Response Surface Methodology Approach to Defining Ultrafiltration of Steepwater from Corn Starch Industry

Zita I. Šereš, Ljubica P. Dokić, Dragana M. Šoronja Simović, Cecilia Hodur, Zsuzsanna Laszlo, Ivana Nikolić, Nikola Maravić

Abstract**—**In this work the concentration of steepwater from corn starch industry is monitored using ultrafiltration membrane. The aim was to examine the conditions of ultrafiltration of steepwater by applying the membrane of 2.5nm. The parameters that vary during the course of ultrafiltration, were the transmembrane pressure, flow rate, while the permeate flux and the dry matter content of permeate and retentate were the dependent parameter constantly monitored during the process. Experiments of ultrafiltration are conducted on the samples of steepwater, which were obtained from the starch wet milling plant „Jabuka“ Pancevo. The procedure of ultrafiltration on a single-channel 250mm lenght, with inner diameter of 6.8mm and outer diameter of 10mm membrane were carried on. The membrane is made of α-Al_2O_3 with TiO_2 layer obtained from GEA (Germany). The experiments are carried out at a flow rate ranging from 100 to 200lh^{-1} and transmembrane pressure of 1-3 bars. During the experiments of steepwater ultrafiltration, the change of permeate flux, dry matter content of permeate and retentate, as well as the absorbance changes of the permeate and retentate were monitored. The experimental results showed that the maximum flux reaches about 40lm^{-2}h^{-1}. For responses obtained after experiments, a polynomial model of the second degree is established to evaluate and quantify the influence of the variables. The quadratic equitation fits with the experimental values, where the coefficient of determination for flux is 0.96. The dry matter content of the retentate is increased for about 6%, while the dry matter content of permeate was reduced for about 35-40%, respectively. During steepwater ultrafiltration in permeate stays 40% less dry matter compared to the feed.

Keywords**—**Ultrafiltration, steepwater, starch industry, ceramic membrane.

I. Introduction

GOVERNMENTS of the developed countries have tried to increase the pressure on the largest waste producers in order to reduce the undesired environmental pollution. For example, the Commission of the European Communities introduced the Integral Pollution and Prevention Control Directive. The purpose of the directive is to achieve integrated prevention and the control of pollution arising from the particular activities listed in its Annex I. Among others, the directive defines the Best Available Techniques (BAT) as the most effective and advanced stage in the development of activities and their operation methods which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment [1], [2]. One of them is membrane technique.

Membrane separation is a filtration technique in which a feed stream is fractionized with a porous membrane. Some of the dissolved solids are held back because their molecular size is too large to allow them to pass through. The size range depends upon the pore sizes of the used membrane. Fractionation of the feed stream occurs, with some molecules being concentrated on the upstream side of the membrane, which is known as the concentrate or retentate. The smaller molecules pass through the membrane into the permeate stream. There are few membrane processes where they can be characterized by driving forces that cause mass transfer of solutes (e.g. difference in concentration – dialysis), difference in electric potential - electro-dialysis), difference in pressure – microfiltration, ultrafiltration, nanofiltration, reverse osmosis) [3]-[5].

The main problem in the performance of ultrafiltration is concentration polarization and fouling of the membrane. Concentration polarization causes deposition of retained compounds on the membrane surface. A number of reviews have described the process in detail [5], [6]. The pure water flux of micro- and ultrafiltration membranes is usually high, but when separation starts through the membrane, the permetae flux falls very quickly, which is caused by the gel formation on the membrane surface. This gel layer forms a secondary barrier to the flow through the membrane [5], [7]. Avoidance of membrane fouling is not possible but it can be limited by the applying a number of different techniques which enhance membrane flux. These techniques might be pre-treatment of feed stream, backflushing, fluidized bed, fluid instability, application of electric, magnetic and ultrasonic fields [5]. There are several papers dealing with the application of membrane filtration for purification of wastewater from starch processing industry or for filtration of the starch suspensions [8], [9]. Membrane filtration is used in order to achieve an increase in the quality of the finished sweetening and syrup products. It has also found its application in the process of water elimination, i.e. dehydration in the course of the production. It is used to isolate proteins from diluted process flows [10].

The aim of this work was to look into the possibility for steepwater ultrafiltration in order to examine the influence of the operating parameters on the permeate flux during

Z. I. Šereš, Lj. Dokić, D. M. Šoronja Simović, I. Nikolić, N. Maravić are with the Faculty of Technology, University of Novi Sad, Bul. Cara Lazara 1, 21000 Novi Sad, Serbia (phone: +381214853685; fax: +38121450413; e-mail:zitas@tf.uns.ac.rs).

C. Hodur and I. Zs. Laszlo are with the Faculty of Engineering, University of Szeged, Moszkva krt. 9-12., Szeged, Hungary, (e-mail: hodur@mk.u-szeged.hu).

steepwater ultrafiltration. Design of experiments (DOE) is the most efficient way to enhance research value and reduce the time needed for experimentation and one of the frequently used methods is response surface methodology (RSM) introduced by Box and Wilson in 1951 [11], [12]. The idea of RSM can be defined as an empirical statistical technique for multiple regression analysis of data obtained from properly designed experiments. It provides a way of rigorously choosing a few points in a design space to efficiently represent all possible points and in that way reduces the number of experimental runs for investigating the influences of different factors as well as their interactions on the response of the interest. RSM was successfully applied for representation of removal of cooper and cobalt ions from aqueous solutions by polymer assisted ultrafiltration [13], [14], optimization of soybean oil degumming using ceramic membrane [15], aroma recovery from beer by pervaporation [16], modeling and optimization in pervaporation [17]. Generally, the results and the optimization can serve for the determination of the suitable operating conditions for the steepwater concentration. The dry matter content could be reduced in the steepwater permeate and the process water in the starch industry could be reused. Thus, the consumption of the process water would be reduced and the nutrients from the steepwater could be exploited as a feed.

II. Experimental

Ultrafiltration experiments were conducted on the samples of steepwater, which were obtained from the corn starch wet milling plant „Jabuka", Pančevo (Serbia). The procedure of ultrafiltration on a single-channel ceramic membrane with 2.5 nm pore sizes on the laboratory apparatus for ultrafiltration has already been published.

The central part of the apparatus is the module with the membrane inside. In this study, use was made of the ceramic membrane of GEA manufacturer (Germany). The membrane is single-channel, 250mm lenght, with the inner diameter of 6.8mm and outer diameter of 10mm. The membrane is made of α-Al_2O_3 with TiO_2 layer. The active membrane surface equals 0.005m^2. The pore sizes of the membrane are 2.5nm. This pore size is much smaller than that usually used for starch wastewater, e.g. ny Cancino-Madariaga and Aguirre [18]. These authors used a 0.2µm PVDF membrane of 7.5m^2. Their experiment was carried out in a real production plant on wastewater solutions with and without a prior sedimentation step. Šaranović et al. [19] investigated microfiltration of wheat starch wastewater on ceramic membrane with 200nm pore sizes, and achieved a dry matter decrease of about 50–60%. For this investigation of steepwater ultrafiltration, the membrane with 2.5nm pore sizes could be used because it contains smaller particles and no starch. Dry matter content was 6.5%, out of which proteins were 50%, lactic acid 26%, carbohydrates (as dextrose) 2.5%, and total ash 21.5%.

The ultrafiltration experiments were planned based on a full 32 factorial designed experiment [20]. In this experiment, the factors, i.e. the independent parameters were the transmembrane pressure (p) and flow rate (Q). Table I shows the values for the independent parameters which varied during the course of filtration.

TABLE I
Varied Values of Independent Variables

Independent variables	Q (L/h)	P (bar)
Varied values	50 / 150/ 200	1 / 2/ 3

Q - flow rate (L/h)
P - transmembrane pressure (bar)

Prior to the main experiments, the water flux of the membrane was measured; the measurement provided the reference to assess the effectiveness of membrane cleaning.

The dependent parameters monitored during the process of ultrafiltration, permeate flux and dry matter content of permeate and retentate were determined at the beginning, during and at the end of ultrafiltration.

The determination of dry matter content in steepwater and of permeate and retentate was based on the following: defined volume of steepwater, permeate or retentate weight in the laboratory glass, with a known mass of the glass. The glass with the content of the sample was put in the water bath. When the water evaporated, the glass with the content was dried at 105oC to a constant weight.

The membrane was cleaned before each experiment with 0.5% solution of Ultrasil 11. The effectiveness in membrane cleaning was assessed by examining the water flux recovery. The cleaning procedure was repeated until the 95% of original water flux was restored.

The influences of transmembrane pressure and flow rate on the permeate flux with the time were analyzed by means of a statistical multifactorial analysis of the experimental data. [19] The experimental data were processed with computer programs Statistica for Windows 8.0 and Origin 6.1.

For responses obtained after experiments, a polynomial model of the second degree is established to evaluate and quantify the influence of the variables:

$$Y=b_0+\sum b_i X_i+\sum b_{ii} X_{ii}^2+\sum \sum b_{ij} X_i X_j \qquad (1)$$

where b_0 represents intercept (constant), b_i the linear, b_{ii} the quadratic and b_{ij} the interaction effect of the factors; Y represents response.

III. Results and Discussion

The main experiments were started based on a full 32 factorial design. At each combination of pressure and flow rate, the ultrafiltration was stopped after cca. 3 hours. Figs. 1 and 2 show the results of these experiments.

The results of fitting the experimental values of the permeate flux after 2.5 hours of ultrafiltration of the second-order polynomial are shown in Table II.

Response fitted with the polynomial model (1) of the second degree is permeate flux- J (l/m2h). Equation (2) is a second-order polynomial (flux as a function of the pressure and flow rate).

$$J=-15.28+36.40\cdot P-0.0728\cdot Q-2.77\cdot P^2+0.0005\cdot P\cdot Q-0{,}1152\cdot Q^2 \quad (2)$$

where:

- J is a permeate flux (l/m^2h),
- P transmembrane pressure (bar),
- Q is a flow rate(l/h).

They approximate well the experimental results for the system (R^2 =0.84). The relatively high value of R^2 obtained for this response indicating good fit of the experimental data to equation [20]. The closer the value of R^2 to the unity, the better the empirical model fits the actual data [21]. The significance of each coefficient was determined through the t-values. The larger the magnitude of the t-value the more significant is the corresponding coefficient. The polynomial model tested for the selected responses were significant at the 95% confidence level (p-value; 0.05, Table II).

TABLE II
RESULTS OF FITTING THE EXPERIMENTAL VALUES OF THE PERMEATE FLUX, AFTER 2.5 HOURS OF ULTRAFILTRATION

Factor	Value	t-value
b0	-15,2834	-0,18835
b1	36,4014	0,99803
b2	-0,0728	-0,07358
b11	-2,7712	-0,34679
b22	0,0005	0,15267
b12	-0,1152	-1,01914
R^2	0,84	

In order to facilitate comparisons of the significance of individual coefficients, they were expressed as a fraction of the largest t-values of the observed correlation [22]. The significance of individual coefficients of average permeate flux correlation are shown in Fig. 1. The most important linear factor influencing permeate flux during the 2.5 hours ultrafiltration is the transmembrane pressure (coefficient - b1). Among the quadratic coefficients the greatest impact on the ultrafiltration process has the quadratic effect of transmembrane pressure, whereas second most significant is the interaction between transmembrane pressure and suspension flow rate.

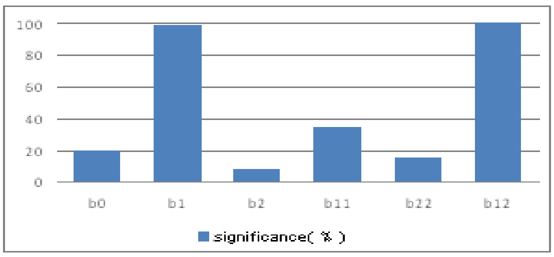

Fig. 1 Significance of the individual coefficient of the average permeate flux correlation

Based on the obtained experimental values and using the program *Statistica 8.0* a regression equation was obtained, which best describes the dependence of the flux on the transmembrane pressure and flow rate, and the graphs depicting two dependent variables are shown in Fig. 2.

Fig. 1 shows the influence of a transmembrane pressure and flow rate of the starch suspension on the value of the flux after reaching the steady state (after 10 minutes). The most important linear factor influencing the permeate flux is the pressure and the Fig. 2 shows that the highest flux values can be achieved (over 35 L/ m^2h) when the flow rate is held around 150 L/h and the transmembrane pressure around 3 bars.

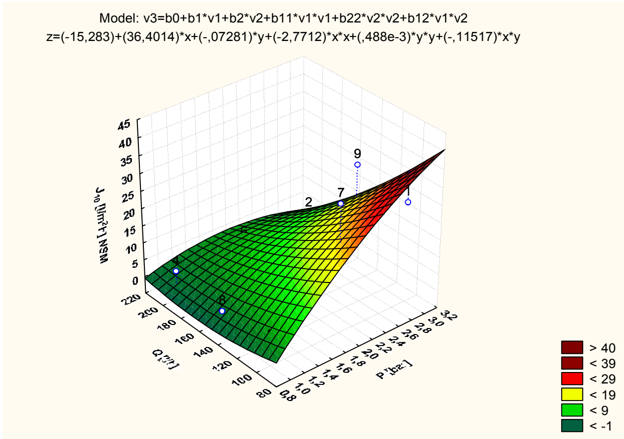

Fig. 2 Dependence of the steepwater permeate flux on the transmembrane pressure and flow rate after reaching steady state

It could be expected that the permeate flux would increase with the transmembrane pressure. However, there is a negative effect of a higher transmembrane pressure: the cake layer may become more compact as the transmembrane pressure increases, leading to a greater flux reduction [21]. Russotti et al. [23] reported that literature data on the influence of the transmembrane pressure on microfiltration of yeast suspensions have been contradictory. In some instances higher steady state fluxes have been reported with the increase of transmembrane pressure, while in other cases higher transmembrane pressure values resulted in lower steady state fluxes. This contradiction in reported results was explained by the fact that permeate flux is strongly influenced by the compressibility of the cake layer formed during filtration process.

At higher steepwater flow rates, with increasing transmembrane pressure, the permeate flux initially increases, eventually reaching a stationary value [18]. A higher steepwater flow rate results in a higher tangential shear stress and the particles on the membrane surface are more unstable [24], [25]. Consequently, less cake mass can be formed under a higher flow rate, which leads to an increase in the average permeate flux. It can be noticed that with increasing flow rate at all transmembrane pressures, the average permeate flux in the increases.

Fig. 3 illustrates a very good correspondence of experimentally obtained and calculated values of flux after reaching a steady state, after 10 minutes of ultrafiltration.

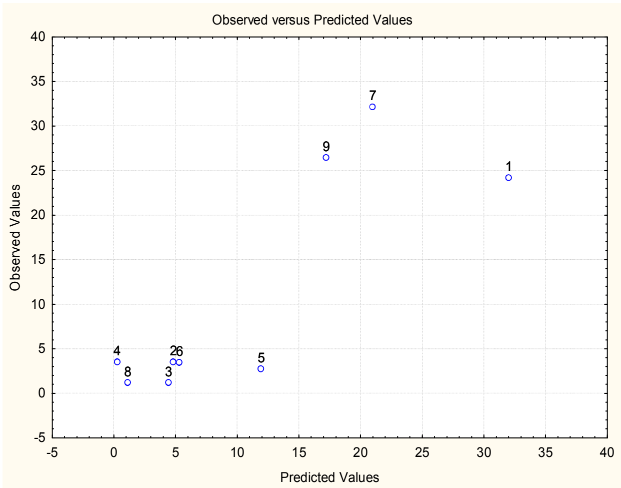

Fig. 3 Correlation between experimentally obtained and calculated values of flux after reaching steady state

Change of the content of dry matter is also one of the most important indicators of changes in the quality of the permeate and retentate after ultrafiltration of steepwater. Higher attention shall be given to the quality of the retentate in relation to the quality of filtered steepwater, and will be expressed in the percentage concentration of the feed mixture after 3 hours of ultrafiltration. Values of changes of dry matter in retentate are presented after 2,5 hours of the ultrafiltration.

The results of fitting the experimental values of the content of dry matter after 2.5 hours of ultrafiltration of the second-order polynomial are shown in Table III.

TABLE III
RESULTS OF FITTING THE EXPERIMENTAL VALUES OF CHANGES OF THE DRY MATTER CONTENT IN RETENTATE

Factor	Value	t-value
b0	17,85667	3,85437
b1	-6,06667	-2,91324
b2	-0,13030	-2,30639
b11	0,35000	0,76714
b22	0,00022	1,21646
b12	0,03000	4,64956
R^2	0,94	

In order to facilitate comparison of the significance of individual coefficients they have been expressed as a fraction of the largest t-values of the observed correlations [22]. Fig. 4 illustrates the significance of the individual changes in the correlation coefficients of dry matter in retentate. The biggest impact on the change in the value of dry matter at the end of ultrafiltration of steepwater has a pressure. However, the quadratic coefficients show a greater impact of a flow rate compared to a pressure. The interaction of transmembrane pressure and flow rate is most significant.

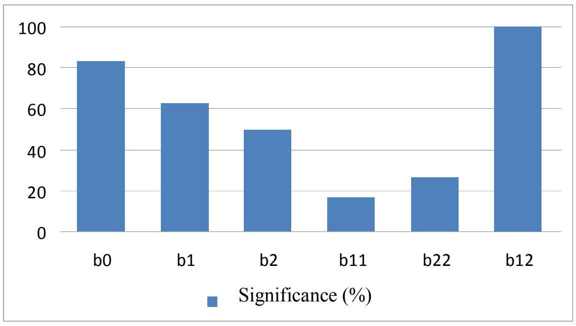

Fig. 4 Significance of the individual coefficients of the changes of dry matter in retentate at the end of ultrafiltration

Fig. 5 shows the effect of transmembrane pressure and flow rate of steepwater on the value of changes of dry matter in retentate. At the lowest values of pressure and flow rate we notice an increase in changes of dry matter content in retentate. A gradual increase in the value of a parameter, pressure or flow rate, leads to the rapid change in decrease of dry matter content in the retentate.

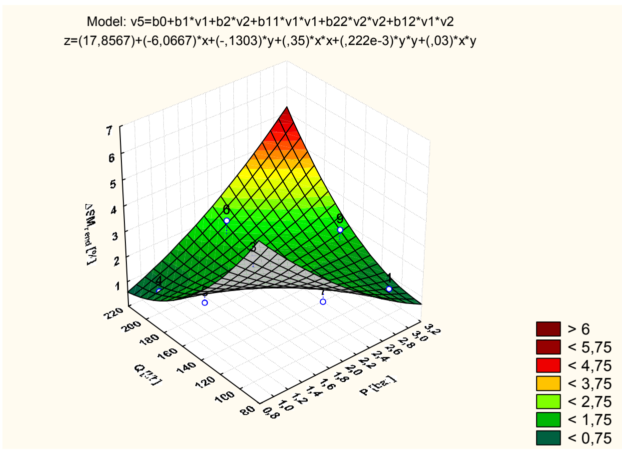

Fig. 5 Dependence of the dry matter content in retentate of flow rate and transmembrane pressure at the end of the ultrafiltration

The best concentration of the retentate (greater than 6%) is achieved at the highest values of pressure and flow rate. When we look at the conditions when the flow rate of steepwater increases the, it reduces the thickness of the bread due to the more intensive removal of the particles from the surface (a higher tangential velocity), its porosity increases, and the influence of a transmembrane pressure is more pronounced and with the increase of a pressure the retentate concentration is decreased.

The best retentate concentracion (greater than 6%) is achieved at the highest values of pressure and flow.

Fig. 6 shows the correlation between the experimentally obtained and calculated values of the changes of dry matter at the end of ultrafiltration.

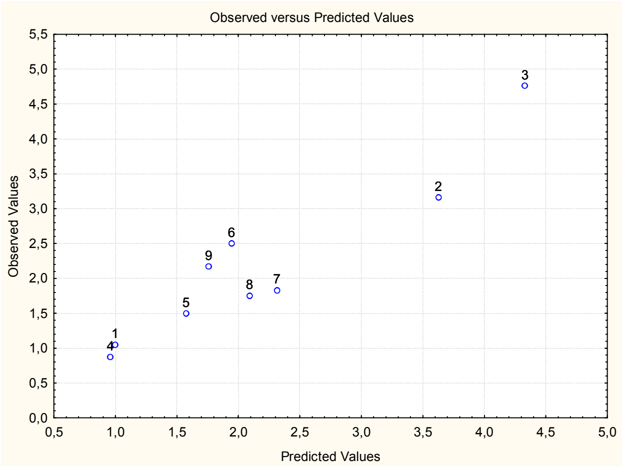

Fig. 6 Correlation between experimentally obtained and calculated values of the changes of dry matter at the end of ultrafiltration

Relative changes in values of the dry matter content of the permeate and retentate compared to the steepwater are ilustrated in Fig. 7. The dry matter content of the retentate is increased for about 6%, while the dry matter content of permeate was reduced for about 40%, respectively. During steepwater ultrafiltration in permeate stays 40% less dry matter compared to the feed.

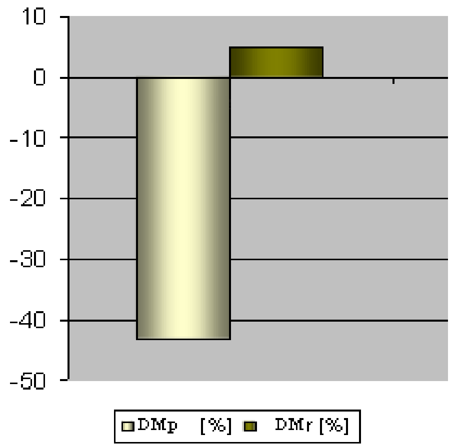

Fig. 7 Relative changes of the dry matter content of the permeate and the retentate in relation to the steepwater

IV. Conclusion

On the basis of the study of the effects of the steepwater ultrafiltration conditions, the following conclusions can be drawn:

The experimental results of permeate flux change and the change of the dry matter content after ultrafiltration with ceramic membrane can be in an adequate way approximated with a polynomial model of the second degree. High values of correlation coefficients indicate the feasibility of this approach. Coefficient values are in the range of from 0.84, for the relative increase of the permeate flux, to 0.94, for a changes of the dry matter content.

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