ULTRASONICALLY ASSISTED ULTRAFILTRATION OF WHEY SOLUTION

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ABSTRACT

The ultrafiltration of whey solutions is a common feature of dairy processes. However, the frequent fouling of ultrafiltration membranes and the subsequent cleaning cycle significantly affects the economics of the process. In this work, we investigated the effect of ultrasonically assisted ultrafiltration. The ultrafiltration of whey solution was investigated in order to determine the main parameters affecting the flux, retention and membrane fouling. The experiments were carried out with an ultrasonic combined laboratory ultrafiltration device, using regenerated cellulose ultrafiltration membranes. The results showed that increasing resistance during filtration is predominantly caused by the concentration polarization, while the participation of membrane fouling in the total resistance is negligible. The ultrasonically assisted ultrafiltration actively reduces the concentration polarization layer resistance. The retention changed slightly with ultrasound power.

PRACTICAL APPLICATIONS

Combination of ultrasound and ultrafiltration processes in dairy industry may enhance the efficiency of whey separation processes during ultrafiltration of why solutions. The given model for describing the filtration mechanism and modified Reynolds number for ultrasonically assisted batch reactor allow the scale up of coupled ultrafiltration process for dairy industry.

INTRODUCTION

Ultrafiltration (UF) is frequently used in the dairy industry for the concentration of whey, which may cause water pollution. The membranes foul during the UF process as the retained particles accumulate on the membrane surface causing a significant reduction in the separation efficiency by decreasing the permeate flux and increasing the pressure drop across the membrane (Muthukumaran et al. 2004, 2005). To reduce the rapid flux decline caused by concentration polarization and membrane fouling, cleaning of the membrane surface is necessary. The typical methods for membrane cleaning which have been used practically include backwashing, gas sparging and chemical cleaning. However, these techniques interrupt the continuous filtration process, leading to a longer processing time and the chemicals sometimes damage the membrane materials and cause secondary pollution. Recently, ultrasound has also been used to improve the permeate flux and

recovery of membrane permeability (Chai et al. 1999; Kyllönen et al. 2005; Latt and Kobayashi 2006). Coupling microfiltration or UF with ultrasonic irradiation has been shown to be effective in reducing fouling problems (Feng et al. 2011). The enhancement of permeate flux by ultrasonication (US) could be improved using higher ultrasonic intensity and lower ultrasonic frequency (Kobayashi et al. 1999, 2003).

The aims of this work were to investigate and to model the combination of UF and US and to determine the membrane filtration parameters and the mechanism of fouling.

MATERIAL AND METHODS

Ultrafiltration of Whey Solutions

Model solutions with whey concentration of 2 wt % were prepared from instant whey powder. The membrane filtration experiments were carried out in a batch stirred cell
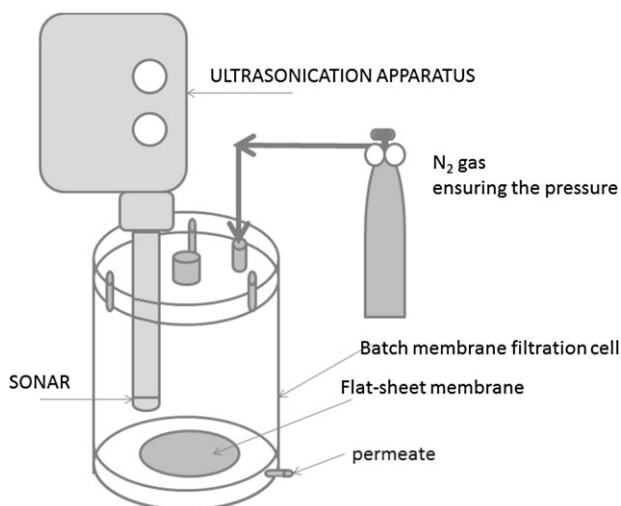
FIG. 1. EXPERIMENTAL DESIGN FOR ULTRASONICALLY ASSISTED ULTRAFILTRATION

FIG. 2. EXPERIMENTAL APPARATUS FOR DETERMINATION OF DIFFUSION COEFFICIENT [DIFFUSION CELL (1), TEST SOLUTION (2), STIRRING BAR (3), A VARIABLE SPEED MAGNETIC STIRRER (4) (ARMFIELD LTD 2011)]

(Merck Millipore, Darmstadt, Germany, Serial N°96) which was built together with an ultrasonic mixer (Fig. 1).

Flat-sheet regenerated cellulose membranes of Amicon (PL series, Merck Millipore, Darmstadt, Germany) with molecular weight cut-offs (MWCO; 3 or 100 kDa) and a membrane effective area of 0.00418 m^2 were used. The capacity of the batch cell is 400 cm^3 and the diameter of the membrane is 0.076 m. Before the UF experiment, the membrane was left immersed in distilled water overnight. The initial feed volume was 200 cm^3 and experiments were carried out at 100 kPa, the pressure was ensured with N$_2$ gas. The measurements were performed in triplicate, in each run a new membrane was used. The sonication experiments were carried out with a US apparatus (UP 100 H Ultrasonic processor, Hielscher Ultrasonics GmbH, Teltow, Germany) with different amplitude A_{US} = 20% and 30% in continuous mode. The maximal power of the ultrasonic apparatus is 100 W, it was operated at 30 kHz.

Diffusion coefficients were determined at 20C with an Armfield CERb apparatus (Armfield Ltd, Ringwood, Great Britain). A specially designed diffusion cell (1) is mounted on top of the stirred vessel and clamped into the desired position using the locking screw. The equipment consists of a variable speed magnetic stirrer (4) and stirring bar (3) for agitation of the test solution (2). The Diffusion apparatus (Fig. 2) uses vertical capillaries 5 mm long with a diameter of 1 mm, which restricts the diffusion to one dimension. The concentration at the lower ends is assumed constant and the concentration at the top ends is effectively zero during the experiment. The diffusion coefficient was determined on the basis if Fick's law by the Eqs. (1) and (2).
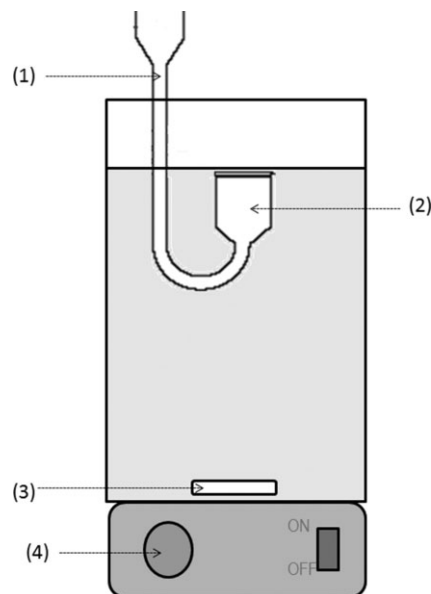
$$\frac{V}{C_M} \cdot \frac{dk}{dt} = -D \frac{d^2\pi}{4} \cdot N \cdot \frac{c_0}{x} \tag{1}$$

$$D = -\frac{4 \cdot V \cdot x}{d^2\pi N c_0 C_M} \frac{dk}{dt} \tag{2}$$

where V is volume of water in outer vessel in liters (L), x is the length of capillaries (cm), d is the diameter of capillaries (cm), N is the number of capillaries (n = 121), c_0 is the concentration of the whey solution, (g/dm^3), C_M is the turbidity change for unit concentration change, (NTU/g/dm^3), $\frac{dk}{dt}$ is the rate of change of turbidity with time, (NTU/s).

Measurements were carried out with 20% whey solution by measuring the change of turbidity in distilled water. The measurements were performed in triplicate, the diffusion coefficient at 20C was found to be 2.75 · 10^{-10} ± 6.48 · 10^{-12} m^2/s.

Viscosity measurements were made with an AND SV-10 vibro-viscometer (A&D Company Ltd, Tokyo, Japan) in a temperature-controlled water bath (Cole-Parmer, Vernon Hills, Illinois, USA) maintained at 20.0 ± 0.1C. The sensor plates operate with a low frequency of 30 Hz and an amplitude of less than 1 mm; the apparatus can measure accuracy of 1% (repeatability) over the range of 0.3–10,000 mPa·s. The density of each solution was measured at 20C with a Densiti 30PX digital density meters (Mettler Toledo, Tokyo, Japan). The turbidity was measured with a Hach Turbidimeter (Hach, Loveland, Colorado, USA).

TABLE 1. FILTRATION LAWS

Fouling mechanism	Filtration law		Constant pressure filtration $J_0 A = \text{constant}$	
Complete pore blocking	$J = J_0 e^{-k_b t}$	(3)	$\ln J = \ln J_0 - k_b \cdot t$	(7)
Gradual pore blocking (standard pore blocking)	$J = J_0 \left(1 + \frac{1}{2} K_S (A \cdot J_0)^{0.5} \cdot t\right)^{-2}$	(4)	$\frac{1}{\sqrt{J}} = \frac{1}{\sqrt{J_0}} + k_s \cdot t$ $k_s = 0.5 K_s A^{0.5}$	(8)
Intermediate filtration	$J = J_0 \cdot (1 + K_i \cdot A \cdot J_0 \cdot t)^{-1}$	(5)	$\frac{1}{J} = \frac{1}{J_0} + k_i \cdot t$ $k_i = K_i A$	(9)
Cake filtration	$J = J_0 \left(1 + 2K_c (A \cdot J_0)^2 \cdot t\right)^{-0.5}$	(6)	$\frac{1}{J^2} = \frac{1}{J_0^2} + k_c \cdot t$ $k_c = 2K_c A^2$	(10)

Theory

The widely used models of fouling mechanisms are cake filtration, intermediate filtration, standard pore blocking and complete pore blocking (Hu and Scott 2008; Banerjee and De 2012) and are formulated in terms of flux per unit of time (Table 1).

In Eqs. (3)–(10), J is the flux, J_0 is the initial flux, the various k are the fouling coefficients and A is a constant. In Eq. (10), A can be expressed as

$$A = \sqrt{\frac{k_c}{2K_c}} \quad (11)$$

The various K terms are the mass transfer coefficients for the associated filtration laws.

In a stirred batch cell, the solute mass transfer coefficient can be calculated from the following correlations (Nicolas et al. 2000; Jadhav et al. 2001)

$$K_c = 0.0443 \frac{D}{b} \cdot Re^{0.75} \cdot Sc^{0.33} \quad \text{if } Re > 3{,}200 \quad (12)$$

where $Re = \frac{\omega \cdot b^2 \cdot \rho}{\eta}$, $Sc = \frac{\eta}{\rho \cdot D}$ and b is the stirring radius, ω is the stirring velocity (in rad/s) and D is the diffusion coefficient (in m²/s).

As this Reynolds number cannot be used in the ultrasonically mixed cell, an equivalent Reynolds number was calculated (Santhanama and Bakhshi 1968) by measuring the equivalent stirring velocity, resulting in the same fluxes as in an ultrasonically mixed UF batch cell. In these cases, the characteristic radius was the radius of the membrane. It was found that the effect of $A_{US} = 20\%$ and 30% ultrasonic mixing is the same as stirring with $n = 270$ min and 660 min and 650 min and 1,000 min rev in the case of 3 and 100 kDa membranes, respectively.

With the assumption of a convection-diffusion mechanism during filtration, the flux is generally expressed by a simplified equation (Schwarze et al. 2010):

$$J = K_c \cdot \ln\left(\frac{c_M - c_P}{c_F - c_P}\right) \quad (13)$$

where c_M is the concentration on the membrane surface, c_P is the permeate concentration, c_F is the feed concentration and J is the flux. The polarization layer concentration was calculated according to the following equation

$$c_M = (c_F - c_P) e^{\frac{J_c}{K_c}} + c_P \quad (14)$$

The membrane resistance was calculated as (Kertész et al. 2012)

$$R_M = \frac{\Delta p}{J_w \eta_w} \quad [m^{-1}] \quad (15)$$

where R_M is the membrane resistance, Δp is the pressure difference between the two sides of the membrane (Pa), J_W is the water flux of the clean membrane and η_W is the viscosity of the water (Pa·s).

The fouling resistance was determined by measuring the water flux through the membrane after the UF and rinsing it with deionized water to remove any particles of residue layer from the surface by subtracting the resistance of the clean membrane:

$$R_F = \frac{\Delta p}{J_{WA} \eta_W} - R_M \quad (16)$$

where J_{WA} is the water flux after the concentration test. The resistance of the polarization layer can be calculated as

$$R_G = \frac{\Delta p}{J_C \eta_{WW}} - R_F - R_M \quad (17)$$

where R_G is the polarization layer resistance (m⁻¹), R_F is the fouling resistance (mainly resulting from the fouled pores) (m⁻¹), J_c is the constant flux at the end of the concentration and η_{ww} is the wastewater viscosity.

RT, the total resistance (m⁻¹), can be evaluated from the steady-state flux using the resistance-in-series model:
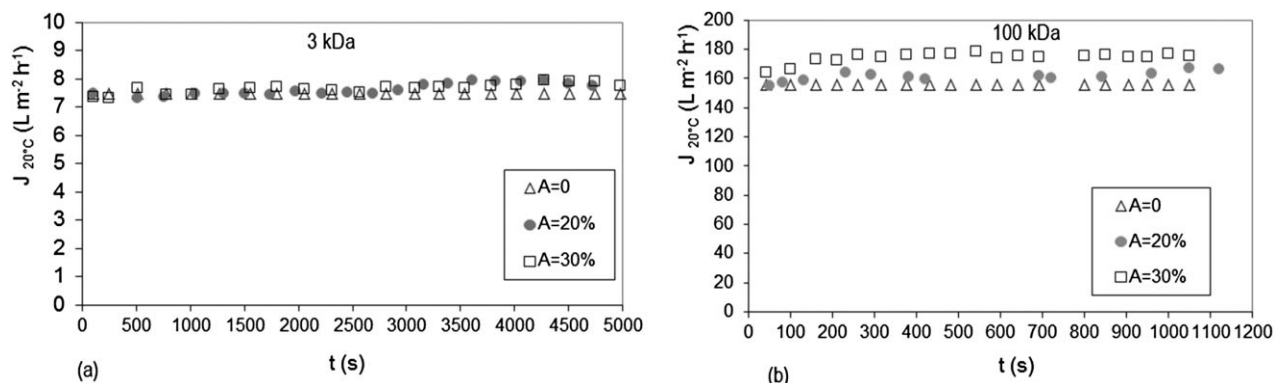
FIG. 3. (A) WATER FLUXES OF REGENERATED CELLULOSE 3 KDA MEMBRANES WITH AND WITHOUT ULTRASONICATION. (B) WATER FLUXES OF REGENERATED CELLULOSE 100 KDA MEMBRANES WITH AND WITHOUT ULTRASONICATION

$$R_T = R_M + R_F + R_P \qquad (18)$$

RESULTS AND DISCUSSION

US Caused Flux Changing

In the first series of experiments, the effects of the ultrasonic process on the clear water flux were examined. As the ultrasonic treatment cause warming of the solution, in order to examine the effect of US, the fluxes were normalized to 20C (Fig. 3).

It was found that the water fluxes through the membrane were not affected by US in case of 3 kDa membrane, but in case of 100 kDa, the water fluxes slightly increased by US. This phenomenon can probably be explained by the fact that acoustic streaming and/or cavitation causes turbulence, which may cause decreased friction of water in membrane pores, resulting in increased water permeability. On the other hand, this phenomenon can only be observed during sonication. The water flux decreased back to the value measured in an unstirred cell when the sonication stopped, indicating that the membrane was not damaged during sonication.

Whey Solution Filtration

In the next series of experiments, whey solution with 2 wt % dry whey content was filtered through membranes with 3 and 100 kDa cut-off weights in unstirred, stirred and ultrasonically mixed batch cells. The linearized filtration laws (Eqs. 7–10) were plotted to measured data and the best correlation was achieved by plotting the cake filtration model. This showed that the UF of whey is gel layer controlled throughout in all cases.

On the basis of Eqs. (11)–(13), the mass transfer coefficients and the fluxes of the cake filtration model were calcu-

lated. As Figs 4 and 5 and Tables 2 and 3 show, the simulated flux data are in good correlation with measured data.

The mass transfer coefficients in stirred or ultrasonically mixed cells show that the mass transfer coefficient increases with increasing ultrasound intensity. The k_c fouling coefficient decreased with membrane pore size, stirring and ultrasonic intensity.

The calculated concentration on the surface of the membrane (c_M) (Tables 2 and 3) increased with membrane pore size: this phenomenon can be explained by the convection-diffusion mechanism of the process. The concentration in the polarization layer is proportional to J/K_c (Eq. 14); because the stabilized fluxes at lower MWCO are very low, the diffusion from the polarization layer to the feed solution
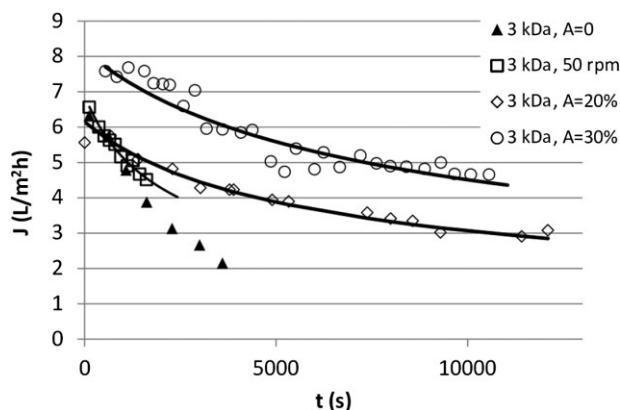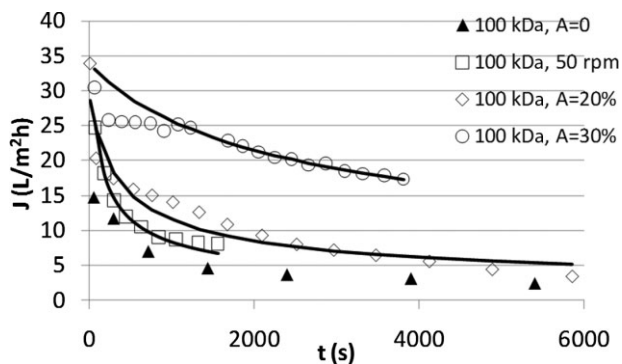

FIG. 4. TYPICAL CURVES OF FLUXES AS A FUNCTION OF TIME DURING ULTRAFILTRATION OF 2% WHEY SOLUTION ON 3 KDA REGENERATED CELLULOSE MEMBRANES WITH AND WITHOUT STIRRING OR ULTRASONICATION. THE CONTINUOUS LINES REPRESENT THE CALCULATED FLUXES ON THE BASIS OF EQ. (10), THE TABLE 2 SHOWS THE CALCULATED FOULING AND MASS TRANSFER COEFFICIENTS
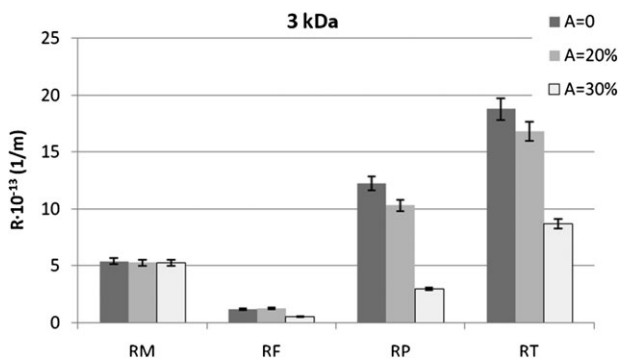
FIG. 5. TYPICAL CURVES OF FLUXES AS A FUNCTION OF TIME DURING ULTRAFILTRATION OF 2% WHEY SOLUTION ON 100 KDA REGENERATED CELLULOSE MEMBRANES WITH AND WITHOUT STIRRING OR ULTRASONICATION. THE CONTINUOUS LINES REPRESENT THE CALCULATED FLUXES ON THE BASIS OF EQ. (10), THE TABLE 3 SHOWS THE CALCULATED FOULING AND MASS TRANSFER COEFFICIENTS
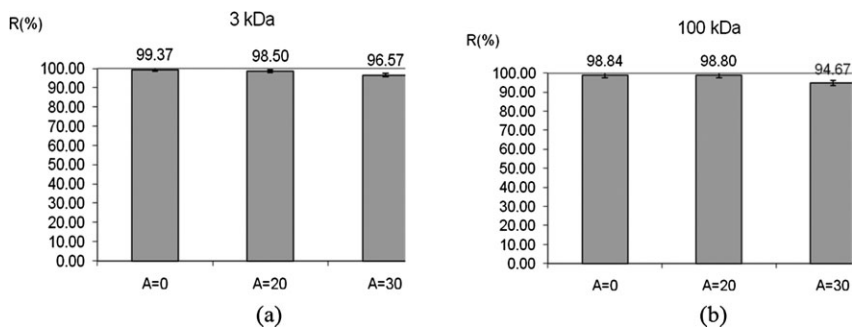

FIG. 7. FILTRATION RESISTANCES DURING ULTRAFILTRATION OF 2 WT % WHEY SOLUTION IN UNSTIRRED AND ULTRASONICALLY MIXED BATCH CELLS USING A 3 KDA ULTRAFILTRATION MEMBRANE

is more expressed, while convection is the major mechanism at higher fluxes. On the other hand, in the case of 100 kDa membranes, the ultrasound decreased the c_M, probably because of decreased retention.

The calculated retention from turbidity decreased with increasing MWCO but it remained above 90% in all cases, as shown in Fig. 6.

Filtration resistances were calculated through the use of Eqs. (15)–(18). The membrane resistances (R_M), fouling resistances (R_F), polarization layer resistances (R_P) and total resistances (R_T) presented in Figs 7 and 8. reveal that the resistance is mainly because of the build-up of a polarization layer and the polarization layer resistance decreases with US intensity, both in the case of 3 and 100 kDa membranes. A comparison of the calculated R_T and the k_c

TABLE 2. CALCULATED MASS TRANSFER COEFFICIENTS AND FOULING COEFFICIENTS IN A STIRRED OR ULTRASONICALLY MIXED BATCH CELL USING 3 KDA ULTRAFILTRATION MEMBRANE

Ultrasonication intensity, W/m²	K_c (m/s)	k_c (m⁴/L⁶/h)	$R\%$	c_M (wt %)
Unstirred cell	–	$5.28 \cdot 10^{-5}$	99.37	–
$A_{US} = 0$, $n = 50$ rpm	$3.97 \cdot 10^{-6}$	$2.05 \cdot 10^{-5}$	–	3.64
$A_{US} = 20\%$	$2.56 \cdot 10^{-5}$	$8.00 \cdot 10^{-6}$	98.50	4.07
$A_{US} = 30\%$	$3.75 \cdot 10^{-5}$	$3.41 \cdot 10^{-6}$	96.57	4.06

TABLE 3. CALCULATED MASS TRANSFER COEFFICIENTS AND FOULING COEFFICIENTS IN A STIRRED OR ULTRASONICALLY MIXED BATCH CELL USING 100 KDA ULTRAFILTRATION MEMBRANE

Ultrasonication intensity, W/m²	K_c (m/s)	(m⁴/L⁶/h)	k_c (m⁴/L⁶/h) 100 kDa	c_M (wt %) 100 kDa
Unstirred cell	–	$5.28 \cdot 10^{-5}$	$3.12 \cdot 10^{-5}$	–
$A_{US} = 0$, $n = 50$ rpm	$3.97 \cdot 10^{-6}$	$2.05 \cdot 10^{-5}$	$1.37 \cdot 10^{-5}$	7.10
$A_{US} = 20\%$	$2.56 \cdot 10^{-5}$	$8.00 \cdot 10^{-6}$	$6.34 \cdot 10^{-6}$	4.29
$A_{US} = 30\%$	$3.75 \cdot 10^{-5}$	$3.41 \cdot 10^{-6}$	$6.43 \cdot 10^{-7}$	4.48

FIG. 6. RETENTION VALUES DURING ULTRAFILTRATION OF 2% WHEY SOLUTION ON 3 KDA (A) AND 100 KDA (B) REGENERATED CELLULOSE MEMBRANES WITH AND WITHOUT ULTRASONICATION
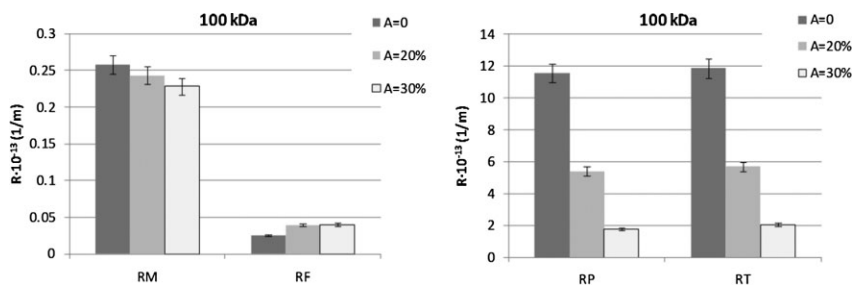
FIG. 8. FILTRATION RESISTANCES DURING ULTRAFILTRATION OF A 2 WT % WHEY SOLUTION IN UNSTIRRED AND ULTRASONICALLY MIXED BATCH CELLS USING A 100 KDA ULTRAFILTRATION MEMBRANE

indicated that these parameters decreased in parallel with increasing ultrasound intensity.

The analysis of variance tests were performed to understand the interactive effect of different operating parameters during experimental runs. Analysis of the effects of the ultrasound intensity and the membrane pore size on retention and fouling coefficient demonstrated that the ultrasound intensity affected both the retention and the membrane fouling coefficient (Figs 8–10).

It was found that in case of lower ultrasound intensity, the change of retention was not significant, but higher US intensity significantly decreased the retention. The fouling coefficient significantly decreased by increasing US intensity even in case of lower US intensity. The results indicated that the pore size of the UF membrane does not affect significantly the retention or the fouling coefficient.

CONCLUSIONS

Following the use of UF coupled with ultrasound with a regenerated cellulose membrane to determine the main fil-

tration parameters of a model whey solution, analysis of the fall in flux with time indicated that the cake formation model gave the best correlation to the experimental data. It was shown that an equivalent Reynolds number can be used for calculating the mass transfer coefficient in a batch cell, modeling the effect of ultrasonic mixing on the flux.

The resistances-in-series model also revealed that the increase in resistance during UF is mainly caused by the concentration polarization, while the membrane fouling in the total resistance is negligible. The results show that the ultrasonication effectively decreased the polarization layer resistance.

The statistical analysis of the result showed that higher performance US significantly decrease the membrane fouling caused by concentration polarization, but application of higher US power decreases the retention also. This means that in the practice the ultrasonic power should be optimized to achieve decreased fouling (thus increased flux) with appropriate retention.
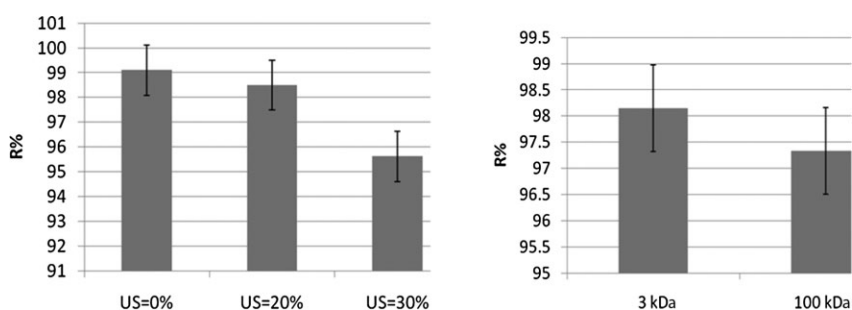

FIG. 9. EFFECT OF ULTRASOUND INTENSITY AND MEMBRANE PORE SIZE ON RETENTION ON THE BASIS OF ANALYSIS OF VARIANCE WITH $P = 0.05$ SIGNIFICANT DIFFERENCES
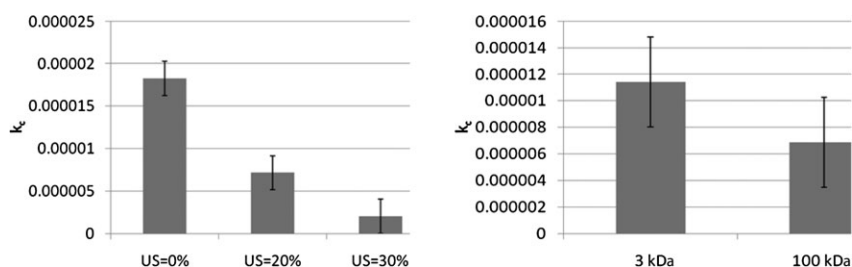

FIG. 10. EFFECT OF ULTRASOUND INTENSITY AND MEMBRANE PORE SIZE ON FOULING COEFFICIENT ON THE BASIS OF ANALYSIS OF VARIANCE WITH $P = 0.05$ SIGNIFICANT DIFFERENCES

NOMENCLATURE

J – flux (L/m²/h)

J_0 – initial flux

J_c – constant flux at the end of the concentration test (L/m²/h)

J_{WA} – water flux after concentration tests (L/m²/h)

J_w – water flux (L/m²/h)

k_c – fouling coefficient

A – experimental constant

A_{US} – expert amplitude of ultrasonic transducer mental constant

K_c – mass transfer coefficient (m/s)

b – stirring radius (m^{-1})

ω – stirring velocity (rad/s)

D – diffusion coefficient (m²/s)

Re – Reynolds number

Sc – Schmidt number

η – dynamic viscosity (Pa·s)

ρ – density (kg/m³)

c_M – concentration on membrane surface (wt %)

c_P – permeate concentration (wt %)

c_F – feed concentration (wt %)

R_M – membrane resistance (m^{-1})

R_F – fouling resistance (m^{-1})

R_G – polarization layer resistance (m^{-1})

R_T – total resistance (m^{-1})

Δp – transmembrane pressure (Pa)

η_w – viscosity of the water (Pa·s)

η_{ww} – viscosity of the wastewater (Pa·s)

ACKNOWLEDGMENTS

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