VigorOx® WWT II
Wastewater Disinfection Technology

Aquatic Toxicity and Fate of VigorOx® WWT II

PeroxyChem

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Definitions/Acronyms

EC_{50} The dose causing incapacitation to 50% of the population tested, determined by running several doses and estimating the EC_{50} statistically.

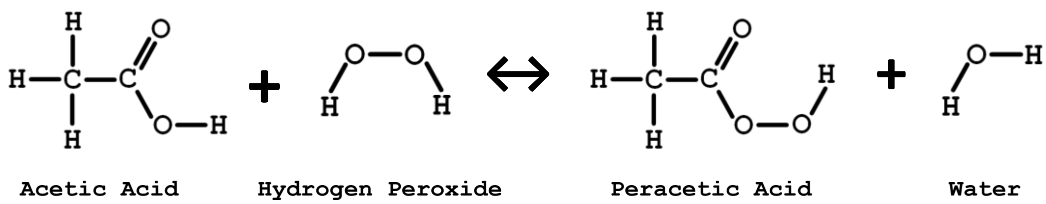
LC_{50} The dose causing lethality to 50% of the population tested, determined by running several doses and estimating the LC_{50} statistically.

IC_{50} The concentration of a substance which inhibits specific biological function in 50% of the test population

NOEC The highest dose tested that does not cause any toxic effects to the organisms tested.

Background

VigorOx® WWT II is an equilibrium peracetic acid solution that contains 15% peractic acid (PAA) by weight at full concentration. The solution exists as an equilibrium of PAA, hydrogen peroxide, acetic acid and water as per:



The environmental fate and ecotoxicity of peracetic acid solutions has been detailed in the report[1] "Peracetic Acid and Its Equilibrium Solutions" by the European Centre for Ecotoxicology and Toxicology of Chemicals. Peracetic acid can be considered a reduced risk, alternative disinfectant based on its effectiveness, its physical - chemical properties and its low exposure potential and risk to the environment.

VigorOx WWT II is used for treating effluent wastewater from municipal and industrial treatment plants to reduce the coliform bacterial count to meet Federal, State and Local laws before water is discharged into a waterway. The typical in-use PAA concentrations will be less than 10 mg/L (ppm) with targeted outflow concentrations around 1 ppm or less, depending on the application and treatment requirements. Peracetic acid is an ideal disinfectant for wastewater application to efficiently and reliably control bacteria under normal operational conditions, including the range of wastewater flow rates and wastewater qualities, without producing toxic, mutagenic or carcinogenic disinfection by-products or persistent disinfectant residues that have adverse environmental effects[1]. This paper will review the environmental fate and ecotoxicological data for peracetic acid and the associated benefits as it applies to treating wastewater effluent.

Aquatic Fate of VigorOx WWT II

The aquatic fate of PAA is almost exclusively determined by degradation in the water phase and is due to a number of mechanisms, including abiotic decomposition, hydrolysis, biodegradation or reaction with organic compounds, and dilution. Hydrolysis results in the breakdown of PAA to acetic acid (vinegar) and hydrogen peroxide, which subsequently decomposes to oxygen and water. The rate of degradation is dependent upon temperature, pH and the presence of metals and oxidizeable organic components. It has been shown that at 20 °C, the decrease in PAA concentration is[2]:

Type of water	pH	Nominal PAA concentration (mg/L)	Measured Concentration (mg/L)		
			Day 0	Day 1	Day 2
Drinking water	6	10	10.3	0.5	0
Seawater	7	10	12.1	0.5	0

Table 1: The decay of peracetic acid at 20 °C in two water matrices.

Addition of COD (chemical oxidant demand), BOD (biological demand) or TSS (total suspended solids) would be expected to increase the degradation rate of the PAA, thereby reducing the longevity of PAA in the environment and its impact on aquatic life. As a result, peracetic acid does not persist long in the environment, unlike disinfection by-products (DBPs) generated by chlorination, and breaks down to the innocuous end products of water and vinegar. No other adverse reactions are known. Also, hydrogen peroxide has a very short lifetime within the environment, and results in the end products of water and oxygen.

The low octanol-water partition coefficient (K_{ow}) of peracetic acid and hydrogen peroxide, 0.3 and 0.4 respectively, indicate bioaccumulation in aquatic organisms is not likely. Additionally, the degradation product acetic acid will not bioaccumulate (K_{ow} = 0.68). The soil - sediment adsorption coefficients are also low. The US EPA June 3, 2010 *Summary for Product Chemistry, Environmental Fate, and Ecotoxicity Data for the Chlorine Registration Review Decision Document*[3] concludes that there is no potential for bioaccumulation or bioconcentration of peracetic acid. As a result, the environmental impact from peracetic acid will be minimal and short-lived

Aquatic Toxicity

The following table was compiled from reference 1 and the references therein. It shows the impact of various peracetic acid formulations on standard aquatic species conducted according to guideline laboratory study protocols.

Species	Duration	Composition (%)			Endpoint EC_{50} or LC_{50}	NOEC	Code of Reliability[d]
	(hours)	PAA	H_2O_2	Acetic Acid	(mg PAA / L)	(mg PAA / L)	
Algae							
Selenastrum capricornutum[a]	120	5.2	20	NS	0.18	0.13	2b
Selenastrum capricornutum[a]	72	18	0.3	NS	< 1.0	< 1.0	2b
Selenastrum capricornutum[a]	72	0.35	7	NS	0.035 – 0.35	0.035	2b
Invertebrates					**Immobility EC_{50}**		
Daphnia magna	48	15	14	28	0.50	0.15	2b
Daphnia magna	48	4.5	27.5	NS	1.1	0.45	2b
Daphnia magna	48	15.5	22	15	0.69	0.16	2b
Daphnia magna	48	5.2	20	NS	0.73	0.56	2b
Daphnia magna	48	18	0.3	NS	< 1.0	< 1.0	2b
Daphnia magna	48	0.35	7	NS	0.035 – 0.350	> 0.0.35	2b
					Lethality LC_{50}		
Crangon crangon[b]	96	12	20	8	15	6.7	2e
Mytilus edulis[b] **embryo**	48	12.5	19	18	0.27	0.13	2e
Crassostrea gigas[b] **embryo**	48	12.5	19	18	0.28	0.13	2e
Fish							
Oncorhynchus mykiss[c]	96	15	14	28	2.0	1.5	2b
Oncorhynchus mykiss[c]	96	15.5	22	15	0.91	0.16	2b
Oncorhynchus mykiss[c]	96	4.5	27.5	NS	1.0	0.45	2b
Oncorhynchus mykiss[c]	96	5.2	20	NS	1.6	0.82	2b
Lepomis macrochirus	96	4.5	27.5	NS	1.2	0.45	2b
Lepomis macrochirus	96	15.5	22	15	3.3	2.7	2b
Lepomis macrochirus	96	5.2	20	NS	1.1	0.47	2b
Brachydanio rerio	96	18	0.3	NS	1.0	< 1.0	2b
Brachydanio rerio	96	0.35	7	NS	~ 0.35	> 0.035	2b
Pleuronectes platessa[b]	96	12	20	8	11	6.7	2e

Table 2: Toxicity of Peracetic Acid Solutions on Aquatic Species

[a] presently known as *Pseudokirchneriella subccapitata* or *Rhaphidocelis subcapitata*
[b] saltwater species
[c] previous name *Salmo gairdneri*
NS – not stated

[d]Klimisch study Code of Reliability:
1 = reliable without restriction
2 = reliable with restrictions: 2b – guideline study with acceptable restrictions; 2e – study well documented, meets generally accepted scientific principles, acceptable for assessment. Reliability 2 (reliable with restrictions) - the concentration of the test substance was not monitored.

OECD Guideline 203 (Fish, Acute Toxicity Test, 2003) - 96 h LC_{50} for rainbow trout (*O. mykiss)* equals 0.53 mg/L

From the laboratory data presented above, a relationship is observed between the size of the organism and its sensitivity to peracetic acid. The smaller the test organism, the greater the sensitivity as compared to larger test organisms. It is suggested the small organisms are more sensitive to peracetic acid because their body-surface to body-weight ratio is high, which enables a higher uptake of PAA per gram body weight. Additionally, longer exposure times leads to more PAA toxicity to the organism. Peracetic acid toxicity to marine - estuarine organisms is found to be lower compared to fresh water species due to its shorter half life (< 1 hour) in the salt water environment.

The US EPA has classified the aquatic toxicity of PAA as highly toxic to algae *(Selenastrum capricornutum)* and aquatic invertebrates *(Daphnia magna)*, and moderately to slightly toxic to fish based on laboratory test results. Peracetic acid is less impactful to aquatic organisms than chlorine (see below).

Aquatic toxicity testing specific to VigorOx® WWT II at Waste Water Treatment Sites

Unlike laboratory studies, where test parameters are tightly controlled to produce dose lethality, peracetic acid dosed in wastewater effluent is rapidly biodegraded by multiple routes, including reaction with organic carbon and metals. In addition, dilution and dispersion into the receiving body of water further reduces the peracetic acid environmental concentration and impact to aquatic organisms as demonstrated. The aquatic toxicity of VigroOx WWT II in actual wastewaters is demonstrated in the following case studies.

1. Seven Day Chronic Static Renewal Definitive

Study performed by Hydrosphere Research for Clay County Utility Authority, Orange Park, FL

Test methods

Species	Dilution Series (%)	Test Method
C.dubia (water flea)	0, 12.5, 25, 50, 75, 100	EPA-821-R-02-013, method 1002.0
P. promelas (fathead minnow)	0, 12.5, 25, 50, 75, 100	EPA-821-R-02-013, method 1000.0

Table 3: Test methods for the chronic testing

Chronic Tests Results

Percent Effluent	*C. dubia*		*P. promelas*	
	Final Survival (%)	Three Brood Totals (Ave # of neonates / female)	Final Survival (%)	Average Dry Weight (mg / fish)
Control	100	34.5	100	0.682
12.5	100	32.8	100	0.613
25	100	32.6	100	0.662
50	100	32.8	100	0.730
75	100	30.1	100	0.774
100	100	28.3	100	0.743
IC_{25}	> 100%		> 100%	

Table 4: Results for the Chronic Test on VigorOx WWT II

Conclusions:

- No chronic toxicity was exhibited for either the water flea or flathead minnow species
- Both species achieved an IC_{25} > 100% effluent

2. Whole Effluent Toxicity Testing

Study performed by North Shore Sanitary District

VigorOx WWT II dosing: ~ 0.8 mg/L
VigorOx WWT II residual ~ 0.04 mg/L

Ceriodaphina dubia acute toxicity
48 hour, juvenile (< 24 hours old)

Treatment	Lab control	6.25% effluent	12.5% effluent	25% effluent	50% effluent	100% effluent
Number of live organisms	20 of 20	20 of 20	20 of 20	20 of 20	20 of 20	20 of 20
Survival (%)	100	100	100	100	100	100
pH	7.2 – 8.1	7.4 – 8.3	7.6 – 8.4	7.7 – 8.4	7.6 – 8.4	7.5 – 8.4
Temp. range (deg C)	24.3 – 24.4	24.1 – 24.2	24.0 – 24.2	24.0 – 24.2	23.7 – 24.1	23.7 – 24.0
Dissolved Oxygen (mg/L)	7.8 – 7.8	7.8 – 7.9	7.6 – 7.8	7.8 – 8.1	7.8 – 8.3	7.8 – 9.0

Table 5: Acute toxicity test results on *C. dubia* with VigorOx WWT II

Fathead Minnow (*Pimephales promelas)* 96 hour acute toxicity
96 hour, larvae (1 – 14 days old)

Treatment	Lab control	6.25% effluent	12.5% effluent	25% effluent	50% effluent	100% effluent
Number of live organisms	20 of 20	20 of 20	20 of 20	20 of 20	20 of 20	20 of 20
Survival (%)	100	100	100	100	100	100
pH	7.2 – 8.4	7.4 – 8.3	7.6 – 8.3	7.7 – 8.3	7.6 – 8.3	7.5 – 8.4
Temp. range (deg C)	23.9 – 25.3	23.8 – 25.4	23.9 – 25.4	23.8 – 25.3	23.9 – 25.3	23.8 – 25.3
Dissolved Oxygen (mg/L)	7.2 – 7.9	7.2 – 8.1	6.9 – 8.0	7.1 – 8.1	6.9 – 8.3	6.8 – 9.0

Table 6: Acute toxicity test results on *P. promelas* with VigorOx WWT II

Conclusions:

- No chronic toxicity was exhibited for either the water flea or flathead minnow species
- Both species achieved an IC_{25} > 100% effluent

Comparison to Chlorine

The US EPA summary report[3] states that chlorine is highly to very highly toxic to all forms of aquatic life. The following table was compiled from reference 3 and the references therein. It shows the impact of chlorine on standard aquatic species conducted according to guideline laboratory study protocols.

Species	% active	Study Duration (hours)	Endpoint EC_{50} or LC_{50}	Toxicity unit	Toxicology Category
Fish					
Oncorhynchus mykiss	29	96	0.2	ppm	Highly toxic
Leponis macrochirus	29	96	0.28	ppm	Highly toxic
Invertebrates					
Daphnia magna	29	48	0.037	ppb	Very highly toxide

Table 7: The Impact of Hypochlorite on Aquatic Toxicity

In general, comparing Table 7 to Table 2, chlorine EC_{50} or LC_{50} values are an order of magnitude lower than those for peracetic acid solutions.

In addition, in the presence of naturally occurring organic matter, chlorine may generate a number of disinfection by-products, including trihalomethanes (such as chloroform and bromodichloromethane) and haloacetic acids. The US EPA currently regulates trihalomethanes in drinking water at 80 ppm and haloacetic acid at 60 ppm due to their potential chronic health effects. Trihalomethanes and haloacetic acids degrade very poorly in the environment, and as a result, can remain within the environment for very long times.

VigorOx WWT II does not generate either trihalomethanes or haloacetic acids, as it does not contain chlorine.

General Conclusions

VigorOx® WWT II peracetic acid provides superior wastewater disinfection without the generation of disinfection by-products (DBPs) such as trihalomethes or haloacetic acids. It is short lived in the environment and breaks down to the innocuous end-products, water and vinegar (acetic acid). Impacts by this product on aquatic fauna will be limited to the initial mixing zone, and due to its degradation rate in the environment and dilution into the receiving body, is not expected to have any significant aquatic toxicity impact beyond this zone.

VigorOx WWT II:

- Has a short lifetime in the environment
- Does not generate chlorinated disinfection by-products
- Generally has an aquatic toxicity an order of magnitude less than chlorine
- Environmental impacts will be limited to the mixing zone due to decomposition and dilution
- Will not bio-accumulate or bio-concentrate

Appendix

1. J. Koivunen, Teinonen-Tanski, H. "Peracetic Acid (PAA) disinfection of primary, secondary and tertiary treated municipal wastewaters". **Water Research** 39, p 4445, 2005.
2. European Centre for Ecotoxicology and Toxicology of Chemicals. JACC #40, "Peracetic Acid (CAS No 79-21-0) and Its Equilibrium Solutions", January 2001.
3. US EPA. "Summary of Product Chemistry, Environmental Fate, and Ecotoxicity Data for the chlorine Registration Review Decision Document", June 3, 2010.