

J.T. Kent, J.H. Tay

Department of Civil Engineering, University of Calgary, Calgary, Alberta, Canada. T2N 1N4.
Email: jordan.kent@ucalgary.ca

Introduction

Table 1. Common ESOC categories [3]

| ESOC Categories |
|---------------------------------|
| Detergents |
| Steroids |
| Endocrine modulating substances |
| Plasticizers |
| Pharmaceuticals |
| Antibiotics |
| Personal care products |
| Fire retardants |
| Nanoparticles |

Emerging substances of concern (ESOC) are a newly recognized type of pollutant that is currently found in wastewater, surface water, and drinking water in many jurisdictions.[1] ESOC end up in the environment due to either wastewater discharge or surface runoff into the rivers and lakes.[2] ESOC can be either man-made chemicals or naturally occurring chemicals that are in higher than normal concentrations due to human development. There are potentially over 15 million compounds that could classify as ESOC, typically categories are shown in Table 1.[3]

Current wastewater treatment processes are not designed to specifically target ESOC and any removal is incidental.[4] Technologies currently being evaluated for ESOC removal include, activated carbon, ozonation, chlorination, reverse osmosis and activated sludge.[5a, 5b] While effective, many of these technologies are difficult to scale up for use in wastewater treatment plants due to high costs, complex operation, or health concerns. Activated sludge is the industry standard for removal of organic contaminants because of its effectiveness and low cost. While being more economical, activated sludge is less effective at removing ESOC compounds than other methods.[6a, 6b] Aerobic granular sludge may be a solution to this problem by combining the economic benefit of biologic wastewater treatment with the possibility of higher ESOC removal efficiency.

This research will determine whether aerobic granular sludge can be used to remove select ESOC that have been identified by the City of Calgary. Table 2 shows some of the compounds identified by the City of Calgary and the recommended medical dose if applicable.[7] To conduct this research an aerobic granule sludge system will be created and then select ESOC will be introduced into the feed while the effluent and sludge health are monitored.

Table 2. ESOC monitored by City of Calgary and recommended medical dose [7]

| ESOC | Recommended dose |
|-------------------------------|------------------|
| Ibuprofen | 1600 mg/d |
| Naproxen | 1000 mg/d |
| Carbamazepine | 1200 mg/d |
| Venlafaxine | 225 mg/d |
| Nonylphenol | n/a |
| Fluoxetine | 80 mg/d |
| 17 α -ethynylestradiol | 0.02 mg/d |
| Gemfibrozil | 1200 mg/d |

Research Objectives

Research Questions:

- 1) What is the removal efficiency for pharmaceuticals and personal care products (PPCP) when using aerobic granular sludge in a sequencing batch reactor?
- 2) What fraction of ESOC removal is due to degradation of the PPCP, compared to absorption of the PPCP into the granule structure?
- 3) What is the effect on the bulk aerobic granular sludge health when ESOC are added to the influent?

Objectives:

- ❖ Establish a stable aerobic granular sludge bioreactor
- ❖ Determine optimal air up-flow velocity in the bioreactor for aerobic granule formation
- ❖ Sustain granular sludge system on low OLR feed representative of influent to City of Calgary WWTPs
- ❖ Develop a reliable method of quantification for each ESOC compound
- ❖ Measure ESOC removal, granular sludge health, and amount absorbed into granules

Out of Scope:

- ❖ Using real wastewater as feed for the experiment
- ❖ Identifying metabolites that are formed by the partial degradation of ESOC compounds
- ❖ Identifying the types of bacteria and their role in ESOC removal

Determine Optimal Air Flowrate

The shear in the bioreactor is arguably the most important factor determining whether healthy activated sludge becomes aerobic granular sludge. Unlike manual mixing methods, the shear from rising gas bubbles is able to provide the impetus for granule growth without breaking the granules apart. The optimal air superficial air velocity for granule formation is reported in literature as ranging from 1.2 cm/s to 3.6 cm/s.[8]

A superficial air velocity of 2.6 cm/s was used to form the first initial granules. However, after the initial visible granules broke up, a test was conducted to confirm the ideal air velocity to promote granule growth. Figure 2 shows the results of this test where the air rate was changed step wise from 1.97 cm/s, to 3.28 cm/s, and then back down to 1.84 cm/s.

It is clearly seen in Figure 2 that the low range air velocity is better for granule growth, while the higher flowrate resulted in a reduction in granule size. At both air velocities the size of the granules stabilized, but the higher air velocity resulted in a significantly smaller average granule size. Using these results, a lower air velocity has been used to increase the granules size into the visible range once again.

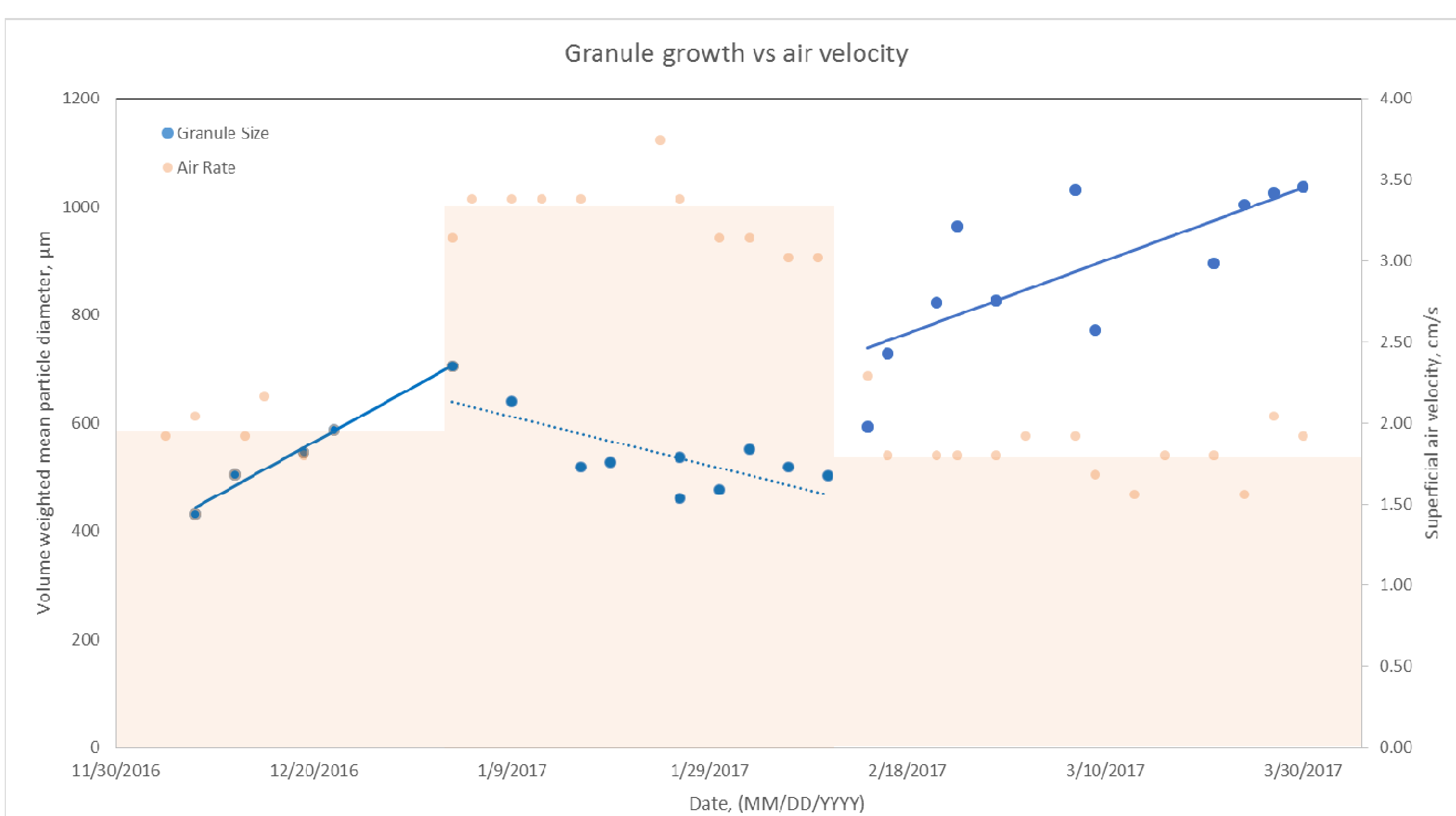


Figure 2. Comparing the average granule size resulting from different air velocities in the bioreactor.

Future Plans

Two of the five objectives, 1) to establish a stable aerobic granular sludge system and 2) to determine the best air velocity for granule growth, have been completed already. One objective, 3) to sustain a granule sludge system at low OLR, has been started. The MLSS of the sludge bed appears to have stabilized but there is the potential for additional sludge loss. As well, the phosphorus removal efficiency must be increased from 14%, until this has been achieved this objective will not be considered complete.

The two remaining objectives, 4) developing a reliable method of ESOC quantification and, 5) measuring the efficiencies and mechanism of ESOC removal, will be completed over the next eight months.

In order to complete the current project the proposed milestones are:

- ❖ Recover the phosphate removal capabilities of the system
- ❖ Create standards for each ESOC and practice the analytical method used to detect these compounds
- ❖ Introduce selected ESOC from Table 2 into the aerobic granular sludge feed water
- ❖ Utilize equipment available at the ACWA facility and University of Calgary to measure ESOC removal
- ❖ Identify the main mechanism of removal (degradation or adsorption) for each ESOC added
- ❖ Determine minimum air needed to maintain an aerobic granular sludge reactor (time permitting)

References:

- [1] Petrović, Mira, Susana Gonzalez, and Damià Barceló. "Analysis and removal of emerging contaminants in wastewater and drinking water." *TrAC Trends in Analytical Chemistry* 22.10 (2003): 685-696.
- [2] Lapworth, D. J., et al. "Emerging organic contaminants in groundwater: a review of sources, fate and occurrence." *Environmental pollution* 163 (2012): 287-303.
- [3] Kolpin, Dana W., et al. "Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999–2000: A national reconnaissance." *Environmental science & technology* 36.8 (2002): 1202-1211.
- [4] Kasprzyk-Hordern, Barbara, Richard M. Dinsdale, and Alan J. Guwy. "The removal of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs during wastewater treatment and its impact on the quality of receiving waters." *Water research* 43.2 (2009): 363-380.
- [5a] Adams, Craig, et al. "Removal of antibiotics from surface and distilled water in conventional water treatment processes." *Journal of environmental engineering* 128.3 (2002): 253-260.

- [5b] Westerhoff, Paul, et al. "Fate of endocrine-disruptor, pharmaceutical, and personal care product chemicals during simulated drinking water treatment processes." *Environmental science & technology* 39.17 (2005): 6649-6663.
- [6a] Lishman, Lori, et al. "Occurrence and reductions of pharmaceuticals and personal care products and estrogens by municipal wastewater treatment plants in Ontario, Canada." *Science of the Total Environment* 367.2 (2006): 544-558.
- [6b] Chen, Chun-Yao, Chun-Kang Wang, and Yang-Hsin Shih. "Microbial degradation of 4-monomethylbrominated diphenyl ether in an aerobic sludge and the DGGE analysis of diversity." *Journal of Environmental Science and Health Part B* 45.5 (2010): 379-385.
- [7] <http://www.drugs.com; http://www.rxlist.com/alesse-drug.htm> (17 α -ethynylestradiol)
- [8] Tay, J.-H., Q.-S. Liu, and Yu Liu. "The effects of shear force on the formation, structure and metabolism of aerobic granules." *Applied microbiology and biotechnology* 57.1-2 (2001): 227-233.

Establish a Stable Granular System

The bioreactor has been continuously operating since August 2016. Recycled activated sludge from Pine Creek Wastewater Treatment Plant (WWTP) was used to inoculate the system. The operating conditions of the bioreactor were set to form granules. The first visible granules were formed 14 days after inoculation, however, after 47 days of operation the granules had become unstable and disintegrated.

Following the disintegration of the visible granules the system still qualified as granular and experiments were done to determine the optimum conditions for granule growth. By February 21, 2017 the granules had grown large enough to become visible again. Table 3 summarizes the changes in the sludge prior to and after the granulation process. Figure 1 shows the change in sludge structure during the granulation process.

Table 3. Bulk sludge characteristics when in floccular structure compared to granular structure.

| | Initial Sludge | Granular Sludge (Mature) |
|---|-----------------|--------------------------|
| | August 17, 2016 | May 11, 2017 |
| Sludge volume index (SVI), mL/g | 128 | 15 |
| Mixed liquor suspended solids (MLSS), mg/L | 3386 | 9167 |
| Volume weighted mean particle diameter, μ m | 150 | 826* |

* This is the average diameter of all sludge particles. The size of the granules without the flocs is 2977 μ m, as shown in Figure 1.

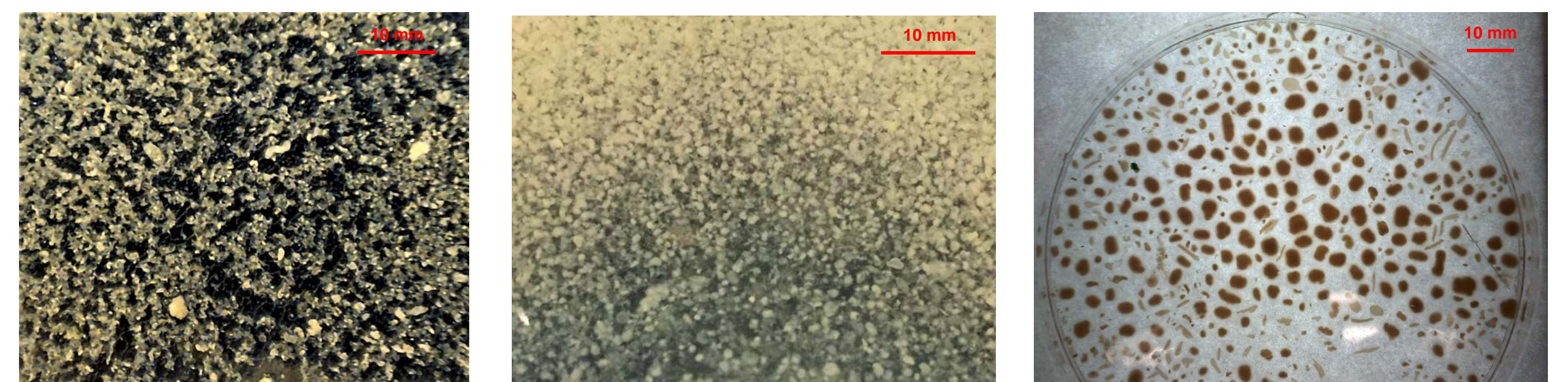


Figure 1. The transition of the aerobic sludge from floccular structure (left), to small granules (middle), to mature granules (right).

Operating Conditions:

- The operating conditions used to grow and maintain a stable granular system:
- ❖ Organic loading rate (OLR) = 1.1 to 3.4 kg/m³/d
 - ❖ Superficial air velocity = 1.84 cm/s
 - ❖ Hydraulic residence time (HRT) = 9 hours

Performance:

- Average removal efficiency of the mature aerobic granular sludge was:
- ❖ Chemical oxygen demand (COD) = 94 %
 - ❖ Ammonium (NH₄⁺) = 86 %
 - ❖ Phosphate (PO₄³⁻) = 73 %

Reduced Feed OLR

After establishing a stable aerobic granular sludge system the feed was changed to a feed representing the influent wastewater to City of Calgary WWTPs.

- ❖ The nutrient ratio of Calgary's wastewater is; 100 (Carbon) : 4.2 (Nitrogen) : 1.3 (Phosphorus)
- ❖ The COD of the influent wastewater is 532 mg/L, based on the removal of BOD in the primary treatment stage the COD entering the second phase of the wastewater treatment plant is approximately 415 mg/L.

This was a significant reduction in the feed concentration for the granules and so a loss of sludge was expected. Figure 3 shows the decrease in the mixed liquor suspended solids (MLSS), an indicator of microbial density, as the food concentration is reduced from an average of 3.2 kg/m³/d to 0.4 kg/m³/d. The MLSS drops from 14400 mg/L to a stable value near 6000 mg/L. While many granules did breakup and wash out the sludge is still primarily composed of granules, not flocs.

Sludge bed seems to have stabilized, however there are two issues that remain to be solved before the project can continue.

- 1) The food to microbe (F:M) ratio dropped from 0.21 to 0.08 when the feed concentration was reduced. This means that continued sludge bed reduction might occur over time. This is acceptable as long as removal rates remain high.
- 2) The phosphate removal has dropped from an average of 73% removal to an average of 14% removal. This is not acceptable and the cause is still undetermined.

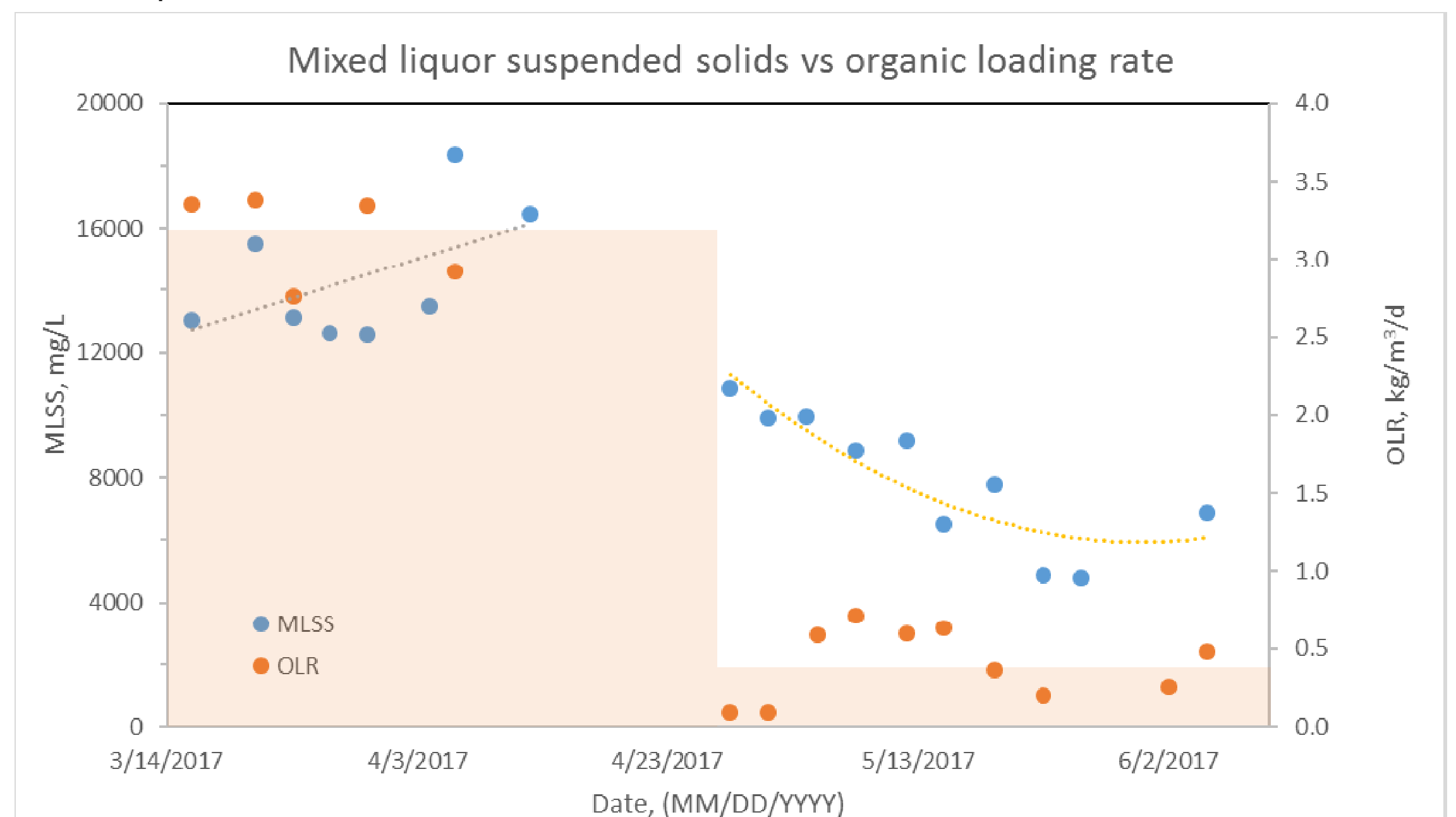


Figure 3. The effect of organic loading rate (OLR) on the mixed liquor suspended solids (MLSS)