Study about the treatability of an industrial stream by means advanced BM Respirometry

Emilio Serrano[1]
[1]Respirometry specialist – eserrano@surcis.com

When it is needed to know whether a particular type of industrial stream can be treated biologically, either because it is expected to be incorporated into the global influent of the treatment process or because has to be individually eliminated in a new biological treatment, it is necessary to know its biodegradable character, degree of toxicity or possible inhibition that could cause in the microorganisms of the biomass responsible of its degradation as fundamental parameters.

It is quite possible that the percentage of biodegradability is not sufficient, as it might be the case that a very biodegradable discharge may contain a high percentage of very slowly biodegradable COD giving way to the well known consequences that this can entail.

Likewise, it may be about low BOD/DQO ratio, either because the BOD is really low or also due to a toxic effect that the sample has been generating during the BOD test performance.

In fact, this same toxic effect can be translated to the bCOD/DQO (Biodegradable COD / COD) where, by varying the ratio [sample volume/ sludge volume] in the respirometry tests, there is the possibility to generate different levels of apparent biodegradability degrees, when the reality is that the relatively low values of DQOb are the consequence of a certain degree of toxicity that was being generated during the respirometry tests performance.

Key words:
Biological treatment, respirometry, specific biodegradability to the sludge, toxicity biodegradable COD (bCOD), , endogenous respiration, yield coefficient, respiration rate, COD utilization rate,

1. Introduction

Faced with the problem of reliable analyses to determine the treatability of an industrial stream, BM Respirometry is erected as an important tool when, for a given ratio [sample volume] / [sludge volume] as a first step to the protocol of treatability, is able to determine the degree of its biodegradability, possible toxicity to the microorganisms and the effect that toxicity could make on the specific biodegradability. This not only results in significant time saving, but also the analysis of the combined effect of biodegradability – toxicity.

Once the results of this type of tests have been obtained, when confirmed the presence of toxicity, we can optionally go to a second step in which we could determine the maximum allowed flow to be treated without any toxicity.

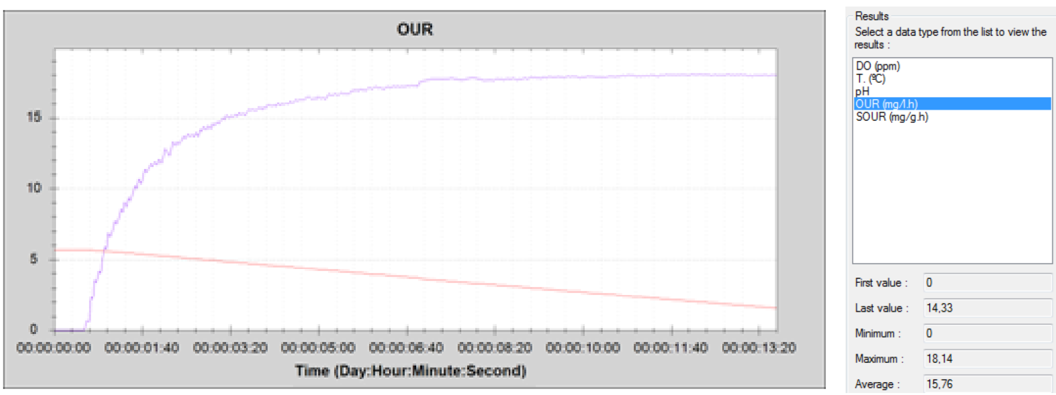
2. Operation modes of a BM respirometer

The BM respirometry systems from Surcis, S.L. (www.surcis.com) include three different operational modes, thus opening up an important range of possibilities to allow a wide range of applications related with the biological wastewater treatment. All operation modes also include programmable automatic temperature control. BM-Advance models also include a programmable pH control.

2.1. OUR mode

The OUR operation mode is a traditional batch respirometry, optimized by a perfect isolation of the atmosphere of the chamber in which the test is running, and with the ability to calculate partial values of OUR & SOUR at different levels of dissolved oxygen.

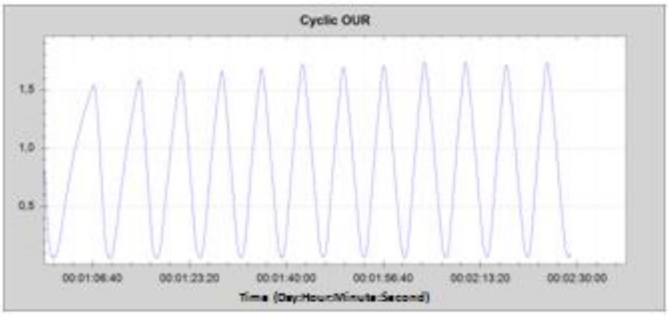
Figure 1. Example of DO and OUR respirograms and result in OUR mode operation



2.2. Cyclic OUR mode

On this mode, the analyzer performs a cyclic chain of OUR & SOUR measurements based on a previously DO threshold within two pre-programmed set-points (high and low) on the test settings board.
Those set-points can be modified during the test performance.

Figura 2. Example of DO respirogram and results in Cyclic OUR mode operation



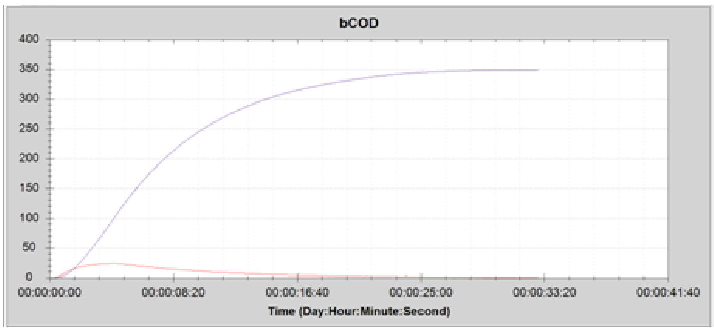
Time	OUR (mg/L.h)	SOUR (mg/g.h)
00:00:53	4,08	2,27
00:00:54	4,67	2,59
00:00:55	4,58	2,54
00:00:56	4,5	2,5
00:00:57	4,42	2,46
00:00:58	4,97	2,76
00:00:59	4,88	2,71
00:01:00	4,8	2,67
00:01:01	4,72	2,62
00:01:02	5,23	2,91
00:01:03	5,14	2,86

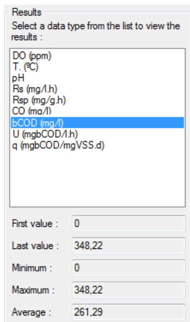
2.3. R mode

It is an optimized respirometry LFS type with recirculation (according to Water Association – IWA classification), where the test is running in liquid phase, on dynamic mode and permanent oxygenation. Generally speaking, the measurement system can be considered as a complete mixed batch system where aeration and recirculation are kept active throughout the test performance.

The R-test in the BM Respirometry normally requires one liter of active sludge under endogenous respiration phase (effluent or recirculation sludge) and a certain amount of sample. Thus, with the automatically controlled temperature and pH conditions, the initial oxygen of the endogenous sludge (baseline) is measured and, once the sample is added, the corresponding dynamic respiration rates (Rs) are continuously measured. Likewise, simultaneously, the BM software integrates the Rs values over time for automatically calculating the consumed oxygen (CO), the biodegradable COD (bCOD) and specific COD utilization rate (q), among others.

Figura 3. Example of bCOD respirogram and result in R mode operaqtion





The BM software is designed to work with small sample volumes with a sample volume/sludge volume ratio could be in between 1/1000 and 100/1000. In this way the test duration is relatively small (1/2 to 3 hours) he selection of the most appropriate ratio is based on the sample COD under the criterion of using a very low ratio when the COD is very high and vice versa.
In any case, the software will apply the corresponding dilution and extrapolation factors to perform the appropriate calculations and give out the correct results.

When the Rs values significantly cross down the baseline (horizontal axis), towards the negative value zone, this means that the endogenous respiration rate has got a significant reduction in its value and thereby detecting that the sample has been causing a toxicity in the active sludge during the test performance.

3. Case of study about the treatability of an industrial stream

This case comes from one of the recent works that the company Surcis has been carrying out within its program of activities related to BM Respirometry.

In this case, the company SIGMA (www.aguasigma.com) requested SURCIS, S.L. to make a study of the treatability of a current with the aim of studying the possibilities of its individual biological treatment in a new treatment plant.

To this end, at the request of Surcis, this company supplied the sample to be studied and an activated sludge with which to perform the respirometry tests.

3.1. Data

Type of industry: manufacture of varnishes
Water with a very high Glycol proportion
Total COD = Soluble COD = 20.045 mg/L
In principle, it is presumed a low BOD/COD ratio (according to data provided by the industry)

3.2. Objectives of the study

The main objectives in the present study are the following:

1. Analysis of the sludge health utilized in the study.
2. Determination of the biodegradable COD (bCOD) at different sample volume/sludge volume ratios.
3. Detection of possible toxicity in the tests of biodegradable COD.
4. Minimum sample volume/sludge volume ratio for a non-toxicity treatment process.
5. Equivalence of the representative respirometry test and a new biological process to establish the calculation basis in absence of toxicity.

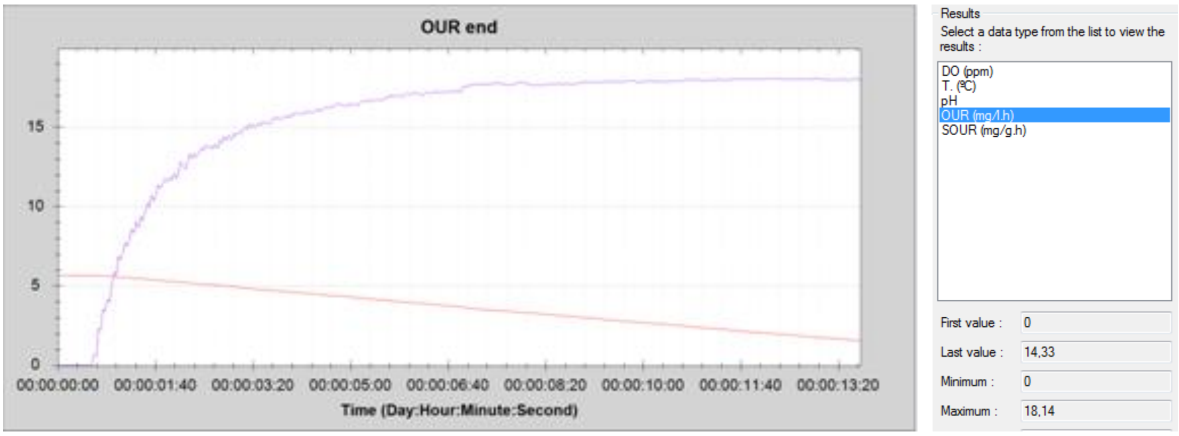
3.3. Respirometry

This study is carried out by means a BM respirometer (BM-Advance model) by means one OUR test and several dynamic R tests, within optimal conditions of dissolved oxygen (> 2,5 ppm), pH (7,7) and Temperature (25 ºC)

3.3.1. Endogenous respiration rate (OUR_{end})

As a first step, the endogenous respiration rate is determined (Figure 4) from the effluent sludge, after having been aerated for a period >12 hours and got a stable activity.

Figure 4. Respirogram and result of endogenous OUR in OUR mode



OUR_{end} = 18 mg O_2/l.h

OUR_{end} value is directly proportional to the active microorganism concentration in the sludge, for that reason it can be taken as a reference in a toxicity assessment.

El valor del OURend es directamente proporcional a la concentración de los microorganismos activos en fango. Por ello, puede tomarse como referencia en una valoración de toxicidad.

3.3.2. Yield coefficient (Y_H)

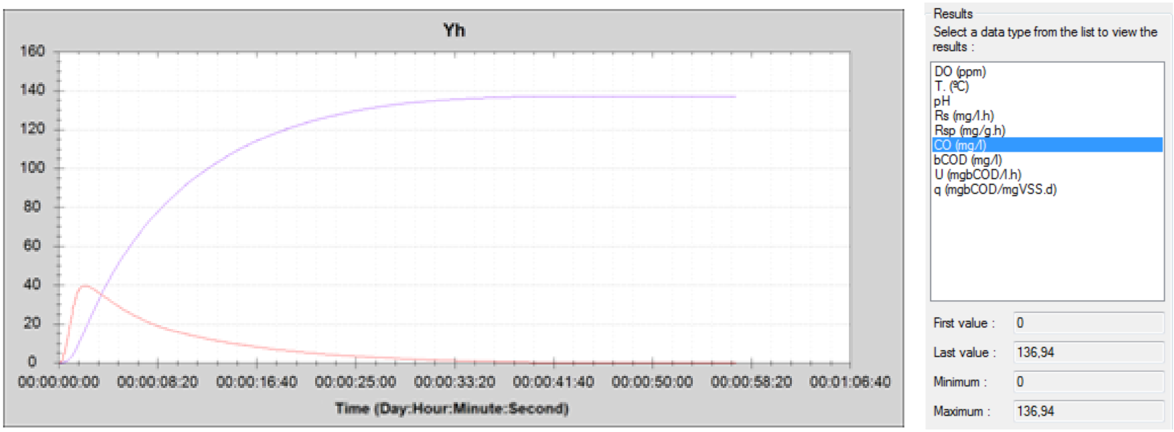
The yield coefficient Y_H is directly related to the heterotrophic biomass growing and it is linked to its biological health.

The Y_H, when expressed in oxygen consumption units, represents the oxygen portion of biodegradable COD intended for biomass reproduction. For this reason, this coefficient becomes part of the mathematical formula of the biodegradable fractions of the COD calculation.

The respirometry test to determine the Y_H is carried out by making use of a R test (Figure 5), where the sample is an organic standard solution (sodium acetate) with an already known COD (COD_{ac})

COD_{ac} = 360 mg/l

Figure 5. Consumed oxygen (CO) respirogram by the organic standard



CO = 136 mg/l

$Y_{H.O2}$ (mg O_2/mg DQO) = 1 – OC / DQO_{ac} (1)

$Y_{H.O2}$= 0,62 mg O_2/mg DQO

<u>Y_H assessment</u>

The value 0.62 that we have obtained as $Y_{H.O2}$ is in the normal range (0.5-0.75) For that reason, we can assume that the biomass growing is normal and that the sludge keeps under normal conditions of activity when a standard non-inhibitory organic substrate is reacting with.

3.3.3. Treatability

The study of treatability is initiated by a biodegradable COD test (DQOb) in order to determine its specific biodegradability (percentage of DQOb in total COD) to the reference sludge

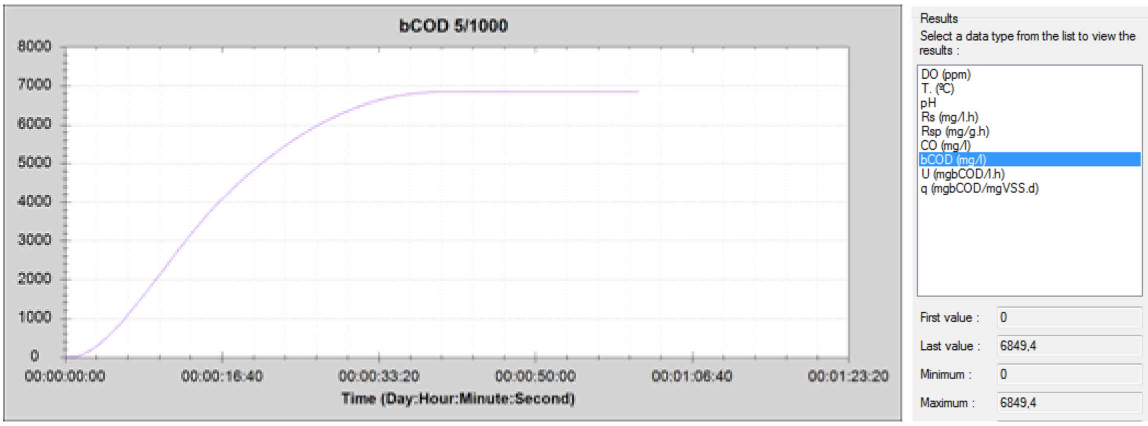
In the event that during this initial test any toxicity to the sludge occurred, some additional tests would be carried out reducing the sample/sludge ratio into a level where the toxicity ceases and thus determine the limit value of volume or flow that the sludge could be treated without any toxicity presence.

3.3.3.1. Biodegradable COD (bCOD) at the sample/sludge ratio volume of 5/1000

Given the relatively high concentration of COD (20,045 mg/l), following the recommendation of the Surcis Applications Guide, the bCOD test is initiated by selecting a sample/sludge volume ratio of 5/1000 (5 ml of sample in 1000 ml of active sludge)

The bCOD value obtained for this sample/sludge ratio (Figure 6) represents the biodegradable fraction to the active sludge.

Figure 6. bCOD respirogram and result



bCOD = 6.849 mg/L

Biodegradability to the sludge: Percentage de bCOD en total COD (%) = 100 * DQOb / DQO (2)
Biodegradability to the sludge ≈ 34 %

bCOD result assessment from the R test at 5/1000 volume ratio

The bCOD and biodegradability to the sludge at the 5/1000 ratio are extremely low. These results lead to consider the possibility of some toxicity presence in the sample and, for this reason, the test will be then analyzed starting from the exogenous respiration rate (Rs) trajectory and its relationship with the endogenous respiration.

3.3.3.2. Toxicity detection in the test at the sample/sludge volume ratio of 5/1000

The toxicity detection and its assessment can be perfectly seen in the Rs respirogram of the bCOD test (Figure 7), where an important toxicity degree is detected when the respiration rate trajectory (Rs) becomes negative (- Rs) and remains there.

Toxicity detection assessment

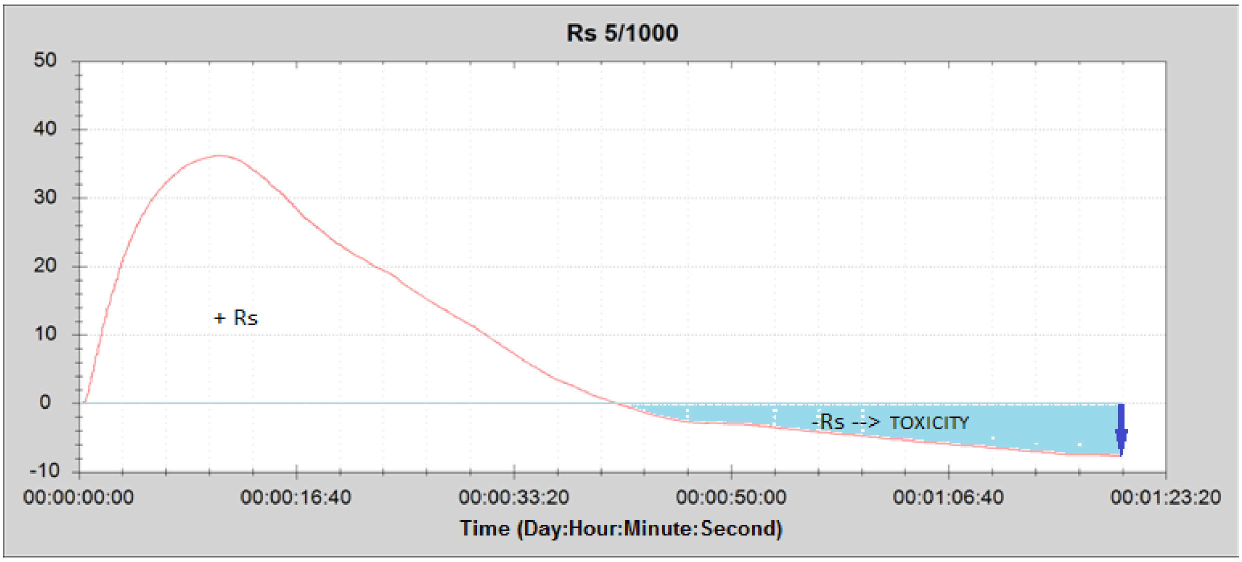
As can be seen in the Rs respirograms (figure 7), the Rs values go below the baseline. For that reason they become negative with a sufficiently representative trend. This means that, during the test performance, there has been a significant drop in the endogenous respiration value which, in R mode represents the baseline.

The toxicity degree is then calculated as follows:

TOX (%) = 100 [1 – (OUR_{end} – Rs negative) / OURend] (3)
TOX = 42 %

It is this level of toxicity that lowers the value of bCOD and its biodegradability value.

Figure 7. Rs values respirogram in the bCOD test



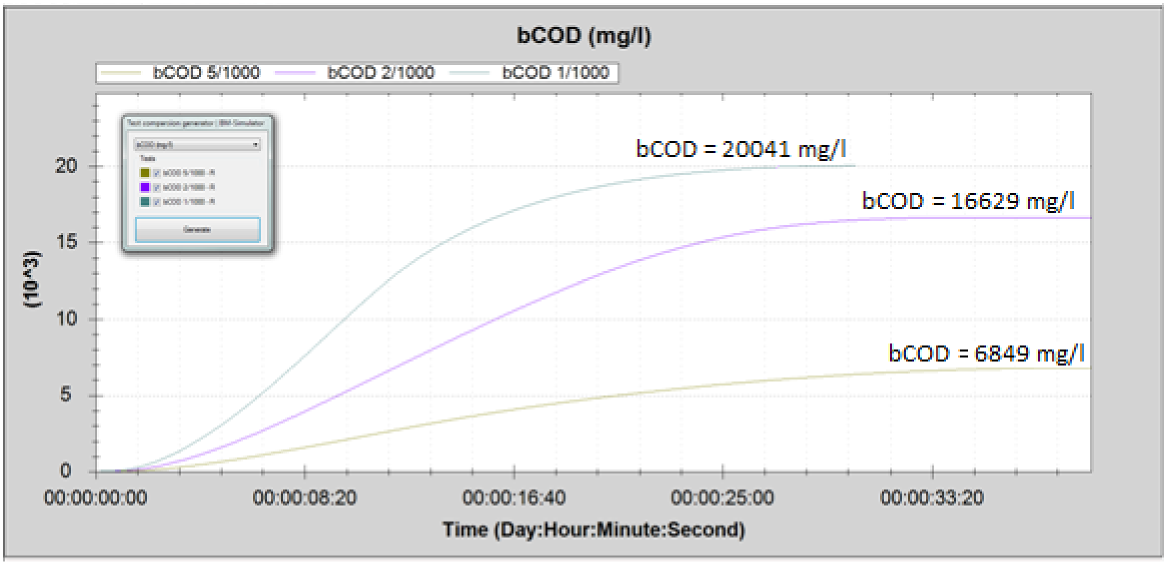
- Rs = Decrement vs endogenous respiration = 7.7 mg O_2/l.h

3.3.3.3. bCOD results from the R test at different sample/sludge volume ratios

Following the established working protocol, in addition to the respirometry test already carried out at the 5/1000 ratio, where a marked toxicity was detected, two additional tests for the 2/1000 and 1/1000 ratios are carried out to analyze the evolution of toxicity to different sample/sludge ratios.

In order to simplify the presentation of the study and perform a comparative analysis of results, we have made use of the option "Test Comparison Generator" of the BM software, to present graphically the results obtained and overlaying the different bCOD respirograms (Figure 8).

Figura 8. Overlying of bCOD respirograms from the tests with different sample/sludge ratios of 1/1000, 2/1000 y 5/1000



From the results obtained in the test we can take as reference those corresponding to the ratio 1/1000 in which a biodegradability of 100% is observed and, therefore, without any symptoms of interfering inhibition in the bCOD value.
With regard to the results obtained with ratios 2/1000 and 5/1000 we can clearly see that, by increasing the sample/sludge ratio, the bCOD value is progressively decreasing and in turn and logically also its biodegradability in the active sludge.

Table.1 bCOD and bCOD/COD values from the R tests at different sample/sludge volume ratios

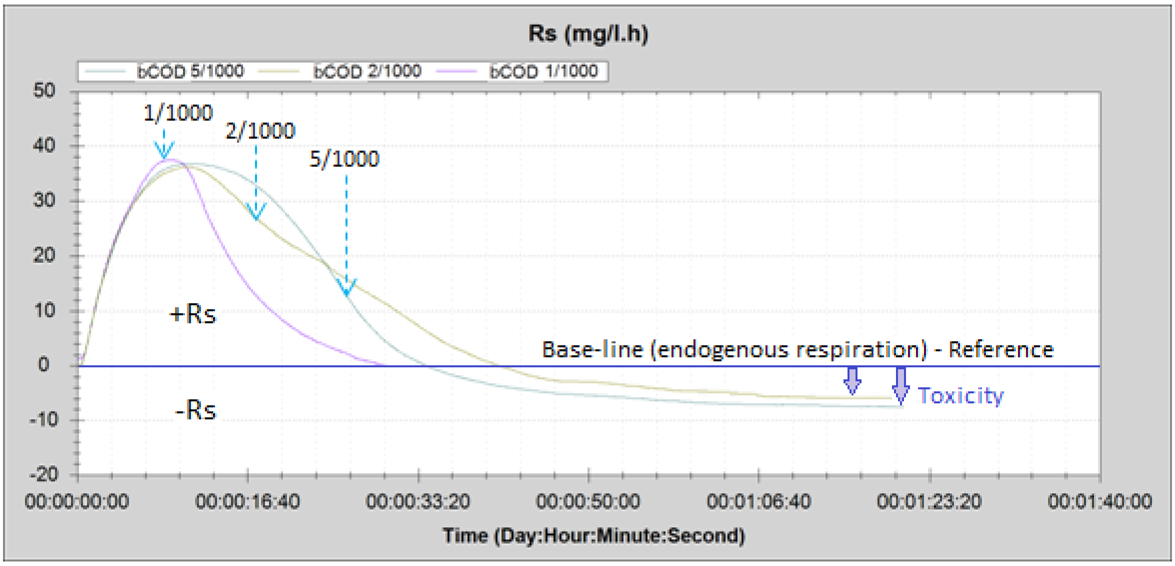
Sample/sludge volumen ratio	bCOD (mg/l)	bCOD/COD
1/1000	20.041	≈ 1
2/1000	16.629	0,83
5/1000	6.849	0,34

For all of this, it becomes clear that a different volume dose of sample in the sludge volume generates an inhibitory effect on the bCOD value, which in all likelihood would be the consequence of a toxicity effect generated in the active biomass of the sludge during the test performance.

3.3.3.4. Exogenous respiration rate (Rs) in the different bCOD tests at different sample/sludge volume ratios with toxicity detection

In order to confirm the presence of toxicity, we resort again to the "Test Comparison Generator" by selecting now the exogenous respiration rate (Rs) and presenting the respirograms overlapping of this parameter (Figure 9)

Figure 9. Rs respirograms overlying for the different sample/sludge ratios in the bCOD tests



Analysis of the Rs results for the different simple/sludge volumen ratios

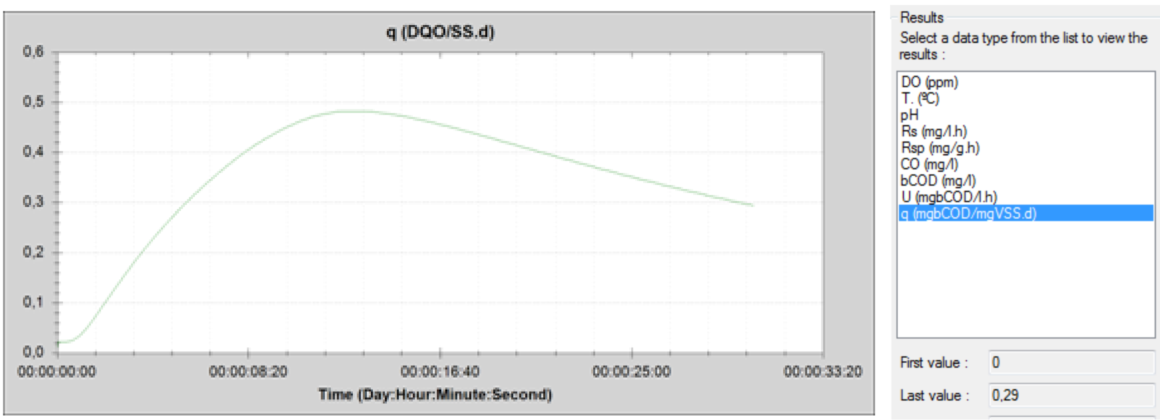
Analyzing the trajectory of Rs respirograms in the tests to different sample/sludge volume ratios we can see that during the tests corresponding to the sample/mud ratios of 5/1000 and 2/1000 the Rs values cross the baseline (breathing endogenous) in the negative zone (-Rs) and therefore significant toxicity detected.

However, for the ratio 1/1000, the Rs values always remain in a positive zone, thus demonstrating a total absence of toxicity. For this reason, we can set the ratio 1/1000 as the safety limit value for future design calculations.

3.4. Equivalence of the R test at 1/1000 volume ratio with a new process to treat the industrial stream

The equivalence for a new biological process to treat the industrial stream can be driven from the value of the DQOb utilization rate (q) that the BM software calculates automatically and simultaneously to the bCOD, Rs among others.

Figura 10. Respirograma de la tasa de utilización de la DQOb en el ensayo de relación muestra/fango de 1/1000



LMSS = 3500 mg/l

q = 0,29 COD / (MLSS/d)

Given the fact that the value of the COD is practically the same as bCOD, we can assume that the value of q is maximum COD loading rate value for a new process to treat the industrial current, for 100% performance and total absence of toxicity.

q ≈ CM ≈ 0,29 kgDQO/kgMLSS/d

This mode of calculation is not intended to figure out a definitive value but rather to establish a coherent basis for calculation. In this way, may be the definitive process design could also go to achieve a slightly lower than 100% performance, but quite enough to get the permitted levels of the required quality in the final effluent.

3.5. Global summary

- The assessment of the Y_H, along with the endogenous respiration rate (OUR_{end}) values, gives way to the suitability of the reference sludge for the study development.

- By means the R test with a sample/sludge ratio of 1/1000, it is determined that the industrial stream can be 100 % biodegradable.

- From the results of respirometry and the fact that the total COD is the same as the soluble, it is assumed that there is no differentiation between total biodegradable COD (bCOD) and readily biodegradable COD (rbCOD) fractions.

- The values of the bCOD/COD ratio in the sample/sludge ratio assays of 2/1000 and 5/1000 are significantly reduced from that obtained with the 1/1000 ratio due to the inhibition of the bCOD value caused by the sample during the tests performance.

- A significant degree of toxicity (>40%) appears during the test for sample/sludge volume ratios of 2/1000 and 5/1000, not shown in the 1/100 volume ratio test.

- Although in the test for 2/1000 volume ratio the bCOD/COD ratio is 0.83 (which could be apparently considered as permissible), it would not be however advisable to use the results from this test for a new process design since the detected toxicity could be cumulative over time.

- The results obtained from the evolution of the respiration rate (Rs) are leading us to set the sample/sludge volumes ratio of 1/1000 as safety limit value, on which we can ensure the complete bCOD elimination within total absence of toxicity.

- By fixing the 1/1000 sample/sludge as a safety ratio, the results obtained from the test on this ratio can be established to design a new process. In this way, under optimal pH, temperature and oxygen conditions, it will able to get a completely bCOD removal in the absence of Toxicity.

- This study further could demonstrate that the presumed data of low BOD/COD ratio is not due to low biodegradability but rather to the presence of toxicity that likely had significantly reduced the BOD value during the test performance.

Additional comment

The results obtained refer to the reaction of the sample with the reference active sludge in its current state. However, there is a possibility that this type of industrial sample during a certain period of sludge acclimatization might improve its level of treatability.

3.6. Conclusions

- In this study it is demonstrated that BM Respirometry, having regard the wide possibilities of the software, enables studies related to the treatability within relatively short time and for reliable results.

- In the case of the study at issue it is shown that, depending on the sample/sludge volume ratio used, there may be a manifest decrease in the biodegradability due to certain degree of toxicity that it is progressively generated during the bCOD test performance.

- The toxicity presence in only one or two test at different sample/sludge volume ratio was not enough reason to exclude the possibility for a new aerobic treatment process since, as decreasing the sample/sludge volume ratio in the different bCOD tests, it was found there is a certain ratio in which the toxicity disappears completely and the biodegradability degree becomes 100 %. Consequently, the results from this test could be used to establish the calculation basis for a new aerobic process to treat the industrial stream.

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