Practical
BM Respirometry
for activated sludge process

Surcis S.L.

Complementary Reagents
for BM respirometry use

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# Chemical reagents for BM respirometry operation

BM respirometry may need some complementary to carry out some tests approached for specific applications.

Chemical Reagent	Application	Comments
Sodium acetate	Organic standard used as a sludge activity reference Determination of heterotrophic yield coefficient (Y_H)	It could be other applications.
Zinc sulphate	To get a truly soluble sample by means the wastewater floculation (with pH control), followed of the supernatant filtration at 0.45 µm. This filtered sample will be used in a R mode test for the automatic determinatioon of the readily biodegradble COD fraction (S_S) in the BM respirometer.	When the wastewater does not contain any colloidal biodegradable COD, we could avoid the step of flocculation and go directly to the 0.45 µm filtratation. Sometimes a truly soluble sample is also posible by means of the filtration of wastewater sample at 0.1 – 0.2 µm .
Allyl Thiourea (ATU)	For ntrification inhibition	It would only be necessary when the ASP includes a nitrification process.
Ammonium Chloride	Ammonium-nitrogen standard to determine the exogenous respiration rate and as a reference in toxicity tests specifically related to nitrification. [1 mg NH_4Cl = 0.26 mg NH_4-N]	Ammonim chloride will only be necssary when the ASP includes a nitrification process in it.

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External small aeration system

This can be a simple aeration system composed by small air-pump, tubing and air-diffusers.
The BM user can get it from any normal domestic aquarium shop for a very low price.

This device is normally used to aerate the effluent activated sludge with enough time to eliminate any rest of substrate pending to be biologically removed and pass the sludge into an endogenous respiration state (endogenous sludge)
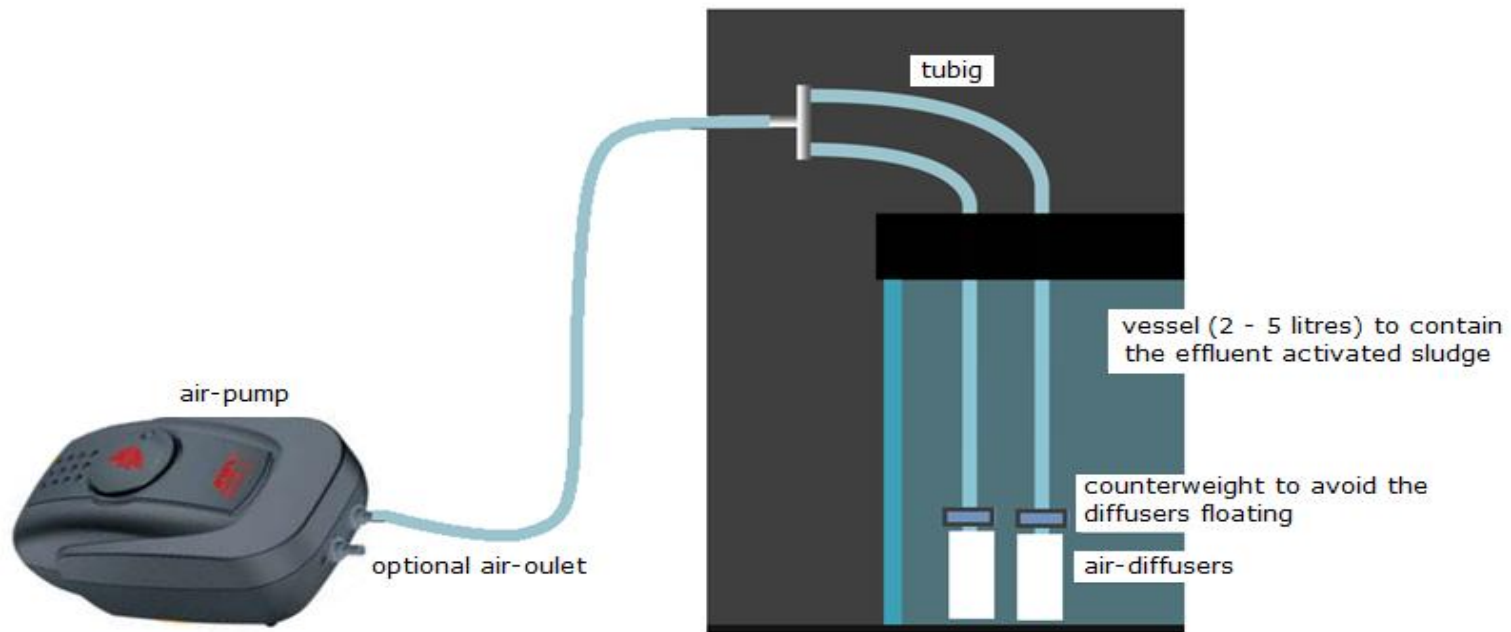
In case the laboratory can provide any other reliable air supply source, we could connect it to the tubing and make use of it instead of the air-pump.
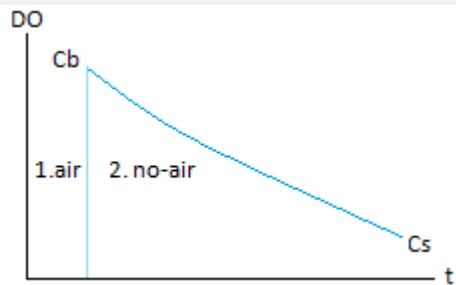
BM Respirometry

Three different operation modes

While most of the respirometers on the market offer only one operation mode, the BM respirometers have three different operation modes: OUR mode, Cyclic OUR mode, and R mode. Each mode develops different respirograms for automatic parameters including D.O., Temperature, and pH (in BM-Advance) from where specific applications can be made.

In a single batch reactor, the measuring system can work as LSS and LFS batch respirometry. The system is optimized by a one-sense membrane device, that together with a dividing plate, is able to isolate the measuring chamber and avoid bubbles against the DO sensor.
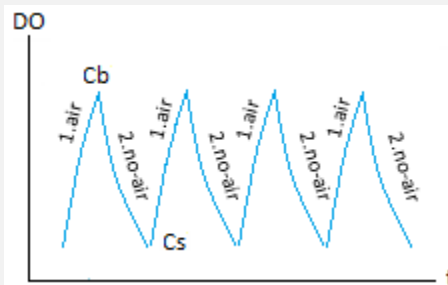
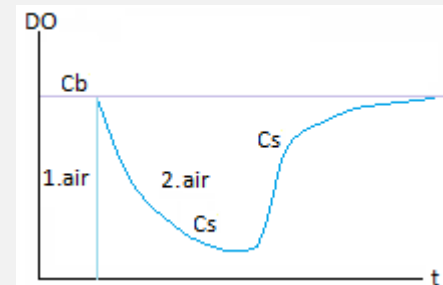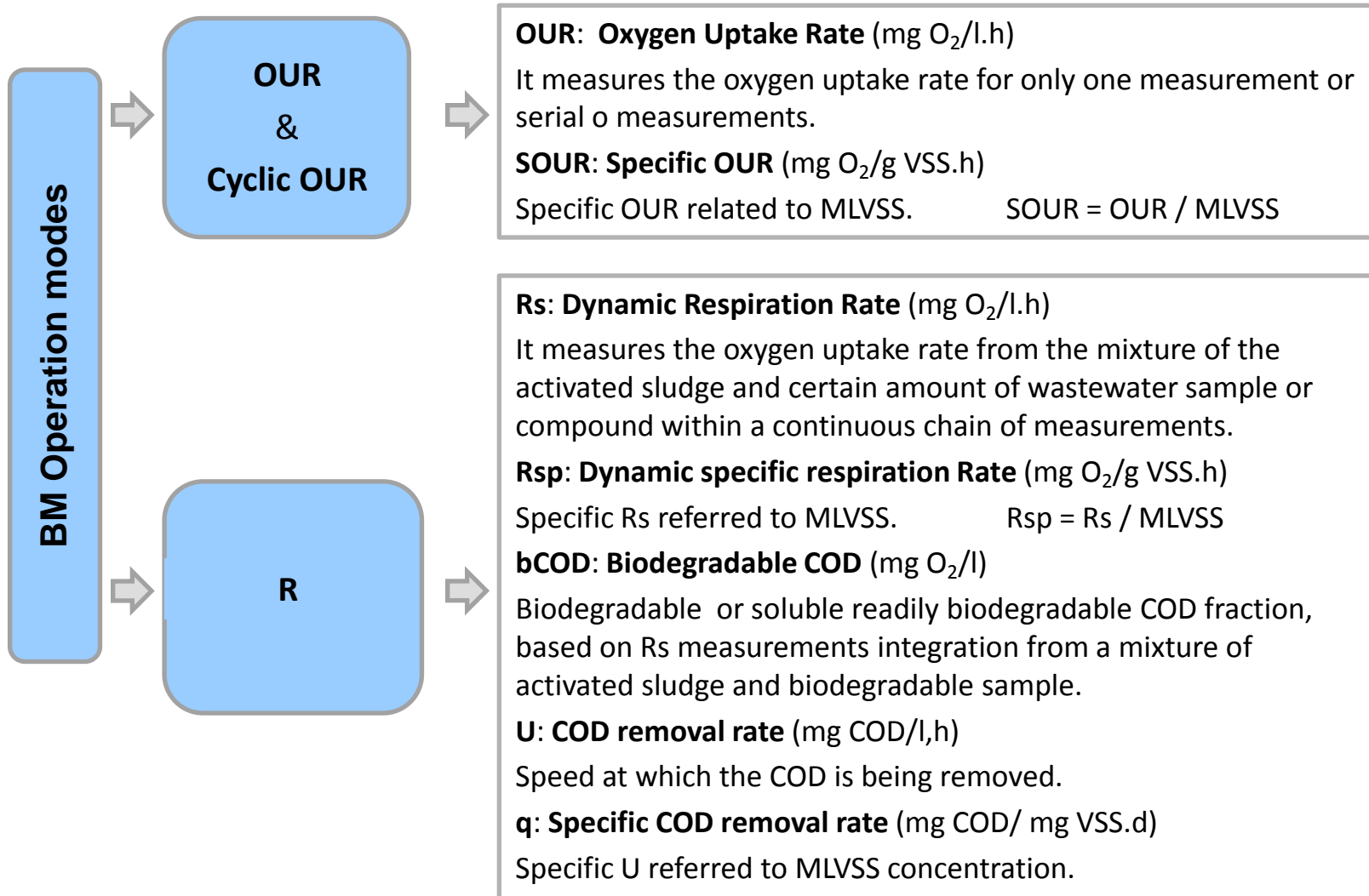| OUR	Cyclic OUR	R
This mode is making use of the LSS respirometry type. The OUR mode consists of a single test to measure the OUR and/or SOUR parameters (by manually setting the MLVSS concentration). It also has the option the get a partial SOUR for any period within the respirogram.	The cyclic OUR mode consists of a progressive sequence of OUR measurements, generated from the DO trajectory when it fluctuates between the DO. Low and DO. High set-points that were set at the start of the test.	The R mode corresponds to a modified LFS respirometry type test. The measuring system can be considered as a completely mixed batch reactor. In this mode, we get the important advantage to work with a small volume of samples in order to minimize the test time for an important package of several simultaneous parameters measurement.

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Main automatic parameters in BM respirometer for the different operations modes

BM Operation modes

OUR & Cyclic OUR

OUR: Oxygen Uptake Rate (mg O_2/l.h)

It measures the oxygen uptake rate for only one measurement or serial o measurements.

SOUR: Specific OUR (mg O_2/g VSS.h)

Specific OUR related to MLVSS.   SOUR = OUR / MLVSS

R

Rs: Dynamic Respiration Rate (mg O_2/l.h)

It measures the oxygen uptake rate from the mixture of the activated sludge and certain amount of wastewater sample or compound within a continuous chain of measurements.

Rsp: Dynamic specific respiration Rate (mg O_2/g VSS.h)

Specific Rs referred to MLVSS.   Rsp = Rs / MLVSS

bCOD: Biodegradable COD (mg O_2/l)

Biodegradable or soluble readily biodegradable COD fraction, based on Rs measurements integration from a mixture of activated sludge and biodegradable sample.

U: COD removal rate (mg COD/l,h)

Speed at which the COD is being removed.

q: Specific COD removal rate (mg COD/ mg VSS.d)

Specific U referred to MLVSS concentration.

Primary assessment
of the activated sludge process
and biomass health

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🤚 Taking the pulse to the activated sludge process

The UNFED SOUR is the SOUR value corresponding to the effluent sludge (end of the aerobic process)

By comparing the UNFED SOUR with the reference value (ref) from a guide table, we can make a primary assessment of how the process is currently performing.

Process type	F/M (BOD/SS.d)	SRT (d)	UNFED SOUR ref (mgO$_2$/gVSS.h)
High loading	> 0.4	4	10 - 15
Medium loading	0.2 – 0.4	4 - 10	7 - 10
Low loading	0.07 – 0.2	10 - 30	3 - 7
Very low loading (extended aeration)	< 0.7		

Actual UNFED SOUR Vs. UNFED SOUR ref. (Table)	Assessment
>> ref	Overloading
= or +/- ref	Good performance
< ref	Low loading
<< ref	Very low loading or Toxicity symptoms

For any activated sludge process were the effluent sludge is not well defined, it also exists the option to perform the UNFED SOUR in a well aerated mixture composed by effluent + aerated returned sludge on equivalent volumes to the effluent flow / RAS flow ratio: [Q (effluent) / Q (RAS) = V (effluent) / V (RAS)]

Endogenous respiration rate

It is about the endogenous oxygen uptake rate test (OUR end) of the activated sludge after being aerated for a sufficient time to eliminate any kind of degradable subtrate.

Normally the endogenous respiration state can be recognized when the oxygen readings are stable within its oxygen saturation level.
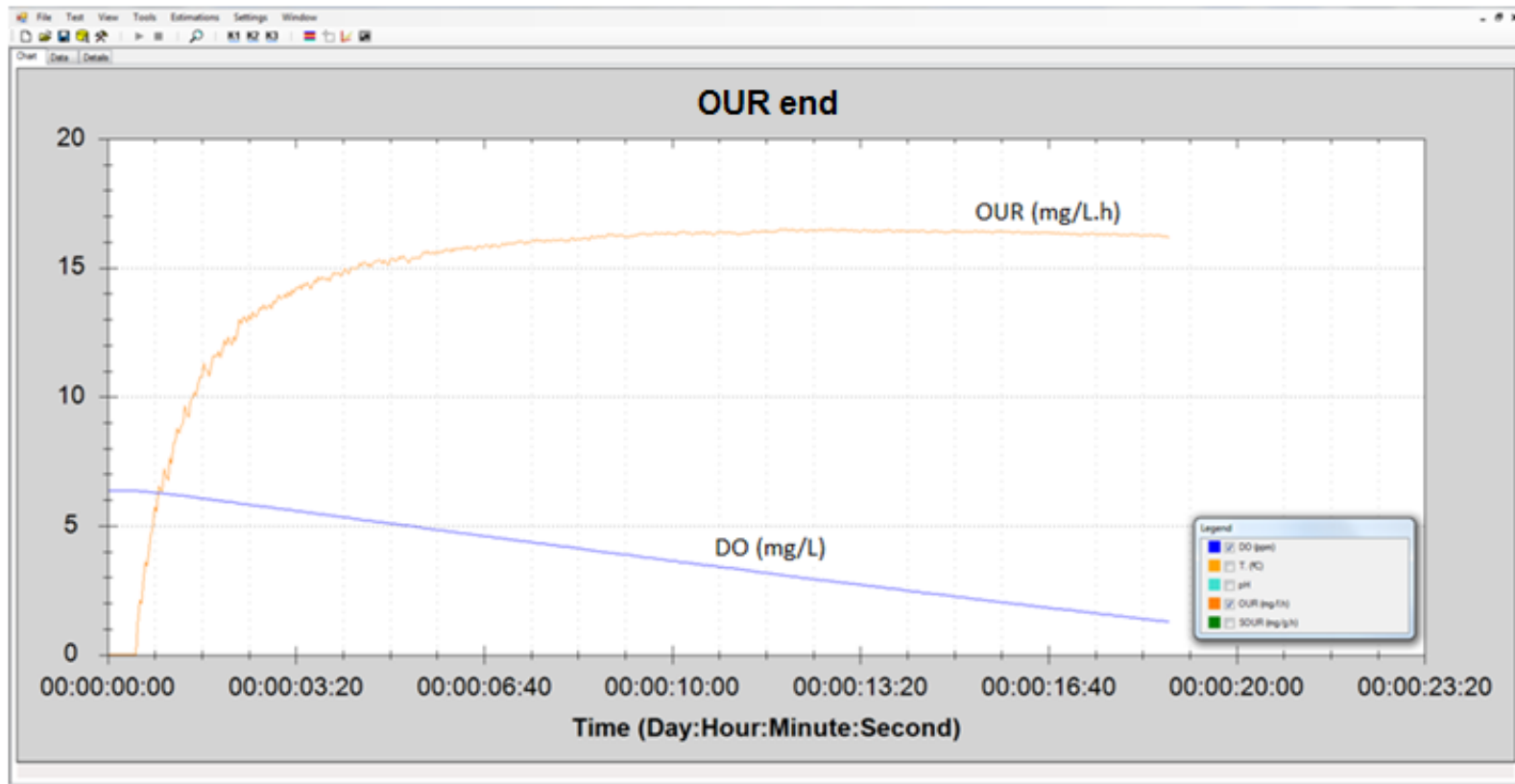
DO and OUR respirogram for OUR end

OUR$_{end}$ assessment

Table guide of usual OUR$_{end}$ values

MLVSS (mg/l)	OUR$_{end}$ (mg/l.h)
1000	2 – 3.5
1500	3 - 5
2000	4 - 7
2500	5 – 8.5
3000	6 - 10
3500	7 - 12
4000	8 – 13.5
4500	9 – 15.5

<u>Some reasons for which the OUR end value could be below its normal range</u>

1. Low active biomass

2. Toxicity

2. Sludge was too long aerated in its process to get its endogenous respiration state (*)

(*) For high and medium loading process, where the UNFED SOUR is usually in range, the endogenous respiration is normally reached after aerating the effluent sludge for 12 hours. For low and very low loading process, where the UNFED SOUR is also in range, the endogenous state is usually reached after aerating the effluent sludge for 2 ~ 4 hours.

Total active biomass concentration
calculated from endogenous respiration

$$\mathbf{X} = 24 * OUR_{end} / (f_{cv} * b)$$

X: Total Active biomass concentration (mg/l)
OUR_{end}: Endogenous respiration (mg/l.h)
f_{CV}: Oxygen uptake per unit of biomass = 1.42 (O_2/X_V)
b: Decay rate of biomass in endogenous respiration = 0,3

Source: Respirometry for Environmental Science and Engineering – James G. Young & Robert M. Cowan. 200

The active biomass concentration should present a variable percentage in the range of 14–35 % of the total amount of MLVSS in the activated sludge.

Some reasons for which the X value could be below its normal range

When the OUR_{end} result is significantly lower than the habitual range, the most probable is that there is a low active biomass concentration, and here are some of the probable reasons:

1. Too low F/M
2. Too low readily biodegradable COD percentage in the total COD (< 12%)
3. One or more process conditions (T, DO, pH) are out of range.
3. Nutrients deficit.
4. The process is currently under toxicity or it had got a recent toxicity

COD fractions

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Yield coefficient of heterotrophic biomass (I)

Heterotrophic yield coefficient (Y_H) is a fundamental parameter for the automatic COD fractions determinations throughout the R mode
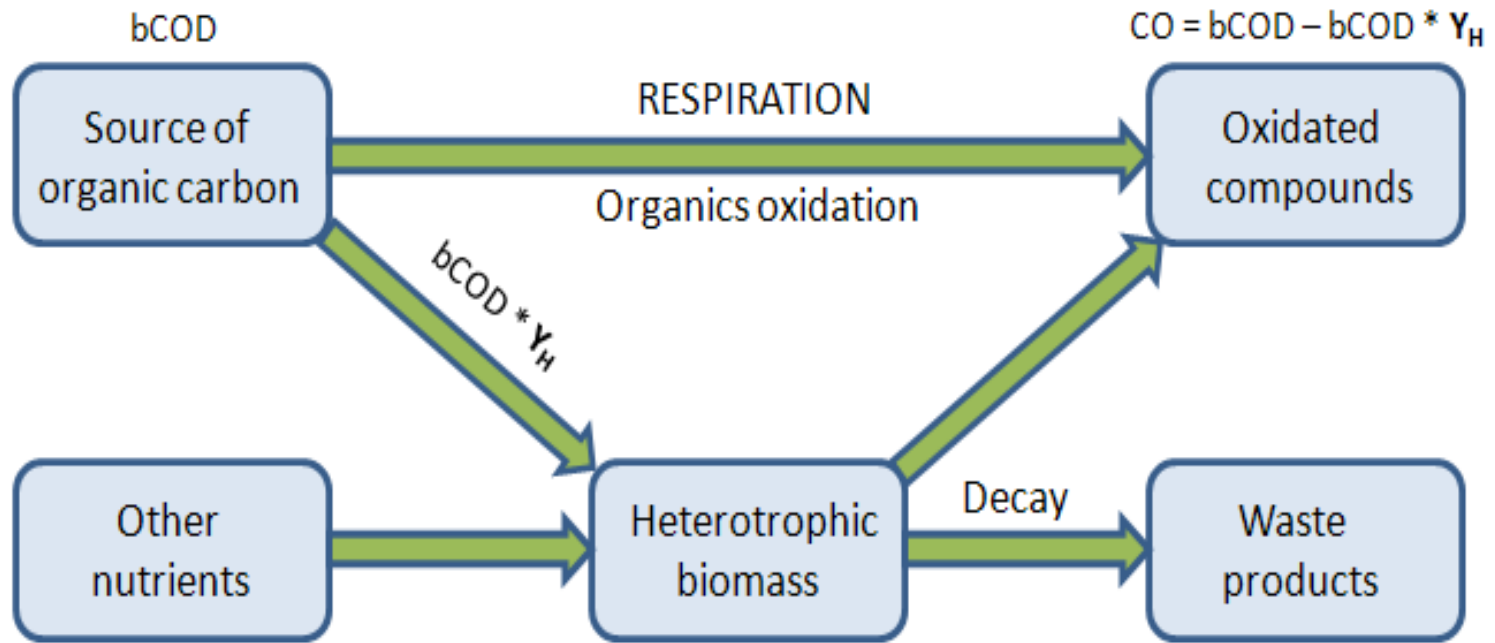
$$bCOD = CO / (1 - Y_H)$$

Heterotrophic yield coefficient (II)

Yield coefficent is determined by means a single R test, by making use a sodium acetate solution sample of known COD (COD_{ac}). In that test, the BM software will automatically give out the cosumed oxygen result (CO), and then the yield coefficient is calculated from CO and CODac.
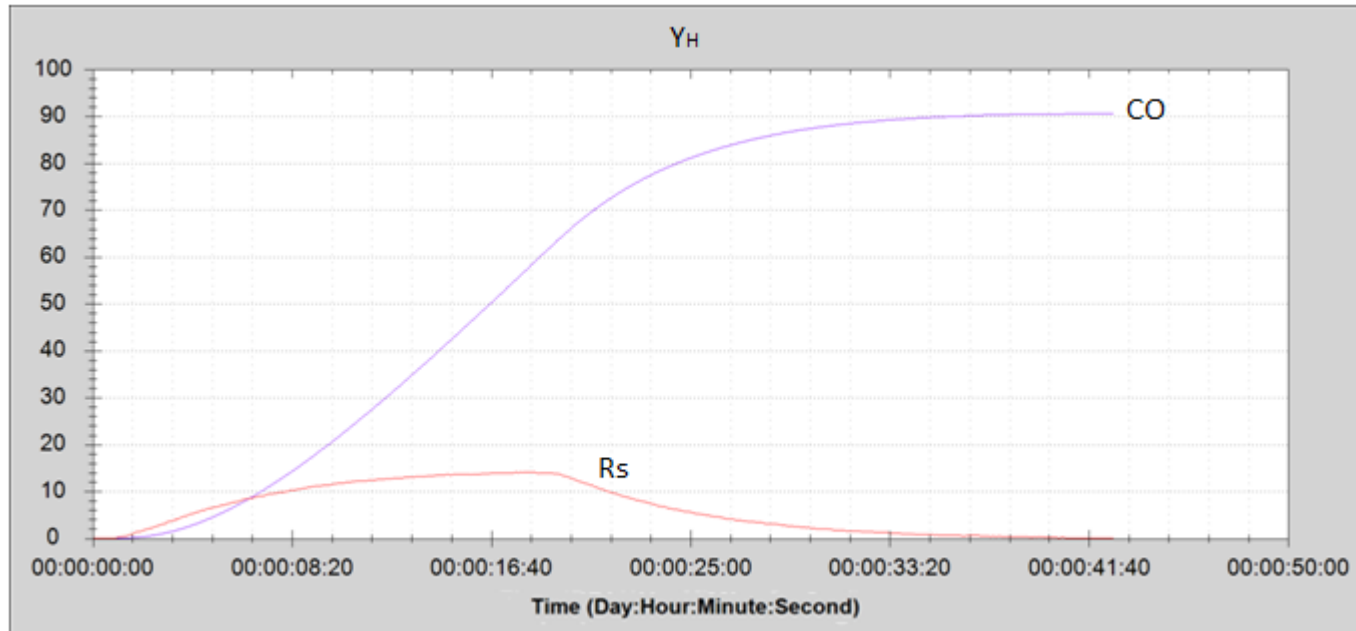
Rs Respirogram for Y_H

$$Y_{H.02} (O_2/COD) = 1 - CO / COD_{ac}$$

$Y_{H.O2}$: Yield coefficient refrered to O_2 consumption (O_2/COD)

COD_{ac}: COD of the sodium acetate sample = 270 - 320 mg/L)

Wastewater COD fractions (I)

```
                        ┌─────────────┐
                        │     COD     │
                        │  total COD  │
                        └──────┬──────┘
              ┌────────────────┴────────────────┐
      ┌───────┴────────┐              ┌──────────┴──────────┐
      │      bCOD      │              │        iCOD         │
      │ Biodegradable  │              │     inert COD       │
      │     COD        │              │    15 – 25% DQO     │
      │  70 – 95% COD  │              └──────────┬──────────┘
      └───────┬────────┘                         │
     ┌────────┴────────┐              ┌───────────┴──────────┐
```

| Sₛ (rbCOD) soluble readily biodegradable COD 10 – 30% DQO | Xₛ (sbCOD) slowly biodegradable COD 50 – 70% DQO | S_I soluble inert COD | X_I Inert particulate COD |

S_S **(rbCOD)** soluble readily biodegradable COD 10 – 30% DQO

X_S **(sbCOD)** slowly biodegradable COD 50 – 70% DQO

S_I soluble inert COD

X_I Inert particulate COD

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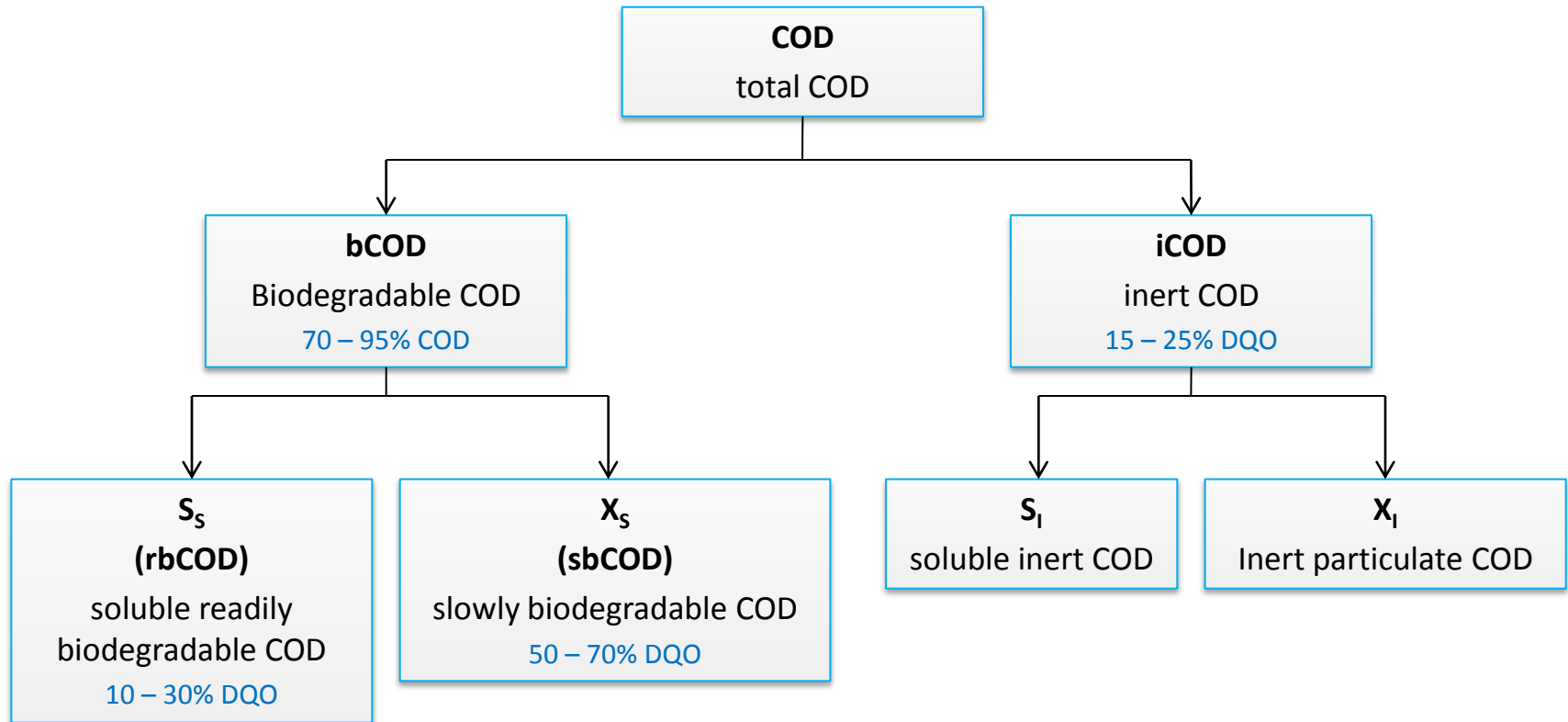
Main wastewater COD fractions (II)

Respirometry R tests
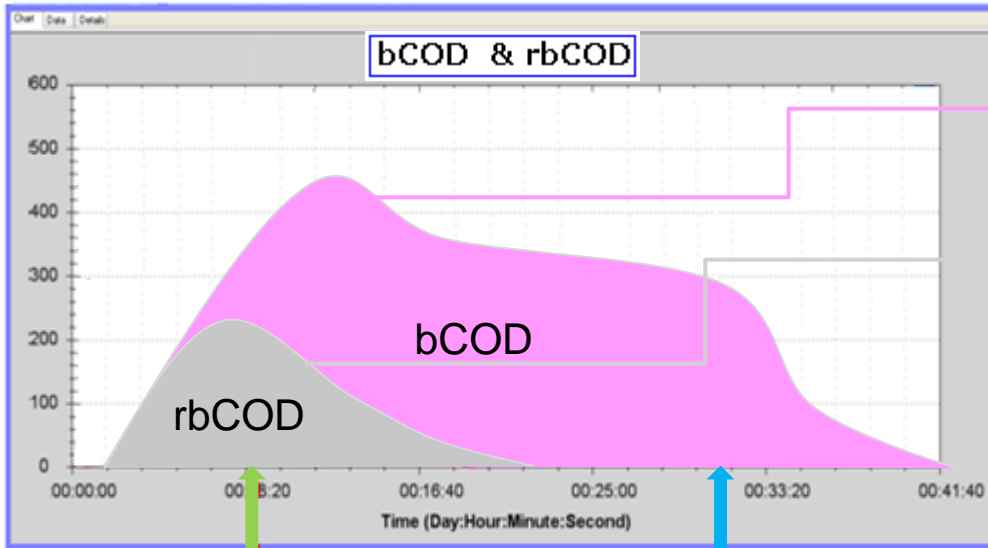
activated sludge (basic or endg.) + filtered w.water

activated sludge (basic or endg.) + Non-filtered w.water

COD → bCOD, iCOD

bCOD → rbCOD, sbCOD

$$COD - bCOD = iCOD$$
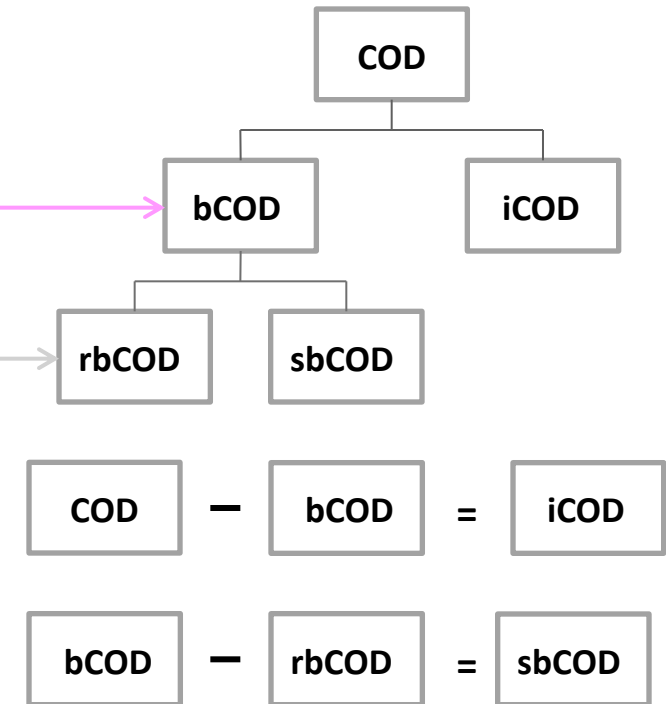
$$bCOD - rbCOD = sbCOD$$

bCOD: biodegradable COD (total)
iCOD: inert COD (no-degradable)
rbCOD: readily biodegradable COD (S_S)
sbCOD: slowly biodegradable COD (X_S)

Biodegradable & Redily biodegradable COD

The biodegradable COD (from normal ww sample) or readily biodegradable COD (from soluble ww sample) is automatically obtained from R test each. In this test is important to take into account that nitrifier biomass must inhibit the nitrifier biomass (in case the process includes nitrification), before the test, by adding the corresponding inhibitor dose to the endogenous sluge (3 – 4 mg ATU / g VSS) and allowing enough time for inhibition.
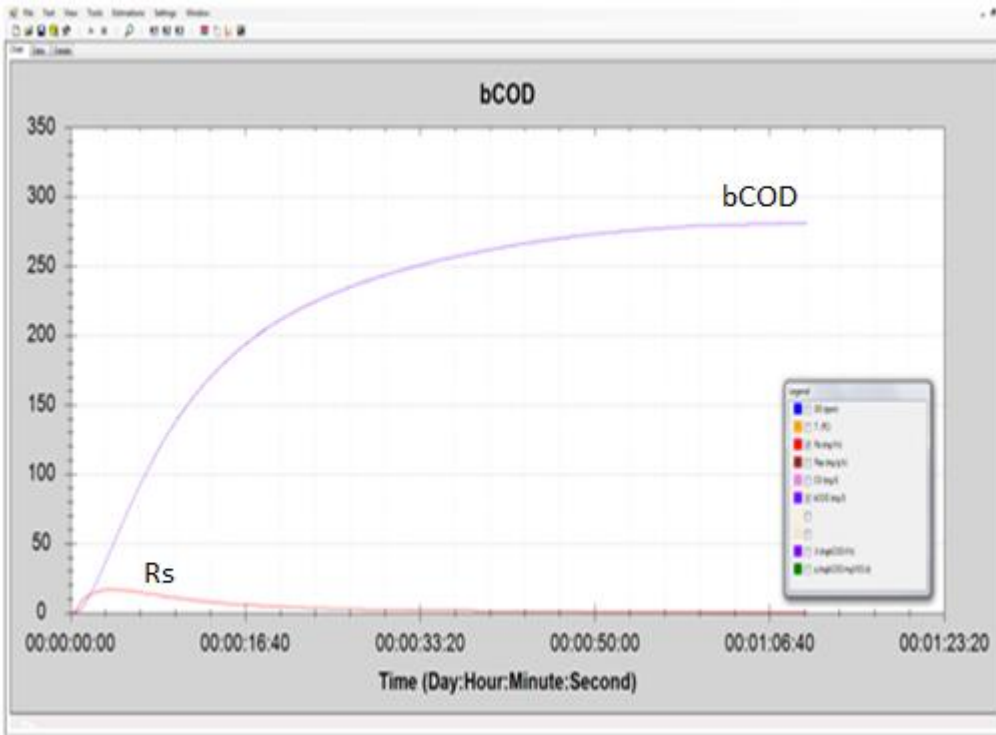
Rs and bCOD Respirograms

bCOD final result

bCOD and rbCOD in one single R test

Wherever possible to distinguish the readily biodegradable part in the Rs respirogram for bCOD, in the settings board we can make use of the option "Force Cb" to raise the base-line to the turning point.

In this way, we can cut the Rs respirogram, convert the turning point level as a new base-line, and automatically create a new respirogram corresponding to the readily biodegradable COD.
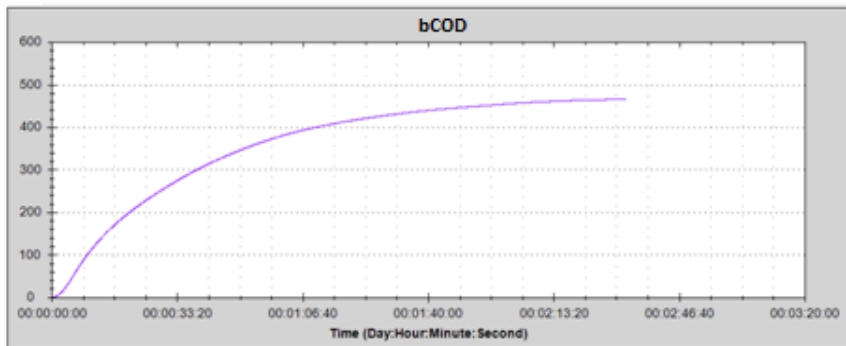
Thus determine the biodegradable and readily biodegradable COD from one single test
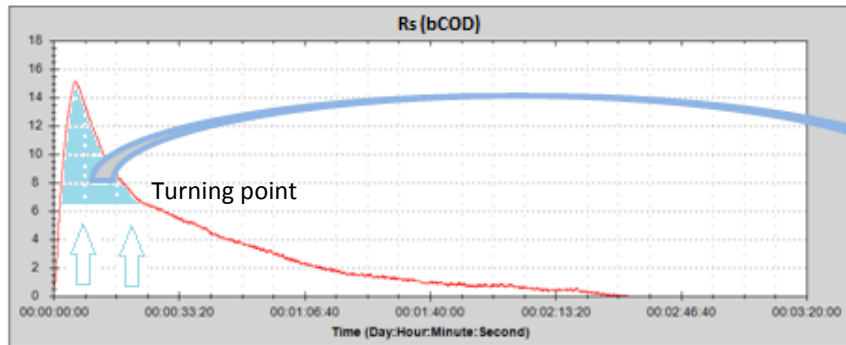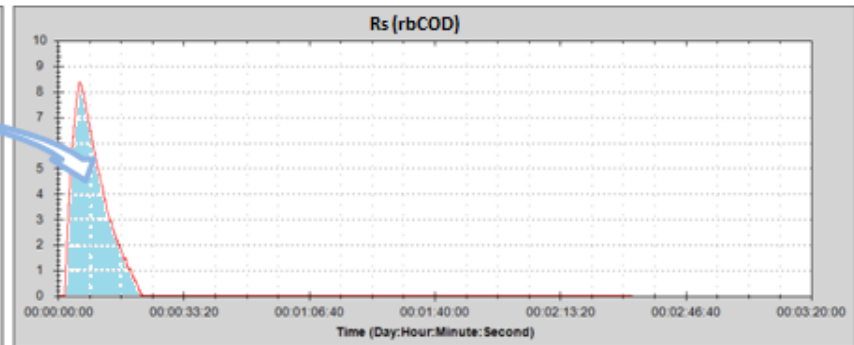
Rs respirogram for bCOD | Rs respirogram for rbCOD (S_s)
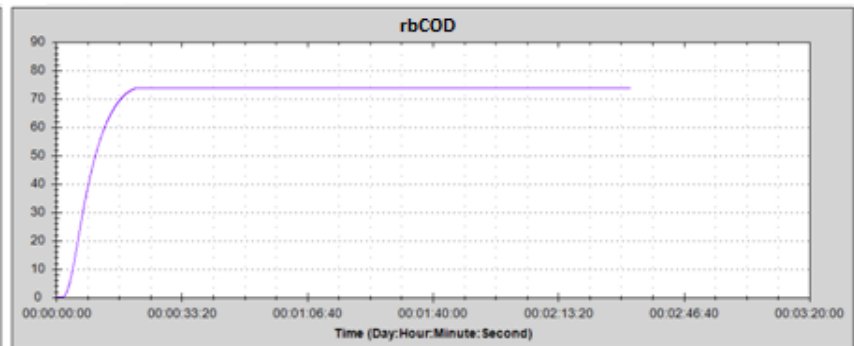
bCOD respirogram | rbCOD (S_s) respirogram

Source: Influent fractionation using a respirometric method for the characterization of primary sedimentation
Ellen Vanassche, 2014 - Faculty of Bioscience Engineering – UNIVERSY OF GENT (Belgium)
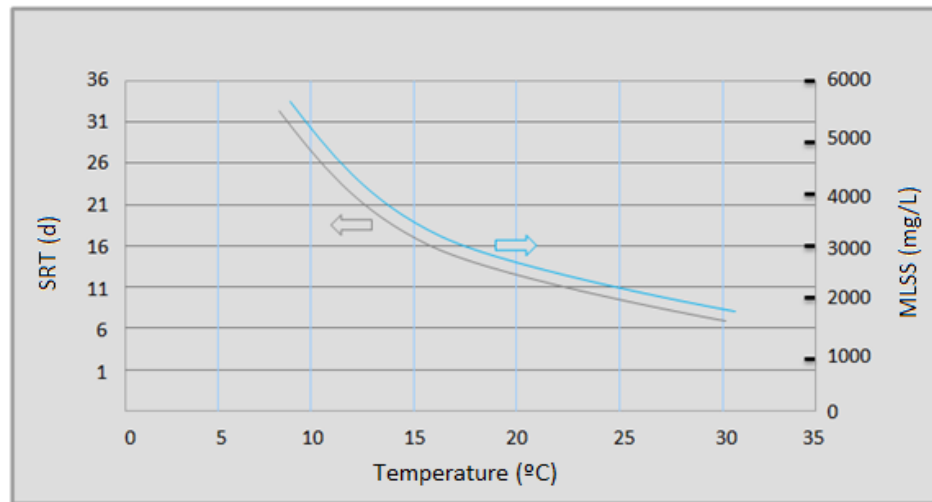
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Nitrification

Optimal nitrification conditions

1.

pH	7.3 to 8,3
T	> 15 to 28 ºC
OD	1 a 3 ppm
COD/TKN	< 5
Enough HRT for nitrification in the reactor	
Without any inhibitory or toxic compound	

2. Coherent SRT and MLSS:

Active nitrifier biomass concentration

The active nitrifier biomass can be determined from its endogenous OUR, calculated from the the difference between the total endogenous and the heterotrophic endogenous OUR.

The heterotrophic endogenous OUR is test is obtained from the same sludge that we used to get the total endogeous OUR by adding a controlled dose of Allyl-Thiourea (ATU) to inhibit the nitrifier biomass activity.

$$\textbf{OUR}_{\textbf{end.N}} = OUR_{end} - OUR_{H.end}$$

$OUR_{end.N}$: OUR of nitrifier biomass

$OUR_{H.end}$: Heterotrophic endogenous OUR
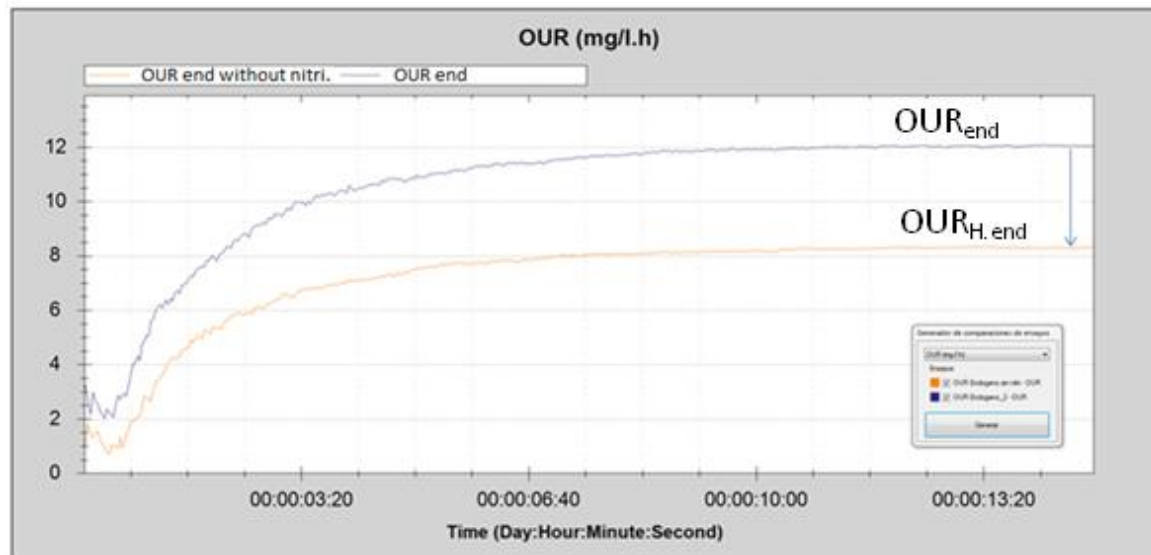
Combined OURend and OURH.end respirograms

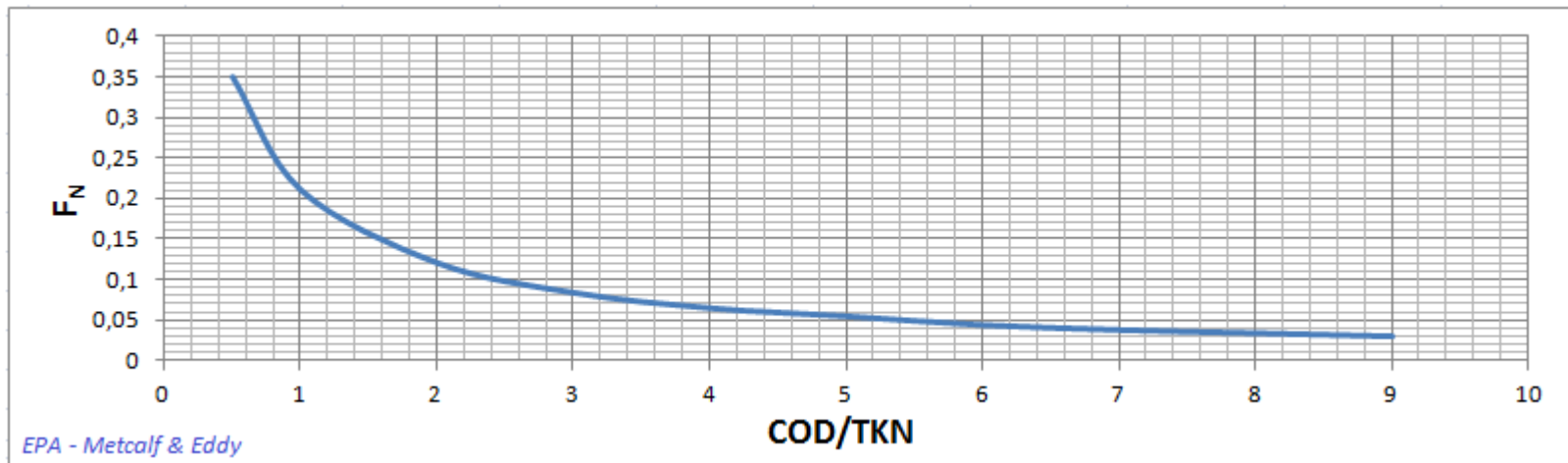$$\textbf{X}_{\textbf{A}} = 24 * OUR_{end.N} / (f_{cv} * b_A)$$

f_{cv}: Oxygen demand per unit of biomass = 1.42 (O_2/X_A):
b_A: Decay rate in the nitrifier endogenous respiration = 0,17. $1,04^{(t-20)}$ (d^{-1}) (Metcalf & Eddy)

Nitrifier biomass concentracion assessment

The condition for a coherent nitrifier biomass $\longrightarrow$ $X_A \geq F_N * VSS$

Reference values

EPA - Metcalf & Eddy

F_N: % nitrifier in VSS / 100

Possible reasons for which the actual nitrifier biomass concentration is lower than the reference value

1. The process is not operating under one or more correct conditions of DO, pH, Temperature.

2. BOD/TKN > 5

3. BOD/TKN ≥ 5 + Low temperature (< 15ºC) for a long time.

3. Low temperature (< 15ºC) for a long time

4. Presence of toxic compound in the influent wastewater.

5. Nutrients defficiency

6. Others.

Maximum nitrification rate

The maximum respiration rate can be obtained from one R test (working at saturation oxygen level) until reaching the maximum respiration rate due to nitrification. The sample is one single ammonium chloride dose with an ammonia content in the range of the typical maximum ammonia concentration in the influent. The respirometric test has to be set to to the same <u>temperature and pH of the process</u> (very important)
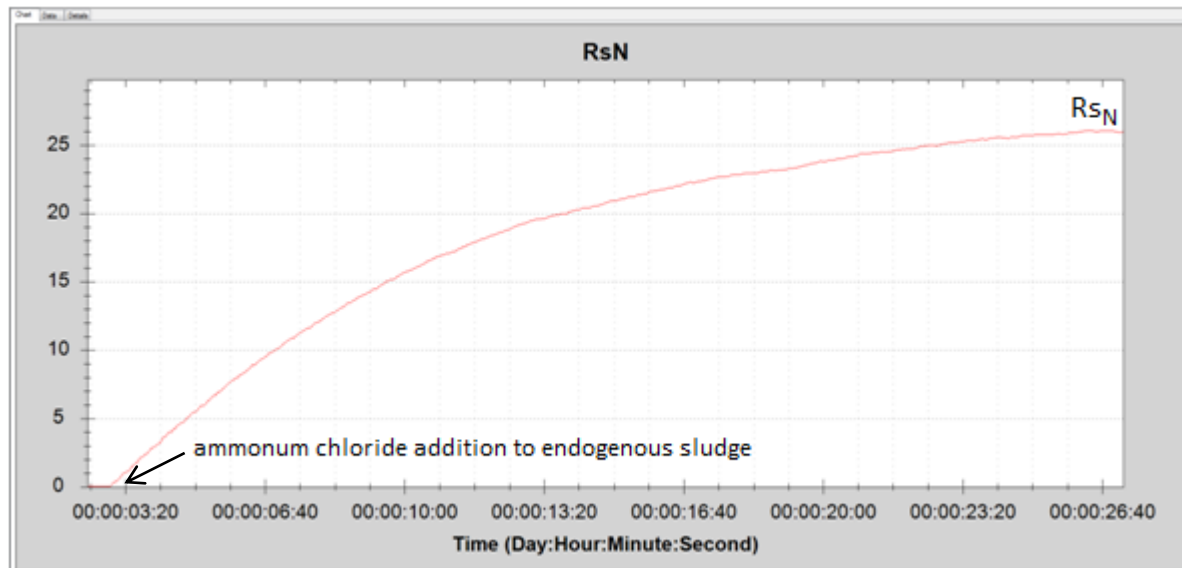
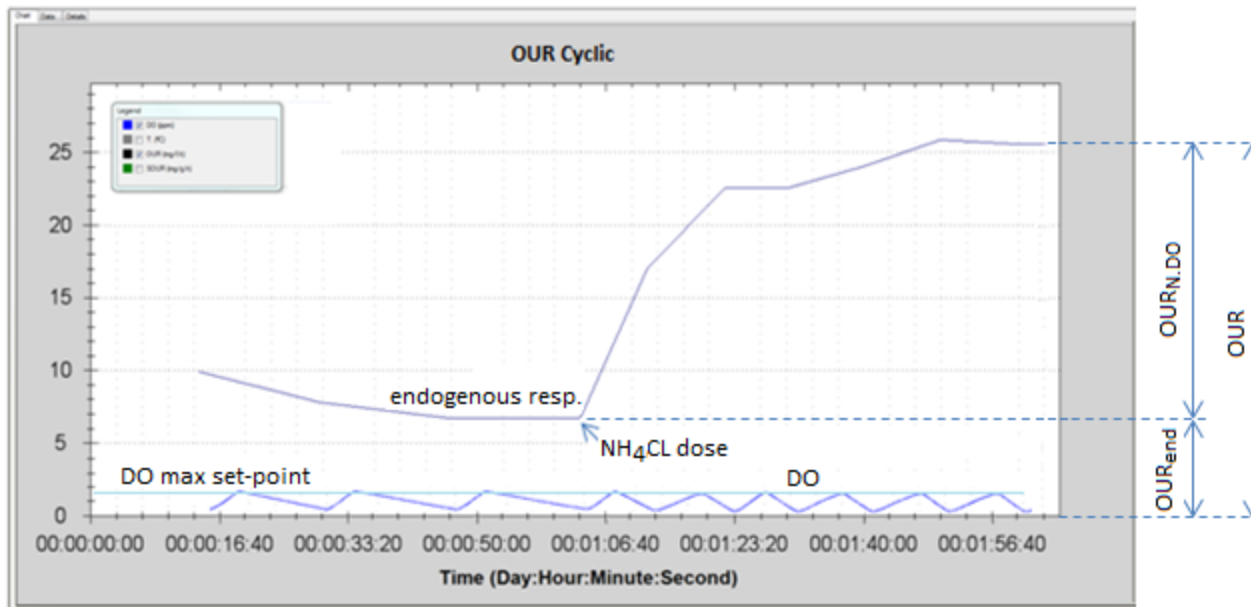Rs respirogram for Rs_N determination

$$\mathbf{AUR_{max}} = Rs_N / 4.57$$

AUR_{max} : Maximum nitrification rate under oxygen saturation (mg /l/h N)
Rs_N: Maximum exogenous respiration rate due to nitrification (mg /l/h O_2)
4.57: mg O_2 consumed per mg of ammonium nitrogen being nitrified (mg /mg O_2/N)

Practical procedure to calculate
the oxygen half-saturation coefficient for nitrification

The procedure is based on the relationship between the maximum respiration rate (Rs_N), and the respiration rate corresponding to a representative DO ($OUR_{N.DO}$) for the same sample concentration of ammonia (ammonim chloride dose) used in the Rs_N test. The $OUR_{N.DO}$ is determined by making use of the OUR Cyclic operation mode, with pH and temperature equivalents to the real process, where the maximum DO set-point is set to one representative level of the process below 3 ppm.

Combined OUR & DO respirograms for $OUR_{N.DO}$ determination

$$OUR_{N.DO} = Rs_N * DO / (K_{DO} + DO) \rightarrow \mathbf{K_{DO}} = DO * (Rs_N / OUR_{N.DO} - 1)$$

K_{DO} : Oxygen half saturation coefficient (mg/l O_2) - *A default value of 0.5 is usually well accepted* -
DO: Dissolved oxygen corresponding to the maximum DO setting-point in the Cyclic OUR test (mg/l)
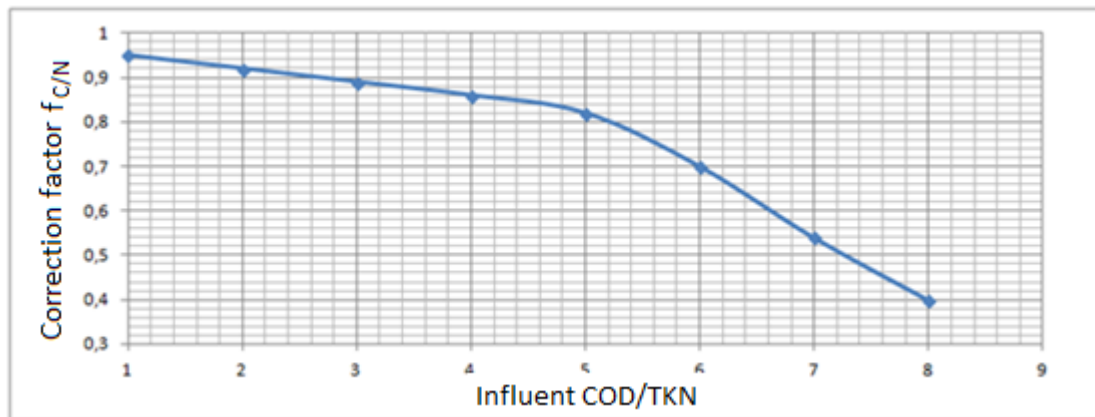
Actual nitrification rate

Here, we refers to the nitrification rate value calculated from the actual dissolved oxygen in the process.

$$\textbf{AUR} = f_{C/N} * AUR_{max} * OD / (K_{OD} + OD)$$

AUR: Actual nitrification rate (mg /l/h N-NH$_4$)

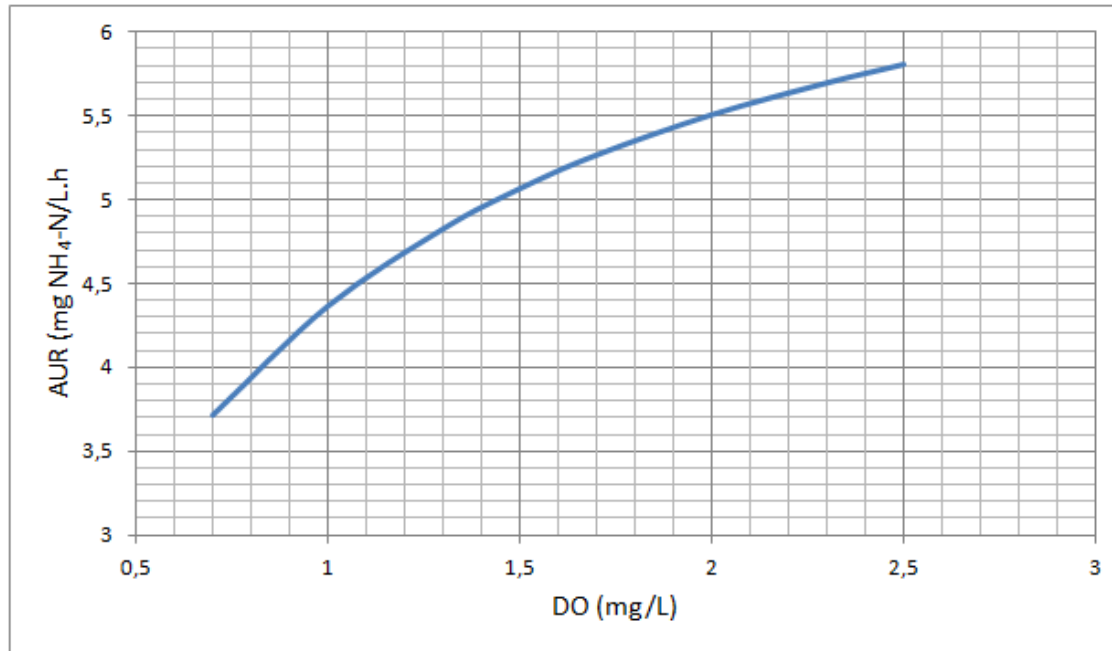OD : Bulk dissolved oxygen level in the nitrification process (mg/l)

$f_{C/N}$: Correction factor due to COD/TKN ratio influence

AUR for different operating DO values

$$AUR = f_{C/N} * AUR_{max} * OD / (K_{OD} + OD)$$

From AUR formula, we can obtain the corresponding AUR values and generate a curve for the process operation at the different DO values.

Actual ammonia being nitrified

$$S_N = TKN_O - TKN_e - S_{sy}$$

S_N: Actual ammonium-nitrogen concentration being nitrified (mg/l NH_4-N)
TKN_O: Influent TKN (mg/l N)
TKN_e: Effluent soluble TKN (mg/l N)
S_{sy}: Nitrogen utilized in the cell synthesis = 0.05 * BOD

Ammonia that should be nitrified

$$S'_N = TKN_O - TKN'_e - S_{sy}$$

S'_N: Ammonium-nitrogen concentration that should be nitrified (mg/l NH_4-N)
TKN_O: Influent TKN (mg/l N)
TKN'_e: TKN that should be in the effluent according to the required nitrification efficiency (mg/l N)
S_{sy}: Nitrogen utilized in the cell synthesis = 0.05 * BOD

Estimation of the required nitrification rate

$$AUR' = (S'_N / S_N) * AUR$$

AUR': Nitrification rate to get the required nitrification efficiency (mg /l/h N-NH_4)

Possible reasons for which the actual nitrification rate could be less than the required nitrification rate

1. The process is not operating under one or more correct conditions of DO, pH, Temperature.

2. The sludge age (SRT) is lower than the one on which the process should be operating.

3. The concentration of the active nitrifier biomass is too low.
     This could be because of
          . BOD/TKN > 5
          . Conditions are out of normal range
          . Inhibition effect

5. Toxicity

6. Others

Actual nitrification capacity

From the actual AUR and HRT for nitrification (HRT_N), we can estimate the corresponding ammonium-nitrogen that the ASP is able to nitrify within the actual conditions on which it is operating.
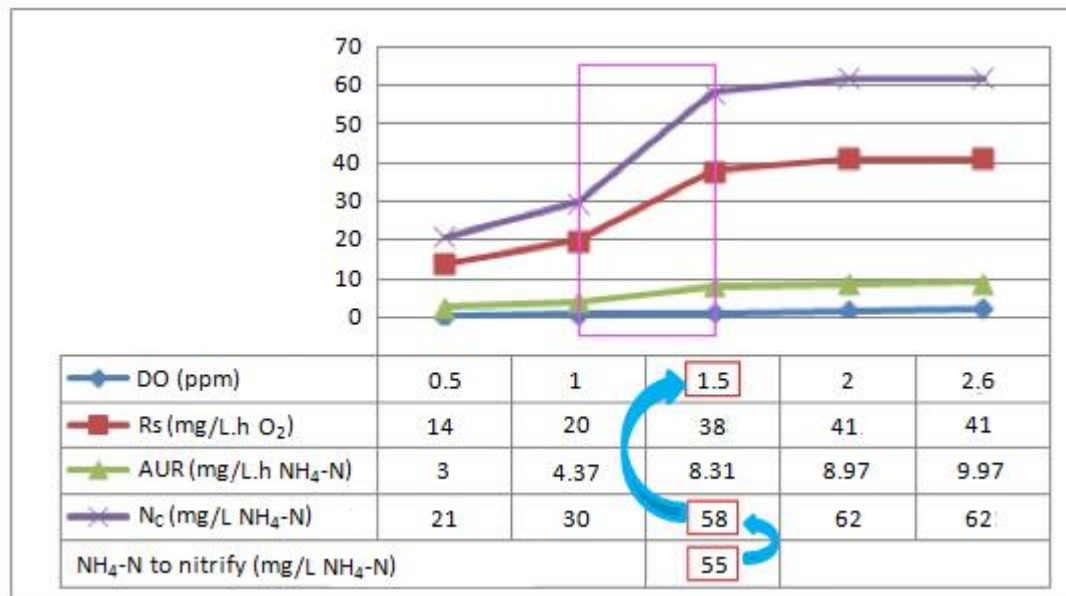
$$N_C = AUR * HRT_N$$

N_C: Nitrification capacity (mg/l NH_4-N)

Theoretical minimum DO for nitrification operation

From the AUR results for different DO levels, the corresponding C_N can be calculated.
Then, the way to get the minimum DO is to select the nearest N_C value just above the ammonia to nitrify.

	0.5	1	1.5	2	2.6
DO (ppm)	0.5	1	1.5	2	2.6
Rs (mg/L.h O_2)	14	20	38	41.	41
AUR (mg/L.h NH_4-N)	3	4.37	8.31	8.97	9.97
N_C (mg/L NH_4-N)	21	30	58	62	62
NH_4-N to nitrify (mg/L NH_4-N)			55		

Maximum nitrifier biomass growing rate

$$\mu_{A.max} = 24 * AUR_{max} * Y_A / X_A$$

$\mu_{A.max}$: Maximum nitrifier biomass growing rate (d^{-1})

Y_A: Yield coefficient ≈ 0,12 (Metcalf & Eddy)

Minimum sluge age for nitrification

$$SRT_{min} = 1 / (\mu_{A.max} - b_A)$$

SRT_{min}: Minimum sludge age for nitrification (d)

Temp	Death & Decay Rate b_A (days^{-1})
10°C	0.02
15°C	0.03
20°C	0.04
25°C	0.05

Source: EPA – Long Island. Sound Study, NY - 2000

The sludge age condition for nitrification $\longrightarrow$ SRT ≥ SRT$_{min}$

Practical operation protocol for the nitrification under energy optimization frame

In this protocol we asume the temperature and pH conditions are within the normal range and the process has the capability to control the DO level under the approach of its minimum range.
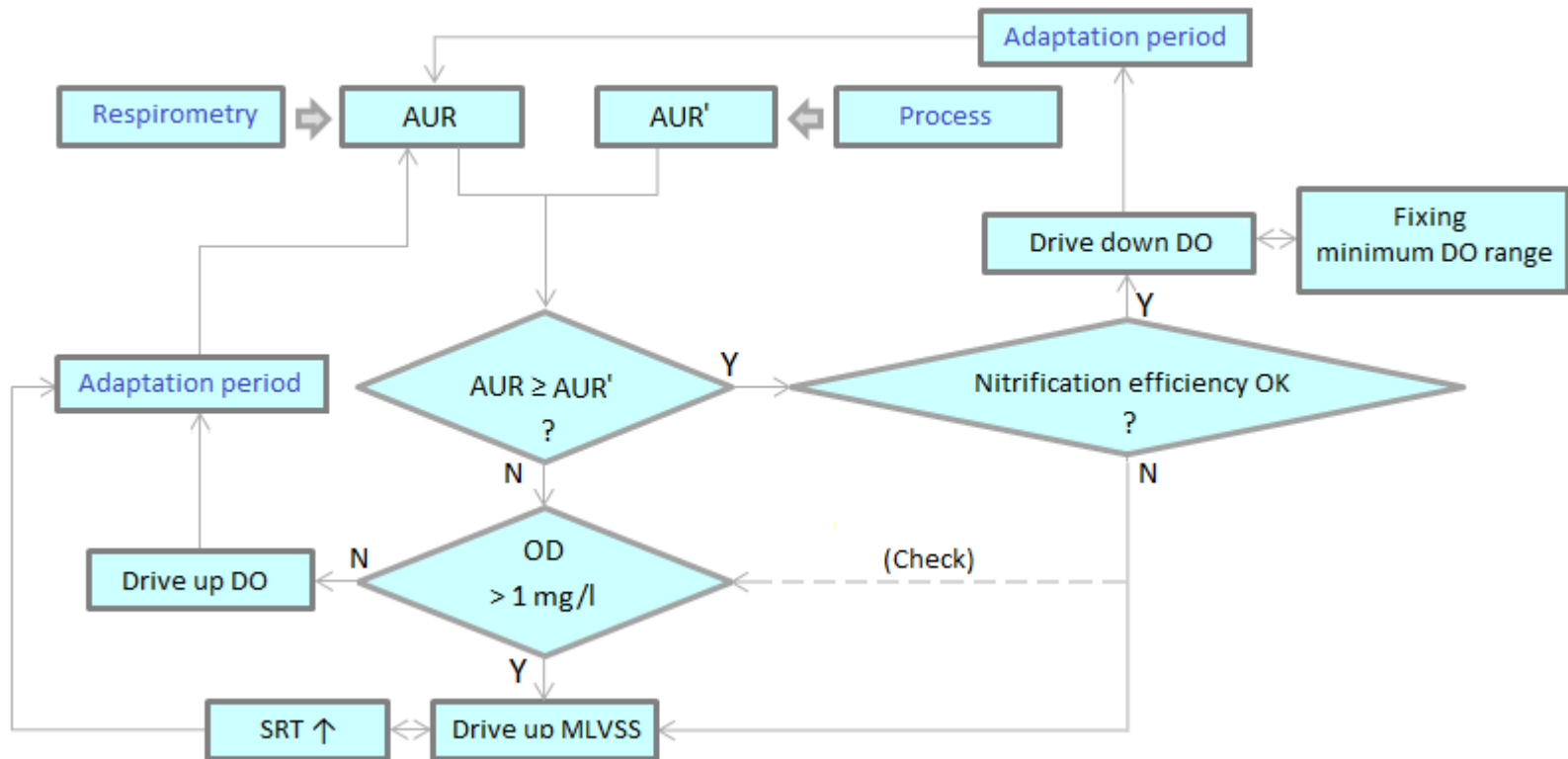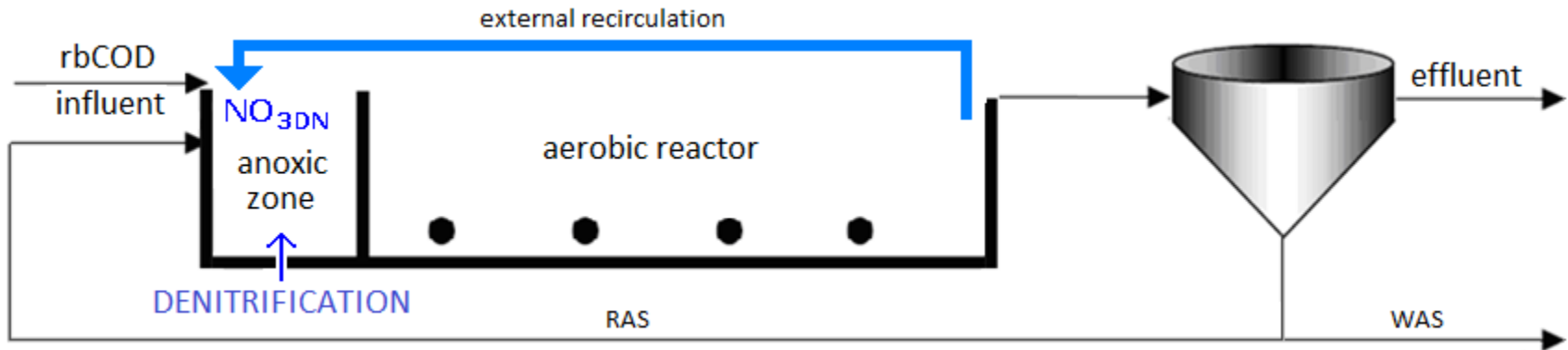
Denitrification optimization

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Conditions for denitrification process

Conditions	
pH	6.5 a 8 (optimal)
BOD/TKN	2.5 to 5
Soluble biodegradable COD/N-NO$_{3.DN}$	≥ 2.83
DO	< 0.3 ppm
Denitrification zone with enough HRT to perform the process	
Without any inhibitor nor toxic compounds	

# Oxygen demand of the soluble organic matter utilized in denitrification

external recirculation

rbCOD influent

NO_{3DN}

anoxic zone

aerobic reactor

effluent

DENITRIFICATION

RAS

WAS

| Consumed oxygen / Nitrate to denitrify ratio	$C\,O/\,[NO_{3.DN}] \geq 2.86$ $[NO_{3.DN}]$: Nitrate to denitrify (mg N-NO$_3$/l)
rbCOD required by the denitrification	$rbCOD_{DN} \geq 2.86 * [NO_{3.DN}] * (1 - Y_H)$
Total COD required by the denitrification	$COD_{DN} \geq (COD/rbCOD) * rbCOD_{DN}$

Toxicity

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Two situations for toxicity

1. Toxicity already present in the activated sludge process
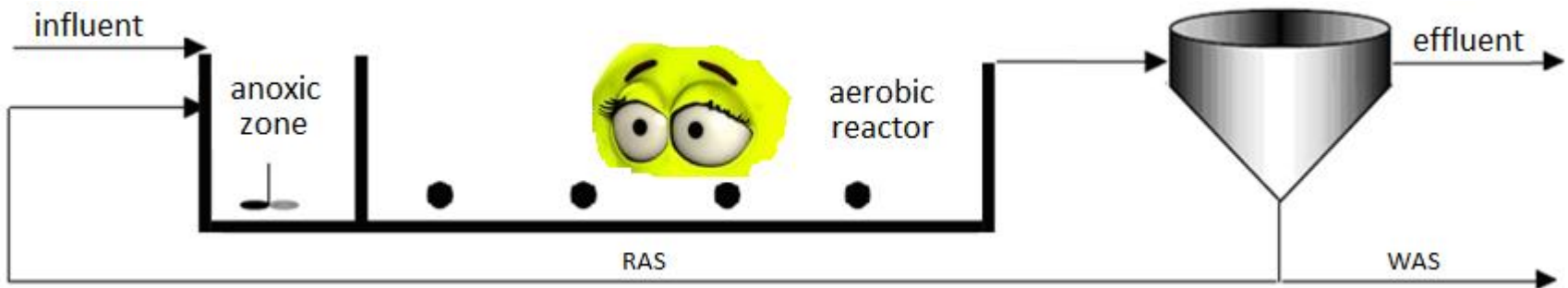
2. Toxicity in the influent wastewater or compound

Symptoms for a toxicity already present in the activated sludge process detected by respirometry
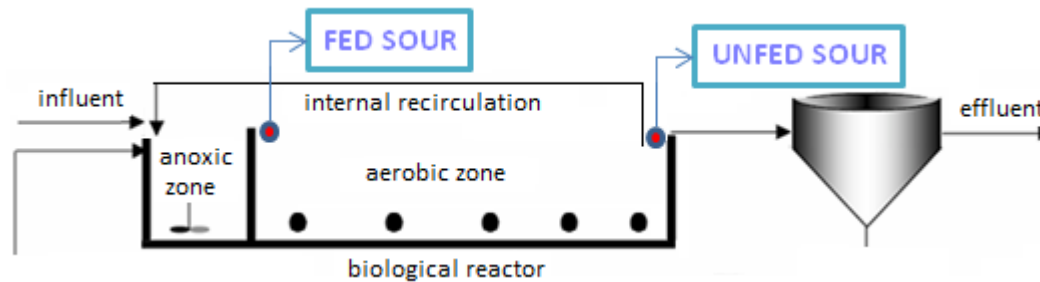
Respirometry	Symptom
UNFED SOUR	<< Reference values in the **Table UNFED SOUR vs SRT** (page 9)
FED SOUR / UNFED SOUR	< 1.3
OUR_{end}	<< Reference values in Table OURend vs MLVSS (page 11)

Short term toxicity

The method is based on one R test (using endogenous RAS sludge) where its added a readily biodegradable standard substrate (e.g. sodium acetate) with sufficient concentration to get its maximum respiration and, once this has been achieved, adding sucessive doses of sample to compare the respiration rate in progress with the maximum respiration rate reached in the test (reference)
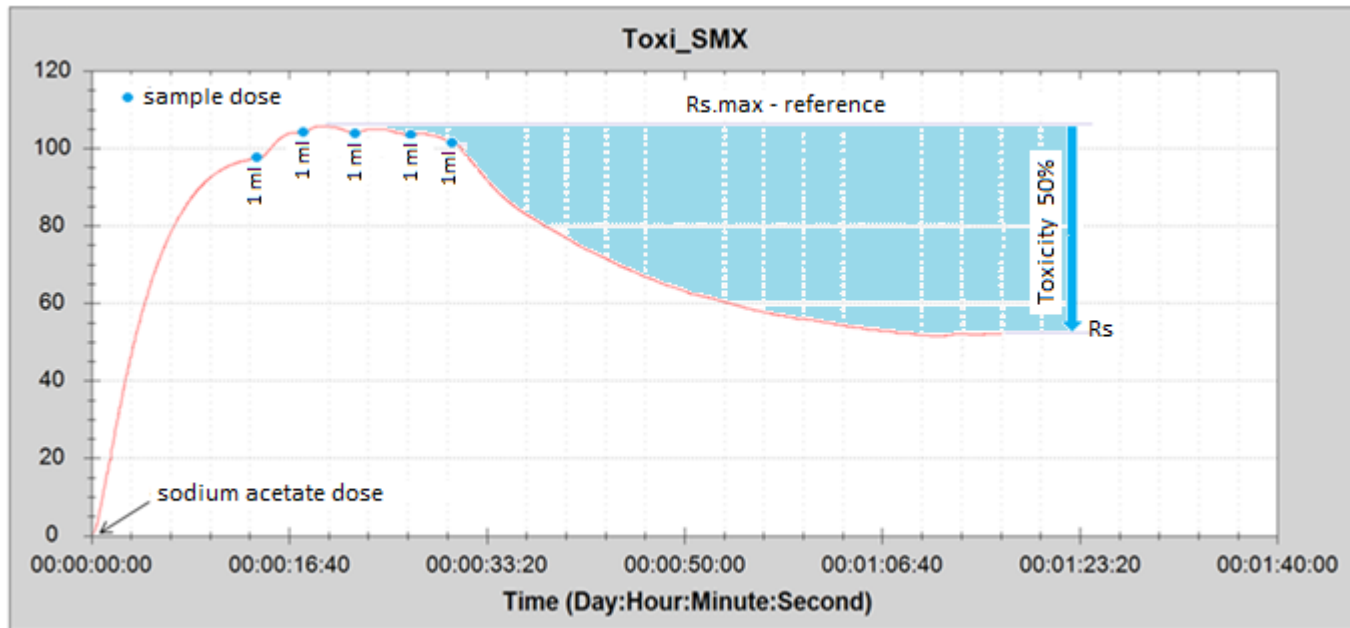
Rs respirogram for short term toxicity

Toxicity (%) = 100 * (Rs.max – Rs) / Rs.max

Additional calculations from short term toxicity

Sample / Sludge ratio for a determined toxicity in the ASP

$V_{m.tox} / V_{RAS}$ = Σ sample doses (ml) / RAS sludge in respirometer reactor (1000 ml)

$V_{m.tox}$: Sample volume from which the toxicity effect is starting
V_{fRAS}: Returned activated sludge volume

Minimum sample flow in the ASP for toxicity

$Q_{i.tox}$ = Q_{RAS} * ($V_{m.tox} / V_{RAS}$)

$Q_{i.tox}$: Minimum influent flow of the sample in the activated sludge process to start toxicity effect (m^3/h)
Q_{RAS} : Returned activated sludge flow (m^3/h)

Minimum F/M in the ASP

F/M_{min} = $Q_{i.tox}$ * BOD / (V * MLVSS)

F/M_{min} : Minimum loading rate (F/M) to start toxicity (BOD /VSS.d)

All the above calculations can also be applied for a determined accepted % of toxicity

Toxicity for global biomass or specific for nitrifiers

This method is based on the preparation of one mixed-liquor with RAS sludge and distilled water (reference) and one o several more mixed-liquor with RAS sludge and sample/s to be analyzed.

Condition for the mixed-liquors: [sample or disitilled water volume / RAS sludge volume] = [Influent flow / RAS flow]

The prepared mixed-liquors are passed into endogenous respiration state to carry out R tests for each one, by adding the same amount of estándar (sodium acetate or ammonium chloride or both) until achieving the maxium respiration rate (Rs.max). The possible toxicity is then assessed by comparing the Rs.max from the reference with the Rs.max corresponding to the samples to analyze.
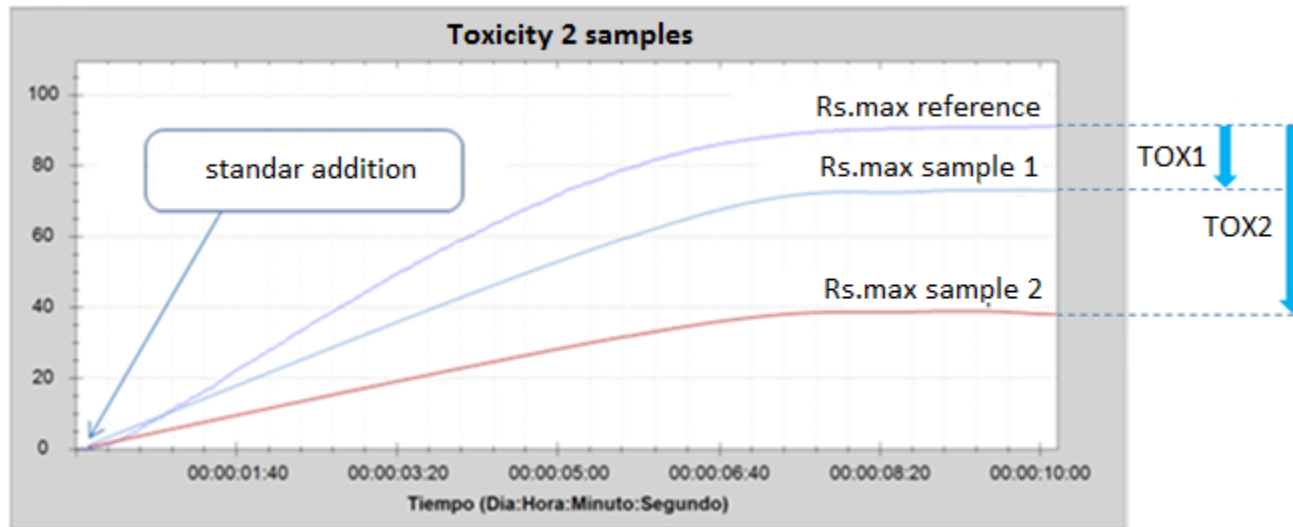
Combined Rs respirograms to asses 2 samples toxicity

Toxicity (%) = 100 * (Rs.max ref. – Rs sample) / Rs.max ref.

This method is valid both to analyze a global toxicity (by adding sodium acetate) or a specific toxicity for nitrification (by adding ammonium chloride)

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