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EFFECTS OF OZONATION ON THE ULTRAFILTRATION OF MEAT INDUSTRY WASTEWATER

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Abstract

Water is currently becoming a strategically important material, and the importance of water and wastewater treatment technologies is therefore increasing. Wastewater from the food industry has many special features originating from its high organic matter content. Meat industry wastewater additionally has a high fat content. We investigated the effects of ultrafiltration and ozonation, individually and in combination, for the treatment of meat industrial wastewater. Ozone gas was generated from oxygen with an Ozomatic Modular 4 ozone generator (Wedeco Ltd., Germany), and filtration was carried out with a micellar-enhanced ultrafiltration (MEUF) apparatus, through a flat membrane with a surface area of 40 cm^2. The experimental data revealed that pre-ozonation of the wastewater affected ultrafiltration. The flux was higher and persisted longer than in the case of non-ozonated samples. The chemical oxygen demand was decreased by ozonation treatment. The duration of ozonation and the subsequent ultrafiltration exhibited a very interesting relationship. The most important effect of ozonation was observed on membrane fouling. The fouling mechanism was modelled, and the rate constants of flux decline (k_1) and deposit removal from the membrane (k_2) were calculated. The effect of the Reynolds number was also shown. The aim of our work was to study the industrial effects of combined cleaning techniques, i.e. ozonation on meat processing wastewater. The optimum ozonation time was 2 to 10 min before ultrafiltration with a PES membrane with a cut-off of 5 kDa.

Key words: fouling, modelling, ozonation, ultrafiltration

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1. Introduction

The food industry is one of the most important consumers of water in Hungary. The wastewater from the food industry is rich in organic components, and therefore has very high biochemical and chemical oxygen demands, a high fat content and high concentrations of dry residue, sediment and total suspended matter. Meat-processing plants use around 62 Mm^3 of water per year (Beszédes et al., 2017; Sroka et al., 2004). The preferred wastewater treatment technologies are those that supply water that can be discharged into receiving water bodies or reused for industrial purposes.

The tightening of environmental regulations (http://www.eugris.info/FurtherDescription.asp?Ca=1&Cy=4&DocID=B&DocTitle=Policy_and_regulatory&T=Hungary&e=365) and the decrease in the cost of membrane technology (Schafer et al., 2001; http://www.amtaorg.com/wp-content/uploads/6_MembraneDesalinationCosts.pdf) have resulted in pressure-driven membrane techniques that are ever more applicable in wastewater treatment (Seres et al., 2016).

Ultrafiltration is one of the most applicable methods among the membrane separation techniques for these purposes. The cut-off interval of ultrafiltration membranes (MWCO 100 kDa – 5 kDa) has made this method popular in tasks where high molecular weight macromolecules must be separated.

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Nowadays, this technique is used for the recovery of valuable compounds, i.e. from pectin-containing solutions and phenol-containing beverages (Galanakis et al., 2010) as well as for the separation of β-glucan from oat mill waste (Patsioura et al., 2011) or phenolic compounds from winery sludge (Galanakis et al., 2013). However, membrane fouling is an important phenomenon that limits the applicability of membrane techniques for wastewater treatment. Membrane fouling is characterised by a decline in flux, due to the deposition and accumulation of materials on the membrane surface or within the pore structure (Cheryan, 1998). Flux decline can be expressed by the fouling coefficient, which is the power of the flux equation (Kertész et al., 2011; László et al., 2009).

There are various well-known chemical and mechanical methods by which to decrease fouling, and different forms of pretreatment have been applied successfully for this purpose (László and Hodúr, 2007; Moussavi and Khosravi 2017; Rehman, 2012). Ozonation has been used as a pretreatment before membrane separation, not only for wastewater but also for potable water (Yüksel, 2004). Ozone is a strong oxidant and a potent disinfecting agent. Ozonation may lower the chemical oxygen demand (COD) of wastewaters. The efficiency of ozone as a pre- and post-treatment in upward-flow anaerobic sludge blanket treatment has been investigated in connection with canning and winery wastewaters, and COD reductions have been achieved (Sigge et al., 2005). Different kinds of pre-treatments, e.g. ozonation, can be applied to influence the transmembrane flux, reversible and irreversible fouling, and permeate quality (Masse et al., 2007).

In the work reported here, the effects of pre-ozonation on the ultrafiltration of meat industrial wastewater were investigated. Certain coefficients and factors were calculated to characterise the extent of these effects. A modelling system was used for the calculation of the rate constant of the flux decline and the rate constant of the removal of the deposit from the membrane, as described earlier (Makardij et al., 2002).

In mathematical form, these may be expressed as follows (Eq. 1):

$$-\frac{dJ}{dt} = k_1 c_0 J - k_2 Re^n \qquad (1)$$

where c_0 is the feed concentration (kg m^{-3}), k_1 is the rate constant of the flux decline (m^3 kg^{-1} s^{-1}), k_2 is the rate constant of the removal of the deposit from the membrane, and Re is the Reynolds number, (i.e. $Re = \frac{d \cdot v \cdot \rho}{\eta}$), ρ is the retentate density (kg m^{-3}), v is the retentate cross-flow velocity (m s^{-1}), η is the viscosity of the retentate (Pa s) and d is the diameter or the hydraulic mean diameter of the channel through which the feed fluid flows. The power n needs to be determined experimentally.

Eq. (1) defines the local permeate flux at any position in the membrane. If the permeate flux is small compared to the total flow, then both c_0 and the Reynolds number may be assumed to be equal to their values at the feed entry point (Makardij et al., 2002).

2. Materials and methods

The wastewater originated from a Hungarian meat-processing plant which functions both as a slaughterhouse and as a meat processing plant. The characteristics of the processed wastewater are provided in Table 1.

Table 1. Characteristics of the sample wastewater

	Conductivity (μS)	***Turbidity (NTU)***	***COD (mg dm^{-3})***	***pH***
Feed	1001	53	955	8.26

Separation was carried out with a stirred ultrafiltration batch device with a capacity of 400 cm^3, equipped with a 40 cm^2 polyether sulphone (PES) membrane with a cut-off value of 5 kD. During filtration, the sample was mixed continuously with a magnetic stirrer (500 rpm).

Both the selectivity and the efficiency are shown by the retention (R) (Eq. 2):

$$R = \left(1 - \frac{c}{c_0}\right) \cdot 100\,(\%) \qquad (2)$$

where c is the concentration of the permeate (%) or (mg dm^{-3}) and the c_0 is the concentration of the feed (%) or (mg dm^{-3}).

The permeate flux can be described as a function of time (Eq. 3):

$$J = J_0 t^{-K} \qquad (3)$$

where J_0 is the initial permeate flux (dm^3 m^{-2} h^{-1}), t is the filtration time (h) and K is the fouling index (Kertész et al., 2011).

For the ozonation process, an ozone generator was used (Ozomatic Modular 4, Wedeco Ltd., Gemany), operating via a silent electric discharge. The ozone-containing gas was bubbled continuously through a 6 dm^3 batch reactor during the treatment. The treatment time was 2, 5 or 10 min; the gas flow rate was 3 dm^3 min^{-1}.

The COD was determined in test tubes (Lovibond, Germany) with an ET 108 digester (Lovibond Germany) and a PC Checkit photometer (Lovibond, Germany). Turbidity was measured by a Nepholometer measuring the relative amount of light able to pass through the solution, and is reported as NTU (Nepholometric Turbidity Units). An HQ440D digital multimeter (Hach Lange) was used to measure conductivity and pH.

Scanning electron microscopy was performed with a Hitachi S-4700 field emission scanning electron microscope operated at an acceleration voltage of 10 kV in ultra-high resolution mode. To analyze the gel layer, after ozonation and without ozone pre-

treatment, 500x top magnification pictures were taken and compared.

To determine the rate constants characterizing the ultrafiltration process itself, we followed the method of Makardij et al. (2002). Makardij developed a new modelling method with which to characterize fouling in cases of microfiltration and ultrafiltration. This modelling system generates two rate constants characterizing the membrane process itself: k_1 – the rate constant for flux decline ($m^3\ kg^{-1}\ s^{-1}$) and k_2 – the rate constant for the removal of the deposit from the membrane. Using Eq. (1) and specifying the initial conditions as follows (Eqs. 4-5):

$$t = 0 \quad J = J_0 \quad and \quad k_1 c_0 J \quad » \quad k_2 Re_n \tag{4}$$

k_1 may be calculated from the initial flux by dropping the second term of the right-hand side of Eq. (1).

$$k_1 = \frac{\frac{dJ}{dt}}{c_0 J_0} \tag{5}$$

Approaching a steady state (6) gives Eq. (7):

$$\frac{dJ}{dt} \Rightarrow 0 \tag{6}$$

and thus

$$k_2 \approx k_1 \left(\frac{c_0 J}{Re^n} \right)_{equilibrium} \tag{7}$$

Eq. (7) can be used to calculate the values of k_1 from the measurement of the initial flux decline, i.e. from the integral form (Eq. 8) of simplified Eq. (1).

$$-\frac{dJ}{dt} = a(J - b) \tag{8}$$

Where

$$a = k_1 c_0 \tag{9}$$

and

$$b = \frac{k_2}{k_1 c_0} \mathrm{Re}^n \tag{10}$$

The Reynolds number in the case of mixing was calculated as follows (Eq. 11):

$$Re_{mix} = \frac{d^2 n \rho}{\eta} \tag{11}$$

where: ρ is the retentate density (kg m^{-3}), n is the rotation rate of the stirrer (s^{-1}), η is the viscosity of the retentate (Pas) and d is the diameter of the stirrer (m).

Integrating Eq. (8) from t=0 to t>0 gives Eq. (12):

$$J = b + (J_0 - b)e^{-at} \tag{12}$$

3. Results and discussions

Samples of the meat industrial wastewater were treated in a batch ozone-reactor for 2, 5 or 10 min and ultrafiltered with a UF device, and the permeate flux values were plotted vs. time. A power equation could be fitted to the points. The main data of the function analysis are shown in Table 2.

Table 2. The initial fluxes and fouling indices at different ozonation times

	Ozonation time (min)			
	0	***2***	***5***	***10***
Initial flux J_0 ($dm^3m^2h^{-1}$)	145.56	62.25	63.85	42.96
Fouling index K	-0.1986	-0.1244	-0.1318	-0.0858

The initial permeate flux of the untreated material was higher than those of the treated samples, but the decreasing tendency reflects the fouling ability, expressed by the fouling index K. The value of K revealed that the non-ozonated wastewater easily fouled the membrane. The ozonated samples had less negative values of K, which means that ozone caused the degradation of large molecules which were then able to pass through the membrane; there was a smaller chance of the development of such an extensive resistance layer on the surface of the membrane. The same results were found by László et al. (2009) in their investigation into the nanofiltration of ozonated dairy wastewater.

Fig. 1 depicts the relative fluxes, J/J_0, vs. time. The J/J_0 values were highest for samples ozonated for 10 min, and lowest for the untreated samples, indicating the improvement in flux due to ozonation.

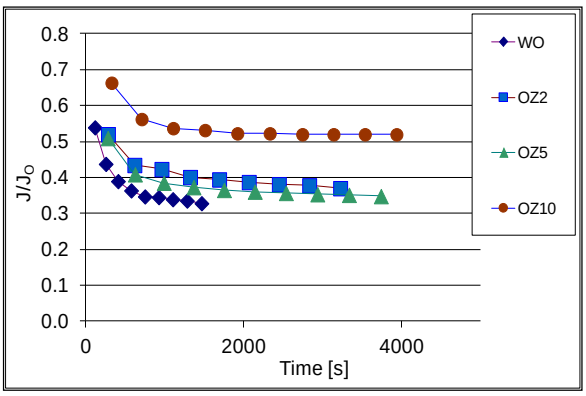


Fig. 1. Relative fluxes as a function of time (WO – without ozonation, OZ2 – ozonation for 2 min, OZ5 – ozonation for 5 min, OZ10 – ozonation for 10 min)

Despite the beneficial effect of a longer ozonation period on the fouling indices in Fig. 1 and

Table 2, the retention data in Fig. 2 point to a beneficial effect of a shorter ozonation process. The retention values were calculated from the concentrations relating to the chemical oxygen demand using Eq. (2).

The relationship between the ozonation time and the retention is inversely linear. A shorter ozonation process mainly caused flocculation, as reported by Bonneville et al. (2001), and the bigger flocculant aggregates could not pass through the membrane, thereby increasing the membrane layer resistance. These samples gave smaller flux values than predicted. A similar flocculation and aggregation mechanism was found by Liang et al. (2014) as well. However, a longer process allows sufficient time for degradation, so the resulting smaller molecules were more likely to reach the permeate side, thereby increasing the flux values and decreasing retention. This flux increase was detected by Fan et al. (2014), and the control of membrane fouling with ozone was also helpful.

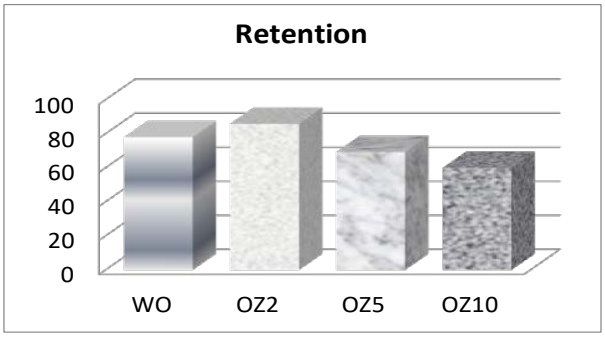


Fig. 2. Retention values calculated via COD % for different ozone-treated samples (WO – without ozonation, OZ2 – ozonation for 2 min, OZ5 – ozonation for 5 min, OZ10 – ozonation for 10 min)

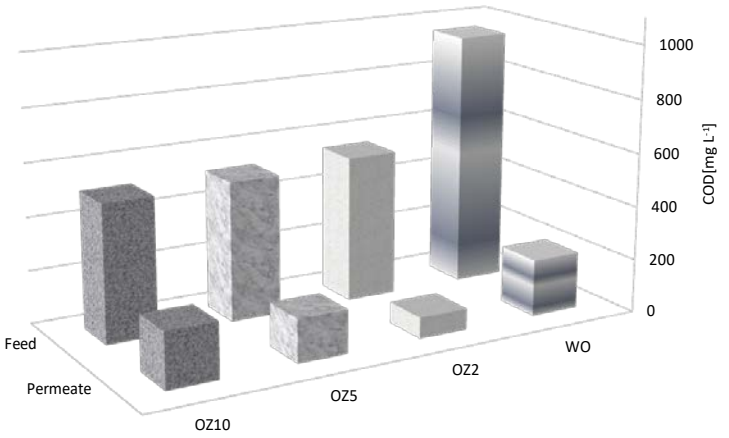
This was confirmed by the results in Fig. 3, which illustrate the COD data of the different samples.

It is clear that the permeate phases from the ozonated samples had lower COD values than that of the untreated sample, and there was an inverse linear relationship between the duration of ozonation and the COD. A very similar tendency was demonstrated by Kiss et al. (2013) after the ozonation of phenol-containing thermal water.

The results show that the COD values of the permeate phases after ozonation for 2 or 5 min met the requirements of the Regulations of the Ministry of Hungarian Environmental Protection (150 mg dm^{-3}). Ozonation for 10 min gave a slightly higher COD, probably due to the digestive effect of ozone on oxidisable organic compounds or particles in the sample. The breakdown effect of the ozonation was shown by Wu et al. (2012) using bamboo industry wastewater; the chromatogram from gel permeation chromatography revealed that ozonation resulted in the breakdown of high molecular weight compounds into lower molecular weight components but could not completely mineralise the organic matter.

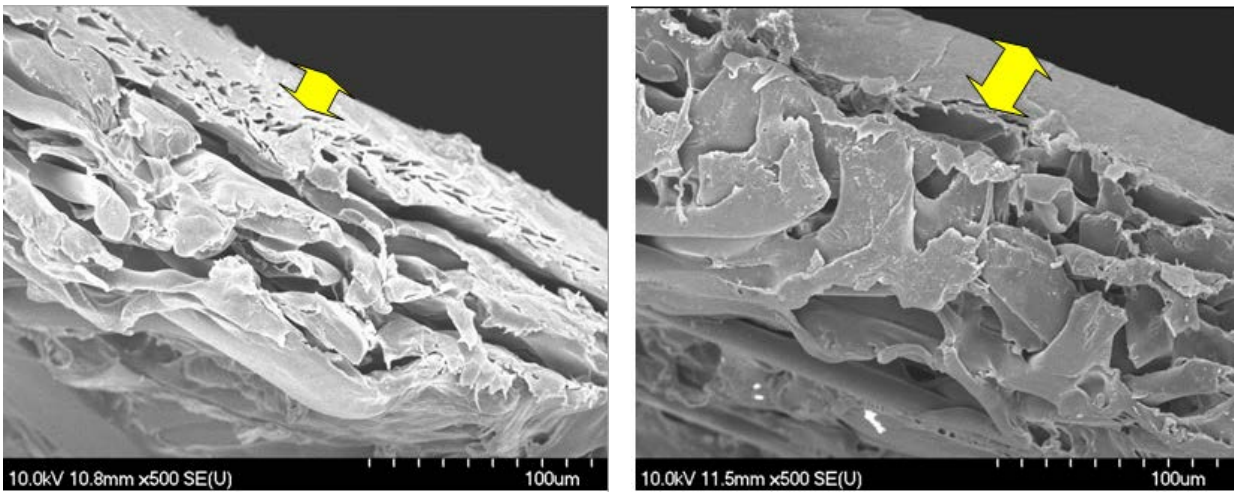
Makardij et al. (2002) developed a new modelling method with which to characterise fouling in cases of microfiltration and ultrafiltration. This modelling system generates two rate constants characterising the membrane process itself: k_1 - the rate constant for flux decline ($m^3\,kg^{-1}\,s^{-1}$) and k_2 - the rate constant for the removal of the deposit from the membrane. The values are presented in Table 3.

The data show that the k_1 values were larger than the k_2 values, which demonstrates that the fouling mechanism has a stronger effect on membrane separation than that of deposit removal. However, there were differences between the samples. The k_2 constants reveal that the ability to remove the deposit was one order of magnitude higher in the case of the samples ozonated for 10 min than for those ozonated for 2 min or 5 min. The k_1 values increased exponentially ($y = 2.3\ e^{0.17x}$, $R^2 = 0.9481$) with the duration of ozonation.



	Permeate	Feed
WO	210	955
OZ2	77	548
OZ5	160	522
OZ10	205	513

Fig. 3. The COD data of non-ozonated or pre-ozonated and ultrafiltered samples (WO – without ozonation, OZ2 – ozonation for 2 min, OZ5 – ozonation for 5 min, OZ10 – ozonation 10 min)



(a) (b)

Fig. 4. Cross-section of the ultrafiltration membrane after separation of (a) a sample ozonated for 10 min (OZ10) and (b) a non-ozonated sample (WO). SEM photos, 500x magnification

The developed gel layer and the cross-section of the separation and supported layer of the membrane are presented in Fig. 4. The arrows show the thickness of the gel layer deposited after ultrafiltration of a 10 min ozonated sample and an untreated sample. The layer on the membrane surface following 10 min of ozonation was thinner than the layer from the sample without ozonation. The long period of ozonation had a breaking effect, so the smaller molecular weight components could enter the pores of membrane, but only a small part could pass through the membrane. Some portion became stuck inside the membrane, which is expressed by the value of k_1.

Table 3. Rate constants of flux decline (k_1) and removal of the deposit (k_2)

	WO3	***OZ2***	***OZ5***	***OZ10***
k_1	2.67E-05	3.61E-05	4.46E-05	1.55E-04
k_2	1.02E-11	6.56E-12	7.95E-12	2.68E-11

4. Conclusions

The results of this study show that ozonation pretreatment for at least 10 min degrades large organic molecules into smaller fragments. This size reduction results in a higher relative flux and a smaller fouling index. These values predict longer operating/management options.

The findings demonstrate that ultrafiltration with a cut-off of 5 kD following ozonation for 2 or 5 min is a satisfactory purification method for such wastewater, since the COD of the permeate met the requirements of the Regulations of the Hungarian Ministry of Environmental Protection (150 mg dm^{-3}). A longer period of ozonation led to a slightly higher COD, but also a higher permeate flux. Calculations based on the Makardij model show that the fouling mechanism has a stronger effect on membrane separation than deposit removal. Further experimental studies would be useful to establish the optimum duration of ozonation in relation to COD.

Nomenclature

k_1 – rate constant of the flux decline ($m^3\,kg^{-1}\,s^{-1}$),
k_2 – rate constant of the deposit removal from the membrane
c_0 – feed concentration ($kg\,m^{-3}$),
Re – Reynolds number, (-)
ρ – density ($kg\,m^{-3}$),
v – cross-flow velocity ($m\,s^{-1}$),
η – viscosity (Pas),
d – diameter or the hydraulic mean diameter of the channel, through which the feed fluid flows (m),
J – flux ($dm^3m^{-2}h^{-1}$)
J_0 – initial flux ($dm^3m^{-2}h^{-1}$)
k – fouling index (-)
t – time
COD – chemical oxygen demand ($mgdm^{-3}$)
WO – sample without ozonation
$OZ2$ – sample ozonated for 2 min
$OZ5$ – sample ozonated for 5 min
$OZ10$ – sample ozonated for 10 min

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