DOCTORAL (PhD) THESES

Summary

INVESTIGATION OF THE PURIFICATION OF DAIRY WASTEWATER USING ADVANCED OXIDATION PROCESSES AND MEMBRANE FILTERATION

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Mosonmagyaróvár
2022

Contents

1. Objective

The basic goal of my research work is to increase the efficiency of membrane filtration with chemical methods connected to membrane separation, primarily with advanced oxidation processes in the case of real and model dairy wastewater.

During the work, I investigate what chemical transformations take place in the material to be filtered during the oxidation pretreatment, how changes between the material and the membrane, and how the process and process parameters of membrane filtration can be optimized with this knowledge. The expected results of the research work form the basis for the development of novel wastewater treatment systems that can also be used in practice, which can be operated efficiently, with minimal waste generation, with good efficiency and, last but not least, flexibly.

My goal is to develop a combined wastewater treatment technology, or at least a part of it, that can be operated sustainably and can be integrated into the circular economy.

2. Experimental material and method

2.1. Preparation of model wastewaters

During my experimental work, I always dissolved the components of the model wastewater in a volume of 600 ml of distilled water and used mixing during all dissolution, pH adjustment, pH measurement, ionic strength measurement and pipetting. I used a magnetic stirrer for mixing. Its rotation speed during filtration, for pH measurement, conductivity measurement and sampling for COD determination was 350 rpm. When dissolving the natrium-caseinate, I used 650-800 rpm for 5-8 minutes.

The concentration of the solution for lactose was 1.53 g/L. For the sake of comparability, I also used a lactose concentration of 1.53 g/L in the other model solutions that did not contain only lactose.

I chose the concentration of the solution containing casein or lactose and casein as 1.12 g/L for casein, and for this 600 ml of distilled water I measured 0.67 g of the protein. I added the protein in small portions to the 600 ml of distilled water with continuous stirring to reduce the clumping of the casein. The pH of the solution was adjusted to 9 with 1 M NaOH. The solution was then homogenized with ultrasound *(Hielscher UP200S)* for 10 minutes. After that, I let the solution heated to about 45 ^{o}C cool down to room temperature before I started the filtration. It should be noted that the solutions containing natrium-caseinate alone, as well as lactose, contain minimal casein, approx. 2%, they have a lower concentration due to the natrium content, since 0.67 g of mass was also measured for 600 ml of distilled water.

In the case of non-pretreated solutions, I measured the pH, conductivity, and turbidity of the solution to be filtered, the concentrate, and the permeate, and I took a sample into the test tubes to determine its chemical oxygen demand. After mixing, but even before the pretreatment, I measured the above-mentioned parameters for the solutions with Fenton-treatment, and took a sample of it in test tubes for the purpose of determining the chemical oxygen demand.

Furthermore, in order to form a transition between the simple models containing only casein and lactose and real wastewaters, I prepared model solutions with a concentration of 0.3% by weight from milk powder *(Milkquick, Instantpack Kft., Hungary*), which contain 0.32 g/g of protein, 0, They contained 05 g/g fat and 0.5 g/g lactose. I used this model to investigate the relationships between oxidation capacity and fluxes.
The characteristics of the model wastewaters are listed in Table 1.

Table 1. Characteristics of the model wastewater

	COD (mg/L)	***Turbidity (NTU)***	***pH***	***Conductivity (µS/cm)***
natrium-caseinate model wastewater	~1200	~15	~7	~400
natrium-caseinate+lactose model wastewater	~2400	~20	~7	~700

2.2. Real dairy wastewaters

After the basic experiments were carried out with the model dairy wastewater - and I examined the operation and changes of the filtration mechanism - I replaced the model with real dairy wastewater, which is produced at the end of real production technological processes as a by-product to be treated, which represents additional problems and costs for the companies. In the course of my work, I also performed series of experiments with two different dairy wastewaters.

2.2.1. General dairy raw wastewater

One of the dairy wastewaters comes from a general processing plant where milk, milk drinks, fermented products, curds, creams and milk desserts are produced. The waste water was raw waste water flowing directly from the production technology, before the cleaning processes. In accordance with the official regulations, the production units characterized their wastewater as follows (Table 2):

Table 2. Characteristics of general dairy wastewater

	COD (mg/L)	***Turbidity (NTU)***	***pH***	***Conductivity (µS/cm)***
Raw wastewater	~3200	~200–250	5.7–6.4	~1200–1400

2.2.2. Mozzarella cheese factory raw wastewater

The other wastewater comes from the production unit of a mozzarella product manufacturer, where different types of mozzarellas, mascarpone and ricotta are produced. The wastewater was raw wastewater flowing directly from the production technology, before the cleaning processes. In accordance with official regulations, the production units characterized their wastewater as follows (Table 3):

Table 3. Characteristics of raw mozzarella wastewater

	COD (mg/L)	***Turbidity (NTU)***	***pH***	***Conductivity (µS/cm)***
Raw wastewater	~4100	~300–350	5.2–6.7	~1400–1600

2.3. Experimental methods

I developed the experimental methods with the help of my supervisors and consultant, the basis for which was provided by my diploma thesis and the literature used. Previously, I carried out a similar research project: I dealt with the purification of oil-containing industrial wastewater by combining membrane separation and high-efficiency oxidation processes. While developing the process, I tried to comply with the basic principles of the circular economy, as well as to focus on areas that are still little known, such as possible toxic effect of oxidation pretreatments.

2.3.1. Fenton-reaction as pretreatment

For the Fenton-reaction, I measured out 400 ml of the prepared 600 ml solution in each case. The pH of the solution was adjusted to pH = 4 with a 1% H_2SO_4 solution, and then 0.23 g of $FeSO_4 \times 7\ H_2O$ was added. Only in the case of the solution containing lactose with a pretreatment time of 0 minutes, 0.57 g of the aqueous salt was added to the solution. After the complete dissolution of the salt, I lowered the pH further by adding acid to 3, and then added 400 µl of a 30% hydrogen peroxide solution. After the waiting time (0, 30, 60, 90) minutes, the pH was adjusted to 7 by adding 1M NaOH. The 0-minute pretreatment means that after adding the reagents, I performed the filtration without an oxidation effect (generation of reactive radicals). The unreacted hydrogen peroxide present in the solution must be removed, otherwise an incorrect chemical oxygen demand value will be obtained, as the residue reacts with the solution in the test tube. For its removal, 4 ml of catalase *(Sigma-Aldrich*) enzyme solution with a concentration of 0.2 mg/ml was administered. The enzyme solution was freshly prepared on each measurement day and stored in the refrigerator until use. After the addition of the enzyme, a further 10-15 minutes of waiting followed before the filtration of the solution began (Figure 1).

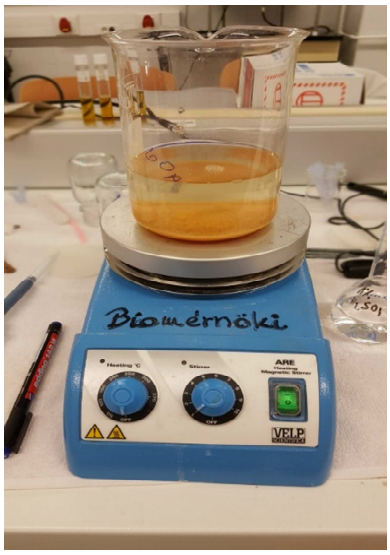

Figure 1. Model dairy wastewater pretreated with Fenton-reaction

2.3.2. Ozone pretreatment

I produced the ozone from oxygen *(Linde, 3.0)* with an ozone generator (*Ozomatic Modular 4*) operating on the principle of corona discharge. With continuous stirring, I bubbled the resulting ozone through the solution to be filtered using a diffuser, the volume of which was 400 ml in each case (Figure 2). The duration of the pretreatment was 5, 10 and 20 minutes, the oxygen flow rate was 1 L/min. To determine the concentration of absorbed ozone, I used a UV/VIS spectrophotometer (*Nanocolor NUV 0113*) at a wavelength of 254 nm. After the instrumental determination of the absorbance. I calculated the exact concentration of ozone based on the Lambert-Beer law. (1)

$$A = \varepsilon \cdot c \cdot l \qquad (1)$$

where ε is the molar absorption coefficient [dm3/mol cm], c is the concentration [mol dm_{-3}] and l is the path length, i.e. the thickness of the tested sample [cm].

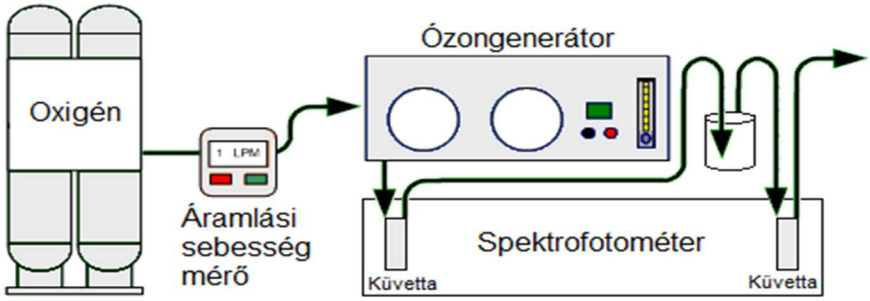

Figure 2. Ozone pretreatment flow chart

2.3.3. Determination of the oxidation capacity (oxygen-equivalent-chemical-oxidation-capacity)

I used oxygen-equivalent chemical oxidation capacity to compare the performance of different high-efficiency oxidation processes. OCC: (kgO_2/m_3) Indicates how much oxygen is "used up" during the purification of 1 m_3 of wastewater for oxidation processes (2):

$$OCC=1.000[O_3] =0.471[H_2O_2] \qquad (2)$$

where $[O_3]$ is the required ozone concentration (kg O_3/m_3), $[H_2O_2]$ is the required hydrogen peroxide concentration (kg H_2O_2/m_3) .

Based on these, I calculated the amount of ozone using the absorbance values and the Lambert-Beer law, and the amount of H_2O_2 using a simple pair of ratios.

2.3.4. Membrane filtration equipment

For the filtration, I used a mixed cell Millipore (USA) membrane filter that can be equipped with a 7.6 cm diameter membrane and provides intermittent filtration. (Figure 3).

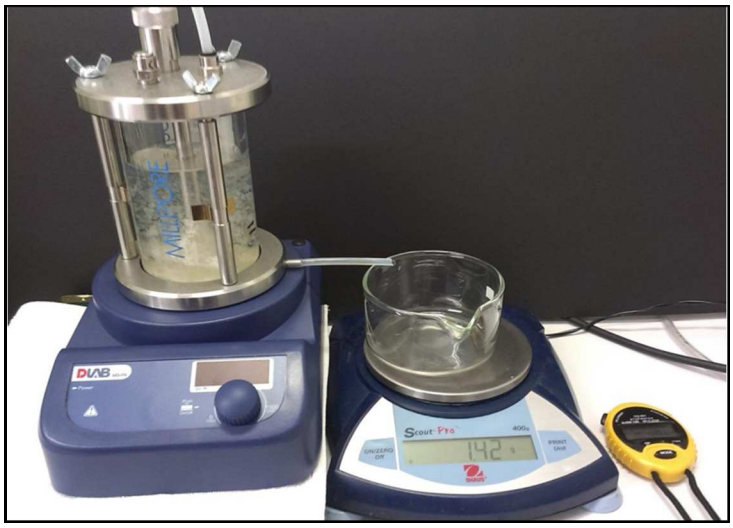

Figure 3. Millipore stirrable cell membrane filter equipment

It's maximum capacity is 300 mL, but during the measurements I filled it with 250 mL of solution. The used membrane can be attached to the lower part of the device.
The membrane used during the filtration was a 0.2 micrometer pore size polyether sulfone (PES) hydrophilic membrane sold by New Logic Research Inc. I soaked the membranes in distilled water for 24 hours before each measurement.

2.3.5. Membrane filtration process

Each time, as a first step, I assembled the thoroughly cleaned equipment, while inserting the pre-cut and soaked membrane. Next came the adjustment of the appropriate pressure value and mixing speed. This was followed by the measurement of the flux of distilled water. I filled about 250 cm^3 into the filter vessel and filtered until 50 g of permeate flowed through. I then poured out the distilled water remaining in the filter and poured 250 cm^3 of solution into the filter vessel. In the case of all filtrations (except parameter optimizations), the applied transmembrane pressure was 3 bar, which was provided from a

nitrogen bottle. During each experiment, I performed the filtrations up to a fivefold compression ratio, that is, I filtered 200 g (~200 ml) of permeate from 250 mL of wastewater. The mass of the permeate was recorded by a scale connected to a computer, and the elapsed time was recorded by the computer. I used the phyScale program for the measurement. The program recorded the elapsed time and the current mass of the permeate at preset intervals. It saved the data in a manageable format in Microsoft Excel, in which I could perform the necessary additional calculations. After that, I thoroughly rinsed the surface of the membrane with distilled water and put the membrane back into the cleaned filter device. I measured the flux of the distilled water again, and continued the filtration until 50 g of permeate was produced.

2.3.6. Analytical methods

In order to characterize the prepared solutions and the permeate and concentrate produced during filtration, I measured their pH, conductivity, turbidity, chemical oxygen demand, and conducted experiments in order to achieve accurate component analysis.

2.3.7. Determination of chemical oxygen demand

The chemical oxygen demand (COD) indicates the amount of O_2 required to chemically oxidize the organic and inorganic material in a unit volume of the sample. To characterize the chemical oxygen demand [mg/L] of the model wastewaters to be treated and the filtrates and permeates, test tubes based on oxidation with potassium dichromate (*Hanna Instruments*), a Lovibond ET 108 destruction unit (2 hours of destruction at 150°C), and a Lovibond COD I used a Vario spectrophotometer.
In order to determine chemical oxygen demand, I added the solution to test tubes for determining chemical oxygen demand with an automatic pipette.

I used two types of test tubes in parallel, one measuring range 0-1500 mg/L COD (mid range) and one measuring range 0-15,000 mg/L COD (high range), in order to obtain more accurate results.
In the former case, 2×1000 µl and in the latter 2×100 µl were pipetted out.
In the case of non-pretreated and pretreated measurements, I performed three parallel measurements.
The results are for the solution prepared for filtration, the permeate and the concentrate. For those solutions where pretreatment is applied, one more COD sampling was carried out in addition to the previous ones. Sampling was done after dissolving the components of the solution, but even before adding Fenton-reagent.

2.3.8. Biogas determination

The biogas production was carried out in three parallel, batch-mode, mesophilic conditions, at 40°C and for 40 days, in an anaerobic laboratory digester equipped with a pressure measuring head (*Oxitop Control AN12 measuring system, WTW Gmbh, Germany*) (Figure 4). I inoculated the digester with acclimatized sludge from a municipal wastewater treatment plant (Hódmezővásárhely, Hungary) in order to eliminate the possible delay phase of the anaerobic biological degradation process. After inoculation, nitrogen gas was flowed through the reactor to prevent contact with air. The pH was adjusted to 7.2 with a solution of 1 M NaOH and 1 M HCl.
The total capacity of the digesters was 1000 ml, therefore the volume of the mixed sample was 70 ml, 50 ml of the retentate and 20 ml of the sludge, taking into account our previous work and the pressure range of the equipment. The pressure values were automatically stored by the barometric heads every 2 hours.

Figure 4. Biogas samples in the reactor

2.3.9. Methane content analysis

The methane content was determined on an Agilent 6890 gas chromatograph equipped with an S/SL input and a flame ionization detector. The analytical column was an HP-PLOT Q PT (30mx0.53mmx40um). The share ratio was 9:1. The oven temperature was set at a constant 80 °C and the column flow rate was 4.5 mL/min. The carrier gas was hydrogen (purity 5.0). I performed the sample injection manually with a gas-tight Hamilton 1710SL syringe with a valve lock.

2.3.10. Membrane fouling models and calculations

In order to investigate the membrane fouling mechanisms, the filtration resistances were determined based on the model of resistors connected in series (1-4). I calculated the membrane resistances as follows (3):

$$R_M = \frac{\Delta p}{Jw \cdot \eta w} \qquad (3)$$

where RM is the membrane resistance, Δp is the pressure difference between the two sides of the membrane [MPa], J_W is the water flux of the clean membrane, η_W is the water viscosity [Pa·s].

RT is the total resistance [m–1], can be calculated using the model of resistors connected in series (4)

$$R_T = R_M + R_{irrev} + R_{rev} \quad (4)$$

where Rirrev is the irreversible resistance (mainly due to clogging of the pores) and Rrev is the reversible resistance, RM is the membrane's own resistance [m–1].

The irreversible resistance can be determined by carefully washing the surface of the membrane with distilled water after filtration, measuring the water flux and looking at the difference compared to the clean membrane (5):

$$R_{irrev} = \frac{\Delta p}{J_{WA} \cdot \eta_W} - R_M \quad (5)$$

where J_{WA} is the water flux after filtration.

The reversible resistance is calculated as follows (6)

$$R_{rev} = \frac{\Delta p}{Jc \cdot \eta_{WW}} - R_{irrev} - R_M \quad (6)$$

where Jc is the constant flux at the end of the filtration and ηww is the viscosity of the wastewater.

The mathematical modeling of the fouling mechanism is described by the Hermia model. I used the Hermia model linearized for each

measurement (Table 4). To evaluate the results, I adjusted these models to experimental data. Due to the easier and more comprehensible overview, I typically illustrated the filtering resistances, since when the available flux increases, the filtering resistance decreases (and vice versa), I felt it was unnecessary to present the diagrams of the flux curves and resistances as well.

Table 4. Models of membrane filtration [Hermia, 1982]

Fouling model	**Equation**	**Linearized equation (Filtering at constant pressure J_{0A}=constant)**
complete blocking	$J = J_0 \cdot e^{-kb \cdot t}$	$lnJ = lnJ_0 - k_b \cdot t$
pore blocking	$J = J_0 \cdot (1+0,5 \cdot K_S \cdot (A \cdot J_0)^{0,5} \cdot t)^{-2}$	$1/\sqrt{J} = 1/\sqrt{J_0} + k_s \cdot t$ $k_s = 0,5 \cdot K_s \cdot A^{0,5}$
Fouling between pores	$J = J_0 \cdot (1+K_i \cdot A \cdot J_0 \cdot t)^{-1}$	$1/J = 1/J_0 + k_i \cdot t$ $k_i = K_i \cdot A$
Cake layer fouling	$J = J_0 \cdot (1+2 \cdot K_c \cdot (A \cdot J_0)^2 \cdot t^{0,5}$	$1/J^2 = 1/J_0^2 + k_c \cdot t$ $k_c = 2 \cdot K_c \cdot A^2$

where J is the flux, J_0 is the initial flux, the various k are the plugging coefficients, and A is a constant.

2.3.11. Statistical methods and calculation of standard deviations

I performed all measurements three times in parallel and calculated the standard deviations using the standard deviation function of Microsoft Excel, and then plotted them where relevant.

3. Results

3.1. Fit of fouling models for model dairy wastewaters

During the evaluation of my measurements, I determined which fouling model best fits the given filters. (Figure 5.)

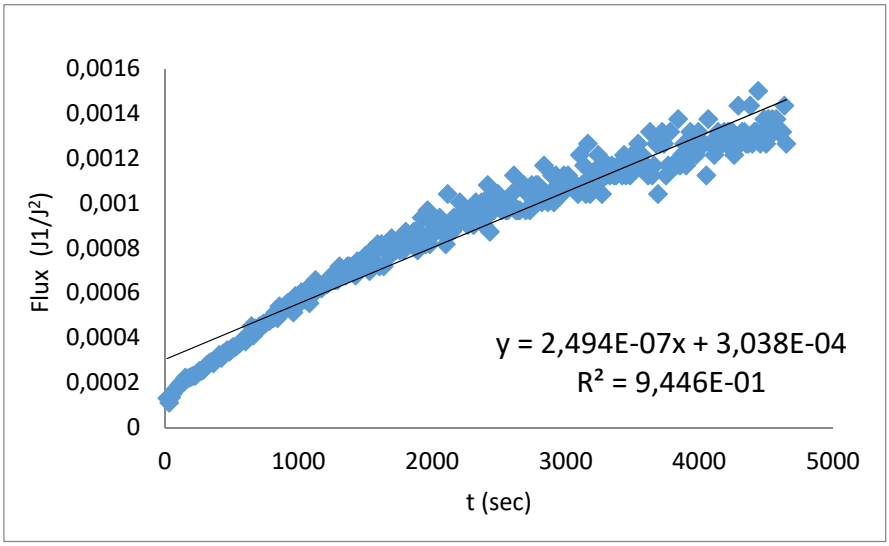

Figure 5. Typical diagram for fitting the cake layer fouling model during membrane filtration of model dairy wastewaters

After performing the filtrations, I found that, regardless of the type of pretreatments, during the filtration of the model's dairy wastewater, in a significant part of the 4 fouling models, the cake layer is the most typical, here the R^2 values were the highest, which indicates the fit of the model.
I have included these results in a table for easier overview (Table 5).

Table 5. The percentage fit of the Hermia models for the membrane filtration of the different model dairy wastewaters

	Complete fouling	Standard fouling	Partial fouling	Cake layer fouling
Caseine	80,9	84,6	87,7	**92,4**
Caseine + 5’ ozone	83,6	87,0	89,7	**93,5**
Caseine + 10’ ozone	84,5	86,8	88,2	**88,3**
Caseine + 20’ ozone	85,4	86,2	87,3	**89,1**
Caseine + 0’ Fenton	95,3	96,5	97,4	**98,6**
Caseine + 30’ Fenton	94,1	95,4	96,5	**98,0**
Caseine + 60’ Fenton	**92,7**	92,5	92,3	91,7
Caseine + 90’ Fenton	72,6	76,5	79,8	**84,9**
Caseine +lactose	78,3	82,8	86,5	**92,0**
Caseine +lactose + 5’ ozone	87,4	89,6	87,4	**90,9**
Caseine +lactose + 10’ ozone	84,7	88,0	89,2	**89,9**
Caseine+lactose + 20’ ozone	87,9	91,2	93,4	**94,9**
Caseine +lactose + 0’ Fenton	88,8	91,5	93,7	**96,2**
Caseine + lactose + 30’ Fenton	84,7	87,9	90,4	**93,6**
Caseine + lactose + 60’ Fenton	77,7	81,6	84,7	**88,9**
Caseine + lactose + 90’ Fenton	86,4	89,2	91,5	**94,5**

3.2. Effect of oxidation capacity on membrane filtration

In order to be able to compare and characterize two different pretreatment methods with a common denominator, I calculated the oxidation capacity (OCC). The essence of this is that I get (see material, tool, method chapter) how many kg of oxygen are "used up" during oxidation to clean one cubic meter of wastewater.
In the first series of experiments (Figure 6), I investigated how the initial flux changes in the case of a process with different oxidation capabilities. I already used milk powder as a model here, in order to form a transition between simple models and real dairy wastewater. I have found that regardless of OCC, the initial flux is greatest with the addition of Fenton-reagents (without the oxidation effect) due to the coagulating/flocculating effect of the reagents. And in the case of untreated wastewater and ozone-pretreated wastewater, it is lower, since the particles in untreated and ozone-pretreated wastewater can clog the pores of the membrane already at the start of filtration.

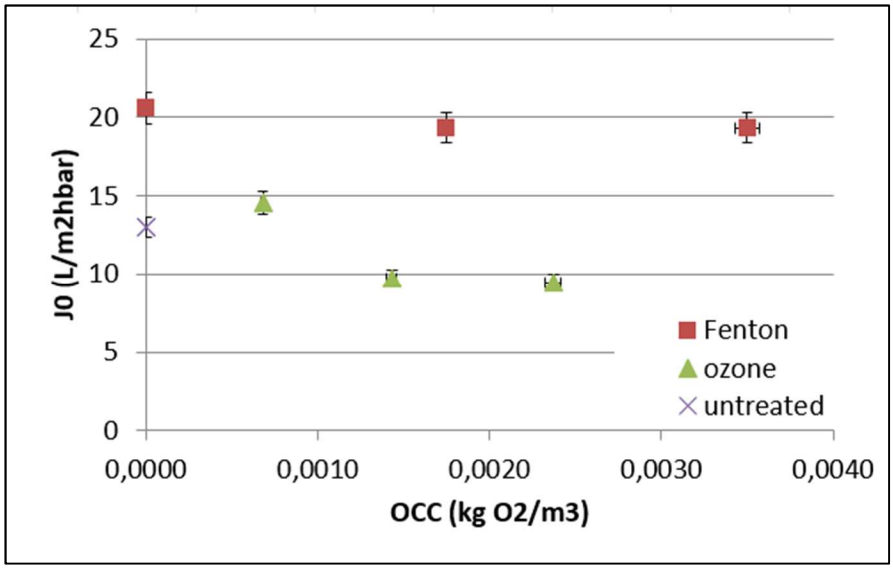

Figure 6. Changes in initial flux values as a function of oxidation capacity

In figure 7, I show how the clogging index changes as a function of the oxidation capacity. I found that increasing the OCC increases the foling index(k). This supports what is shown in Figure 6, that by increasing the OCC, due to the oxidation, the particles become smaller and can clog the pores of the membrane, thus increasing the foluling index and decreasing the initial flux.

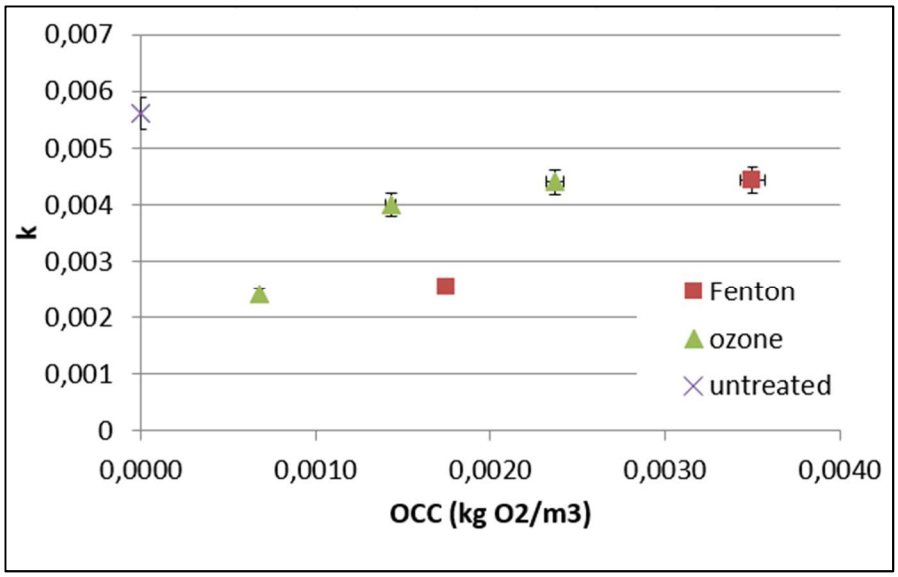

Figure 7. The change of the fouling index as a function of the oxidation capacity

3.3. The effect of pretreatments on the filtration mechanism

After comparing the two different pre-oxidation treatments, I examined how the filtration resistances and pollutant retentions develop in model dairy wastewaters. I used natrium-caseinate and later lactose to prepare the model wastewaters. Casein proteins can increase the fouling of membranes, moreover, this effect increases if they crumble due to oxidation, and lactose can enter the permeate in addition to influencing the filtration process, thus increasing its chemical oxygen demand.

In the first series of experiments, I pretreated a 1.2 g/L natrium-caseinate solution with ozone for 5, 10, 20 minutes. With the Fenton-reaction, the length of the pretreatments was 0, 30, 60 and 90 minutes, and the [H2O2]:[Fe] ratio was 5:1. Based on the resistances connected in series (Experimental material and method 4.3.9.), I found that the ozone treatment increased the filtering (reversible and irreversible) resistances, thereby reducing the flux. (Figure 8)

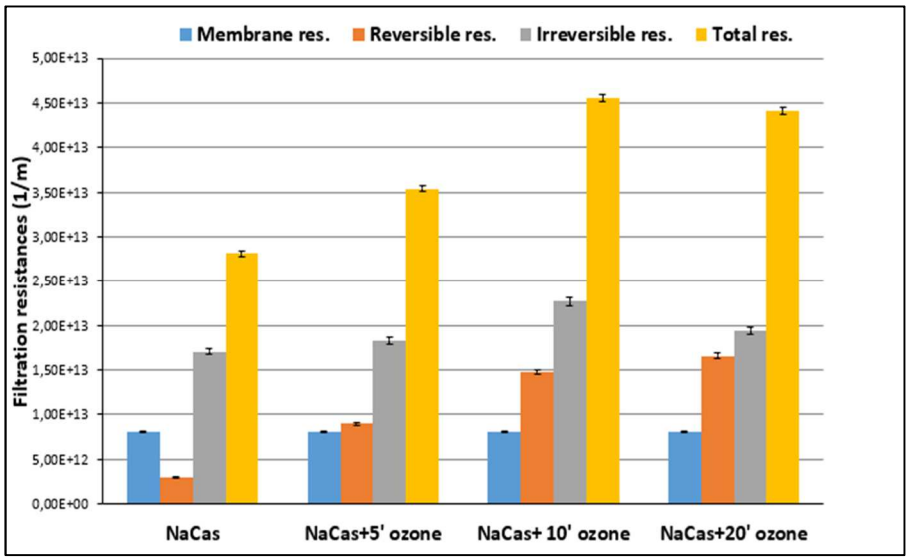

Figure 8 Filtration resistances in the case of ozone pretreatment of model wastewater containing natrium-caseinate

The Fenton-reaction as a pretreatment significantly reduced both reversible and irreversible resistance (Figure 9); already without an oxidation reaction, just by adding Fenton-reagents. Short-term oxidation further reduced the filtration resistances, thus increasing the flux, while longer-term (90 min) treatment decreased the flux, probably due to the fragmentation of larger molecules, which can cause membrane fouling.

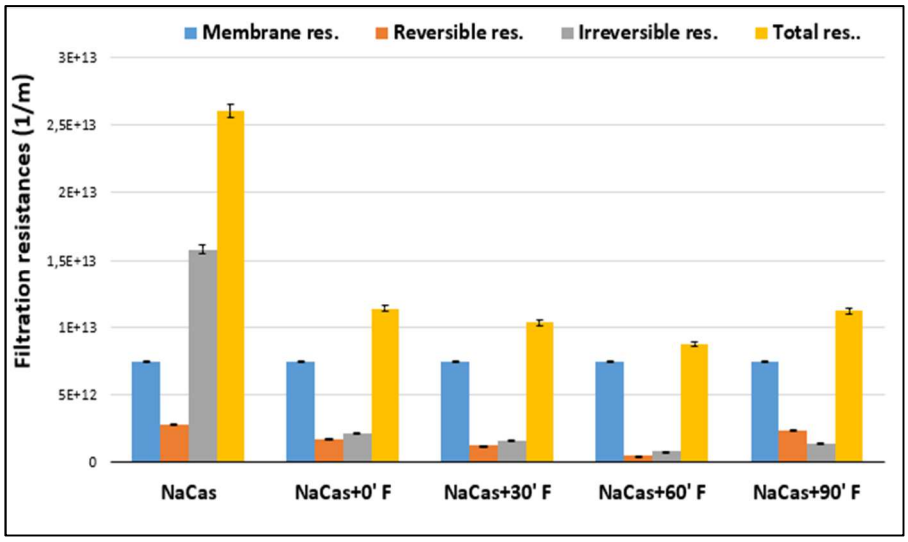

Figure 9 Filtration resistances in the case of pretreatment of model wastewaters containing natrium-caseinate with 5:1 [H_2O_2]:[Fe]Fenton-reagent

3.4. Effect of lactose on the filtration mechanism

Since dairy waste waters often contain lactose, which can significantly affect filterability, in the next series of experiments I investigated the filtration resistance in the presence of lactose. (Figure 10) I found that the presence of lactose increased the total resistance of the natrium-caseinate solution, which could only be reduced by adding Fenton-reagents. In this case, the oxidizing effect of the Fenton-reaction reduced the total resistance, as the irreversible resistance decreased significantly.

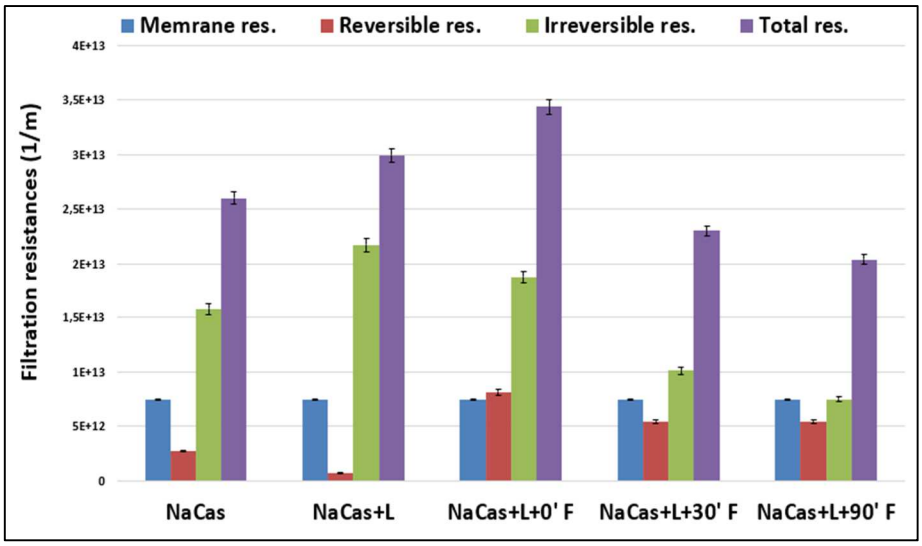

Figure 10 Filtration resistances in the case of pretreatment of model wastewaters containing natrium-caseinate and lactose with a 5:1 $[H_2O_2]$:[Fe] Fenton-reagent

3.5. Results achieved with the combined treatment of general dairy wastewater

In the first series of experiments with real dairy wastewater from general milk processing technology (similar to the previous chapters), I pretreated the samples with ozone for 5, 10, or 20 minutes, and with the Fenton-reaction for 0, 30, or 90 minutes. Then, I filtered the pretreated samples with a membrane and calculated the filtration resistances based on the measured fluxes. These calculations revealed that the ozone pretreatment increased the relative fluxes in all cases, and the 10-minute pretreatment resulted in the highest values. At the same time, pretreatments with the Fenton-reaction reduced the relative fluxes. In order to obtain and visualize additional information about the nature of the pre-fouling, I plotted and compared the filter resistances (Figure 11).

I found that the 10-minute ozone pretreatment reduced the filtration resistances to the greatest extent. Pretreatment with the Fenton reaction

increased the total resistance by increasing the irreversible resistance. The reason for this may be that in this wastewater, the agglomerated particles formed with the help of Fenton-reagents are smaller as a result of the oxidation pretreatment, partially or completely blocking the pores of the membrane, which can make it difficult or even impossible to filter and clean the membrane. In this wastewater, the effect of increasing the membrane resistance of lactose and Fenton-reagents is more effective, which I also experienced with the model wastewaters.

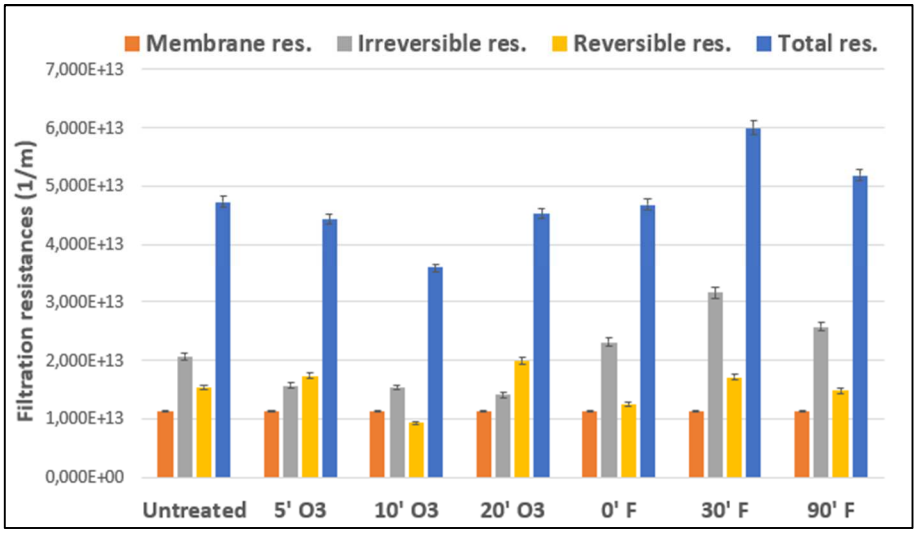

Figure 11. Effects of oxidation pretreatments on filtration resistances

3.6. Changes in cleaning efficiencies as a result of pretreatments in mozzarella dairy wastewater

After performing the filtrations, I measured and compared the cleaning efficiency (Figure 12). The oxidation treatment alone (without filtration) also reduced the COD of the wastewater, but only to a small extent (6-12%), while most of the pollutants can be removed by membrane filtration. The highest cleaning efficiency was observed with the 10-minute pretreatment (72%), and the cleaning efficiency decreased with further increase in the duration of the ozone treatment.

Among the Fenton-reactions, the 0-minute Fenton-reaction (without oxidation) was the most effective (70%), which is due to the coagulation-flocculation effect of the Fenton-reagents. Nevertheless, the ozone treatment and the short-term Fenton reaction achieved the highest (62.5%) cleaning efficiency. The chemical oxygen demand of the permeate was thus reduced below 1200 mg/L chemical oxygen demand. Dairy wastewater treated in this way may be suitable for further purification with municipal wastewater, or for the production of water that can be recycled with a second membrane filtration step (nanofiltration or reverse osmosis).

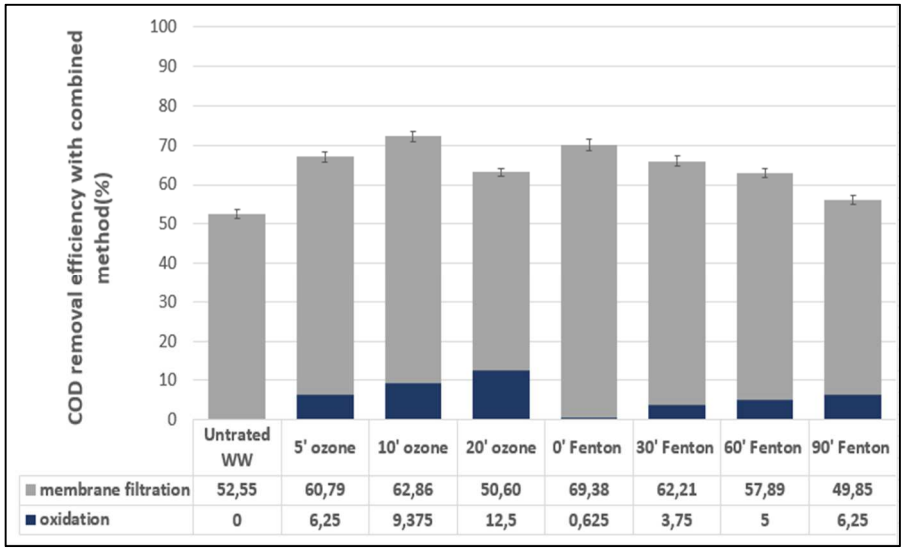

Figure 12. COD removal efficiency from dairy wastewater by pretreatment with ozone and Fenton-reaction

3.7. Determination of methane content in the produced biogas

In order for the produced biogas to be utilized energetically, it is also necessary to examine its methane content, since the higher the methane content, the greater part of the biogas can actually be utilized (Figure 13). I found that the methane content was high even in the untreated

samples, and the pretreatments further increased it. In the untreated mixture, 60% of the biogas was methane. This value increased to 70% after the ozone pretreatment and to 68% after the Fenton reaction. It can therefore be said that the oxidation pretreatments increase not only the amount of biogas, but also the methane content of the biogas produced from the concentrate

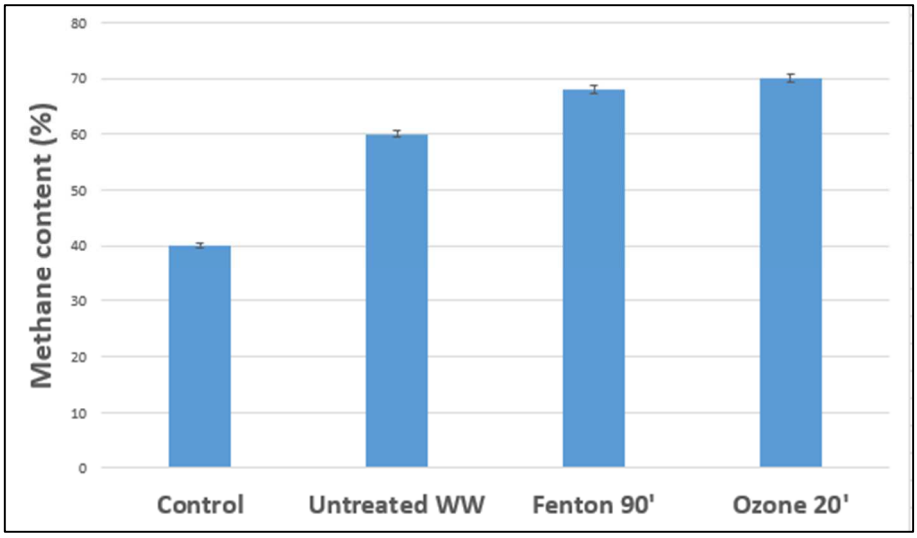

Figure 13. Changes in the methane content of biogas produced from wastewater concentrate as a result of oxidation pretreatments

3.8. Summary of results

Overall, it can be said that during membrane filtration of dairy wastewater after pretreatment with ozonation and Fenton reaction, cake layer filtration is typical. The filtering mechanisms are aided by the coagulating/(micro)flocculating effect of the pretreatments, which can also increase the cleaning efficiency with adequate oxidation capacity. However, by increasing the oxidation pretreatments, the particles become smaller and clog the membrane, which can also impair the filtration and cleaning efficiency. This effect increases in the presence of lactose, as well as in the presence of other pollutants in real

wastewater. Biogas with a high methane content can be developed from the concentrate of real wastewater, which can be used for energy purposes, so the process fits into the topic of the circular economy and, after further tests, it can also be used industrially.

4. Summary of thesis points, new scientific results

1. I proved that in this work, in addition to the presented conditions and filtration parameters, during the filtration of the model's dairy wastewater, regardless of the type and duration of the pretreatments, in a significant part (with the exception of one) of the 4 fouling models, cake layer is the most typical, here were the highest R_2 values, which indicates the fit of the model. (Chapter 5.1.1). The fits can be improved if the initial measurement points are omitted, but the entire mechanism is best described by the cake layer filtration model.
   a. I proved that the initial flux is independent of the oxidation capacity. Even without oxidation, Fenton-reagents increase the flux due to their coagulating/flocculating effect
   b. particles of raw and ozone-pretreated wastewater more easily clog the pores of the membrane, therefore the flux decreases. (Chapter 5.2.6)
2. I proved that the Fenton reagents by themselves significantly reduce the filtration resistances when filtering model wastewater containing only casein. However, if lactose is added to the model, the filtration resistances start to increase and the oxidation effect of the Fenton reaction is also needed to reduce the resistances again
      i. compared to untreated wastewater, the total resistance is reduced by 40% even with the addition of Fenton-reagents if the model wastewater only contains casein
      ii. if the model wastewater also contains lactose, the resistances will first start to increase, the flocculates will be of a different size, the filtration mechanism will change and the cake layer and particles entering the pores will clog the membrane
      iii. as the oxidation effect of the reaction prevails, the resistance begins to decrease again, the size of the flocculates

and membrane fouling particles is favorably affected by the reaction

3. I proved that in the case of general dairy wastewater, the 10-minute pretreatment (0.328 kg/m3 ozone) gave the lowest filtration resistance and the highest cleaning efficiency (62.86%), and in addition, the methane content of the biogas produced was 64%, so for energy purposes can be utilized.
4. I proved that (chapters 5.2.6 and 5.3.4 and 5.4.3) the amount of oxidizing material required to achieve the lowest resistance and highest cleaning efficiency under the present conditions with the developed method is as follows:
   a. the. casein-containing model for wastewater
      i. 0.069 kg/m3 in the case of a 5-minute ozone pretreatment
      ii. 60 0.325 kg/m3 in the case of a 60-minute Fenton reaction pretreatment
   b. mozzarella wastewater
      i. 0.283 kg/m3 in the case of a 20-minute ozone pretreatment
      ii. 0.154 kg/m3 in case of pretreatment with Fenton reaction for 60 minutes
   c. general dairy wastewater
      i. 0.328 kg/m3 in the case of a 10-minute ozone pretreatment
      ii. 0 kg/m3 in the case of pretreatment with a 0-minute Fenton reaction (here, the addition of reagents without oxidation gave the best values)

5. Published publications on the topic of the dissertation – IF: 2,536

1. Zakar M., Beszédes S., Lakatos E., Keszthelyi-Szabó G., László Zs. (2021): Dairy wastewater utilization by combination of oxidation pre-treatment and ultrafiltration. Environmental Engineering and Management Journal. Vol. 20, No. 11.Q3
2. Zakar M., Farkas D.I., Lakatos E., Keszthelyi-Szabó G.,László ZS. (2020): Purification of model dairy wastewaters by ozone, Fenton pre-treatment and membrane filtration. Periodicapolytechnica Chemical Engineering. Vol. 64 : 3 pp. 357-363., 7 p. Q3
3. Zakar M., Lakatos E., Keszthelyi-Szabó G., László Zs. (2017): Purification of dairy wastewaters by advanced oxidation processes and membrane filtration. Analecta Technica Szegedinensia Vol. 11 : 1 pp. 32-38., 7 p.
4. Zakar M.; Kovács I., Muhi P.; Lakatos E., Keszthelyi-Szabó G., László Zs. (2017): The effect of advanced oxidation pre-treatment on the membrane filtration parameters of dairy wastewater. Hungarian Journal of Industry and Chemistry Vol. 45:2 pp. 23-27.
   Analecta Technica Szegedinensia (2017) 11 : 1 pp. 32-38., 7

6. Conference announcements related to the topic of the dissertation

1. Zakar M., Farkas D.I., Beszédes S., Lakatos E., Keszthelyi-Szabó G., László Zs. (2019): Real dairy wastewater treatment by coupled advanced oxidation processes and membrane filtration Book of Abstracts - 6th European Conference on Environmetal Applications of Advanced Oxidation Processes - Portorose, Slovenia, 26-30 June
2. Zakar M., Farkas D.I., Szabó A., Lakatos E., Keszthelyi-Szabó G., László Zs. (2019): A Fenton-reakció és az ózonos előkezelés hatásának vizsgálata modell tejipari szennyvíz membránszűrése során XXI. Századi vízgazdálkodás a tudományok metszéspontjában : II. Víztudományi Nemzetközi Konferencia Szarvas, Magyarország : Szent István Egyetem Agrár- és Gazdaságtudományi Kar (2019) 380 p. pp. 186-192., 7 p.
3. Zakar M., Farkas I.D., Kertész Sz., Lakatos E., Keszthelyi-Szabó G., Šereš Z., László Zs. (2018): Investigation of the effect of ozone

pretreatment in the membrane filtration of real dairy wastewater. International Conference on Science, Technology, Engineering and Economy : ICOSTEE 2018

4. Zakar M., Farkas I.D., Lakatos E., Keszthelyi-Szabó G., László Zs. (2018): A Fenton-reakció előkezelésként való alkalmazásának hatása valós tejipari szennyvizek membránszűrése során XXXVII. Óvári Tudományos Napok Összefoglalói
5. Zakar M., Lakatos E., Keszthelyi-Szabó G., László Zs. (2018) Fenton-reakció és ózonos előkezelés összehasonlítása kazein tartalmú modell tejipari szennyvizek membránszűrése során Műszaki, technológiai és gazdasági kihívások a 21. században : Nemzetközi magyar nyelvű konferenciasorozat. Absztrakt kötet
6. Zakar M., Veréb G., Kovács I., Hodúr C., László Zs. (2018): Applying ozonization as pre pr pro treatment combined with membrane filtration for the purification of oil contaminated waters International Conference on Science and Technique Based on Applied and Fundamental Research : Book of Abstracts
7. Zakar M., Veréb G., Hodúr C., Keszthelyi-Szabó G., Lakatos E., László, Zs.(2018): Élelmiszeripari szennyvizek kezelése ózonkezelés és membránszeparáció kombinálásával XXXVI. Óvári Tudományos Nap : Hagyomány és innováció az agrár- és élelmiszergazdaságban I-II
8. Zakar M., Farkas I.D., Lakatos E., Keszthelyi-Szabó G., László Zs. (2018): Purification of model dairy wastewaters by Fenton pretreatment and membrane filtration. 10th Eastern European IWA Young Water Professionals Conference. Croatia
9. Zakar M., Veréb G., Hodúr C., Keszthelyi-Szabó G., László Zs. (2016): Purification of industrial wastewater with the combination of ozonation and membrane separation. Proceedings of the 22nd International Symposium on Analytical and Environmental Problems. Szeged