Innovative technologies for reuse of petrochemical condensates.

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1. Introduction

In the (petro)chemical industry, the importance of steam is highly emphasized as an essential heat transfer and reaction medium, as well as a diluent during crude feed cracking. Steam with very high quality is required to guarantee the stable and lasting performance of the plant and with this respect, the type of water source introduced into the boiler system for generation of steam needs to meet very stringent requirements and limitations.

The variety of process applications of steam leads to the generation of a broad range of condensate streams with different composition and specifics, which are further considered when these streams are contemplated for return and reuse in the steam/water cycle. The more heavily contaminated condensates are unsuitable for direct reuse or polishing and are treated at the Waste Water Treatment Plant (WWTP), leaving an opportunity for development of improved condensate treatment for higher steam/condensate recycle ratios and an increased water and energy efficiency.

As part of a project under the scope of the Institute for Sustainable Process Technology (ISPT) and together with several partners (Dow Benelux BV, Terneuzen, Ghent University, Evides Industriewater, Sitech, KWR Watercycle Research Institute, Kurita), this research aims to achieve more efficient production of steam in the (petro)chemical industry by enhancing the recycling of process condensates as high quality water and by reducing the freshwater intake intensity and dependence.

In order to study the main principals and requirements to reach this goal, a specific research case was initiated at the site of the chemical company Dow Benelux BV, Terneuzen, which is located in a water stressed Delta. This production site requires a fresh water supply of 22 million m^3 per year from which only 1-2 million m^3 are locally sourced and the rest is either delivered from recycling water or abstracted from the natural park Biesbosch. Because of that, the company strives to decrease the intake and necessity of high quality fresh water and to rely only on more sustainable reused process water at the site. This goal has been realized up to 80%, but nevertheless, Dow aims to achieve 100% reuse.

1.2. Technologies of choice

The production process itself generates condensate streams at elevated temperatures, in which complex organics such as acetate, propionate, formate, phenol and emulsion breakers are still present. Due to the nature of these pollutants, such streams are sent to the WWTP.

By strategically by-passing the WWTP and applying an individual treatment on the condensate, a higher energy efficiency and improved water recovery can be achieved. Such approach would further decrease the load to the WWTP. Because of that, different treatment approaches were preselected amongst which Membrane Distillation (MD) and Membrane Aerated Biofilm Reactor (MABR).

2. Materials and methods

2.1 Membrane Distillation (MD)

Membrane distillation is a thermally driven (possible low grade waste heat) process which normally operates in the range between 30˚C–80˚C and applies a microporous hydrophobic membrane for the separation of a vapor from a liquid stream. In general, MD exists in different configurations, based on the principle that a vapor pressure difference is created across the membrane; Direct Contact MD (DCMD), Air Gap MD (AGMD), Sweep Gas MD (SGMD) and Vacuum MD (VMD).

2.1.1. Lab scale DCMD experiments with synthetic solutions

Due to the availability of waste heat in the condensate stream from Dow Benelux, MD was chosen as a technique for simultaneous water and energy recovery. The influence of key operational conditions on the process efficiency, such as the temperature difference between the feed and the distillate (ΔT), the average temperature of both streams ($T_{average}$) and the flow rate, were studied in a lab scale DCMD, treating a synthetic solution containing the main pollutants measured in the condensate: acetate (200mg/L), propionate (40mg/L) and phenol (30mg/L) with a pH value between 8.5-9.

The experimental set-up consisted of an acrylic MD module with an active surface area of 163 cm^2 and counter current supply of feed and distillate. The temperature on both sides of the system were maintained by two heat exchangers and detected by Resistance Temperature Detector (RTD) sensors with an accuracy of 0.01˚C. The collected data was continuously logged via the program LabView.

2.1.2. Set of parameters and operational conditions

The values selected for these parameters were chosen to represent a full scale MD configuration and secured to incorporate their influence on the amount and quality of the obtained distillate, making the lab scale results comparable to a real system. It was specifically taken into account that common driving force (ΔT) has been reported in the literature within the range of 2K to 10K, because on full scale the temperature drops along the membrane matrix due to temperature polarization.

The same process specific was also considered when talking about the average temperature in the module on a full scale system. In practice, 80°C is usually applied on the feed side and 20°C on the distillate side resulting in an average temperature of 50˚C. Based on a Design of Experiments (DOE) approach, for each studied parameter a high (ΔT = 20°C; $T_{average}$= 60°C, flow rate = 90L/h) and low level (ΔT = 10˚C; $T_{average}$= 40˚C, flow rate = 60L/h) were given and 8 sets of conditions were tested.

At the beginning of the experiments, a bench mark test with Demi Water (DW) was conducted and repeated after a set of 2-3 experiments at the following conditions: T_F = 60˚C, T_D = 45˚C and flow rate F = 60L/h. The obtained flux was compared with the initially attained value and used to evaluate the integrity of the membrane.

2.1.3. Sampling procedure and analyzes

Samples were taken at the inlet of the feed and the outlet of the distillate of the MD module at every hour and they were immediately analyzed for pH and conductivity. The composition of the samples was further examined for the presence of phenol via HACH spectrophotometry and for organic acids by Ion Chromatography (IC).

The rejection efficiency of the present compounds was determined via the following equation:

$$Rejection\ Efficiency\ (RE, \%) = \frac{C_{F_0} - C_D}{C_{F_0}} * 100\ \%$$

where C_{F_0} is the concentration of the component in the feed solution and C_D is the amount of the same pollutant in the distillate.

2.2. Biological treatment: MABR

In order to achieve higher effluent purity, a biological treatment step was also considered. An MABR was selected, where the membranes serve as the supplier of oxygen (~200mbar) for the treatment and as a support for the development of a biofilm. The wastewater surrounding the membranes provides the carbon source and nutrients needed for the growth of the biomass (Figure 1).

Because of the stated advantages, an MABR pilot unit with two identical 55L reactors was designed by OxyMem (Ireland) to study the treatment efficiency of the condensate stream generated at Dow, Figure 1. The system is operated in series in order to achieve the highest possible removal efficiency.

The pilot was inoculated with sludge from the WWTP of the company and was operated in a batch mode for 2-5 days, after which it was continuously supplied with synthetic feed. The composition of the mixture was adjusted gradually in order to reach the full load of all chemicals present in the condensate with the intention to replace it in time with real condensate. In order to assure all necessary elements for a healthy biofilm, macronutrients (N and P) as well as micronutrients were additionally added.

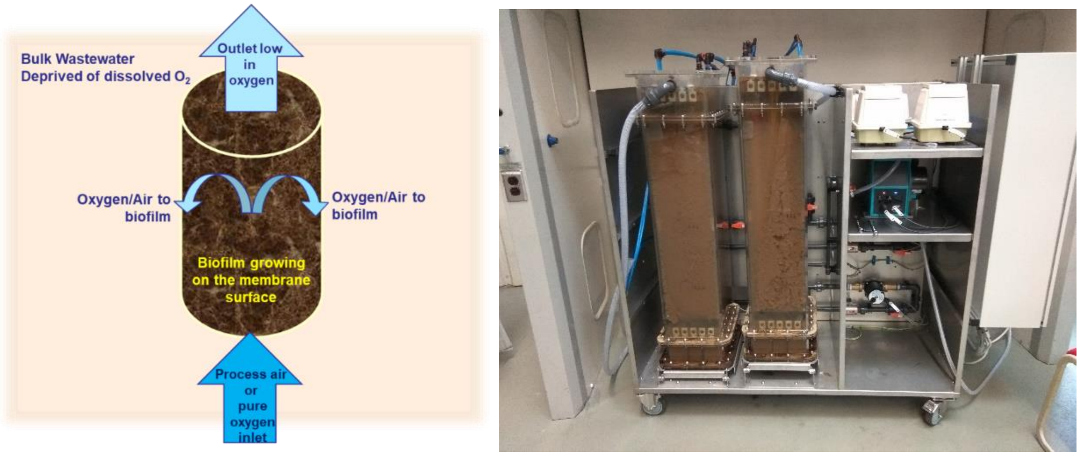

Figure 1 OxyMem MABR twin pilot at Dow, Terneuzen - main concept (left) and after inoculation (right)

The pilot system was operated at an HRT of 10 h per reactor, which resulted in a total flow rate to the system of 128 L/day. Since the main driving force for oxygen supply is through diffusion from the silicon membranes to the biofilm (Figure 1), mixing around the fibers is very important and this is conducted by recirculation pumps with a flow rate of up to 1200L/h. In addition, an ideal biofilm thickness is maintained via scouring, which removes the excess biomass.

The process performance is continuously evaluated by monitoring the main effluent quality parameters such as total organic carbon (TOC = TC-IC), total nitrogen (TN), ammonia (NH_3), nitrite (NO_2^-) and nitrate (NO_3^-) and by additional analyses on the amount of acids via IC and phenol HACH test kits.

3. Results

3.1. MD experiments

The low rejection of phenol observed during the experiments is probably due to its high pKa. For instance, since the pH of the treated synthetic mixture was highly basic (8.5-9) in order to resemble the real condensate, at this pH acetic and propionic acids were certainly above their dissociation constants of pKa = 4.76 at 25˚C and pKa = 4.88 at 25˚C, respectively. The acids in the feed were greatly rejected, which could be hypothetically explained by the presence of their unprotonated forms. On the other hand, phenol was less retained and has a pKa of 9.99, which could lower its removal since a fraction of phenol will still be in its protonated and more volatile form.

3.2. MABR experiments

The removal efficiency of each individual carbon constituent was monitored and regularly evaluated. Based on the collected data was concluded that the system is able to deplete the present organic acids with an average removal efficiency for acetate, propionate and formate of 95.5%, 83.7% and 57.9%, respectively. When looking into the extent to which phenol was also biodegraded, was noted a particularly high removal effectiveness of 93.3% on an average. Furthermore, in the effluent of the first MABR unit is continuously detected a hardly biodegradable carbon fraction, which persistently remains in the system and leads to an average removal of approximately 75% in R1.

In addition, the applied operational parameters such as air and mixing flow rate, the location of dosed nutrients, the carbon load and pH of the feed have proven their individual influence and importance to the system's performance. For instance, introducing the nutrients mixture directly into R1 rather than into its mixing loop has led to an improved mixing flow from 300L/h to 950L/h, but also to lower (0.5 mg/L) dissolved oxygen concentration in the bulk. Such depleted of oxygen environment secured the completion of denitrification, but on the other hand influenced the removal of the targeted carbon pollutants.

4. Future perspectives

It is of great importance for the real application of the MABR system that a load in the expected magnitude to the full scale reactors is tested on the pilot scale as well as to examine the limits and capacity of the process. Moreover, in order to achieve higher TOC removal a restart and re-inoculation of R2 has been considered as a polishing step for degradation of the persistent carbon fraction in the effluent of R1.

With respect to the MD configuration, future experiments with elevated pH (10.5-13) are planned as a methodology to achieve the highest phenol retention. In addition, given the nature of the pollutants of interest a comparison between the performance and rejection capability of a hydrophobic and an oleophobic membranes will be made.