# Course « Water and wastewater treatment », Fall 2020

**Part I « Wastewater treatment » by Prof. Holliger**

## Homework 1

**Homework 1-1 : « Carbonaceous oxygen demand of bacteria and organic matter »**

An approximate empirical formula for bacterial cells is $C_5H_7O_2N$, the one for organic matter $C_{18}H_{19}O_9N$. What would be the carbonaceous chemical oxygen demand for 1 g of bacterial cells or 1 g of organic matter ?

***Solution***

With the general formula for oxidation of organic matter

($C_nH_aO_bN_c + (n + a/4 - b/2 - 3c/4)\ O_2 \rightarrow nCO_2 + (a/2 - 3c/2)H_2O + cNH_3$),

one can elucidate the number of moles needed for complete oxidation of organics into water, carbon dioxide and ammonia:

**COD of 1g of cells**

$C_5H_7O_2N + 5\ O_2 \rightarrow 5\ CO_2 + 2\ H_2O + NH_3$

mol wt organic matter = 5x12 + 7x1 + 2x16 + 1x14 = 113 g/mol

$$COD = \frac{5 \text{ mol } O_2}{\text{mol cells}} \times \frac{32 \text{ g } O_2\text{/mol}}{113\text{g cells/mol}} \times 1 \text{ g cells} = \mathbf{1.416 \text{ g } O_2 \text{ per g of cells}}$$

**COD of 1g of organic matter**

$C_{18}H_{19}O_9N + 17.5\ O_2 \rightarrow 18\ CO_2 + 8\ H_2O + NH_3$

mol wt organic matter = 18x12 + 19x1 + 9x16 + 1x14 = 393 g/mol

$$COD = \frac{17.5 \text{ mol } O_2}{\text{mol OM}} \times \frac{32 \text{ g } O_2\text{/mol}}{393\text{g OM/mol}} \times 1 \text{ g organic matter} = \mathbf{1.425 \text{ g } O_2 \text{ per g of organic matter}}$$

**Homework 1-2 : « Wastewater parameters of an industrial wastewater »**

The analysis of an industrial wastewater has given the following results :

- TOC : 150 g / $m^3$
- DOC : 0 g / $m^3$
- TKN : 35 g / $m^3$

According to the company, the wastewater contains exclusively organic matter with a composition of $C_{18}H_{19}O_9N$ and ammonium nitrogen.

a) What is the concentration of the volatile suspended solids (VSS) of this wastewater ?

b) What is the ammonium concentration of the wastewater ?

c) How much chemical oxygen demand (COD) is in this wastewater ?

d) After primary treatment in a clarifier, a sludge is obtained with 6% SS. What are the concentrations of TOC, DOC, and $NH_4$-N of this sludge ?

***Solution***

a) The molecular mass of organic matter ($C_{18}H_{19}O_9N$) is equal to : (18x12) + (19x1) + (9x16) + (1x14) = 393 g/mol; TOC is 150 g / $m^3$, and all the carbon is in the particulate fraction since there is no dissolved organic carbon DOC. One mole of organic matter contains 216 g of carbon (18x12).

   Hence, there is (150/216) = 0,69 mol organic matter per $m^3$ in this wastewater.

   The concentration of **VSS** is therefore (0,69 x 393) = **273 $g_{VSS}$ / $m^3$**

b) TKN, the Kjeldahl nitrogen, measure organic nitrogen and inorganic nitrogen in the form of ammonium.

   There is one mole nitrogen per mole of organic matter, hence, the organic nitrogen present has also a concentration of 0,69 mol / $m^3$.

   This corresponds to (0,69x14) = 9,66 g / $m^3$, the rest of TKN (35-9,66) = **25,34 $g_N$ / $m^3$** is **ammonium nitrogen**.

c) $C_{18}H_{19}O_9N + 17{,}5O_2 \rightarrow 18CO_2 + 8H_2O + NH_3$ (calculated with the formula under 1.1)

   The COD is therefore (17,5x0,69x32) = **386,4 $g_{O2}$ / $m^3$**

d) The VSS concentration in the wastewater is 0.273 kg/$m^3$, in the sludge it is 60 kg/$m^3$, and VSS is equal to TSS. Hence, the sludge is 219.78-times more concentrated in VSS than the wastewater.

   **TOC** = 219.78 x 0.150 = **32.967 kg/$m^3$** ;
   **DOC = 0 g/$m^3$,** there is still no DOC;
   **$NH_4$-N = 25,34 $g_N$/$m^3$,** since dissolved compounds are not more concentrated in the sludge**.**

**Homework 1-3 : « Incoherence in measured wastewater parameters »**

To improve anaerobic digestion of waste sludge (primary and secondary sludge together), a company proposes to treat the effluent of the anaerobic digester by a hydrothermal treatment and to transform non-degraded organic matter (especially the particulate matter) into solubilized organic molecules. The idea is that this liquid could then be recycled into the anaerobic digestion process and the solubilized organic matter transformed into biogas. In order to do a test on laboratory-scale to investigate whether this hydrothermal treatment liquid can be digested anaerobically, a detailed analysis was carried out on different parameters:

| Parameter | Unit | Average |
|---|---|---|
| volatile solids (VS) | [mg/L] | 1457 |
| fixed solids (IS) | [mg/L] | 610 |
| total organic carbon (TOC) | [mg C/L] | 2016 |
| total inorganic carbon (TIC) | [mg C/L] | 1301 |
| chemical oxygen demand (COD) | [mg O2/L] | 7480 |
| Kjehldahl nitrogen (TKN) | [mg N-TKN/L] | 1865 |
| ammonium nitrogen (N-NH4) | [mg N-NH4/L] | 2320 |

When having a closer look at these values, it is quite obvious that there is incoherence in this data. Identify the incoherence in the data by comparing the different parameters and by making some back-of-the-envelope calculations, and explain why the data is incoherent.

*Remark: If you need the chemical composition of the solubilized organic matter in the hydrothermal treatment liquid, you can use* $C_{18}H_{19}O_9N$ *which has a COD of 1.42* $g_{O2}\ g_{OM}^{-1}$.

## ***Solution***

*The most obvious incoherence is the following:*

- *The VS have a lower concentration than TOC but TOC only measures the carbon of organic matter. Hence, VS should be normally higher than TOC. However, if there are many volatile organic compounds present in the water sample that volatilize during drying of the water sample at 100°C, this difference could be real.*
- *IS is also lower than TIC but normally inorganic carbon does not volatilize. There is also a problem between these two parameters. In addition, there is quite some ammonium nitrogen present in the sample. Only if the pH would be high and ammonium nitrogen would be mainly present as free ammonia ($NH_3$) it would volatilize during drying. We should have some information on pH of the sample to be able to estimate whether this makes sense.*
- *Kjehldahl nitrogen comprises organic nitrogen and ammonium nitrogen. However, the concentration of TKN is lower than $N\text{-}NH_4$ which does not make sense. There must be an analytical error.*
- *Finally one can compare the TOC and COD measurements. From TOC we can conclude that we have 9.3 mM (2016/216) organic matter in the sample which means 3668 mg OM/L (9.3x393). This represents a COD of 5208 mg $O_2$/L (3668x1.42). This value is much lower than the measured COD. However there is the possibility that the organic matter in the water sample has a completely different composition than average organic matter of wastewater. In this case the organic matter must be in a much more reduced state in order to have such a high COD.*

**Homework 1-4 : « Return sludge – waste sludge »**

An activated sludge WWTP treats the wastewater of 50'000 PE ($Q_0$ = 17'500 $m^3$ $d^{-1}$) and the sludge production ($X_{produced}$) is 135 $g_{TSS}$ $m^{-3}{}_{WW}$. The activated sludge concentration ($X_{AT}$) in the aeration tank is maintained at 3.5 $kg_{TSS}$ $m^{-3}$. One pumps 17'000 $m^3$ $d^{-1}$ sludge, return and waste sludge combined. The effluent of the secondary clarifier contains 15 $g_{TSS}$ $m^{-3}$.

a) How much sludge in $m^3$ does one has to remove from the total sludge volume pumped per day as waste sludge assuming that $Q_e = Q_0$ ?

b) How many times does the sludge in average return in the aeration tank before leaving the WWTP via the effluent and the waste sludge ?

*HINT: For a) assume that $Q_r$ is about equal to $Q_r$+$Q_w$ since $Q_W$ is very small.*

***Solution***

a) The **waste sludge production** is equal to the total sludge production minus the sludge leaving with the effluent of the secondary clarifier :

$(Q_0 \times X_{produced}) – (Q_0 \times X_e)$ = 2100 $kg_{TSS}$ $d^{-1}$

In the following, one has to calculate the waste sludge concentration $X_w$ which is the same as the return sludge concentration $X_r$. For this, one can make a mass balance over the secondary clarifier (influent equal to effluent, no growth) with $Q_r \approx Q_r + Q_w$ :

$(Q_0 + Q_r)\ X_{AT} = (Q_0 \times X_e) + (Q_r \times X_r)$

$X_r = ((Q_0 + Q_r)\ X_{AT}) - Q_0 \times X_e) / Q_r$

$X_w = X_r$ = ((17'500 + 17'000) × 3'500 – 17'500 × 15) / 17'000 = 7088 $g_{TSS}$ $m^{-3}$

The volume to be wasted per day :

$\mathbf{Q_w}$ = 2100 $kg_{TSS}$ $d^{-1}$ / 7,1 $kg_{TSS}$ $m^{-3}$ = **296 $m^3$ $d^{-1}$** (approximately 1.7% of $Q_0$)

b) This problem can be solved by comparing the amount of sludge that is entering the aeration tank per day by the return sludge (influent biomass can be neglected) with the amount of sludge produced per day.

The quantity of return sludge brought to the aeration tank per day is :

(17'000 – $Q_w$) × $X_r$ = 118'600 $kg_{TSS}$ $d^{-1}$.

The mass of sludge produced per day is :

$Q_0 \times X_{produced}$ = 2'360 $kg_{TSS}$ $d^{-1}$.

The sludge circulated on average **50-times** (118.6500/2'360) through the aeration tank before leaving the WWTP via the effluent.