

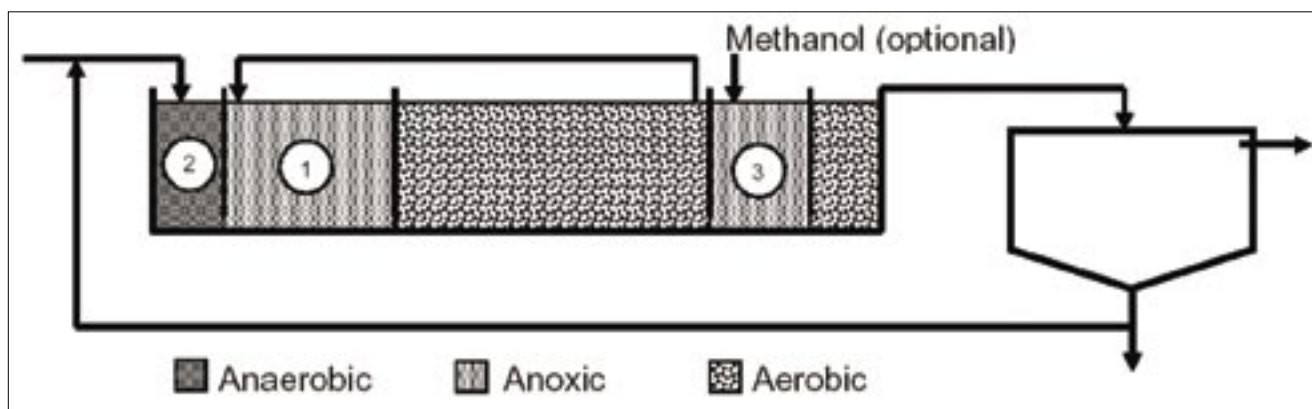
Black magic can work wonders for wastewater treatment

Hach wastewater specialist, **Mr Bob Dabkowski**, details the theory of oxidation reduction potential (ORP), a background into common biological nutrient removal (BNR) systems, and the basic application of ORP sensors into these common BNR systems

Oxidation reduction potential (ORP) is commonly a misunderstood science. Applying ORP to wastewater treatment is often considered a mystery and sometimes called “black magic”. It is easy to overlook this simple sensor and the complex data it brings to the wastewater treatment professional. Unlike dissolved oxygen control in aeration basins, ORP control in BNR systems focuses on optimisation of the process and not necessarily cost savings, although some cost savings may be realised.



Once understood, ORP can be quite beneficial in the operation of a BNR system



The five-stage Bardenpho process

Theory of ORP

ORP theory is best summarised as an indication of the solution's ability to oxidise or reduce another solution. It can also be defined as the sum of all the potentials in the water. Every ion, compound, and element in water exhibits a potential — the sum of these potentials is the ORP value of the water. The ORP value of the water tells the treatment professional if the environment of the water is oxidative (positive millivolt values), or reductive (negative millivolt values).

A simple way to think of ORP is through dechlorination. Chlorine is a strong oxidant — adding chlorine to the water changes the ORP to a positive value, indicating an oxidative solution. The chlorinated solution oxidises organics and also kills microorganisms. Since this strongly oxidative solution would be harmful to the environment, it needs to be neutralised by adding a strong reductant, such as sodium bisulfite. Sodium bisulfite reduces the chlorine present to harmless chloride where it can be discharged to a receiving body. This is a simplified view of dechlorination to help understand the nature of ORP, since in the real world there are other compounds exerting a background ORP on the solution.

In BNR wastewater systems, it is often necessary to know the ORP of the various treatment basins to optimise the system. In order for bacteria to respire, they need to donate an electron to a final electron acceptor. In aerobic environments this final electron acceptor is typically an oxidant (such as oxygen), in anaerobic environments the final electron acceptor is typically a reducer (such as sulfate). ORP measurements help understand the bacteria's environment: A reductive solution (negative ORP) is generally capable of donating an electron, while an oxidative solution (positive ORP) is generally capable of accepting an electron. This environmental condition can be a critical limiting factor in BNR systems.

Introduction to BNR

As new effluent permits reduce the amount of nutrients wastewater treatment plants are allowed to discharge into receiving bodies, simple, cost effective means to treat the waste are readily embraced. Removing nitrogen and phosphorous biologically provides the lowest operating cost when running properly, and therefore is gaining popularity.

All combined BNR systems share common elements: An anaerobic zone free of dissolved oxygen and nitrate, an anoxic zone containing nitrates, and an aerobic zone rich with dissolved oxygen.

After primary clarification, the wastewater typically flows into an anaerobic zone first, where the anaerobic environment favours the respiration of Phosphate Accumulating Organisms (PAOs). In the anaerobic zone, the PAOs break down large intercellular polyphosphate compounds into simple orthophosphate and release it into the water.

The next zone is typically anoxic, with nitrates created in the subsequent aerobic zone recycled to the head of this anoxic zone. In this anoxic environment, separate heterotrophic bacteria break down nitrate into nitrite and finally nitrogen gas. The nitrogen gas is released to the atmosphere through mixing in the aeration basin. The aerobic zone serves two purposes for BNR: The conversion of ammonia to nitrate, and the uptake of the previously released phosphate into cellular material of the PAOs. The nitrate is recycled into the anoxic zone where it is converted to nitrogen gas, and the phosphate is removed through normal wasting of the activated sludge.

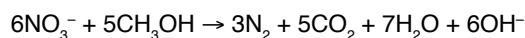
Another way to think of nutrient removal is from the perspective of the nutrient itself, and how it is removed biologically.

Nitrogen removal

Nitrogen removal is done through two process treatment steps, one aerobic and one anoxic. The aerobic process, called "nitrification", converts ammonium to nitrate.



The next step in the process is removal of nitrate, by a process called "denitrification". Denitrification occurs when wastewater environment is anoxic, or there is a lack of "free" oxygen but combined oxygen is available as nitrate. These conditions are important for the removal of nitrate because facultative bacteria can utilise both oxygen and nitrate in their metabolic processes. If oxygen is present, they will favour oxygen and will not remove nitrate. When oxygen is absent, facultative bacteria convert nitrate to nitrogen gas.



Phosphorous removal

Phosphorous removal is a two-step process, anaerobic fermentation followed by aerobic treatment.

Phosphorous removal begins with anaerobic treatment. Free and combined oxygen are not available and the products of anaerobic fermentation are primarily volatile acids. Phosphate consuming bacteria (PAOs) assimilate volatile fatty acids. The energy required for this assimilation comes from intercellular phosphate, which is then released to the mixed liquor. At this point in the process there is an increase in phosphate in the mixed liquor.

The next phase of phosphorous removal is aerobic treatment. Phosphate consuming bacteria now have a large supply of energy, in the form of stored volatile fatty acids, for metabolism and growth. There is a large increase in the mass of phosphate-consuming bacteria and these bacteria now absorb both the initial phosphate and reabsorb the phosphate released during anaerobic treatment. The phosphate is now part of the bacterial cell mass and is removed as sludge in the clarifier.

While there are many different process variations in order to achieve the biological removal of nitrogen and phosphorous, all share the same anaerobic, anoxic, and aerobic zones described above.

Most systems cannot rely on biological removal alone, but must also supplement with carbon addition, chemical precipitation and/or filtration in order to meet effluent permit requirements. Chemical treatments increase the opportunity for advanced instrumentation, but will not be described in this article.

Applying ORP sensors in BNR systems

The Water Environment Federation recently published *Manual of Practice No. 29, Biological Nutrient Removal (BNR) Operation in Wastewater Treatment Plants*, and offers nine different processes which remove both nitrogen and phosphorous biologically. Five of the most common combined

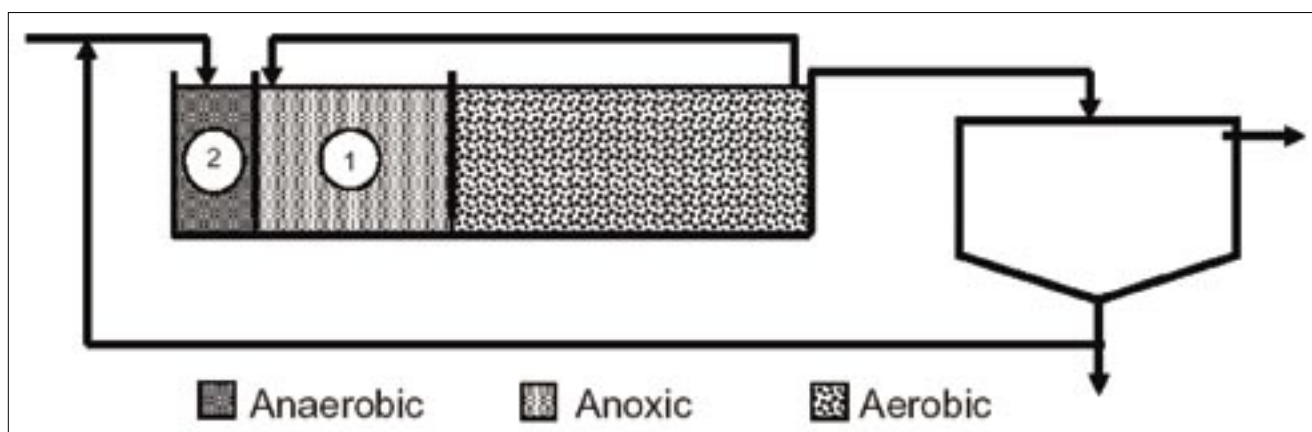
BNR processes will be described, along with application details for ORP measurement and control. As with any process control measurement, it is necessary to install the sensor in a manner that is representative of the entire zone. A typical rule of thumb for wastewater installations is to install the ORP sensor in the middle of the basin, approximately 1/4 of the depth of the basin (i.e. 10-ft deep basin, submerge sensor about 2.5-ft deep).

In the five-stage Bardenpho process, there are three locations that would benefit from an ORP measurement. The first, and most important application is in the first anoxic zone where a majority of the denitrification is taking place. Factors affecting the ORP of this zone are the amount of recycled aerobic water, the amount of anaerobic effluent from the first zone, along with the biological state of the bacteria from each zone. The ORP in this zone should be between -100 and 100 mV, indicating a fairly neutral solution for the denitrification to take place.

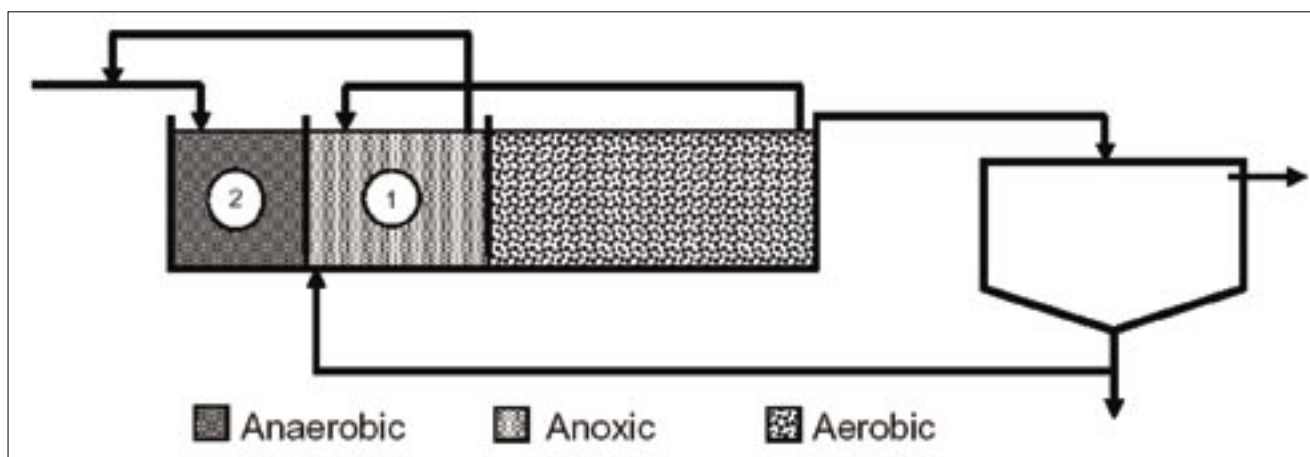
The second location for an ORP sensor would be in the initial anaerobic zone, also known as a fermentation zone. This basin requires a strongly negative ORP in order to break down the polyphosphates as mentioned earlier. Look for ORP values less than -150 mV to ensure adequate electron donors for the respiration of the PAOs.

The second anoxic zone is the third location for ORP measurement. This zone is in essence a "polishing step" for denitrification. The ORP in this zone is especially important if methanol is being added as a food source to further denitrify the water. While the methanol addition is best determined by pilot studies, it can be controlled through the ORP measurement combined with COD, Total Inorganic Nitrogen (TIN) and volatile TSS testing.

The three-stage Phoredox process is a very common method of performing nutrient removal since it requires the least amount of alterations to the typical conventional activated sludge plant. It is not the most efficient system, due to the nitrates in the Return Activated Sludge (RAS) inhibiting proper phosphorous release in the anaerobic zone. Facilities employing this A²/O process that are facing tighter permit limits than it can produce are forced to amend their process



The three-stage Phoredox (A²/O) process



The University of Cape Town and Virginia initiative processes

in order to meet the new limits, which results in additional capital costs.

Similar to the five-stage Bardenpho process, the first and most important location for ORP measurement is in the anoxic zone where the denitrification is taking place. The factors affecting the ORP of this zone are also the same as the Bardenpho: The amount of recycled aerobic mixed liquor, the amount of anaerobic effluent from the first zone, along with the biological state of the bacteria from each zone. Like most anoxic zones, the ORP should be between -100 and 100 mV.

The anaerobic zone is the second location for an ORP measurement. In this zone we are breaking down the polyphosphates and releasing orthophosphates, the PAOs which do this require a strongly reducing environment. Look for ORP values less than -150 mV in the anaerobic zone.

While it is possible to install an ORP sensor in the aerobic zone, typically in the A^2/O process it is not necessary since DO is a better, more efficient control. ORP could indicate an inactive sludge in the aerobic zone even though DO levels could be around 2 mg/L. An occasional ORP measurement by a portable ORP meter would be sufficient to ensure a positive millivolt potential (a negative ORP reading would indicate an inactive sludge, and BOD/SOUR tests could confirm this).

However similar to the three-stage Phoredox (A^2/O) process, the University of Cape Town and Virginia Initiative Processes (UCT and VIP) have added features that provide much more control and flexibility. Major differences between them are that the UCT and VIP system recycles the RAS into the anoxic zone — keeping nitrates from interfering with the phosphorous removal by adding an additional denitrification step before the RAS is then returned to the anaerobic zone. The philosophy behind this process is that if there is not enough influent carbon to remove nitrogen and phosphorous, the preference should be given to phosphorous removal.

ORP measurements and installations are the same as for the A^2/O system. The first and most important location for ORP measurement is in the anoxic zone where the denitrification is taking place. The difference is the factors affecting the ORP

of this zone: The amount of recycled aerobic mixed liquor, the amount of nitrates in the RAS, the amount of anaerobic effluent from the first zone. Again, like most anoxic zones, the ORP should be between -100 and 100 mV.

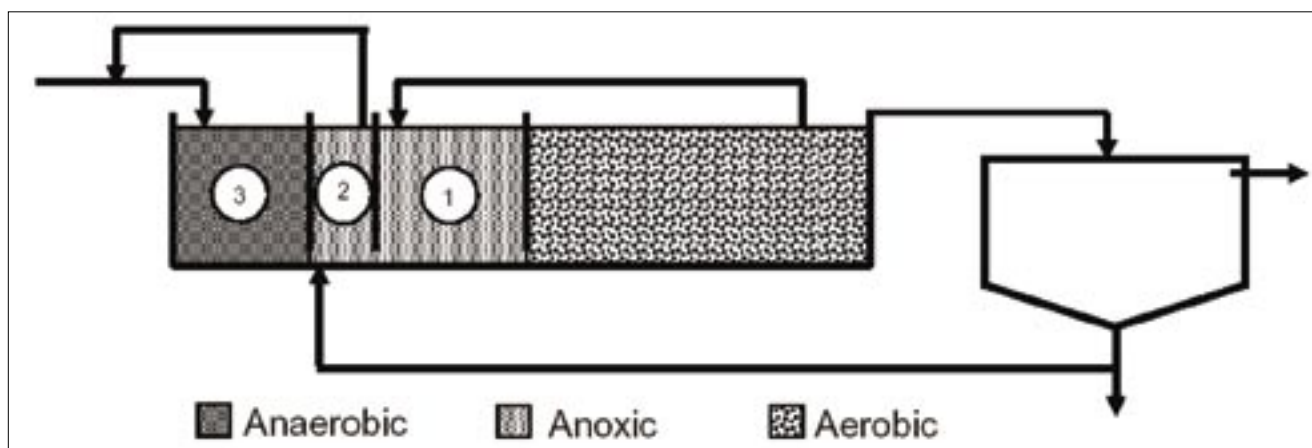
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The difference between the standard UCT and VIP process and the modified UCT process is that an additional anoxic zone is created solely for the purpose of denitrifying the RAS before it is returned to the anaerobic zone. This way it is free from the influence of the recycled aerobic zone nitrates and further increases flexibility in the “phosphorous first” philosophy.

In addition to the two ORP sensors used in the UCT and VIP processes, an additional ORP sensor installed in the first anoxic zone would help ensure an environment for denitrification of the RAS. In this first anoxic zone ORP values should be between -100 and 100 mV, with the most likely scenario being between -100 and 0 mV.

The modified Johannesburg process allows for quick denitrification of the RAS through an initial “preanoxic” zone which is typically twice the solids concentration of the mixed liquor (solids in the remaining zones). The primary effluent wastewater is introduced into an anaerobic zone where it mixes with the denitrified RAS to begin the phosphorous removal stage. Water is recycled from the end of the anaerobic zone to the preanoxic zone, feeding the denitrifying bacteria any readily available organic compounds not consumed by the PAOs in the anaerobic zone. Similar to the other processes, a second anoxic zone allows for initial denitrification of the primary effluent, followed by an aerobic zone for nitrification and removal of organics. Nitrified aerobic mixed liquor is recycled to the second anoxic zone for denitrification.

The best location for the first ORP sensor is in the preanoxic zone, and would best be installed with a self-cleaning system such as an air blast. Premature fouling of the sensor could



The modified UCT process

be a concern due to the high level of suspended solids in this preanoxic zone. Also, with the addition of the anaerobic recycle stream, it is quite possible for this zone to become inactive if the detention time increased significantly. Controlling the ORP in this zone between -100 and 100 mV is critical to proper denitrification and seeding of the remaining process. If this zone is mixed using on/off aeration, ORP control becomes even more important to ensure it does not become aerobic.

To ensure a proper anaerobic and reducing environment for the PAOs, the second ORP sensor should be installed in the anaerobic zone. Similar to the other anaerobic zones, look for ORP values less than -150 mV.

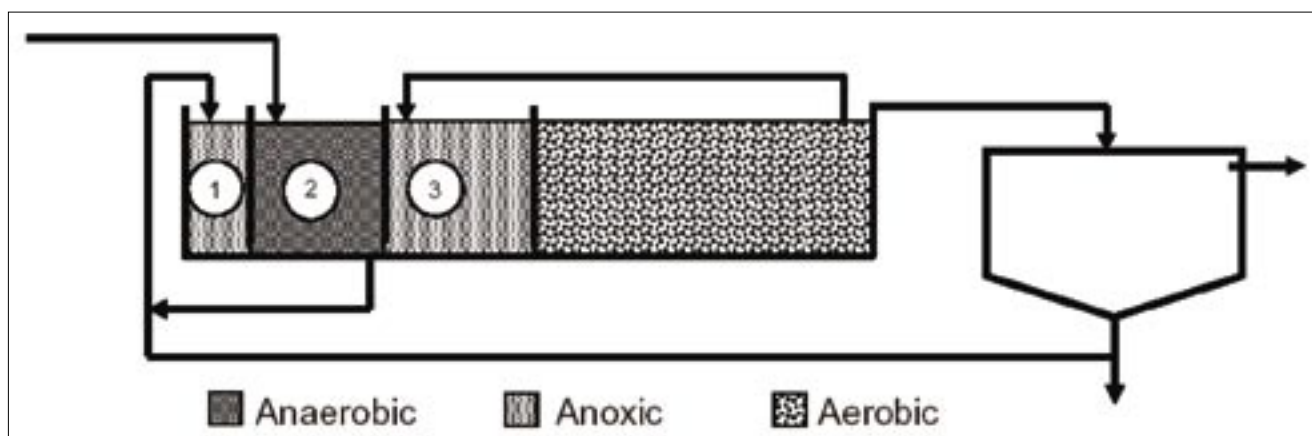
The third ORP sensor is best installed in the second anoxic zone. This second anoxic zone is responsible for the majority of the denitrification taking place, and it is necessary to ensure a fairly neutral environment. As with other anoxic zones, ORP values should be between -100 and 100 mV. ORP in this zone will ensure that an appropriate amount of aerobic effluent is recycled for the biomass present.

Summary

Once understood, ORP can be quite beneficial in the operation of a BNR system. As with any control parameter, it is necessary to ensure the sample is representative of the larger system, that the method is reliable, and of course reproducible. Combined with other testing to confirm the site-specific conditions, online ORP can be a simple and cost effective solution for process control and optimisation.

While there are many different processes to accomplish removal of nutrients in wastewater, the same basics apply to BNR systems. All consist of an anaerobic zone, anoxic zone, and aerobic zone, typically accomplishing similar functions between systems. Knowing how these zones affect the bacteria and how ORP relates to the environment of each zone allows for the instrumentation professional to make application recommendations with ease. **WWA**

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The modified Johannesburg process