The efficiency of nitrogen removal in synthetic laundry wastewater using a submerged membrane bioreactor at different total nitrogen volume loadings and MLSS concentrations

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The aim of this study was to determine the effect of various total nitrogen volume loadings and various mixed liquor suspended solids (MLSS) concentrations in the submerged membrane bioreactor on the nitrification and the efficiency of nitrogen removal from soft synthetic wastewater. In the first part of the research the total nitrogen volume loading was increased from 0.063 to 0.315 g L^{-1} d^{-1}. The activated sludge was not removed from the reactor and therefore the concentration increased from the initial 4 g L^{-1} to a maximum value of 25.6 g L^{-1}. The results for removal of total nitrogen showed that the treatment effect was highest at the total nitrogen volume loading of 0.19 g L^{-1} d^{-1}, with 84 % removal efficiency. In the second part of the research the total nitrogen volume loading was held constant at 0.19 g L^{-1} d^{-1} and the MLSS concentrations were varied between 10 and 15 g L^{-1}. The results in this part of the research showed that nitrification did not occur when the activated sludge concentration was 10 g L^{-1} and that nitrification started when the activated sludge concentration increased. The research shows the connection between biomass concentration and nitrification degree in the MBR.
Key words: *membrane bioreactor; biodegradation; volume load; activated sludge concentration; nitrification*

1. Introduction

A membrane bioreactor (MBR) is a system that combines a reactor, in which the process of biological treatment occurs, and a membrane unit, in which the separation process of activated sludge and treated water occurs (Judd, 2006) [1]. The MBR allows a higher biomass concentration of mixed liquor suspended solids (MLSS) in the reactor, up to 40 g L^{-1}, while in the conventional biological treatment processes the biomass concentration is lower than 5 g L^{-1} (Marrot et al., 2004) [2]. MBR systems provide a lower rate biomass production at higher sludge age, shorter hydraulic retention time, high removal of solids and organic matter and good retention of activated sludge (Ersu et al., 2008) [3]. The system is also more flexible in comparison with the conventional treatment plants (Visvanathan et al., 2000) [4]. With higher MLSS concentrations the effective nitrification and denitrification can be achieved without extended aeration. The removal of nitrogen components from wastewater has become one of the most important concerns in water pollution control, since these components can be toxic to aquatic life and cause oxygen depletion and eutrophication in receiving water (Rađenović et al., 2008) [5]. The long sludge retention time (SRT) also increases the retention of microorganisms with relatively slow growth rates, such as nitrifying bacteria, thus promoting nitrification (Teck et al., 2009) [6]. Some authors believe that there should be a minimal rate of sludge waste in order to keep an optimal range of sludge concentration in the MBR. When no sludge is withdrawn from the reactor, accumulation of inorganic compounds can be expected (Rađenović et al., 2008) [5].

The pollution of laundry wastewater, which can be biodegradable (Altenbaher et al., 2010; Altenbaher et al., 2011) [7, 8], is dependent on the origin of the linen, the soil degree of the linen and the type of laundering process. Therefore, the aim of this study was to discover more information about the biological treatment of soft wastewater, which is also produced in industrial laundering processes. We investigated the difference in the efficiency of total nitrogen (TN) removal according to the constant and changeable biomass concentration used. This study aimed to offer useful information about the maximum total nitrogen volume loadings which can still be biodegradable and about the most appropriate MLSS concentration in the reactor for laundry wastewater. According to the results the optimal operation conditions of the MBR reactor for total nitrogen removal will be determined and this will provide basic information for the treatment of various polluted wastewaters from industrial laundries.

2. Material and methods

2.1. Experimental set-up

The membrane bioreactor consisted of an anoxic (V = 10 L) and an aerobic part (V = 30 L). In the aerobic part two chlorinated polyethylene flat sheet microfiltration membranes (Kubota) were installed, with a pore size of 0.4 μm and effective area of 0.1 m^2 per membrane. Aeration was provided continuously underneath the membranes so as to partially prevent membrane fouling and supply air to the bioreactor. The activated sludge used in the study was taken from an aerobic reactor at the local wastewater treatment plant (Maribor, Slovenia). The soft synthetic wastewater simulating laundry wastewater was prepared daily from a meat peptone (Fluka 70174) at a concentration of 1 g L^{-1} of distilled water. The properties of the synthetic wastewater are as follows: average pH =5.65; alkalinity < 50 mg/L). Wastewater inflow and filtration of treated water (permeate) was achieved by using two Masterflex L/S digital pumps. In order to prevent overflow, a level sensor was used to maintain a constant liquid level in the reactor by controlling the operation of the feed pump. The process scheme is noted in Fig.1.

2.2. Different total nitrogen volume loading

In this study synthetic laundry wastewater with a total nitrogen value (TN) of (112 ± 20) mg L^{-1} and COD of (505 ± 80) mg L^{-1} was supplied into the submerged MBR. The loading of total nitrogen was increased during the study with the change of the inflow (Q) from 1 to 5 L h^{-1} through 5 phases (Tab.1) noted as I to V and it was 0.063 do 0.315 g TN L^{-1} d^{-1}. According to the flow in different phases the following parameters were also determined: chemical oxygen demand (COD) and hydraulic retention time. All data is noted in table 1. The duration of each phase was different and was dependent on the adaptation of activated sludge to synthetic water by beginning with low concentrations for adaptation, followed by increased concentration of synthetic wastewater and extended adaptation time. During a three month period (172 days) for each phase

Tab.1 Operating conditions during different total nitrogen volume loading

Parameter	Phase I	Phase II	Phase III	Phase IV	Phase V
Q (L h^{-1})	1	2	3	4	5
TN (g L^{-1} d^{-1})	0.063	0.126	0.19	0.252	0.315
COD (g L^{-1} d^{-1})	0.317	0.634	0.954	1.268	1.585
HRT (h)	40	20	13.3	10	8

Where Q means flow, TN means total nitrogen, COD means chemical oxygen demand and HRT means hydraulic retention time

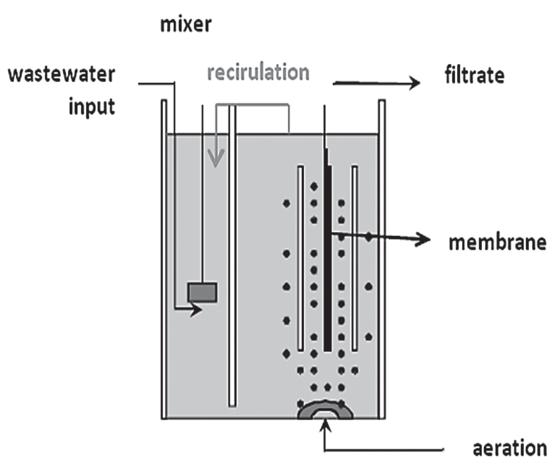

Fig.1 Process scheme of laboratory membrane reactor

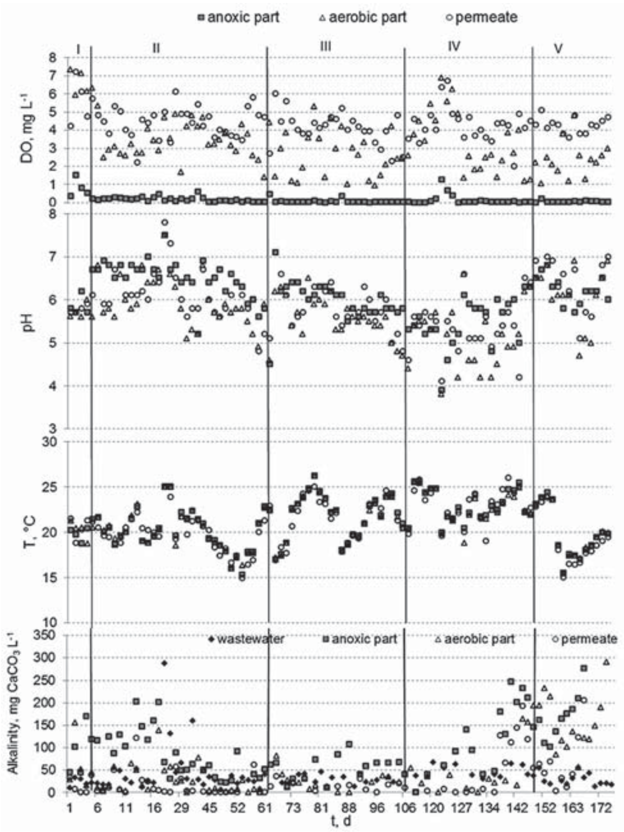

Fig.2 Daily measurements of DO, pH, T and alkalinity in wastewater, anoxic part, aerobic part and permeate for each phase at different total nitrogen volume loading (DO= dissolved oxygen

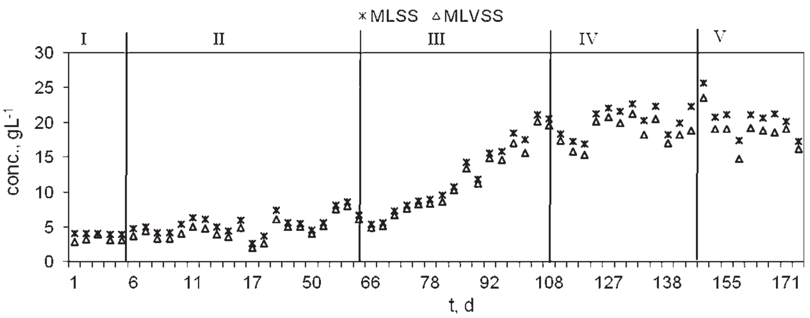

Fig.3 MLSS and MLVSS concentrations for each phase at different total nitrogen volume loading (MLSS = mixed liquor suspended solids, MLVSS = mixed liquor volatile suspended solids)

with different total nitrogen loading the following parameters were determined:

- dissolved oxygen (DO), pH, value, temperature and alkalinity (Fig.2) for each phase in anoxic part, aerobic part and permeate;
- MLSS and MLVSS concentration (Fig.3) and TN removal and COD removal in wastewater (Fig.4) for each phase;
- ammonium, nitrite and nitrate concentrations (Fig.5) for each phase in wastewater, anoxic part, aerobic part and permeate.

2.1. Fixed activated sludge concentrations

In the second part of the research the effect of three different MLSS concentrations (10, 12.5 and 15 g L^{-1}) on the nitrogen removal efficiency were tested. The total nitrogen volume loading was held constant at 0.19 g L^{-1} d^{-1}. The results from this part of the research indicated the most appropriate MLSS concentration for a MBR plant used for laundry wastewater. The following parameters were determined during a 107 days period:

- dissolved oxygen (DO), pH, value, temperature and alkalinity (Fig.5) in anoxic part, aerobic part and permeate for each MLSS concentration in anoxic part, aerobic part and permeate;
- TN concentration in wastewater and permeate (Fig.6) for each MLSS concentration;
- ammonium, nitrite and nitrate concentrations (Fig.7) for each MLSS concentration in wastewater, anoxic part, aerobic part and permeate.

2.1. Analytical methods

The effects of the treatment were followed by determination of the COD (SIST SIST ISO 6060) [9], total nitrogen (SIST EN 12260) [10], ammonium (SIST ISO 5664) [11], nitrite (SIST EN 26777) [12] and nitrate (SIST ISO 7890-1) [13] for influent, anoxic part, aerobic part and permeate. The samples from the reactor were filtrated through filter paper with a pore size 3-5 μm. Alkalinity (SIST ISO 9963-1) [14], temperature (SIST DIN 38404-4) [15], dissolved oxygen (DO) (SIST EN 25814) [16] and pH (SIST ISO 10523) [17] were measured daily. MLSS/MLVSS concentrations (SIST ISO 11923) [18] were measured three times per week.

3. Results and discussion

3.1. Different volume loading of total nitrogen

3.1.1. Operational conditions at different loading of total nitrogen

DO concentration (Fig.2) in the aerobic part was always above 1 mg L^{-1}, and occasionally even higher than 3

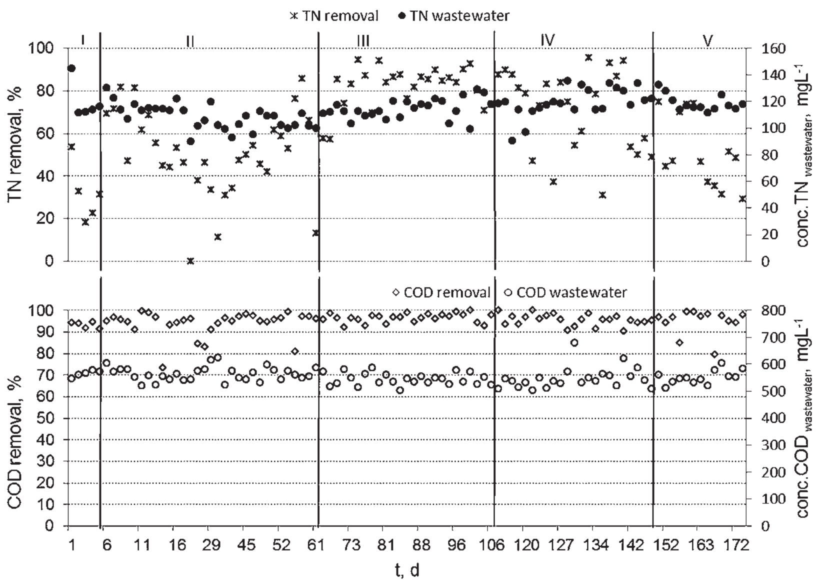

Fig.4 TN and COD removal efficiencies and concentrations in wastewater for each phase at different total nitrogen volume loading (TN = total nitrogen, COD = chemical oxygen demand)

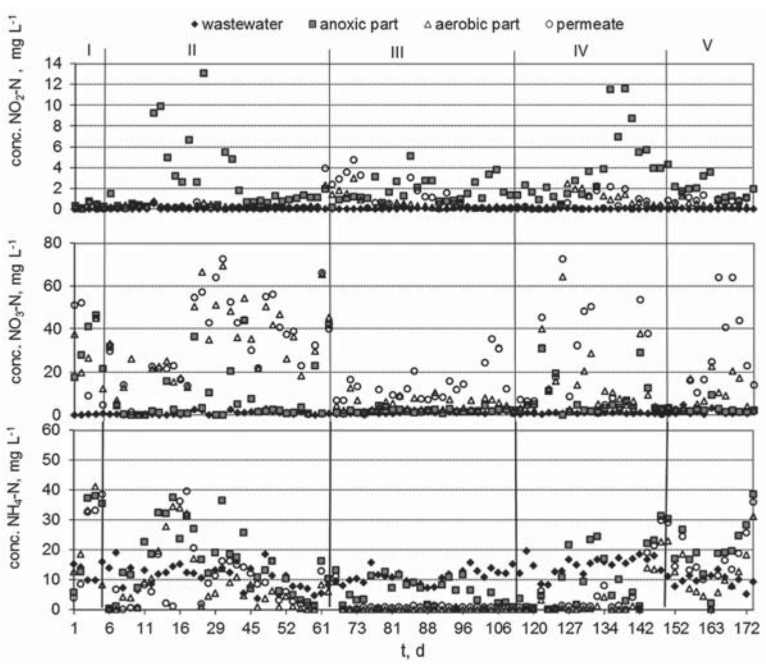

Fig.5 Ammonium, nitrite and nitrate concentrations for each phase at different total nitrogen volume loading

mg L^{-1} which, in essence, does not improve the effect of treatment, but only increases the aeration costs, although on the other hand too low a concentration can lead to growth of filamentous bacteria in the activated sludge (Roš, 2001) [19]. The concentration of DO in the anoxic part was always below 0.5 mg L^{-1}, except in three cases when the aeration diffusers passed into this part of the reactor.

During the study the pH value was low between 3.9 and 7.1 for the anoxic part and between 3.8 and 7.5 for the aerobic part of the reactor. Incomplete nitrification in this part of research could also be the consequence of low pH values. When the pH value is outside the range between 7.2 and 8.5, the metabolism of autotrophic microorganisms is impaired (Marsili-Libelli and Tabani, 2002; Rađenović et al., 2008) [20, 5]. The pH is very important for biological treatment, whereas microorganisms remain sufficiently active only in a narrow pH range between 6.5 and 9. Outside this area the biological activity can be inhibited or even stopped. Nitrification reactions are also particularly sensitive to pH. During the nitrification process the pH value can be reduced to such an extent due to the formation of mineral acids that the biological activity is inhibited (Roš, 2001) [19].

Temperature was measured daily and was between 15.3 and 26.2 °C (Fig.2) which is suitable for an optimal performance of the MBR (Rađenović et al., 2008) [5].

The alkalinity of the wastewater was due to the use of soft water very low (below 50 mg $CaCO_3$ L^{-1}), except on the 25th, 26th and 36th days of treatment, where the softening device was out of order and tap water was used (Fig.2). Henze et al. (1995) [21] reports that the nitrification process reduces the alkalinity in water and this is essential for the nitrification of relatively soft water where the pH in the water can be so low that the nitrification process is limited or stops completely. Incomplete nitrification in this research could also be the consequence of using soft wastewater and, therefore achieving low alkalinity in the reactor.

3.1.2. MLSS/MLVSS concentrations at different loading of total nitrogen

During the operation the activated sludge was not removed from the reactor and therefore the concentration increased from the initial 4 g L^{-1} to the highest value 25.6 g L^{-1} on the 141st day of operation (Fig.3). For the first six days of operation the MLSS concentration was constant, the initial growth phase started at a phase II and then reached the highest level (from 5 g L^{-1} to 21 g L^{-1}) at a total nitrogen

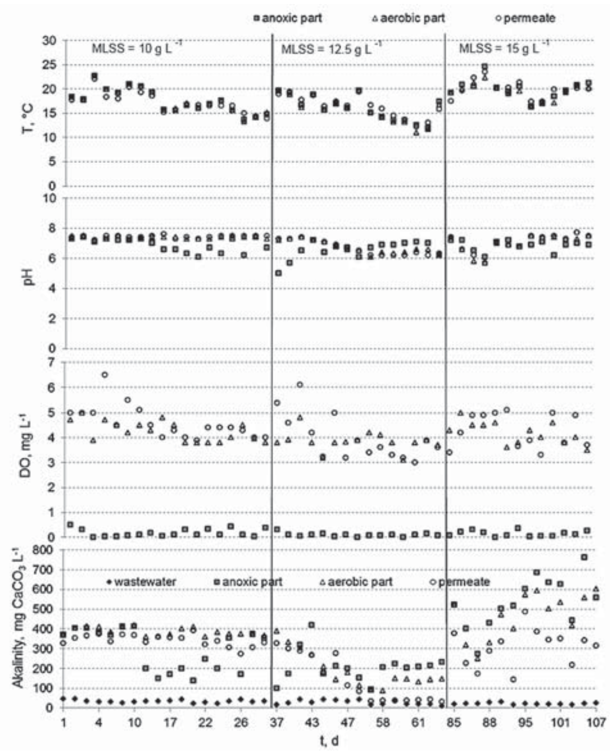

Fig.6 Daily measurements of DO, pH, T and alkalinity in wastewater, anoxic part, aerobic part and permeate at different MLSS concentrations (DO = dissolved oxygen, MLSS = mixed liquor suspended solids)

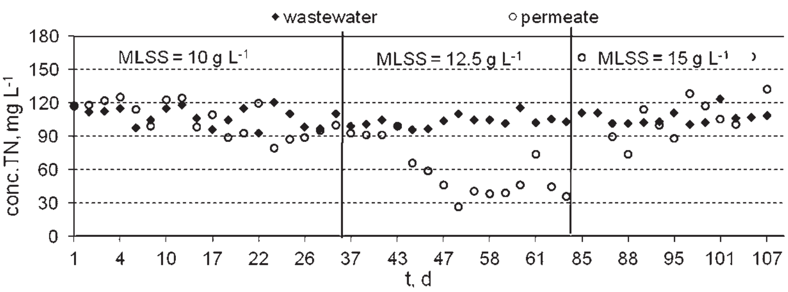

Fig.7 Total nitrogen (TN) concentration in wastewater and in permeate at different MLSS concentrations (MLSS = mixed liquor suspended solids)

volume loading of 0.19 g L^{-1} d^{-1} (phase III). Later, the growth of activated sludge was reduced and the MLSS concentration was on average 20 g L^{-1}. Similar findings were observed for MLVSS (Mixed liquor volatile suspended solids) concentrations with an average of 25 g L^{-1}.

3.1.3. Total nitrogen and COD removal at different loading of total nitrogen

Nitrification is the primary important process in removing the total nitrogen content from wastewater. Incomplete nitrification decreases the TN removal efficiency of the system (Rajesh Banu et al., 2009) [22]. The removal results for COD in the treatment process showed that the effect of treatment was very high for all phases and it was 93, 94, 97 % for phases I-III and 95 % for phases IV and V (Fig.4).

The removal results for total nitrogen (Fig.4) in the treatment process showed that the effect of treatment was highest at phase III, where the concentrations of total nitrogen in permeate were on average 19 mg L^{-1}, and the removal efficiency of the total nitrogen was 84 % for synthetic laundry wastewater. The effect of treatment was lower for the other phases and it was 31, 51, 68 and 49 % for phase I, II, IV and V respectively. The results showed higher nitrogen assimilation into biomass (lower NO_3 concentrations) in phase III, where the MLSS concentration also increased. Because the MBRs operated in a long SRT the sludge yield was often very low. Thus, the contribution by assimilation to the TN removal would be low and nitrification-denitrification would play a more important role in the removal of nitrogen from wastewater.

Fig.5 explains nitrification processes in the MBR system. The results indicate that the nitrification process was very good in phase III, where all the ammonia was oxidized completely. Henze et al. (1995), reports that nitrite will only appear in a large amount when the considered process is nonstationary, for example because of varying loads, washout or other operational problems in the treatment plants. Therefore, the changing total nitrogen volume loading (from phase to phase) could be the reason for the increase and subsequent decrease of nitrite concentration in the aerobic part of the reactor. DO concentration in the range between 0.3 and 0.5 mg L^{-1} is suitable for partial nitrification (Xue et al., 2009) [23], therefore this could be the reason for the occasional higher amount of nitrite in the anoxic part of the reactor.

The results from the first part of the research show that, in spite of the very low alkalinity of soft wastewater, the nitrogen removal efficiency can still be high. The effect of the treatment is largely dependent on the increment concentration of activated sludge, because as this research pointed out, the efficiency is lower when biomass concentration is nearly constant. Nutrient assimilation into biomass is therefore very important and it should be taken into the consideration during treatment with MBRs

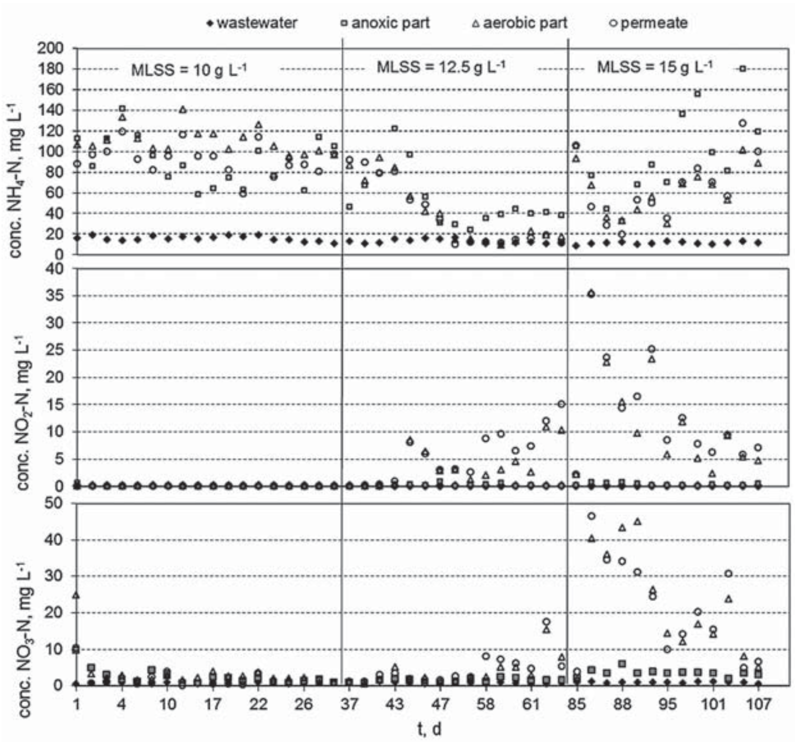

Fig.8 Ammonium, nitrite and nitrate concentrations in wastewater, anoxic part, aerobic part and permeate at different MLSS concentrations (MLSS = mixed liquor suspended solids)

where very long SRTs are used and therefore sludge yield is low.

3.2. Fixed MLSS concentrations

3.2.1. MLSS concentration and volumetric load

MLSS concentration was measured daily and was held constant at 10 g L^{-1}, 12.5 g L^{-1} or 15 g L^{-1} with a deviation of 0.5 g L^{-1}.The surplus activated sludge was withdrawn. Different volumetric loads were tested with synthetic wastewater where different peptone concentrations were added to achieve different nitrogen concentrations.

3.2.2. Operational conditions during fixed MLSS concentrations

T, pH, DO and alkalinity were also measured during this part of the research (Fig.6). The temperature in the reactor was between 10 and 25 °C, the pH value was between 5 and 7.4 in the anoxic part and between 5.7 and 7.5 in the aerobic part, and the DO concentration was below 0.5 mg L^{-1} in the anoxic part and above 3 mg L^{-1} in the aerobic part. Although the composition of synthetic wastewater yielded low alkalinity of wastewater, the alkalinity in the anoxic part of the reactor ranged between 100 and 450 mg $CaCO_3$ L^{-1} when the MLSS concentration was 10 and 12.5 g L^{-1} respectively and up to 760 mg $CaCO_3$ L^{-1} when the MLSS concentration was 15 g L^{-1}. When nitrification began (at MLSS concentration 12.5 g L^{-1}), the alkalinity was significantly lower and when alkalinity lowers it causes a drop in the pH and a lower efficiency of the process (Henze et al., 1995) [21].

3.2.3. Nitrogen removal during fixed MLSS concentrations

The daily values of nitrogen components showed no nitrification at the MLSS concentration 10 g L^{-1} and incomplete nitrification at the MLSS concentration 12.5 g L^{-1} and 15 g L^{-1} (Fig.7). The maximal TN removal efficiency was at MLSS concentration 12.5 g L^{-1} where it was 41 % compared to the concentrations 10 g L^{-1} and 15 g L^{-1} where it was maximally 34 % and 27 %, respectively (Fig.8) and which is, however, less than other researchers achieved (Fu et al., 2009; Rajesh Banu et al., 2009; Teck et al., 2009) [24, 22, 6]. Dong et al. (2009) [25] reports that the total nitrogen removal may also depend on the concentration of dissolved oxygen in the reactor and that with an increase in DO concentration from 0.1 mg L^{-1} to 2 mg L^{-1} the TN removal increases greatly, but at a DO concentration of 4 mg L^{-1} the efficiency is reduced significantly. A similar effect was achieved in this research between day 43 and 68, when the DO was below 4 mg L^{-1} and the TN concentration in the permeate was significantly lower (Fig.6 and Fig.8).

According to the results in the second part of the research, it could be concluded that, with daily withdrawal of the surplus activated sludge, the nitrification was low when the MLSS concentration was 10 g L^{-1} and therefore the decrease in TN concentration was the consequence of the assimilation into biomass. With increasing MLSS concentration, the degree of nitrification increased and therefore the nitrate concentration in the aerobic part was high. Better TN removal efficiency could be achieved with internal recycling from the aerobic to the anoxic part of the reactor, which would reduce the nitrate concentration in the effluent (Baeza et al., 2004; Ersu et al., 2008) [26, 3] and this will therefore be a subject for further research.

4. Conclusions

The anoxic/aerobic membrane bioreactor was in the first part of the research operated under longer SRT and with five different total nitrogen volume loadings for synthetic laundry wastewater. The removal results for total nitrogen in the treatment process showed that the removal efficiency had increased at the total nitrogen volume loading 0.19 g L^{-1} d^{-1}, where it was more than 84 %, and the concentration of total nitrogen in permeate was on average 19 mg L^{-1}. However, this has also been achieved because nitrogen was assimilated into the biomass. With further increase in volume loading, the removal efficiency decreased because the MLSS concentration was almost constant.

In the second part of the research the reactor operated with three different MLSS concentrations, while the total nitrogen volume loading was held constant at 0.19 g L^{-1} d^{-1}. Results from this part of the research showed that the MLSS concentration in the reactor is a very important parameter and when increasing in volume loading the MLSS concentration must also be increased otherwise lower nitrification will be observed. However the pH values are also important for nitrification, but because in this part of the study they were almost in the optimum range and should not have a negative impact on nitrification. Membrane bioreactors operate at high concentrations of activated sludge leading to lower sensitivity, thus highly polluted waters can be successfully treated than during classical treatment processes. However, since high active sludge concentrations can cause membrane fouling, and optimum needs to be found.

For the treatment of synthetic laundry wastewater with an MBR there should be a balance between the MLSS concentration and volume loading which will assure appropriate efficiency as was shown with the results at the burden of 0.19 g TN L^{-1} d^{-1} the MLSS concentration of 10 mg/l active sludge was too low to enable nitrification.

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