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# Treatment of beverage production wastewater by membrane bioreactor

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## Abstract

The paper reports on the results of treatment of wastewater from the bottling of water and soft drinks with a membrane bioreactor (MBR) pilot plant. The existing conventional activated sludge process could not produce effluent suitable for discharge due to significant fluctuations of wastewater composition and flow rate. MBR successfully removed pollutants measured as COD, BOD and TOC from the wastewater with an efficiency of over 90%. The main factors negatively influencing the MBR treatment were low biomass concentration and low HRT, which were significant in the case of highly polluted wastewater. Membrane fouling was more pronounced during the first 10 days of the filtration and then gradually slowed down. The most significant fouling was caused by scale precipitation, which was responsible for 70–80% of the loss of membrane permeability. After 60 days of continuous filtration, it was possible to restore the original permeability of the membrane through intensive chemical cleaning with hypochlorite, acid and alkaline solutions.

*Keywords:* Activated sludge; Membrane bioreactor; Wastewater

## 1. Introduction

Membrane bioreactor (MBR) technology, which combines biological activated sludge process (ASP) and membrane filtration, has become more popular, abundant and accepted in recent years for the treatment of many types of wastewater where conventional ASP cannot cope with either the composition of wastewater or the fluc-

tuations of wastewater flow rate. It is also used in cases where demand on the quality of effluent exceeds the capability of ASP [1,2]. Although MBR capital and operational costs somewhat exceed the costs of conventional process, it seems that the upgrade of the conventional process occurs even in cases where conventional treatment works well. It can be related to the increase of water price and the need for water reuse, as well as with the more stringent regulations on effluent quality.

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The limiting step in the conventional treatment is the separation of sludge from the treated water. Without good sedimentation in the secondary settler, parts of the sludge end up in treated water which leads to poor efficiency of the treatment process. Sedimentation of the sludge is influenced by the characteristics of the microbial flocs as a function of their physiological state. The occurrence of sludge with poor settling characteristics, often called the bulking sludge, is connected with growth of filamentous bacteria which proliferate in unfavorable biological conditions such as low dissolved oxygen concentration, low food to microorganism ratio and nutrient deficiency [3]. While dissolved oxygen concentration can be provided by a proper aeration system, problems with variations in wastewater flow rate and composition can seriously affect the performance of the ASP. Therefore, the bacterial community in the ASP has to be kept in conditions favorable for floc formation. By doing so, microorganisms in the activated sludge are being kept in the exponential growth phase in which they produce large quantities of excess biomass. Favorable conditions for sludge sedimentation are usually easy to achieve with municipal wastewater containing a small quantity of industrial wastewater and drainage water. In the cases when drainage water dilutes the wastewater significantly or in the case of various industrial wastewaters, the ASP efficiency can be seriously lowered due to poor sedimentation of microbial flocs.

In order to overcome the limitations of ASP, MBR technology can be successfully employed to treat wastewater in conditions which do not allow successful sedimentation of activated sludge [4]. Since an MBR uses membrane filtration instead of sedimentation to separate bacteria from the treated water, biomass concentration within the bioreactor can be maintained at a much higher level, thus reducing the size of the bioreactor. Without the secondary settler and with a smaller bioreactor, a typical MBR plant footprint can be as low as 25% of that of the ASP for the same

capacity. Sludge retention times (SRT) are in general much longer with an MBR, which gives the slower growing species, which have the ability to decompose less biodegradable compounds, the opportunity to proliferate. Also, since there is no need for the sludge to settle, the bacteria in the bioreactor can be supplied with less substrate than with ASP, which keeps the sludge production in the process much lower, thus reducing the cost of excess sludge handling. Presently, there are a number of examples of successful implementation of MBR across the range of applications [1,5].

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 beverage 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 tested for treatment of such water along with further membrane filtration [6] in order to facilitate water reuse [7]. More stringent regulations and the increase of the price of water stimulate development of the novel approaches to wastewater treatment.

This work reports the results of the treatment of wastewater from a soft drinks production facility. 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 efficiency of the two processes.

## 2. Experimental

The experiments were conducted on a pilot plant MBR with a hollow fiber membrane (Zenon ZeeWee™-10, 0.4 µm pore size, 0.92 m<sup>2</sup> surface area) vertically submerged directly in the 40 L (useful volume) rectangular based (24×24×93 cm)

bioreactor. The pilot plant consisted of laboratory pumps for feed flow and permeate suction, a blower with a diffuser placed under the membrane and a pressure gauge. The membrane was bubbled with a blower connected to the diffuser placed below the membrane with  $6.5 \text{ m}^3 \text{ h}^{-1}$  of air flow, which helped to avoid fouling of the membrane through promoting shear over its surface and produced a stable concentration of dissolved oxygen, which was always above  $6 \text{ mg/L}$  in the bioreactor. Mixing of the bioreactor was also performed by the airflow induced under the membrane. Membrane was backflushed with effluent for 10 s every 9.75 min 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  $5 \text{ L h}^{-1}$ , which gave a permeate flux of  $5.43 \text{ L m}^{-2} \text{ h}^{-1}$  and 8 h hydraulic retention time. The bioreactor was inoculated with activated sludge from a full-size municipal wastewater treatment plant with initial  $10 \text{ g L}^{-1}$  of mixed liquor suspended solids (MLSS) in the bioreactor. After a 38-day adaptation period when activated sludge was fed with tested real wastewater, the continuous treatment experiment was closely monitored during the next 22 days on the site of the wastewater discharge concurrently with the existing full scale treatment plant. The existing treatment plant was a conventional activated sludge process with a primary settler, an equalization tank for pH corrections, an aerated basin, and a secondary settler. Hydraulic retention time of the plant was 5–12 h, depending on the wastewater flow rate. Samples of the raw wastewater and effluents from both MBR and the existing treatment plant were taken several times a day for analyses, which comprised of COD, BOD, inorganic constituents in wastewater and MLSS, all conducted according to standard methods. TOC measurements were done on a Shimadzu TOC analyzer 5000A.

Permeability of the membrane was estimated by measuring transmembrane pressure (TMP) and the water flux ( $J$ ) during filtration of the activated

sludge suspension. At least six pairs of measured flux and stabilized TMP values were used to draw the curve for each permeability calculation which was performed using the linear part of  $J$  vs. TMP curve by the best fit method.

Membrane chemical cleaning was performed either as a backwash cleaning without removing the membrane from the mixed liquor or as an extensive cleaning after the experiment completion, when the membrane was removed from the bioreactor and soaked in several cleaning solutions. For backwash cleaning, the membrane was filled with hypochlorite solution ( $750 \text{ mg/L}$  of active chlorine) throughout the backwash and left for 2 h, followed by cleaning solution discharge, and then filled with hydrochloric acid diluted to pH 2. For extensive cleaning, the membrane was soaked in several cleaning solutions with aeration applied under the membrane. The cleaning solutions and the duration of their application for soaking were respectively: tap water for 2 h; hypochlorite solution ( $750 \text{ mg/L}$ ) for 24 h; hydrochloric acid (pH = 2) for 1 h; sodium hydroxide (pH = 12) for 8 h; hypochlorite solution ( $750 \text{ mg/L}$ ) for 24 h.

### 3. Results and discussion

The facility investigated for this study was bottling a natural spring water plant, which was also used for bottling soft drinks. The dynamics of production also dictate the generation of the wastewater, which is discharged into a nearby river after equalization, neutralization and ASP treatment. The wastewater from the investigated facility showed significant variations in composition as shown in Table 1. As the production was switching from water to soft drinks bottling, the composition of wastewater was affected accordingly, which resulted in noted variations. Wastewater from steam production used within the facility, as well as sanitary wastewater, ended up in the wastewater to be treated biologically, thus further enhancing the variations in wastewater composition. As can be seen from Table 1,

Table 1

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

	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
pH	7.06	5.29	9.85	1.06	6.5-8
Conductivity (μS/cm)	2600	900	6100	1200	—
Total hardness (mg CaO/L)	27.4	7.2	52.9	13.3	—
Chloride (mg/L)	760	87	1525	374	—

besides the parameters concerning organic load, the wastewater contained high concentrations of chloride and had high total hardness, which generates high conductivity. COD fluctuated between 200 and 3000 mg/L as can be seen from both Table 1 and Fig. 1.

Peak COD values were usually noted after soft drink bottling operation, when cleaning of the bottling line took place and components of soft drinks such as sugars and colors ended up in

the wastewater. These periods of occurrence of heavily polluted water were rather short but the volumes of such waters were usually large. As can be seen from Fig. 1, the existing ASP had serious problems in treating these waters, which resulted in high values of COD in its effluent. Fig. 2 gives the TOC concentrations of wastewater as well as ASP and MBR effluents. They are in concordance with COD with a ratio of COD and TOC concentrations of about 3.8, which indicate

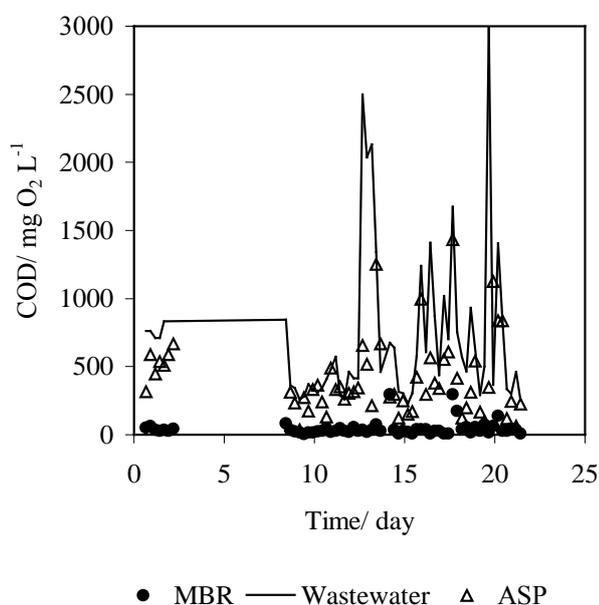


Fig. 1. COD of the wastewater, MBR and ASP effluents.

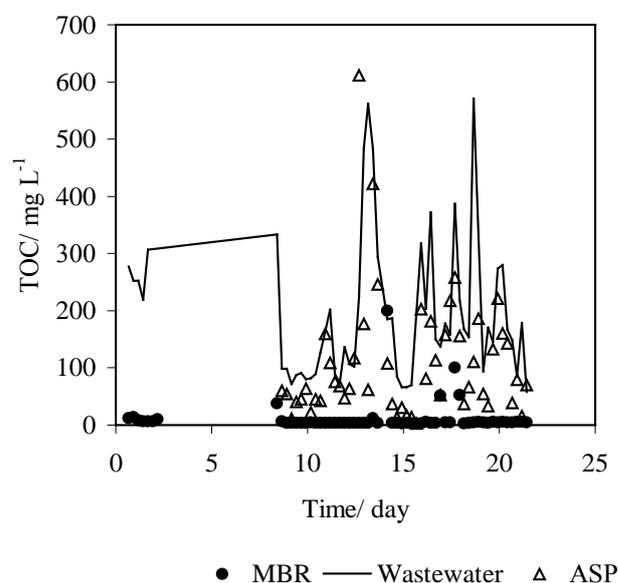


Fig. 2. TOC of wastewater, MBR and ASP effluents.

the oxidation state of carbon in wastewater suitable for biological treatment. The somewhat low ratio of BOD and COD in the wastewater contrasts the prediction of good biodegradability. It can be concluded from Figs. 1 and 2 that the existing ASP treatment clearly could not treat the wastewater sufficiently enough to meet the discharge regulations. The main reason for this incapability was the low concentration of activated sludge in the aerated basin of the plant, usually under 1 g/L. The low concentration of the sludge was a result of long periods with low organic loading from the lightly polluted wastewater into the aerated basin, which lead to the starvation of the bacteria of the activated sludge. The starvation resulted in the bulking of the sludge, which caused a major loss of bacterial population. The occasional high organic loads could not enhance growth and retention of the bacteria in the bioreactor. What is more, the high salt concentration caused by the regeneration of the ion exchange water softening unit and the neutralization of the 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.

Unlike the conventional plant, the MBR treatment was quite efficient and stable in removal of organic constituents, with both COD and TOC reduced by 94% on average. It was mostly the result of higher activated sludge biomass concentration in the bioreactor, which was caused by its retention by the membrane. Bacteria in the activated sludge were capable of efficient biodegradation of the pollutants from the wastewater while the membrane retained suspended solids, thus further enhancing the effluent quality. However, there were some exceptions to the observed high removal efficiency when higher concentrations of both COD and TOC were measured in the MBR effluent. These events were probably caused by sudden increases in the organic load of the wastewater, when microorganisms did not have enough time for complete degradation. In order to further

investigate the degradation rate of such wastewater, two experiments were undertaken. The first was a batch laboratory treatment of high strength wastewater and the second was an experiment with the collected highly polluted wastewater treated in pilot MBR with differing hydraulic retention times (HRT). The results of batch treatment with altering concentrations of wastewater and changing of the MLSS are presented on the Fig. 3. The results suggest that the degradation time of the pollutants from the wastewater is only 2 h for wastewater with TOC around 250 mg/L. The curves of TOC removal were very similar for MLSS concentrations of 5.48 and 2.79 g/L, indicating that both MLSS concentrations were sufficient for the treatment. In contrast to that, wastewater with higher TOC (around 500 mg/L) needed a longer time for the degradation of pollutants, which could not be removed in less than 5 h. What is more, the MLSS concentration had a significant influence on the rate of degradation. From the batch experiment it was evident that MLSS and contact time between bacteria and

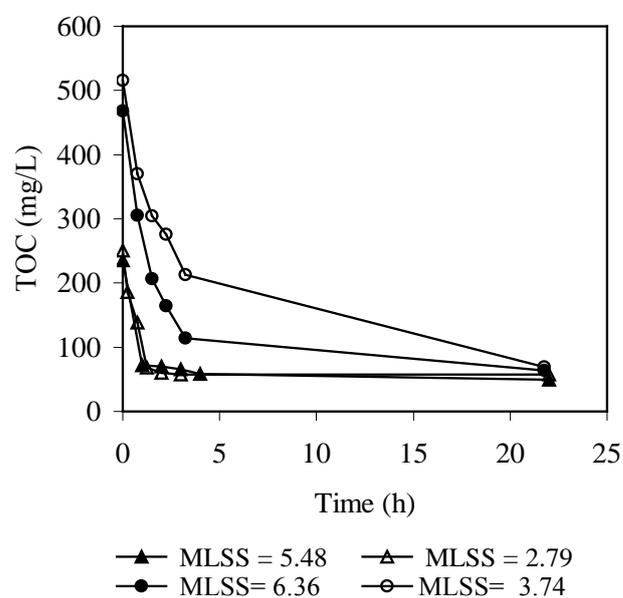


Fig. 3. TOC removal from real wastewater in the batch experiment for different MLSS (g/L).

wastewater were significant factors influencing treatment efficiency.

The experiments were then transferred to a pilot scale with highly polluted wastewater. The TOC of the MBR effluent with collected wastewater, with an average TOC of 800 mg/L at different HRTs, is presented in Fig. 4. From the results of the experiment, it can be clearly seen that HRT significantly influenced treatment efficiency. 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 a 5 h HRT, a sudden increase in organic content of the effluent was observed. A five-hour 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 a satisfactory level.

MLSS was slowly decreasing from 9.8 g/L at the beginning of the experiment to 8 g/L at its end. This slow decrease was probably caused by the organic loading rate into the bioreactor, which was insufficient to sustain the inoculated concentration of the biomass. The low sludge produc-

tion rate, or even complete stagnation of MLSS for MBRs, has been reported earlier [8], 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 a reduction of sludge production. The lower production of excess sludge is considered as an advantage of MBR technology over ASP.

Table 2 summarizes the compared results 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, probably due to a low MLSS concentration, MBR succeeded to produce water suitable for discharge.

Membrane performance was monitored through permeability measurement during the pilot trial. Membrane permeability for the filtration of the activated sludge is given in Fig. 5. Membrane permeability for continuous filtration during both adaptation and treatment periods is given here.

The constant permeate flow rate, which gave a permeate flux of  $5.43 \text{ L m}^{-2} \text{ h}^{-1}$ , induced the fouling of the membrane with the constituents of

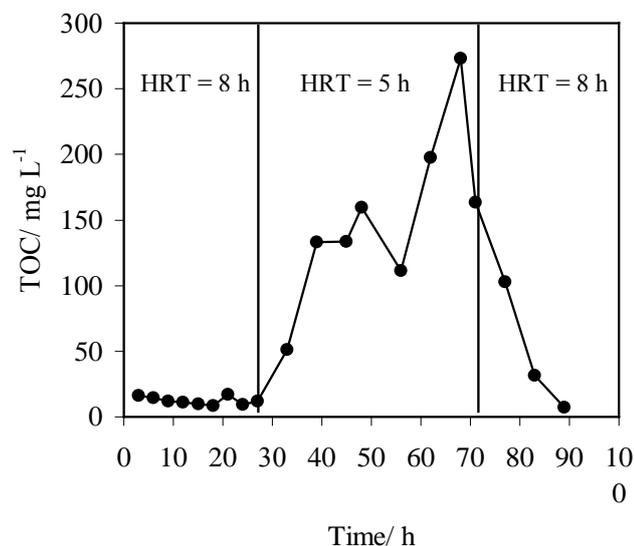


Fig. 4. TOC in MBR effluent for highly polluted wastewaters and HRTs.

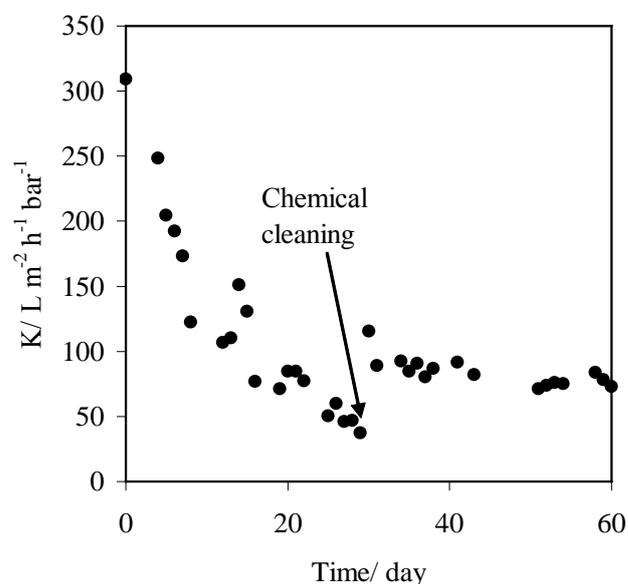


Fig. 5. Membrane fouling as permeability decreases over time.

Table 2  
Comparison of removal efficiency (%) for MBR and ASP

	MBR	ASP
TOC	94	44
COD	94	43
BOD	97	47

the mixed liquor. The rate of the fouling was not constant, with more rapid fouling during the first 10 days of the filtration, followed by a gradual slow down. The whole experiment was conducted with the permeate flux set well under the critical flux estimated in a previous experiments [9]. The concept of the critical flux originally presented by Field et al. [10] states that there exists a flux under which no fouling occurs. Despite the doubts whether this concept is applicable to membrane fouling with complex media such as mixed liquor of activated sludge, the concept is widely accepted for fouling prediction, with most MBRs operating under nominally sub-critical conditions [1]. Pollice et al. [11] reviewed the sub-critical fouling phenomenon in MBR. From the reviewed data, it is evident that even sub-critical operation inevitably leads to fouling. This fouling is often reported to follow a two-stage fouling pattern, which includes slow TMP increase over a long period of time, followed by a rapid increase after a critical time period. In the work of Zhang et al. [12] this pattern is extended with an initial period of conditioning fouling. In the cited work on fouling in MBR under sub-critical conditions, three stages are introduced, including initial conditioning fouling, slow fouling and sudden TMP jump. During the initial conditioning fouling interactions take place between the membrane surface and the soluble components of mixed liquor. This fouling is usually rapid, irreversible by nature and it occurs even for zero flux operation. In the second stage of slow fouling, membrane surface is gradually covered by biopolymers such as extra-cellular polymeric substances (EPS), changing the prop-

erties of the membrane surface and making the attachment of the microbial flocs to the membrane surface easier. This may promote biofilm growth on the membrane surface. Over time, complete or partial pore blocking takes place. This blocking is expected to be inhomogeneous since the air and the liquid flow are distributed unevenly in the MBR. With some regions of the membrane more fouled than others, the flux varies locally, thus exceeding the critical flux in some areas of the membrane surface, leading to a sudden TMP jump characteristic for operation above the critical flux. The fouling behavior in the present work is in concordance with the cited mechanism, only without the observed sharp increase of TMP, probably due to a short duration of the experiment and low applied flux. On day 29, chemical backwash cleaning with hypochlorite solution was performed, followed by acid cleaning with hydrochloric acid. Some of the permeability loss due to fouling was regained but short term cleaning (2 h) could not restore the initial permeability. It should be noted that acidic cleaning was responsible for about 80% of the permeability recovery, while the hypochlorite recovered the rest. These observations indicate significant fouling due to a scale precipitation. When looking at the composition of the wastewater in Table 1, the occasional high concentrations of total hardness can be extracted along with high values of pH. These conditions were favorable for scale formation, so scaling occurred despite the fact that the membrane could not retain inorganic salts.

After the completion of the experiments, the membrane was thoroughly cleansed by soaking the membrane in hypochlorite solution, as well as acidic and alkaline solution. Cleaning was performed by altering the chemical solution used for soaking the membrane. The permeability of the membrane was measured during the cleaning (Fig. 6). As in the first cleaning, the biggest rise in membrane permeability was a result of the acidic soak, which was responsible for 72% of overall permeability recovery, while combined hypochlo-

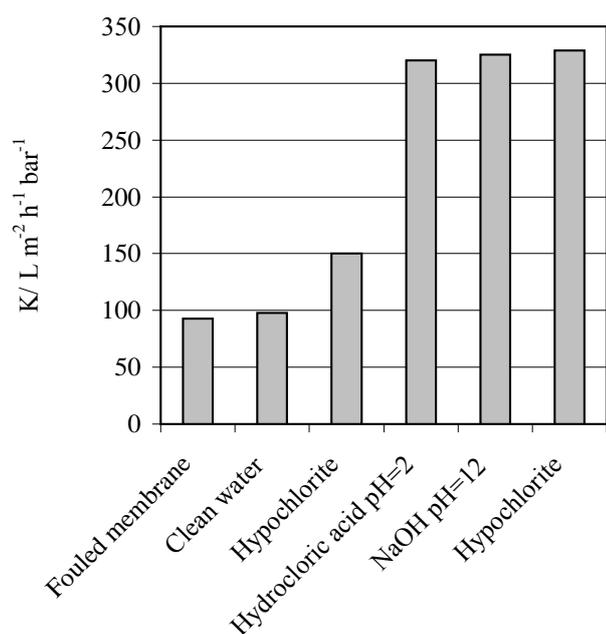


Fig. 6. Permeability of the membrane during chemical cleaning.

rite and NaOH recovered 26% of the permeability. It is obvious that scale was a major foulant in this study. To prevent the synergistic fouling effect of scale and biosolids, which may combine in formation of deposits on the membrane, more frequent acid cleaning is recommended.

#### 4. Conclusions

The results of the pilot MBR testing showed that MBR had a significant advantage in treatment efficiency compared to the conventional activated sludge process for wastewater from the investigated water and soft drink bottling facility. The MBR effluent was suitable for discharge, while the effluent after ASP treatment could not meet the discharge requirements. The main reasons for failure of the ASP were the fluctuations in wastewater composition and flow rate, which prevented the development of a sufficient concentration of activated sludge necessary for treatment. The MBR treatment was influenced by the MLSS concentration in the bioreactor and the

HRT, which were significant in the case of highly polluted wastewater.

Membrane fouling was more pronounced during the first 10 days of the filtration and then gradually slowed down. A filtration regime with frequent backwash, low permeate flux and intensive aeration allowed uninterrupted continuous filtration for 30 days. The most significant fouling was caused by scale precipitation due to occasional high concentration of total hardness in wastewater, accompanied with high pH. It was possible to restore the original permeability of the membrane through intensive chemical cleaning with hypochlorite, acid and alkaline solutions.

Altogether, MBR showed capability in treatment of investigated wastewater from beverage production, which opens the possibility of upgrading the existing ASP in order to meet the discharge requirements.

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