Determination of Readily Biodegradable COD (rbCOD)

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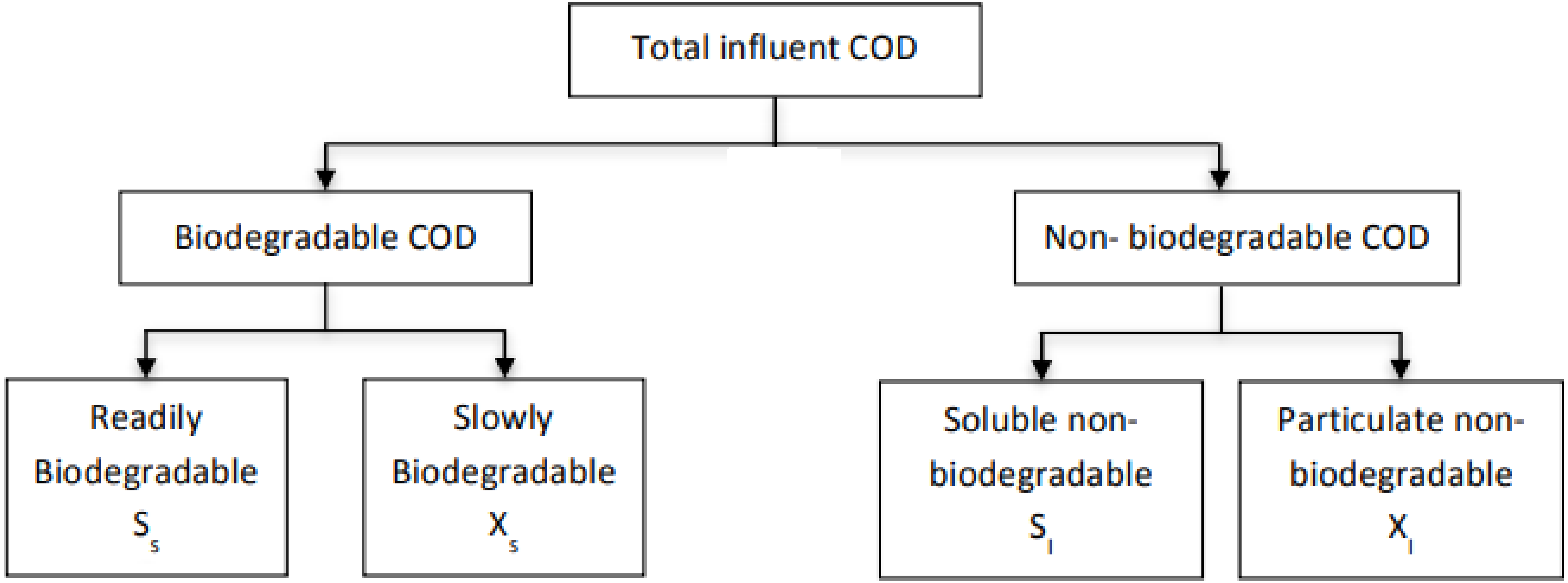
- Wastewater biodegradable and non-biodegradable fractions
- Influence of readily biodegradable COD (rbCOD) and other COD fractions on wastewater treatment
- Determination of rbCOD by:
  - Chemical-physical analysis (estimation)
  - Respirometry
- Conclusions

COD Fractions

Wastewater biodegradable and non-biodegradable fractions

Characterization of wastewater with regard to the organic content is useful from the standpoint of modeling, process control and prediction of effluent quality. Analytical parameters such as Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) are routinely used to reflect the total organics in wastewater. COD is estimated to be a more useful parameter than BOD, but from a modeling standpoint, COD cannot differentiate between biodegradable and inert organic matter or between readily and slowly biodegradable fractions.

Wastewater biodegradable and non-biodegradable fractions

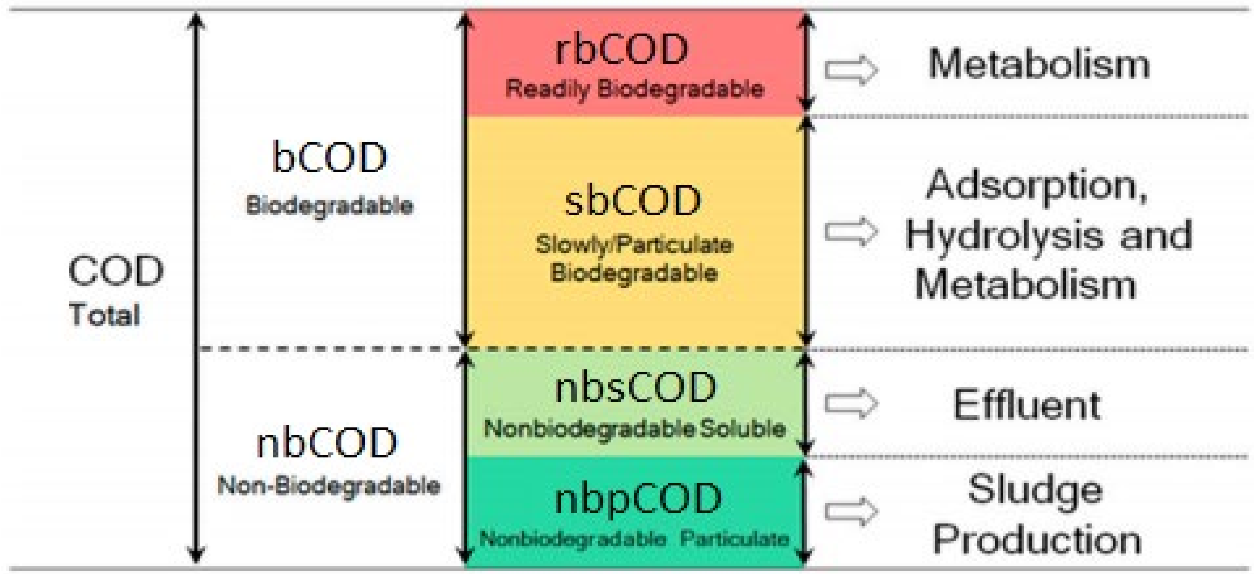


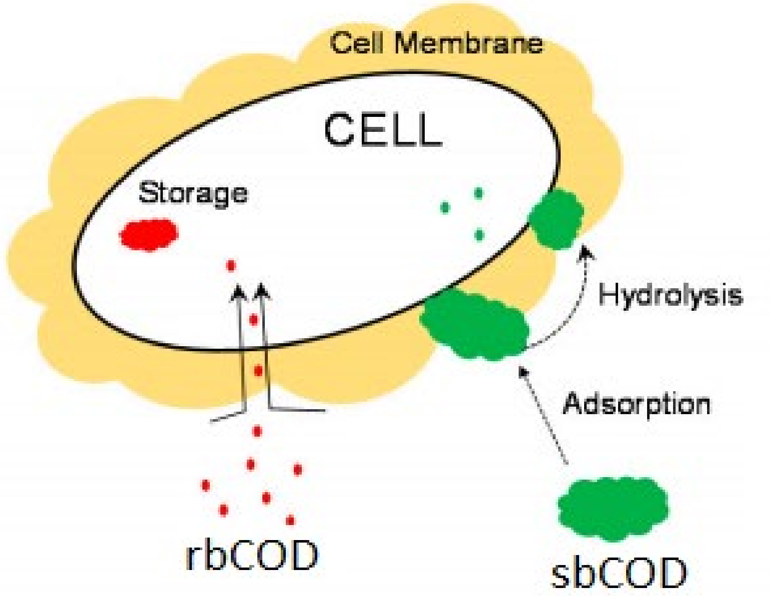
Influent wastewater fractions

Wastewater biodegradable and non-biodegradable fractions

Typical raw and settled portions of wastewater COD fractions in total COD			
Biodegradable COD (bCOD) Raw: 0.75 to 0.85 Settled: 0.80 to 0.95		Non-Biodegradable COD (nbCOD) Raw: 0.15 to 0.25 Settled: 0.05 to 0.20	
rbCOD (S_S) Raw: 0.08 to 0.25 Settled: 0.10 to 0.35	sbCOD (X_S) Raw: 0.50 to 0.77 Settled: 0.45 to 0.85	nbsCOD (S_I) Raw: 0.04 to 0.10 Settled: 0.05 to 0.20	nbpCOD (X_I) Raw: 0.07 to 0.20 Settled: 0.00 to 0.10

Wastewater biodegradable and non-biodegradable fractions





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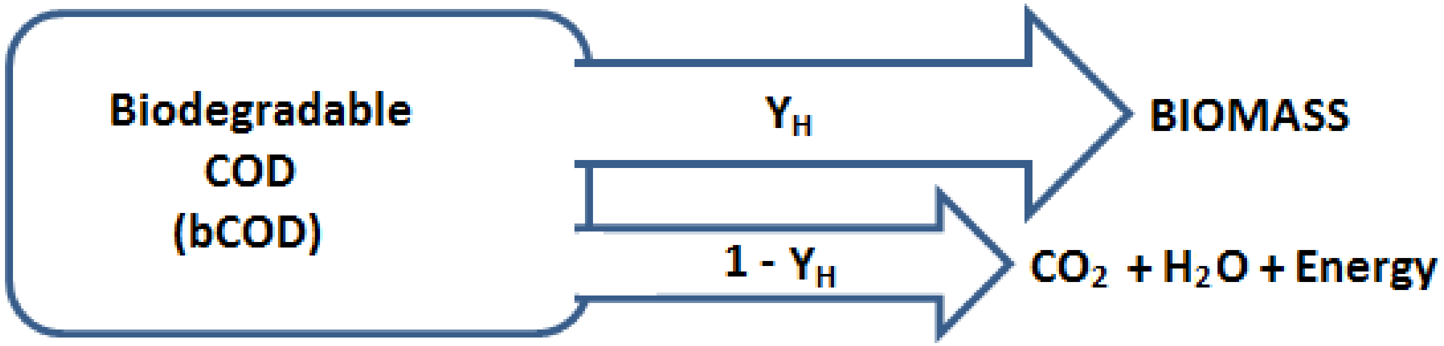
Why biodegradable COD rather than BOD?

BOD only measures the organics used for respiration and ignores what is converted to biomass



BOD ignores the non-biodegradable carbonaceous matter

$$\boxed{\text{non-biodegradable COD (nbCOD)}} = \boxed{\text{COD}} - \boxed{\text{bCOD}}$$

Where:
Y_H - Heterotrophic yield coefficient (mg cell COD / mg COD removed)

Biodegradable COD (bCOD)

- **Biodegradable (bCOD)**

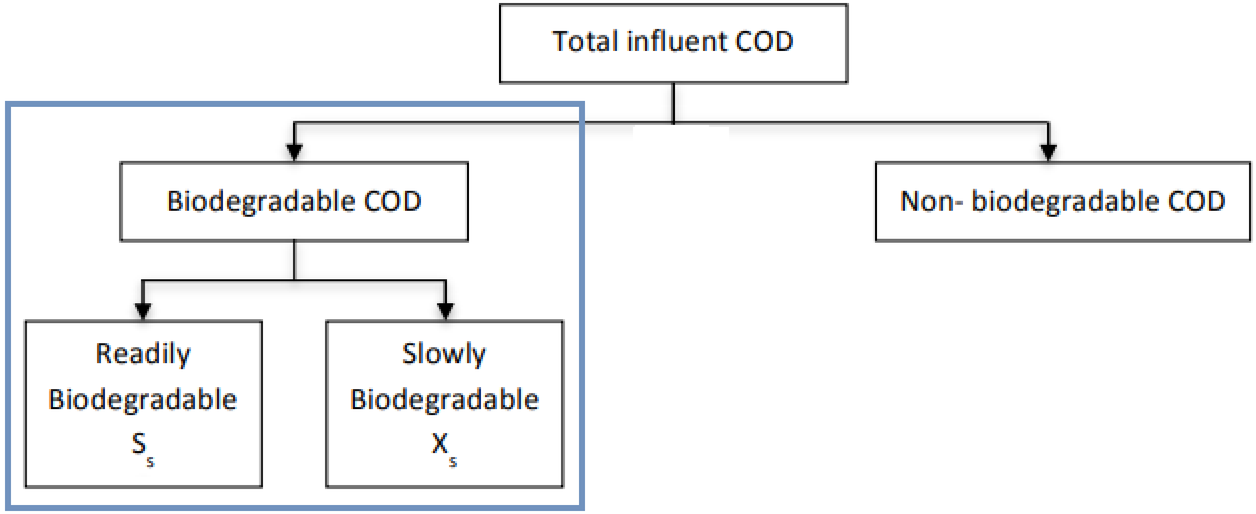
  Consists of the total fraction from COD that can be biodegraded by the heterotrophic microorganisms.

- **Readily biodegradable (rbCOD, S_S)**

  Consists of small molecules that are directly available for biodegradation by heterotrophic microorganisms (volatile fatty acids, alcohols, amino-acids, simple sugars)

- **Slowly biodegradable (sbCOD, X_S)**

  Consists of larger molecules requiring extracellular breakdown (hydrolysis) before being biodegraded by the heterotrophic microorganisms (proteins, FOG, complex carbohydrates)



Influent wastewater fractions

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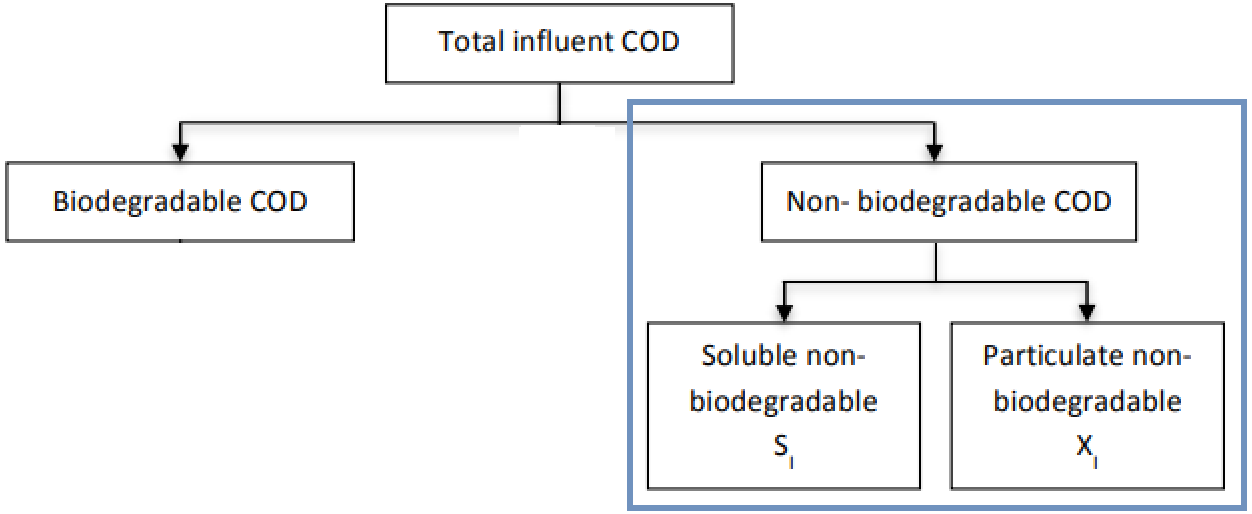
Non-biodegradable COD (nbCOD)

- **Soluble non-biodegradable COD (nbsCOD)**

Soluble fraction is not affected by contact with the biomass, does not undergo any changes during treatment and is discharged with the effluent.

- **Particulate non-biodegradable COD (nbpCOD)**

Particulate fraction forms significant portion of primary and/or waste activated sludge. nbCOD impacts significantly the plant sludge production and digestibility.



Influent wastewater fractions

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Influence of readily biodegradable COD (rbCOD)

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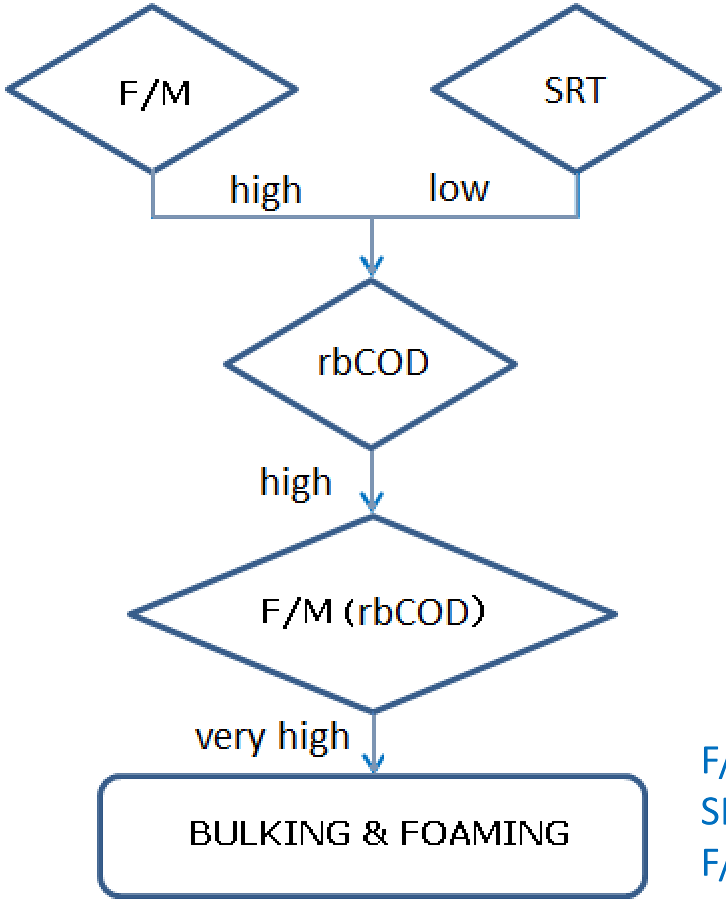
Influence of readily biodegradable COD (rbCOD)

High rbCOD (> 30%) with a high F/M can lead the process towards Bulking & Foaming



F/M: Food/Microorganisms ratio
SRT: Sludge Retention Time (d)
F/M (rbCOD): F/M only related to rbCOD

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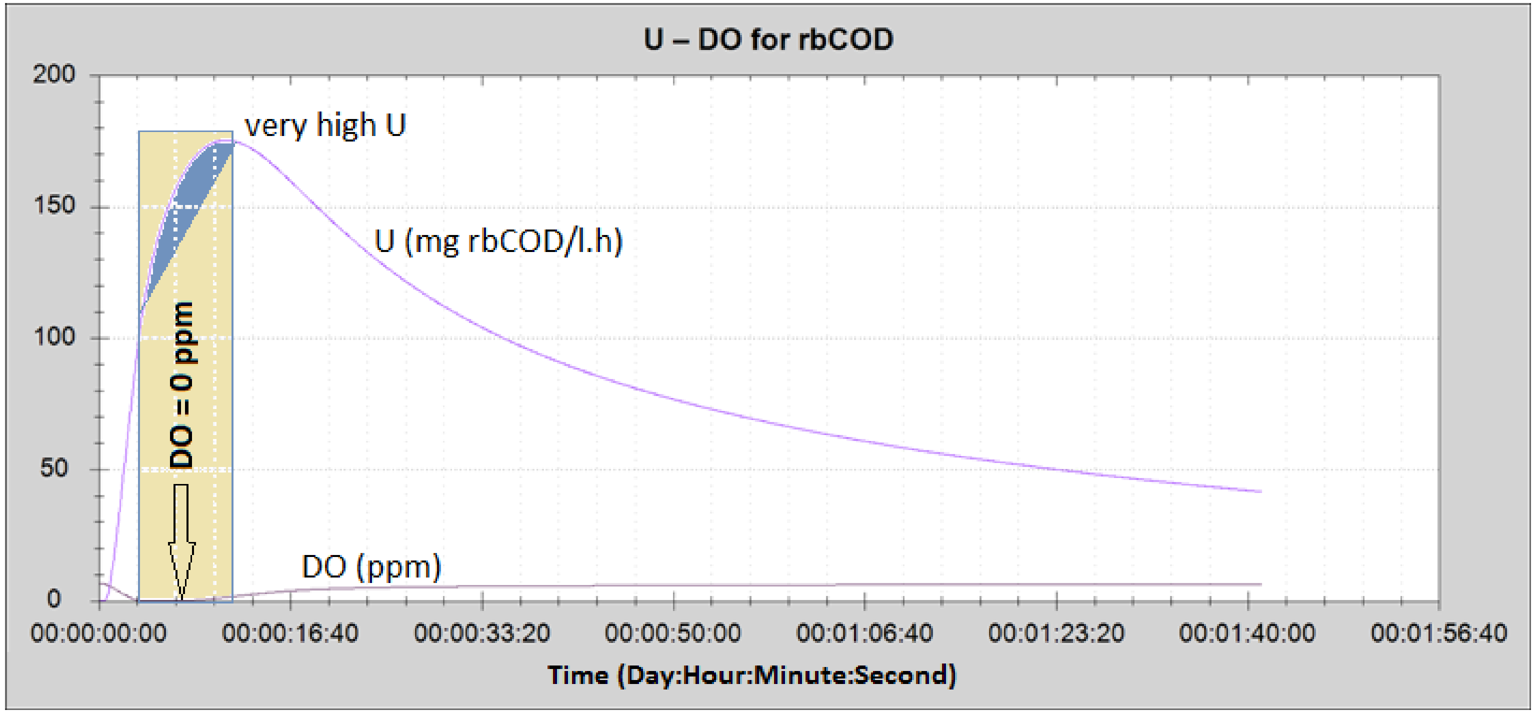
Influence of readily biodegradable COD (rbCOD)

When the aeration tank is operating under limited oxygenation, a rbCOD with high COD uptake rate U can cause a dramatic fall of the dissolved oxygen level to zero ppm, creating an unwanted anoxic zone, which could lead the process towards a poor COD performance and possible septicity.



Simultaneous DO and U Respirograms in respirometer in R test mode for rbCOD determination

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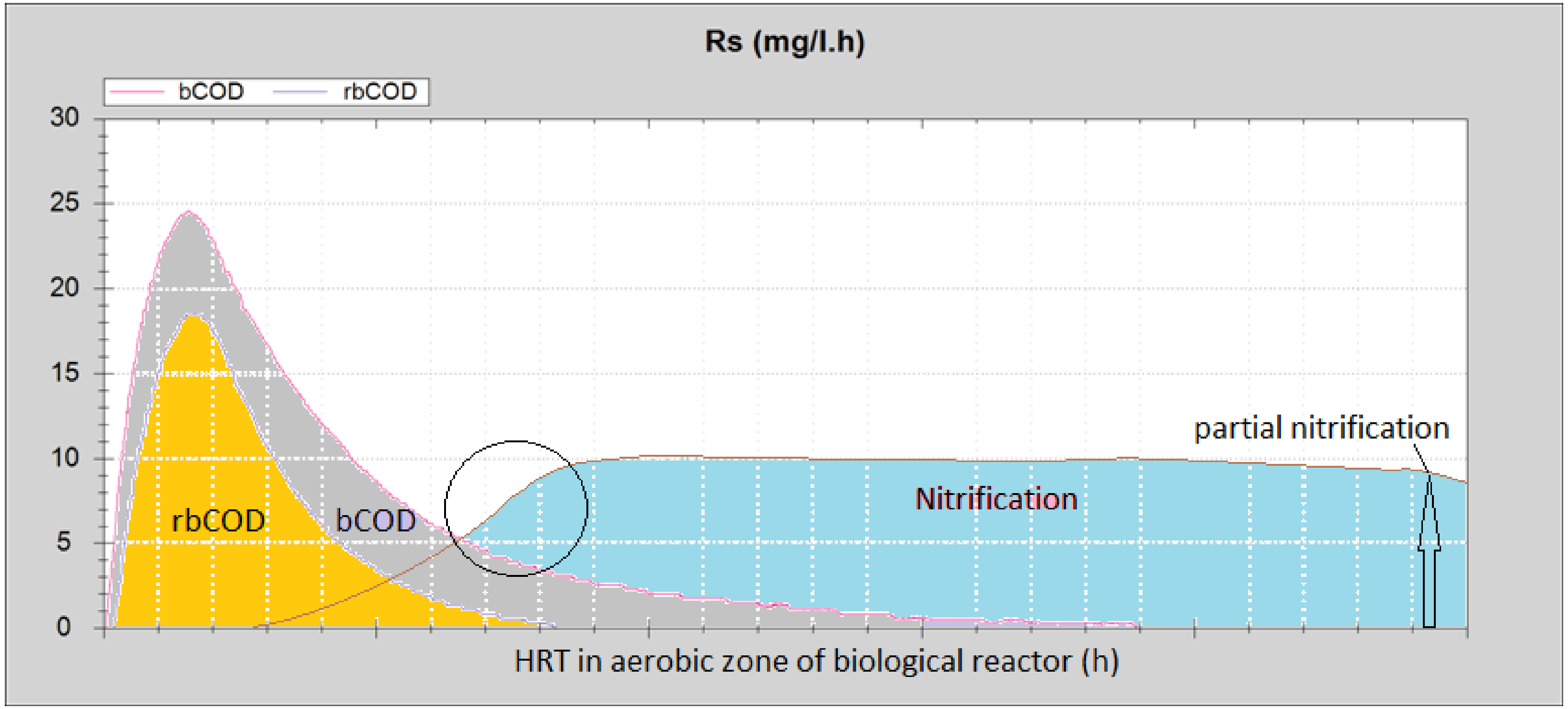
Influence of readily biodegradable COD (rbCOD)

High rbCOD with a limited hydraulic retention time can develop a partial nitrification and risk of nitrite in the effluent.



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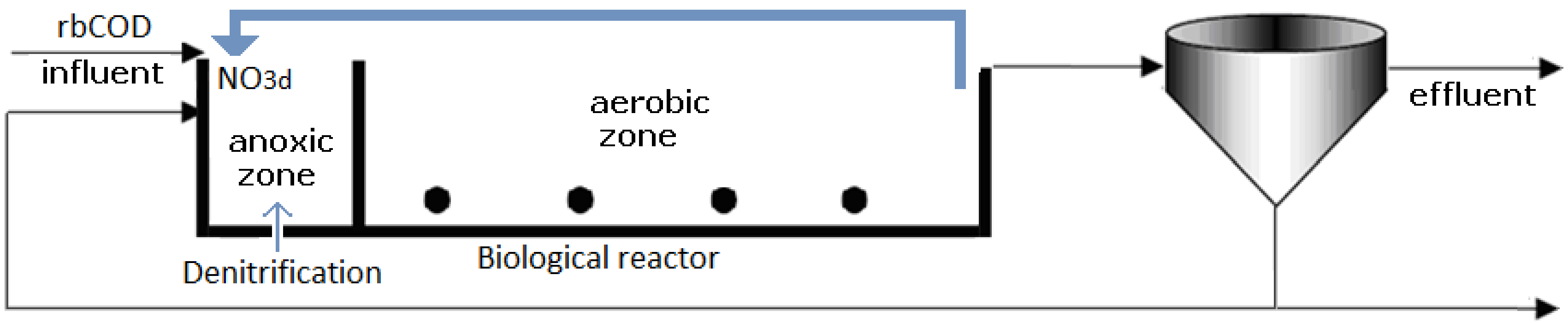
Influence of readily biodegradable COD (rbCOD)

- Enhanced Biological Phosphorus Removal (EBPR)
  - A two-step process of phosphorus release and uptake under alternating anaerobic and aerobic or anoxic conditions where Phosphate Accumulating Organisms or PAOs use rbCOD to accumulate phosphorous (normal cells have 1-2% P where PAOs can have up to 40%)

- rbCOD concentration (especially concentration of VFA) in anaerobic zone is a critical factor for successful biological phosphorous removal.

Influence of readily biodegradable COD (rbCOD)

- The rbCOD, in the influent of the anoxic zone, is the carbonaceous material available for the heterotrophic biomass to develop the denitrification process. For this reason, a lack of rbCOD will lead the process to a poor denitrification performance.



Soluble carbonaceous matter / Nitrate = [rbCOD (1 – Y_H)] / [N_NO_3d] = 2.86 or higher

N_NO_3d (mg/l): Nitrate to denitrify

The Soluble carbonaceous matter / Nitrate ratio should be equal or higher than 2.86 value. When the carbonaceous matter / Nitrate ratio is lower than 2.86, the denitrification performance will be proportionally reduced.

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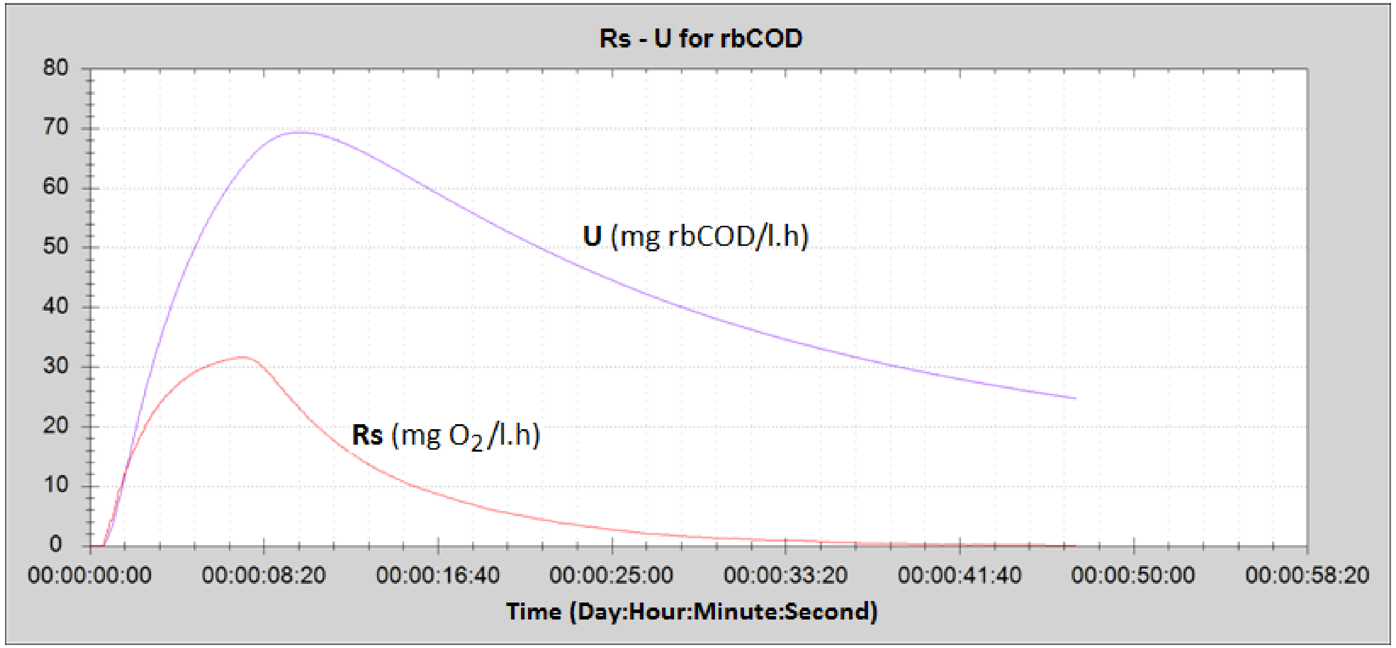
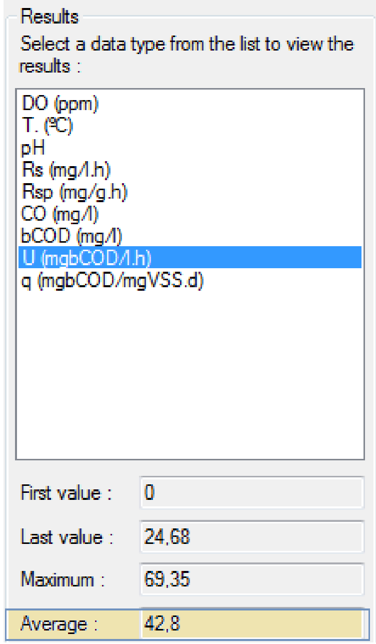
Influence of readily biodegradable COD (rbCOD)

Denitrification develops at the same speed as the rbCOD uptake rate during nitrate oxidation. For this reason, the denitrification rate (NUR) is proportional to the rbCOD uptake rate (U) which is one of the simultaneous parameters that a respirometer can automatically calculate in the R test for rbCOD.



Simultaneous Rs and U Respirograms R test for bCOD determination in a respirometer



Average U result

Denitrification rate : NUR = U (1 – $Y_{H.O2}$) / 2.86

We can calculate the NUR from the U parameter, and check the necessary hydraulic retention time (T_{DN}) in the anoxic zone.

T_{DN} = N_NO_3d / NUR

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Influence of the particulate slowly biodegradable COD (sbCOD)

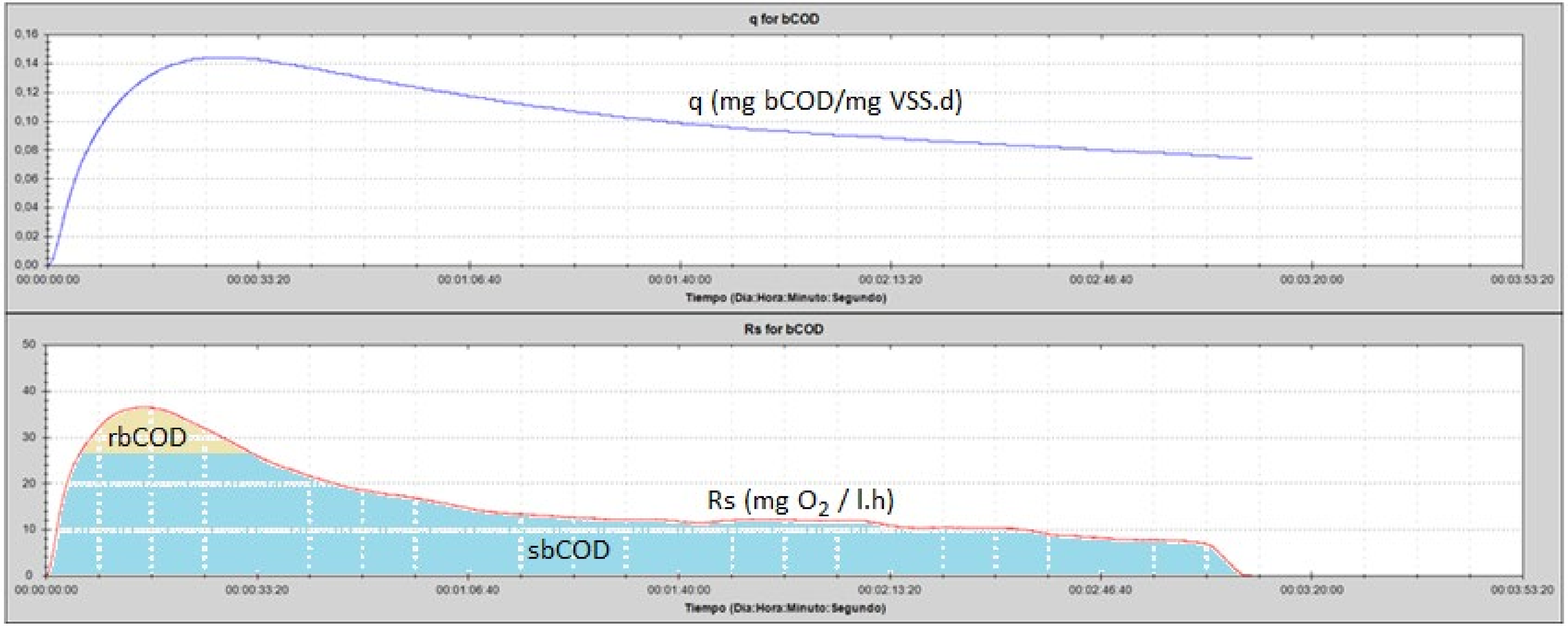
- High value of sbCOD including very low specific COD uptake rate (e.g. FOG) can cause a nutritional lack, leading the process to a filamentous bacteria generation and possible bulking phenomena.

- When the HRT is very limited, a high sbCOD could cause a poor COD performance.

- For wastewater treatments not designed for nitrification, under certain conditions, a high value of sbCOD could lead the process to an unwanted nitrification.

Impact of high slowly biodegradable COD (sbCOD) and low specific substrate uptake rate (q)

When sbCOD is very high (> 70 % of COD), together with a low specific substrate uptake rate (q), it can make a high impact in the activated sludge and lead the process to Foaming & Bulking.



In those conditions, the biomass can experience a dramatic nutritional lack, leading the sludge to deflocculation.

Influence of the non-biodegradable COD

- High percentage of nbCOD (> 25% of COD) can lead the process to a poor performance by getting COD levels out of limits in the effluent.

- When the nbCOD includes a high percentage of particulate portion (nbpCOD), the sludge production can be dramatically increased.

- When the nbCOD includes a high percentage of soluble portion (nbsCOD) it could be a possible cause of lack of soluble biodegradable COD (rbCOD) for the denitrification.

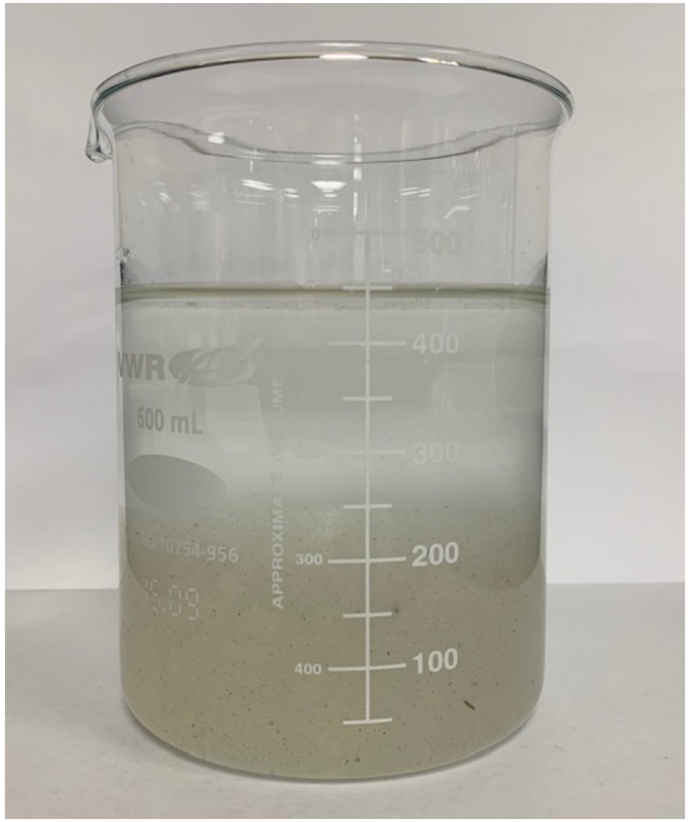
Determination of rbCOD

Estimating Readily Biodegradable COD by chemical-physical method

- Collect samples of influent and effluent
- Analysis steps
  - Flocculation of influent with zinc sulfate
  - Filtration
  - COD analysis
  - Calculations

Estimating Readily Biodegradable COD by chemical-physical method

Influent Flocculation Procedure



- Add 2 mL of 100 g/L zinc sulfate to a 200 mL wastewater sample.
- Mix with magnetic stirrer for 1 minute.
- Adjust pH to 10.5 with 6-M sodium hydroxide (NaOH)
- Settle for a few minutes
- Withdraw clear supernatant
- Filter through 0.45 um filter

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Estimating Readily Biodegradable COD by chemical-physical method

- **Analyze COD of:**

  - Influent
  - Flocculated and Filtered Influent
  - Effluent

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Estimating Readily Biodegradable COD by chemical-physical method

- **Calculations**

$$rbCOD = ffCOD - S_I$$

Where:

ffCOD - COD of Flocculated and Filtered influent

S_I (inert COD) = COD of effluent

Estimating Readily Biodegradable COD by chemical-physical method

Fraction	COD (mg/L)	%
Soluble VFA (S_A) (mg/L)	18.8	(7.7%)
Soluble Non-VFA (S_S) (mg/L)	36.4	(15.0%)
Soluble Unbiodegradable (S_I) (mg/L)	7.0	(2.9%)
Slowly Biodegradable Colloidal (S_{COL}) (mg/L)	21.2	(8.7%)
Slowly Biodegradable Particulate (X_S) (mg/L)	100	(41.0%)
Particulate Unbiodegradable (X_I) (mg/L)	59.9	(24.6%)

Readily Biodegradable (S_S or rbCOD) (mg/L): 55.2 (22.7%)

Slowly Biodegradable (SBCOD) (mg/L): 121 (49.8%)

COD after Flocculation and Filtration (1.2um) (mg/L): 62.2 (25.6%)

COD after Filtration (1.2 um) (mg/L): 83.4 (34.3%)

Total COD (mg/L): 243 (100%)

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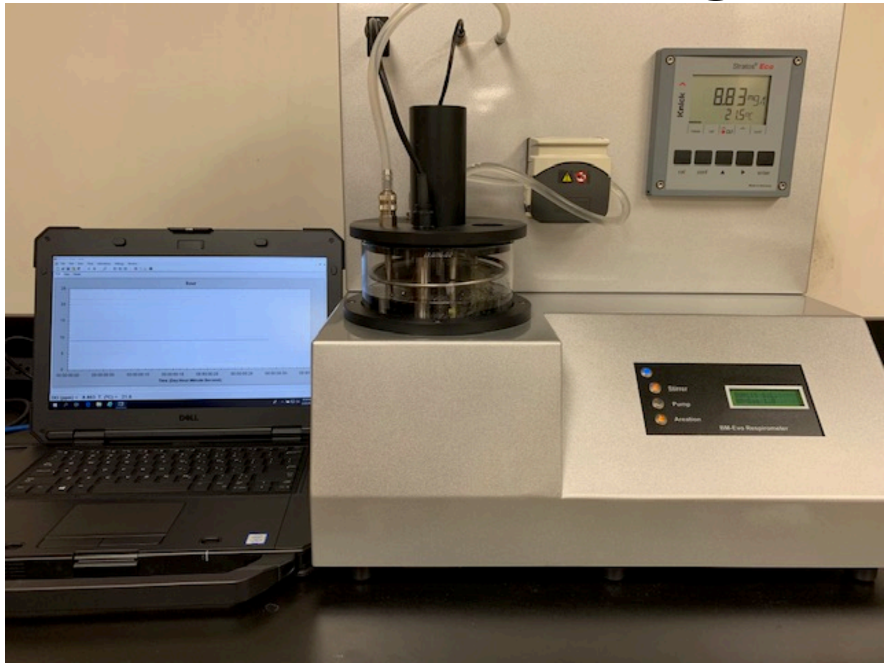
Determining Readily Biodegradable COD by Respirometry

- Collect samples of influent and activated sludge



- Analysis steps
  - Flocculation with zinc sulfate
  - Filtration
  - COD analysis
  - Calculations

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Determining Readily Biodegradable COD by Respirometry

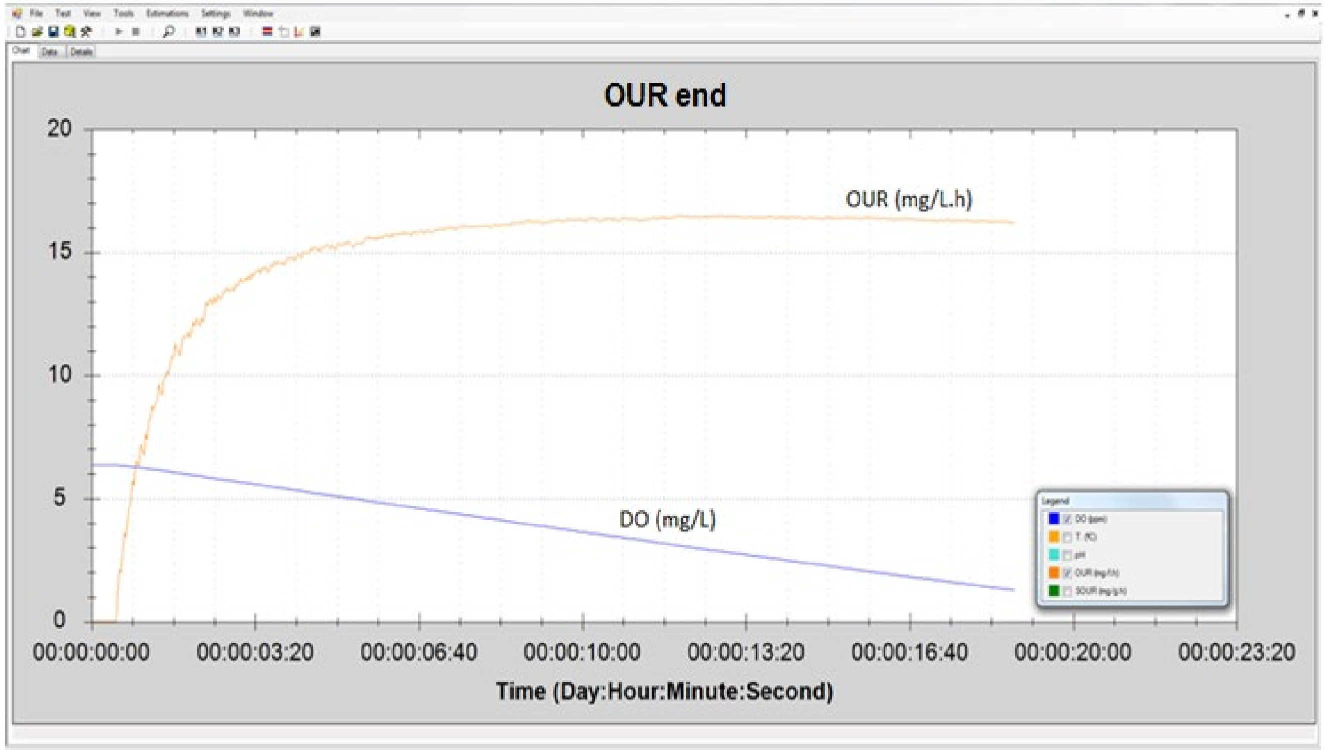
- From an endogenous activated sludge and an influent sample, the respirometer can automatically determine the biodegradable COD (bCOD) and readily biodegradable COD (rbCOD). And from those parameters and total COD, the slowly biodegradable (sbCOD) and non-biodegradable fractions can be calculated.

Determining Readily Biodegradable COD by Respirometry

Endogenous respiration rate

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

Normally the endogenous respiration state can be recognized when the oxygen readings are stable within its oxygen saturation level.



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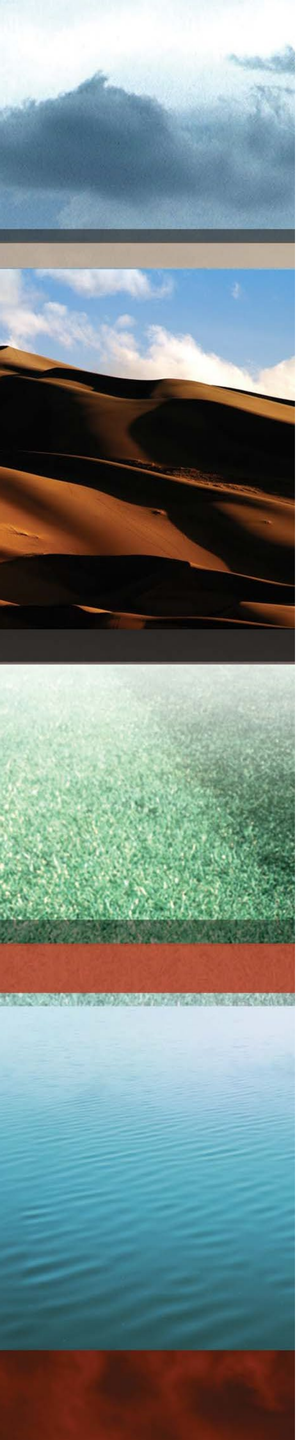

OUR_{end} assessment

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

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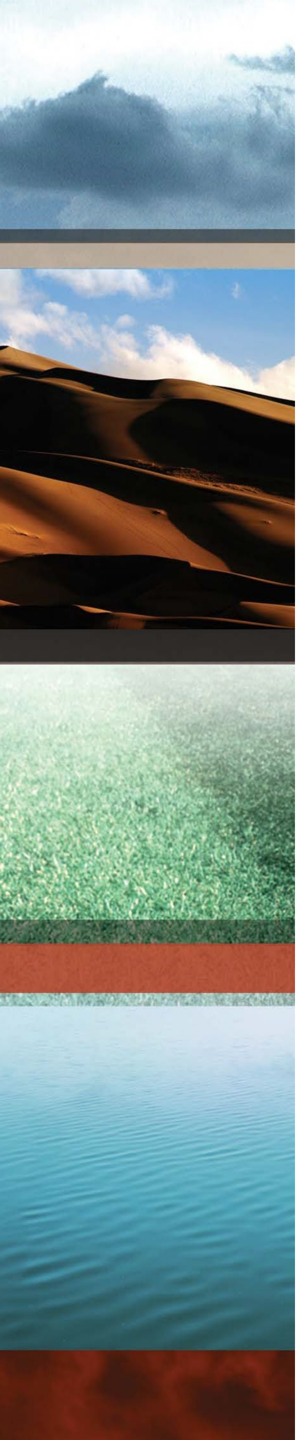

Determining Readily Biodegradable COD by Respirometry

Influent to biological reactor
<u>non-filtered</u> sample

Activated sludge
under endogenous respiration

Influent to biological reactor
<u>soluble</u> sample

R test in BM respirometer
$bCOD = CO / (1 - Y_H)$
(automatic calculation)

→ **bCOD**

R test in BM respirometer
$rbCOD = COs / (1 - Y_H)$
(automatic calculation)

→ **rbCOD**
S_S

COD: total COD
Y_H = heterotrophic yield coefficient
CO = consumed oxygen
COs: CO in soluble sample
bCOD = biodegradable COD
rbCOD (S_S) = readily biodegradable COD

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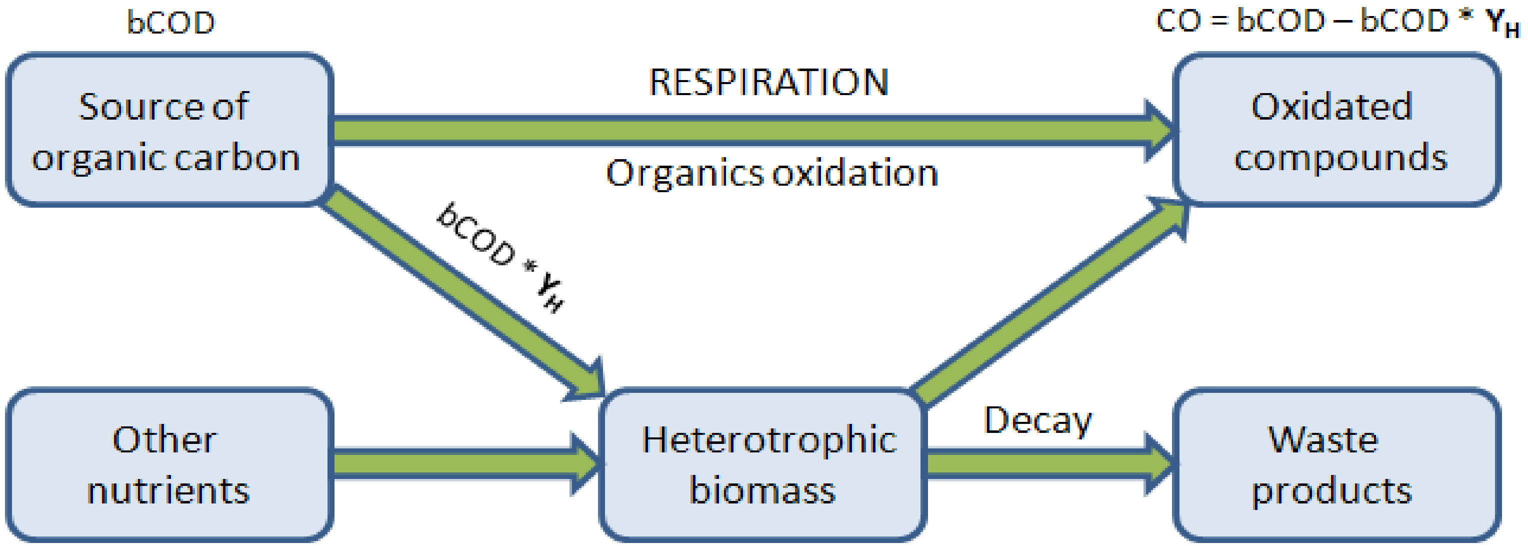
Determining Readily Biodegradable COD by Respirometry

Yield coefficient of heterotrophic biomass

The Y_H is a fundamental parameter by itself and for the bCOD and rbCOD fractions because it represents the part that goes to the heterotrophic biomass growth



$$\mathbf{bCOD} = CO / (1 - \mathbf{Y_H})$$

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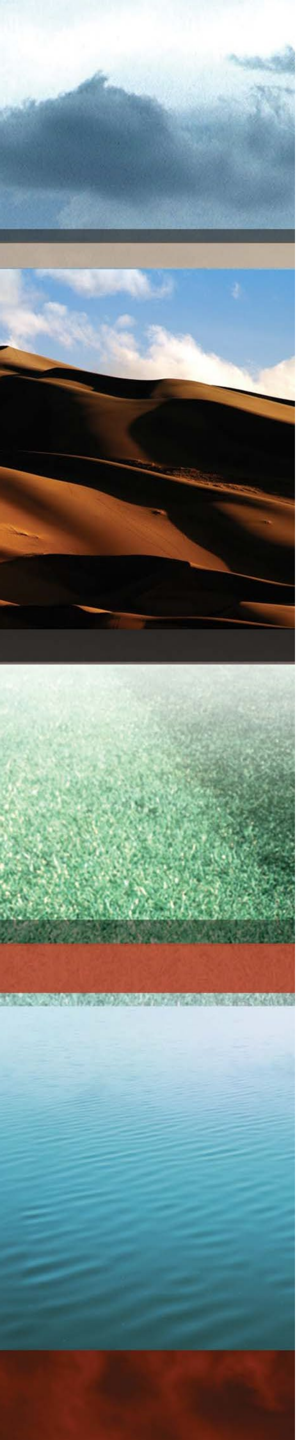
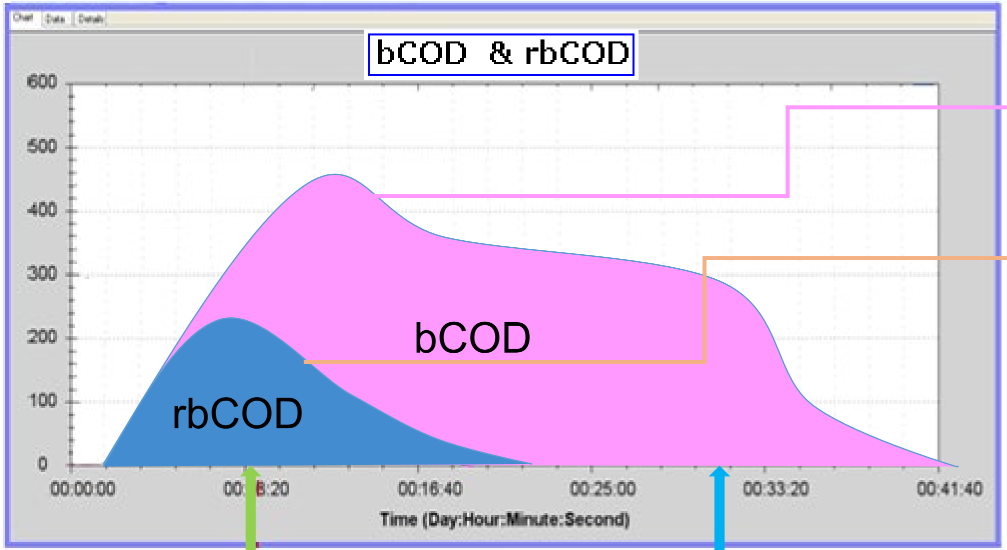


Determining Readily Biodegradable COD by Respirometry



activated sludge (endogenous respiration) + filtered influent	activated sludge (endogenous respiration) + Non-filtered influent

- COD
  - bCOD
    - rbCOD
    - sbCOD
  - nbCOD

COD − bCOD = nbCOD

bCOD − rbCOD = sbCOD

sCOD − rbCOD = nbsCOD

nbCOD − nbsCOD = nbpCOD

bCOD: biodegradable COD (total)
nbCOD: non-biodegradable COD
rbCOD: readily biodegradable COD (S_S)
sbCOD: slowly biodegradable COD (X_S)
sCOD: soluble COD
nbsCOD: non-biodegradable soluble COD
nbpCOD: non-biodegradable particulate COD

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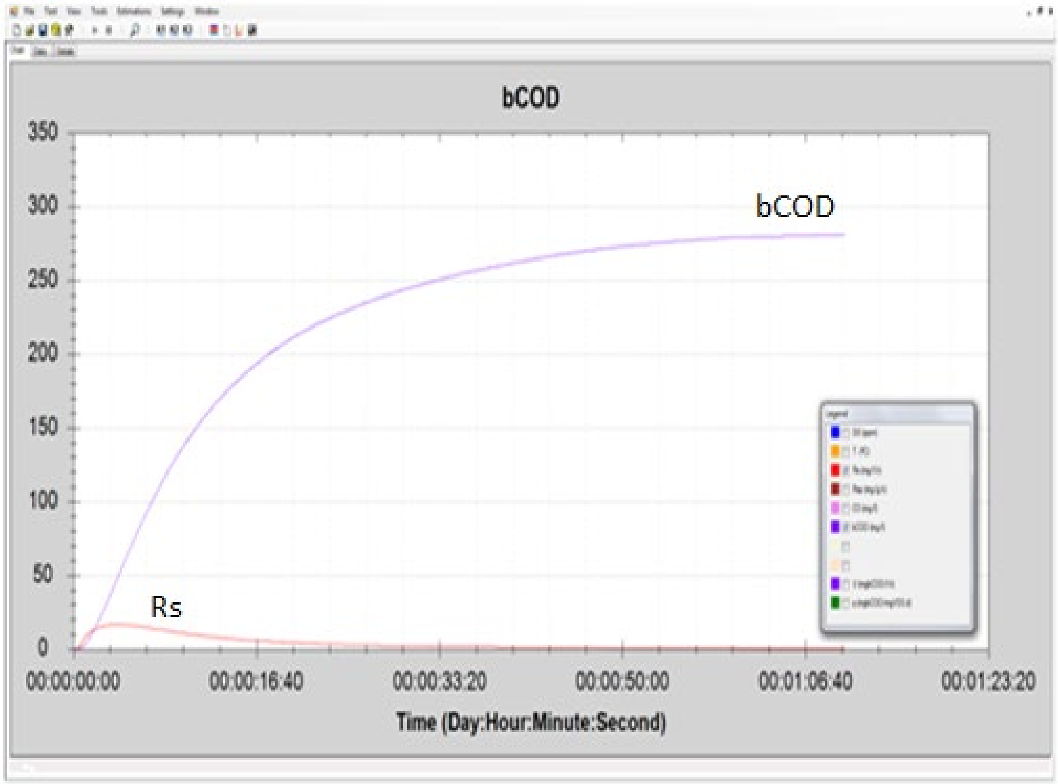
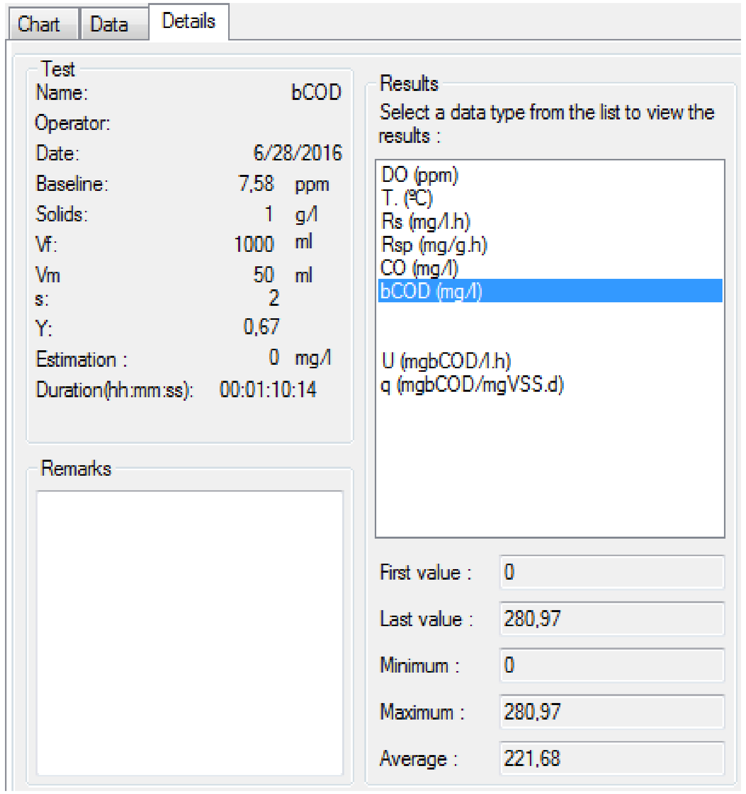
Determining Readily Biodegradable COD by Respirometry



Rs and bCOD Respirograms



bCOD final result

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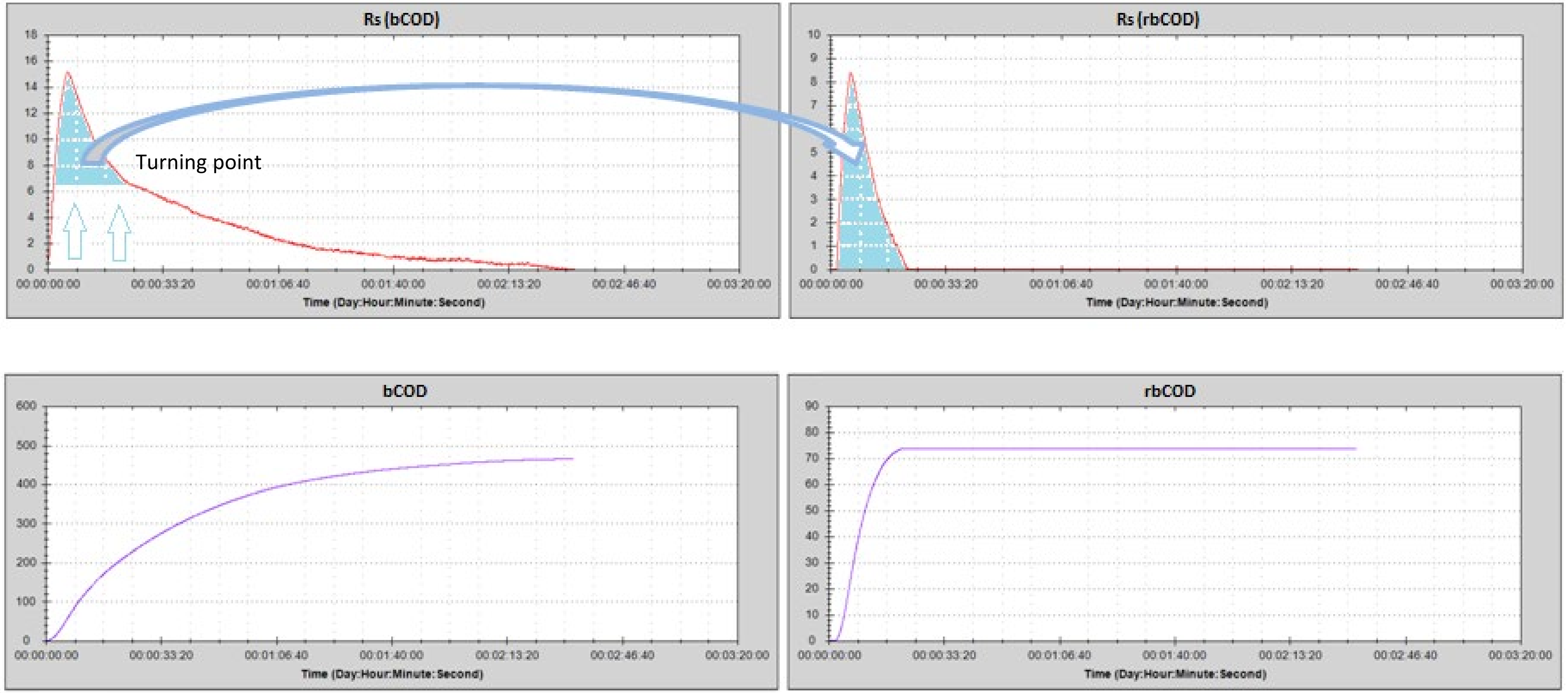
Determining Readily Biodegradable COD by Respirometry



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Conclusions

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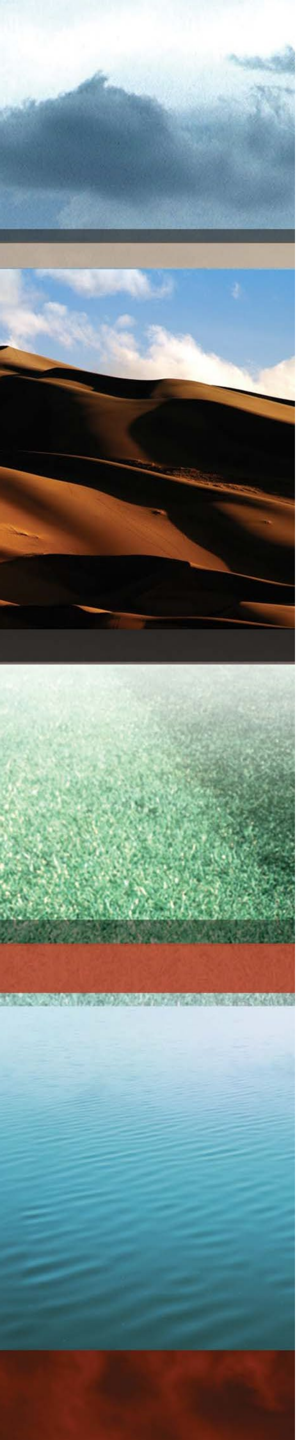

Conclusions

- Comparison of rbCOD determination by both methods

	Chemical-physical	Respirometry & COD analysis
Uses activated sludge to determine COD fractions of wastewater?	-	*
Easy to perform	*	*

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Conclusions

- Comparison of rbCOD determination by both methods

	Chemical-physical	Respirometry & COD analysis
“True” rbCOD determined	-	*
Estimated rbCOD determined	*	-

Conclusions

- Comparison of rbCOD determination by both methods

	Chemical-physical	Respirometry & COD analysis
Can the testing equipment be used for other process control tests?	*	***

Applications of Respirometry

- **Fast pulse of the actual process performance**
  - In only a few minutes it can get a fast diagnostic pulse on how the activated sludge process is performing.
- **Biological treatability**
  - Analyze the ability of the biomass to degrade wastes under specific conditions.
- **COD fractionation**
  - COD fractions determination (included the slowly and non biodegradable COD)
- **Advanced oxidation processes tracking**
  - The combination of COD fractioning, substrate utilization rate and specific inhibition/toxicity permits the perfect tracking of any advanced oxidation system and assess the evolution of the substrate biodegradation character throughout the treatment.

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Applications of Respirometry

- **Nitrification**
  - Determination of the nitrification rate under different DO, temperature and pH conditions, nitrification capacity, minimum sludge age.
- **Denitrification**
  - Determination of the soluble biodegradable COD necessary for denitrification, and denitrification capacity.
- **Toxicity**
  - Inhibition & toxicity for any specific activated sludge.
- **Operative parameters**
  - Loading rate (F/M), Sludge age (MCRT, SRT)
- **Biokinetic parameters**
  - For modeling and simulation software support

Applications of Respirometry

- **Energy optimization**
  - Can analyze the minimum DO level at which the process can operate without any performance detriment.
- **Sequencing Batch Reactor (SBR) optimization**
  - The respirometer can determine appropriate parameters and conditions for optimal operation.
- **Influence of different conditions**
  - By modifying the test conditions we can analyze their influence in the process activity and study the optimal, minimum level and loading capacity.
- **Nutrients**
  - By means the readily biodegradable COD and yield coefficients its possible to analyze the optimal nutrients ratio.

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Thank you

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