Use of Peracetic Acid as a Wastewater Disinfectant to Eliminate the Formation of Chlorinated Disinfection By-products and Inhibit the Activity of Endocrine Disrupting Compounds

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ABSTRACT

While the chlorination process is the most commonly used disinfection technology for municipal wastewater in the US, formation of harmful chlorinated DBPs has become a concern, and is one of the major drivers for wastewater utilities to consider alternative disinfection technologies. Studies in 1970s found that trihalomethanes (THMs), which include chloroform, dichlorobromomethane, dibromochloromethane and bromoform, can be formed from chlorinated disinfection processes[1]. Since that, numerous and even more toxic DBPs have been identified as the result of the wastewater chlorination process. These include, for example nitrosamines[2] and cyanide[3-4]. Some of these DBPs have been identified as human carcinogens or probable human carcinogens. They could also be toxic to aquatic organisms. Once these DBPs are formed, adding a de-chlorination process will not remove them. Depending on site specific conditions, utilities may have discharge limits on DBPs in their National Pollutant Discharge Elimination System (NPDES) permits. For comparison purpose, the corresponding maximum contaminant levels (MCLs) in accordance to the primary drinking water standard in US are also included in the table. Similar to other water quality parameters, the limit values of DBPs in NPDES permits vary from plant to plant, depending primarily on the dilution factor of the wastewater effluent discharging into the receiving stream, the target sensitive aquatic organisms to be protected, and the use designation of the receiving stream.

In addition to disinfection by-products, endocrine disrupting compounds (EDCs) and pharmacological and personal care products (PPCPs) may have a profound impact on human health and sensitive receiving bodies, such as wetlands, through discharge via wastewaters into the environment. EDCs may enter the environment through wastewater discharge as a result of incomplete metabolism of medicinal compounds, such as synthetic estrogen, or through leaching from waste materials, such as the plasticizer bis-phenol A. Disruption of normal endocrine cycles may cause abnormal growth, reproduction and development in wildlife and potentially cause hormonal dysfunction and cancer in humans.

Recently, peracetic acid (PAA) has gained momentum as an alternative disinfection technology to chlorine[5-7]. Peracetic acid is delivered as an equilibrium solution of peracetic acid, hydrogen peroxide, acetic acid (vinegar) and water, and has been used in a variety of industries as a disinfectant and sterilant. While its use as a wastewater disinfectant has been relatively recent, over the past four years, its effectiveness on controlling bacterial microorganisms is well-known[8]. Upon reaction with bacteria and viruses, natural organic matter, reduced metals and suspended solids, PAA decomposes to oxygen, water and acetic acid. As a result, no

chlorinated by-products are formed. In addition, PAA does not survive long under environmental conditions, so its overall impact on the environment is small, as compared to chlorine.

This study investigates the impact of peracetic acid disinfection of wastewater on the formation of chlorinated disinfection by-products and on the inactivation of endocrine disruptor compounds.

KEYWORDS: peracetic acid, disinfection, endocrine disruptor, DBP, by-product, THM, wetlands restoration

INTRODUCTION

Endocrine disruptor compounds (EDC) are a class of chemicals with the ability to interfere with the endocrine (hormonal) processes in mammals. Any hormonal process in the body can potentially be impacted by endocrine disruptors . As a result, EDs have been linked to many health related issues, such as: learning disabilities, brain and cognitive development problems, breast cancer, deformations of limbs, feminizing of males and masculinizing of females, prostate and other cancers. While the impact of EDCs on health are not typically short term (like toxins), long term effects may be drastic.

EDCs are found in many consumer and industrial products and various pharmaceuticals. Disposal of such products may lead to EDCs migrating into the groundwater and drinking supplies, or by passing directly through the body, contaminating wastewater. Due to the potential of relatively low concentrations (< 1 ppb) of EDCs having an impact on hormonal processes, and the relatively poor efficiency of treatment processes in removing EDCs from the water supply, there is significant potential of EDCs in wastewater having a negative impact on sensitive receiving bodies, such as wetlands, creeks and rivers.

This preliminary research shows the potential for peracetic acid (PAA) to deactivate EDCs. Thus, application of PAA as a disinfection technology for wastewaters may provide the additional benefit of deactivating EDCs, reducing the potential impact of wastewaters on sensitive receiving bodies and on human health. In addition, as PAA is not a chlorine based technology, it has been demonstrated that conversion of chlorination to PAA disinfection eliminates the generation of chlorinated disinfection by-products.

METHOD

ED Deactivation Bench Test Procedure

The deactivation of EDCs by PAA was investigated at the bench scale, utilizing stirred jars with spiked distilled (DI) water. Three endocrine disruptors, representing broad categories of EDCs, were used as the target compounds for the study. These included (see Figure 1): 17-beta-estradiol (**E2**, a human sex hormone and steroid; it is the most referenced compound in research and papers concerning EDCs and is the primary female sex hormone), 17-alpha-ethinyl estradiol (**EE2**, a chemical derivative of estradiol; a major ingredient in hormonal contraceptive

formulations; due to its prevalence, it substantially contributes to the EDC concerns in municipal wastewater) and bisphenol-A (**BPA**, a synthetic chemical that structurally resembles EDCs that is commonly found in plastics; it can block endocrine receptors and disrupt an organism's normal endocrine activities).

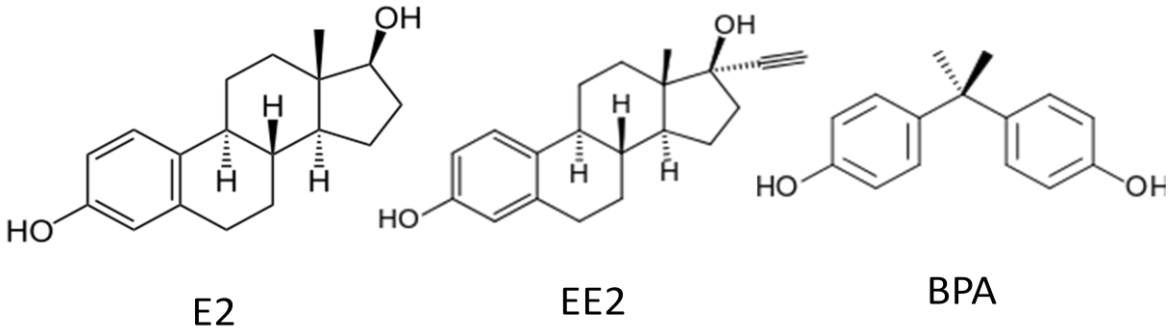

Figure 1 The Three Edocrine Disruptor Compounds used in this Study

Each jar was filled with one liter of DI water and spiked with concentrations of ED per Table 1.

ED	**ED Spike (µg/L)**
E2	5
EE2	9
BPA	21

Table 1: EDC concentrations used during the bench test.

Each "spike" run was also dosed with PAA[9] at one of three concentrations: 1, 5 and 10 ppm. Samples were pulled for analysis at 10 and 20 minutes of contact time. A blank containing distilled water was run for comparison.

For analysis, EDC was extracted from the test solution using solid phase extraction (SPE) at Tulane[10]. Endocrine activity was assessed using a reporter gene assay method[11] and was performed at Xavier University. The purpose of this method was to evaluate the estrogen activity of the compounds before and after PAA treatment. The assay utilizes a T47D[12] derivative that has been stably transfected with the reporter gene. Thus, the T47D ERE luc cell line expresses the endogenous estrogen receptors of T47D and contains an exogenous estrogen responsive reporter gene (luciferase). Therefore, the estrogen specific transcription activity of a chemical is directly related to the luciferase measured in the lysate of treated T47D ERE luc cells. The T47D ERE luc assay procedure presented here is a modified version of published methods[12,13]. All tissue culture materials, such as media and sera, are commercially available.

The T47D ERE luc cells were seeded into 96 well plates and fed media containing treatment compounds. After two days of cultivation, the cell lysates were harvested and evaluated for luciferase activity. The assay monitors estrogen activity, which is quantified using a standard equivalent. The equivalent is a unit for reporting estrogenicity and it is based on the strength and activity of a standard chemical used in the assay. The EDC assays applied in this project use estradiol (E2) as the standard chemical, meaning all recorded activity is based off an estradiol standard. This activity can be measured as a percentage of estrogen activity, with 10^{-10} M

estradiol as 100%. This method does not measure the actual concentration of ED in the sample, but rather the endocrine disrupting capacity of the sample. As a result, a decrease in signal response corresponds to a decrease in the endocrine disruption of that particular compound compared to the reference estradiol.

RESULTS

ED Deactivation Bench Test Results

Results for the control samples demonstrated that there was neither a positive or negative change in EDC activity when dosed with PAA. The PAA did not impact the assessment of EDC reactivation at dosages from 1-ppm to 10-ppm, nor did it exhibit activity of its own. For the lose EDC spiked samples, the following results were observed for E2, EE2 and BPA:

PAA Dosage (ppm)	E2 Activity				
	0 minutes	10 minutes		20 minutes	
	Control (ng/L as E2 Equivalent)	Results (ng/L as E2 Equivalent)	Reduction Percentage	Results (ng/L as E2 Equivalent)	Reduction Percentage
1	94.6	11.9	87%	4.2	96%
5	94.6	19.5	79%	14.5	85%
10	94.6	7.9	92%	9.8	90%

Table 2: PAA Impact on E2 Activity at 5 µg/L concentration

Dosage (ppm)	EE2 Activity				
	0 minutes	10 minutes		20 minutes	
	Control (ng/L as E2 Equivalent)	Results (ng/L as E2 Equivalent)	Reduction Percentage	Results (ng/L as E2 Equivalent)	Reduction Percentage
1	89.0	11.1	88%	2.2	98%
5	89.0	19.0	79%	7.3	92%
10	89.0	2.7	97%	18.1	80%

Table 3: PAA Impact on EE2 Activity at 9 µg/L concentration

Dosage (ppm)	Activity				
	0 minutes	10 minutes		20 minutes	
	Control (ng/L as E2 Equivalent)	Results (ng/L as E2 Equivalent)	Reduction Percentage	Results (ng/L as E2 Equivalent)	Reduction Percentage
1	0.72	0.05	94%	0.44	39%
5	0.72	0.57	21%	-0.02	99.9%
10	0.72	0.11	84%	-0.05	99.9%

Table 4: PAA Impact on BPA Activity at 21 µg/L concentration

As can be seen, peracetic acid significantly reduced the endocrine disrupting capabilities of these three EDCs. Typically greater than a 90% reduction in endocrine activity was observed after 20

minutes of contact time. There is some scatter in the data for BPA, and this may be due to the fact that these BPA concentrations are near the detection limit of this methodology for BPA.

PAA Deactivation of EDs in an Actual Wastewater Treatment Facility

The effectiveness of PAA) in deactiving EDCs in actual wastewaters was investigated using the effluent from a WWTP located in Louisiana. The outflow from this plant is being considered for discharged in the surrounding wetlands to help restore the wetlands following the impact of Hurricane Katrina. The plant currently uses hypochlorite as its disinfection technology, and as a result cannot currently discharge its wastewater into the wetlands. The plant is investing VigorOx WWT II as an alternative technology to aid in protecting sensitive species and allow for discharge into the wetlands.

Testing was performed using a disinfection pilot reactor that was located near the disinfection contact chamber of the WWTP. The primary goal of the addition of PAA is to meet the plant's regulatory bacterial requirement of less than 200 cfu / 100 mL of fecal coliforms. During the pilot testing period, influent fecal counts ranged from 330 to 4950 cfu / 100 mL. A PAA concentration of 2 mg/L was utilized, and was able to exceed the 200 cfu / 100 mL maximum after 7.5 minutes of contact time. 2 – 3 log reductions in total coliform were measured after 19 minutes of contact time.

Background EDC activity was measured, as per the extraction procedure (performed at Tulane University) and receptor gene method (performed at Xavier University) as described above, for the secondary effluent wastewater prior to chlorine disinfection and for effluent wastewater that had undergone chorination. The results are shown below (N = number of samples measured).

Sample	**Activity (ng/L as E2 Equivalent)**
Average Background [Secondary Effluent] (Oct-8 to Oct-10)	11.7 (N=6) Range (1 – 40)
Chlorinated Effluent	29.1 (N=2)
Chlorination Effect	149% Increase in ED activity

Table 5: Average Estrogenicity of the Wastewater Before and After Chlorination

For assessment of the PAA impact on the EDCs, samples were pulled from the pilot reactor through sampling taps prior to addition of PAA, and at locations representing 15 and 20 minutes of PAA contact time. Six total samples were assessed for EDC activity (3 consecutive days on the first week, and 3 consecutive days on the second week). The average estrogenicity of the wastewater following PAA treatment for all samples is shown in Table 6.

Chlorination		PAA Treatment		Comparison of PAA Deactivation to Chlorination
Activity	% Increase	Activity	% Reduction	
29.1	149	8.2	30	179% reduction in EDC activity when PAA replaces chlorination disinfection

Table 6: Average Estrogenicity of PAA Treated Wastewater Compared to Chlorinated Wastewater

Application of PAA was shown to have an overall 30% reduction in the wastewater endocrine activity; whereas chlorination was shown to increase endocrine activity by 149% compared to the background values. This was achieved with a PAA dose designed to meet the bacterial reduction requirements.

Prevention of Disinfection By-Product Formation

Because PAA is not a chlorine based disinfection chemistry, it will not form DBPs, such as halogenated methanes, chlorinated acids or cyanides. However, chlorination may form these toxic compounds, even if a de-chlorination step has been add to the treatment process, as de-chlorination will not remove DPBs.

Two examples from wastewater treatment plants in Florida that demonstrate the benefit of PAA over chlorine as a wastewater disinfectant with respect to the formation of disinfection by-products (DPBs) are discussed below. For the first example, after a comprehensive study with bench scale testing, full scale trialing including cost comparison among different disinfection alternatives (including ozone and UV light disinfection), PAA was found to be the most cost effective alternative to replace their chlorination / de-chlorination system to eliminate trihalomethane (THM)formation and distribution into the environment. The average dose of PAA during the trial was 1.5 mg PAA /L. The average dose of chlorine was 7.0 mg/L (as Cl_2), which provided similar disinfection efficiency as the PAA against fecal coliform and enterococci.

Results indicating the formation of DBPs during the full scale trial, comparing PAA and chlorine / de-chlorination are shown in Table 7. As can be seen from the table, the addition of PAA to the wastewater did not form any THMs; whereas the addition of chlorine yielded an increase in the concentration of THMs.

DBPs	Before Disinfection	After Chlorination	After VigorOx WWT II
Dichlorobromomethane (ppb)	0.6	56.9	0.6
Dibromochloromethane (ppb)	0.8	72.7	0.8
Chloroform (ppb)	0.6	21.6	0.6
Bromoform (ppb)	0.6	19.6	0.6

Table 7. DBP Monitored Results during Full Scale Trial

The second example, from a bench scale study, showed similar results. The DBP analyses from the test are shown in Table 3, demonstrating the benefit of using PAA to address DBP formation.

DBPs	Untreated Samples	PAA-Treated Sample			Chlorine Treated Sample[a]	
		2 mg/L (PAA)	3 mg/L (PAA)	5 mg/L (PAA)	5 mg/L (Cl_2)	10 mg/L (Cl_2)
Bromoform (ppb)[b]	<10	<10	<10	<10	30	70
Dibromochloromethane (ppb)[b]	<5	<5	<5	<5	8.8	21

Table 8. DBP Results during Bench Scale Test (contact time 30 minutes)

a: These chlorine doses provided similar disinfection efficiency as that of 2 mg/L (PAA) and 3 mg/L (PAA) against fecal coliform and enterococci for the wastewater sample
b: Permit limits are 360 ppb for bromoform and 34 ppb for dibromochloromethane.

CONCLUSIONS

Peracetic Acid was shown to reduce the estrogenicity of three major endocrine disrupting compounds: E2, EE2 and BPA at both the bench scale and on actual wastewaters. EDC activity reduction was achieved in the wastewater at concentrations designed to meet the plant's permit requirement for bacterial control. As a result, the application of PAA to control bacteria may provide the additional benefit of reducing the impact of EDCs on the environment. Whereas chlorination potentially serves to increase the EDC activity of wastewater, the inactivation of EDCs by PAA makes PAA a suitable alternative disinfection technology for WWTPs with outflows into sensitive receiving bodies.

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