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A Hot Solution

Nitrification at elevated temperatures is no problem for a refinery MBBR

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Wastewater in refinery applications frequently reaches temperatures in excess of 40°C, making biological treatment a challenge; in particular, nitrification. The Suncor Refinery in Montreal, Quebec, is no exception. The refinery processes 130,000 barrels per day, producing gasoline, distillates, asphalts, heavy fuel oil, petrochemicals, solvents, and feedstock for lubricants.

The process of refining crude oil into finished products such as gasoline and other petrochemicals requires complex systems and generates large quantities of water. The desalter unit requires washwater and heat to remove dissolved salts from the crude oil before it can be further processed. Steam is used in many refining processes: it is used as a stripping agent in distillation and for dilution in the cracking process.

Refinery wastewater contains a range of hydrocarbons as well as ammonia. The most common process used to remove organic carbon and ammonia is biological treatment, either in a suspended growth system such as activated sludge or a fixed-film system such as trickling filters or moving bed biofilm reactors (MBBRs).

Long-term operating data has shown that the MBBR is a robust process that allows nitrification to take place at elevated temperatures. An MBBR was installed at the Suncor refinery to increase the plant's nitrification capacity. As a result, the facility has seen improved treated effluent quality.

Suncor Refinery in Montreal

The wastewater treatment plant at Suncor is typical of refineries. Wastewater flows through an oil separator, followed by dissolved-air flotation. The pretreated effluent is then collected in an equalization tank prior to being pumped to the MBBR. The MBBR effluent is discharged into a lagoon prior to discharge to the Saint Lawrence River.

Figure 1. AnoxKaldnes™ K3 media

MBBR overview

The MBBR process was developed at the Norwegian University of Science and Technology around 25 years ago. It is a completely mixed, continuous flow-through process combining the benefits of fixed-film and suspended-growth processes.

An MBBR consists of a tank equipped with an outlet sieve to retain media, the media itself, and an aeration or mixing system. The aeration system utilizes a medium-bubble design with stainless steel laterals and diffusers. An important feature is that biofilm thickness is controlled by media movement so that oxygen diffusion through the biofilm is encouraged. The MBBR at the Suncor refinery uses AnoxKaldnes™ K3 media, shown in Figure 1. The media is made of high-density polyethylene, with a protected surface area of 500 m^2/m^3 and a specific gravity of 0.95 kg/dm^3. Typical fill ratios range from 10% to 65% of total reactor volume.

Nitrification

The nitrification rate in an MBBR is directly related to the organic loading rate, dissolved oxygen concentration, and temperature. In most industrial applications where the organic load is significant compared to the nitrogen load, a two-stage system is recommended, consisting of carbon removal followed by nitrification. However, the wastewater at the Suncor refinery is relatively dilute compared to other refinery effluents, so the MBBR was designed for combined carbon removal and nitrification to allow existing tanks to be used. The MBBR was designed to achieve discharge requirements of less than 10 mg/L of soluble biochemical oxygen demand (BOD), 0.1 mg/L of phenols, and less than 3 mg/L of ammonia nitrogen (NH_4-N).

The design parameters for the process are given in Table 1.

Table 1. Influent design parameters for an MBBR

Parameter	***Unit***	***Monthly average***	***Daily maximum***	***Peak maximum***
Flow	m^3/d	9800	16,350	27,250
Temperature	°C	40	42	-
TBOD	mg/L	45	100	150
TSS	mg/L	20	40	50
Total oil and grease	mg/L	<15	35	-
Phenols	mg/L	1	2	3
NH_4-N	mg/L	7	15	
PO_4-P	mg/L	0.06	0.2	
pH	units	6.0–9.0		

Temperature

As mentioned earlier, one of the design challenges was water temperature. Although the nitrification requirements are very low (assuming a BOD-to-nitrogen requirement for cellular synthesis of 100:3.5—only 5.9 mg/L of NH_4-N needs to be nitrified under average load conditions), there is little information available on nitrification rates at high temperatures. Many researchers have investigated the impact of temperature on fixed-film systems; however, very few have operated at temperatures in excess of 35°C. The optimal activity of *Nitrosomonas* has been shown to occur at 35°C, while the optimal activity of *Nitrobacter* occurs at 38°C, with a sharp drop-off in activity beyond these temperatures. Due to the limited data available at the time of the Suncor project, a conservative design approach was adopted to ensure that the monthly average discharge concentration could be achieved under all operating conditions.

Treatment results

Effluent monitoring is undertaken on a biweekly basis by Suncor personnel. The MBBR influent and effluent characteristics from February 2011 through May 2014 are summarized in Table 2.

Table 2. MBBR influent and effluent characteristics

Parameter	***Unit***	***MBBR inlet***	***MBBR outlet***
Flow	m^3/d	10,193	
Temperature	°C	23–53 (average 40)	
TCOD	mg/L	165	83
SCOD	mg/L	84	29
TBOD	mg/L	61	14
SBOD	mg/L	37	5
TSS	mg/L	32	39
Total oil and grease	mg/L	15	5.6
Phenols	mg/L	1.4	0.2
N-NH_4	mg/L	8.7	0.7
N-NO_3+ N-NO_2	mg/L	0.4	5.2
T-P	mg/L	0.7	0.2

The temperature and dissolved oxygen profiles in the MBBR are shown in Figure 2. The temperature increased gradually from April through May and remained above 40°C from May until October. The dissolved oxygen profile is almost the direct inverse of the temperature—as temperature increases, the dissolved oxygen concentration decreases.

However, the aeration capacity was sufficient to maintain DO concentrations above 2.5 mg/L under most conditions, ensuring that the nitrification rate would not be limited by oxygen.

Figure 2. Yearly temperature profile

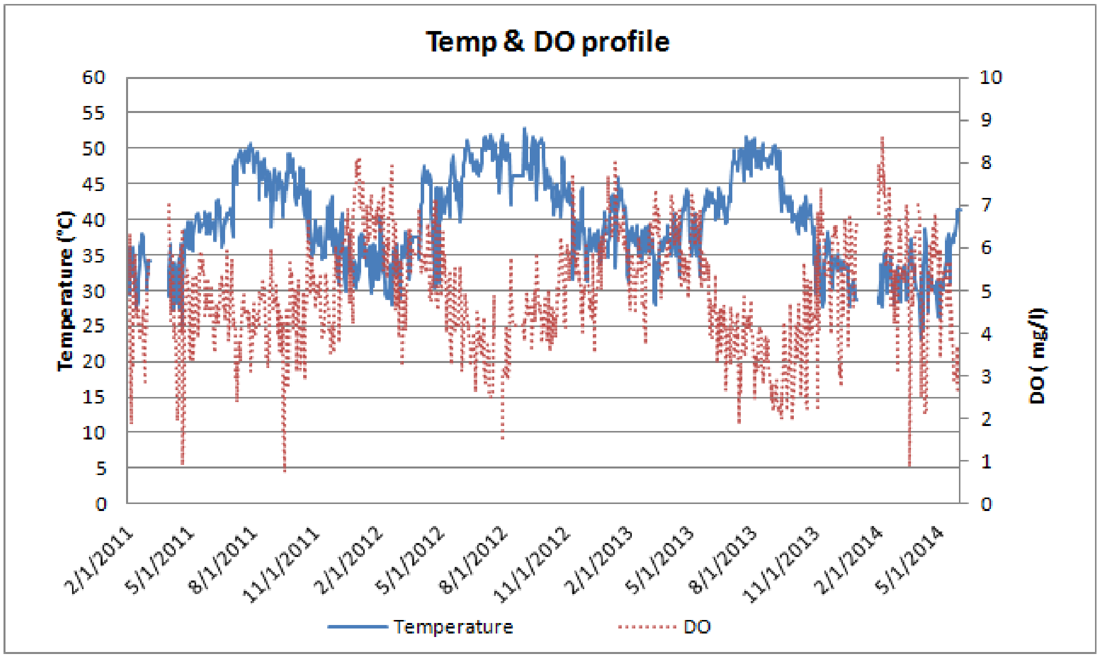

Figure 3 shows inlet and outlet total BOD concentrations over time. BOD removal across the MBBR is consistently meeting discharge requirements, even at temperatures in excess of 45°C. The three data points showing BOD levels higher than 40 mg/L reflect days when the influent load exceeded the maximum daily design load of 1600 kg BOD/d and are not related to high temperature.

Figure 3. TBOD profile across the MBBR

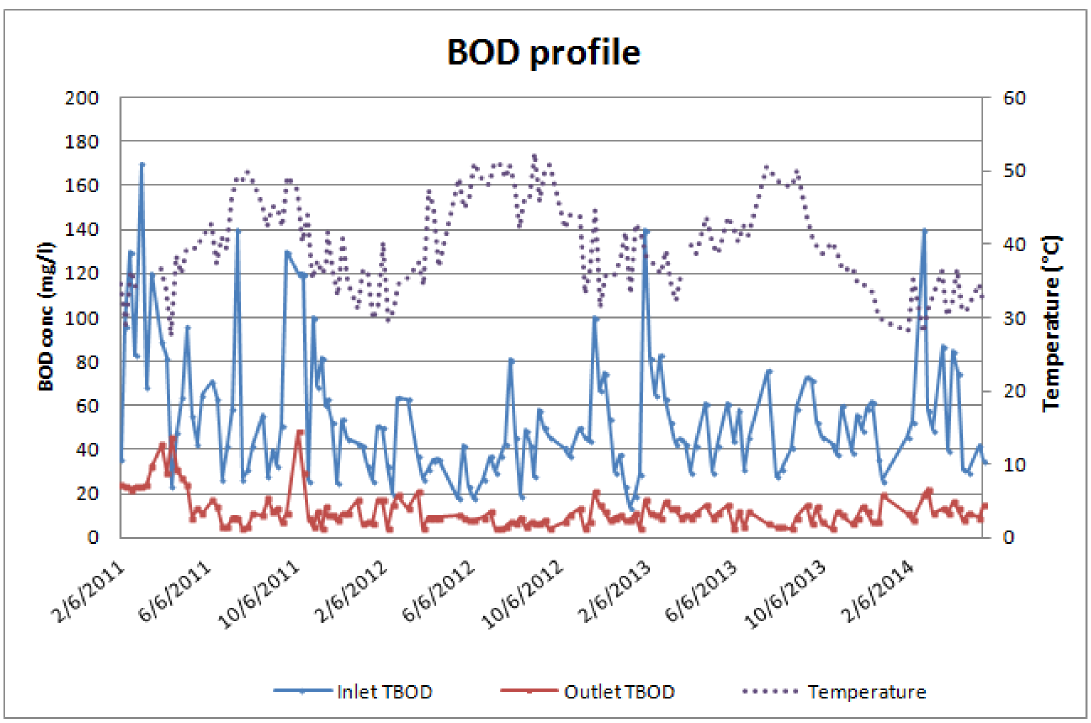

Figure 4. Nitrogen profile across the MBBR

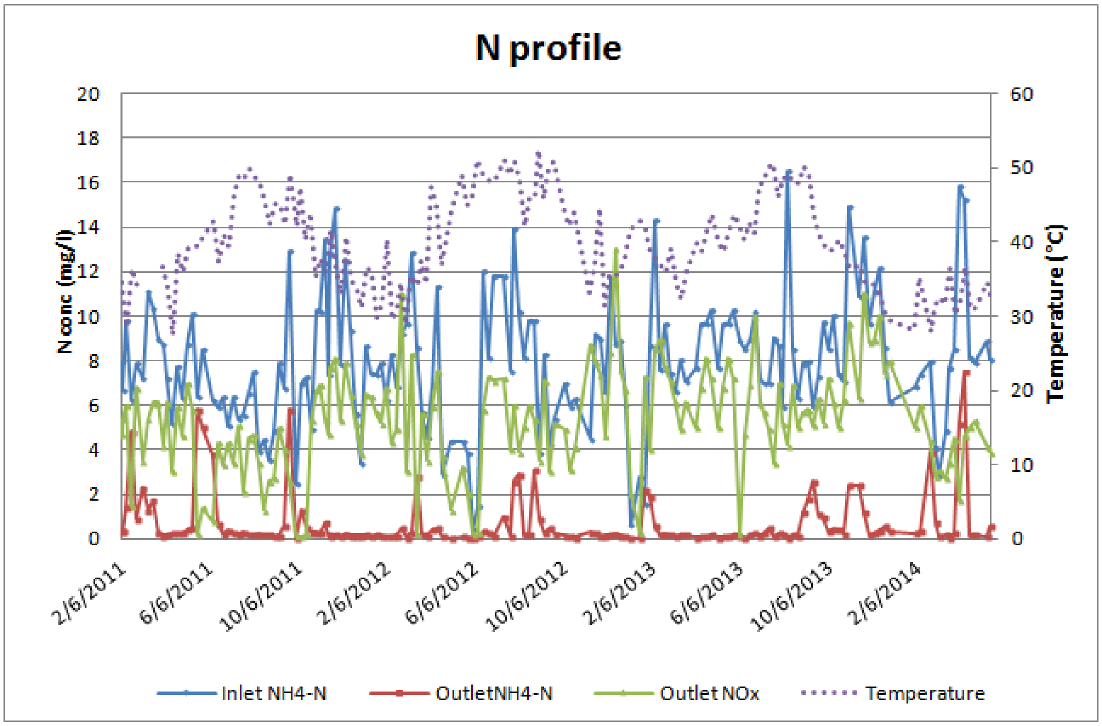

Figure 4 shows the inlet and outlet NH_4-N concentrations with nitrogen oxides in the MBBR effluent. Nitrate production is clear evidence of nitrification activity. To demonstrate nitrification, a nitrogen balance must be undertaken across the system. Nitrogen will be consumed for cellular synthesis. In this case, with an average influent total BOD of 61 mg/L and assuming a BOD:N ratio of 100:3.5 for a low-load system, an average of 2.1 mg/L N will be assimilated. For nitrification to be the dominant ammonia removal process, the total inorganic nitrogen in the effluent must be nearly equal to the inlet total inorganic nitrogen. Based on the data collected, the theoretic nitrate production should be 5.9 mg/L. The observed nitrate production was 4.8 mg/L at the Suncor facility.

Researchers have conducted continuous laboratory studies with MBBRs operated at 35°C, 40°C, and 45°C (Shore J.L., W.S. M'Coy, C.K. Gunsch, and M.A. Deshusses. 2012. "Application of a moving bed biofilm reactor for tertiary ammonia treatment in high temperature industrial wastewater," *Bioresource Technology,* 112, pp. 51–60). They showed that, with acclimatization, nitrification could be sustained at 40°C, but not at 45°C. Their tests were carried out over a short period of time, with a step increase in temperature rather than a long-term gradual increase, which may have resulted in insufficient adaptation time.

The results at the Suncor facility indicate that, provided that the temperature increase is gradual over a period of weeks, nitrification can be sustained at temperatures up to 50°C. This is supported by the nitrogen balance described previously.

Occasional high-effluent NH_4-N concentrations have been observed at the facility; the data were reviewed to determine the cause of the decreased nitrification. However, no clear correlation with the temperature could be found. In most instances, the higher NH_4-N concentration in the effluent could be attributed to a high influent NH_4-N load.

Lower costs overall

Most of the ammonia removal in MBBRs is accomplished through nitrification, as demonstrated by the production of nitrate. It can be deduced that the capacity for complete nitrification at the Suncor system is approximately 150 kg N/d. Being able to operate at elevated temperatures without cooling prior to biological treatment significantly benefits Suncor both in terms of capital and operating expenses, allowing substantial cost savings.

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