Naphthenic Acids and Aerobic Granulation

Tiwari, S.S., Tay, J.H.‡

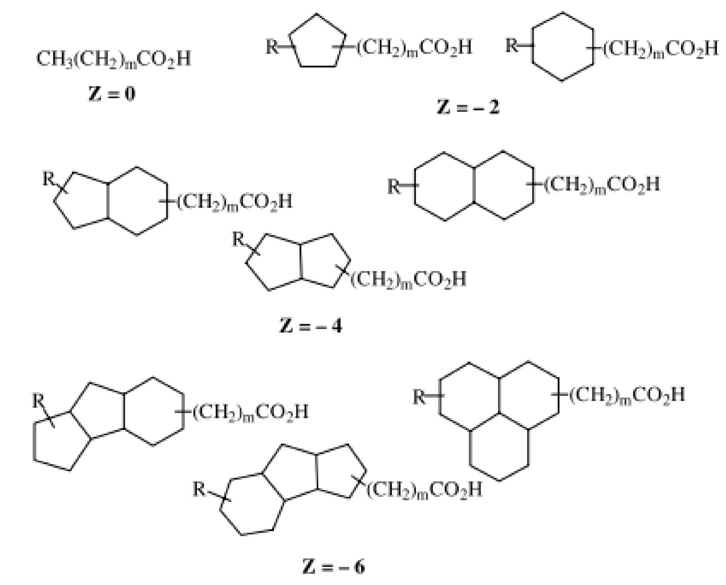
‡University of Calgary, Calgary, Alberta, Canada. T2N 1N4

Email: stiwari@ucalgary.ca; jhatay@ucalgary.ca

Oil Sands Process-Affected Water and Naphthenic Acids

Production of bitumen from North Albertan oil sands requires large quantities of water. Environmental regulations limit the usage of freshwater from the nearby Athabasca River, and hence most of the water is recycled. This water, also known as oil sands process-affected water (OSPW) over time becomes alkaline, abrasive and acutely toxic to aquatic life due to a high concentration of dissolved salts, minerals, trace metals, residual bitumen and naphthenic acids (NAs) (Allen 2008a). NAs occur naturally in petroleum, and their surfactant nature helps in bitumen recovery, but also is a reason for acute toxicity in aquatic organisms and corrosion in facilities in higher concentrations (Brown and Ulrich 2015).

MacKinnon and Boerger (1986) confirmed that NAs were the primary source of acute toxicity in OSPW, and many OSPW treatments have since focused on the treatments of NAs using different strategies (Allen 2008b). Biological treatment, in particular, despite its high efficiency, low cost, and minimal waste generation, has been slow to adapt to the oil sands industry, due to sensitivity of microbes to high salinity and toxic organic chemicals. One technology that has emerged with a strong potential for NA treatment is aerobic granulation biotechnology.



Naphthenic Acids (adapted from Brown and Ulrich (2015))

Aerobic Granulation


Aerobic Granules produced in lab

Granulation is a process by which biomass or microorganisms agglomerate into self-immobilized, dense and compact granules, under controlled loading and operating conditions. Cultured in a previously-inoculated upflow sludge blanket reactor, a constant flow regime of wastewater is established, which provides the mechanical stimulus for biomass to agglomerate into granules ranging from 0.5mm - 2mm in diameter. They constitute a diverse colony of microbes from the surface down to the centre of the granule. This diversity of microbes helps in the complete biodegradation of the various constituents of wastewaters (Show, Lee, and Tay 2012).

In comparison to other biological treatments, aerobic granulation offers high biomass retention, resistance to toxicity, higher COD removal efficiencies even in the presence of salinity, shorter hydraulic retention times (HRT), diverse microbial community formed from the wastewater itself, resistance to shock loads, low sludge growth and minimal operational problems.

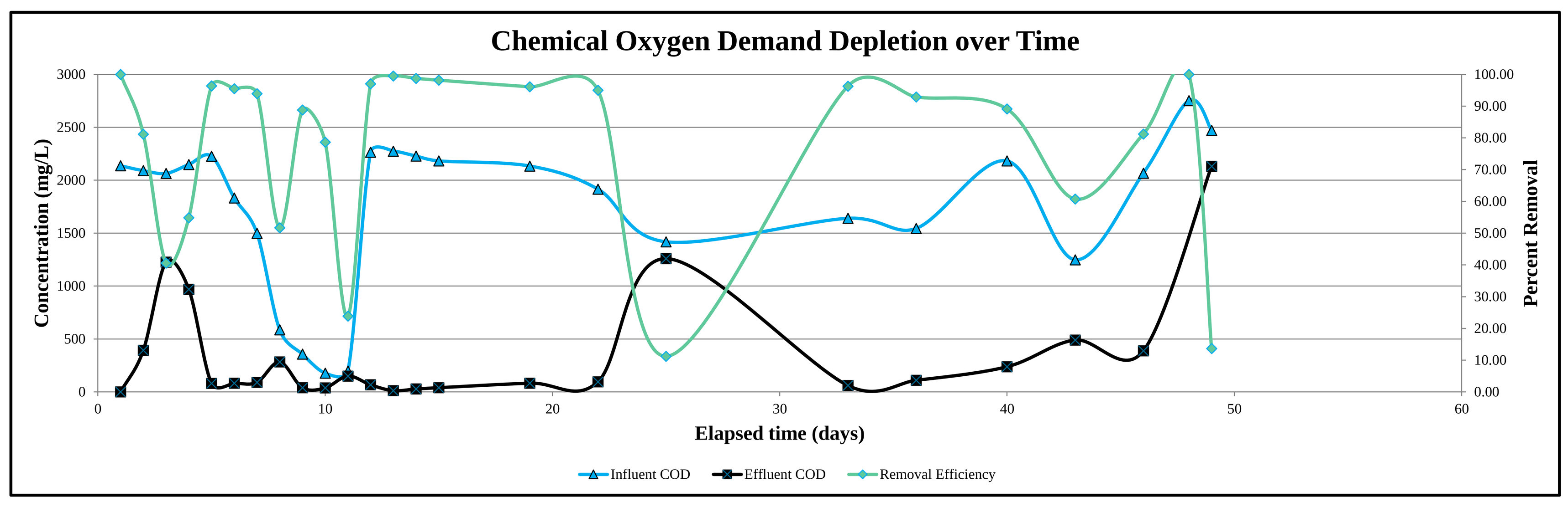
Methods

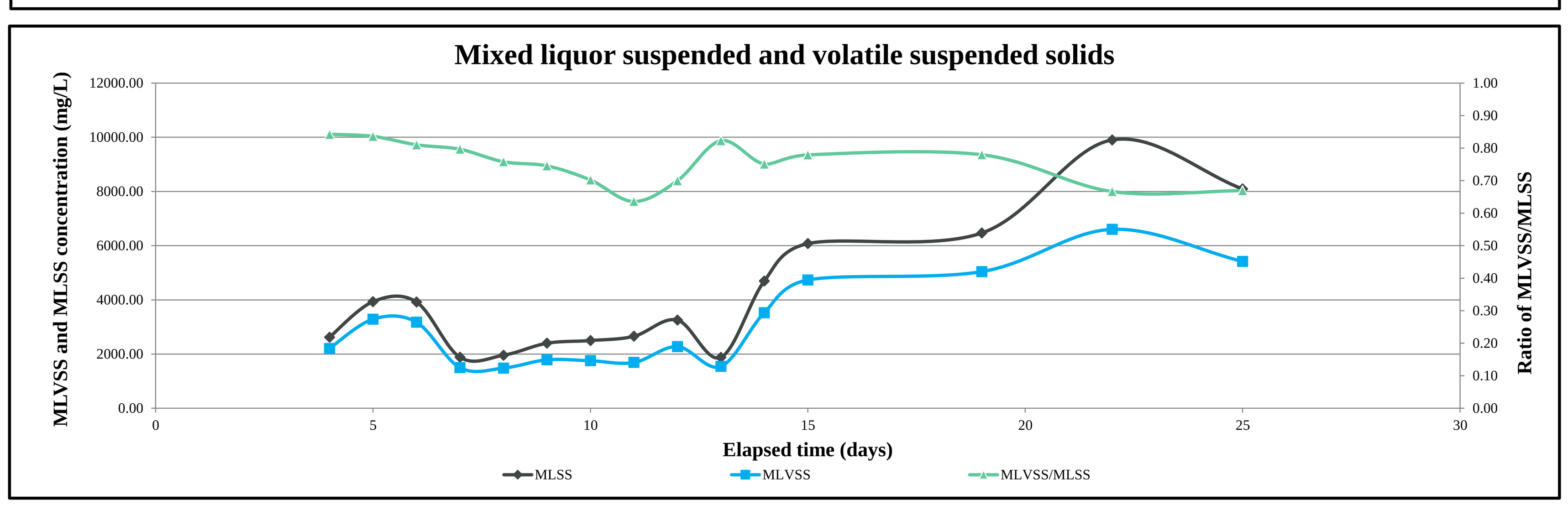

Aerobic Granular Reactor in Initial Stages of Granulation

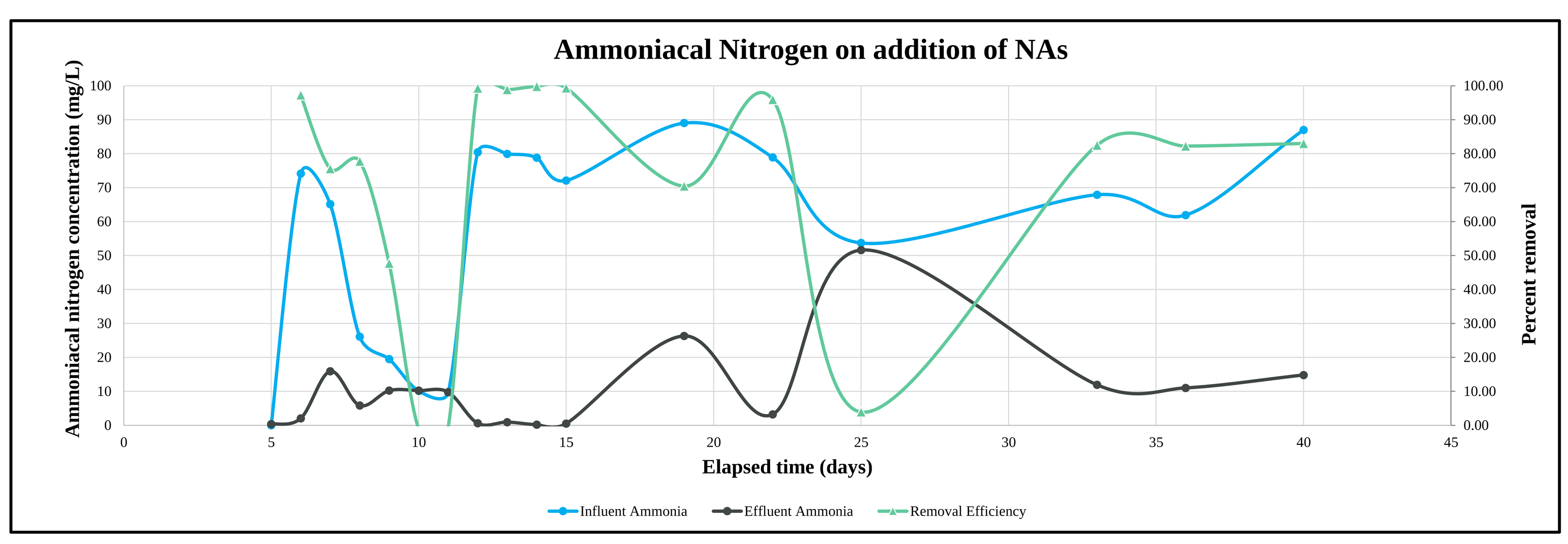
Mature aerobic granules were cultivated in a 5 L sequential aerobic sludge reactor, seeded with 2 L activated sludge from a municipal wastewater treatment plant in Calgary AB, Canada. The granules were fed with an acetate-based synthetic wastewater. Naphthenic acids (Sigma Aldrich 70340) were then added at a 5ppm concentration directly into the wastewater, and results recorded.

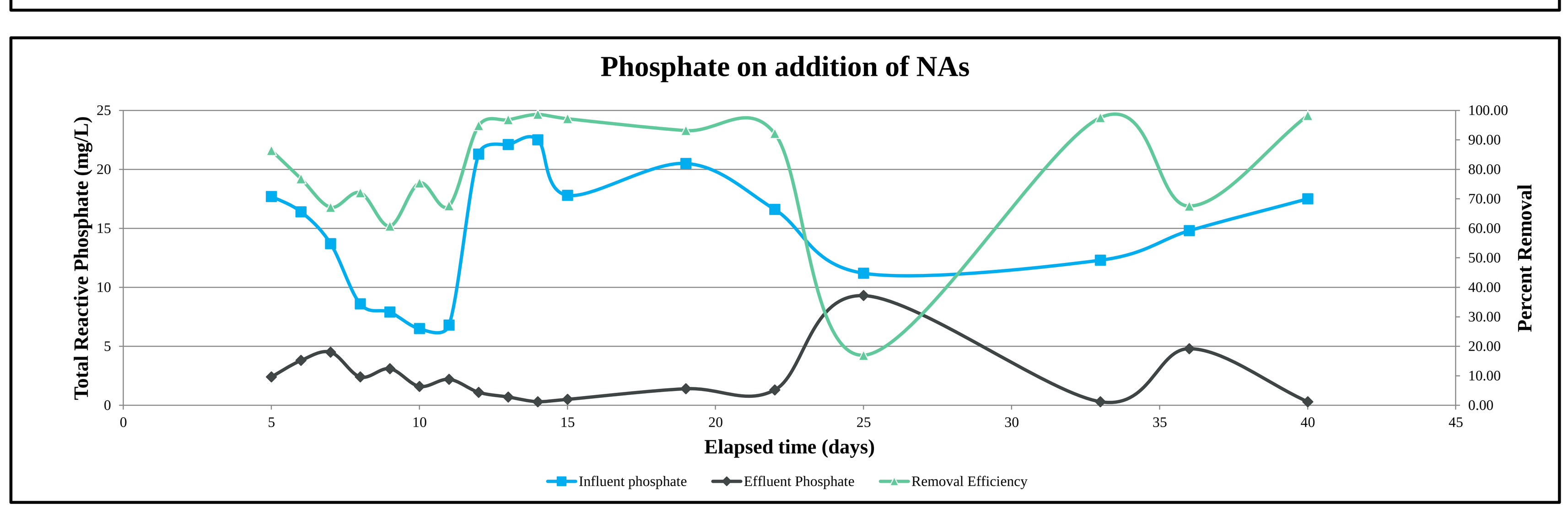
Wastewater samples were analyzed for COD, suspended solids, volatile suspended solids (VSS), NH3-N and PO4-P in accordance with the Standard Methods (APHA 2012). Naphthenic acid analysis requires extraction with dichloromethane, and coupling with gas chromatography – mass spectrometry (GC-MS) techniques for quantification purposes. NA analysis is ongoing currently, and results will be reported in a subsequent article.

Results









Discussion and Future Work

- Despite few system shocks on addition of NAs, COD, ammoniacal nitrogen and phosphate removal efficiencies remained high; and MLVSS/MLSS ratio remained high
- While NA analysis is ongoing, few indirect correlations can be made:
  - Correlations developed by Islam et al. (2014) were employed to study NA degradation, in that a 10% decrease in COD would result in a 29.2% decrease in NA concentration.
  - Addition of ammonium ions creates ammoniated naphthenate salts (Rikka, 2007; Wang et al., 2006), while phosphate addition favours higher rates of biodegradation (Herman et al., 1993; Lai et al., 1996). A degradation of ammoniacal nitrogen can be correlated to degradation of NAs.
- Further tests would correlate degradation of ammoniacal nitrogen with NA degradation.
- Ramp up of influent NA concentrations, without compromising on the granular stability will also be studied.
- Direct measurements of NAs using gas chromatography – mass spectrometry will be performed as well.

References

Allen, E. W. (2008a). *Journal of Environmental Engineering and Science*, *7*(5), 499–524. https://doi.org/10.1139/S08-020
Allen, E. W. (2008b). *Journal of Environmental Engineering and Science*, *7*(5), 499–524. https://doi.org/10.1139/S08-020
American Public Health Association, American Water Works Association, & Water Environment Federation. (2012). *Standard Methods for the Examination of Water and Wastewater*. (22nd ed.). Denver: American Water Works Association.
Brown, L. D., & Ulrich, A. C. (2015). *Chemosphere*, *127*, 276–290. https://doi.org/10.1016/j.chemosphere.2015.02.003
Herman, D. C., Fedorak, P. M., & Costerton, J. W. (1993). *Canadian Journal of Microbiology*, *39*, 576–580.
Islam, M. S., Moreira, J., Chelme-Ayala, P., & Gamal El-Din, M. (2014). *Sci. Total Environ.*, *493C*, 282–290.
Lai, J. W. S., Pinto, L. J., Kiehlmann, E., Bendell-Young, L. I., & Moore, M. M. (1996). *Environmental Toxicology and Chemistry*, *15*(9), 1482–1491.
MacKinnon, M. D., & Boerger, H. (1986). *Water Quality Research Journal of Canada*, *21*(4), 496–512.
Rikka, P. (2007). *Spectrometric Identification of Naphthenic Acids isolated from Crude Oil*. Texas State University-San Marcos.
Show, K. Y., Lee, D. J., & Tay, J. H. (2012). *Applied Biochemistry and Biotechnology*, *167*(6), 1622–1640. https://doi.org/10.1007/s12010-012-9609-8
Wang, Y., Chu, Z., Qiu, B., Liu, C., & Zhang, Y. (2006). *Fuel*, *85*(17), 2489–2493. https://doi.org/10.1016/j.fuel.2006.04.032