

## **Comparative Study of MBR and Activated Sludge in the Treatment of Paper Mill Wastewater**

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### **Abstract**

The study was based on a full scale activated sludge plant (AS) compared to a parallel operated pilot membrane bioreactor (MBR) with flat sheets membranes. Both systems received their influent from an anaerobic bioreactor treating paper mill wastewater. MBR produced an effluent of much better quality than AS in terms of suspended solids, containing 1 mg/L or less in 80% of the monitoring time, while the AS effluent contained 12 mg/L. This could save the necessity of further treatment by filtration in case of MBR. Other effluent quality parameters, such as organic matter (COD and BOD), phosphorous and ammonia nitrogen did not indicate substantial differences between AS and MBR. Calcium carbonate scaling and formation of a bacterial layer on the membrane caused severe flux reduction. The membrane blockage because of scaling and biofouling proved to be very serious, therefore, it required proper and more complicated maintenance than the AS system. This study leads to the conclusion that in case of paper mill wastewater, after anaerobic biotreatment, if there is no need for excellent effluent quality in terms of suspended solids, the replacement of the AS by the MBR would not be strongly justified, mainly because of maintenance cost.

### **Keywords**

Activated sludge, anaerobic pre-treatment, membrane bioreactor, paper mill.

### **Introduction**

Water and fiber are necessary elements in the paper industry. During the papermaking process highly polluted wastewater is generated. The paper industry makes a lot of efforts in order to improve purification and quality of liquid effluents. In recent years papermaking effluents had achieved relatively low levels of contaminants (Webb, 2003). However, the continued tendency to increasing stringency of regulated wastewater discharge standards and the decreasing reserves of fresh water in the world, make paper industry to go on searches of the appropriate solution for the improvement of effluent quality. One of the ways to meet these new standards is by upgrading of existing biological treatment facilities or applying advanced secondary treatment technologies.

Activated sludge treatment (AS) systems are often used for pulp and paper mill wastewater purification, showing high organic matter removal efficiency. However, AS is highly sensitive to external disturbances of physical and/or of chemical nature and this often results in high concentration of suspended solids and turbidity in the effluent, reducing the amount of active biomass in the bioreactor, creating sludge bulking and foaming in aerated basin (Metcalf and Eddy, 1991). In case of paper industry these disturbances may vary from sudden changes in pH or in organic loading rate to toxicity caused by of resins, acids or chlorinated organic compounds. Sarlin et al. (1999) reported that unusual changes in the paper mill wastewater characteristics, caused by spills of biocides, oils, dyes, acids and other chemicals, could reduce biomass activity and have a negative effect on biosolids settleability. Efficient separation between biosolids and the liquid effluent phase is one of the most critical and difficult goals of the AS process for obtaining low total suspended solids (TSS) concentration and turbidity (Metcalf and

Eddy, 1991). Shtahl et al. (2004) reported that in the case of paper mill wastewater treatment by conventional full scale AS, settling and clarification problems were regularly encountered and the process was characterized by high TSS effluent concentration and by high SVI.

Membrane bioreactors (MBR) can be considered as a modification of the conventional AS, using membrane filtration instead of sedimentation. The use of membrane separation technology could improve liquid/biosolids separation. Advantages of the MBR are associated with the production of effluent almost free of TSS and bacteria, much higher MLSS concentration in bioreactor, higher sludge residence time (SRT), smaller bioreactor size and low biomass yields (Cicek et al, 1998). Galil et al. (2003) found that in comparison with AS, the MBR process can produce an effluent of much better quality in terms of organic matter, suspended solids, and nutrients. Dufresne et al. (1998) reported results indicating that lignin concentration and toxicity of 48h-LC<sub>50</sub> for *Daphnia Magna* were significantly lower in MBR than AS effluent during chemi-thermo-mechanical pulp (CTMP) wastewater purification.

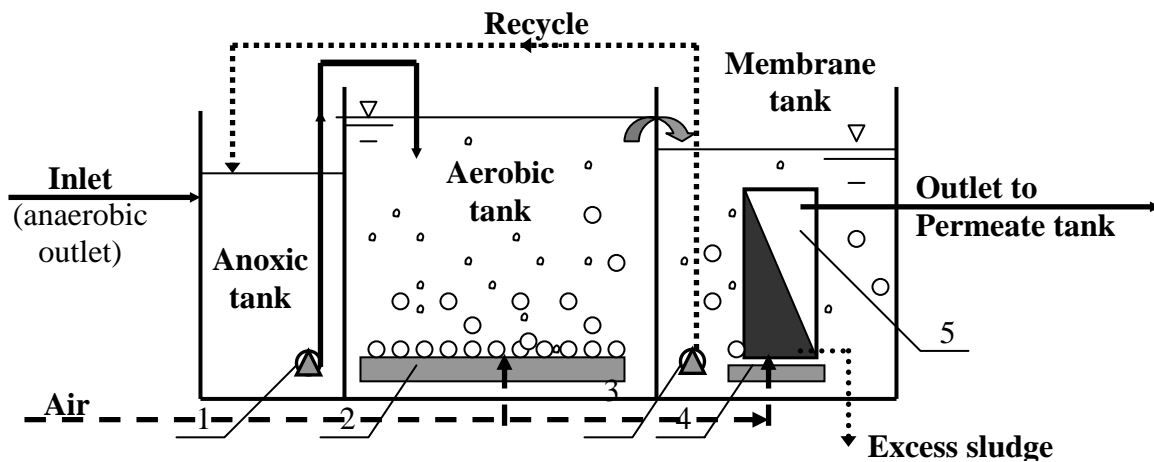
The disadvantages associated with MBR include high investment cost and relatively difficult operation and maintenance. Membrane fouling problems require frequent cleaning procedures by chemicals, with intermittent operation of the system. Additionally, MBR running at high SRT could be accompanied by the accumulation of non-biodegradable organic and inorganic compounds in the bioreactor which could be harmful to the microbial population or to the membrane structure (Cicek et al., 1999).

MBR systems have found broad application in municipal and industrial wastewater treatment (Cicek, 2003). In the case of pulp and paper industry, most of the reported activity of MBR is more at the pilot-scale trial level than full-scale installation. Webb (2001) reported that there are successful full-scale MBR units installed in the paper mills in Netherlands and France showing high effluent quality in term of COD, BOD and TSS. It should be noted that most of the MBR studies and reports focused on the treatment of raw wastewater with mechanical pre-treatment only. However, in the nineties, the combination of anaerobic pre-treatment with aerobic bioprocess became popular especially in the treatment of industrial wastewater in pulp and paper industries. Therefore, the aim of the work presented in this paper was to investigate and compare the performances obtained during the simultaneous operation of MBR pilot and a full-scale AS system operated in parallel on the treatment of the effluent obtained from an anaerobic bioreactor.

## Materials and Methods

The project was carried out the American Israel Paper Mills (AIPM) group, Hedera, Israel. The industrial complex is producing approximately 300,000-ton tissue, fine and packaging papers per year, on the one site and consuming about 2,600,000 m<sup>3</sup> of fresh water per year. The wastewater treatment plant (WWTP) includes equalization tank (750 m<sup>3</sup>), primary treatment by ALGAS drum filter, anaerobic pre-treatment operated since April 2002, and AS. The anaerobic reactor installed in WWTP is an Upflow Anaerobic Sludge Blanket (UASB – Paques' Internal Circulation Reactor) with a tall, slim design reactor (V= 1200 m<sup>3</sup>). The aerobic AS plant includes a completely-mixed aeration basin (V=8500 m<sup>3</sup>) equipped with surface aerators and followed by four clarifiers for biosolids separation. The experimental membrane bioreactor (MBR) pilot was provided by Kubota and operated in parallel with the full-scale AS system. In this type of MBR solids are removed from the treated water by driving the mixed liquor on the outside of the membrane panel through to the inside of the panel. The liquid head above the membranes (1.3 m) proves the driving force needed to move the liquid through the membrane material. The flat sheets of membranes were manufactured from poly-olefin with pore size of 0.1 to 0.4 microns (micro-filtration). The total amount of membranes was 75 with a total surface area of 60 m<sup>2</sup>. The pilot had 4 tanks (anoxic, aerobic, membrane and permeate) with volumes 5, 11, 9 and 7 m<sup>3</sup>, accordingly, as shown in Fig 1. The

aerobic and membrane tanks arranged with fine and coarse bubble air diffusers, accordingly. The operational flux of the MBR system was 20.8 L/m<sup>2</sup>\*hr.



**Figure 1. Schematic diagram of the submerged membrane bioreactor experimental (MBR).**

1 – submerged pump, 2 – fine bubble air diffusers, 3 – recycle sludge pump, 4 - coarse bubble air diffuser, 5 – membrane unit.

The influent treated by either the AS plant or by the MBR pilot was the effluent of the UASB reactor. Table 1 presents the quality of this influent. The average operating parameters of the AS plant and MBR pilot during the 7-month parallel experimental work are summarized in Table 2. Quality parameters such as COD, TSS, DO and MLSS were monitored daily while BOD, NH<sub>4</sub>-N and TP were measured twice per week. The analytical procedures were performed in accordance with the Standard Methods (1997).

**Table 1. Average characteristics of the MBR and AS influent (anaerobic effluent)**

Parameter	Value	Parameter	Value
1 pH	6.57 ± 0.18	6 TSS, mg/L	300 ± 120
2 Total COD, mg/L	910 ± 320	7 TKN, mg/l	30.9 ± 8.5
3 Total BOD, mg/L	430 ± 180	8 NH <sub>4</sub> -N, mg/L	4.3 ± 3.3
4 Ca Hardness, mg/l as CaCO <sub>3</sub>	420 ± 100	9 Total P, mg/L	10.2 ± 1.3
5 Alkalinity, mg/l as CaCO <sub>3</sub>	1100 ± 250	10 SO <sub>4</sub> , mg/L	68 ± 28

**Table 2. Average MBR and AS operating parameters**

Parameter	MBR (lab scale)	AS (full scale)
1 Flow rate, m <sup>3</sup> /day	30	6,100
2 Volume of basins, m <sup>3</sup>	24	8,500
3 HRT, hr	19	33
4 MLSS, gr/L	15	6
5 MLVSS, gr/L	8.7	4.1
6 DO in aeration basin, mg O <sub>2</sub> /L	3.0	2.5
7 F/M, kg BOD <sub>5</sub> /kg MLVSS * day	0.04	0.06
8 SOUR, mgO <sub>2</sub> /gr MLVSS * hr	5.7	6.1
9 SRT, days	24	31

## Results and discussion

Organic matter removal: Results of organic matter removal by AS and by MBR are summarized in Figs. 2, 3 and 4, expressed as COD and BOD. In Fig. 2 we can see that during all the experimental work period effluent COD concentrations were identical for both AS and MBR. The average effluent COD concentrations of AS and MBR were 105 and 102 mg/L, accordingly, with roughly similar fluctuation (Fig. 3). Similar results were also observed in terms of average BOD removal: 1-5 mg/L for MBR and 3-7 mg/L for AS.

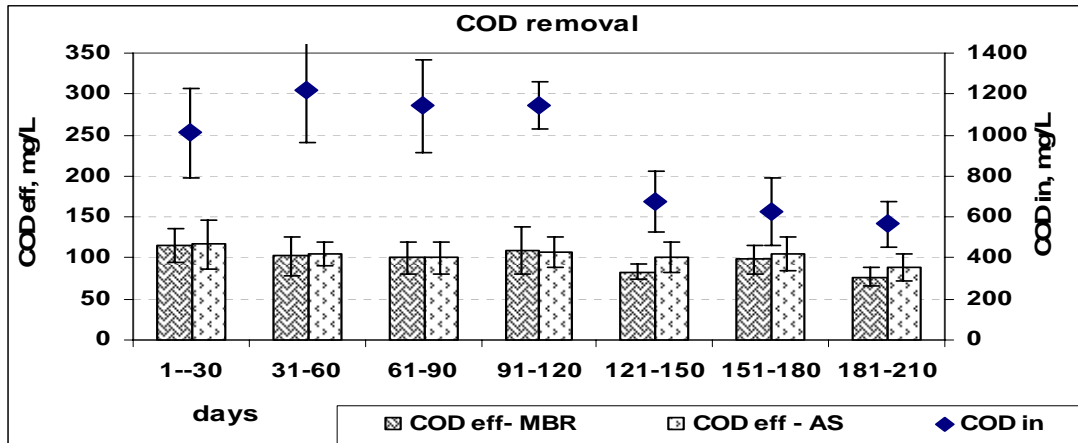


Figure 2. COD in influent and effluent of AS and MBR pilot

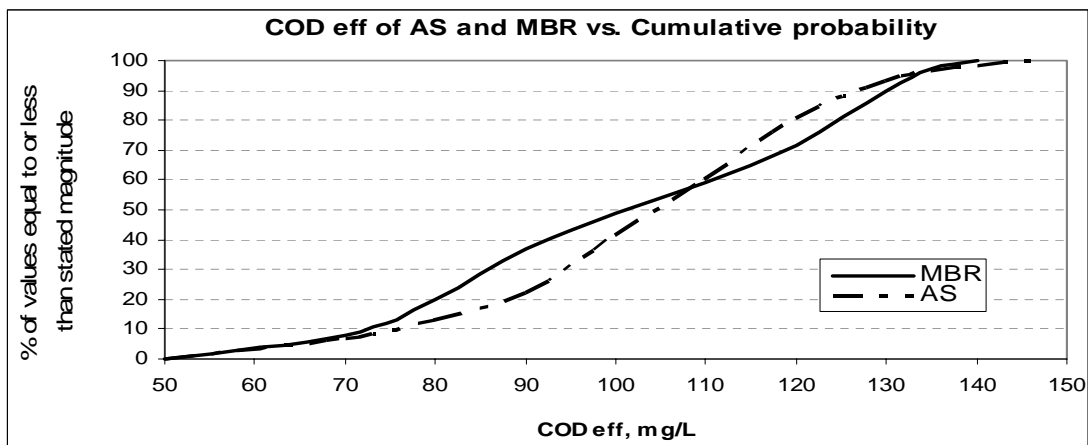
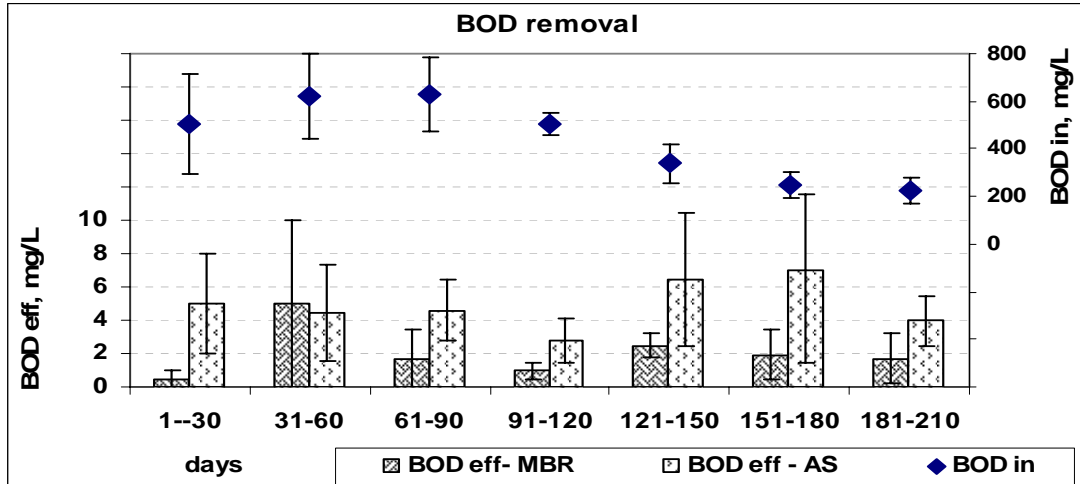
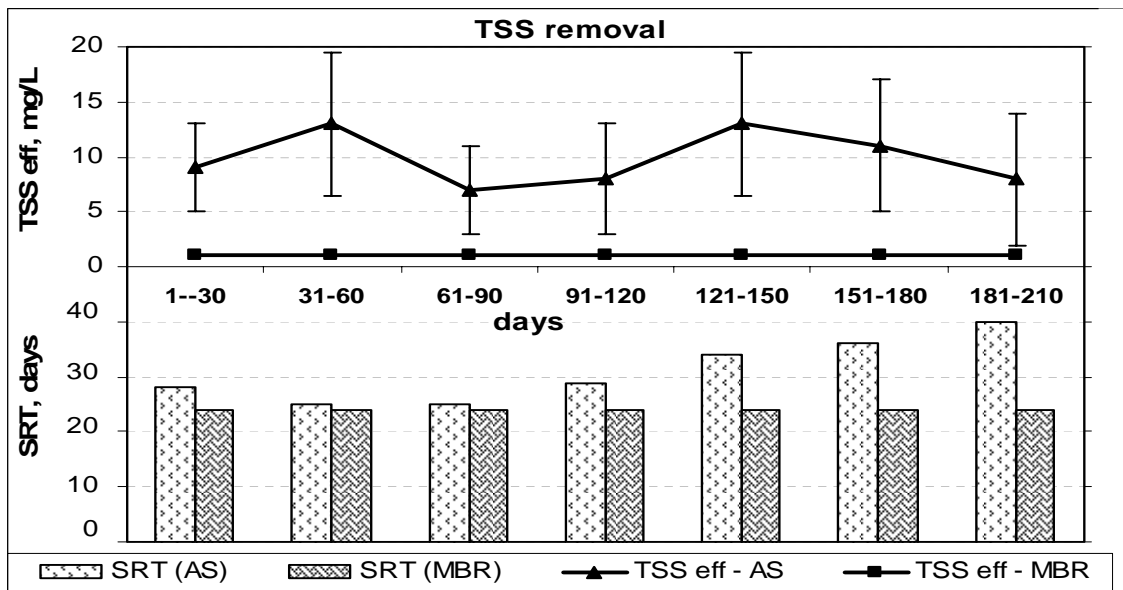


Figure 3. COD in effluent of AS and MBR pilot vs. Cumulative probability



**Figure 4. BOD in influent and effluent of AS and MBR pilot**

Suspended solids removal: Data summarized in Figs. 5 and 6 indicate that, as expected, MBR was dramatically more efficient than AS in the removal of the suspended solids. TSS removal efficiency of MBR was close to 100% during all the time, with effluent values equal to or less than 1 mg/L and without any fluctuation. The effluent TSS concentrations of AS varied from 6 to 13 mg/L, also indicating high fluctuations. It should be noted that the sludge residence time in the MBR was shorter than in AS (24 days vs. 25-40 days, based on average values). The higher MBR suspended solids removal effectiveness was the result of the fact that separation of biosolids by membranes is independent of the biosludge flocculation and settling ability.



**Figure 5. TSS in effluent of AS and MBR vs. SRT**

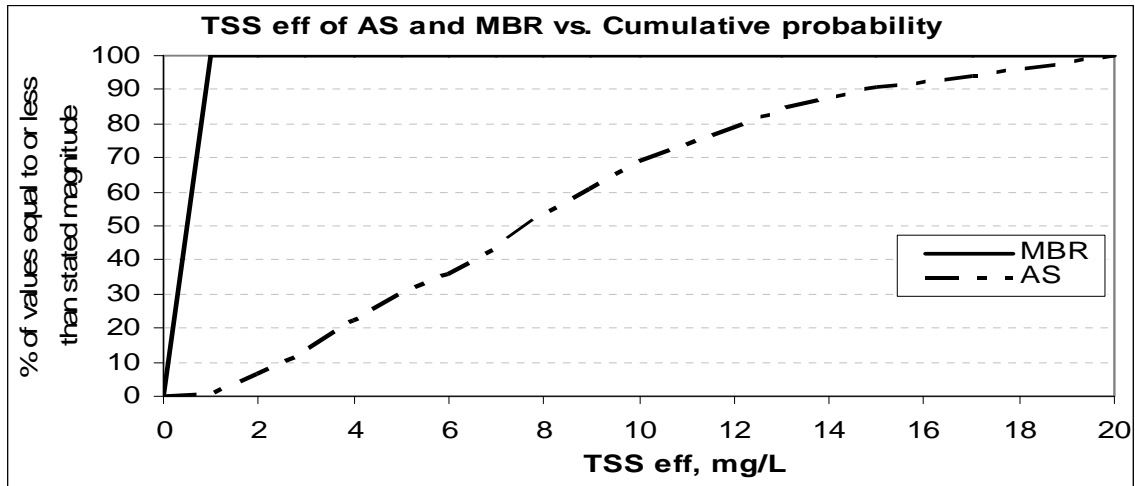


Figure 6. TSS in effluent of AS and MBR pilot vs. Cumulative probability

**Phosphorus removal:** According to the Israeli environmental regulations for paper industry, the average total phosphorous (TP) effluent concentration should not exceed 1 mg/L, therefore, TP removal obtained by the MBR pilot was checked in comparison with the AS. During the first three months of the MBR pilot operation, no special phosphorous removal methods were used, besides the bioprocess itself. In this period the effluent TP concentrations of MBR and AS were about 2-3 and 3-4 mg/L, accordingly (see Fig. 7). Since the effluent TP was higher than permitted by the regulations, ferric chloride solution (40%) was added to the aeration tanks of MBR and AS in order to reduce the effluent phosphorous concentration.

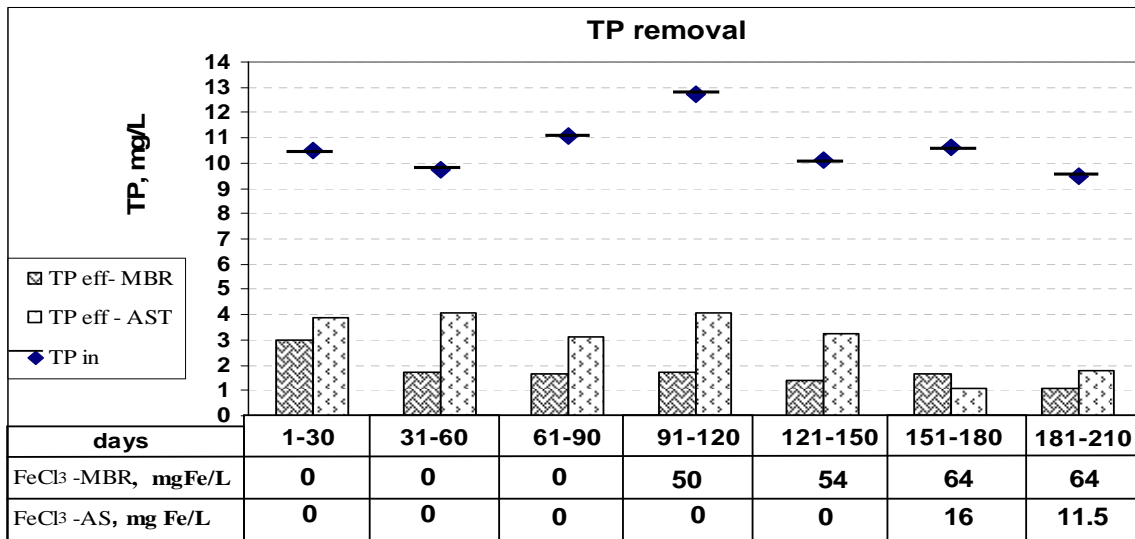
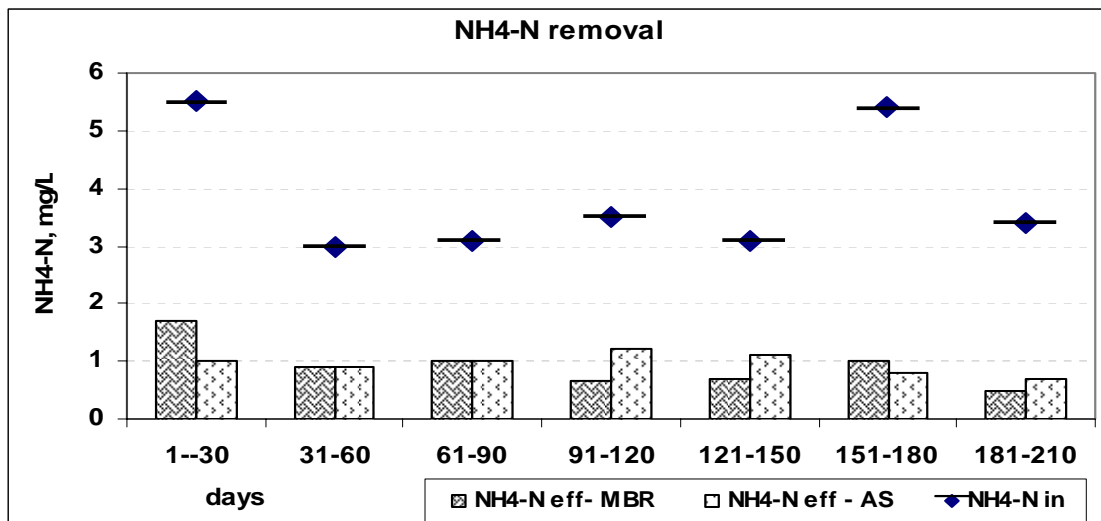


Figure 7. TP in influent and effluent of AS and MBR pilot.

Data in Fig. 7 indicate that in spite of the relatively high ferric chloride doses used for the phosphorous removal (from 50 to 64 mg Fe/L added to the MBR), the desired TP concentration (1.00 mg/L or less) could not be achieved. The same situation was observed in the AS with smaller doses of Fe. Apparently, considerable amounts of ferric chloride were wasted on the reaction with organic and inorganic compounds, which were presented in the mill wastewater. On the other hand, increasing Fe concentration

could damage the membranes and, therefore, 64 mg Fe/L was the maximum concentration used for the improvement of phosphorous removal.

**Nitrogen removal:** Fig. 8 presents results of nitrogen removal by AS and MBR in terms of ammonia nitrogen ( $\text{NH}_4\text{-N}$ ). It can be seen that  $\text{NH}_4\text{-N}$  effluent concentrations were similar for both AS and MBR systems (closed to 1 mg/L). Longer retention time of nitrifying bacteria in the AS bioreactor, and higher amounts of biomass (MLVSS) in the MBR did not substantially change nitrification efficiency in both bioreactors.



**Figure 8. Ammonia nitrogen in influent and effluent of AS and MBR pilot**

**MBR pilot operation problems:** At the beginning of the experimental work, several samples of MBR effluent indicated high total bacteria count (about  $2.9\text{-}6.5 \times 10^6$  CFU/ml). This phenomenon could be explained by the fact that during the first two months of MBR operation the chemical cleaning of the membranes was performed according with the MBR producer directives. This led to the formation of a bacterial layer on the membrane inner part. After implementation of membrane cleaning procedure with citric acid and sodium hypochlorite and increasing of the cleaning frequency (once per 2-3 weeks), the bacterial inner layer disappeared. As a result, bacteria concentration in the MBR effluent decreased.

An additional problem in the MBR operation was a sharp decreasing of the flux, due to sudden membrane plugging. Two reasons could be clearly observed: (a) non uniform air distribution into the membrane tank caused the total blockage of the gap between the membranes by biosolids, leading to diminishing of the membrane flow capacity; (b) the flux reduction was caused by the formation of a  $\text{CaCO}_3$  film on the membrane surface. During the transferring of the mixed liquor from the aerobic tank to the membrane tank of the MBR, a lot of extra carbon dioxide was stripped off by the vigorous circulation and airflow that locally causes calcium deposits due to the changes in pH. In order to solve the calcification problem, approximately 50% of untreated wastewater was moved directly from the Anoxic tank to the Membrane tank of the MBR. It allowed decreasing the calcium problem due to the stabilization of the  $\text{CO}_2$  equilibrium in the Membrane tank.

## Conclusions

The comparison of AS and MBR as the second bio-treatment stage following the anaerobic treatment of paper mill wastewater revealed that the MBR could produce an effluent of much better quality in terms of suspended solids. The very low and uniform TSS concentration in the MBR effluent could exclude the necessity of filtration in order to reach more stringent wastewater discharge standards. The other basic parameters (i.e. COD, BOD, TP and NH<sub>4</sub>-N) did not show substantial differences between AS and MBR.

The membrane blockage because of scaling and biofouling may be very serious for the MBR system. Therefore, the MBR requires frequent and more complicated maintenance than the AS system, especially in the case of paper mill, when calcium concentrations in wastewater are relatively high.

Lerner et al. (submitted) showed that application of the anaerobic pre-treatment significantly improved the performance of the aerobic AS conventional system treating paper mill wastewater. Therefore, if there is no need for the excellent effluent in terms of TSS, the replacement of the AS by the MBR, as a second biotreatment stage, might not be required in the case of paper mill wastewater anaerobic-aerobic treatment.

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