The Impact of Peracetic Acid on Receiving Waters: Biochemical Oxygen Demand and Dissolved Oxygen

INTRODUCTION

The use of peracetic acid (PAA) for wastewater disinfection has seen significant growth in North America over the last several years due to its advantages over chlorine-based chemistries. These advantages include: no formation of chlorinated disinfection byproduct, such as trihalomethanes; lower aquatic toxicity and environmental impact; less influence of wastewater quality, such as TSS, nitrate and ammonia, on disinfection performance; and generally lower concentration or contact time to achieve the target microbial kill. The microbial efficacy of PAA on pathogens within wastewater is well known[1], and several publications have investigated the impact of PAA on the subsequent water quality of a plant's effluent after disinfection[1-3]. This month's edition of the *Disinfection Forum* examines the role PAA plays in the formation of both biochemical oxygen demand (BOD) and dissolved oxygen (DO), two competing mechanisms that impact the health of the plant's receiving stream.

BIOCHEMICAL OXYGEN DEMAND

BOD is the amount of oxygen required for microbial metabolism or organic compounds in the wastewater and receiving stream. The amount of oxygen needed to completely convert the organic compounds to carbon dioxide is termed the Total Biochemical Oxygen Demand. BOD is listed as a pollutant by the U.S. EPA and can impact the health of the aquatic ecosystem through oxygen depletion due to microbial consumption. Influx of organic compounds into the ecosystem may result in a subsequent microbial bloom, which will utilize the available dissolved oxygen. BOD is typically expressed as mg of O_2 / L over a 5 day period at an incubation temperature of 20 °C (BOD_5). As this test measures the consumption of oxygen due to microbial consumption of the organic compounds, disinfectants, such as PAA, must be neutralized prior to the incubation period.

Commercially available PAA solutions contain four components: peracetic acid, acetic acid, hydrogen peroxide and water. As an example, PeroxyChem's VigorOx® WWT II PAA contains 15% percetic acid, 23% hydrogen peroxide, 16% acetic acid, 45% water and 1% sulfuric acid as a process aid. As a result, PAA can generate BOD due to the biological oxidation of acetic acid:

$$CH_3COOH + 2\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O \qquad \text{Eq 1}$$

In addition, PAA will decompose to acetic as follows:

$$2\,CH_3COOOH \rightarrow 2\,CH_3COOH + O_2 \qquad \text{Eq 2}$$

which will also contribute to the BOD.

Combining equations 1 and 2, the theoretical BOD generated from 1 mg of PAA from VigorOx WWT II / L is 1.98 mg O_2 / L water. In comparison, the theoretical BOD generated from other PAA formulations in the market place are shown in Table 1:

PAA wt%	Hydrogen Peroxide wt%	Acetic Acid wt%	Theoretical BOD (mg O2 / L)
15	23	16	1.98
12	18.5	20	2.62
22	5	45	3.02

Table 1: Theoretical BOD contribution from the addition of 1 mg PAA / L for several commercially available PAA products

DISSOLVED OXYGEN

While PAA solutions may generate BOD, and as a result contribute to biological uptake of oxygen from the receiving stream, the deleterious of the BOD may be partially offset by the dissolved oxygen that will be generated by the decomposition of PAA. Equation 2 shows the generation of one mole of oxygen for two moles of PAA that decompose. In addition, as seen in Table 1, PAA solutions contain hydrogen peroxide. The decomposition of hydrogen peroxide is shown in Equation 3, which shows one mole of oxygen formed for two moles of hydrogen peroxide decomposed:

$$2\ H_2O_2 \rightarrow 2\ H_2O + O_2 \qquad \text{Eq 3}$$

Combining Equations 2 and 3, the theoretical DO generated from one 1 mg PAA from VigorOx WWT II / L is 0.93 mg O_2 / L water. As a result, the DO generated by the VigorOx WWT II PAA solution nearly offsets the theoretical BOD formed, giving an "apparent" BOD of 1.05 mg O_2 / L water. Table 2 shows the theoretical DO generated from several commercially available PAA products and the resulting apparent BOD.

PAA wt%	Hydrogen Peroxide wt%	Acetic Acid wt%	Generated DO (mg O2 / L)	Apparent BOD (Theoretical BOD – DO)
15	23	16	0.93	1.05
12	18.5	20	0.94	1.68
22	5	45	0.32	2.70

Table 2: Generated DO and Apparent BOD contributions from 1 ppm PAA / L for several commercially available PAA products

Because the BOD_5 test method requires the quenching of the PAA prior to initiation of the incubation period, the method does give credit to the formation of DO from the PAA. As a result, in states or regions with very low BOD requirements on the effluent wastewater or in situations where the wastewater already has a high BOD value, use of PAA as the disinfection technology may result in BOD values exceeding permitted values. While this is not often the case, in such situations, demonstration of the positive impact of the generated DO may be warranted.

IMPACT OF PAA IN REAL WASTEWATERS

Cavallini[2] performed laboratory testing of PAA in wastewater obtained from the outfall of a treatment plant in Brazil. Their results demonstrated that DO increased within increasing dosages of PAA at several different temperatures, up to 40 mg PAA / L. Above these levels they observed the DO levels level off, which they attributed to supersaturation of the effluent. The research concluded, "since DO is a parameter of great relevance to the quality of bodies of water, the release of effluents with high DO concentrations could be another advantage of PAA application, in addition to deactivation of microorganisms." They also investigated the impact of PAA on BOD, and observed that a dosage of 10 mg PAA / L showed no significant change in the BOD of the effluent. Luukkonen[1] measured BOD following PAA addition up to 8 mg/L to tertiary treated wastewater in a pilot plant setting in Finland. Measured changes in wastewater BOD (BOD_7) after PAA addition were significantly lower than the theoretical BOD (and even showed a decreased in BOD at PAA concentrations below 2 ppm). This echoed work by Baldry[4] in which BOD was observed to fall during full scale PAA trialing. This was possibly attributed to the oxidation of organics by the PAA in the textile-constituent wastewater. To the point, PAA may actually aid in the reduction of BOD due to the oxidation of wastewater organics into smaller constituents. Stampi[3] reported virtually on change, within the standard error, of BOD_5 values in wastewater from a plant utilizing PAA as a disinfectant (contact time 20 minutes with a PAA dose of 1.5 – 2 ppm) pre and post PAA disinfection. A recent pilot trialing of PAA disinfection at a wastewater treatment plant in Georgia showed that cBOD values pre and post PAA addition did not change (average pre-PAA cBOD = 2.43 mg / L, average post-PAA cBOD = 2.46 mg/L) for PAA dose concentrations between 0.5 and 3.0 mg / L.

CONCLUSION

PAA solutions may negatively impact the BOD values of the effluent of a wastewater treatment plant due to the addition of acetic acid. In general, for most wastewater treatment plants, the additional BOD derived from PAA will be minimal and not impact the water quality beyond permitted levels. However, in situations where the BOD permit levels are low or the wastewater already has high BOD content, the addition of PAA may impact the plant's ability to meet permit requirements. In actuality, the BOD is partially offset by the generation of dissolved oxygen due to the decomposition of the peracetic acid and hydrogen peroxide components of the PAA solution. While this offset may not be apparent during standard BOD_5 testing, it has been shown that BOD values in actual wastewaters are lower than the theoretically amount, and in some cases is actually seen to decrease due to the potential oxidation of organic species present in the wastewater.

1. Example: Luukkonen, T, J. Teeriniemi, H. Prokkola, J. Ramo and U. Lassi. “Chemical Aspects of Peracetic Acid Based Wastewater Dsinfection”. **Water SA** 40, p 73 – 80, 2014.

2. Cavallini, G., S. de Campos, J. de Souza and C. de Sousa Vidal. “Evaluation of the Physical – Chemical Characteristics of Wastewater After Disinfection with Peracetic Acid”. **Water Air Soil Pollut** 224, p. 1751 – 1763, 2013.

3. Stampi, S., G. de Luca and F. Zanetti. “Evaluation of the Efficiency of Peracetic Acid in the Disinfection of Sewage Effluents”. **J Appl Microbiology** 91, p 833-838, 2001.

4. Baldry, M., A. Cavadore, M. French, G. Massa, L. Rodrigues, P. Schirch and T. Threadgold. “Effluent Disinfection in Warm Climates with Peracetic Acid”. **Water Sci Tech** 31, p 161-164, 1995.

5. Gruss, A., D. Funk, C. Wilbanks, K. Bell. “PAA – An Alternative for Wastewater Disinfection”. 2015 Annual GAWP Conference, Savannah, GA, 2015.