# State of the art procedure for analysis and control of anoxic denitrification by BM Respirometry in a wastewater treatment

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## ABSTRACT

The removal of nitrogen in a wastewater treatment plant can be completed by the biological process of denitrification under anoxic conditions. For this there are several types of processes, but in general it is carried out by means of facultative heterotrophic bacteria that mainly use a source of organic carbon for synthesis and energy as well as nitrate ($NO3^-$) as a source of oxygen.

Being heterotrophic bacteria, there is a relationship between their aerobic and anoxic activity.
Normally, the external carbon source for denitrification can come from wastewater or from an external source such as methanol (commonly used).

One of the important challenges in denitrification is to know if from the wastewater entering the process organic matter is available in sufficient quantity and quality to obtain the required performance.

In a full-scale WWTP, Henze et al. (1994) recommended a COD/nitrogen (COD/N) ratio of 6 to 11 g COD/g N-NO3 for complete denitrification. However, these ratios may not yield the expected result when the percentages of the easily biodegradable (COD), slowly biodegradable (COD) and inert (COD) fractions of COD fall outside normal ranges.

With all this, the fundamental principle that comes into play in this paper is based on the fact that the denitrification rate has a direct relationship with the rate of elimination of oxygen consumed in biodegradable COD. The priority is on the easily biodegradable COD fraction, but if it were the case that the percentage of the dominant fraction is the slowly biodegradable COD, a denitrification rate could be generated that is slow enough that the nitrate cannot be sufficiently removed within the time limit set by the hydraulic retention time of the anoxic process.

In any case, thanks to advanced respìrometry techniques, we are in a position to develop procedures based on aerobic tests that can be used to determine parameters of the anoxic denitrification process with total and absolute effectiveness.

## 1. INTRODUCTION

Since W. Eckenfelder demonstrated in 1985 that the OUR parameter of sludge was related to the denitrification rate, several authors have dedicated themselves to demonstrating that the rate of oxygen consumed in aerobically biodegradable COD is related to the rate of anoxic denitrification (Henri Spanjers, Peter A. Vanrolleghem – 2004, GA Ekama – 2004, ...)

Therefore, with this principle, it is not necessary to operate in an anoxic medium to obtain the denitrification rate and denitrification capacity.

On this basis, a state of the art procedure is presented here in which by means of Surcis BM Respirometry, operating under aerobic conditions, the removal rate of the biodegradable COD is automatically measured and, with this, the way towards the calculation of the nitrification rate and nitrification capacity is enabled.

This procedure also makes it possible to distinguish between the total biodegradable COD and the readily biodegradable COD used and to analyze the influence of these biodegradable COD fractions on the nitrate removal capacity.

With all this, it is also analyzed whether the anoxic process will need some external source of organic matter to obtain the desired performance.

## 2. BM Respirometer

The BM Respirometry technology is based on a unique system, based on the modified LFS + LSS respirometry, developed by Surcis S.L., which is included in a series of different BM respirometer models.

This technology allows, in the previous test setup and even during its normal performance, the adaptation to different conditions of pH, Temperature, Oxygen and sample / sludge ratio. It also allows the possibility of introducing certain data that can participate in the automatic calculations of fundamental parameters in the treatment process.

The main applications that can be carried out with BM Respirometry are the following: Taking the pulse of the process for its fast assessment, COD fractions, Biodegradability to the sludge, Toxicity, Nitrification rate (AUR), Denitrification rate (NUR), Assessment and monitoring of the aeration system, among many others.

Optionally, by means of a special reactor (bio-carrier), BM respirometers can carry out respirometry tests with moving bed biofilms for MBBR and granular biomass processes.

1. Automatic pH control system
2. pH sensor
3. Dissolved oxygen sensor
4. Stirring motor
5. Homogenization persitaltic pump
6. Reactor
7. Automatic tempering system
8. Leds fon devices control
9. Oxygen and temperatures controller
10. pH controller
11. PC + software

***BM Respirometry System – BM-Advance new model***

**OUR & Cyclic OUR modes**

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 mode**

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.

***Operation modes and automatic parameters in the BM software***

## 3. Points to consider in the relationship between oxygen consumption in the use of biodegradable COD and anoxic denitrification

- Denitrification is carried out in the anoxic environment by means of facultative heterotrophic bacteria, using organic carbon for synthesis and energy, as well as nitrate as a source of oxygen.

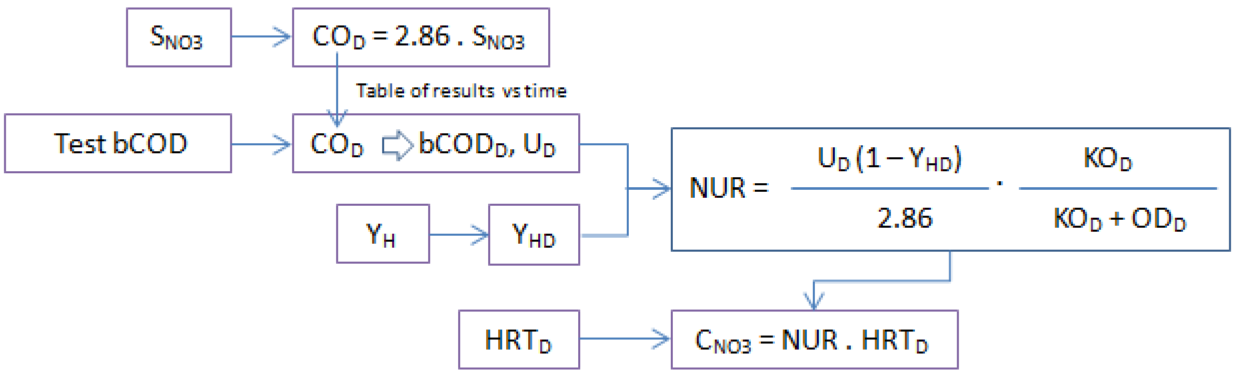
- Under normal conditions, each mg of reduced N_$NO_3$ consumes 2.86 mg of oxygen, produces 0.45 mg of SSVLM and produces 3.57 mg of alkalinity.

- In the process of anoxic denitrification, nitrate alimination is proportional to the removal of COD from organic matter as a source of organic carbon, prioritizing the use of easily biodegradable COD (COD)

**4. Procedure for the determination of denitrification rate, Consumed Oxygen, CODb used in the process and Denitrification capacity**

It is an exclusive procedure of BM Respirometry in which we can highlight its simplicity and extensive parameter information.

**4.1. Diagram**




| | |
|---|---|
| bCOD Test | = BM Respirometry Test for Biodegradable COD on equivalent conditions of temperature and pH |
| $S_{NO3}$ | = Nitrate to be denitrified (mg $NO_3$-N/L) |
| $CO_D$ | = Net oxygen corresponding to bCOD consumed in denitrification (mg/L) |
| $Y_{HD}$ | = Yield coefficient of facultative heterotrophic biomass in denitrification ($O_2$/COD) |
| $Y_H$ | = Yield coefficient of aerobic heterotrophic biomass ($O_2$/COD) |
| $U_D$ | = Utilization rate of cumulative bCOD in denitrification (mg COD/L.h) |
| $[U_D (1-Y_{HD})]$ | = Net oxygen uptake rate from bCOD used in the denitrification (mg $O_2$/l,h) |
| NUR | = Denitrification rate (mg $NO_3$-N/L.h) |
| $K_{OD}$ | = Coefficient of of inhibition due to oxygen in anoxic zone = 0.2 mg/L ( Henze et al 1996) |
| $DO_D$ | = Dissolved oxygen in the anoxic denitrification zone (mg $O_2$/L) – should be < 0.3 mg/L - |
| $TRH_D$ | = Hydraulic retention time of the anoxic denitrification zone (h) |
| $C_{NO3}$ | = Nitrification capacity (mg $NO_3$-N/L) |

The BM respirometry COD test not only includes dynamic respiration rates (Rs), but also other parameters such as oxygen consumed demand (OC) and COD utilization rate (U). And It is precisely these parameters (OC and U) that will be used to obtain the NUR.

In all this, it is important to bear in mind that denitrification uses bCOD without including the part of the oxygen destined for the production of biomass in this process ($Y_{HD}$) and therefore the rate of net oxygen consumption per organic matter used must exclude this oxygen.
With this, the oxygen demand per organic matter used becomes COD (1 – $Y_{HD}$)

1) <u>Relationship between oxygen demand per organic matter and nitrate to be denitrified</u>

The ratio of oxygen consumed (OCD) per biodegradable COD (COD) used to nitrate removed is 2.86. (Henri Spanjers, Peter A. Vanrolleghem - 2004, GA Ekama - 2004, others)

$$2.86 = \frac{OC_D}{S_{NO3}} \qquad (1)$$

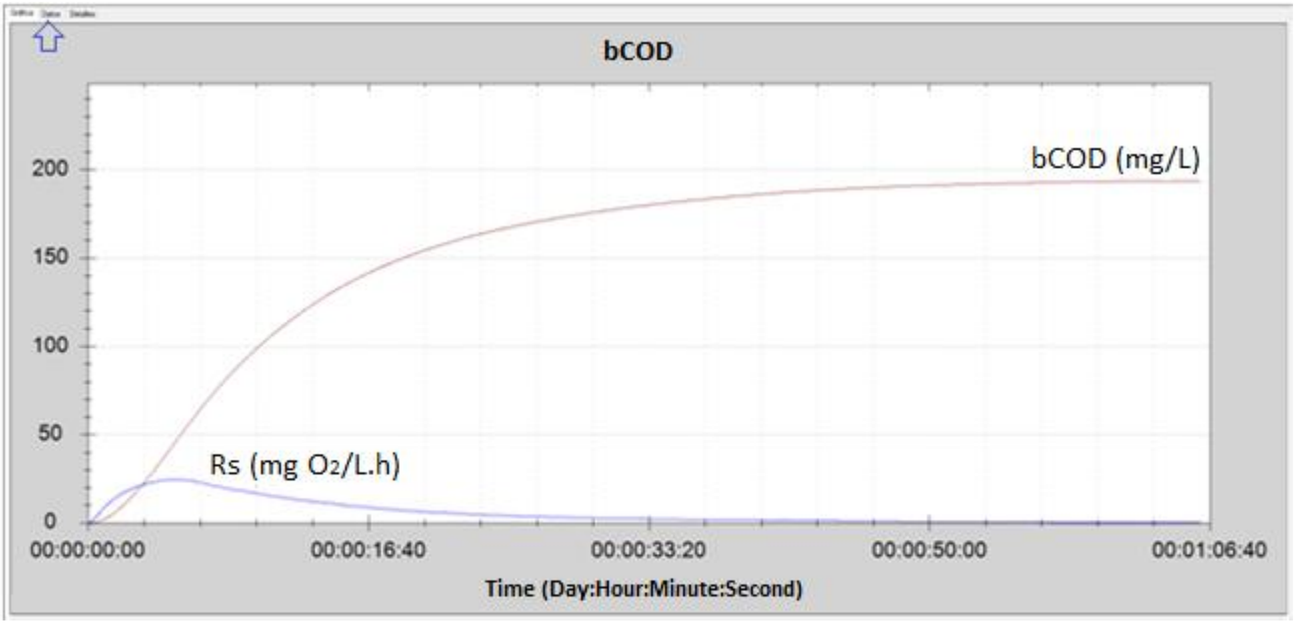
2) <u>Stoichiometric coefficient of facultative heterotrophic biomass in denitrification zone</u>

The stoichiometric yirld coefficient in the anoxic denitrification zone is calculated by applying a correction factor to the stoichiometric coefficient of heterotrophic biomass in the aerobic zone.

$$Y_{HD} = 0.83 \cdot Y_H \qquad (2) \quad \text{(Muller et al., 2003)}$$

3) <u>Automatic determination of COD and COD utilization rate in denitrification</u>

To this end, a respirometry test of the COD of wastewater will be carried out under equivalent pH and temperature conditions.




***Simultaneous respirograms of COD and Rs in a R test of biodegradable COD***

Once the test is finished, in the "Data" tab we can find all the results obtained as a function of time. From this table, we locate the value corresponding to the $OC_D$, which we have previously calculated, and obtain the values of the $U_D$ and $bCOD_D$ for the same time interval.

Chart | Data | Details

| CO (mg/l) | bCOD (mg/l) | U (mgbCOD/l.h) |
|---|---|---|
| 85.99 | 186.94 | 18.64 |
| 86.01 = $CO_D$ | 186.97 = $bCOD_D$ | 18.62 = $U_D$ |

***Obtaining the COD and UD corresponding to OCD in denitrification from the data table***

4) <u>Denitrification rate</u>

Since the direct relationship between the oxygen consumed by biodegradable COD and nitrate removed is 2.86, likewise there is this same relationship between the rate of oxygen consumed by bCOD used and the rate of nitrate removal.

In this case, taking into account that the oxygen corresponding to the biomass yield cannot be accounted for, we will apply the factor (1-YHD) to the UD value to convert the CODb utilization rate to OC utilization rate.

$$OC_D = bCOD_D\,(1 - Y_{HD}) \qquad (3)$$

Threfore

$$NUR = \frac{U_D\,(1\text{-}Y_{HD})}{2.86} \cdot \frac{KO_D}{(KO_D + OD_D)} \qquad (4)$$

5. Nitrification capacity

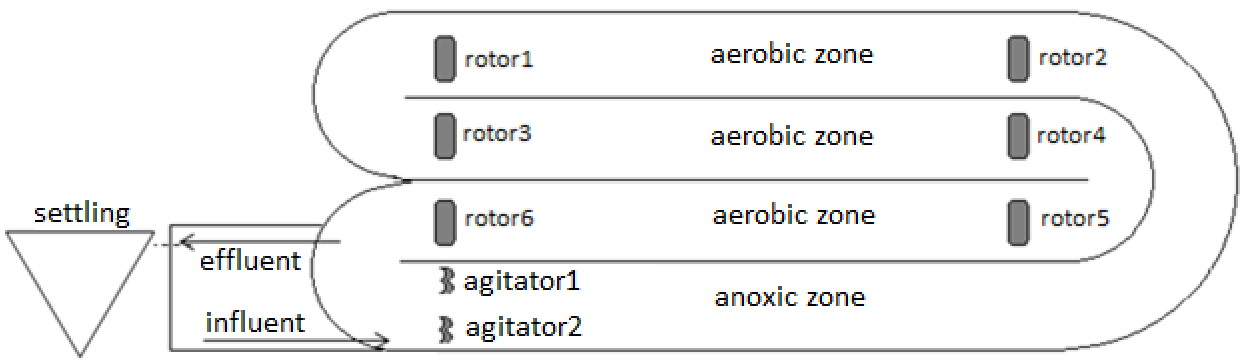
Denitrification capacity measures the nitrate that a process, with a given hydraulic retention time, is able to nitrify.

$C_{NO3}$ = NUR . $HRT_D$ (5)

To note:

- HRT is inversely proportional to NUR.
- NUR is directly dependent on the utiization rate of the cummulative CODb (U).
- The higher the percentage of slowly biodegradable COD used in the NUR, the lower the NUR will be than if the percentage of CODb was mostly readily biodegradable COD, with a proportional impact on the nitrification capacity.
- The dissolved oxygen in the anoxic zone ($DO_D$) also plays an important role, so the higher the $DO_D$, the lower the NUR and terefore the lower nitrification capacity.

**6. Example of nitrification rate and nitrification capacity calculation (real case)**




***Biological reactor : double carrousel – extended aeration***

| Parameter | Influent value | Effluent value |
|---|---|---|
| $Y_H$ (mg $O_2$/COD) | 0.70 | - |
| TKN (mg N/L) | 62 | 2.3 |
| BOD (mg/L) | 280 | 6 |
| HRT anoxic zone (h) | 11.5 | - |
| DO anoxic zone (mg/L) | ~ 0.00 | - |
| Nitrate (mg N-$NO_3$/L) | - | 3.5 |

Nitrifiable N (mg N/L) = TKN influent - $N_{sin}$ - TKN effluent = 62 - 13.7 - 2.3 = 46

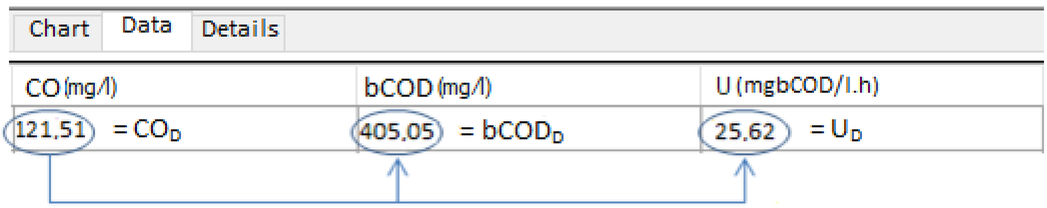
$N_{sin}$: N synthesis of the biomass ≈ 0.05 * BOD removed = 0.05 . (280 - 6) = 13.7

Nitrate to denitrify (mg $NO_3$-N/L): SNO3 = Nitrifiable N – Nitrate effluent = 46 - 3.5 = 42.5

Oxygen consumed in the bCOD utilization: $CO_D$ = 2.86 . SNO3 = 2.86 . 42.5 = 121.5 mg O2/L

$Y_{HD}$ Coefficient = 0.83 . $Y_H$ = 0.83 . 0.70 = 0.58

From the CODOb respirometry test, with the calculated value of $CO_D$, $U_D$ is then obtained in the data table.




Applying the equation (4)

NUR = [25,62 (1 – 0,58) / 2,86] . 02 / (0.2 + 0,0) = 3.76 mg $NO_3$-N/L.h

Applying the equation (5)

$C_{NO3}$ = 3.76 . 11.5 = 43.24 mg N-$NO_3$/L

In this example, the denitrification capacity is higher and very close to the nitrate to be denitrified. ($C_{NO3}$ ~ $S_{NO3}$) Therefore the process should proceed without any problem.

## 7. Conclusion

An exclusive procedure has been presented here in which the BM Respirometry software is able to automatically obtain some basic parameters that can be extrapolated for the calculation of the essential parameters in anoxic denitrification.
In this way, the oxygen used in the biodegradable COD consumed in denitrification and the elimination rate of this biodegradable COD are automatically obtained.
This leads to the calculation of Denitrification Rate (NUR) and Denitrification Capacity ($C_{NO3}$)

This procedure shows that the exclusive technology and software of BM Respirometry can become a fundamental tool for applications related to denitrification.

In addition to all this, it is important to take into account the rest of the applications that BM Respirometry can undertake in order to complete the integral cycle of control, design and research in the biological treatment of wastewater.

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