ABSTRACT: Meat processing industries generate a great amount of wastewater. Because of the remote locations of companies in Northern Finland, they face the problem of low efficiency of traditional biological wastewater purification and the need for a decentralized energy supply system. Membrane separation processes integrated in wastewater purification technology could provide an eco-friendly, and economical solution for the small and medium sized meat processing enterprises (SME’s). The main aim of our research project was to find technology for the treatment of food industry wastewater, which is suitable for producing recyclable process water, and on the other hand, could provide an economical pre-concentration stage before anaerobic digestion (AD).

KEYWORDS: membrane technology, wastewater, food industry

INTRODUCTION

Food processing companies generate a great amount of wastewater because of the processed high water contented raw materials, dehydration processes, and the high water demand of flushing and cleaning procedures. The level of wastewater pollution and the adaptable purification technology is highly dependent on the characteristics of the processed material and the possibility of a separated process waters collection. The purification technologies should be dynamically fitted to the fluctuated wastewater production and to varied composition. The fluctuating wastewater output is a peculiar problem of small meat processor with periodical operating. One of the possible treatment and utilization methods for food industry wastewater is the irrigation onto land, by which the nitrogen and phosphorus content can be utilizable to increase the biomass production but the cation composition of wastewater is not perfectly suited to the demand of plant cultivating. Luo et al. [1] reported that the long term using of meat processing wastewater damages soil quality due to the varying in exchangeable cations of fertilized soil, and this problem makes uncertain the sustainability of the application of effluents for irrigation.

The membrane technology is known as a flexibly adaptable technique for varying capacity and for the diverse chemical composition of processed water [2]. In RO processes, where the fluid is forced through the porous membrane by the pressure difference, the permeate flow rate depends on the permeability of membranes (L), the physical properties of processed fluid (\( \rho, \eta \)) and the pressure gradient (\( dp/dx \)). However, the RO process is additionally affected by diffusion through the membrane (D). The mass flux (N) through the membrane pores can be described by Eq. 1. [3]

\[
N = \frac{\rho L}{\eta} \frac{dp}{dx} - D \frac{dP}{dx}
\]  

Based on the solution-diffusion transport model, the mass flux across the membrane depends on the permeability of the membrane for water (L), the transmembrane pressure (p) and the osmotic pressure difference (\( \pi \)). The osmotic pressure is in large measure affected by the temperature of the fluid (T) and the concentration difference (C) between the two sides of the membrane. For ideal solutions it can be calculated by Eq. 2. using the ideal gas constant (R):
\[ \Delta \pi = \Delta CRT \]  

If the thickness of the membrane (\( l \)), the solubility (\( S \)) and the water partial volume (\( V \)) are known, the water flux can be given by the formula of Wijmans and Baker [4]

\[ J = \frac{DSV}{RTI} (\Delta p - \Delta \pi) \]  

Considering Eq. (1) and Eq. (3), the mass flow through the membrane and the permeate flux are affected by the transmembrane pressure and the temperature. The increasing of the temperature decreases the viscosity of fluids and therefore increases the water and the salt permeability but simultaneously increases the osmotic pressure [5].

The high rejection for organic materials and for detergents makes the RO process suitable for the recycling of food wastewater. Bohdziewicz et al. [6] found that applying RO for meat industrial wastewaters after simultaneous precipitation the organic matter removal efficiency reached the value of 99.8%; the ammonium retention and the total nitrogen retention was 97% and 99%, respectively. In a latter paper of the authors, the performance of RO operation after activated sludge pretreatment was investigated and it was concluded that without chemical precipitation the retention for total nitrogen and total phosphorus was 90% and 97.5%, respectively. The removal of biodegradable materials (expressed by BODs) was just 50%, but despite the lower organic matter removal performance the purified wastewater was found suitable for reuse in the production cycle of the plant [7]. In the study of Vourch et al. [8], the efficiency of a one-stage RO, a combined system of nanofiltration (NF) before RO and a two-stage RO+RO operations for dairy process water treatment was compared and it was concluded that there was no significant difference in the retention for electric conductivity and total organic carbon (TOC) between the RO and the NF+RO system.

With RO operations pure water can be obtained and the UF systems are capable of producing clear and transparent wastewater permeate with reduced bacteria content, but the presence of alive microorganisms in the feed solution can assist in depositing the polarization layer on the membrane surface, facilitating membrane fouling [9]. Kornboonraksa et al. [10] found that in membrane bioreactor the total membrane resistance increased by a large scale and the permeate flux decreased because of the released carbohydrates of piggery wastewater which were deposited easily on the membrane surface due to the microbial degradation.

Under high pressure the diffusion rate is reduced due to the more compact (less porous) deposited layer, and the resistance increases with the enhanced local osmotic pressure. This phenomenon is described as biofilm enhanced osmotic pressure (BEOP) [11-12]. During long-time RO concentration operations the membranes can be considered as non-porous materials for the dissolved solids, flocs and colloids and a so-called surface fouling (external fouling) phenomenon is observed on the feed-side surface of the membrane [13]. During the scale formation the salts of feed can crystallize on the surface of a membrane and additionally the rejected solid can form a cake layer [14]. In the formed cake-layer a complex flow pattern can be observed; moreover, the flow direction may even be the reverse of the pressure gradient because of the inter-connectivity of the neighboring pores [15]. Pore blocking with the adsorption of foulants on the pore wall may occur if the foulants’ size is comparable with something pore sized or smaller [16]. Internal fouling can also be experienced if the structure of the membrane is irreversibly altered due to the extremely high hydrostatic pressure or chemical degradation.

The effect of fouling can be characterized by the flux decline versus operation time, and to examine the flux behavior and the fouling mechanisms the resistance-in-series model can be used in various membrane processes. In the model the relationship between the permeate flux, transmembrane pressure and the total resistance can be described by the series resistance equation

\[ J = \frac{\Delta p}{\eta R_t} \]  

where \( \eta \) is the viscosity of the feed fluid and \( R_t \) is the total resistance.

The \( R_t \) can be defined by the sum of the hydraulic (intrinsic) membrane resistance (\( R_m \)), the polarization layer (external fouling) resistance (\( R_p \)) and the (internal) fouling resistance (\( R_f \)).

\[ R_t = R_m + R_f + R_p \]  

The model is successfully adopted for the examination of flux behavior during the RO concentration of manure [17] or juice [18], separation of oil in water emulsion [19] and for the control of fouling phenomena in several ultrafiltration processes [20-22].

The traditional concept of the membrane water purification systems, when the concentrate is handled as waste stream, can be changed because the concentrated feed streams with high biodegradable organic matter content are utilizable for anaerobic digestion (AD). Furthermore, in the Northern region the temperature sensitive biological wastewater treatment can be replaced with the membrane processes; hereby the time demand of the purification technology can be reduced and the membrane operation can fulfill the requirements of the periodic and fluctuating wastewater product.
According to the above mentioned concept, the dual aim of our work was to concentrate the organic matter content with membrane processes to get a suitable raw material for AD, and on the other hand to produce pure permeate which can be recyclable or reusable. In our work presented in this paper we examined the effect of transmembrane pressure, recirculation flow rate and the temperature of feed on the permeate flux and resistances concentrating meat industrial wastewater. For the calculation of resistances the resistances-in-series model was used to determine the main influential parameters, and to optimize the conditions for RO operation response, surface methodology was applied.

**Materials and Methodology**

**Wastewater sample**

The real wastewater samples originated from a medium-sized meat processing company; the sampling point was after the grease tap. The process water originates from meat processing technology, mainly from the flushing and rinsing of equipment (slicing and packaging machines, smoking chambers). To remove grit and other large-sized solids a cloth filter was used. The characteristic of wastewater is shown in Table 1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mean value</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS (mgL⁻¹)</td>
<td>3210</td>
<td>296</td>
</tr>
<tr>
<td>TOC (mgL⁻¹)</td>
<td>834.1</td>
<td>35.3</td>
</tr>
<tr>
<td>Lipid (mgL⁻¹)</td>
<td>115.1</td>
<td>21.7</td>
</tr>
<tr>
<td>Protein (mgL⁻¹)</td>
<td>379.4</td>
<td>21.2</td>
</tr>
<tr>
<td>pH</td>
<td>6.13</td>
<td>0.23</td>
</tr>
<tr>
<td>Conductivity*</td>
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<td>14.2</td>
</tr>
<tr>
<td>Density*</td>
<td>1005.3</td>
<td>3.2</td>
</tr>
<tr>
<td>Viscosity*</td>
<td>0.877</td>
<td>0.009</td>
</tr>
</tbody>
</table>

* at 30°C

**Analytical measurements**

During the RO and UF operation the total organic carbon (TOC) content, the fat content and the protein content were assayed. TOC content was measured by a Sievers 900 portable TOC analyzer with a membrane conductometric detector (GE Analytical Instruments, U.S.).

The photometrical protein assay was based on the Lowry method [23] using the bovine serum albumin (BSA) standard. The samples were diluted to avoid interference with lipids, ammonium ions and salts and to minimize the effect of the sample on the pH of the reaction mixture.

The lipid content of wastewater samples was determined by partition-gravimetric procedures after extraction according to the Bligh and Dyer method [24]. For the viscosity measurements of wastewater samples a glass capillary viscometer was used.

**Membrane filtration procedure and calculations**

For the pilot-scale filtration test series flow, a B1 module of Paterson Candy International (PCI) was used. The tubular module was equipped by AFC99 polyamide RO (99% nominal retention for NaCl) membranes (ITT PCI Membranes Ltd.). Each 1.2 m long tubular membrane had a 12.5 mm inner diameter, and the total effective membrane area was 0.85 m².

The recirculation flow rate (Q_rec) varies between 600 and 1000 Lh⁻¹. Considering the nominal pressure range of the PCI module and the membranes and, furthermore, based on experimental design, the operating pressure for RO tests was 25-35-45 bar, respectively. The temperature of feed was controlled by a coil-type heat exchanger. In each experiment 60 L wastewater was concentrated to reach a 3.75 value of volume reduction ratio (VRR), calculated by Eq. (6)

\[ VRR = \frac{V_f}{V_f - V_p} \]  

where \( V_f \) is the volume of feed, and \( V_p \) is the volume of permeate.

The retention for total organic carbon (R_TOC), fat (R_fat) and proteins (R_prot) were calculated using the following equation (Eq. 7)

\[ R(\%) = \left( 1 - \frac{c_p}{c_0} \right) \times 100 \]  

where \( c_p \) and \( c_0 \) are the concentration of measured components in the permeate and feed, respectively.

The connection between pressure, permeate flux and the resistance components can be described by Eq. 4. From this general expression the hydraulic resistance of the clean membrane (R_m) can be calculated by the data obtained from the permeate flux (J_w, m⁻²s⁻¹) measurement with deionized water at different transmembrane pressures (Δp, Pa) and from the dynamic viscosity (η_w, Pas).
During the concentration process the solid and dissolved components build up the polarization layer (cake layer), which can be removed by intensive flushing with water. From the pure water flux measured after flushing ($J_f$) and using $R_m$ the fouling resistance can be given by Eq. 9.

$$R_f = \frac{\Delta p}{\eta J_f} - R_m \text{ (m}^{-1})$$

After knowing $R_m$ an $R_f$ and calculating $R_t$ from the permeate flux obtained from the wastewater filtration test the polarization layer resistance can be determined by the combination of Eq. 4. and 5.

### DETERMINATION OF INFLUENTIAL PARAMETERS

To examine the possible interactions between the operating conditions and to optimize the influential parameters for membrane purification, central composite face centered (CCF) experimental design and response surface methodology (RSM) was performed using MODDE 8.0 statistical experimental design software (Umetrics, Sweden). RSM is an adequate method to fit a model by a least squares technique when a combination of independent variables and their interactions affect the desired response [25].

For the modeling and optimization the studied factors were the transmembrane pressure ($p$) of 25 and 45 bar, recirculation flow rate ($Q_{rec}$) of 600 and 1000 Lm$^{-2}$h$^{-1}$ and the temperature of 30° and 40°C (Table 2). The values of pressure and the recirculation flow rate were chosen based on the membrane characteristics and considering the specification of the RO unit and the membrane module. The operating temperatures were varied according to the temperature range of produced industrial process water.

The selected responses were the average permeates flux ($J$), the organic matter retention ($R_{TOC}$), the total resistance ($R_t$) and the polarization layer resistance ($R_p$). To evaluate the reproducibility of the fitted model, five center points were used in the experimental design ($Q_{rec}=800$ Lh$^{-1}$, $p = 35$bar at a temperature of 35°C). In order to reduce the systematic error, the runs of the experiments were randomized.

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>$Q_{rec}$ (Lh$^{-1}$)</th>
<th>$p$ (bar)</th>
<th>Temp. (°C)</th>
<th>$J_{perm}$ (Lm$^{-2}$h$^{-1}$)</th>
<th>$R_t \times 10^{14}$ (m$^{-1}$)</th>
<th>$R_p \times 10^{14}$ (m$^{-1}$)</th>
<th>$R_{TOC}$ (%)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>600</td>
<td>25</td>
<td>30</td>
<td>54.35</td>
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<td>0.716</td>
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</tr>
<tr>
<td>2</td>
<td>1000</td>
<td>25</td>
<td>30</td>
<td>55.04</td>
<td>2.556</td>
<td>0.698</td>
<td>99.20</td>
</tr>
<tr>
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<td>600</td>
<td>45</td>
<td>30</td>
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<td>3.211</td>
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</tr>
<tr>
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<td>40</td>
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<tr>
<td>13</td>
<td>800</td>
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<td>14</td>
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<td>3.024</td>
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<td>99.05</td>
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<td>70.93</td>
<td>2.880</td>
<td>0.925</td>
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<td>19</td>
<td>800</td>
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<td>35</td>
<td>70.96</td>
<td>2.879</td>
<td>0.921</td>
<td>99.17</td>
</tr>
</tbody>
</table>

Retention for TOC, lipids and proteins has not changed significantly with the varying of factors, because the retention of AFC99 membrane for different components is higher than 97%. The calculated value of $R_m$ for the AFC99 membrane was $1.409 \times 10^{14}$ m$^{-1}$. In our case the range of $R_f$ was obtained from $8.761 \times 10^{13}$ to $1.034 \times 10^{14}$ m$^{-1}$ but the change was not significant at the 95% confidence interval; therefore, the fouling resistant cannot be used as a response parameter.

To determine which factors have important effects on the response, one factor is varied while the others are kept at the average value. Fig. 1 shows the effects of single parameters and their interactions on the permeate flux ($J_p$), total resistance ($R_t$) and polarization layer resistance ($R_p$). Our results show that mainly the pressure and the temperature have an effect on the permeate flux, $R_t$ and $R_p$; furthermore, a smaller influence of $Q_{rec}$ was obtained on permeate flux and total resistance. The other factors and the interactions between them have just a negligible effect on response parameters. The significant effect of temperature on flux can be explained by studying Eq. 1 and Eq. 3. With temperature increasing, the permeate diffusivity through the membrane increases and the viscosity decreases simultaneously, which has a positive effect on permeate flux.
Effects for $J_p$

Effects for $R_t$

Effects for $R_p$

Figure 1. Effects of factors and interactions on the permeate flux (a), total resistance (b) and polarization layer resistance (c).

Our calculation, based on the resistance in series model, showed that the hydraulic resistance of the membrane ($R_m$) was in all cases higher than the fouling resistance ($R_f$) and the ratio of $R_m$ to $R_f$ was from 39.3 to 51.9%, depending on the experimental conditions. The main part of $R_m$ in $R_t$ can be explained by the composition of the wastewater, and the low amount of organic matter could not form a thick polarization layer in the turbulent feed flow; furthermore, the concentration of low molecular size compounds was not high enough to significantly increase the internal fouling.

**MODELING AND OPTIMIZATION OF RO PROCESS**

During the refinement the non-significant terms were removed. Since the value of $R_t$ contains the $R_p$, the change of the two parameters are not independent; therefore, $R_p$ was removed from the responses to obtain a correct statistical model. After refinement a quadratic model was refitted with multiple linear regressions (MLR). The mathematical relationship between the independent variables of pressure ($p$, bar), recirculation flow rate ($Q_{rec}$, L/h), temperature ($t$, °C) and the response function for permeate flux ($J_p$, L/m²h⁻¹) and total resistance ($R_t$, m⁻¹) are presented by Eq. (10) and (11), respectively.

\[
J_p = 71.0214 + 8.25p + 0.5659Q_{rec} + 2.711t - 4.989p^2 
\]

\[
R_t = 2.9009 \times 10^{14} + 2.986 \times 10^{13}p - 3.659 \times 10^{12}Q_{rec} - 3.95 \times 10^{12}t + 3.107 \times 10^{10}p^2
\]

The response function predictions were in good agreement with the experimental data; the $R^2$ for $J_p$, and $R_t$ was 0.996 and 0.994, respectively (Fig. 2).

In addition, the goodness of fit ($Q^2$) for $J_p$ and $R_t$ was 0.991 and 0.988, which indicates good predictive power of the models. The reproducibility was over 99.9% and the standard deviations of the fitted models were higher than the standard deviation of the residuals ($R^2_{adj} > 0.98$ in both cases).

Figure 2. Observed versus predicted values for permeate flux and total resistance.
To analyze the effects of factors the characteristic contour plots are shown in Fig. 3. As Fig. 3 shows, the permeate flux is strongly dependent on the pressure and temperature. The difference between operating pressure and osmotic pressure decreased during the concentration and therefore there was a non-linear correlation between the permeate flux and the pressure.

In addition, during the concentration process the deposited cake layer caused a slower diffusion (via longer diffusion path and lower diffusivity) and a higher hydraulic resistance. The temperature increasing caused the viscosity to decrease, which predicted higher permeate flux (Eq. 4), but the higher temperature is also expressed in the higher osmotic pressure, decreasing the driving force of the RO process ($\Delta p - \Delta \pi$). Considering this phenomenon, the relationship between the temperature and permeate flux is also non-linear.

Figure 3. The combined effect of temperature and pressure on permeate flux (a) and $r_t$ total resistance (b)

In our case the highest permeate fluxes can be reach by applying pressure over 37 bar and a temperature over 36.5°C but to achieve the best permeate flux the recirculation flow rate can be set at a value over 750Lh$^{-1}$ (Re number can be over 20,000). In this region the retention for TOC and protein was higher than 97% and 99%, respectively. On the other hand, the pressure increasing from 25 to 45 bar increased the total resistance by approximately 17% but this effect can be reduced by the application of elevated temperature and/or higher recirculation flow rate.

The antagonist effect of the pressure increasing total resistance and permeate flux can be explained by the altering of the structure of the polarization layer. Under high pressure, the formed cake layer has become less porous, which can increase the hydraulic resistance of the layer [26]. Although Hoek et al. [14] reported that the fouling can improve the selectivity of the membrane; this establishment is acceptable just for removal of larger sized molecules via size-exclusion mechanisms.

Using the refitted model, based on the date obtained from the response surface analysis, the optimal condition of the RO process of meat industrial wastewater was determined at a transmembrane pressure of 38.5 bar and a recirculation flow rate of 1000 Lh$^{-1}$ at 40°C.

**CONCLUSION**

The RO concentration of meat industrial wastewater was carried out in a pilot-scale filtration unit equipped by AFC99 polyamide membranes. For the experimental design and optimization, MODDE 8.0 software was used, investigating the effects of the operation pressure, temperature and recirculation flow rate on the organic matter retention, permeate flux and the resistances calculated from the resistances in the series model.

Our results show that the investigated parameters did not significantly affect the retention but the permeate flux and the total resistance are suitable for the response parameter of modeling. Based on our results, the increasing pressure positively affects the permeate flux but at elevated pressure the total resistance increases as well. The increasing of the temperature and the recirculation flow rate could enhance the permeate flux and decrease the total resistance. The fitted quadratic model was significant at the 95% confidence interval and showed good predictive power as well as high reproducibility.

The optimal conditions for RO concentration of meat industrial wastewater were determined at an operating pressure of 38.5 bar, recirculation flow rate of 1000 Lh$^{-1}$ and temperature of 40°C. The TOC content and the conductivity of permeate was lower than 5 ppm and 20 μScm$^{-1}$, respectively, which allows for the recycling and reusing, for example, in cleaning, in the flushing process or for...
cooling water. The average TS content of RO concentrate was higher than 9% with a TOC content of 2.8 gL⁻¹, protein content of 1.2 gL⁻¹ and fat content of 0.35 gL⁻¹.

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