Membrane bioreactors as core technology for water loop closure in a maltery

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ABSTRACT
This paper reports on the potential for water reuse in the malting sector. Core unit of a treatment train to close the water loop was a membrane bioreactor (MBR). Three different commercial submerged membranes were compared in terms of their fouling potential in this application. In a second step, MBR permeate was subjected to reverse osmosis (RO) and several oxidation processes. Neither the MBR permeate nor the RO permeate or oxidized water streams showed an adverse effect on malt quality. The worst case scenario was then tested in a closed water loop over several malting cycles at pilot scale and the effect on water and malt quality investigated.

Key words | closed water loop, maltery, membrane bioreactor

INTRODUCTION
Malting wastewaters are easily degradable and are typically treated biologically. Increases in malting capacity, limited space availability or the desire to anticipate future legislative restrictions with respect to effluent discharge norms or water intake are all factors which favour the upgrade of existing biological treatment systems to membrane bioreactors (MBRs). This opens the way to post-treatment of the MBR effluent in view of water reuse.

Malting of barley involves three production stages: steeping, germination and kilning. Total water use during malting amounts to 4 m³ water/ton barley and is mainly attributed to steeping and the first germination step. Around 20% of the total water consumption is taken up by the barley or lost through evaporation. The remaining 80% is wastewater. If this is treated to process water quality, substantial water savings can be achieved.

In view of wastewater treatment plant upgrade from conventional treatment to MBR and the potential application of water reuse, research was undertaken to compare various submerged MBR membranes for their fouling potential. This included the analyses of extracellular polymeric substances (EPS) which have been described in literature to affect membrane fouling (Rosenberger & Kraume 2002; Le-Clech et al. 2006). In a second step MBR permeate was subjected to post-treatment by reverse osmosis and oxidation processes. The various waters were tested in a micromaltery for their effect on malt quality. Finally, one option was extensively tested in a closed water loop.
loop over several malting cycles and the effects on water and malt quality were evaluated.

**MATERIALS AND METHODS**

**Laboratory reactor systems**

A conventional activated sludge (CAS) system and a MBR were fed in parallel with maltery wastewater. The MBR consisted of one bioreactor vessel, in which three types of membranes were submerged. These were a plate-and-frame membrane in a rotating frame system from Huber, a plate-and-frame membrane module from Kubota and a module of vertically positioned hollow fibre membranes from Puron. The plate-and-frame membranes were operated through filtration–relaxation cycles, the hollow fibre membranes through filtration–backwash cycles. The reactors were monitored for typical membrane and biological parameters (APHA 1995). In addition, samples were taken for EPS determinations.

**EPS determination**

EPS were measured as sugars and proteins using a heat extraction-based method (after Örmece & Vesilind 2002): Sludge samples were centrifuged at 3000 rpm for 5 min to separate the soluble and sludge-bound EPS. The sludge pellets were heated for 1 h at 70°C, centrifuged and the supernatant filtered over 0.45 μm to yield the sludge-bound EPS. Polysaccharide and protein fractions in the soluble and sludge-bound EPS were quantified by the Anthrone and Lowry method respectively, using glucose and γ-globuline as reference compounds.

**Post-treatment tests on MBR effluent**

Effluent samples were collected from a pilot-scale MBR equipped with Puron membranes. To further disinfect the MBR-effluent and to reduce color and COD, it was subjected to different oxidation processes. These included ozonation, peroxide treatment, UV treatment or combinations of these techniques. Tests were performed at different pHs and at variable oxidant concentration levels.

In parallel, MBR permeate was subjected to reverse osmosis to evaluate COD, salt and microorganism retention. Water samples obtained after MBR, oxidation or reverse osmosis treatment were mixed with variable concentrations of drinking water and then subjected to a barley germination test to evaluate the presence of any inhibitory compounds or toxic effects.

**Closed loop tests**

Three types of water were tested for their effect on the actual malting process through tests in a micromaltery: MBR permeate, oxidized MBR permeate and RO permeate. Each water was used in a complete malting cycle treating 8 kg of 4 different barley types. For the final malts, 23 quality parameters were determined and the results compared to those obtained in a standard malting process with drinking water.

In the closed water loop tests, MBR was applied without any post-treatment. A first malting cycle was initiated with drinking water. The wastewater was sent to the MBR. Its effluent was collected, compensated for water losses with drinking water and recycled to the micro-maltery. Water quality as well as malt quality parameters were routinely monitored. Per week 2 malting cycles were performed each with 2 barley varieties.

**RESULTS AND DISCUSSION**

**Comparison of 3 submerged membranes in laboratory-scale system**

In the laboratory-scale test, CAS effluent typically had a higher COD than the 3 MBR permeates (Figure 1).
The effluent COD of the CAS followed the COD evolution in the influent and peaked between day 40 and 60 due to a high concentration of suspended solids. For the three MBR permeates, the CODs were similar during the first weeks of operation. After day 45, the Puron effluent typically had a higher COD than the Huber and Kubota membranes.

After a difficult start-up period, all membranes were operated for longer periods of time without chemical cleaning. Operational fluxes were then increased to accelerate the membrane fouling process. From the recovery of permeabilities after different cleaning procedures, it could be concluded that the Puron membrane was mainly fouled by biological material, whereas the Huber and Kubota membrane fouling was due to biological and other organic material.

EPS analyses on the sludges (not shown), indicated that the majority of EPS in the MBR sludge consisted of proteins and that the sludge-bound EPS fraction was larger than the soluble fraction. Towards the end of the test period, nearly all EPS occur as sludge-bound material.

For the three submerged MBR membranes tested, the amount of proteins and polysaccharides retained by the membranes was calculated from the concentration difference between reactor supernatant and permeate as this can be considered a measure for the amount of EPS available for membrane fouling. Although the removal percentages were lower for the proteins than for the polysaccharides, the absolute amount of proteins removed was much larger for all three membranes. Therefore, we may probably assume that in particular the proteins contributed to membrane fouling.

When the membrane filtration resistance was plotted against the retained protein concentration (Figure 2), it turned out to be fairly constant up to 300 mg/l. Above that value membrane fouling increased very strongly for the Kubota and Huber membranes. For the Puron membrane, protein retention was never that high, so the membrane behaviour in those conditions is not known.

This relation between filtration resistance and protein retention seems to correspond with conclusions drawn from the effect of different membrane cleaning procedures where the Kubota and Huber membrane fouling was shown to also have an organic component. These were probably proteins. For the Puron membrane, the filtration resistance seems independent of EPS. Whether this is related to the backwash which was applied to the Puron membranes only, is not clear. In any case, the tests indicated that at the same EPS concentration and composition, different membranes coupled to the same bioreactor may show a different fouling behaviour.

Post-treatment tests on MBR effluent

No significant COD decrease was obtained when MBR permeate was treated with peroxide alone. The combination of peroxide with UV however, led to a COD removal of 63% at a peroxide dose of 3 g/g COD. Ozonation gave much stronger COD reductions up to 90%. Final COD values of 20 mg/l could be obtained at ozon doses of 2 g/g COD. Probably, this difference in efficiency is partly due to differences in operational protocols (continuous ozonation tests versus batchwise peroxide tests). The combination of ozonation and UV further improved the COD removal efficiencies at lower ozon doses.

Application of reverse osmosis on the MBR permeate resulted in a complete elimination of COD, color and microorganisms.

None of the post-treatment technologies yielded a water quality which had a negative impact on the barley germination process.

Closed loop tests

In a first step, MBR permeate, RO-permeate and oxidized permeate were used for micromalting. Since water losses will occur in the malting process, real conditions were mimicked by making up mixtures of around 20% drinking water/80% reuse water. The oxidation treatment used for these tests was peroxide + UV, since a preliminary cost calculation showed that ozonation + UV would not be
economical under the present conditions. All tests gave malts of qualities similar to the ones obtained in the reference situation using drinking water alone.

For the long-term closed water loop tests, preference was given to a treatment scheme consisting solely of MBR. On the one hand, this was the economically most interesting scenario. On the other hand, this could be considered the worst case for COD and conductivity accumulation in the recycled water.

In the closed water loop tests, 36 maltings were performed. Because of high evaporation losses in the experimental set-up, more drinking water had to be supplemented than originally planned. This resulted in an average ratio of 60% MBR permeate/40% drinking water.

The micromaltery effluent (which is also the MBR influent) showed high variability in COD and BOD (Figure 3). This was the result of differences in release of (in)organic compounds during the various stages of the malting process and from the two tested barley varieties. The MBR system coped very well with these strong fluctuations in incoming wastewater composition, and stably removed all BOD. On the other hand, both COD and conductivity continuously increased (see Figure 4).

The malt quality remained very constant throughout the test period for the parameters measured. No negative effect could be attributed to the direct reuse of MBR permeate when compared to drinking water. Although the current tests give a first indication that MBR treatment may suffice to achieve a water quality suited for reuse in malteries, longer term closed water loop tests will have to confirm these results for a wider range of barley varieties.

CONCLUSIONS

Comparison of three submerged MBR membranes showed that their fouling behaviour in the same biological matrix may vary substantially. Differences in permeate quality were however limited.

Long-term tests with direct reuse of MBR permeate supplemented with drinking water did not show any deterioration in malt quality parameters. Implementation at full-scale will however require more extensive testing over longer periods of time. In case recalcitrant COD and/or salt accumulation becomes problematic, both oxidation and reverse osmosis treatment can be efficient countermeasures.

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REFERENCES


