

Study on the treatability of a new polymer stream in the wastewater treatment plant of REPSOL Puertollano refinery (Spain)

Introduction to BM respirometry

The use of the BM advanced respirometry system enables the user to get the precise calculation of the operating parameters and limit set points that any activated sludge actually needs within the framework of an energy optimization. For that reason, the proper use of this respirometry is more than justified; and not only because of getting the parameters for a good process performance, but also to keep a healthy biomass and prevent possible potential problems.

However, because of the wide range of applications and possibilities that BM respirometry can offer, it is critical to get a protocol that can be adapted to any specific process and carried out by the plant operator within his available timeframe.

For this protocol here explained we can use any of the BM respirometers, but in case the pH could play a critical role in its performance, it would be recommended the model BM-Advance which includes an automatic pH monitoring and control system.



BM-Advance respirometry system

The BM respirometer can be programmed with three different operation modes (OUR, Cyclic OUR and R) and can be set for different conditions of DO, Temperature, pH, sample volumes. Those conditions can be changed during the test performance. All simultaneous measurements can be displayed on tabular or graphic mode during the test and respirograms can be overlaid. The R test, since we can use small amount of wastewater sample, the tests can be run in very short term.

Parameters measured in BM respirometry:

OUR (mgO ₂ /L.h)	Oxygen Uptake Rate.
SOUR (mgO ₂ /gVSS.h)	Specific OUR - by introducing the MLVSS concentration -
Rs (mgO ₂ /L.h)	Dynamic Respiration Rate.
Rsp (mgO ₂ /gVSS.h)	Specific Rs - by introducing the MLVSS concentration -
CO (mg/L)	Consumed Oxygen
bcOD & rbCOD (mg/L)	Biodegradable & Readily biodegradable COD – by introducing Y _H –
U (mg COD/L.h)	COD utilization rate
q (COD/SS.d)	Specific COD utilization rate

1. Study

This study comprised part of a Respirometry training course given to operators responsible for the wastewater treatment plant in REPSOL Puertollano refinery.

The plant operator informed us that it was forecasted to include a new polymer PQ stream to the influent of the treatment plant and wanted to know its treatability in terms of toxicity degree, biodegradability, and maximum permitted flow and COD loading to be treated.

Therefore, the main objectives of the study were:

1. Determine the maximum polymer PQ stream addition rate into the influent without provoking a significant inhibition in the activated sludge process.
2. Analyze the biodegradability of this polymer PQ in terms of biodegradable COD / total COD ratio.
3. Calculate de maximum permitted flow of the polymer PQ in the total influent to the biological reactor
4. Calculate de maximum permitted COD loading of the polymer PQ.

2. Main Polymer PQ and ASP data

Polymer COD: $COD_{PQ} = 1190 \text{ mg/L}$

Biological reactor = 4 lanes of 3000 m^3 each, connected in parallel

Average influent: $Q_i = 1000 \text{ m}^3/\text{h}$

RAS flow: $Q_{RAS} = 750 \text{ m}^3/\text{h}$

MLVSS = 3000 mg/L

HRT = 7 hours



One of the lanes of the biological reactor

4. General procedure

1. We perform a dynamic R test in the respirometer.

We start the test by fixing the base-line from the DO value of the endogenous returned sludge (RAS).

2. Once we have got the DO base-line, we add a controlled high dose of a standard substrate (sodium acetate) to reach its specific saturation and create an initial respiration rate.
3. Then, we are adding consecutive doses of the stream aliquot of compound in the respirometer reactor until reaching the break point where the exogenous respiration rate chain (R_s) starts significantly to drop as a clear sign of toxicity.
4. By summing the total volume of aliquot doses we have added, we determine the maximum [sample volume] / [RAS volume] ratio where the toxicity starts to be present.
5. Assuming that [aliquot volume] / [RAS volume] in the BM respirometer reactor = [stream flow in influent] / [RAS flow], we can calculate the maximum permitted flow before reaching a toxicity.
6. Now we perform another R test to get the corresponding biodegradable COD (bCOD)
7. The bCOD/COD ratio will figure out the specific biodegradability (%)
8. Then, with the bCOD/COD and permitted flow we can calculate the corresponding maximum permitted COD loading.

5. Points of the study

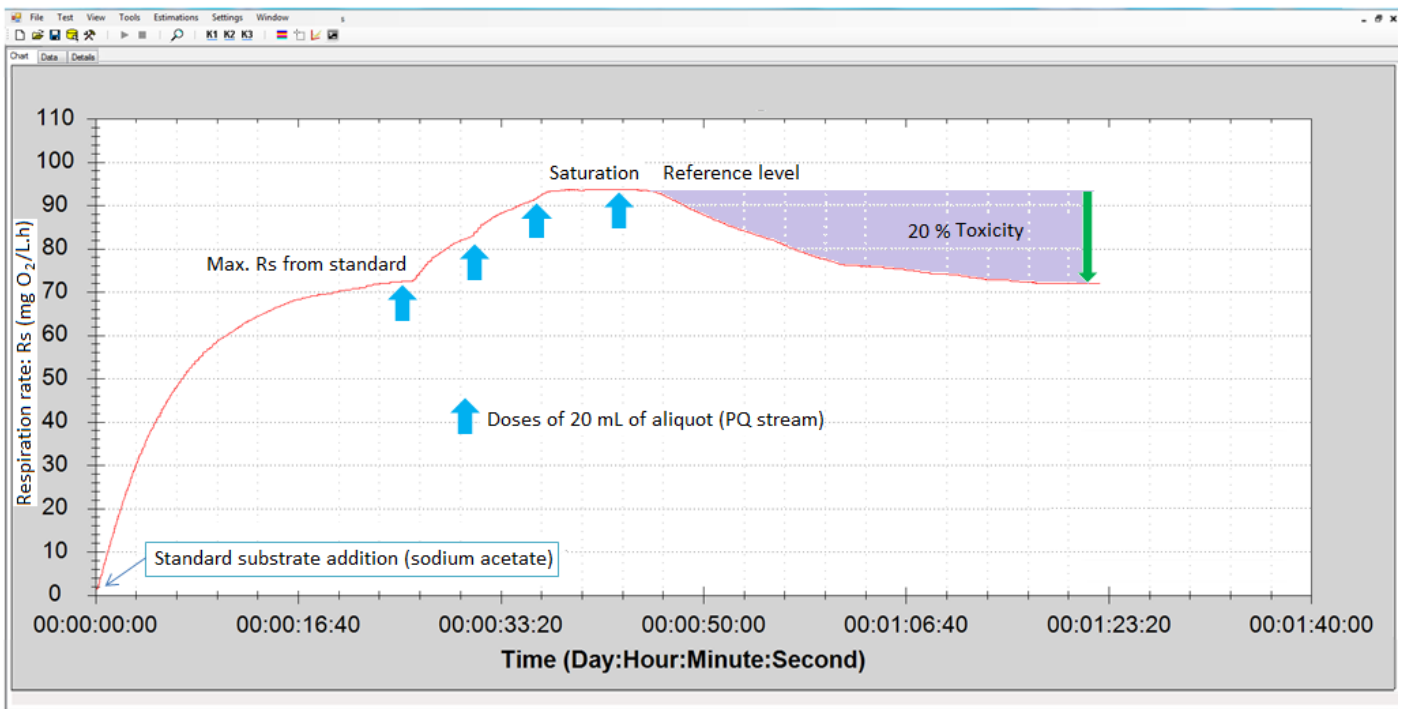
The following important parameters and procedures were carried out:

1. Dynamic Toxicity of the polymer PQ in the activated sludge
2. Maximum permitted flow of the polymer PQ stream and COD loading in the ASP influent.
3. Heterotrophic yield coefficient.
4. Polymer biodegradability referred to specific activated sludge process and COD_{PQ} fractions
5. Percentage of polymer COD that could be removed within the available hydraulic retention time.
6. Summary of the main results
7. Conclusions

5.1. Toxicity

With BM respirometer it is possible to determine an equivalent toxicity using different methods.

For this specific study we were carrying out a method based on the addition of consecutive doses of sample in the activated sludge of the respirometer reactor which was previously conducted to a maximum respiration rate level by means the addition of one standard substrate in excess.



Rs respirogram for Toxicity

We could observe that, once we have started adding the 20 ml polymer doses, there was any toxic effect until the 4th dose (80 ml) and, just by adding the 5th dose (100 ml), the respiration rate (Rs) started to decrease until certain level which represented a 20 % toxicity

5.2. Maximum permitted polymer PQ flow and COD loading in the influent to biological reactor

Taking into account that the flows ratio is equivalent to the volumes ratio, we can assume the following:

$$V_{PQ,max} / V_{RAS} = Q_{PQ,max} / Q_{RAS}$$

$V_{PQ,max}$: Total added PQ volume in the respirometer reactor until toxicity = 4 doses * 20 = 80 mL

V_{RAS} : Volume of endogenous RAS in the respirometer = 1000 mL

Q_{RAS} : Actual RAS flow in the ASP = 750 m³/h

$Q_{PQ,max}$: Maximum permitted PQ stream in the influent to ASP

$$Q_{PQ,max} = Q_{RAS} * V_{PQ,max} / V_{RAS}$$

$$V_{PQ,max} / V_{RAS} = 80 / 1000 = 0,08 \rightarrow 8\%$$

Therefore, the maximum permitted flow of the PQ stream will be calculated as follows:

$$Q_{PQ,max} = 0,08 * Q_{RAS} = 0,08 * 750 = 60 \text{ m}^3/\text{h}$$

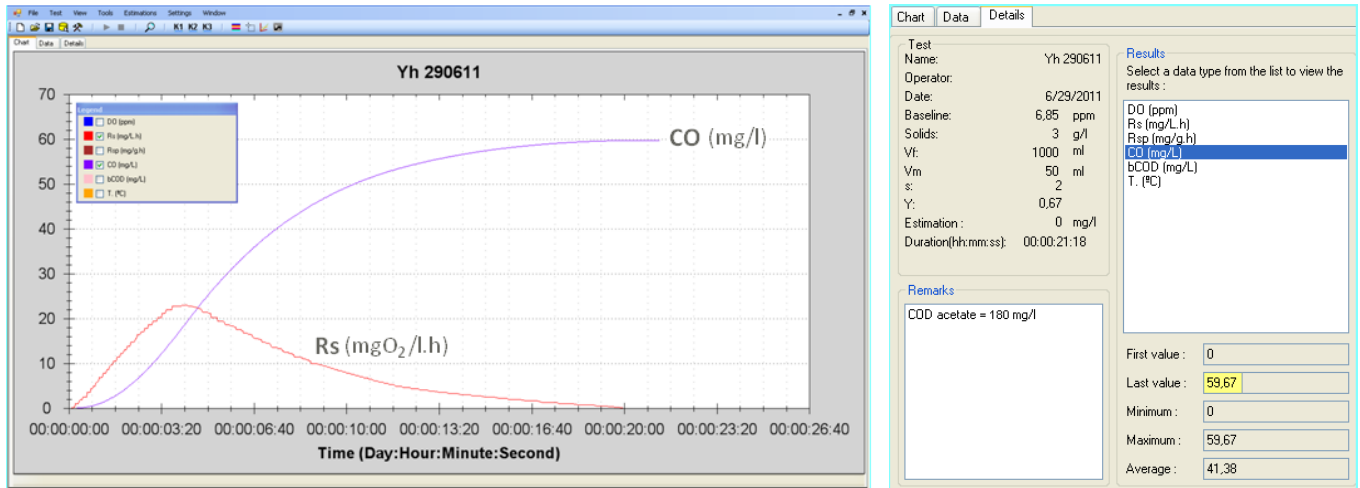
Once we know the maximum permitted flow, we can then calculate the corresponding COD loading

$$DQO_{PQ} \text{ loading} = Q_{PQ,max} * COD_{PQ} = 60 * 1190 = 71400 \text{ kg DQO/h}$$

5.3. Y_H determination

The Y_H is also determined by means a R test by making use of a solution of sodium acetate of known COD (180 mg/l). In this test, we start fixing the DO base line from the 1 litre of endogenous RAS in the reactor vessel of the respirometer and then adding a known volume of sodium acetate solution sample.

In the test configuration the yield coefficient (Y_H) should be introduced in the test configuration in order the software to automatically determine the corresponding biodegradable COD (bCOD).



Rs & CO respirograms for Y_H

The R test perform a continuous chain of R_s measurements from which the BM software will automatically determine the corresponding accumulated consumed oxygen (CO) over the time. Then, with the COD of the sodium acetate solution (COD_{ac}), we calculate the corresponding Y_H (CO/COD)

$$Y_H = 1 - CO / COD_{ac}; \quad Y_H = 1 - 59.67 / 180 = 0.67$$

$$Y_H = 0.67 \text{ (CO/COD)}$$

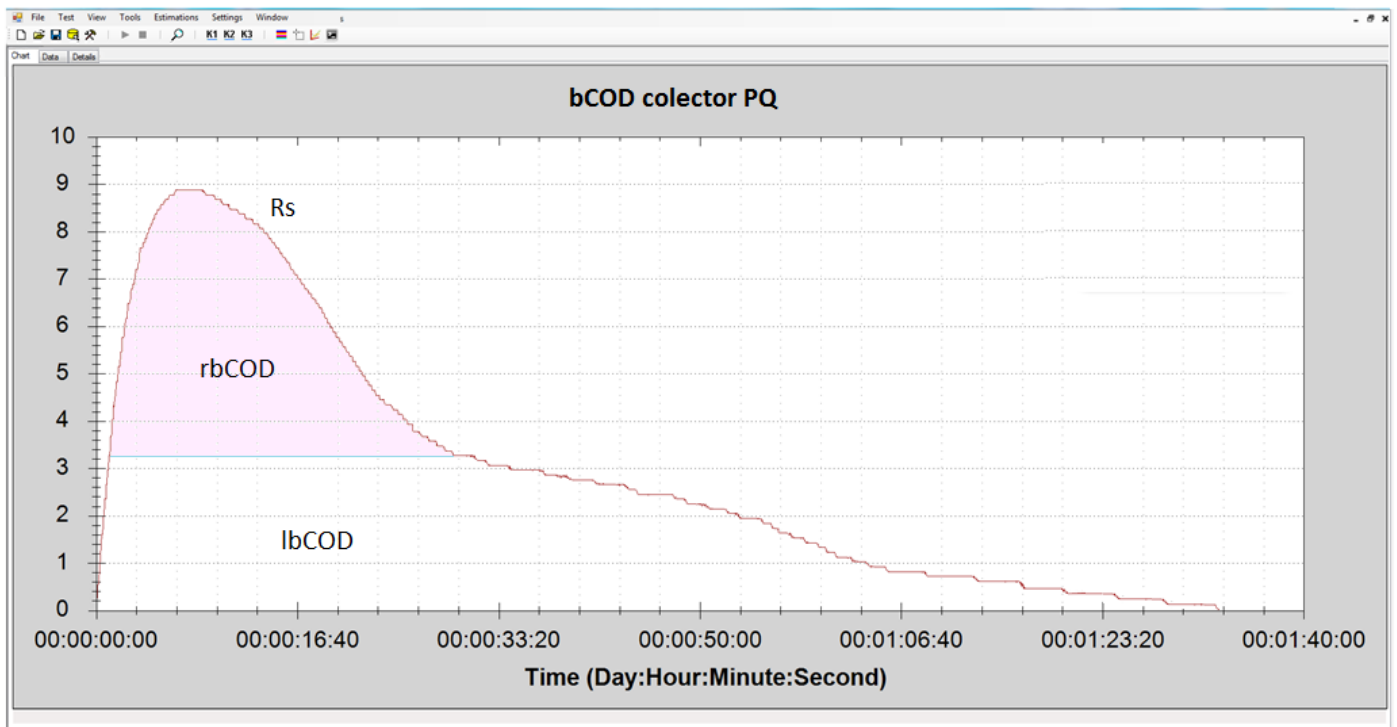
5.4. Polymer biodegradability referred to the specific activated sludge of the plant and COD_{PQ} fractions

We understand biodegradability (%) to the specific activated sludge the % of the total biodegradable COD (bCOD) in its total COD (COD)

We already know the COD of the polymer (1190 mg/L), and by means one dynamic R test we get the bCOD (888 mg/l) in the BM-EVO respirometer.

For that, we start fixing the DO base line from the 1 litre of endogenous RAS in the reactor vessel of the respirometer and then adding a known volume of polymer sample.

The BM software automatically determines the value of bCOD [$bCOD = CO / (1 - Y_H)$] and also U, q simultaneously



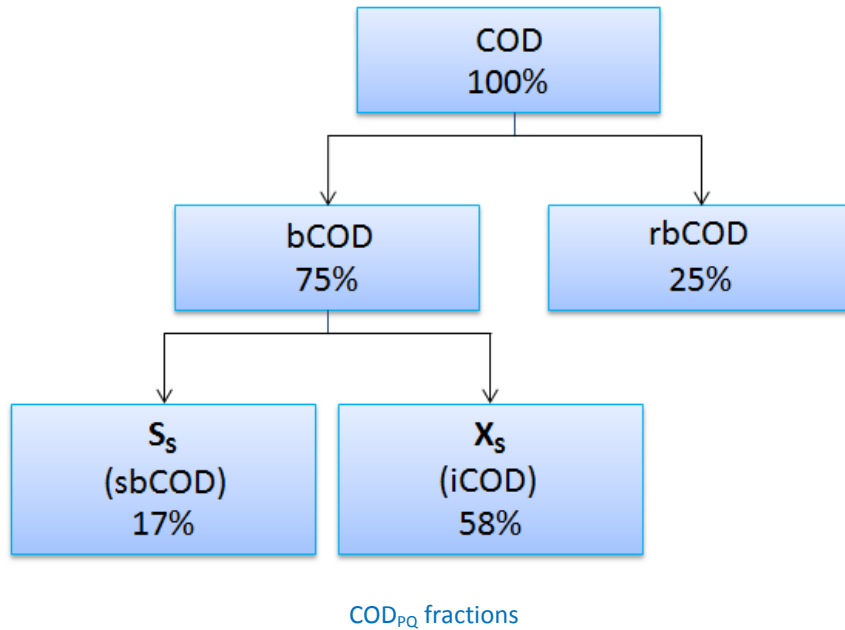
Rs respirogram for bCOD

Test	Results	Results
Name: DBOb Colector PQ	Select a data type from the list to view the results :	Select a data type from the list to view the results :
Operator:	DO (ppm)	DO (ppm)
Date: 6/29/2011	T. (°C)	T. (°C)
Baseline: 6.58 ppm	Rs (mg/l/h)	Rs (mg/l/h)
Solids: 3 g/l	Rsp (mg/g.h)	Rsp (mg/g.h)
Vf: 1000 ml	CO (mg/l)	CO (mg/l)
Vm: 50 ml	bCOD (mg/l)	bCOD (mg/l)
s: 1	U (mgbCOD/l.h)	U (mgbCOD/l.h)
Y: 0.67	q (mgbCOD/mgVSS.d)	q (mgbCOD/mgVSS.d)
Estimation: 0 mg/l		
Duration(hh:mm:ss): 00:01:23:18		
Remarks	First value : 0	First value : 0
1000 ml fango recirculación aireado	Last value : 887,96	Last value : 30,13
50 ml muestra efluente Colector	Minimum : 0	Minimum : 0
Petroquímica (1.190 mg/l de DQO)	Maximum : 887,96	Maximum : 70,11
	Average : 625,13	Average : 62,16

bCOD and U results from the R test

With these results we can make up the percentage of the COD fractions in COD_{PQ} :

- Biodegradable COD_{PQ} ($bCOD_{PQ}$) = 888 mg/L \rightarrow 75 % COD_{PQ}
- Readily biodegradable COD_{PQ} ($rbCOD_{PQ}$) \rightarrow 17% COD_{PQ}
- Slowly biodegradable COD_{PQ} : $sbCOD = [bCOD_{PQ} - rbCOD_{PQ}] \rightarrow$ 58% COD_{PQ}
- Inert COD_{PQ} : $iCOD_{PQ} = [COD_{PQ} - bCOD_{PQ}] \rightarrow$ 25% COD_{PQ}



5.5. Percentage of the polymer COD that can be removed within the available hydraulic retention time of the process

From U average we obtain the average time (T_{PQ}) for a complete degradation of the polymer:

$$T_{PQ} = \text{bCOD}_{PQ} / U \text{ average} = 888 / 30 = 29.6 \text{ horas}$$

Since the HRT of the process is 7 hours and the required T_{PQ} is 29.6 hours, we will get now the ability to calculate the maximum percentage of bCOD_{PQ} (E_{PQ}) that could be eliminated:

$$E_{PQ} = 100 * 7 / 29.6 \approx 24 \%$$

6. Summary of the main results

Parameter	Description	Value
Q_{PQ_max}	Maximum permissible flow to be treated without reaching any toxic level.	$8\% * Q_r$ = 60 m ³ /h
Biodegradability	$100 * \text{bCOD}_{PQ} / \text{DQO}_{PQ}$	75 %
T_{PQ}	Necessary time for a complete degradation of the bCOD_{PQ}	29,6 horas
E_{PQ}	Maximum percentage of bCOD_{PQ} (E_{PQ}) that could be eliminated in the biological treatment	24%

7. Conclusions

1. The toxic effect of polymer PQ is manifested in the actual activated sludge for a flow equal to or greater than 8% of the recirculation activated sludge (RAS) flow.
2. When the flow rate falls below 8% of the RAS flow, the s PQ polymer has a specific biodegradability of 75%
3. By keeping the current concentration of MLVSS and conditions, the hydraulic time necessary for the complete degradation of the polymer PQ is 29.6 hours.
4. Since only the current process has got a HRT of 7 hours, only 24% of the polymer PQ could be removed.

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