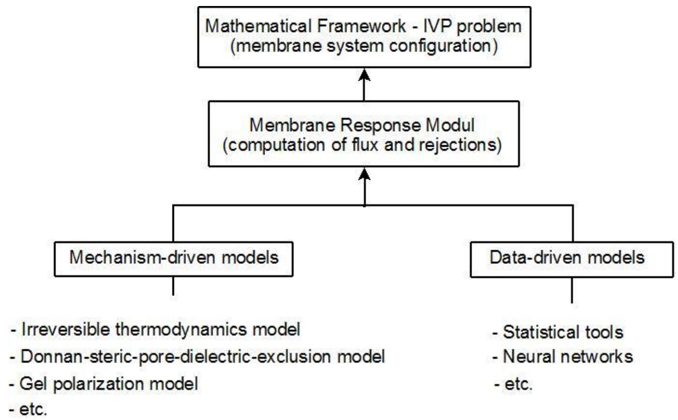

Figure 4. FLOW-CHART OF THE SIMULATION APPROACH

RESULTS AND DISCUSSION

The experimental data obtained from the experimental run no. 1 was processed with data-driven modelling techniques (RSM, PLSR and artificial neural networks). Then, the resulting quantitative expressions for flux *q* and rejections R_i were integrated in the proposed mathematical framework. Runge-Kutta integration scheme is implemented for integrating the feed volume along with the concentrations for the studied interval of the operational time. Figs. 5 and 6 are representative figures of the simulation outputs for whey diafiltration using response surface methodology and neural network approach, respectively. A good agreement between predicted and experimental results can be achieved.

CONCLUSION

A mathematical framework is provided for simulation of whey diafiltration processes. Either transport models or real-life experimental data can be employed, without having to modify the governing equations of the framework. The proposed procedure is applicable for different batch diafiltration concepts and for multi-component systems. We have proposed an experimental design that minimizes the a-priori experimentation and permits the extraction of high-quality information from the experimental data. To convert raw data into useful information, we have successfully employed statistical tools (RSM, PLSR) and artificial neural networks. The modeling technique has been validated with a number of process runs by adjusting diffe-

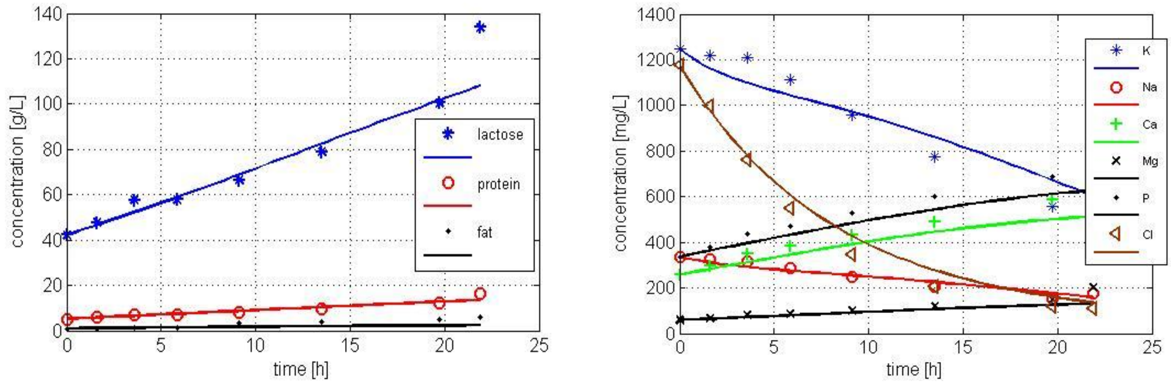

Figure 5. ORGANIC COMPOUNDS (LEFT SIDE) AND IONIC SPECIES (RIGHT SIDE) AS FUNCTION OF OPERATIONAL TIME FOR VARIABLE-VOLUME DIAFILTRATION WITH A=0.75. EXPERIMENTAL DATA ARE ILLUSTRATED WITH SYMBOLS AND ESTIMATED VALUES WITH CONTINUOUS LINES

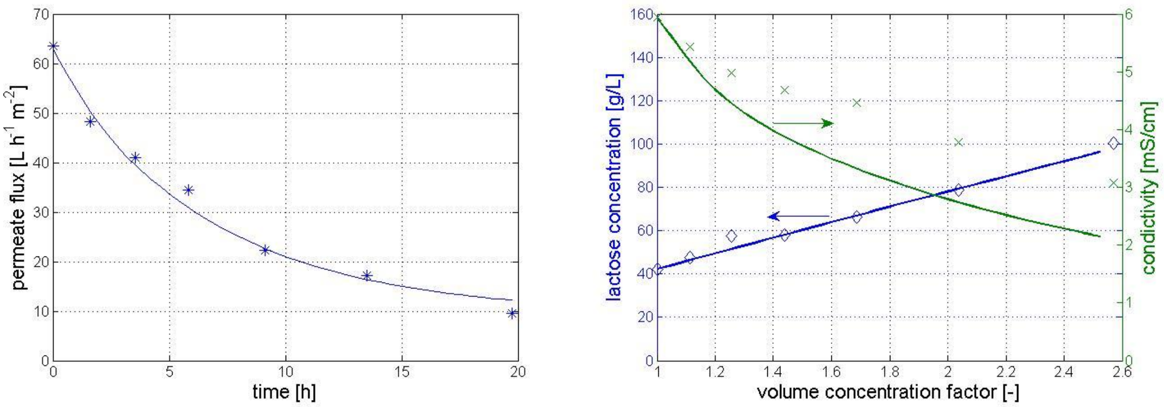

Figure 6. SIMULATION OF THE DYNAMICS OF SWEET WHEY DIAFILTRATION WITH ARTIFICIAL NEURAL NETWORK APPROACH. PERMEATE FLUX VS OPERATIONAL TIME (LEFT SIDE); CONDUCTIVITY AND LACTOSE CONCENTRATION AS FUNCTION OF VOLUME CONCENTRATION FACTOR (RIGHT SIDE). EXPERIMENTAL DATA ARE ILLUSTRATED WITH SYMBOLS AND ESTIMATED VALUES WITH CONTINUOUS LINES

rent diluant utilization schemes. A good agreement between simulated and measured filtration data was found.

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IZVOD

EKSPERIMENTALNA I NUMERIČKA ISPITIVANJA DESALINACIJE SURUTKE PRIMENOM NANOFILTRACIJE

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Surutka je sporedni proizvod dobijen tokom prerade mleka u sir ili kazein. Surutka se proizvodi u velikim količinama u celom svetu: godišnji obim surutke proizvedene u svetu prelazi 160 miliona tona. Primena nanofiltracije čini surutku pogodnim dodatkom u ljudskoj ishrani. U radu je data simulacija metode za predviđanje dinamike procesa membranske filtracije u višekomponentnim sistemima kao što je surutka. Eksperimentalni podaci su dobijeni tokom laboratorijske nanonfiltracije slatke i kisele surutke. Upotrebljeni su modeli koji minimiziraju neophodne apriori eksperimente i omogućavaju pretvaranje sirovih podataka u korisne informacije. Integrisani su statistički alati i tehnike učenja pomoću mašina u predloženom matematičkom okviru. Rezultati prikazuju da ovakve tehnike mogu da modeluju višekomponentne sisteme gde je dostupna limitirana informacija o njihovom stvarnom hemijskom sastavu.

Ključne reči: desalinacija • dijafiltracija • nanofiltracija • simulacija • surutka