WFL Publisher
Science and Technology
Meri-Rastilantie 3 B, FI-00980
Helsinki, Finland
e-mail: info@world-food.net

Journal of Food, Agriculture & Environment Vol.11 (1): 221-226. 2013

www.world-food.net

Optimization of wine decolorization by microfiltration on polyurethane membranes

Igor Cretescu [1], Alexandru Savin [1], Carmen Cimpeanu [2], Roxana Dana Bucur [3]* and Maria Harja [1]

[1] Faculty of Chemical Engineering and Environmental Protection, 73, D. Mangeron Street, 700050, Iasi, Romania. [2] University of Agronomical Sciences and Veterinary Medicine of Bucharest, 59, Marasti, 011464, Bucharest, Romania. [3] "Ion Ionescu de la Brad" University of Agricultural Sciences and Veterinary Medicine of Iasi, Faculty of Agriculture, 3, Mihail Sadoveanu Alley, 700490, Iasi, Romania. e-mail: icre@ch.tuiasi.ro, asavin@ch.tuiasi.ro, carmencimpeanu@yahoo.com, rbucur@uaiasi.ro, maria_harja06@yahoo.com

Received 2 October 2012, accepted 19 January 2013.

Abstract

Partial removal of colored compounds, responsible for wine properties (i.e. astringency), was studied in term of wine decolorisation, using microfiltration on modified polyurethane membrane. The microfiltration treatment process of the Cabernet Sauvignon red wine was investigated in order to improve the wine quality. The main influencing experimental factors on the wine microfiltration efficiency, taking into consideration in this study were the vacuum intensity (in term of microfiltration pressure) and initial intensity of wine colour (in term of optical density/colour intensity measured in absorbance units). A mathematical model was developed based on experimental design according to 2^2 second-order rotatable composite central design methodology. The optimal values corresponding to the maximum decolorization rate in terms of wine microfiltration efficiency and wine properties were found for a vacuum of 34 mm Hg and an initial wine optical density of 2.8.

Key words: Wine microfiltration, polyurethane membrane, colour intensity, Cabernet Sauvignon, optimization.

Introduction

Food safety and quality represent fields of actual and high interest, for both producers and consumers. In order to assure the quality levels of food products, membrane techniques have been used in the last decades [1, 2]. The quality of wines, in general, and of red wines [3, 4], in particular, might be controlled and enhanced by involving membrane techniques in various operations within the technological flux. By using membrane separations, the contents of dye compounds, tannin, flavour and ethylic alcohol might be controlled, thus contributing to obtain some colours, flavours and aromas that satisfy various preferences [5-7].

In establishing the membrane technique, the nature and structure of membrane play an important role. The structural constituents of membrane must neither interact chemically with wine compounds nor dissolved into wine and as a consequence affect the quality.

For food usages, there are known membranes achieved from various materials, covering a wide range of chemical compounds. Membranes based on polyurethane and modified celluloses have been studied and applied in controlling the characteristics of food products such as dairy products, wine, and so on [8, 9].

The red wine resulted from pressing fermented marc has in some particular cases, high astringency. That is why it is desirable to recover the alcohol, which leads to economical losses due to instead of red wine; finally it is obtained a distillate with a low content of alcohol and thus a low market value [2].

Compared with conventional methods such as treatment with bentonite or gluing with gelatin, membrane separation is selective in removing chemical compounds that generates astringency.

The use of polysulphone membranes in the ultrafiltration of wines shows that they reduce the astringency, but are far to meet the quality requirements of wines due to the retention of flavours. In addition, low permeate flows through polysulphone membranes are caused by instantaneous adsorption of phenolic compounds in wines, and thus it is generated a secondary layer (gel layer) on the membrane surface, that increases the resistance to flow.

Cellulose membranes allow initially high and constant flow rates, followed by a slight decline with the increase of the number of reuses. This decrease in flow rate could be associated only with the increase of wine viscosity due to the excessive accumulation of polyphenols and coloured compounds.

When the wine treatment is based on ultrafiltration, important losses of the flavors occur, while the wine treatment by microfiltration provides additional advantages on the conservation of color and aromatic contents.

In order to eliminate some of the above mentioned disadvantages related to ultrafiltration and polysulphone membranes, the wine treatment by microfiltration will be further investigated in this study, using polyurethane membrane prepared by means of an original method. These have a composite structure made of polyurethane and cellulose derivates.

The study is focused on both process modeling and finding the optimum operating parameters for the microfiltration process of the Cabernet Sauvignon red wine, in order to improve the wine quality through selective and efficient removal of undesirable colored compounds.

---

* Corresponding Author:
Roxana Dana Bucur (e-mail: rbucur@uaiasi.ro)

Materials and Methods

Materials, procedures and analysis: The scheme of the microfiltration set-up used in the experimental investigations is shown in Fig. 1.

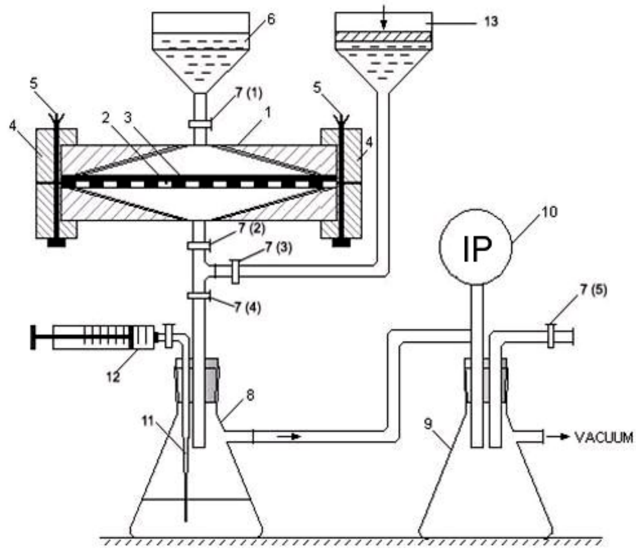

Figure 1. Microfiltration set-up with frontal module: 1 - microfiltration module, 2 - metallic support of membrane 3 - microfiltration membrane, 4 - flange, 5 - sealing screw, 6 - raw wine, 7 - valves, 8 - permeate collecting vessel, 9 - buffer vessel, 10 - vacuumeter, 11 - capillary, 12 - sampling syringe, 13 - washing and unclogging solution.

In the process of wine microfiltration, an asymmetric polyurethane membrane prepared according to a method described in our previous works [8, 10] was used as filtration material. The basic characteristics of membrane are presented in Table 1.

Table 1. Characteristics of polyurethane membrane.

Filtrating material	Porosity ε, (%)	Permeability to water P, ($m^3/h{\cdot}m^2$)	Mean pore diameter (μm)	Thickness (μm)
Polyurethane membrane	73.71	0.1592	1.2-1.7	175

The integrity of membranes was tested using an air flow, and a very low vacuum (1 mm Hg).

The experiments were performed using Cabernet Sauvignon red wine (Ştefăneşti Vineyard, Argeş, Romania, harvest of 2006) having an ethylic alcohol concentration of 11.20% (at 20°C), and a high concentration of coloured compounds, corresponding to the initial color intensity of wine (in term of optical density of 2.8 absorbance units).

In order to obtain wines of different initial concentration of coloured compounds, mixtures were prepared from the raw wine having the highest concentration of coloured compounds and various volumes of alcohol solution in water 11.20% vol., corresponding to different dilution degrees, D (1 wine volume: D volumes of aqueous alcoholic solution).

The determination of optical characteristics of wines and permeate samples was achieved by molecular absorption spectrophotometry [11], using an UV-VIS SPECORD (Carl Zeiss, Jena) spectrophotometer.

Multivariate experimental design: The central composite rotatable experimental design (CCD) was used for the response surface modelling and optimization of the microfiltration process. The significant experimental factors taken into consideration were: x_1 the value of the vacuum applied below the membrane needed to achieve the microfiltration process, x_2 the initial colour intensity of red wine, I_{C_0}. Decolorization rate of wine Y (%) is the considered response. The variation range of the independent variables was established based on a series of preliminary tests, and are shown in Table 2.

Table 2. Real and coded values of the investigated factors in the microfiltration process ($\alpha = 1.414$).

Process variables	Coded variables	Real values of codified levels				
		$-\alpha$	-1	0	+1	$+\alpha$
Vacuum, mm Hg	x_1	10	19	40	61	70
Initial color intensity	x_2	1.0	1.265	1.890	2.535	2.790

Calculations in this paper, related to the modelling and optimization of microfiltration process of wine, were performed by means of MathCAD and Matlab software.

Results and Discussion

Microfiltration of Cabernet Sauvignon red wine: The concentration of coloured products that might provide colour, bitterness and astringency to red wines is determined based on the wine colour intensity achieved from the visible spectrum of wine shown in Fig. 2.

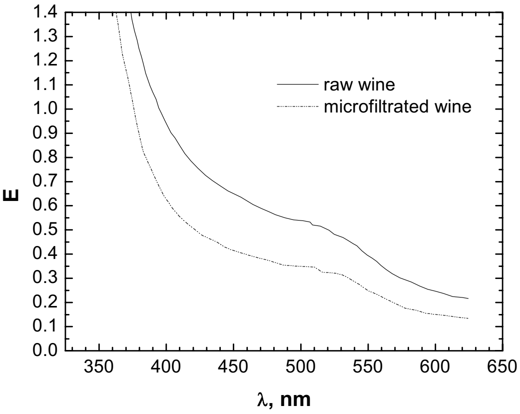

Figure 2. Visible spectra of strong coloured red wine, Cabernet Sauvignon type; 1 - raw wine, 2- wine microfiltrated on polyurethane membrane.

In case of red wines, the intensity is expressed as the sum of absorptions of radiations with wavelengths of 420, 520 and 620 nm, respectively, and the colour tint is expressed by the absorption ratio at 420 and 520 nm [12]:

$$I = E_{0.420} + E_{0.520} + E_{0.620} \tag{1}$$

$$T = E_{0.420} / E_{0.520} \tag{2}$$

It can be noticed that the extinction values of permeate wine are reduced by microfiltration from 0.62 to 0.405, in case of the wavelength of 420 nm, from 0.445 to 0.28, at 520 nm, and from 0.31 to 0.15, at 620 nm. Hence, it can be stated that the polyurethane membrane is effective in retaining the colored materials from the wine.

Influence of pressure gradient on membrane: In a series of experiments, the wine microfiltration was carried out on polyurethane membranes, at several values of vacuum applied below the membrane. The intensity of the obtained permeate colour, I_{PC}, as a function of the vacuum is shown in Fig. 3.

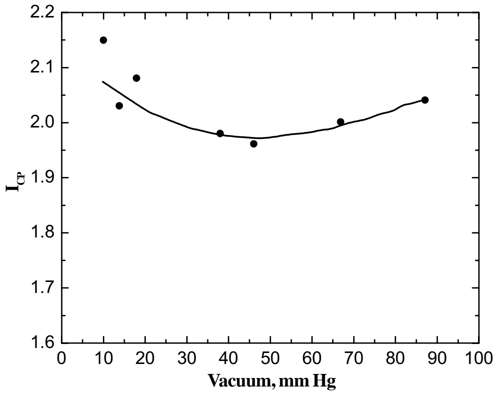

Figure 3. Permeate colour intensity, I_{PC}, as a function of the vacuum from below the membrane.

At the vacuum of 10 mm Hg, the membrane porosity was reduced by the compression of membrane structure and pore blocking with coloured substances, which leads to the decrease of dyes and solvent (water and alcohol) flow rates. The alcohol in the collected permeate is evaporated which leads to an increase of dye concentration in permeate. At the vacuum of 40 mm Hg, the evaporation of alcohol from permeate was reduced, and the colour intensity of permeated wine decreaseds. However, the pressure drop on the membrane maintains a diminished porosity compared to the initial structure.

At vacuum of 70-80 mm Hg, the porosity was less affected, and alcohol was removed from permeate in low amounts, the colour intensity resulted in permeate was given by a higher quantity of dye passing through pores. The influence of coloured compounds from wine on its membrane separation process is in agreement with the mechanism described by Brock [13].

The coloured particles greater than pore size are stopped on the membrane surface and may block some of the pores, contributing to the reduction of flow rate.

Particles with smaller dimension than pore diameters are embedded in the membrane matrix. Some particles may pass through the membrane matrix and reach into the permeate composition, while others adhere to the membrane matrix altering the porosity, thus determining a decrease of the solvent flow rate and the flow of other particles through membrane.

When the vacuum applied below the membrane is very low (10-20 mmHg), membrane matrix blocking is achieved after a short time from the beginning of the process, and the flow rate through membrane is reduced fast. Large particles of coloured compounds no longer pass through the membrane, while permeate in the collecting vessel is concentrated by ethanol evaporation.

Influence of colored materials concentration: In another series of experiments, it was established how the concentration in coloured materials in the initial wine and permeate influences the permeate flow.

Rapid formation of the cake layer reduced the flow rate of permeate after about 3-4 min of operation of the microfilter equipped with a polyurethane membrane. Further decrease of permeate flow rate by 2-3% was due to partial pore fouling (Fig. 4). By feeding the membrane module with fresh wine over the retentiate on the membrane, the concentration of species that form the solute was reduced, retentiate viscosity decreased, and consequently the permeate flow rate increased.

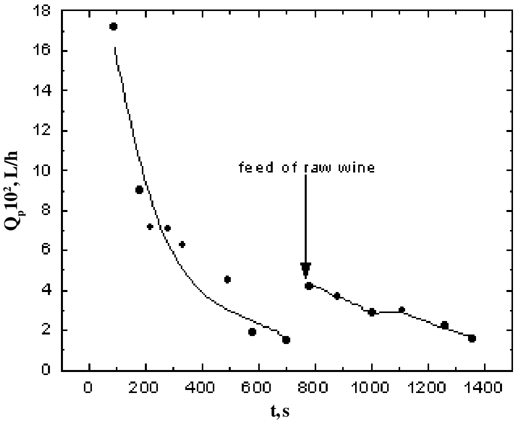

Figure 4. Variation of permeate flow rate in time and with the addition of red wine containing the same concentration of dye, at vacuum of 150 mm Hg, dilution D = 2.

The two series of experiments emphasize that the pressure gradient on the membrane and solute concentration in the wine fed in the microfiltration influences the process and permeate quality. Further, it was proceed to study the influences of these two factors over the process.

Modeling by active experiment of the decolorization process by microfiltration of red wine with different concentrations of coloured compounds: By recording the visible spectra for each synthetic mixture obtained by diluting the initial wine, the extinctions were determined, and based on them the intensity of the initial colour of diluted wine was calculated. In Fig. 5 the colour intensity is plotted as a function of dilution.

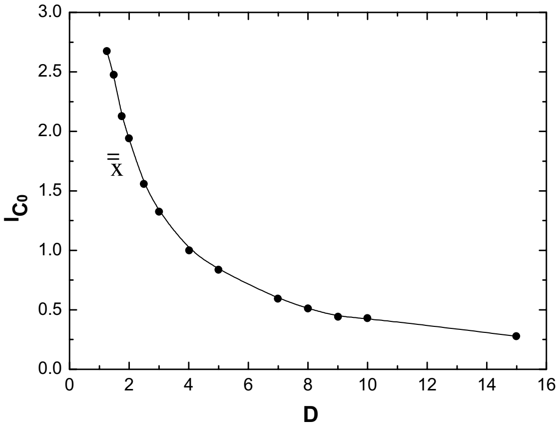

Figure 5. Initial colour intensity of raw wine (I_{C_0}) as a function of dilution (D).

The analytical form of this function is $I_{C_0} = 3.7938 \times D^{-0.984}$. By means of this function, the needed dilutions were determined in order to obtain raw wine of various initial colour intensities in accordance with the values of the experimental design.

The decolorization rate of Cabernet Sauvignon red wine was calculated on the basis of the intensity values of the initial colour and that obtained after microfiltration according to the relationship:

$$Y\% = \frac{I_i - I_f}{I_i} \cdot 100 \qquad (3)$$

where I_i and I_f are colour intensity of raw wine and permeated wine, respectively.

Classical research methodology involves the obtaining of experimental results by successive modifications of the process parameters, leading to a low efficiency during experimental optimization. A completely different approach arises when the research subject is investigated using statistical methods in all stages of the experiment. This mode of solving problems is called active experiment and requires programming or planning of the experiments. The investigation of processes by active experiment has advantages for modelling and optimization of processes in environmental engineering and chemical and food technologies[14-20].

In order to determine a regression equation for the microfiltration process, an experimental program was established that provides simultaneous modification of the values of process variables. The microfiltration process of wine was modelling using a second order model, based on 2^2 experimental design matrix, according to central composite rotatable design program, which involve the experimental values of the decolorization rate for N = 13 experiments (Table 3).

Regression coefficients[14, 21] of the empirical model were calculated by means of the least squares method using equation 4:

where $\overline{b}$ is the column matrix of the regression coefficients having

$$\overline{b} = \left(\overline{\overline{X}}^T \cdot \overline{\overline{X}} \right)^{-1} \overline{\overline{X}}^T \cdot \overline{Y} \qquad (4)$$

the dimension (u×1); $\overline{\overline{X}}$ - matrix of the experimental program having the dimension (N×u); $\overline{Y}$- column matrix (N×1) containing the experimental results of the decolorization rate determined in accordance with the experimental plan; N - number of experiments, u - number of regression coefficients in the empirical model equation. Based on the experimental plan (Table 3), it was developed a nonlinear mathematical model (regression equation) that approximates with certain accuracy the microfiltration process of red wine. Written in coded coordinates, the mathematical model has the following expression:

$$\hat{Y} = 24.546 - 0.881x_1 + 3.894x_2 - 2.097x_1^2 + 3.306x_2^2 + 0.59x_1x_2 \qquad (5)$$

where $-1.414 \leq x_1 \leq +1.414$ and $-1.414 \leq x_2 \leq +1.414$ (coded coordinates).

Table 3. Experimental design for studying of wine microfiltration process.

N	Factor - 1		Factor - 2		Wine decolorization rate
	x_1	P, mmHg	x_2	I_{Co}	Y, %
1	-1	19	-1	1.260	26.19
2	1	61	-1	1.260	22.22
3	-1	19	1	2.535	26.48
4	1	61	1	2.535	24.90
5	-1.414	10	0	1.890	21.69
6	1.414	70	0	1.890	20.63
7	0	40	-1.414	1.0	22.00
8	0	40	1.414	2.790	41.93
9	0	40	0	1.890	27.51
10	0	40	0	1.890	20.63
11	0	40	0	1.890	24.34
12	0	40	0	1.890	24.33
13	0	40	0	1.890	25.92

In real coordinates, the equation of the mathematical model is:

$$\hat{Y} = 39.94 + 0.247 \cdot P - 26.717 \cdot I_{Co} - 4.659\,.\,10\text{-}3 \cdot P^2 + 8.199 \cdot I_{Co}^{\ 2} + 0.044 \cdot P \cdot I_{Co} \qquad (6)$$

where $10 \leq P \leq 70$ (mm Hg) and $1 \leq I_{Co} \leq 2.790$ (real coordinates).

The agreement between the mathematical model and the experimental results was statistically verified by applying Fischer Test[21] for the significance level of p = 0.05 and freedom degrees f_1 = 7 and f_2 = 4. The calculated value of Fischer criterion is 4.43. The tabulated value of Fischer criterion for the significance of p = 0.05 and freedom degrees f_1 = 7 and f_2 = 4 is of 6.09. Due to $F_C<F_T$, the validity of the mathematical model is statistically accepted, and thus it can be stated that model is adequate. This adequacy is described in Fig. 6, where the experimental values of the decolorization rate Y(%) are compared with those calculated according to the empirical model. Also, a satisfactory agreement can be noticed between the mathematical model and experimental results.

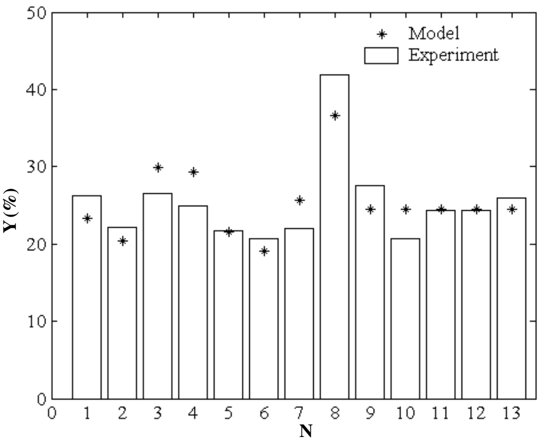

Figure 6. Experimental values of microfiltration efficiency compared with those calculated according to the suggested mathematical model.

Fig. 7 shows the response surface of the regression equation, and in Fig. 8 the contour lines corresponding to the response surface. In these figs, it can be noticed that the significant factor is the initial colour intensity I_{Co} of Cabernet Sauvignon wine.

The increase of the value of this factor contributes to the increase of the wine decolorization rate. The absolute pressure from below the membrane, within the investigated operation range, has a less relevant influence on the decolorization rate in comparison with the intensity of initial colour, I_{Co}. The response surface shown in Fig. 7, and the contour lines in Fig. 8, point out that the microfiltration is efficient at values of pressure from below the membrane ranged between 30 and 40 mm Hg.

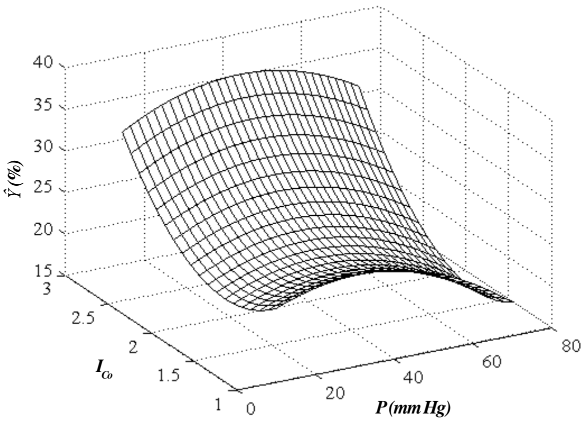

Figure 7. Response surface of regression equation showing the dependence of the wine decolorization rate (microfiltration efficiency) on I_{Co} and P variables.

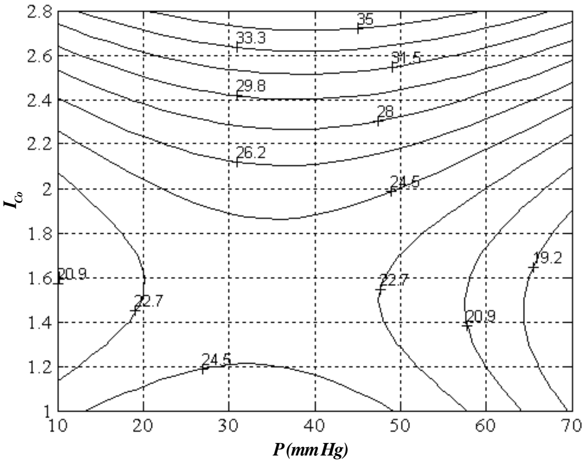

Figure 8. Contour lines corresponding to the response surface, i.e. the dependence of wine decolorization rate (microfiltration efficiency) on I_{Co} and P variables.

Optimization of red wine decolorization process: By means of statistical modelling, a second-degree polynomial equation was obtained whose adequacy was verified statistically. Thus, it can be stated that the mathematical model describes satisfactorily the investigated experimental domain. In order to determine the optimal conditions of microfiltration process, ensuring the highest decolorization rate of wine, the canonical analysis was used by means of which the regression equation (4) was brought into the canonical form. The canonical transformation of the regression equation lies in the selection of a new system of coordinates having the origin in the stationary point [19].

The stationary point was determined by solving the system of equations obtained through the derivation of the objective function in relation to each decision variable and equalization to zero, having the following coordinates (coded values): $\overline{x}^* = \{-0.29\ -0.563\}^T$. The value of the objective function in this point is $\hat{Y}(\overline{x}_S) = 23.578$. The regression equation (2) written in canonical form becomes:

$$\hat{Y} - 23.578 = -2.113 \cdot \zeta_1 + 3.22 \cdot \zeta_2 \qquad (7)$$

where ζ_1 and ζ_2 represent the factor values in the new system of axes (canonical axes), and the corresponding canonical coefficients represent the values of the quadratic and interaction coefficients matrix in the regression equation (4). Due to the canonical coefficients have different signs, the response surface represents a hyperbolic paraboloid and for optimizing the process, it was used the method of moving along the canonical axes. In correspondence with the new system of coordinates, it was realized the move along the ζ_2 axe for which the canonical coefficient is positive, and the value of the objective function is maximizing. Further, the objective function was given different values $\hat{Y} > 23.578$ and the corresponding regimes ware calculated. Due to the movement was carried out along the ζ_2 canonical axe, $\zeta_1 = 0$, and equation (7) can be written as:

$$\xi_2 = \pm\sqrt{\left(\hat{Y} - 23.578\right)/3.322} \qquad (8)$$

The passing from (ζ_i) canonical coordinates to the coded values of factors (x_i) was achieved by means of the following system of equations:

$$\begin{cases} x_1 = \left(\xi_1 + x_{S1}\right) cos\,\beta - \left(\xi_2 + x_{S2}\right) sin\,\beta \\ x_2 = \left(\xi_1 + x_{S1}\right) sin\,\beta + \left(\xi_2 + x_{S2}\right) cos\,\beta \end{cases} \qquad (9)$$

where β is the angle between the axes of the new coordinate system in relation to those of the old system.

Thus, the identification of the optimal conditions was performed investigating the response surface in the canonical space, and the two possible regimes were established: $\overline{x}^* = \{-0.294\ 1.429\}^T$ and $\overline{x}^* = \{-0.282\ -2.553\}^T$. Since the second regime is located at a distance much beyond the investigated experimental range, the optimal point in coded coordinates is $\overline{x}^* = \{-0.294\ 1.429\}^T$ and the calculated value of the objective function in this point is $\hat{Y}(\overline{x}^*) = 36.691$. Real optimal values of the factors involved in the microfiltration process of red wine, which give the best decolorization rate, are presented in Table 4.

Table 4. Optimal values of the factors giving the maximum decolorization rate of Cabernet Sauvignon wine.

P (mm Hg)	I_{Co}	Y % (exp.)	ŷ%(calc.)
34	2.800	36.20	36.691

These composite polyurethane membranes exhibited an excellent behaviour in respect with the main purpose presented in this article. In order to improve the membrane performances, especially the membrane selectivity toward different organic compounds from wines, the polyurethane membranes could be modified according to some procedures described in literature [21-22].

Conclusions

The efficiency of using asymmetrical polyurethane membranes was emphasized in the microfiltration of Cabernet Sauvignon red wine in order to diminish the content of coloured substances that might also give astringency and acidity.

The vacuum used in microfiltration and the initial concentration of coloured compounds in wine were considered as factors, and their influence on the characteristics of filtrated wine and separation process performance, respectively, were monitored.

The gradual formation of the cake layer decreases rapidly the permeate flow rate after approximately 3-4 min of operation of the microfiltration module. The subsequent decrease of permeate flow rate of 2-3% is due to partial pore fouling.

Modelling of decolorization process by microfiltration of Cabernet Sauvignon red wine with high content of coloured compounds was achieved through active experiment program using a second-order central-composite rotatable design.

The model allowed determining the optimal conditions of microfiltration in order to obtain red wine with a certain intensity of colour.

Optimal values of the factors involved in the microfiltration process were determined by the canonical analysis of regression equation. Thus, the maximum efficiency of the wine microfiltration process expressed by the decolorization rate corresponds to a vacuum of 34 mm Hg and an initial intensity of the wine colour of 2.8.

Conclusions

These composite polyurethane membranes exhibited an excellent behaviour in respect with the main purpose presented in this article. In order to improve the membrane performances, especially the membrane selectivity toward different organic compounds from wines, the polyurethane membranes could be modified according to some procedures described in literature [22,23].

Acknowledgements

The research presented in this paper was partially achieved in the frame of CNCSIS project type A, cod 1070/2004-2007, financed by the Romanian Government. Many thanks to Professor dr. Mariana Bezdadea for membrane preparation and corresponding know-how transfer.

References

[1] Mafart, P. and Beliard, E. 2004. Genie Industriel Alimentaire. Tome 2-Techniques separatives. 2nd edn. Tec & Doc Lavoisier, Paris, 206 p.

[2] Shrikhande, A. J. and Kupina, S. A. 1993. Ultrafiltration: A new approach for quality improvement of pressed wine. In Gump, B. H.and Pruett, D. J. (eds). Beer and Wine Production: Analysis, Characterization and Technological Advances. An American Chemical Society Publication, Washington, pp. 197- 218.

[3] Budić-Leto, I., Gajdoš Kljusurić, J., Zdunić, G., Tomić-Potrebuješ, I., Pezo, I. and Lovrić, T. 2012. Comparison of the descriptive sensory attributes of taste and chemical parameters of Croatian dessert wine Prošek using multivariate analysis. Journal of Food, Agriculture & Environment **10**(1):132-136.

[4] Poiana, M. A., Dobrei, A., Stoin, D. and Ghita, A. 2008. The influence of viticultural region and the ageing process on the color structure and antioxidant profile of Cabernet Sauvignon red wines. Journal of Food, Agriculture & Environment **6**(3&4):104 -108.

[5] Vernhet, A. and Moutounet, M. 2002. Fouling of organic microfiltration membranes by wine constituents: Importance, relative impact of wine polysccharides and polyphenols and incidence of membrane properties. J. Membrane Sci. **201**:103-122.

[6] Vernhet, A., Cartalade, D. and Moutounet, M. 2003. Contribution to the understanding of fouling build-up during microfiltration of wines. J. Membrane Sci. **211**:357-370.

[7] Takacs, L., Vatai, G. and Korany, K. 2007. Production of alcohol free wine by pervaporation, J. Food Eng. **78**:118-125.

[8] Bourceanu, M., Cretescu, I. and Bezdadea M. 2008, Techniques and Performances in Membrane Separation. Cermi, Iasi, 154 p.

[9] Zavastin, D. E., Cretescu, I. and Bezdadea, M. 2012. Study of separative performances of a cellulose acetate-polyurethane blend membrane for the treatment of some phenolic aqueous solutions. J. Env. Protect. Ecol. **13**:497-505.

[10] Zavastin, D. E., Cretescu, I., Bezdadea, M., Bourceanu, M., Dragan, M., Lisa, G., Mangalagiu, I., Vasic, V. and Savic, J. 2010. Preparation, characterization and applicability of cellulose acetate-polyurethane blend membrane in separation techniques. Colloids surface A-Physicochem. Eng. Aspects. **370**:120-128.

[11] Alecu, A., Saucier, C. and Cretescu, I. 2008. The study of catalytic degradation of malvidin-3-glucoside from red wines, using molecular absorption spectrophotometry. Rev. Chim. **59**:314-317.

[12] O. I. V. 2013. Recueil des methodes internacionales d'analyse des vins et des mouts, Vol 1. Paris. 513 p. http://www.oiv.int/oiv/info/frmethodesinternationalesvin.

[13] Brock, T. D. 1983. Membrane Filtration: A User's Guide and Reference Manual. Springer-Verlag, New York, 381 p.

[14] Marchitan, N., Cojocaru, C., Mereuta, A., Duca, G., Cretescu, I. and Gonta, M. 2010. Modelling and optimization of tartaric acid reactive extraction from aqueous solutions: A comparison between response surface methodology and artificial neural network. Separ. Purif. Technol. **75**:273-285.

[15] Secula, M. S., Suditu, G. D., Poulios, I., Cojocaru, C. and Cretescu, I. 2008. Response surface optimization of the photocatalytic decolorization of a simulated dyestuff effluent. Chem. Eng. J. **141**:18-26.

[16] Suman, I., Cojocaru, C., Creţescu, I., Duca, G., Malina Jr., J. F. and Covaliov, V. 2007. Mathematical modeling and optimization of the anaerobic treatment of the winery waste. Rev. Chim. **58**:1134-1141.

[17] Barbuta, M., Diaconescu, R. M. and Harja, M. 2012. Using neural networks for prediction of properties of polymer concrete with fly ash. J. Mat. Civil Eng. **24**:523-528.

[18] Yan, Z., Zheng, R., Yin, F., Shu, G., Zhou, X., Liao,C.L. and Dai, Z.-K. 2010. Multi-objective optimization of decoloration and lactosucrose recovery through artificial neural network and genetic algorithm. J. Food Agric. Enviro. **8**(3&4):121-127.

[19] Harja, M., Buema, G., Sutiman, D. M., Munteanu, C. and Bucur, D. 2012. Low cost adsorbents obtained from ash for copper removal. Korean Journal of Chemical Engineering **29**(12):1735-1744.

[20] Harja, M., Bucur D., Cimpeanu, S. M., Ciocinta, R. C. and Gurita, A. A. 2012. Conversion of ash on zeolites for soil application. Journal of Food, Agriculture & Environment **10**(2):1056-1059.

[21] Jiju, A. 2003. Design of Experiments for Engineers and Scientists. Butterworth-Heinemann, Oxford, 176 p.

[22] Ciobanu, G., Luca, C., Ilisei, S. and Luca, A. C. 2012. New polyurethane - hydroxyapatite composites membranes. Environmental Engineering and Management Journal **11**(2):291-295.

[23] Bezdadea, M., Savin, A. and Ciobanu, G. 1993. Use of glycidyls in the modification of polyurethane membrane structures. Polymer Intern. **32**:407-410.