# TREATMENT OF FOOD INDUSTRY WASTEWATERS IN MEMBRANE BIOREACTOR

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Application of membrane bioreactor (MBR) was investigated as a treatment process for two different types of food industry wastewaters: an oil plant wastewater and wastewater from beverage production.

In beverage production membrane bioreactor achieved effective and stable organic compounds removal from the wastewater (COD=94 %, TOC=94 %, BOD<sub>5</sub>= 98 %) during all period of experiment. Facility had conventional activated sludge wastewater treatment which could not treat wastewater satisfactorily due to the frequent changes in the wastewater composition and flow rate. Therefore, membrane bioreactor with immersed membrane was tested for wastewater treatment to compare the two technologies.

Average percent of COD removal with membrane bioreactor for treatment of wastewater from vegetable oil production was 75%, while fats and oils were removed with an average of 86%. Best treatment efficiency was achieved by treatment of mixed wastewaters from all of the sources where COD was removed with 91% and oil and grease with 95% efficiency.

Activated sludge was successfully kept in the bioreactor by immersed membrane so that stable concentration of activated sludge biomass could be maintained in spite of large fluctuations in the composition of the wastewater. Stable and uninterrupted filtration was obtained by using backwash cleaning and by maintaining constant flow and aeration rate.

This type of wastewater treatment ensures large return of processed water for reuse, which enables more efficient water management and considerable reduction in wastewater discharge cost.

Key words: activated sludge, food industry wastewater, beverage production, oil plant, membrane bioreactor

# INTRODUCTION

#### 1. About MBR

Membrane bioreactors (MBR) which combine biological activated sludge process (ASP) and membrane separation are now widely used for wastewater treatment and reclamation. The reactor is operated similar to a conventional activated sludge process but without the need for secondary clarification. They are used in cases when conventional ASP cannot cope with either composition of wastewater or fluctuations of wastewater flow rate. It is also used in cases where demand on the quality of effluent exceeds the capability of ASP. The limiting step in the conventional treatment is the separation of sludge from the treated water. Without a good sedimentation in secondary settler parts of the sludge end up in treated water which leads to poor efficiency of the treatment process.

Advantages of MBR over conventional activated sludge (ASP) technology comprises better effluent quality, smaller footprint, higher concentration of MLSS (mixed liquor suspended solids), less excess sludge production and generally more stable process. Principal limitation of the MBR process lies in membrane fouling as a consequence of the interactions between the membrane and the mixed liquor, which affects overall process performance. Membrane separation is carried out either with cross-flow filtration in side-stream MBRs or with submerged membranes which operate in dead-end mode.

In the past decade, submerged vacuum driven membranes have become more attractive for their much lower energy consumption and lower transmembrane pressure than predominantly used tubular cross-flow membranes. There is possibility of using the aeration in the bioreactor to prevent fouling by creating turbulent cross flow over the membrane surface. They can be easily installed in the existing conventional plants thus increasing their capacity without a need to build bigger reactors. Although MBR capital and operational costs exceeds costs of conventional process it seems that upgrade of conventional process occurs even in cases when conventional treatment works well. It can be related with increase of water price and need for water reuse as well as with more stringent regulations on effluent quality.

#### 2. Wastewater from beverage industry

In the first part of investigation of MBR treatment applicability for treatment of food industry wastewaters, pilot testing was conducted in beverage industry. In most beverage industries, spent process water generated in different individual operations (bottle washing, juice production, cleaning of tanks and pipes, etc.) is mixed and equalized onsite in large tanks prior to discharge into the municipal sewage system. Treatment of wastewater from beverages production facilities usually comprises some sort of physical pre-treatment for removal of suspended matter followed by biological treatment, either aerobic or anaerobic. MBR was also investigated for treatment of such water along with further membrane filtration (1) in order to facilitate water reuse (2).

The existing conventional ASP has not been able to treat wastewater sufficiently and therefore a pilot plant testing with MBR was conducted in parallel with conventional treatment to compare the efficiencies of the two processes.

#### 3. Wastewater from vegetable oil industry

In the second part of investigation of MBR treatment applicability, experiment was conducted on the. wastewater from vegetable oil industry. Discharge of vegetable oil industry effluents is posing a serious threat to water resources. Production of refined vegetable oil include many technological processes such as pre-treatment of oilseeds, manufacturing, refining and modification of oils. The effluent mainly comes from degumming, deacidification and deodorisation steps (3) which are part of refining process. Acid splitting is also part of refining process in which sulphuric acid is added to the soap stock causing free fatty acids to be separated from the medium. The resulting effluent is highly acidic. (4)

The composition of wastewater may vary widely from day to day depending on operating conditions and type of oil processed. Because of complexity of wastewater and variations in quantity and characteristic, the choice of wastewater treatment methods depends on many local conditions (5). Many authors have discussed physical methods like ultrafiltration (6) and reverse osmosis (7); physicochemical methods which includes precipitation, coagulation, flocculation and flotation (5), (8), (9); physicochemical methods followed by biological processes (4),(10), (11); biological methods (12) and other methods like thermochemical treatment (13) and photocatalysis (14) for oily wastewater treatment.

## EXPERIMENTAL

Experiments with both types of wastewater were conducted on a pilot plant MBR with a hollow fiber membrane (Zenon ZeeWee<sup>TM</sup>-10, 0.4 µm pore size, 0.93 m<sup>2</sup> surface area) vertically submerged directly in the 40 L (useful volume) rectangular based (24x24x93 cm) bioreactor. The pilot plant consisted of laboratory pumps for feed flow and permeate suction; a blower with a diffuser placed under the membrane; a pressure gauge. The membrane was bubbled with a blower connected to the diffuser placed below the membrane with 6.5 m<sup>3</sup> h<sup>-1</sup> of air flow, which helped to avoid fouling of the membrane through promoting shear over its surface and produced stable dissolved oxygen concentration which was always above 6 mg/L in the bioreactor. Mixing of the bioreactor was also performed by airflow induced below the membrane. Membrane was backflushed with effluent for 10 seconds every 9.75 minutes with the backflush rate 1.5 times bigger than the effluent flow rate in order to remove deposits on the membrane surface. The flow rate of feed water was 5 L h<sup>-1</sup> which gave a permeate flux of 5.43 L m<sup>2</sup> h<sup>1</sup> and 8 h hydraulic retention time. The bioreactor was inoculated with activated sludge from a full-size municipal wastewater treatment plant with initial 10 g L<sup>1</sup> of mixed liquor suspended solids (MLSS) in the bioreactor for the experiment with wastewater from vegetable oil production and 8 g L-1 for the with wastewater from beverage production. MBR membrane characteristics are presented in Table 1.

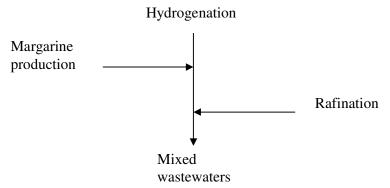
Table 1. MBR membrane characteristics

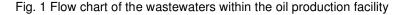
membrane type	hollow fibre
Dimensions of module (mm)	692.15 × 109.54
Dimensions. fibre length (m)	0.52
Filtration area (m <sup>2</sup> )	0.93
Nominal pore size (µm)	0.4
Cross section area (cm <sup>2</sup> )	94 cm <sup>2</sup>

Resistance R <sub>m</sub> (m <sup>-1</sup> )	6.5 x 10 <sup>11</sup>
Maximal pressure (bar)	0.55
Maximal temperature (°C)	40
Maximal concentration of active chlorine (mg L <sup>-1</sup> )	1000
optimal pH. (for washing)	5-9 (2-10.5)

In first experiment with wastewater from beverage production samples of the raw wastewater and effluents from both MBR and existing conventional biological treatment plant were taken several times a day for analyses which comprised COD, BOD, inorganic constituents in wastewater and MLSS, all conducted according to standard methods. TOC measurements were done on Shimadzu TOC analyzer 5000A.

In the second experiment with wastewater from oil plant production samples of the effluents from MBR were analysed daily. The facility was situated in 5 positions within the oil production factory (Fig1.). Oil and grease from margarine production wastewater and from rafination plant wastewater were removed by flotation before entering the sewer. Wastewater was directly pumped out of the sewer into MBR pilot plant. The experiment was performed on wastewaters from hydrogenation plant, plant for margarine production, mixed wastewaters from hydrogenation and margarine production, and mixed wastewaters before entering the public sewer. The aim of this experiment was to determinate what is the most efficient, and less expensive way for wastewater treatment. Wastewater after treatment must fulfil legal requirements.





Parameters of concern were chemical oxygen demand (COD), oil and grease, total dry matter, pH, suspended solids, electrical conductivity and total organic carbon (TOC). Parameters were measured by standard analytical methods.

## **RESULTS AND DISSCUSION**

# 1. Wastewater from beverage production

In the first experiment investigated facility was bottling plant for natural spring water which also served for bottling of soft drinks. The dynamics of production dictates also the generation of the wastewater which is discharged into a nearby river after egalization, neutralization and biological treatment. The wastewater from the investigated facility showed significant variations in composition as shown in Table 2. As the production was switching from the water to soft drinks bottling, composition of wastewater was affected accordingly which resulted in noted variations. COD fluctuated between 200 and 3000 mg/L as can be seen both from Table 2 and Fig. 2.

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	Average	Minimum	Maximum	Standard deviation	Limit for discharge
COD (mg O <sub>2</sub> /L)	722	228	2990	585	125
BOD (mg O <sub>2</sub> /L)	232	130	350	111	25
TOC (mg/L)	194	58	571	125	30
рН	7.06	5.29	9.85	1.06	6.5-8

Table 2. Average composition of wastewater during the experiment and limit values for discharge according to Croatian wastewater regulation

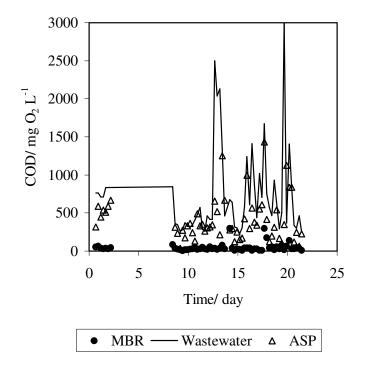


Fig. 2 COD of the wastewater, MBR and ASP effluents

High peek values of COD were usually noted after the soft drink bottling campaign when cleaning of the bottling line took place and components of soft drinks such as sugars and colors ended up in the wastewater. As can bee seen from the Fig 2, the existing ASP had serious problems in treating these waters which resulted in high values of COD in its effluent. Fig. 3 gives the TOC concentrations of wastewater as well as ASP and MBR effluents. They are in concordance with COD with the ratio between COD and TOC concentrations about 3.8 which indicate oxidation state of carbon in the wastewater suitable for biological treatment. It can be concluded from Figures. 2 and 3 that existing ASP treatment clearly could not treat the wastewater sufficiently enough to meet the regulations for discharge. The main reason for this incapability was low concentration of the activated sludge in the aerated basin of the plant, usually bellow 1g/L. Low concentration of the sludge was a result of long periods with low organic loading from the low polluted wastewater into the aerated basin which lead to the starvation of the bacteria of the activated sludge. Result of the starvation was bulking of the sludge which caused major loss of the bacterial population. The occasional high organic loads could not enhance growth and retention of the bacteria in the bioreactor. What is more, high salt concentration caused by regeneration of water softening column and neutralization of alkaline cleaning solution for the bottling production lines, as well as fluctuations in pH could also have diminished the activity of the activated sludge and its ability to form flocs.

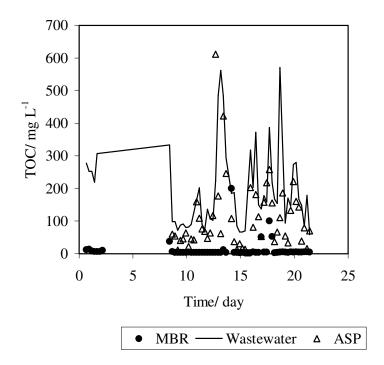
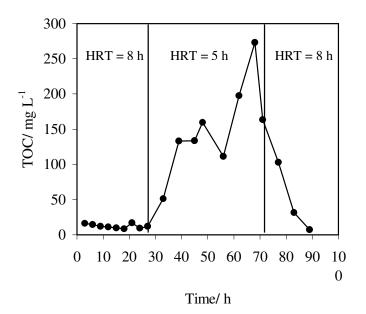
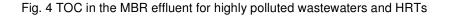


Fig. 3 TOC of the wastewater, MBR and ASP effluents

Unlike the conventional plant, the MBR treatment was quite efficient and stable in removal of organic constituents with both COD and TOC averagely reduced by 94%. It was mostly the result of higher activated sludge biomass concentration in the bioreactor as a result of its retention by the membrane. Activated sludge was capable for efficient biodegradation of the pollutants from the wastewater while the membrane retained suspended solids thus further enhancing the effluent quality.

To investigate further degradation rate of such wastewater experiment with highly polluted wastewater was conducted with two hydraulic retention times (HRT). The TOC of the MBR effluent with collected wastewater having average TOC of 800 mg/L at different HRTs is presented on the Fig. 4. From the results of the experiment it can be clearly seen that HRT influenced the treatment efficiency significantly. Successful treatment was achieved at the beginning of the experiment when HRT was set at 8 h. When the wastewater flow rate was increased to give 5 h HRT, sudden increase in organic content of the effluent was observed. Five hours HRT was clearly not sufficient for microorganisms to degrade the organic matter from the wastewater completely while prolonging the HRT again to 8 h improved the treatment efficiency to satisfactory level. (Fig. 4)





MLSS was slowly decreasing from the 9.8 g/L at the beginning of the experiment to 8 g/L at its end. This slow decrease was probably caused by organic loading rate to the bioreactor which was insufficient to sustain the inoculated concentration of the biomass. The low sludge production rate, or even complete stagnation of MLSS for MBRs, has been reported earlier (15) and explained by low food to micro-organism ratio (i.e. little substrate per unit biomass) which lead to competition among the micro-organisms and resulted in reduction of sludge production. The lower production of excess sludge is considered as an advantage of the MBR technology over ASP.

Table 3 summarizes the compared results of removal efficiency for ASP and MBR. The superiority of MBR treatment is clearly evident for all parameters of organic pollution. While ASP failed to treat water sufficiently, MBR succeeded to produce water suitable for discharge.

	MBR	ASP
TOC	94	44
COD	94	43
BOD	97	47

Table 3 Comparison of removal efficiency (%) for MBR and ASP

## 2. Wastewater from oil and grease production

#### 2.1. Mixed WASTEWATERS

In Table 4 is shown the composition of mixed wastewaters from all of the wastewater sources within the oil and grease production. This wastewater had lowest variations of all investigated wastewaters due to egalization. Moreover, the acidic wastewater from the reifinement process neutralized within the collecting pipeline with alkaline wastewater from margarine production thus giving suitable media for biological treatment. As a result of the egalization of the wastewaters, more than 91% of COD was removed and the effluent quality showed little if any dependence on the fluctuation of COD in the feed water. COD in effluent was between 25-109 mgO<sub>2</sub>L<sup>-1</sup>. Oil and grease removal with MBR was also very high with 94.5% average efficiency. (Fig.5) Average values in effluent

were 8.4 mg  $O_2 L^{-1}$ . All of the investigated pollutants in MBR effluent were considerably lower than legal requirements for wastewater disposal in public sewage system.

	COD (mg O <sub>2</sub> L <sup>-1</sup> )	Oil and grease (mg L <sup>-1</sup> )	pН	Suspended solids (mg L <sup>-1</sup> )	Conductivity (μScm <sup>-1</sup> )
mean	677.1	172.3	6.83	210.5	1470
min.	575	83	6.59	126	1180
max.	830	271	6.99	322	1680
Stan. Dev.	112.3	68.3	0.2	82.2	221.8

Table 4. Composition of collected wastewater

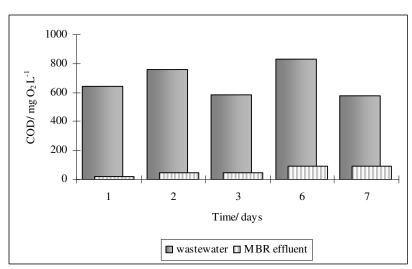


Fig 5 COD during treatment of collected wastewaters with MBR

### 2.2. WASTEWATER FROM HYDROGENATION PROCESS

Composition of wastewater from oil hydrogenation is shown in Table 5. The wastewater with COD ranging from 85 to 800 mg  $O_2 L^{-1}$  with rather high concentrations of oils and stable pH seemed suitable for biological treatment.

	COD (mg O <sub>2</sub> L <sup>-1</sup> )	Oil and grease (mg L <sup>-1</sup> )	pН	Suspended solids (mg L <sup>-1</sup> )	Conductivity (μScm <sup>-1</sup> )
mean	415	74.4	7.48	91	492
min.	86	16.9	6.57	13	350
max.	798	201.2	8.18	289	820
Stan. Dev.	230	70	0.5	101.3	176.3

Table 5.Composition of wastewater from oil hydrogenation

On Fig.6 is given the removal efficiency of COD during treatment of wastewater from oil hydrogenation with MBR. The quality of the effluent from the MBR was uniform with no visible influence of the COD concentration in the wastewater. Average removal efficiency of COD was 77,7%, of oil and grease was also 77%. Since the membrane pores of 0.4  $\mu$ m retained suspended matter, its complete removal was achieved.

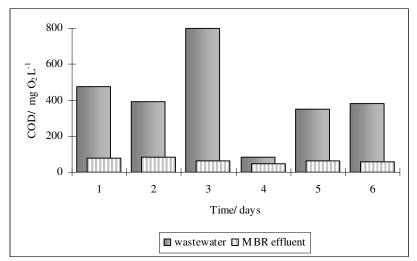


Fig.6 COD during treatment of wastewater from oil hydrogenation with MBR

# 2.3. WASTEWATER FROM MARGARINE PRODUCTION

As can be seen in Table 6, wastewater from margarine production had much higher CODs then wastewater from the hydrogenation along with high concentration of oil. However the fluctuations of pH from 6 to 12 caused by alkaline cleaning of margarine production line were notable and such water was evidently unsuitable for biological treatment. Therefore a neutralization step prior to MBR stage was necessary since such high values of pH could the inhibit activity of mixed culture of the activated sludge.

	COD (mg O <sub>2</sub> L <sup>-1</sup> )	Oil and grease (mg L <sup>-1</sup> )	рН	Suspended solids (mg L <sup>-1</sup> )	Conductivity (µScm <sup>-1</sup> )
mean	2020.9	575.8	8.36	284.6	1829
min.	608.7	100	6.64	227	600
max.	4173.9	1119	12.1	380	4600
Stan. Dev.	1620	367	2.02	83.2	1456.4

Table 6 . Composition of wastewater from margarine production

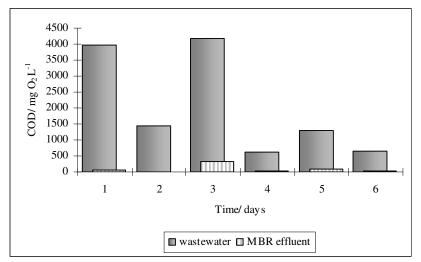


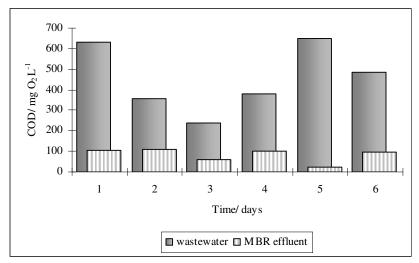
Fig. 7 COD during treatment of wastewater from margarine production with MBR

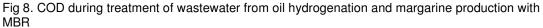
# 2.4. MIXED WASTEWATERS FROM HYDROGENATION PROCESS AND MARGARINE PRODUCTION

As can be noted from the composition of the mixed wastewaters from margarine production and oil hydrogenation (Table 7), the fluctuations of pH was attenuated by their mixing while COD showed lower values then in case of margarine production wastewater with less fluctuations. No attempt to neutralize these water prior to MBR was made but due to a short duration of high pH occurrence in the water there was no significant ph rise in the bioreactor. Figure 8 show efficient removal of organic compounds measured as COD . Average removal efficiency was 79.6%. Absolute removal of suspended solids by MBR membrane also contributed to removal of COD. (16) Ng, et al.(2000) ascribe up to 80% of organic compounds removal to membrane filtration. Oil and grease floated in the bioreactor because of aeration and were retained on the surface, and hence could not pass through the membrane which was submerged into mixed liquor. The consequence was its better degradation due to a prolonged residence time in the bioreactor. Removal efficiency of COD is shown on Fig. 8 and averagely it was 79.6%. Oil and grease removal efficiency were 81.6%. MBR technology in general is expected to show better removal of oil and grease than conventional activated sludge technology where easily floatable oils end up with treated water in the secondary settler. Also, the oil contaminated sludge is often considered as hazardous waste and has to be disposed with special care.

	COD (mg O <sub>2</sub> L <sup>-1</sup> )	Oil and grease (mg L <sup>-1</sup> )	Total dry matter (mg L <sup>-1</sup> )	рН	Suspended solids (mg L <sup>-1</sup> )	Conductivity (μScm <sup>-1</sup> )
mean	457	96.5	1189	8.34	91	813
min.	236	83.3	841	7.09	50	620
max.	630	118.8	1874	10.3	144	1250
Stan. Dev.	162.2	12.7	363.2	1.09	31.4	248

Table 7	Composition of wastewater	from oil	hydrogenation	and mar	narine production
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## CONCLUSIONS

The results of the experiment in beverage production showed that MBR had significant advantage in treatment efficiency compared to conventional activated sludge process for investigated wastewater. MBR effluent was suitable for discharge while effluent after ASP treatment could not meet the discharge requirements. The main reasons for failure of the ASP were fluctuations in wastewater composition and flow rate that prevented development of the sufficient concentration of the activated sludge necessary for the treatment. The MBR treatment was influenced by MLSS concentration in the bioreactor and HRT that were significant in the case of highly polluted wastewater.

In the experiment with wastewater from vegetable oil production, MBR also treated successfully all investigated wastewaters generated within the facility. Best results were achieved on mixed wastewater from all of sources throughout the facility with 91% removal of COD and 95% removal of fats and oils. To provide adequate wastewater treatment with MBR, pretreatment consisting of partial removal of fats and oils by flotation along with the neutralization of the wastewater should be applied

The high quality of MBR effluent opens possibility for re-use of the effluent in investigated industrial processes, which can significantly reduce the demand for fresh water.

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