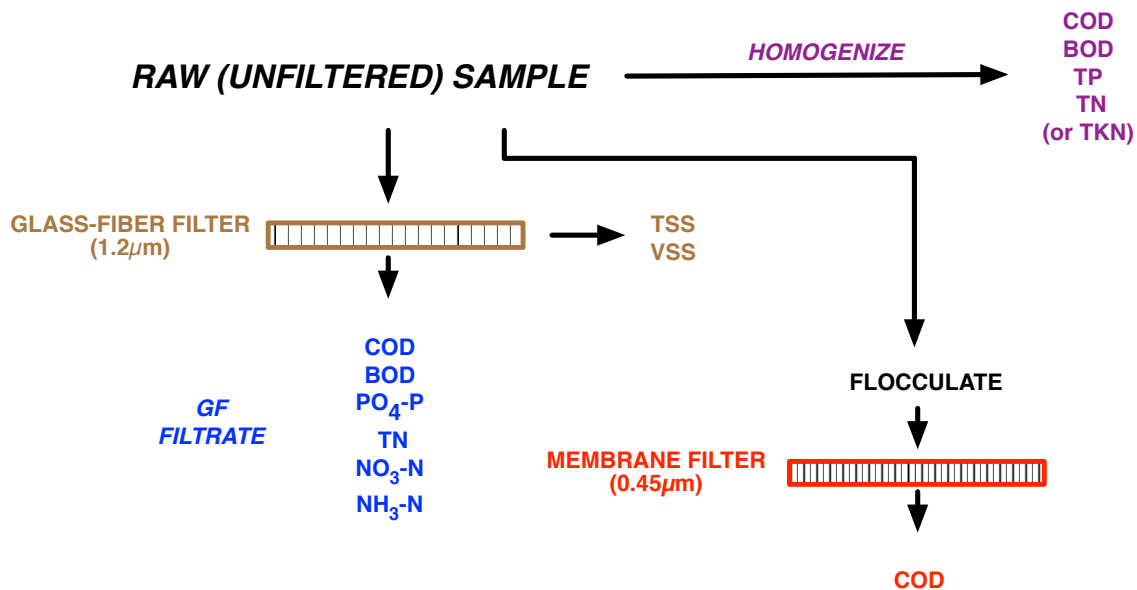


Analysis Chain for Supplemental Sampling

The suggested range of analyses for COD, BOD, N and P species to be performed on raw influent wastewater samples is laid out in the diagram below. Essentially the same analyses should be performed on primary effluent samples if the plant incorporates PSTs.

In addition to these analyses, measurements of pH and Alkalinity should be included.

Depending on the project objectives, certain other analyses should be performed; for example, VFA, Total S, sulfate.



On the **influent sample**, the following procedure should be implemented:

- Divide the sample into three sub-samples (being careful to shake/mix up the main sample very well).
- Homogenize¹ one of the sub-samples and analyze for “total” parameters (e.g. COD, BOD, TN, etc.)
- Use the second sub-sample for TSS and VSS analyses. Keep the filtrate, and on a portion of that, analyze for COD, NH₃-N, PO₄-P, etc.
- Flocculate and filter the third sub-sample using the method of Mamais *et al.* (1993) and analyze the filtrate for COD.
- It is important that each series of analyses starts with the same sample.

¹ The meaning of **homogenize** in the above procedure: we usually run the sample in a blender at high speed for 1-2 minutes. The objective here is to break up the little “bits” so that when we do something like total COD on an unfiltered sample we try and increase the chance that we’re getting a representative measure of the COD associated with both soluble and particulate material. Also be careful to shake well before taking any sub-samples (*i.e.* before measuring a volume for solids analysis).

ffCOD Analysis Method:

The method is based on a physical separation, which involves pre-flocculation of the sample followed by filtration (referred to as the ffCOD). It is assumed that the flocculation step will remove the colloidal material, resulting in a filtrate that contains only “truly soluble” material.

The unbiodegradable soluble COD must be subtracted from the raw wastewater ffCOD to obtain the influent readily biodegradable COD, *i.e.*, the RBCOD is estimated by determining the ffCOD of the raw influent, and subtracting from it the filtered effluent COD.

Materials/Equipment List:

- Zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$)
- 6 M sodium hydroxide
- Distilled/deionized water
- 500 mL beaker
- pH analyser
- Stir plate
- 0.45 μm membrane filters
- Filtration apparatus
- 0 to 10 mL pipette

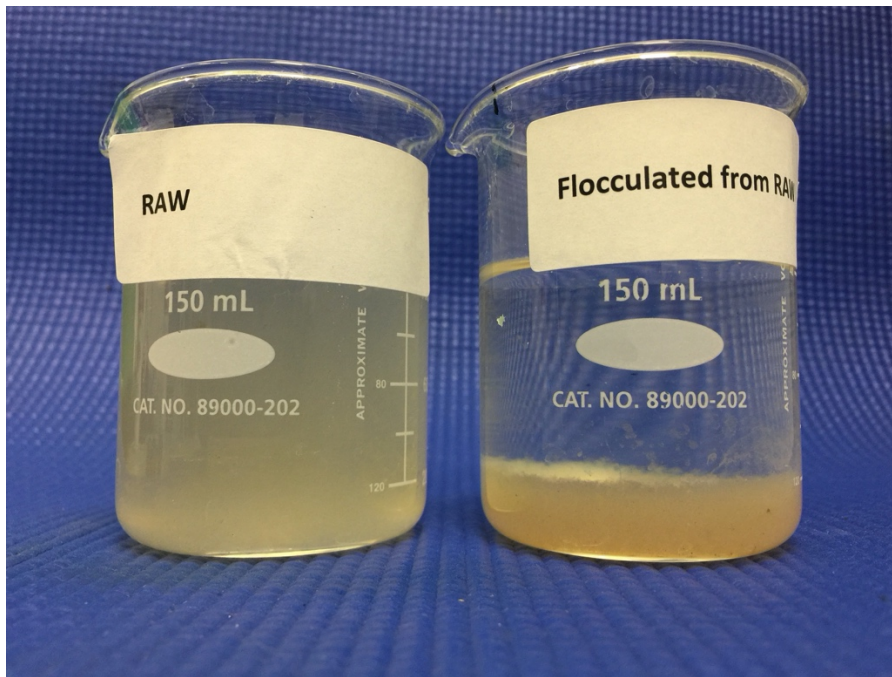
Stock Solution Preparation:

Make up a stock solution of zinc sulfate as follows:

- Dissolve 20 g of zinc sulfate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) into 200 mL of distilled/deionized water.

ffCOD Procedure:

- Pipette 2 mL of the 100 g/L zinc sulfate stock solution into a 200 mL raw wastewater sample (or 1 mL 100 g/L zinc sulfate stock solution into a 100 mL sample).
- Mixed the sample vigorously for approximately 1 minute (*i.e.* use a pH analyzer stir plate).
- Turn the mixer to low, set up a pH probe in the sample and add 6 M sodium hydroxide solution drop-wise until the pH is adjusted to approximately 10.5.
- You should see flocs start to form in the sample.
- Gently mix the sample for several minutes (*e.g.* 10-15).
- Turn off the mixer and allow the sample to settle. A fairly clear supernatant should be evident.
- Withdraw 40-50 mL of the clear supernatant with a pipette (avoiding pulling up any of the settled solids) and filter this supernatant through a 0.45 μm membrane filter.
- Analyze the filtrate for COD.



Related references:

Mamais, D., D. Jenkins and P. Pitt (1993) A Rapid Physical-chemical Method for the Determination of Readily Biodegradable Soluble COD in Municipal Wastewater. *Water Res.*, 27(1):195-197.

Wentzel, M.C., Mbewe, A., Lakay, M.T., Ekama, G.A. (2000) Evaluation of a Modified Flocculation Filtration Method to Determine Wastewater Readily Biodegradable COD. Presented at the WISA 2000 Biennial Conference, Sun City, South Africa, 28 May – 1 June 2000.