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The Ultimate BOD

A much better nickname

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Example of a BOD determination

200 mL of waste water was collected, aerated and seeded with bacteria. The dissolved oxygen content was 7.6 mg/L initially. After 5 days, the dissolved oxygen content had dropped to 2.8 mg/L. What is the BOD₅ and the ultimate BOD?

(Note: The [dissolved O₂] would be determined by the Winkler Method or another of the O₂ titrations already discussed.)

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The BOD₅

7.6 mg/L – 2.8 mg/L = 4.8 mg/L

BOD₅ = 4.8 mg/L

How do we get the ultimate BOD from that?

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It's all about the kinetic model

BOD reactions have "1st order kinetics"

"1st order kinetics" refers to the dependence on concentration

$$\text{Rate} = -\frac{\Delta[\text{react}]}{\Delta\text{time}} = \frac{\Delta[\text{prod}]}{\Delta\text{time}} = k[\text{react}]^1$$

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The Rate Law

$$\text{Rate} = -\frac{\Delta[\text{react}]}{\Delta\text{time}} = \frac{\Delta[\text{prod}]}{\Delta\text{time}} = k[\text{react}]^1$$

What's that funky "k"?

k is called the "rate constant", it's the only thing that is constant in this kinetic scheme.

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A word about k

The "rate constant", k :

- Depends on the reaction
- Depends on the type of bacteria (in the case of BOD)
- Depends on the temperature

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The Rate Law

$$\text{Rate} = - \frac{\Delta[\text{react}]}{\Delta\text{time}} = \frac{\Delta[\text{prod}]}{\Delta\text{time}} = k [\text{react}]^1$$

Which reactant?
To do this test, you need O₂, organic waste,
and bacteria.

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**A Man's Got to Eat –
and so do bacteria**

$$- \frac{\Delta[\text{Organic waste}]}{\Delta\text{time}} = k [\text{Organic waste}]^1$$

This gives the rate at any time based on the
amount of waste left and the "rate constant",
k.

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But I thought this was a test for O₂?

Well, it's not and get over it!

Actually, we test for O₂, but only so that we
know the [organic waste]

If we're going to test for O₂, we need to rewrite
the rate law in terms of the [O₂] rather than
the [organic waste].

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Reformulating the Rate Law

Rate = $-\frac{\Delta[\text{Organic}]}{\Delta\text{time}} = k [\text{Organic}]^1$

How would we change this to reflect O₂?

What are the Rules?
Units! Units! Units!
(probably not that helpful here)
Moles! Moles! Moles!

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It's all relative....

A + 2 B = 3 C

If [A] changes by 1 mole, [B] changes by 2 moles.

If [Organic Waste] changes by a certain amount, there is a stoichiometrically equivalent amount of **oxygen demanded** by the bacteria to make the change.

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Equivalence

$-\frac{\Delta[\text{Organic waste}]}{\Delta\text{time}} = k [\text{Organic waste}]^1$

$-X \frac{\Delta[\text{O}_2]}{\Delta\text{time}} = k [\text{O}_2]$

What's "X"?
It's the stoichiometry

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Equivalence

- $\frac{-\Delta[\text{O}_2]}{\Delta\text{time}} = k [\text{O}_2]$
- Δtime

Or

- $\frac{\Delta[\text{O}_2]}{\Delta\text{time}} = k' [\text{O}_2]$
- Δtime

Where k' contains the stoichiometry difference!

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IT'S NOT REAL OXYGEN!

Remember, "oxygen demand" isn't the oxygen there, it's the oxygen used up to get there!

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A Kinetic Model based on O₂

- $\frac{\Delta\text{O}_2}{\Delta\text{time}} = k' \text{O}_2$
- Δtime

So what? (you might be asking)

So, you can now use oxygen used as a measure of organic waste that must be there.

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BUT FIRST....
.....A QUESTION!

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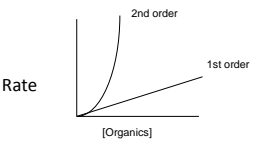
Is the assumption good?
We've "assumed" that the kinetics are 1st order and depend only on the concentration of organics. This, of course, is an informed decision by environmental scientists.
Is it a good assumption?

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It really doesn't matter!
Suppose the decay is really 2nd order...
What would that mean?
Rate = $-\frac{\Delta [\text{Organics}]}{\Delta \text{time}} = k [\text{Organics}]^2$
And so...

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Decay rate of the decay rate is faster

$$\text{Rate} = - \frac{\Delta [\text{Organics}]}{\Delta \text{time}} = k [\text{Organics}]^2$$


The graph plots Rate on the y-axis and [Organics] on the x-axis. Two curves originate from the origin: a straight line labeled '1st order' and a curve that curves upwards labeled '2nd order'.

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What does this mean for [Org]?

$$- \frac{\Delta [\text{Organics}]}{\Delta \text{time}} = k [\text{Organics}]^2$$
$$- \frac{\Delta [\text{Organics}]}{\Delta \text{time}} = k [\text{Organic waste}]^1$$

We can calculate the [Organics] at any time by determining the "Integrated Rate Law"

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What does this mean for [Org]?

$$- \frac{\Delta [\text{Organics}]}{[\text{Organics}]^2} = k \Delta \text{time}$$
$$- \frac{\Delta [\text{Organics}]}{[\text{Organics}]^1} = k \Delta \text{time}$$

If you assume that the difference in infinitesimal, it's a differential equation.

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Anybody know how to do this?

$$-\frac{\Delta [\text{Organics}]}{[\text{Organics}]^2} = k \Delta \text{time}$$

$$-\frac{\Delta [\text{Organics}]}{[\text{Organics}]^2} = k \Delta \text{time}$$

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The Integrated 2nd Order Rate Law

$$-\frac{\Delta [\text{Organics}]}{[\text{Organics}]^2} = k \Delta \text{time}$$

$$\int_{[\text{Org}]_i}^{[\text{Org}]_f} \frac{d[\text{Organics}]}{[\text{Organics}]^2} = k \int_0^t d \text{time}$$

$$\frac{1}{[\text{Org}]_f} - \frac{1}{[\text{Org}]_i} = [kt - k(0)] = kt$$

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The Integrated 1st Order Rate Law

$$-\frac{\Delta [\text{Organics}]}{[\text{Organics}]^1} = k \Delta \text{time}$$

$$\int_{[\text{Org}]_i}^{[\text{Org}]_f} \frac{d[\text{Organics}]}{[\text{Organics}]} = -k \int_0^t d \text{time}$$

$$\ln [\text{Org}]_f - \ln [\text{Org}]_i = -kt$$

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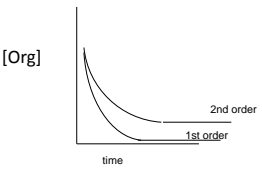
The Integrated Rate Laws

$$\frac{1}{[\text{Org}]_f} - \frac{1}{[\text{Org}]_i} = kt$$
$$\ln [\text{Org}]_f - \ln [\text{Org}]_i = -kt$$

These give you the concentration of organic waste (or corresponding oxygen demand) at any time!

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If you plot them...



[Org]

time

2nd order

1st order

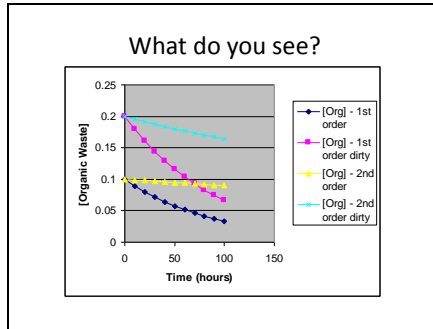
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So what?

The original question was: Was 1st order kinetics a good assumption?

How does this help us answer that?

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It just doesn't matter...

At any given point in the curve, the dirtier sample "looks dirtier" - it shows a higher [Organics] or higher Oxygen Demand.

It takes more or less time to get to [Organics] = 0, but this is only an issue if you really need to know how long it takes.

Bigger BOD, dirtier water. PERIOD!
(and since we choose the bacteria, we have some control)

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The Integrated Rate Law

$\ln [Org]_t - \ln [Org]_{t=0} = -kt$

$\ln [O_2]_t - \ln [O_2]_{t=0} = -kt$

$\ln \{ [O_2]_t / [O_2]_{t=0} \} = -kt$

Keep in mind, $[O_2]_{t=0}$ is the BOD - the theoretical amount of Oxygen required to achieve complete biochemical degradation of the organic waste.

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The Integrated Rate Law

$\ln \{ [O_2]_t / [O_2]_{t=0} \} = -kt$

You can also refer to "BOD exerted" – which is how much of the total BOD has been used:
 $BODE = [O_2]_{t=0} - [O_2]_t$

This is the number that gets measured, since in the end we can't measure "theoretical oxygen required", only the actual oxygen used.

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The Integrated Rate Law

$\ln \{ [O_2]_t / [O_2]_{t=0} \} = -kt$
or
 $[O_2]_t / [O_2]_{t=0} = e^{-kt}$

$BODE = [O_2]_{t=0} - [O_2]_t = [O_2]_{t=0} (1 - e^{-kt})$
 $BODE = [O_2]_0 (1 - e^{-kt}) = BOD (1 - e^{-kt})$

Do I need to know k?

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You could calculate it

If you have more than 1 measurement of O_2 concentration - then you could calculate it.

The standard value is usually taken to be 0.23 day^{-1} in the absence of an independent determination of it.

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Ultimate BOD

If you determine the BOD after 5 days, this is called "the 5 day BOD" (BOD_5). If you determine the BOD after 20 days, this is called "the 20 day BOD" (BOD_{20}). These are really BOD exerted values.

The "ultimate BOD" is the amount of oxygen required to decompose all of the organic material after "infinite time". This is usually simply calculated from the 5 or 20 day data. (Who can wait for infinity?)

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Example of a BOD determination

200 mL of waste water was collected, aerated and seeded with bacteria. The dissolved oxygen content was 7.6 mg/L initially. After 5 days, the dissolved oxygen content had dropped to 2.8 mg/L. What is the BOD_5 and the ultimate BOD?

(Note: The [dissolved O_2] would be determined by the Winkler Method or another of the O_2 titrations already discussed.)

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The BOD_5

$7.6 \text{ mg/L} - 2.8 \text{ mg/L} = 4.8 \text{ mg/L}$

$BOD_5 = 4.8 \text{ mg/L}$

How do we get the ultimate BOD from that?

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We assume the model & the k

$k = 0.23 \text{ day}^{-1}$

$\text{BOD}_5 = \text{BOD} (1 - e^{-kt})$

$4.8 \text{ mg/L} = \text{BOD} (1 - e^{-(0.23 \text{ day}^{-1})(5 \text{ days})})$

$4.8 \text{ mg/L} = \text{BOD} (1 - 0.3166) = \text{BOD} (0.6833)$

Ultimate BOD = 7.02 mg/L

What does this number mean?

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It's pretty clean water

7.02 mg/L is quite clean.

To compare, a solution of 300 mg/L of glucose has an ultimate BOD of 320 mg/L – and that water is barely sweet.

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Limitations?

1. Non-biodegradable organic waste is unaccounted for.
2. Very dirty water will use up all dissolved oxygen before the 5 days is over.
3. Other aerobic activity (biological or just chemical) is counted.

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Solutions?

1. You could try a different mix of bacteria. Or you can determine the COD and compare it.
2. Dilution is your friend!

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Determining BOD in a very dirty sample.

200 mL of waste water was collected, aerated and seeded with bacteria. The dissolved oxygen content was 6.9 mg/L initially. After 5 days, the dissolved oxygen content had dropped to 0 mg/L. A second test was run using a 2 mL sample of waste water diluted to 200 mL and aerated and seeded. The dissolved oxygen content was 7.6 mg/L initially. After 5 days, the dissolved oxygen content had dropped to 4.3 mg/L. What is the BOD_5 and the ultimate BOD?

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The Solution

$7.6 \text{ mg/L} - 4.3 \text{ mg/L} = 3.3 \text{ mg/L}$

? $BOD_5 = 3.3 \text{ mg/L}$?

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The Solution

$7.6 \text{ mg/L} - 4.3 \text{ mg/L} = 3.3 \text{ mg/L}$

$\text{BOD}_5 = \frac{3.3 \text{ mg/L}}{2 \text{ mL}/200 \text{ mL}} = 330 \text{ mg/L}$

Another way to look at this:
 $\frac{3.3 \text{ mg}}{\text{L diluted waste}} * \frac{.200 \text{ L diluted waste}}{.002 \text{ L original sample}}$

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Ultimate BOD calculation

$k = 0.23 \text{ day}^{-1}$

$\text{BOD}_5 = \text{BOD} (1 - e^{-kt})$

$330 \text{ mg/L} = \text{BOD} (1 - e^{-(0.23 \text{ day}^{-1})(5 \text{ days})})$

$330 \text{ mg/L} = \text{BOD} (1 - 0.3166) = \text{BOD} (0.6833)$

Ultimate BOD = 483 mg/L

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BOD₂₀ vs BOD₅ vs BOD

BOD is determined by bacterial action. This is not a steady, stable thing. In addition, there are accuracy limitations for the titrations.

Typically BOD₂₀ is more accurate than BOD₅ because it averages out more of the day to day fluctuations.

BOD is calculated from BOD₅ and BOD₂₀, so it has all the same errors as those PLUS it has the limitation on the accuracy of k.

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Increased accuracy

Do multiple 20 day tests.

Or do a 20 day test with a 5 day test point.
Calculate k from the 2 pieces of data and use that k to calculate the ultimate BOD.

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Bottom Line

It's a method of comparison.

The number doesn't need to be 100% accurate, it just needs to be determined in the same manner as the number it is being compared to.

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BUT...

The biggest problem is the presence of non-biodegradable organics (humus) that will be unaccounted for. You could have the dirtiest water ever and have it test as perfectly clean in the BOD test. So, you never rely solely on the BOD.
