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MODELLING OF MULTI-STEP MICROFILTRATION PROCESS FOR SOLVENT EXCHANGE

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Industrial-scale microfiltration (MF) separation is applied to process a dispersed ternary system containing an organic solvent, water and fine particles. The objective of the separation is to exchange the organic solvent with water and concentrate the water-particle dispersion. The MF separation is carried out in a multi-step batch operation including pre-concentration, dilution mode, and post-concentration process steps. In this study, we present a practical computational algorithm which can be used as a basis for process simulations of both concentration and dilution modes. The numerical method is based on mass balance processing and on empirical relations of the rejection and the permeate flux to the feed composition. These empirical relations are obtained from the experimental data of a single test-run with the process liquid. We discuss the input data of the code and the respective experimental design with the necessary sampling. Finally, we provide optimum-search techniques considering economical aspects and technological demands.

Keywords: microfiltration, modelling, solvent exchange, diafiltration, optimization

Introduction

One of the major solvent consuming processes in the chemical and the pharmaceutical manufacturing is solvent exchange. Organic solvents are widely used as reaction media for chemical synthesis, raw materials, and as cleaning agents [1].

Membrane technology has a great potential to improve the performance of many liquid phase synthesis reactions by reducing the need for complex solvent handling operations. Membrane separation can provide a cheaper solution over the conventional solvent exchange via distillation, when the solvent to be removed has a lower boiling point than the replacing solvent [2].

In batch membrane system design, a common separation strategy for selective removal of components with low retentions is to employ a multi-step membrane process. A multi-step batch process is a chain of operations of a defined number and order that are carried out consecutively using the same membrane module. There are two basic operation modes: the concentration and the dilution mode. In a general case, a multi-step process consists of three steps (e.g. operations): pre-concentration, dilution mode and post-concentration steps. This concept is one of the conventional process techniques to achieve high purification of macro-solutes with an economically acceptable flux [3].

Batch membrane separation has been presented in a number of different forms in the past, which is, and continues to be an active area of interest both academically and industrially. The classical mathematical modelling [4,5] uses the concentration factor as a basis for the calculations, while numerical techniques [6,7] handle the permeate flux and the component rejections as (time-dependent) state functions of the feed composition.

In this study, we present a practical computational algorithm which can be used for the simulation of batch operations. The numerical method is based on mass balance processing and on empirical relations of the rejection and the permeate flux to the feed composition. These empirical relations are obtained from experimental data that were obtained from a test-run with the process liquid. We discuss the input data of the computational algorithm and the respective experimental design with the necessary sampling. Finally, we provide optimum-search techniques considering economical aspects and technological demands.

Although real-life experimental data are used in this study, the latter strictly focuses on the mathematical programming approach, and it does not aim to give a detailed insight into the properties of the applied colloidal system and the confidential technological specifications of the industrial settings.

Problem statement

Industrial-scale MF separation is applied to process a ternary dispersed system containing an organic solvent, water and fine particles. The objective of the separation

is to exchange the organic solvent with water, and concentrate the water-particle dispersion. The schematic configuration of the industrial membrane filtration plant is shown in *Fig. 1*.

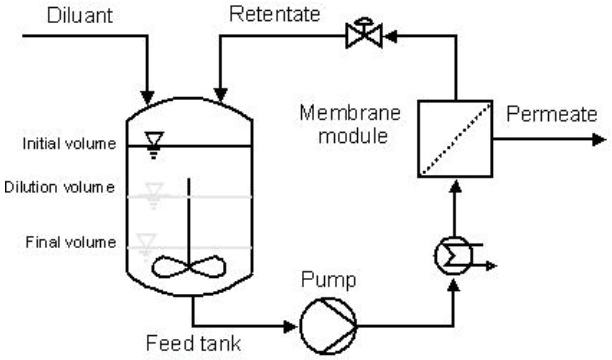

Figure 1: Schematic representation of the batch configuration

Two basic modes of batch operation are considered: the concentration and the dilution mode. In the concentration mode, the retentate stream is completely recycled into the feed tank, and the permeate stream is collected separately, that results in a continuous volume decrease in the feed tank. In the dilution mode, a diluant is added into the feed tank at a rate equal to the permeation rate. A level sensor is activated in the feed tank, which keeps the adjusted level of the feed volume constant by continuous addition of the wash water. The total weight of the particle in the feed tank remains constant due to the complete rejection, but the solvent passes through the membrane. Since the permeate stream is replaced with wash water, there is a continuous decrease of solvent concentration in the feed tank during the dilution mode.

The colloidal dispersion is produced batch-wise via chemical synthesis. This ca. 250 kg dispersion is the initial feed for the MF process, and it contains ca. 10 w/w% fine particles and ca. 30 w/w% solvent. The MF separation is carried out in a multi-step batch operation including pre-concentration, dilution mode, and post-concentration process steps. Due to technical requirements, the solvent concentration has to be reduced to 0.05 w/w%, and the dispersion concentrated to 100 kg. As far as the membrane separation performance is concerned, the water and solvent permeation rates through the MF membrane are equal, and the dispersed particles are completely rejected by the membrane. The stability of the colloidal system can also affect the MF process performance. At certain feed composition range, the dispersion becomes unstable. This phenomenon can lead to sludge formation which can completely plug the membrane. Thus, extra care is needed in the process design.

The objective of this study is to define the mathematical basis of the chemical engineering problem by building a model based on real-life experimental data. The problem is attacked with suitable mathematical programming techniques that gives quantitative prediction for the unit operation steps, and provides the optimum operational settings for the overall multi-step separation process.

Modelling concept

The multi-step process is carried out at constant pressure and temperature, and the same hydrodynamic conditions are maintained during the operation. Thus, at any time and at any step of the process, the permeate flux can be described solely as a non-linear function of the actual feed composition. The computational technique summarized in the scheme of *Fig. 2* was developed in order to predict the changes of the feed tank volume and the feed composition during the membrane filtration process.

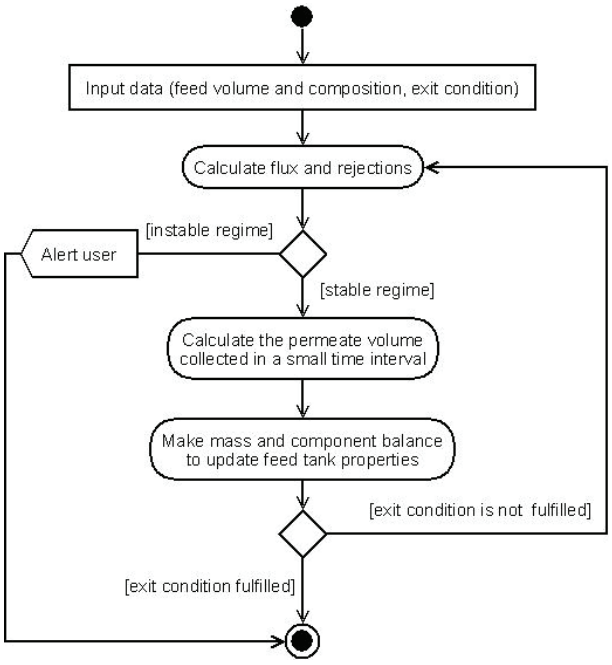

Figure 2: UML activity diagram of the process simulation

It is assumed that the initial feed concentration of both particle c^F_p and solvent c^F_s are known. For simulation purpose, we prior define a sufficiently small time interval Δt. If the relationship between permeate flux and feed composition is known, than the permeate flux can be calculated for the initial feed dispersion at the beginning of the process. Therefore, the small volume of the permeate ΔV, which passes through the membrane in the small time-interval, can be quantified. The relationship between flux and feed composition, e.g. $J = J(c^F_p, c^F_s)$, can be obtained from theoretical membrane transport models. However, in this study, we use a practical approach based on experimental data. This approach ensures the derivation of a reliable relation from a limited number of experimental data without prior approximations. The function $J = J(c^F_p, c^F_s)$ was empirically determined during a test-run with the process stream. Complete particle retention is proved with analytical measurements, and the water and solvent permeation rates through the membrane are found to be equal. Thus, the mass of each component in the very small permeated volume ΔV can be estimated.

Thereafter, mass and component balances for both permeate and feed tank can be used to determine the new compositions and total masses. Then, the above described procedure can be repeated with the new values. Obviously, in dilution mode operation, we assume a wash-water volume inlet into the feed tank, which is equal to the ΔV permeated volume. The exit condition of the cycle is the prior defined volume, which is collected in the permeate tank, or alternatively, the solvent concentration in the feed tank. During the computational cycle, the feed composition is checked to determine whether the dispersion is stable and separation can be continued.

This code can be run either in concentration or in dilution mode and multi-step process can be built up from individual blocks by defining the input arguments of a latter step as the output arguments of the previous step. The number and the order of the individual steps can be freely chosen by the user. This practical computational technique is not restricted to MF applications, and one can simulate diverse modes of operations. In a recent study [7], a similar numerical approach is presented for the simulation of the separation of inorganic salts from organic molecules with multi-step batch nanofiltration.

Process simulation

The permeate flux was experimentally determined for different feed compositions during one test-run of the industrial-scale membrane plant on place at the chemical company. The initial ca. 250 kg feed was concentrated to ca. 160 kg, and thereafter, 90 kg water was added into the feed tank. Then this procedure was repeated several times. Although membrane cleaning was not performed in between the concentration mode operations during the test-run, an increased permeate flux was always observed after each concentration step. This may indicate that fouling has minor importance during the process. During this test-run, the permeate flux was measured periodically, and at the same time, samples were taken from the permeate stream for solvent concentration analysis. The solvent/water ratio in the permeate stream was always equal to the actual solvent/water ratio of the feed tank. The total particle mass in the feed tank was 28 kg, and it remained constant during the operation due to complete rejection. The particle concentration in the feed tank was determined by monitoring the total feed volume at the time of sampling. The experimental data of the permeate flux as function of particle and solvent feed concentrations are shown in *Fig. 3.* Both particle and solvent feed concentrations have significant contributions to the observed permeate flux.

The unstable composition regime, that is where no permeate flux can be measured, is well visible in Fig. 3. Based on the experimental data, this regime is empirically defined by the set of feed concentrations which satisfy

$$0.142 \le c^F_p \le 0.17 \qquad \text{and} \qquad 0.018 \le c^F_s \le 0.092,$$

where c^F_p and c^F_s are the particle and the solvent concentration in the feed tank, respectively.

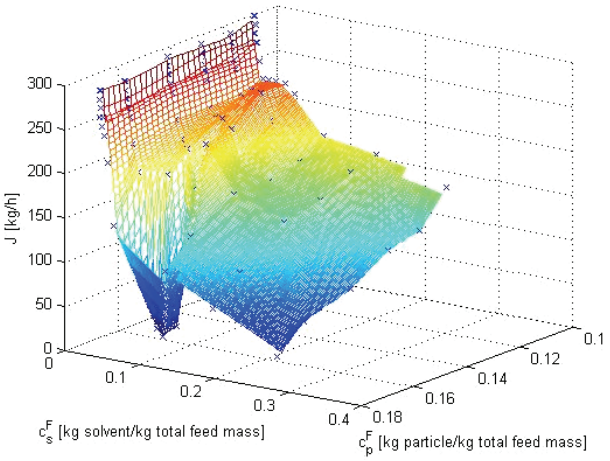

Figure 3: Experimental data of permeate flux (illustrated with x) in the function of particle and solvent concentration (Lines are to guide eyes.)

It is important to understand that the pronounced flux decline in the above defined region is provoked by the physical-chemical changes in the colloidal system, and the membrane permeation decline is a response to these radical dispersion-based changes. The experimental values of permeate flux follow a uniform trend which is broken only in the unstable regime. Thus, it seems reasonable to determine the overall trend for the permeate flux, and to handle the instable regime separately. The permeate flux can be expressed in terms of c^F_p and c^F_s by fitting the non-zero experimental results using an equation like:

$$J = \left(x_1\, e^{-x_2\, c_s^F}\right) c_p^{F\,2} + \left(x_3\, e^{-x_4\, c_s^F}\right) c_p^F + \left(x_5\, e^{-x_6\, c_s^F}\right),$$

where x_i, i = 1, 2, … 6 are the fitting parameters.

The estimated empirical plane and the set of coefficients are shown in *Fig. 4.*

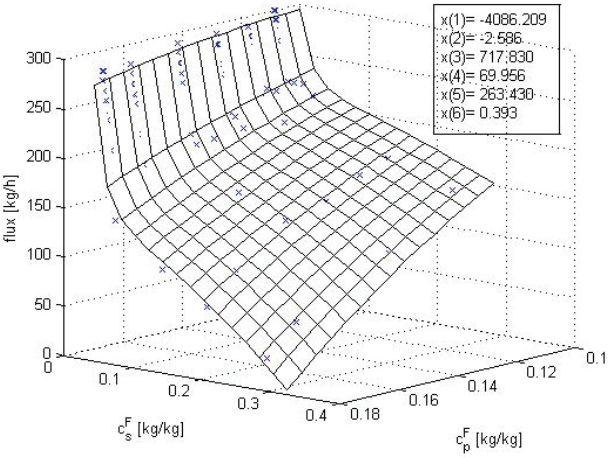

Figure 4: Estimated (solid lines) and experimental data (*) of permeate flux in the function of solvent and particle concentration
(Curve-fitting is based on non-zero flux data.)

The changes in the permeate flux and in the concentrations in feed tank are calculated through the computational procedure using the actual (time-dependent) feed concentrations. This dynamic method differs from the conventional calculation procedures that are based on volume concentration factors.

The currently applied process has three operational steps. First, the initial feed is pre-concentrated. This step is characterized with the pre-concentration grade m_{pre}, which is defined as the total mass of the dispersion in the feed tank when the second step, the dilution mode, starts. Thus, for example a pre-concentration grade m_{pre}=200 kg means that the initial 250 kg dispersion is concentrated to 200 kg before the dilution mode starts.

Fig. 5 shows the complete simulation of a 3-step process. The feed was first concentrated to 200 kg, then dilution mode operation was carried out by applying 1100 L wash-water, and finally the dispersion was concentrated to 100 kg. The permeate flux and the solvent concentration in the feed tank can be predicted over the operation time as shown in Fig. 5.

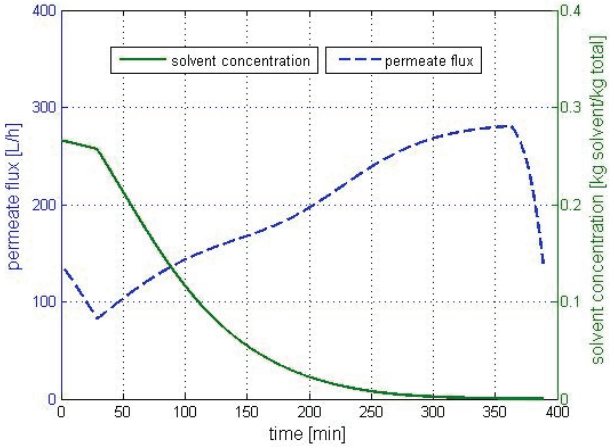

*Figure 5: S*imulation example for a three-step process including pre-concentration, dilution mode, and post-concentration steps

During the pre-concentration step, the increasing feed concentration causes a decreasing flux. It is a conventional wisdom that the amount of wash-water is minimized if it is added where the feed concentration is high [8]. However, as shown in Fig. 4, high feed concentrations lead to lower solvent fluxes through the membrane. Thus, an optimum pre-concentration grade exists for performing the dilution mode.

Process optimization

The aim of the optimization is to find the set of operation parameters that result in the most economical process, and satisfy the given technological demands of the final product. Thus, the total processing cost is the objective function that has to be minimized; the operational parameters of pre-concentration grade m_{pre} and xdiluant volume V_D are the decision variables, and the given technological requirements are the constraints of the optimization. We define a product quality and a product mass constraint, e.g. the final solvent concentration has to be reduced under a limit value of c_{limit}=0.05 w/w% and the final product mass m^{final} of 100 kg has to be obtained.

The objective function can be defined as the total cost per unit of product produced. The total cost is a sum of two terms, which are the operational cost of the pump and the cost of the utilized dilution water.

The mathematical problem can be described as follows:

$$\text{Minimize} \qquad f(m_{pre},V_D) = k_1 t + k_2 V_D$$

subject to the constraints

$$m^{final} = 100 \text{ kg} \qquad \text{and} \qquad c_s^{final} \le c_{limit}$$

where $f(m_{pre},V_D)$ is the objective function, t is the total operation time, V_D is the dilution water consumption, while k_1 and k_2 are constants. The constant k_1 is a product of the power consumption of the pump and the electricity price, and k_2 is the unit price of the utilized dilution water.

Computer simulation of 3-step processes was performed for sets of m_{pre} and V_D input parameters. Thus, in the first process step, the dispersion was concentrated to a pre-concentration grade m_{pre}, then the diluant volume of V_D was applied to wash out the solvent, and finally the dispersion was concentrated to 100 kg in the last step. During these 3-step processes, membrane plugging caused by sludge formation can occur when the composition in the feed tank becomes instable. *Fig. 6* shows the instable area for the applied operational parameters.

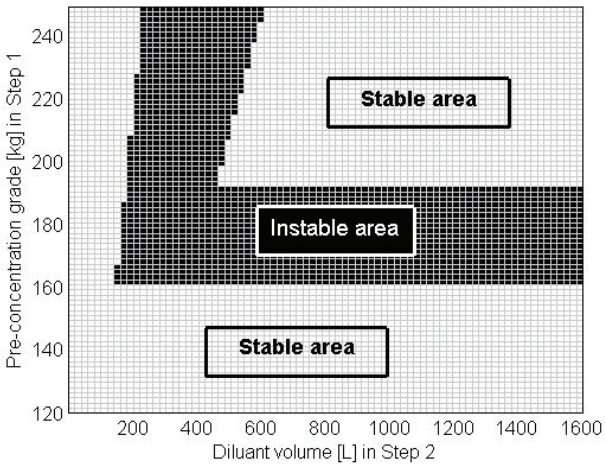

Figure 6: Instable dispersion area illustrated for the applied operational parameters

A flux decline can also occur due to high feed concentration as shown in Fig. 4. With other words, the dispersion can not be concentrated to a too high extend, because in that case no permeate flux can be gained. Obviously, the location of the optimum is affected, not only by the pre-concentrated grade, but also by the extent to which the solvent concentration is reduced in the dilution mode step. The applied diluant volume V_D has to be sufficiently big in order to exchange the

solvent in the feed tank. If V_D is too low, the final solvent concentration can not be reduced to the desired limit value. These issues all contribute to a reduced feasible region in the (m_{pre},V_D) matrix. Fig. 6 shows the calculated objective function values in the feasible range.

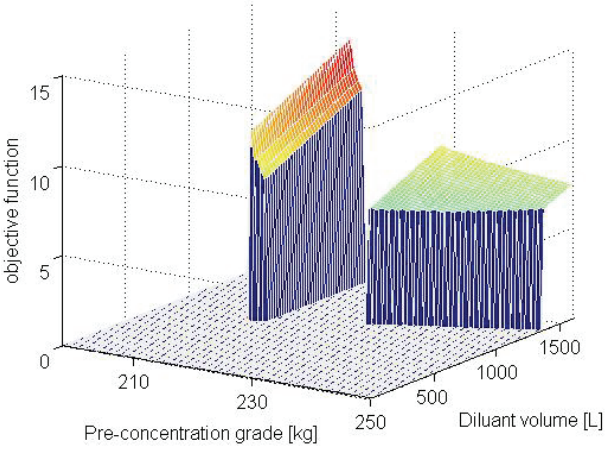

Figure 7: Objective function in the feasible range as function of pre-concentration grade and diluant volume

As shown in Fig. 6, for each pre-concentration grade m_{pre} can be found a diluant volume V_D, where the quality demand for the final solvent content is satisfied. The optimum operational parameters (m_{pre},V_D) are given by the minimum value of the half-plane of the calculated objective function in the feasible range, and it can be directly read from the graph. It should be noted that the outcome of the optimization is not generally valid. A change in the constants k_1 and k_2 of the objective function, or the utilization of an other type of membrane would result in a different set of optimum operational parameters.

Summary

A numerical technique is presented to simulate and optimize multi-step batch membrane processes for solvent exchange. This technique can be also used to simulate membrane filtration processes where not only the flux, but also the rejections of the components are dependent on the feed composition. The approach followed in this work did not use the volume concentration factor as a basis for the calculations, but rather the flux as a state function of the feed concentrations.

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