

Technical paper

Removal Efficiency of COD, Total P and Total N Components from Municipal Wastewater using Hollow-fibre MBR

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Received: 15-12-2010

Abstract

The membrane bioreactor (MBR) integrates well within the conventionally activated sludge system regarding advanced membrane separation for wastewater treatment. Over the last decade, a number of MBR systems have been constructed worldwide and this system is now accepted as a technology of choice for wastewater treatment especially for municipal wastewater. The aim of this work was to investigate and compare submerged MBR with conventionally-activated sludge system for the treatment of municipal wastewater in Maribor, Slovenia. It can be concluded from the results, that the efficiencies being determined by the parameters were satisfied, such as, chemical oxygen demand, total phosphorous, and total nitrogen, which were 97%, 75%, and 90%, respectively. The efficiencies of ultrafiltration membrane for the same parameters were also determined, and compared with biological treatment. The results of this analysis show an additional effect regarding an improvement in the quality of the permeate but primary treatment is also very important. For successfully application of MBR system smaller grid for primary treatment is needed.

Keywords: Municipal wastewater treatment, membrane bioreactor, membrane filtration, biological treatment

1. Introduction

The lack of fresh water is becoming an increasingly serious problem in many countries. This situation is being aggravated further by the pollution of fresh water resources, such as lakes, rivers, and water ground. This is due to the discharging of untreated wastewater from both industrial enterprises and municipalities, these being the main sources of water pollution. These problems have become worse since water ground reservoirs have also become exhausted.¹

Biological treatment is an important aspect for industrial and municipal wastewater treatment and reuse processes.² The most commonly used is the conventionally-activated sludge process (CASP). In order to improve the efficiency of CASP, much effort has been directed towards increasing sludge concentrations in bioreactors. However, a relatively low sludge concentration (2–4 g/L) is required to achieve a good settling-effect in the secondary clarifier.³ This limitation has been an inherent disadvantage of CASP.

The membrane bioreactor is one of the next generations of wastewater treatment processes to be developed from either CAS or trickling filter systems. Since the regulation of wastewater has noticeably increased in many countries, membrane bioreactors (MBRs) can be an attractive option for wastewater treatment.⁴ MBR is a new type of biological wastewater treatment, in which activated sludge treatment is directly combined with membrane technology.⁵ This process is characterized by the use of a membrane, either submerged or externally configured to a suspended growth bioreactor. This membrane retains biomass solids and macromolecules, and replaces the traditional sedimentation tank used in the conventionally-activated sludge process.⁵ Ultrafiltration membrane is able to retain up to 100% of the bacterial cell. As biomass accumulates in MBRs, nutrient concentration plummets to very low levels, thus providing better conditions for slow-

growing bacteria, such as the development of nitrifying bacteria to develop.⁶ Therefore, MBRs can provide complete nitrification and de-nitrification.⁷ A total nitrogen concentration in the effluent below 10 mg/L is attainable and even below 3 mg/L in warm climate. A recent study showed that MBRs sufficiently remove carbon, phosphorus, and nitrogen at 95%, 88%, and 89%, respectively.⁸ MBRs also offer several advantages when compared to conventional processes. Among other benefits, MBRs provide a lower footprint, lower sludge production, rapid start-up of biological processes, and high-quality effluent production.⁹ These acknowledgements were achieved over long years of MBR development but recently, after larger European projects, it was realized, that the numerous mentioned advantages of MBR technology are doubtful when considering the costs of its operational system.¹⁰ Despite these conclusions, interest in MBR processes has increased significantly over recent years. More than 400 MBR plants had been constructed by 2005, and about 300 references to industrial applications (> 20 m³/d) have been listed together with 100 municipal wastewater treatment plants (WWTPs > 500 p.e.). On average, the capacities of industrial applications are, in the order of magnitude, smaller than the municipal applications (median flows of 180 m³/d and 2500 m³/d, respectively). Over the coming years, at least 70 new MBR plants are predicted for construction, annually.¹¹ The research and commercial applications of membrane bioreactor technology are advancing rapidly around the world, for both municipal and industrial wastewater treatments.¹²

The aim of this paper was to study the submerged MBR treatment of municipal wastewater collected at the wastewater municipal treatment plant (WWTP) in Maribor, Slovenia, and the removal efficiency of organic components, such as chemical oxygen demand, phosphorous, and nitrogen. A pilot-scale hollow-fibre ultrafiltration unit was installed at the WWTP Maribor, Slovenia. The performance of a bench-scale membrane bioreactor, fed with real municipal wastewater, was operated over a total period of six months. The operation of this system was tested at different primary treatments of municipal wastewater samples. The operational conditions for both wastewater treatments were also studied.

2. Experimental

2.1. Materials and Methods

A pilot-scale UF membrane system was installed at the Maribor municipal wastewater treatment plant, Slovenia. The Maribor wastewater municipal treatment plant has a capacity of 195000 PE. The biological unit's treatment capacity is 5000 m³/h. This WWTP, with conventionally-activated sludge treatment, mainly receives domestic wastewater and a small portion of industrial wastewater. This treatment includes the tertiary treatments regar-

ding nitrification, de-nitrification, and enhanced phosphorous removal.

2.2. Physico-chemical Analyses

Chemical analyses of the samples commenced, on a regular basis, in the middle of May 2008, when optimal conditions were established, and when the system had been stabilized. The chemical demands of oxygen (COD), total phosphorus (TP), and total nitrogen (TN) from the inflow samples were monitored according to ISO standard methods.

In addition, the effluent nitrate (NO₃⁻) and ammonia concentrations (N-NH₄⁺), were also measured.

Chemical analyses were performed using Merck's tests.

Equation (1) was used for computing the removal efficiency (R_E).

$$R_E = \left(1 - \frac{\gamma_{j,i}}{\gamma_{j,v}} \right) \times 100\% \quad (1)$$

where:

R_E – efficiency (%)
 γ_{j,i} – effluent mass concentration of component j (mg/L)
 γ_{j,v} – influent mass concentration of component j (mg/L)

2.3. MBR-pilot Plant

The UF pilot system was a Zenon ZeeWeed-10 (ZW-10) outside/in a hollow-fibre 0.93 m² membrane. An ultrafiltration membrane retains particles larger than 0.04 μm. The MBR process operated continuously from March 2008 to August 2008 at the municipal WWTP in Maribor. The wastewater employed in this study was actual wastewater taken from the influent WWTP, and the characteristics of this wastewater are shown in Table 1.

A schematic view of the experimental system used in this study, is shown in Figure 1. The MBR system contained the biological sludge taken from the sludge return line at the wastewater treatment plant.

The process using a membrane bioreactor is composed of two primary parts, the biological unit responsible for the biodegradation of the waste compounds, and the membrane module for the physical separation of the treated water from mixed liquor.

The same conditions for hydraulic retention time (HRT) were achieved during our experiments, due to the fact that the WWTP worked on HRTs of 7 h and 30 h during the rainy and dry seasons, respectively. The MBR system was operated for six months, however, the time presented here was during May, June, and July 2008 and, therefore, a HRT of 20 h was established.

The biological unit (V = 35 L) consists of separate anoxic cells with average dissolved oxygen (DO) concentrations of 0.5 mgO₂/L and aerobic cells of average DO of

Table 1: Composition of the WWTP influent.

Parameters	May			June			July		
	COD (mgO ₂ /L)	TP (mg/L)	TN (mg/L)	COD (mgO ₂ /L)	TP (mg/L)	TN (mg/L)	COD (mgO ₂ /L)	TP (mg/L)	TN (mg/L)
Average	898.33	11.67	62.5	718.29	8.73	44.79	769	10.61	47.38
St. dev	75.40	1.47	7.81	262.44	2.23	21.61	195.30	2.90	13.04
Min	816	9.7	58	308	3.9	12	400	5.3	21
Max	1026	13.2	78	1188	12.4	78	954	14.6	59

5 mgO₂/L, thus providing the environment necessary for the biochemical oxygen demand (BOD) removal, the nitrification, and the de-nitrification processes, to occur. This oxidized and nitrified recycle stream is blended with raw sewage (carbon source) to allow de-nitrification to occur within the anoxic zone.

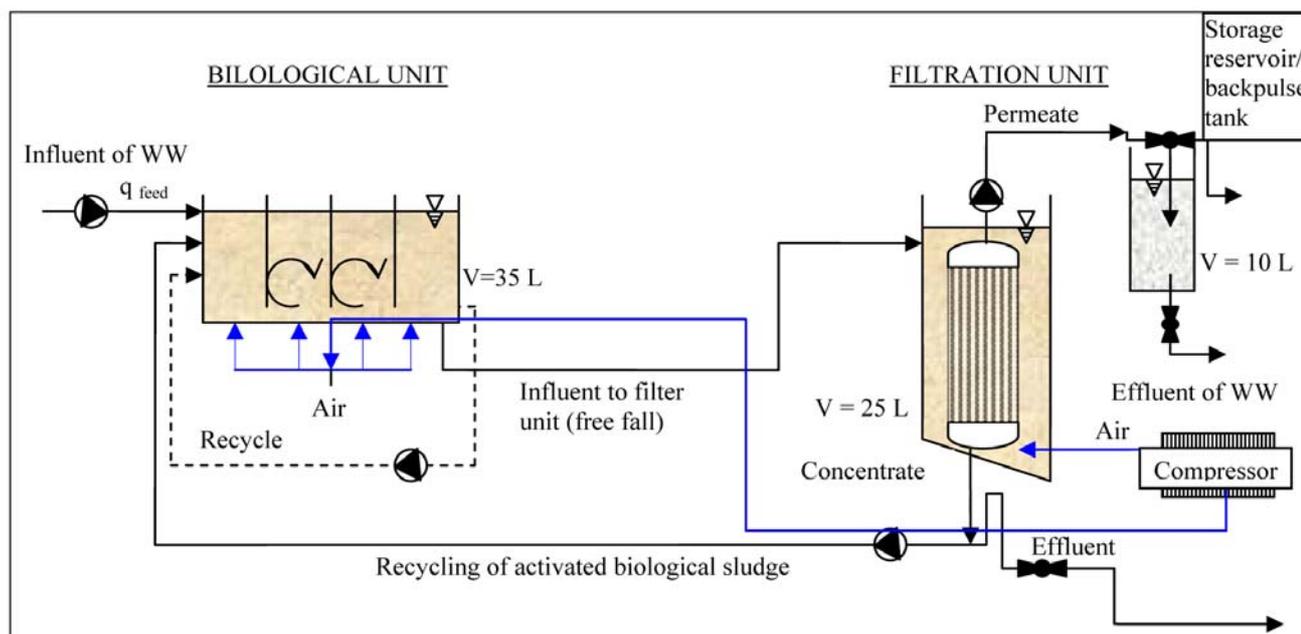
From the biological unit, the activated sludge flowed using gravity, to the filtration unit ($V = 25$ litres) where a membrane module with hollow-fibre was immersed. The influent flow was 3 L/h and the HRT achieved was 20 h, the same as the WWTP. A vacuum is applied to the module headers to draw the wastewater from the process tank through the membrane. Air is fed to the underside of the membranes to prevent solids from binding on the surfaces of the membranes. The average concentration of the DO unit was 5 mg O₂/L.

One 15 L backwash storage tank, filled with permeate is provided for the periodic backwashing of the membranes. Permeate is extracted by imposing negative pressure on the membrane. The operational cycles lasted 6 min, and included permeate extraction (5.5 min) and backwash (0.5 min).

3. Results and Discussion

The process was observed for a period of six months (March to August 2008) and during this period stable operational conditions could be seen within three months (May to July 2008). Therefore, this paper presents the results from May to July 2008. The measurements of physical parameters pH and the temperatures within the system, as well as the biochemical characteristics of the processes COD, TP and TN, were carried out in parallel on both the MBR and the WWTP. A comparison was also presented between both systems regarding COD, TP and TN using the same established HRT.

The same pretreatment was used for MBR because the WWTP for the primary treatment used grids of 10 mm. Although the inflow passed through a 10 mm screen prior to entering the MBR tank, a problem still occurred when holding the flow constant, due to pipe-blocking. A stable operation of MBR was not established. Therefore, an additional small 2 mm screen was used for mechanical pretreatment, after which the flow remained constant for the whole period when operating the MBR system. Prior

**Figure 1:** Schematic diagram of the MBR pilot plant.

to this grid removal, the pipes were constantly blocked and pipe-cleaning had to be carried out every second day. It is evident that the primary treatment of sewage is of particular importance for the successful operation of an MBR system. Most of the European MBR plants operate with 3–5 mm during stage I, and 0.5 mm during the stage II screen pre-treatment step.¹³

Once a stable flow has been established, activated sludge was added in the bio and filtration units. Activated sludge re-circulated from the last part into the first part of the bio-unit. The concentration of sludge in the MBR plant increased during the operation. Figure 2 shows the Mixed Liquor Suspended Solids (MLSS) concentration in MBR over the three months. The activated sludge added to the bioreactor was taken from the WWTP, and it took a short time to adjust to its new conditions.

A period of 25 days was needed for the microorganisms to adapt to the new operating conditions. The biomass concentration decreased during this period.

After the 25th day, MLSS continuously increased and reached a value of 9 g/L. A MLSS concentration of 9 g/l is normally expected, however, most pilot plants work with concentrations between 12 and 15 g/L. These values were not achieved due to membrane fouling. On the other hand, the conventional devices at WWTP have a common biomass concentration of activated sludge of around 4 g/L.⁴ This concentration for the MBR system was perhaps low, but when compared with conventional WWTP, it was higher.

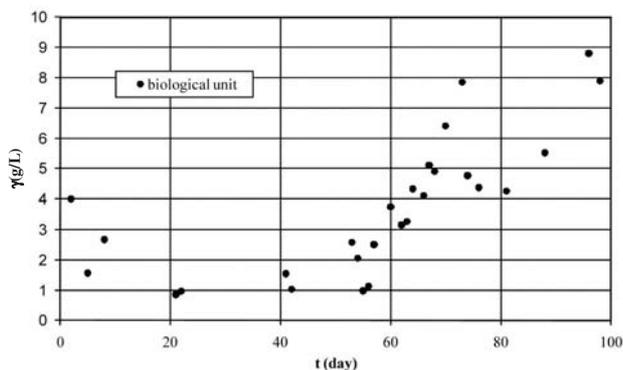


Figure 2: MLSS in the bio-unit during the operation.

3. 1. COD efficiency

The input and output values of the COD were monitored, as presented in Figure 3, during the period of stable operating conditions (from 30 to 100 days) when the biomass concentration of activated sludge was within a phase of stable growth (after the inoculation of MBR, decay of the biomass, and a period of stabilization under new conditions, from 0 to 30 days).

The COD values in the feed are somewhat higher than the usual values for municipal wastewater, and are

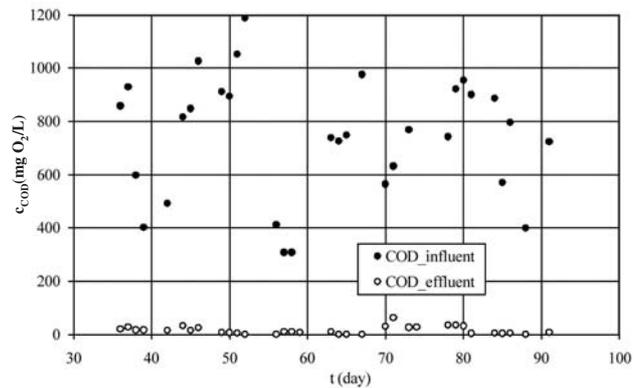


Figure 3: Chemical oxygen demand (COD) concentration measurements versus time.

within the range of 300–1200 mg O₂/L because the WWTP mainly receives domestic wastewater and a small portion of industrial wastewater. Despite this, the effluent COD values measured after the implementation process in the membrane bioreactor are satisfactory and in accordance with the regulations.¹⁴ The results of the removal efficiencies were calculated according to equation 1 and show that the removal efficiency of organic matter expressed as COD was the lowest at the beginning of the May, and grew during the remaining two months of the experiment. These efficiency improvements should be sought in the biomass concentration of the activated sludge, which during that period had gone through phases of adjustment after the inoculation of the bioreactor and the growth phase. Therefore, as an indicator of this assertion, the correlation between the observed parameters was done between the removal efficiency of the organic load with the biomass concentration within a membrane bioreactor. MLSS was determined every third day and the correlation showed the average monthly value of MLSS concentration for each month.

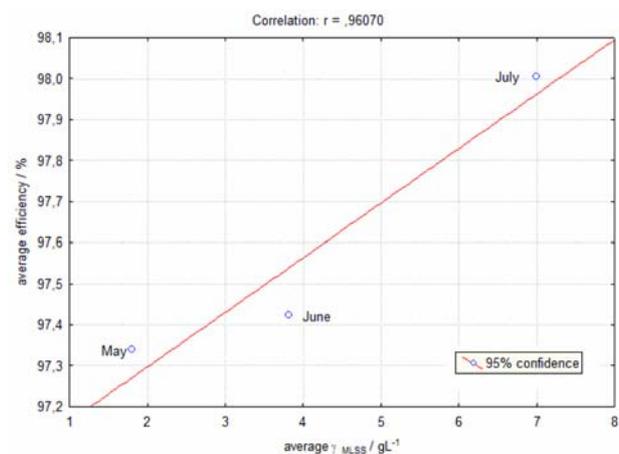


Figure 4: Correlation between monthly average removal efficiency and the average biomass concentration, MLSS.

The results of the correlation analyses for each month, are shown in Figure 4 where the positive correlation of $r = 0.9607$ can be seen. The average removal efficiency increased with any increase in the biomass concentration of activated sludge over a three month period of stable MBR operating conditions. As the average MLSS concentration increased from 1.8 g/l in May to 7 g/l in July, the efficiency regarding the removal organic matter as COD also increased from 97.3 to 98%, respectively.

3. 2. Total Phosphorus (TP) Efficiency

The total phosphorus concentration measured from day 35, is shown in Figure 5. Up to the end of the trial, the influent concentration varied between 8 and 15 mg/L, whilst the concentration decreased in the effluent. The effluent concentration still remained above 2 mg/L. In the period from 35 to 50 days, the concentrations were above 4 mg/L. No coagulants were used for additional chemical phosphorus removal. The removal of phosphorus can be related to the biological process of binding the phosphorus onto microorganisms in activated sludge. A low capacity when binding the phosphorous on the microorganism results in low removal efficiency. For better removal of phosphorus, the addition of coagulants into the process is necessary, or using the physico-chemical methods before MBR.

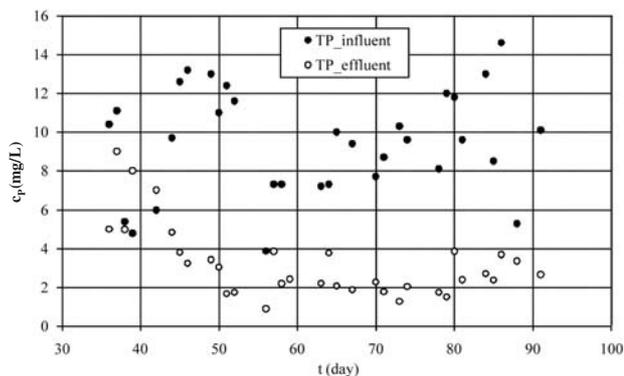


Figure 5: Total phosphorus (TP) concentration measurements versus time.

3. 3. Total nitrogen (TN) Efficiency

The total nitrogen (TN) components were measured as concentrations of $\text{NH}_4^+\text{-N}$, NO_3^- in the effluent, and total N in the influent and effluent over the three months of stable operation and by considering those processes of nitrification and de-nitrification that require special conditions (aerobic and anoxic), as presented in Figures 6.

The biological unit consisted of two parts, namely aerobic conditions ($\text{DO} = 5 \text{ mg O}_2/\text{L}$) were maintained in the first part, and the anoxic conditions (DO below $0.5 \text{ mg O}_2/\text{L}$) in the second part.

These conditions in the biological unit were favourable for the processes of nitrification and de-nitrification, which can be seen from the results when determining the N-parameters. After the initial phase of the adaptation and population growth of nitrifying bacteria, which depended on the concentrations of these bacteria within the activated sludge with which the MBR was inoculated, and on the quantity of inoculated sludge, a stable nitrification was established with very low concentration of total nitrogen at the exit from the MBR.

It can be seen from Figure 6 that, the concentration of NO_3^- decreased from 50 to 2 mg/L over the period from 35 to 50 day. This decrease showed a successful nitrification process. Within this period, the pH value also decreased from 7.6 to 6.7. After day 50, the $\text{NH}_4^+\text{-N}$ began to decrease to 0.01 mg/L. As can be seen, the nitrogen compounds in the effluent were mostly removed and nitrogen gas was formed, indicating stable nitrification behaviour.

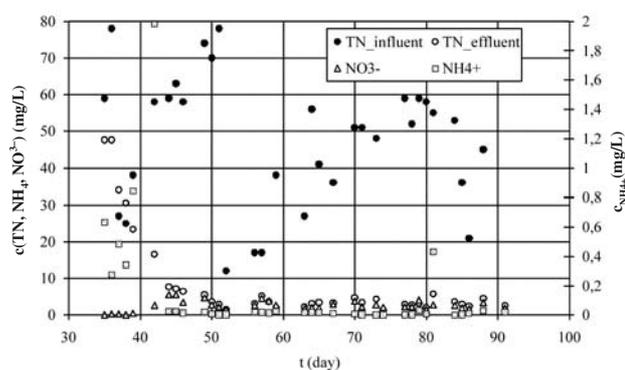


Figure 6: Total nitrogen (TN) concentration measurements versus time.

3. 4. Comparison of Efficient Removal of WWTP and MBR

Considering that the MBR process treated municipal wastewater which flowed to the WWTP Maribor for further treatment, it is reasonable to compare the effectiveness of this treatment between both systems. On startup, and during the operation of the MBR system, we tried to work and operate under similar or the same conditions as normal WWTP operating conditions (HRT).

Figure 7 shows the efficiency of treatment in the WWTP and by the process of MBR from 35 to 90 day. Treatment efficiency was compared for the chemical oxygen demand, total phosphorus, and the total nitrogen. The efficiencies of MBR treatment were higher than WWTP for COD and TN, being 97% and 90%, respectively, whilst the efficiencies of TP was lower (75%) than WWTP (95%), due to the pre-treatment (coagulation) used in WWTP.

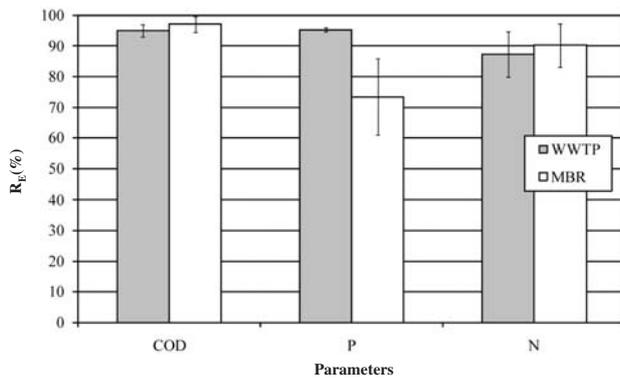


Figure 7: Comparison of the treatment efficiencies of certain parameters between the WWTP and MBR processes.

By considering the configuration of the MBR pilot plant consisting of two units, biological and filtration units, the analyses of removal efficiency was conducted for the COD, TP, and TN components for each unit. Only the results for June are presented (from the 49 to 77) days of operation, due to the stable nitrification process (Figures 8, 9 and 10).

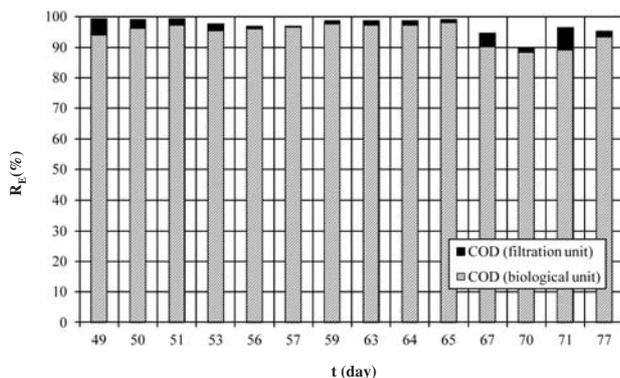


Figure 8: COD removal efficiency in bio- and filtration unit.

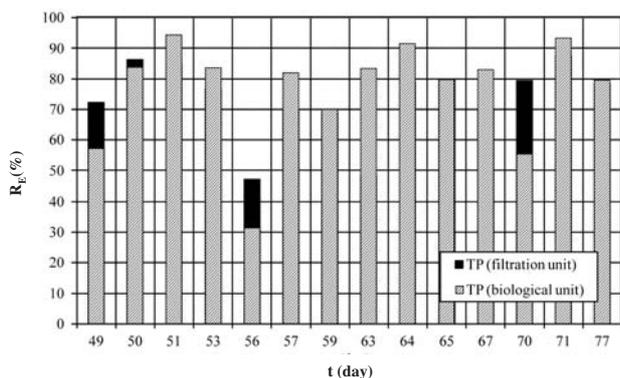


Figure 9: Total P removal efficiency in bio- and filtration unit.

It is obvious from Figure 8 that the COD removal efficiencies were achieved within the biological unit, whilst filtration improved the wastewater quality by up to 100%. Some fluctuation occurred during days 67 to 70 due to

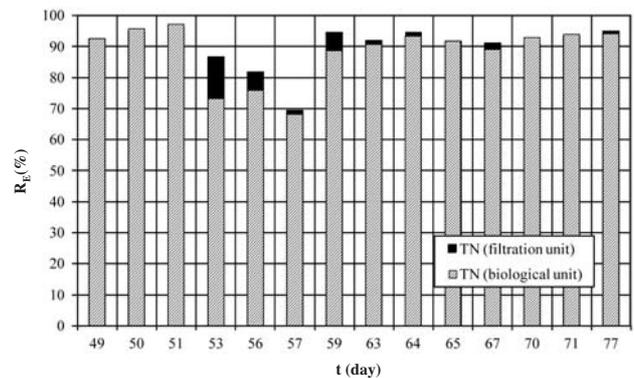


Figure 10: Total N removal efficiency in bio- and filtration unit.

heavy rain, and some time was needed to stabilize the system. The efficiencies were, therefore, a little lower.

The phosphorus removal efficiencies were between 50% and 90%. The enhanced phosphorus removal could be accomplished by configuring an anaerobic zone or by adding chemicals. It is obvious from Figure 10 that major nitrogen removal efficiencies were achieved within the biological unit, whilst filtration improved the wastewater quality, especially in the case where the biological treatment was poor. Ultrafiltration improved the efficiency by 10%. In accordance with other authors, the COD removal was constantly higher than 98% and the total nitrogen removal was between 90% and 95%.^{15,16,17} Only slight oscillation was observed in the concentration due to changing weather conditions (pH, T, influent flow, dilution of wastewater due to rainfall).

Although, biological phosphorus removal requires principally different operational conditions than total nitrogen (TN) removal, i.e. high biomass yields and short sludge retention times, its feasibility using MBR has been demonstrated.⁸

4. Conclusion

Over the last decade, the number of MBR systems constructed worldwide has risen exponentially, due to their advantages over conventionally-activated sludge systems. The aim of this work was to investigate the efficiency of submerged MBRs for municipal wastewater treatment and the removal of COD, N-component and P-component, and to compare its efficiency with the municipal wastewater treatment plant (WWTP) in Maribor, Slovenia. It can be concluded from the results, that the pretreatment is one of the most critical factors for guaranteeing a stable and continuous MBR operation. If only a 10 mm screen is used, the operation is still unstable, whilst at least 2 mm of sieving allows for the efficient pretreatment and stable operation of MBR. From the efficiency results for chemical oxygen demand and the total nitrogen, bet-

ween MBR and WWTP which varied from 90% to 99%, we can conclude that MBR system is very efficient and the operation is stable when using municipal wastewater. The phosphorus removal efficiencies were between 50% and 90%. and a comparison could not be done here due to the different pretreatment processes in WWTP.

5. References

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Povzetek

Membranski bioreaktor (MBR) za obdelavo odpadnih voda združuje prednosti konvencionalnega čiščenja z aktivnim blatom in napredne membranske filtracije. Po vsem svetu v zadnjem desetletju število postavitvev MBR sistemov izjemno narašča in s tem je ta nova tehnologija potrjena kot uspešna in učinkovita za obdelavo odpadnih vod, posebej komunalnih. Namen raziskave je bil razviti in primerjati učinek čiščenja MBR, ki ima vgrajeno potopljeno membrano, s konvencionalno čistilno napravo za obdelavo komunalnih odpadnih vod v Mariboru, Slovenija. Rezultati so pokazali, da je bilo čiščenje z MBR učinkovito, kar kažejo zadovoljive vrednosti parametrov kot so KPK, skupni fosfor in skupni dušik, katerih učinkovitosti znašajo 97 %, 75 % in 90 %. Za enake parametre smo raziskali učinkovitosti z uporabo UF membrane, ki smo jih primerjali z biološkim čiščenjem. Ugotovili smo, da membrana še dodatno prispeva k učinkovitosti, saj je kakovost permeata bila zelo visoka. Seveda pa je pomembno tudi primarno čiščenje, saj smo ugotovili, da za uspešno delovanje MBR sistema potrebujemo sita z manjšimi porami v primerjavi s konvencionalnim čiščenjem.