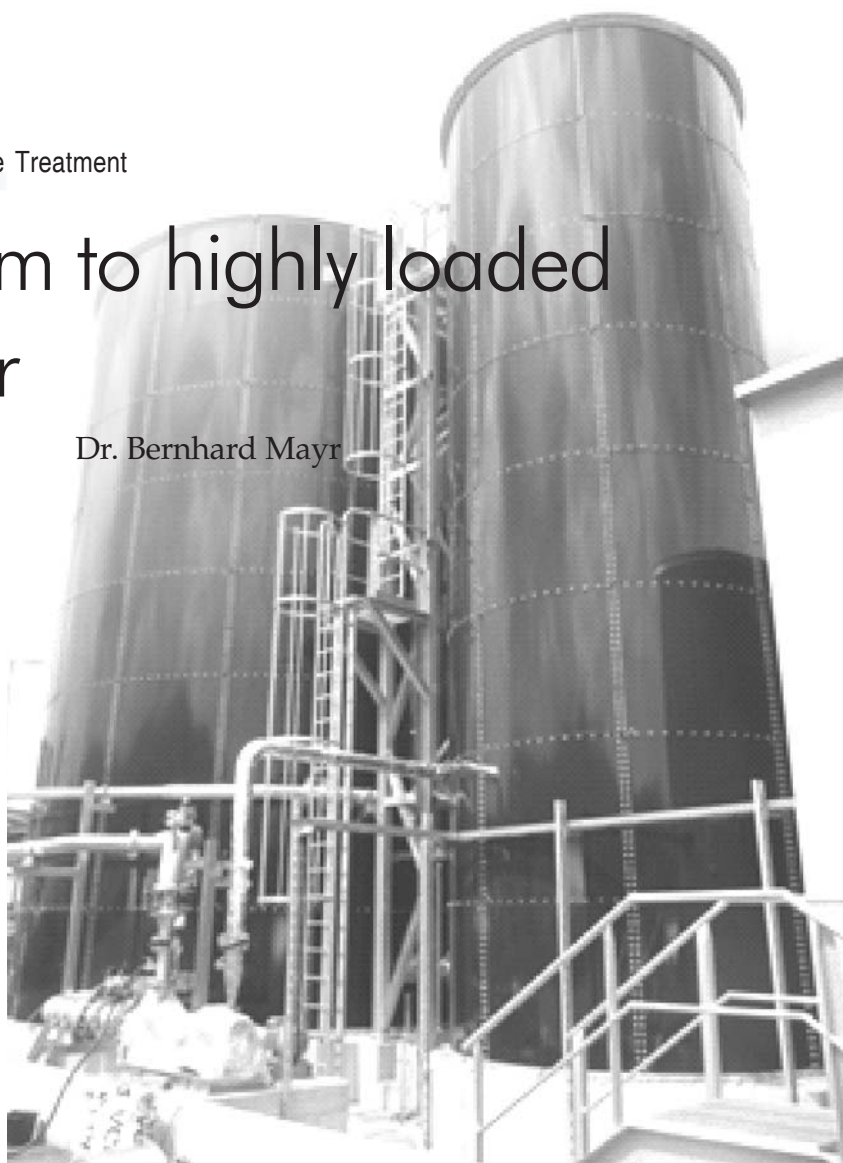


Applying MBR-system to highly loaded organic waste water

Dr. Bernhard Mayr

In the paper practical experience from large scale case studies of Membrane Bioreactor (MBR) systems is presented. In the first case, a full scale MBR installation to treat highly loaded landfill leachate is described. In the second case, a MBR plant to clean strongly concentrated waste water from renewable fuel production and from an animal fat refining is presented. Energy from the biological oxidation process, the influence of ammonia effluent concentration, nutrient supply, foaming and the feasibility of anaerobic pre-treatment are discussed in this paper. Long term behavior of cross-flow membranes is shown as well.



Introduction

MBR systems are well known and established for a wide range of applications. Due to the ability to adjust and control sludge age and to decouple hydraulic and sludge residence time it is possible to reach high degradation rates even for hard organic compounds (expressed as chemical oxygen demand - COD) which are present e.g. in landfill leachate. The cross-flow membrane separation process demands more energy than conventional sludge sedimentation. If highly concentrated organic waste water is processed, the energy demand for oxidizing organic compounds becomes significant also in terms of operating costs and therefore an anaerobic pre-treatment is often considered as an alternative.

In this paper, practical experience from two projects is presented. First case describes a full scale MBR installation to treat landfill leachate with a COD concentration of 25.000 mg/l and an ammonia concentration of 4.000 mg/l. Landfill leachate is produced as a result of the anaerobic

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microbial degradation and compression of solid waste on landfills and it is characterized by high organic and ammonium concentration. Organic compounds in waste water have been treated successfully by the activated sludge process. A removal of ammonium and organic nitrogen compounds by the combined aerobic and anoxic biological treatment (so called nitrification/denitrification process) has been widely integrated in biological treatment processes. The elimination of high nitrogen content by means of the conventional nitrification/denitrification regime asks for a sufficient supply of carbon source during the anoxic phase. Therefore an anaerobic pre-treatment was not taken into account, since it would deplete easily degradable carbon (expressed as biological oxygen demand - BOD).

In the second case, a MBR plant to clean waste water from renewable fuel production and a used fat refining plant (with an average COD concentration of 150.000 mg/l and poor nutrient content) is presented. In this case two reasons were responsible to consider a MBR installation. Firstly, the low emission limit for COD required a biological degradation process and secondly, a straight forward approach with minimal process components was a pre-condition, in order to keep operating costs low and process reliability high.

Materials and Methods

In this paper, results from theoretical designs based also on simulation models and from laboratory and pilot testing stage are compared to data obtained from start-up of the full scale plants.

MBR for leachate treatment

The following pictures show some process equipment of

the waste water treatment plant.

Pilot Plant

The pilot plant combined biological wastewater treatment via denitrification and nitrification processes with ceramic cross-flow microfiltration (MF), to separate the purified water from the biomass. A reverse osmosis (RO) unit was used to polish the effluent to ensure the stipulated emission limits. The experimental setup consisted of two separated tanks with a total capacity of 0.62 m³. 0.15 m³ of the total capacity was used as primary anoxic denitrification and 0.47 m³ was used for successive oxidative nitrification process.

Large Scale implementation

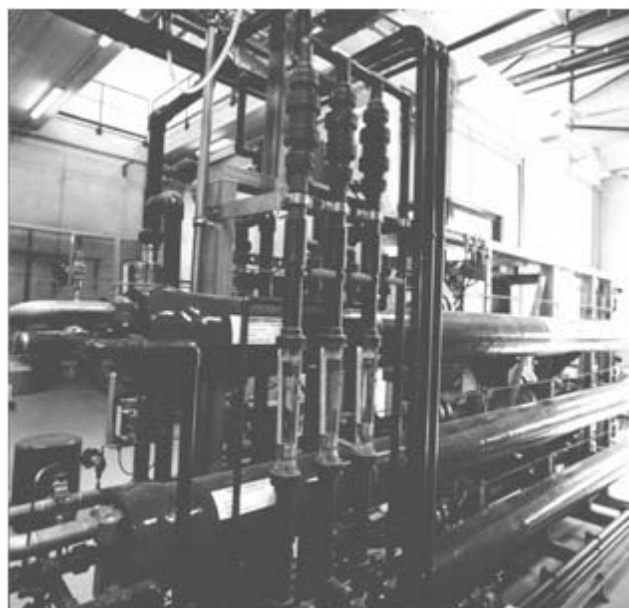
The design of the large scale plant was based on the results of pilot testing in respect to membrane flux and sludge load of the bioreactors. The biological leachate treatment was performed in non-pressurized bioreactors (**Figure 1**). Leachate was supplied to the upstream anoxic denitrification tank. Oxygen from nitrate was used to digest easily degradable organic compounds while ammonia flows through this tank largely unchanged and reaches the jet-aerated nitrification tank. Aerobic conditions prevailing in this tank, oxidized ammonia to nitrate and carried out aerobic metabolism of COD compounds.

The main characteristics of the large scale plant were as follows:

- Throughput: 100 m³/d
- Denitrification: one tank with 130 m³ operated in plug



Ceramic cross-flow microfiltration



Reverse Osmosis

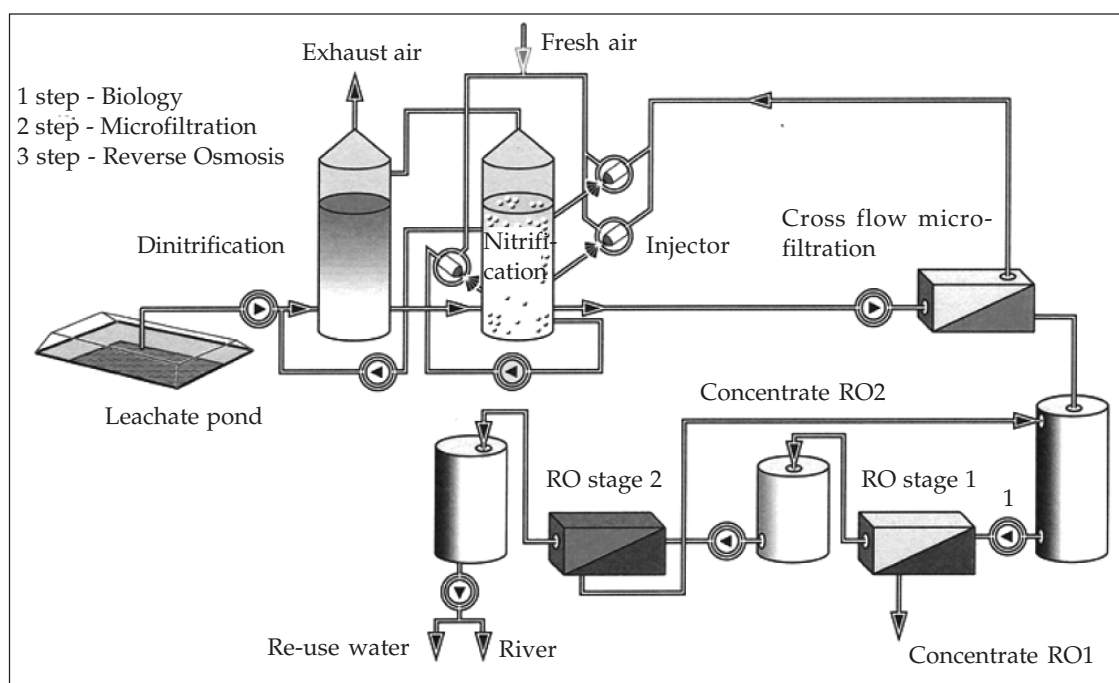


Fig1: Basic flow sheet of large scale installation for landfill leachate

flow mode

- Nitrification: two Continuous stirred tank reactor (CSTR) reactors with a total volume of 260 m³, 10 pcs of air-injectors
- Cross-flow microfiltration: 40 m² membrane surface, operating transmembrane pressure 2.5 bar
- Cooling tower 200 kW
- Sludge handling with decanter press

The plant was equipped with four recirculation circuits:

- The first circuit (50 m³/h) was used for recirculation of nitrate and microorganisms from the nitrification to the anoxic denitrification.
- The second circuit (240 m³/h) connected to in the nitrification tank was used for feeding the cross-flow MF and the remaining pressure after the membrane modules was used for injector aeration.
- Other circuits were used for aeration by means of ejector. Medium was taken from the bottom of the tank and after an increase in pressure was inserted back through the injectors. In the injectors the necessary process air was sucked in and introduced as fine bubbles to enhance efficient utilization of oxygen.
- An additional circuit (60 m³/h) was installed for cooling purposes.

For biomass removal a ceramic MF was used. The ceramic modules have a maximum pore diameter of 0.2 microns and are equipped with an automatic back-flushing

device. Modules have an open channel diameter of 8 mm on the feed side.

In order to directly discharge the biologically and physically pre-cleaned leachate to a small receiving river the emission limits were set to COD < 50 mg/l, NH₄ < 10 mg/l and N_{tot} < 50 mg/l.

A reverse osmosis system with spiral wound modules was used to eliminate ionic

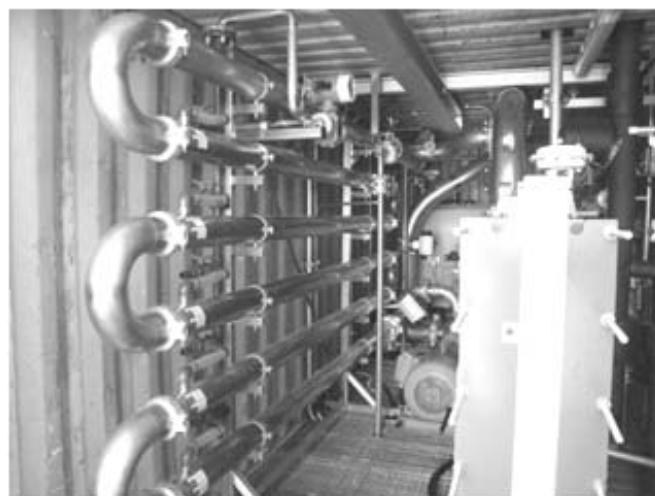
and non-biodegradable molecular impurities.

MBR for treatment of waste water from renewable fuel production

Design approaches and pilot plant tests

The goal was to develop a wastewater treatment concept which enables a cost efficient reduction of the organic compounds expressed as COD from values of around 150.000 mgCOD/l to < 5.000 mgCOD/l.

Several experiments were carried out in pilot scale on site and in laboratory scale:



Organic cross-flow microfiltration

- Use of reverse osmosis to recover methanol and to reduce COD load
- Combination of anaerobic digestion with a conventional activated sludge process (sedimentation)
- Combination of anaerobic digestion with an aerobic MBR
- Aerobic MBR as a stand-alone solution

For the reverse osmosis experiments a disc-tube type pilot plant was used. This unit was equipped with 172 membrane sheets with a total membrane area of 7.7 m² mounted in an 8" tube. It was possible to operate the system up to 60 bar. Anaerobic digestion was done in a 30 m³ CSTR tank with wall heating. As an inoculum, 6 m³ fermentation broth from a biogas plant was used. The conventional activated sludge process was tested in a 2 m³ aerated CSTR tank and a 0.7 m³ secondary clarifier. The effluent of the anaerobic CSTR was used as feed of the aerobic installation. The MBR was established by installation of a MF cross-flow unit with a membrane area of 1.35 m² and a pore size of 0.04 µm, after the secondary clarifier of the above mentioned aerobic unit. pH Value, electric conductivity, DS(dry solids) and oDS (organic dry solids), COD, gas production and quality (CH₄, CO₂, O₂, H₂S) were monitored.

In order to increase the safety of process design a process simulation on base of the ASM1 model was done. The flow sheet of the model took into account that the selector is insufficiently mixed and therefore was divided into two separated zones as shown in **Figure 2**.

The following parameters were used for modeling the process (**Table 1**):

Table 1: parameters for simulation of highload organic waste water plant

| | | |
|--|------|-------------------|
| Amount | 1,05 | m ³ /h |
| COD feed concentration | 120 | kg/m ³ |
| NH ₄ feed concentration | 0,05 | kg/m ³ |
| NO ₃ feed concentration | 0 | kg/m ³ |
| Excess sludge | 9,16 | m ³ /d |
| Sludge residence time | 56 | d |
| temperature | 35 | °C |
| Oxygen concentration in aerated part of selector | 1 | mg/l |
| Oxygen concentration in aerobic tank | 1 | mg/l |

Large Scale implementation

The design of the membrane unit was based on tests and measurements as described previously. The design of the aerobic unit was done according to the ATV-DVWK A 131 guideline with some specific adaptations. The plant was able to process 30 m³/d of highly loaded organic waste water, with a COD concentration of up to 150.000 mg/l. It consisted of a slightly aerated selector (125 m³) and an aerated tank (400 m³). Connected to the large aerated tank, were one circuit for cross-flow MF, cooler and injector aeration ending in the selector (60 m³/h) and a second circuit for injector aeration (400 m³/h). Several anti-foam measures were integrated to prevent foaming.

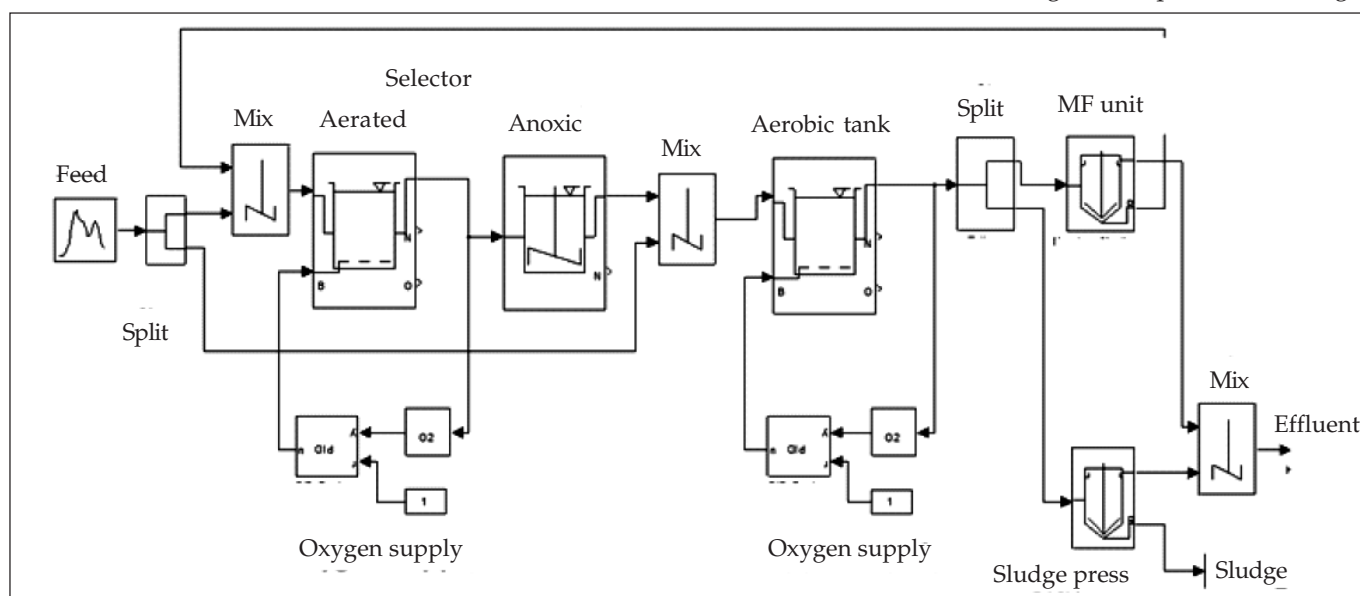


Fig 2: flow sheet of ASM1 simulation model

Table 2: Characteristics of the leachate plant

| Parameter | Pilot scale | Large scale | units |
|---------------------------------|-------------|-------------|-------------------------------------|
| Volume tot | 0,62 | 390 | m ³ |
| Inflow | 0.1 | 100 | m ³ /d |
| pH-Wert | 7.6 – 8.7 | 8,2 | |
| Electric conductivity | 42 | 36 | mS/cm |
| COD | 22 - 35 | 15 | kg/m ³ |
| BOD ₅ | — | 5.3 | kg/m ³ |
| Ammonium | 4.2 – 6.2 | 4.0 | kg/m ³ |
| DW | 25 | 35 | kg/m ³ |
| Area MF | 0,55 | 40 | m ² |
| B _R COD | 4,60 | 3,85 | kg/(m ³ .d) |
| B _R -NH ₄ | 0,84 | 1,03 | kg/(m ³ .d) |
| B _{TS} COD | 0,18 | 0,11 | kg/(kg.d) |
| B _{TS} NH ₄ | 0,034 | 0,029 | kg/(kg.d) |
| Biomass growth factor | 0,07 | 0,13 | kg _{TS} /kg _{COD} |
| Flux MF | 164 | 104 | l/(m ² .h) |
| Transmembranepressure | 3,50 | 2,50 | bar |
| Permeability MF | 46,8 | 41,7 | l/(m ² .h.bar) |

Results and Discussion

MBR for leachate treatment

Both heat and sludge production are hard to quantify exactly under pilot conditions and therefore scale up should be based on calculations, making use of recognized guidelines, which were not available for this specific case. Because of these uncertainties, cooling and sludge press was installed as soon as reliable large scale operational data was available. Thereafter the plant was able to treat all leachate to ensure direct discharge quality (COD < 50 mg/l, NH₄-N < 10 mg/l, NO₂-N < 1 mg/l, N_{tot} < 50 mg/l), even in periods of heavy rain.

Particular attention in the design of the large scale installation must be laid on the operating parameters found in Table 2.

Carbon source for denitrification

Because of the highly loaded and variable composition of leachate it may, from past experiences, lead to a sudden shortage of easily degradable carbon for the denitrification process. As a consequence, pH will decrease and a massive increase in nitrate concentration will lead to an inhibition of nitrification. For this reason, a continu-

ous monitoring of pH and nitrate levels is an essential prerequisite for trouble-free operation of the biology. This problem never occurred during pilot tests as the landfill leachate contained sufficient degradable carbon. Since small amounts of sludge were landfilled, the degradable compounds depleted quickly and the addition of carbon source (acetic acid) became necessary.

Foaming

Foaming occurred during the pilot test phase. Therefore, an antifoam control system consisting of a special foam suction system coupled to the injectors and free head space over the maximum liquid level, was implemented in the large scale system. Under normal operating conditions these measures proved to be sufficient. However, depending on certain unknown ingredients in the feed or due to biological problems, strong foaming happened and even sometimes in the anoxic denitrification tank. While at the beginning, 2 – 5 l/d of antifoam was sufficient this amount increased to more than 200 l/d as the operation proceeded (by 6 months). It can be safely said that the biology adapted to the

usually hard degradable ingredients of the anti-foam agent. As a consequence several antifoam products were tested under pilot test conditions and additional nozzles were installed to spray down the foam from the top.

Monitoring of feed characteristics to ensure flux of MF unit

Although the limiting fouling layers could be removed by intensive chemical cleaning, these efforts exceeded the planned maintenance activities. Therefore the MF was expanded from 25 to 40 m² with an additional third module in series by increasing the height of the rack and using a more powerful pump. Anyhow, due to the constantly fluctuating and unidentifiable ingredients in the leachate or due to unknown interactions with the biology repeatedly, spontaneous and sometimes massive blockages of the microfiltration occurred. This problem could be handled to a certain extent by controlling the inflow system by making use of two independent leachate basins and through the use of individual purification strategies. Derived from Table 2., it can be concluded that volumetric load rate and the necessary oxygen uptake can be successfully scaled up from pilot scale, even if the scale-up ratio is far larger than 100. Problems might occur in the

scale-up of the membrane unit, since influences from the biological system might significantly impact the behavior of membrane operation, both flux and maintenance efforts. The same is true for foaming conditions and for the specific yield of biomass related to COD.

MBR for treatment of waste water from renewable fuel production

Previous experiments with reverse osmosis showed that a major part, namely up to 80 % of the COD, consists of very small organic molecules, i.e. mainly methanol. Although it is possible to restrain larger components like glycerol or propandiol in the concentrate, it is not possible to ensure low COD values in the permeate due to the high permeability of methanol. Therefore, the permeate cannot be discharged directly to a river or to most sewer networks. Furthermore, significant biofouling was observed and the membrane itself as well as the material of the spacer discs showed significant signs of wear after few weeks of operation.

Although laboratory tests with anaerobic digestion, based on addition of high load organic waste water to an inoculum derived from a communal digestion plant were promising, the larger anaerobic CSTR pilot plant, which was started with sludge from a biogas plant, did not confirm these findings. Stable operation could not be reached and the test run had to be stopped after a collapse of the biology only after 8 weeks of operation. The reason for this unsuccessful experiment was not known for sure, but it was assumed that some ingredients in the waste water were harmful for anaerobic microorganism. Aerobic membrane bioreactor (MBR) was considered as simplest, most reliable and economically feasible solution.

Since this variant of sole aerobic treatment was not tested in pilot scale, a residual risk was remaining during scale-up. Therefore a process simulation was undertaken. The results of the simulation for steady state operation based on the ASM1 model show that a steady process is feasible. The applied model was appropriate and lead to reliable results. The simulation showed that the given feed rate of COD (126 kg/h) can be oxidized to an extent higher than 95% at a biomass concentration of about 22.6 kg/m^3 ($= 25 \text{ kg OCOD/m}^3$). However, only 11 kg/m^3 of which is active biomass. For the survival of the biomass, however, a much higher content of ammonium in the inflow was necessary: 5 kg/m^3 , since ammonium was a major limiting factor for biomass growth.

The simulation further predicted that an aeration rate of $196 \text{ kgO}_2/\text{h}$ will be adequate.

During simulation the following parameters have proven to be particularly critical system parameters:

- COD load
- supply of NH_4 , P_2O_5 , K_2O and other nutrients
- oxygen uptake rate

All three parameters are limiting for the growth of biomass and must be supplied in sufficient quantities and in a suitable ratio to each other. The amount of active biomass in the selector and aerobic tank increases due to a slower death rate when the temperature is lowered, from 30°C to 20°C . The model predicts that less active biomass in the system will lead to lower concentrations in the effluent after MF and decanter. Simulation results further show that COD reduction degree is to be expected between 96.8% (at 35°C) and 94.4% (at 20°C).

Oxygen demand increases with temperature due to the increased biomass growth and lower oxygen solubility. The waste water derived mainly from distillation processes requires the addition of nutrients in long-term operation, but the quantity and quality could neither be defined in experiments nor simulation, because the aerobic pilot tests were done using nutrient rich effluent of the anaerobic pilot test run, which itself was started with a nutrient containing sludge from a biogas plant. The degradation rate of COD was higher than 95 %, thus ensuring emissions lower than 5.000 mg/l . The biological process is robust and no toxic inhibitions have been recognized so far. The membranes of the organic cross-flow microfiltration had to be changed once after some fibers and other debris harmed the surface during start-up. Since then the membranes are operating at design flux and regular chemical cleanings are done according to standard operating procedures.

The following operation and scale-up experience was learned in case of waste water from renewable fuel production:

Cooling system

Based on the experience from the highly loaded leachate, the cooling capacity of the large scale plant was designed calculating the power demand for aeration and microfiltration and a certain surplus was taken into account for microbial oxidation of organic compounds. This estimation proved to be sufficient, but problems occurred because fibers in the inoculum blocked the plate heat exchanger as well as the microfiltration inlet several times. After an additional and time-consuming filtering this problem was solved.

Sludge withdrawal and decanter press

Again the decanter press was installed after the process was already fully established and the supplier of the press could make laboratory tests in order to define the best flocculent. This approach prohibits any improper design and is possible due to the fact that biomass growth rate is low and the biomass content in the bioreactors can be adjusted and also increased up to 50 kg/m³ in ejector aerated MBR systems equipped with cross-flow filtration systems. The amount of surplus sludge is in the range of 0.12 kgDW/kgCOD and higher than predicted by the simulation model.

Nutrient supply

The carbon rich waste water with high amounts of methanol, glycerol and fats makes it necessary to provide a wide range of nutrients. Therefore as base supply, an agricultural fertilizer was dosed and the content of nitrogen, phosphorus and potassium among others is monitored by regular offline analysis.

Foaming

Although several measures to prevent or fight foaming were already included in the installation, like foam overflow and destruction, free head space, anti-foam dosing and a sufficient nutrient supply, foaming still caused several problems. Incomplete mixing of the selector contributed to the foaming as well. In order to improve the mixing behavior, the volumetric energy dissipation was increased by lowering the liquid level in both tanks significantly, while the pumping capacity in the mentioned circuits was kept constant. This additional measure solved the foaming problem successfully.

Summary

Nowadays, highly loaded organic waste water should be treated by anaerobic means simply because biogas and consequently energy can be derived from the process. Two case studies are presented in this paper where an aerobic MBR installation was realized in contrary to this statement. The reasons for this design approach differ. In the case of landfill leachate, biological degradation of ammonia requires a carbon source in the denitrification step and in contrast to this need an anaerobic treatment would easily deplete degradable carbon and consequently increase an expensive external carbon supply. This would be economically or ecologically unviable.

In the second case of waste water from renewable fuel production, an anaerobic process could not be implemented successfully due to insufficient nutrient supply

and/or toxic ingredients in the waste water. Also the biogas would show a very high content of hydrogen-sulfide and the amount would be too low to yield significant revenue if used as fuel in a steam boiler or cogeneration-unit. Another approach based on reverse osmosis as standalone solution failed likewise.

It was proven that aerobic MBRs are much less sensitive to process fluctuations and also toxic ingredients. The MBR concept is straight forward, consisting of comparatively less process equipment and follows the basic industrial idea of keeping the process simple. Consequently, the large scale plants were built as aerobic MBRs, taking into account the drawback of significantly higher energy costs. After initial adjustments, both plant ensured the stipulated emission limits were met and the cross-flow membrane units were performing excellently.

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