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Lab scale experiments using a submerged MBR under thermophilic aerobic conditions for the treatment of paper mill deinking wastewater

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ABSTRACT

This paper describes the results of laboratory experiments using a thermophilic aerobic MBR (TMBR) at 50 °C. An innovative use of submerged flat-sheet MBR modules to treat circuit wastewater from the paper industry was studied. Two experiments were conducted with a flux of 8–13 L/m^2/h without chemical membrane cleaning. COD and BOD_5 elimination rates were 83% and 99%, respectively. Calcium was reduced from 110 to 180 mg/L in the inflow to 35–60 mg/L in the permeate. However, only negligible membrane scaling occurred. The observed sludge yield was very low and amounted to 0.07–0.29 g MLSS/g $COD_{eliminated}$. Consequently, the nutrient supply of ammonia and phosphate can be lower compared to a mesophilic process. Molecular-biological FISH analysis revealed a likewise high diversity of microorganisms in the TMBR compared to the mesophilic sludge used for start-up. Furthermore, ammonia-oxidising bacteria were detected at thermophilic operation.

1. Introduction

Paper production requires large volumes of fresh water. The wastewater is typically treated by end-of-pipe technologies and subsequently discharged into the receiving water. Process integrated treatment methods make water circuit concepts possible which allow the water in the paper production process to be reused. The lower the specific effluent volume, the higher are the detrimental substance concentrations in the water circuit like COD, BOD_5 or calcium. Common technologies for the integrated treatment of circuit waters, however, are processes that merely remove solids based on flotation, sedimentation or filtration methods (Jung and Pauly, 2011). The combination of biological treatment and ultrafiltration in a MBR makes it possible to eliminate dissolved detrimental substances (COD, BOD_5, calcium) as well as solids. Compared to common applications of MBR technology, its use in paper industry makes thermophilic operation possible at 40–60 °C. This creates new opportunities as well as risks due to the changed operating conditions and process properties.

A few studies have already been published on thermophilic aerobic wastewater treatment. According to LaPara and Alleman (1999), the first paper published on this technology was by Rudolfs and Amberg (1953). The crucial advantages and drawbacks of the thermophilic process were reported by Suvilampi and Rintala (2003) as well as by LaPara and Alleman (1999). According to these reviews, the higher temperature results in higher substrate degradation rates due to faster reaction kinetics and higher specific biomass growth rates. In any case, a lower net sludge yield was observed due to an increased endogenous respiration rate of the microorganisms that went hand in hand with a higher decay rate. The main drawback of the process is the poor sludge settleability. The lack of formation of stable flocs is characteristic of thermophilic aerobic sludge. Indeed, the shape of very loose flocs and small particle sizes are typical (Vogelaar, 2002). Langevin and Liao (2010) assumed the reason was the difference in the species of microorganisms, especially a greater number of filamentous bacteria in the population. In addition, the significant impact of increased EPS (extracellular polymeric substances) concentrations and differences in the charge or hydrophobicity of the particle surface were discussed (Langevin and Liao, 2010).

Generally speaking, the ammonia and phosphate concentrations in wastewaters from the paper industry are far below the concentrations typical of municipal effluents. Indeed, most paper mills add nitrogen and phosphorus upstream of the biological wastewater treatment plant (Möbius, 2009). Low degradation rates

Abbreviations: FISH, fluorescence in situ hybridization; ICP-MS, inductive coupled plasma mass spectrometry; ICP-OES, inductive coupled plasma atomic emission spectroscopy; MLSS, mixed liquor suspended solids; MLVSS, mixed liquor volatile suspended solids; TKN, total Kjeldahl nitrogen; TMBR, thermophilic membrane bioreactor; TMP, transmembrane pressure.

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of ammonia and phosphate are rather positive in the wastewater treatment plants of paper mills, since fewer chemicals need to be added subsequently. However, according to state-of-the-art literature, nitrification does not occur at temperatures exceeding 45 °C (LaPara and Alleman, 1999; Juteau, 2006).

The change in sludge characteristics, especially poor sedimentation properties, has so far prevented the widespread use of industrial scale application of the thermophilic aerobic process, at least in the paper industry. If a MBR can be used as an alternative to conventional sedimentation, the industry would benefit from the advantages of the thermophilic process. At the same time, the problem of poor sludge settleability would be solved.

Mesophilic MBR technology is already being used in industrial wastewater treatment and is still the object of many research projects. Moreover, there are currently nine MBR plants in operation in paper mills all over Europe (Simstich and Öller, 2010). Until now, the current state of technological development of a thermophilic MBR (TMBR) has been performed primarily in laboratory and pilot studies. There are only two industrial scale plants reported in the literature (Ramaerkers et al., 2001; Bertanza et al., 2010). The risk associated with a TMBR is the known correlation between decreasing flux and decreasing particle size. Smaller sludge flocs lead to a higher density of the particle layer on the membrane which in turn results in an increased pressure drop (Meng et al., 2006). Hence, a lower flux could be expected in a TMBR. The effect of flux decrease due to smaller floc sized was also observed by Yang et al. (2010). The higher temperature counteracts this effect due to the lower viscosity of the activated sludge which should result in an increase of flux.

Virtually all of the existing literature on the TMBR relates to the same type of membrane module used, the side-stream design of an external MBR system (Ragona and Hall, 1998; Bérubé and Hall, 2000; LaPara et al., 2001b; Huuhilo et al., 2002; Lopetegul and Sancho, 2003; Kurian et al., 2005; Visvanathan et al., 2007; Abeynayaka and Visvanathan, 2011). There are very few exceptions. The submerged type of MBR was studied at thermophilic temperatures and so far only published by Dias et al. (2005), Zhang et al. (2006), Al-Amri et al. (2010) and Sousa et al. (2011). The use of side-stream modules has the characteristics of a higher transmembrane pressure TMP (transmembrane pressure) resulting in greater flux and they are considered to be more unsusceptible to fouling due to increased cross-flow velocities (Abeynayaka and Visvanathan, 2011; Judd, 2011). But the alternative MBR system with submerged modules has the advantages of a far lower energy demand and a less complex design as well as a smaller footprint. These are the reasons why the submerged system is preferably used for large scale MBR plants (Lesjean et al., 2009).

The aim of the research experiments reported here was to study the opportunities and challenges of a submerged MBR in thermophilic operation with real wastewater from paper mills. The technological feasibility of the TMBR was studied in long-term laboratory experiments. One main focus was the effect of the typical small sized flocs of thermophilic sludge on the membrane operation in terms of flux and TMP.

2. Methods

2.1. Analysis

The parameters BOD_5, DOC, total phosphorus P_{tot}, TKN, TNb (total nitrogen bound), temperature, conductivity, pH, total suspended solids TSS, mixed liquor suspended solids MLSS and volatile suspended solids VSS were measured according to the German Standard Methods for the Examination of Water, Wastewater and Sludge (DEV) (Wasserchemische Gesellschaft, 2011). The parameters COD, Ca^{2+}, PO_4^{3-}, SO_4^{2-}, NH_4^+, NO_2^-, NO_3^- were measured by photometric cuvette tests from HACH-LANGE GmbH, Germany. All influent samples were filtered through a 12–15 µm paper filter. Since the influent samples of experiment B still exhibited some turbidity after filtering, these samples were filtered again using a 0.45 µm filter. The COD was only measured in the dissolved state. The particle size distribution was measured by laser scattering with a detection range of 0.3–300 µm (Mastersizer MicroPlus, Malvern Instruments GmbH, Germany). FISH analysis was carried out by vermicon AG, Munich/Germany. Elements like barium, iron, magnesium, sodium or silicon were analysed by ICP-MS/ICP-OES according to standard methods ISO 11885 and ISO 17294-2.

2.2. Characteristics of paper mill wastewater

The used real wastewater was obtained from two different paper mills (designated "experiment A" and "experiment B") that produce several 100,000 tonnes of graphic paper per year. The raw material used in the mills is a mixture of recovered paper, pulp and mechanical wood pulp, each making up about one-third of the raw material. The wastewater was taken from the effluent of the deinking plant where the recovered paper was processed and the water temperature typically ranged between 40 and 50 °C.

The wastewater was supplied weekly for the laboratory experiments and stored at 10–15 °C in 1000 l tanks. Table 1 shows the characteristics of the influent samples used in the two experiments. The BOD_5/COD ratio of about 0.45 was within the typical range for wastewater from the paper industry. Scaling phenomena were expected with respect to the high calcium concentrations. The low concentrations of phosphate and ammonia were also typical for wastewater from the paper industry and made it necessary to add urea and KH_2PO_4 prior to TMBR treatment. The influent concentrations of nitrogen and phosphorus were chosen so that permeate concentrations of NH_4^+ and PO_4^{3-} of 0.5 to 2 mg/l could be achieved. The aim was to ensure a sufficient nutrient feed for the microorganisms. In experiment A, the BOD_5:N:P ratio ranged from 100:0.2:0.13 to 100:3.75:0.34 during the optimisation process. To study further the effects of the nutrient concentrations, the influent BOD_5:N:P ratios in experiment B were raised to 100:8.5:1.25 step by step. The fact that the nutrient supply was continuously high enough for the microorganisms was verified as well by monitoring the TKN nitrogen and P_{tot} phosphorus concentrations in the dry matter of the MLSS Table 2.

Table 1
Influent characteristics (mean values).

	COD mg/l	BOD_5 mg/l	pH -	Cond. mS/cm	Ca^{2+} mg/l	SO_4^{2-} mg/l	PO_4^{3-} mg/l	NH_4^+ mg/l	Ba mg/l	Fe mg/l	Mg mg/l	Na mg/l	Si mg/l
Experiment A	2597	1151	6.6	3.0	113	351	1.9	0.11	0.053	0.33	11	680	75
Standard deviation	203	237	0.3	0.2	22	75	0.9	0.10	–	–	–	–	–
n	8	8	7	7	7	8	6	8	1	1	1	1	1
Experiment B	1403	658	7.3	3.3	179	783	0.6	0.52	0.035	0.16	9.3	900	4.6
Standard deviation	204	93	0.2	0.3	23	92	0.5	0.27	–	–	–	–	–
n	16	8	16	16	13	8	20	15	1	1	1	1	1