

Biological Nutrient Removal

Applications for Monitoring Oxidation Reduction Potential OWEA ~ June 26th, 2019



Today's topics

- The Science of ORP
- Applications for ORP monitoring
- Technology for ORP monitoring
- Case Studies
- Sensor Care and Parting Thoughts





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The Science of ORP



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What is Oxidation-Reduction or Redox?

• An oxidation-

reduction (redox) reaction is a type of chemical reaction that involves a transfer of electrons between two species.

 The oxidation number of a molecule, atom, or ion changes by gaining or losing an electron.





What is Oxidation-Reduction or Redox?

LEO goes GER



- Loss of electrons is oxidation
- Gain of electrons is reduction



Why Do We Care?

- Oxidation-reduction potential
- aka: ORP
- aka: Redox

Indicates the water's relative state to receive or gain electrons



Growing Bugs Are Happy Bugs!

Bacteria require 4 things for growth:

- 1. Carbon
- 2. Nutrients
- 3. Energy
- Reducing Power the ability to transfer electrons

Source: Biological Wastewater Treatment, 2nd ed., Grady, C.P., Daigger, G.T., Lim, H.C., 1999.



Bugs get energy and reducing power from oxidation-reduction (Redox) reactions

Treatment Function	Energy source	Reducing power
	(e⁻ donor)	(e ⁻ acceptor)
BOD removal	Organic C	O ₂
Nitrification	NH_4^+	O ₂
Denitrification	Organic C	NO _x
Fermentation	Organic C	Organic C





What has ORP have to do with it?

ORP measures electron donating ability.

- Electron tower: most negative (e⁻ donors) at top to most positive (e⁻ acceptors) at bottom.
- Electrons donated from the top of the tower can be "caught" by acceptors at various levels.
- The greater the "fall" the more energy is released



 $E_0'(V)$

-0.50

-0.40

-0.30

-0.20

- -0.10

.15 v

Fermentation

Carbon is

donor and

acceptor

Couple

CO2/glucose (-0.43) 24 e-

CO₂/methanol (-0.38) 6 e

NAD+/NADH (-0.32) 2 e

CO2/acetate (-0.28) 8 e-

2H+/H2 (-0.42) 2 e-

Sº/H2S (-0.28) 2 e-

SO42-/H2S (-0.22) 8 e

Sounds complicated, huh?

It is, but....



It can be <u>very</u> simple if only interested in measuring e⁻



ORP Sensor is similar to pH sensor

The measurement is the raw signal, millivolts (mV)



Reference electrode Reference junction Electrolyte Measuring electrode

*YSI SensoLyt PtA electrode (109 125Y)





Applications for ORP Monitoring



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Wastewater Activated Sludge Process





Sludge Activity

Oxic = aerobic = DO is the primary e- accepter

Anoxic = No DO. NO_3 is primary e- accepter

Anaerobic = No DO or NO₃, need something else



Oxidation Reduction Potential (ORP)



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ORP as a DO Sensor

Think of ORP as a DO sensor that measures negative

DO > 1.0 mg/L: primarily O_2

- No direct meaning as to the status of nitrification
- +100 to +400 mV ORP for nitrification pricess

DO < 1.0 mg/L: O_2 + other e⁻ acceptors

- No direct meaning as to the status of denitrification
- -100 to -100 mV ORP for denitrification process

DO < 0.1 mg/L: primarily other e⁻ acceptors

- No direct meaning as to the status of denitrification
- -100 to -400 mV ORP for denitrification process



ORP as a "N" Sensor

ORP can indicate what forms of N are present

- NO_3 and NO_2
- Ammonium and TKN
- Little to no dissolved 'N' (and no DO)

ORP (mV)

+



ORP as a "P" Sensor Well, it can't really do that

- 'P' is neither oxidized or reduced during biological-P removal
- However, it can tell you when conditions are ripe for uptake and release







Monitoring Methods



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Monitoring Methods









Monitoring Methods









Case Studies



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Englewood, CO

- Switched to ORP control: Cl₂ residual analyzer required continual operator attention.
- DPD test kit was getting interference; Difficult to set the proper dosage.
- Sodium bisulfite overdosed to assure compliance with chlorine residual limit





ORP Monitoring System







ORP /Ammonium Monitoring System



Image courtesy of Greg Farmer

Extended Aeration Process

Goal: minimize aeration & chlorine

- Measuring ORP in anoxic zone
- NH₃-N target in effluent: 2 3 mg/L
- Upper ORP SP: -200 mV
- Lower ORP SP: -270 mV
- NH₃-N maintained between 1 and 3.5 mg/L
- DO near 0 mg/L
 - Nitrate also low

Intermittent Aeration Process

Sequencing Batch Reactor, SBR, cyclic activated sludge

time (hour)

Reproduced G Olsson, M Nielsen, Z Yuan, A Lynggaard-Jensen, J-P Steyer (2005) *Science & Technical Report No. 15, Instrumentation, Control, and Automation in Wastewater Systems,* with permission from the copyright holders, IWA Publishing

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Sensor Care

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Calibration, Cleaning and Replacement

- Calibration: 1-point offset correction
- YSI 3682 Zobell solution: +231 mV @25°C (platinum Ag/AgCI) Cleaning:
- In general use the same practices as you would a pH sensor
- Junction: running water / soft brush
- Platinum: Wet and blot dry (avoid rubbing)
- Short-term soak in household dish soap for grease removal

Replacement:

 Electrodes should last many months to years (IQSN electrodes warrantied for 6 months)

Parting Thoughts

- ORP is relative not comparable between brands, between applications
- ORP accuracy +/- 20 mV
- Response may be slow up to 24 hours to stabilize in natural waters (but very fast in Zobell)
- ORP measurement is affected by temperature but not corrected for it.

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