

The Importance of Low pH Environments in the Treatment of Wastewater Containing High Carbohydrate Wastes.

Key concepts:

- Organic digestion/degradation depends in part upon presence of hydroxyl radicals:
 - ▶ **Fermenting Organisms produce H₂O₂**
 - ▶ Hydroxyls come from H₂O₂ + UV
 - ▶ H₂O₂ also oxidises and produces free Oxygen in contact with organic material
 - ▶ Sunlight Produces H₂O₂ and also contains UV
- Fermenting organisms produce enzymes and low level Acids – these are critical because:
 - ▶ Hydroxyl degradation is much more efficient in low pH
 - ▶ Low level organic acids are the key element in settling rates of solids
 - ▶ Some enzymes (e.g. amylase) react with H₂O₂ rapidly
- Fermenting organisms produce Highly UNBUFFERED low pH in water. Very small pH adjustments can have huge impacts on the pH and flow-on effects – kills the microbes and results in no/low settling of solids.
 - ▶ H₂O₂ produced by Fermenting microbes oxidises Sulphides, Amines and other odour compounds naturally (hence balanced ponds don't smell)
 - ▶ H₂O₂ produced by fermenters in "anoxic" environments adds oxygen and allows them to maintain an oxygen balance
 - ▶ Fermenters compete with odour creating organisms and organisms which produce corrosive elements (sulphuric acid, etc)
- Flocculants, Surfactants and emulsifiers reduce the capacity of fermenting organisms to feed/maintain population growth.

Understanding interruptions in organic waste breakdown

The digestion of carbohydrate-rich wastes in an aqueous environment is commonly seen as a mathematical equation involving normal parameters of time, space and oxygen input. Much focus has also been given to the production of enzymes by microbes or introduction of enzymes as a means of degrading carbohydrates. In this article we focus on another product of fermentative processes, hydrogen peroxide, and its importance in the digestion process.

There are commonly failures of waste treatment mechanisms which appear “unexplained” and which plant operators find difficult to rectify. Our experience shows that such events are typically grouped around two basic misconceptions:

Firstly that low pH is problematic for aerated treatment processes and secondly that sedimentation rates are dependant on dissolved oxygen levels in the secondary (aerated) phase of the process. Generally speaking, “breakdown” events follow or are associated with expected or real high load periods.

When faced with a significant or unusual input of carbohydrate-rich material, the standard reaction is to add lime or a similar pH adjuster and try to adjust sedimentation by first increasing aeration schedules and secondly by adding flocculants and/or surfactants.

In reality, our observations suggest that **both of these reactions result in a rapid decline in microbial activity and can lead to a significant lengthening of the recovery time for the treatment plant.** Additionally, these reactions often result in the complete interruption of organic digestion and end in the “dumping” of some very difficult waste material and a total “re-start” of the process.

Understanding why this occurs requires a further look at the reaction which takes place in the degrading of carbohydrates and organic material.

Importance of Hydrogen Peroxide in Digestion of Carbohydrates

Perhaps the most effective tool in the breakdown of carbohydrates is the hydroxyl radical (HO, sometimes incorrectly confused with Hydroxide radicals 'OH'). It has been shown that hydroxyl radicals attack the linkages which keep carbohydrates together. (<http://chemistry.umeche.maine.edu/Fort/Oxygen2b.html>)

Much work has been done on Advanced Oxidation processes which depend upon the advanced formation of hydroxyl radicals using various techniques involving UV, Ozone and Hydrogen Peroxide. Without going into depth here, the important factors to note in this are that all such studies conclude that attack on carbohydrates and indeed on organic compounds in general by hydroxyl radicals produced by UV + H₂O₂ is significantly more consistent at lower pH levels. In fact, the generation of hydroxyls and their effectiveness in degrading such compounds has been shown to work best in the 3-7 pH range. (mokrini et al

<http://www.photobiology.com/IUPAC98/esplugas/phenol.html>)

Use of Ozone and peroxide as an oxidation source has been shown to be more effective at higher pH levels; however there are other limits to the effectiveness of a program for heavily loaded wastewater that relies on Ozone injection.

For our purposes, the addition of a concentrated source of hydroxyls using a mechanically-based advanced oxidation source or the concentrated addition of Hydrogen Peroxide is generally not cost effective on the scale needed to effect consistent treatment of large-scale waste water streams. In fact the time element involved in direct dosage often precludes the process.

Microbes and Sunlight produce H₂O₂

There are two important sources of hydrogen peroxide which need to be considered. The first is the production of H₂O₂ as a metabolite of fermenting microbes. (<http://www.h2o2.com/intro/overview.html>). Some fermentative organisms such as lacto-bacillus and other fermenting bacteria produce H₂O₂ in large amounts as part of their metabolic processes. This process has been noted previously and is seen as part of the ability such organisms have to discourage competitors and overcome some pathogenic organisms. (http://www.ncbi.nlm.nih.gov/entrez/query.fcgi?cmd=Retrieve&db=PubMed&list_uids=14570275&dopt=Abstract). Many other microbes also produce H₂O₂ as a by-product of their conversion of food in water. When considering the ability of a treatment plant to consistently degrade organic material and in particular carbohydrates, looking at the production of H₂O₂ is an important factor.

The second important source of H₂O₂ is sunlight on water. It is interesting to note that, as in the case of Ozone in the upper atmosphere; energy from the sun produces H₂O₂; and UV from the sun also degrades H₂O₂ in a continuous cycle. This effect has particularly been noted in studies of conversion of substances in atmospheric moisture. (http://www.ametsoc.org/POLICY/aciddepo_2003.html)

Several studies have also shown that the use of UV and H₂O₂ in tandem has the result of producing significant numbers of Hydroxyls in water. Any pond which is open to sunlight will naturally contain a measure of Hydrogen Peroxide produced in the water by the action of the sunlight on the water itself. Consequently, it will also contain a measure of Hydroxyl anions produced by the effect of UV on the peroxide which has been produced.

In tandem, a source of peroxide, combined with a source of UV are extremely effective in the degradation of carbohydrates and other organic compounds in water.

Consistent H₂O₂ means keep the right bugs alive

It is extremely important therefore to preserve those elements which are responsible for the production of peroxide in the body of water concerned.

Critical in this discussion is the subject of pH. It has been repeatedly shown that higher pH leads to a lower and less consistent level of hydroxyl attack on organic compounds in water – particularly carbohydrates.

It is no secret that organisms responsible for rapid consumption of carbohydrates prefer – and in fact produce – low pH environments. This is generally taken to be related to low-level organic acids which are produced by these types of organisms. **Artificially adjusting pH using lime and other materials significantly inhibits the growth rate of populations of these types of organisms.**

Additionally, **mokrini et al** have shown that inclusion of hydroxyl scavengers in the water will affect the level of breakdown which occurs. It is important to note that Lime and other alkali adjusters also have the effect of acting as adsorbents which attract hydroxyl radicals – effectively reducing the breakdown capacity further.

No need to fear low pH

In general, we find that reactions to low pH are directly related to the fear of odour production and corrosion issues. This comes about because of the typical understanding that hydrogen sulphide and amines, etc are produced whenever pH is lower than neutral. Again, this is a misconception. In reality, there are two distinct organic pathways which may be present and the results which occur depend entirely upon which group of organisms are allowed to dominate. In fact, Hydrogen Peroxide is perhaps the most effective oxidiser of Hydrogen sulphide, amines and other such odour generators commonly found. Additionally, the presence of Hydrogen Peroxide and its subsequent by-products directly counteracts the effects of thiosulphide production (sulphuric acid responsible for corrosion). **There are microbes which control odour by producing oxidisers such as H₂O₂ and other substances in low pH environments which directly oxidise the odour substances. Where a balance of microbial activity is present – including fermentative organisms like lactobacillus—low pH will not necessarily result in odour.**

It is understood that Sulphate Reducing Bacteria (SRB) commonly inhabit anoxic sludges and are responsible for large-scale, rapid production of hydrogen sulphide. What is not commonly understood is that the natural counter for these organisms is those which produce H₂O₂ and low-level organic acids. H₂O₂ both oxidises hydrogen sulphide and allows a residual of oxygen in these situations. Additionally, there are also organisms (the purple-non-sulphur bacteria) which directly compete with SRB for sulphate. These bacteria do not produce sulphide compounds and can be cultured in most waste situations without difficulty.

However, key factor in this is; organisms which naturally counter the effects of SRB and Thibacillus produce products (low-level acids and nitrogen compounds such as amino acids) which both lower pH **and significantly reduce the buffering capacity of the water body**. This means that introduction of Lime or similar pH adjustment when such organisms have previously been predominant will result in a rapid upward movement in pH. This rapid increase in pH is compounded further by the addition of oxygen which overwhelms the weakly acidic effect of CO₂ produced under less highly

aerated circumstances. Both of these factors subsequently result in microbial die-back in populations of those organisms which are primarily responsible for the break-down of carbohydrates and other organic substances.

Sedimentation and pH change

Importantly, rapid changes to the sedimentation rates of solids in water are also observed following rapid increases in pH. Remembering that organic acids and the production of them involving nitrogen consumption are the primary element supporting the sedimentation of solids in a healthy treatment plant, it is no surprise that rapid upward change in pH will result in a reduced ability to support settling in the treatment works. Unfortunately, the addition of surfactants and other agents used to chemically induce sedimentation at this point adversely impacts on the recovery of the plant. There is a little understood interruption of the metabolic rate of fermentative organisms which occurs upon the introduction of alkali-based surfactants, emulsifiers and flocculants. In addition, some flocculants, (such as aluminium sulphate, ferrous compounds, etc) are toxic to the organisms required and greatly favour the growth of SRB. (Holder & Hauser)

Aerobic or Anaerobic?

It must also be remembered that the concept of a totally "aerobic" environment and a totally "anaerobic" or "anoxic" environment as mutually exclusive elements in a waste treatment circumstance are misleading. Dissolved oxygen concentrations up to 5 ppm (common in most aerobic treatment plants) do not preclude the rapid growth of some fermenting organisms (including lactobacillus). It is interesting to note that many of these organisms – which are associated automatically with anaerobic, acidic environments—are actually cultured in an aerobic environment in our factory. Additionally, organisms which produce both enzymes for carbohydrate digestion (e.g. amylase by lactobacillus niger) and H₂O₂ as part of their metabolic activity end up allowing/creating free oxygen as the enzymes and peroxide react. (<http://www.h2o2.com/intro/faq.html#22>). The reality is that a cycle of oxygen and hydrogen use exists and is critical to both respiratory and metabolic activity in a range of organisms prevalent in both low oxygen and higher oxygen environments. Additionally, there are organisms (heterotrophs) which are able to work in both aerobic and anaerobic conditions, and which can help to form a "bridge" between the states of oxygen concentration in water in a similar way that photosynthetic plants are able to operate in air. In most discussions, this centres on the relationship between carbon and oxygen. In water, the relationship between hydrogen and oxygen is also extremely important in understanding the breakdown pathway for organic material and is a contributor to the ability of organisms to work in conditions of fluctuating oxygen concentration.

Neutral pH from a biological process?

It has often been noted that there is a natural cycle of biological activity in water which results in neutral pH. In general, this is related to the predominance of aerobic organisms and of phototrophic activity in the water. However it is important to note that this process is not complete until the level of organic matter in the water is greatly reduced. In fact, dependence on neutral pH as a guide to healthy activity can be quite misleading. There are, for example, events which see high levels of ammonia being formed where high BOD exists (eutrophication). This can occur simultaneously with the production of organic acids to produce a "neutral" overall pH in water for a time. What is not a popular thought is that in order to reach a stage of low organic load, a period of low pH (and corresponding rapid digestion) is necessary. When this is complete, a gradual return to neutral pH will occur. In a continual flow-through situation; **management of time in process is considerably more important than artificial adjustment of pH in respect of biological pH control.**

Need for pH Adjustment after high-load events?

It has also been noted that continued Advanced Oxidation with hydroxyl radicals will result in a low pH reading (in some cases 4 -5.5) in final effluent waters. This is quite easily understood if we understand pH to be a measure of free hydrogen. In cases where high relative organic load is experienced over a short period where strong populations of fermenting organisms predominate, advanced oxidation can occur, resulting in low pH of effluent waters which are virtually devoid of organic matter and show very low values for BOD, TSS and biological counts. We have been able to replicate this process using Ozone/UV and Peroxide input in mechanical circumstances. Key in this discussion is that the **pH reading experienced is not due to the presence of residual organic material in the form of undigested organic acids in this case.** In fact, the measure of low pH in such circumstances records the presence of residual radicals formed in part from the degradation of H₂O₂. Confirmation of this is seen in the ease with which pH balancing is achieved in such circumstances, not by the addition of alkali substances, but by simply running the effluent through/over an adsorption material such as marble chip. It is recommended that such a "molecular filtration" process be preferred to introduction of lime or other pH adjustment being both more cost-effective and more reliable, provided that provision is made to periodically remove and "regenerate" filtration media as adsorption sites can be filled over time. (The process of adsorption is easily reversed by exposure to sunshine)