Lab Exercise #6: Wastewater

Objective:
To characterize the performance of the Amherst Wastewater Treatment Plant.

Introduction

Plant Description

The Amherst wastewater treatment plant is located immediately west of the athletic fields (Circled in red below).

When you arrive on site, please enter the south end of the main building (circled in red below).

The current plant went on line in 1979, replacing a smaller primary treatment facility. It has a design flow of 7 MGD, but typically treats no more than 3.5-4 MGD. Raw Amherst wastewater is almost entirely residential, with very little industrial component, although it does receive wastewater from UMass.
Wastewater is first passed through a grinder and a grit chamber to remove sand and other solids that might harm the pumps and valves. The primary clarifiers are 70 feet in
diameter with mechanical sludge collection. The rake drive is powered by a 1 HP motor. The tanks hold about 0.32 MG and also include a skimmer and beaching plate. Primary effluent BOD$_5$ is typically about 80 mg/L.

Figure 4. North End of plant showing 3 Primary Clarifiers and Preliminary Treatment Building

Figure 5. One of the Primary Clarifiers, currently out of Service
The Amherst Wastewater Treatment Plant employs conventional activated sludge. Each aeration basin holds 0.208 MG, with 3 such basins in use under normal operation.

Figure 6. Aerial View of Activated Sludge Tanks (on left).

Figure 7. Activated Sludge Tank from the ground showing surface Aerator
The secondary clarifiers are 85 feet in diameter with draft tubes for vacuum sludge collection. A 2 HP motor is mounted above the center well.
Water from the secondary settling tanks enters a wet well just south of the clarifiers. From here there are two 100 HP pumps and a third 20 HP pump that can be used to send the effluent to the Connecticut River. At this point chlorine is injected (only during warmer months) at a typical usage rate of 40 lb/day. The water leaves the plant with a residual of about 0.5 mg/L. The effluent pipe is 36 inches in diameter and about 1.8 miles long. This provides adequate chlorine contact time as required, without the need for a chlorine contact tank.

Sludge is collected from the primary and secondary clarifiers. The flow of 1° sludge is about 20% of the flow of 2° sludge. The primary is about 6% solids whereas the secondary is only about 0.5% solids. These are mixed and thickened in the main building. The Ashbrook gravity belt thickener (http://www.as-h.com/us/en-us/Aquabelt.aspx) is used with polymer addition and it is operated about 5 hrs per day. The final blended solids content after thickening is about 7%. Since the closing of the Amherst landfill, all thickened sludge has been taken to other locations. Most currently goes to Fitchberg, MA where it is further dewatered, incinerated and then ash is placed in a landfill.

Operation of the biological treatment system is generally based on a target F/M of 0.30 (based on BOD_s). The MLVSS target is 2,700 mg/L, which usually results in a sludge age of about 10 days.

Chemical Oxygen Demand (from Hach literature)

The Chemical Oxygen Demand (COD) test uses a strong chemical oxidant in an acid solution and heat to oxidize organic carbon to CO_2 and H_2O. By definition, chemical oxygen demand is “a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant.” *Oxygen demand is determined by measuring the amount of oxidant consumed using titrimetric or photometric methods. The test is not adversely affected by toxic substances, and test data is available in 1-1/2 to 3 hours, providing faster water quality assessment and process control.

COD test results can also be used to estimate the BOD results on a given sample. An empirical relationship exists between BOD, COD and TOC. However, the specific relationship must be established for each sample. Once correlation has been established, the test is useful for monitoring and control.

When organic matter is oxidized by dichromate in sulfuric acid, most of the carbon is converted to CO_2. Hydrogen present is converted to H_2O. The reaction is illustrated using the primary standard, potassium acid phthalate (KHP), as an example:

\[
2 \text{KC}_8\text{H}_5\text{O}_4 + 10 \text{K}_2\text{Cr}_2\text{O}_7 + 41 \text{H}_2\text{SO}_4 \rightarrow 16 \text{CO}_2 + 46 \text{H}_2\text{O} + 10 \text{Cr}_2(\text{SO}_4)_3 + 11 \text{K}_2\text{SO}_4
\]

Dichromate ions (Cr_2O_7^{2-}) form orange-colored solutions. When dichromate is reduced to chromic ion (Cr^{3+}), the solution becomes green. Intermediate valence states may also occur. The COD can be determined by measuring the loss of dichromate (at ~420 nm) or the formation of chromic ion (at about 600 nm). Most tests make use of the 420 nm wavelength due to better sensitivity.
Apparatus used in the micro digestion method consists of a COD Reactor with a 25-vial capacity. The Hach COD Reactor will maintain a temperature of 150 ± 2 °C. Caps on Hach COD Reagent vials are specially designed to provide a positive seal when used in the COD Reactor. They will not withstand temperatures above 120 °C. The caps reach a temperature of about 85 °C when used with the COD Reactor, even though the digestion mixture maintains 150 °C. This temperature difference provides the refluxing action necessary for the recovery of volatile organics.

Nitrate Determination by the Cadmium Reduction Method

Nitrate (NO$_3^-$) is reduced almost quantitatively to nitrite (NO$_2^-$) in the presence of cadmium (Cd). The macro method uses commercially available Cd granules treated with copper sulfate (CuSO$_4$) and packed in a glass column. The Hach kit uses reagents in powder pillows. The NO$_2^-$ produced from Cd reduction is subsequently determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine dihydrochloride to form a highly colored azo dye that is measured using a color comparator or a spectrophotometer (@543 nm). A correction may be made for any nitrite (NO$_2^-$) originally present in the sample by analyzing without the reduction step. The applicable range of this method is 0.01 to 1.0 mg NO$_3^-$-N/L.

Use of Analytical Balances

An analytical balance is required for the determination of solids in environmental samples. It is also used for preparation of standard solutions, as required for calibrating the nitrate method. A cut-away diagram of a typical modern analytical balance is shown below.

1. Balance Beam 
2. Concentric Weights 
3. Fixed counterweight 
4. zero-point adjust 
5. Scale-deflection adjustment weight 
6. Graduation plate 
7. Parallelogram suspension 
8. Knife edges 
9. Sample 
10. Weight-lifting mechanism 
11. Weight control knobs 
12. Light bulb 
13. Mirrors 
14. Readout Panel 
15. Air damping
The correct weighing procedure depends somewhat on the design of the balance. Most mechanical single pan analytical balances have a knife edge supported balance beam. Such balances are always equipped with a pan release lever which raises and lowers the fulcrum off of a finely-machined knife edge. In the Environmental Engineering Teaching Laboratory we have a Mettler H80 which employs a taught band fulcrum support system, rather than a knife edge. It, therefore, does not require a pan release. The Mettler H80 is pictured on the following page. The numbers refer to the following:

1. Level indicator
2. Weight control knob for 10 g increments
3. Weight control knob for 1 g increments
4. Power switch for optical scale
5. Weighing pan
6. Leveling feet
7. Sliding door, right
8. Zero adjustment knob
9. Readout
10. Micrometer knob
11. Image definition adjustment
12. Cover plate of lighting system
13. Power cable
14. Sliding door, left
Some general rules should be kept in mind when using an analytical balance:

1. Allow samples to reach room temperature before weighing. Samples that are too hot will set up convection currents and the apparent sample weight will be incorrect. A slowly drifting apparent sample weight is indicative of this problem.

2. Chemicals should be placed in a weighing bottle, a plastic weighing tray, or coated weighing paper. Weighing paper is best for small quantities (usually <1g); weighing trays are used for larger amounts; and stoppered weighing bottles are recommended for reactive, volatile, toxic or hygroscopic substances. In the absence of a weighing bottle, a small beaker and watch glass may be substituted. Never place chemicals directly on the pan!

3. The analytical balance should be kept clean at all times. If a solid is spilled inside the weighing chamber, carefully remove it with the balance brush. The desiccant should be replaced
or regenerated when it changes color. Used weighing papers and trays should be immediately discarded.

The procedure for weighing with the Mettler H80 is as follows:

1. Insure that the balance is level by verifying that the air bubble is in the center of the circular marking of the level indicator (1).
2. Verify that the weight control knobs (2,3) and micrometer knob (10) are in the zero position.
3. Carefully clean off the pan (5) with the soft brush provided.
4. Actuate power switch (4). Optical scale image appears.
5. Close both doors and adjust zero point, if necessary, with the zero adjustment knob (8).
6. Open one door and place the empty weighing vessel on the center of the pan. Its weight is referred to as the "tare", and the process of weighing it is called "taring". Objects to be weighed may be moved by hand prior to determination of the tare and after final weighing only. Should the sample container need to be moved between taring and final weighing, use either clean, dry rubber gloves (not latex), tongs, or a paper loop. Fingerprints will add significant mass to small samples.
7. Close the glass doors tightly to avoid unsettling air currents.
8. Turn weight control knob (2) until optical scale image moves through readout field, the turn knob (2) back one step.
9. Turn weight control knob (3) until optical scale moves into readout field.
10. Turn micrometer knob (10) until next scale division line is exactly in center of index fork.

![Figure 12: Mettler H80 Readout](image)

11. Read weight.
12. Open door and remove object from pan.
13. Return weight control knobs (2,3) and micrometer knob (10) to zero, and brush off pan and weighing chamber, if necessary.
14. Repeat steps 3-13 for weighing vessel plus sample.
1. Compensating stirrup
2. Front Knife edge
3. Overhead pan brake
4. Weight Carriage
5. Built-in weights
6. Weighing pan
7. Weight control mechanism
8. Optical projection screen
9. Micrometer mirror
10. Micrometer plane glass
11. Arrestment cam
12. Zero-point mirror
13. Arrestment rod
14. Objective focus control
15. Optical scale and objective
16. Air damper
17. Sensitivity adjustment
18. Macro zero adjustment
19. Beam
20. Main bearing

Figure 13: Sartorius 2400 series balance
Measurement of Solids

**Suspended Solids (Non-filtrable Residue).** Suspended solids is measured directly by drying and weighing the solids retained during filtration. This approach is much more accurate for most waters than the indirect method of subtracting dissolved solids from total solids. Whatman 934AH glass fiber filters (nominal pore size 1.4 microns) are most commonly used. These may be placed in small aluminum foil weighing pans. The filters may be identified by etching a number into the small tab on the weighing pans. Filters should be weighed, heated and dried while remaining in the aluminum pans. They should only be removed for actual filtering operations. They should always be handled with tongs, and one must be careful not to tear them or leave fragments on the filtration apparatus. Precision has been found to be ±5 mg/L at low concentrations, increasing up to ±20 mg/L at values of 200 mg/L or more.

1. Prewash a 934AH glass fiber filter by rinsing three times with 20 mL of distilled water. Maintain suction until the filter is dry.
2. Dry this filter at 103-105°C for 1 hour, and cool in a desiccator.
3. Weigh the filter, then pass a water sample of sufficient volume to yield 50-200 mg suspended solids through it. Smaller volumes will result in reduced accuracy.
4. Dry for at least one hour at 103-105°C.
5. Cool in a desiccator and weigh. As always, the sample should be re-heated in accordance with #4 and re-weighed to achieve a constant weight (a drop of no more than 0.5 mg).

**Volatile Solids and Fixed Solids**

*Fixed solids* are those that remain as residue after ignition at 550°C for 15 minutes. The weight of material lost is called the volatile solids. Thus the total operational definition for volatile solids would be: all matter lost upon ignition at 550°C for 15 minutes, but not lost upon
drying at 103-105°C for 1 hour. The portion lost upon ignition is generally assumed to be equivalent to the organic fraction. The portion remaining is considered the inorganic fraction. For waters of moderate to high hardness, most of this is calcium carbonate which decomposes only at temperatures exceeding 800°C. When igniting a filter with suspended matter, one must be especially careful of the temperature; above 600°C glass fiber filters begin to melt and can lose a significant amount of weight in 15 minutes.

Combining the fractionations resulting from ignition and filtration, one arrives at a total of 9 separate categories: total solids (TS), fixed solids, volatile solids, total dissolved solids (TDS), fixed dissolved solids, volatile dissolved solids, total suspended solids (TSS), fixed suspended solids, and volatile suspended solids (VSS). In practice, only four of these (TS, TDS, TSS, and VSS) are commonly used. When comparing fixed solids with inorganic content, one would expect positive bias from incomplete oxidation of organic matter, and negative bias from decomposition of certain inorganics. Ammonium salts may be lost during low temperature drying or upon ignition. Most others are stable under the conditions used for volatile solids determination with the exception of magnesium carbonate (equation 1). Volatile solids may be effected by these as well as loss of recalcitrant waters of crystallation (positive bias), and previous losses of organic matter to volatilization during low-temperature drying (negative bias). A modest interlaboratory study found an average standard deviation of 11 mg/L on a sample of 170 mg/L volatile solids.

\[
\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2 \uparrow \tag{1}
\]

Analysis of sludge, sediment, and soil for fixed and volatile solids presents additional problems. Both negative and positive biases can be acute, so greater care must be taken in ignition temperature and time. Again, ammonium compounds (often present in sludge in the form of ammonium bicarbonate) may be lost during low temperature drying and therefore should not introduce a bias in volatile solids analysis (equation 2). However, occluded water can be especially problematic. Standard practice is to use a 1-hour ignition time. With sludge, sediment and soil, nearly all of the solids are in the undissolved state. Therefore, only total, total volatile, and total fixed fractions are normally determined.

\[
\text{NH}_4\text{HCO}_3 \rightarrow \text{NH}_3 \uparrow + \text{H}_2\text{O} \uparrow + \text{CO}_2 \uparrow \tag{2}
\]

1. Dry and weigh a vessel containing the solids to be analyzed. For volatile and fixed suspended solids analysis, the filter (with residue) prepared for suspended solids analysis and dried to a constant weight may be used. For volatile and fixed total (or dissolved) solids, the evaporating dish (with residue) prepared for total (or dissolved) solids analysis dried to a constant weight should be used.
2. Ignite the sample and vessel in a preheated muffle furnace set at 550±50°C for 15-20 min (water & wastewater) or 1 hour (sludge, sediment & soil).
3. Cool for 15 minutes in the open air in an area protected from dust.
4. Place vessel in a desiccator for final cooling to room temperature and weigh. Due to the approximate nature of this test samples are not generally re-heated and dried to a constant weight.
Laboratory #6 Procedure

The lab TA will collect 5 samples at various points (raw, primary effluent, secondary effluent, mixed liquor, waste activated sludge) in the plant and return them to UMass for analysis of solids and COD by the class. Measure solids (TSS and VSS) on all 5, but COD and nitrate on only the three as below. In each lab period we will form 5 groups (A-E) and each will be responsible for sample analysis as listed below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Solids</th>
<th>COD</th>
<th>Nitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw WW</td>
<td>A</td>
<td>A</td>
<td>X</td>
</tr>
<tr>
<td>Primary Effluent</td>
<td>B</td>
<td>B</td>
<td>X</td>
</tr>
<tr>
<td>Secondary Effluent</td>
<td>C</td>
<td>C</td>
<td>X</td>
</tr>
<tr>
<td>Mixed Liquor Activated Sludge</td>
<td>D</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Waste Activated Sludge</td>
<td>E</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calibration Standard I</td>
<td>D</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Calibration Standard II</td>
<td>E</td>
<td></td>
<td>X</td>
</tr>
</tbody>
</table>

A. Determination of Wastewater Suspended Solids

1. Select a pre-dried glass fiber filter and aluminum pan from the desiccator (1 per group), handling it with tweezers or a gloved hand. Place a mark on the pan tab so that you can identify your filter/pan and measure its weight \((W_1)\) on the analytical balance. This is referred to as the “tare”.
2. Using tweezers, place the filter on a filter base. Clamp the reservoir on the base, locking in the filter paper.
3. Connect the filter flask and pump.
4. Turn on pump and pour a pre-measured volume of sample into the filter reservoir. Recommended volumes are 1000 mL for secondary effluent, 50 mL for raw wastewater and primary effluent and 10 mL for the sludge samples.
5. Wash down sides of reservoir with distilled water from a squeeze bottle.
6. Using tweezers, carefully place the filter back onto its aluminum pan and place the pan + filter into the 103°C drying oven.
7. Following one hour of drying remove all filters and pans from the 103°C oven and place in desiccator to cool.
8. Weigh each filter/pan unit \((W_2)\) after it has returned to room temperature (about 15 min).
9. Place each pan and filter in the 550°C furnace for 15 min.
10. Following the 15 min ignition period transfer each pan and filter to the desiccator.
11. Weigh each filter/pan unit \((W_3)\) after it has returned to room temperature (about 20 min).

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1 A decision was made not to measure nitrate because the plant is not currently in nitrifying mode.
B. Micro COD Test (from Hach literature)

1. Turn on the COD Reactor and preheat to 150 °C.
2. Mix the sample thoroughly so that you can remove a representative sub-sample.
3. Remove the cap of a COD Reagent vial and transfer 2.00 mL of sample into the vial.
4. Replace the vial cap tightly. Hold the vial by the cap and invert several times over a sink to mix. (CAUTION! Dichromate COD vials will become very hot during mixing.)
5. Place the vials into the pre-heated COD Reactor. Heat the vials for 2 hours.
6. Remove the vials from the reactor and cool to room temperature.
7. Adjust wavelength on spectrophotometer to 420 nm. Measure absorbance.
8. Compare absorbance with values from COD standards (Potassium Acid Phthalate, or KHP).

C. Nitrate Nitrogen Determination (from Hach literature)

Do the following for all samples plus a blank (deionized water) and a 10 mg/L nitrate standard:

1. Add 0.5 mL of sample or standard to a 10 mL test tube
2. Add 4.5 mL of deionized water
3. Open one NitraVer 6 Nitrate Reagent Powder Pillow and add contents of this pillow to the diluted sample in the test tube
4. Shake for 3 minutes and allow the sample to stand undisturbed for an additional 30 seconds, allowing cadmium particles to settle
5. Carefully pour the supernatant into a second test tube
6. Open one NitraVer 3 Nitrate Reagent Powder Pillow and add contents of this pillow to the decanted sample in the second test tube
7. Stopper this tube and shake for 30 seconds. A red color will develop if nitrate is present.
8. Allow at least 10 minutes, but not more than 20 minutes before measuring absorbance.
9. Adjust the wavelength on the spectrophotometer to 540 nm. Zero the spectrophotometer and measure absorbance of the sample at 540 nm wavelength.

Lab Preparation (done by TA)

Assemble Glassware and related lab supplies
- Vacuum flasks and filter holders
- Glass fiber filters, aluminum pans
- Graduated Cylinders form measuring sample volume for solids analysis
- COD vials
- Nitrate glassware
- Pipets for measuring sample volume for COD test

Assemble and Test out Equipment
- Both ovens
- Analytical Balance
- COD kits and reactors
- Nitrate kits

Prepare and Dry Filters
- Pre-heat filters in oven and place each on a separate aluminum pan in the dessicator

Steps for completing the lab write-up

Data Presentation
a) Present your data (TSS, VSS, COD and nitrate) in a logical tabular format. You should also graph the COD and nitrate data.
b) What is the ratio of mixed liquor VSS to TSS? Is this typical for activated sludge mixed liquor?
c) Calculate the percent COD removal across primary and secondary treatment.
d) To what extent is the plant nitrifying?
Plant Assessment

e) Estimate overflow rate for the primary and secondary clarifiers in meters/day. Assume average flow of 3.5 MGD and two clarifiers of each type in service. Also determine the average water depth in the primary clarifiers.

f) Compare your data for MLVSS with the plant target MLVSS

g) Calculate the COD-based F/M ratio. How does this compare to the plant target value? Keep in mind that the COD concentration is usually 1.5 to 2.5 times the BOD₅ concentration.

h) Calculate the hydraulic retention time in the aeration basins

i) Calculate the average waste activated sludge flow rate \( Q_w \) in gallons per minute that must be maintained to assure a target of 10 days sludge age \( (\Theta_c) \) assuming the MLVSS and waste activated sludge VSS that you measured.