GUIDANCE

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Advanced Oxidation Processes (AOP) for the Oxidation of Microcontaminants

Currently, Oklahoma Department of Environmental Quality (DEQ) does not have official regulations addressing advanced oxidation processes (AOP). This guidance document is intended to provide general design information to assist the utility in the investigation and use of this technology. This document is intended to be used for guidance purposes only. The responsible engineer and the sponsoring utility are ultimately responsible for the proper selection and implementation of the AOP technology. The DEQ has a Variance Committee (OAC:656-3-7) to review processes or equipment not specifically covered by the standards in Chapter 656 provided the permittee requests a variance. This document is intended to provide an outline for the utility to prepare the technology document and backup information for DEQ review of the variance request.

Definitions

Hydroxyl radical – (OH·), the highly reactive, neutral form of the hydroxide ion (OH⁻)
Microcontaminant – An impurity, in this case in water, that is microscopic in size

Abbreviations

AOP – Advanced oxidation processes
DEQ – Department of Environmental Quality
DV – Design value
MIB – Methylisoborneol
SD – Standard deviation
UV – Ultraviolet

References
See citations

Applicable OAC Sections
None

Advanced Oxidation Processes (AOP)

In general, AOP is the in-situ generation of radical species for oxidation and ultimately the destruction of a wide range of microcontaminants in the process stream. AOP can be effectively used to remove potentially harmful microcontaminants that may pose an exposure risk for humans through Category 1 water reuse.

As show in Table 1, the hydroxyl radical has the highest oxidation potential of various oxidants.

Table 1 – Electrochemical Oxidation Potential (EOP) for Common Oxidants	
Oxidant	**(EOP), V**
Hydroxyl Radical	+2.80
Ozone	+2.07
Hydrogen Peroxide	+1.78
Permanganate	+1.67
Chlorine Dioxide	+1.50
Chlorine (Metcalf et al. 2003)	+1.36

The following Table 2 compares the reaction rate for some selected contaminants with ozone versus hydroxyl radical.

Table 2 – Reaction Rate Comparison between Ozone and Hydroxyl Radical ($M^{-1}S^{-1}$)		
Contaminant	Ozone	Hydroxyl Radical ($M^{-1}S^{-1}$)
Phenol	1300	$1x10^7 - 1x10^{10}$
Naphthalene	3000	$1x10^7 - 1x10^{10}$
Benzene	2	$1x10^7 - 1x10^{10}$
PCE	0.1	$1x10^7 - 1x10^{10}$
TCE	10-20	$1x10^7 - 1x10^{10}$
Atrazine	10-20	$1x10^7 - 1x10^{10}$

Hydroxyl radicals are nonselective oxidants that very rapidly degrade microcontaminants. Table 2 – Reaction Rate Comparison presents the reaction of different species with ozone and hydroxyl radicals. As demonstrated above the hydroxyl radical is a non-selective oxidant. It has a fairly uniform rate of reaction and can oxidize at an extremely fast rate for almost all microcontaniments found in reuse water. (AWWA 1999)

Common technologies for the production of hydroxyl radicals or other radical species include the following:

**Hydrogen Peroxide/Ozone (H_2O_2/O_3)**

The reaction chemistry is presented below. – Ozone and Hydrogen Peroxide to produce the hydroxyl radical. (AWWA 1999)

$$H_2O_2 = HO_2^- + H_2$$
$$HO_2^- + O_3 \rightarrow OH\cdot + O_2^- + O_2$$
(AWWA 1999)
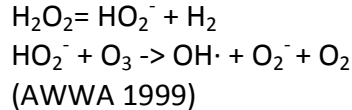
As powerful an oxidant as ozone is, the hydroxyl radical has a greater EOP. (Metcalf et al. 2003) This is one of the reasons the hydroxyl radical is a non-selective species with extremely high reactive rates.

UV/ Hydrogen peroxide

Ultraviolet (UV) light is in the high-energy end of the light spectrum with wavelength less than the visible light (400 nm) but greater than that of x-rays (100 nm). A standard UV disinfection reactor will not remove most microcontaminants. Currently, there is an AOP that utilizes UV light and hydrogen peroxide to produce the hydroxyl radical. The process in which the hydroxyl radical is formed is as follows:

$$H_2O_2 + UV \rightarrow 2\ OH\cdot$$
(AWWA 2011)
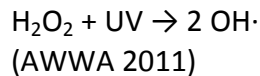
Once the hydroxyl radical has been propagated, it will auto decompose hydrogen peroxide to produce additional hydroxyl radicals in the following manner:

$$H_2O_2 + OH\cdot \rightarrow H_2O + HO_2\cdot$$
$$HO_2\cdot + H_2O_2 \rightarrow H_2O + O_2 + OH\cdot$$
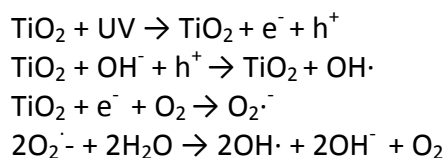(AWWA 2011)
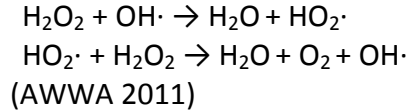
UV/ Chlorine

Research has recently been conducted into the feasibility and ability of UV/ HOCl (Cl$_2$) as an AOP to degrade microcontaminants. Hydroxyl radical is produced from photolysis of hypochlorite (OCl$^-$) and hypochlorous acid (HOCl) at wavelengths less than 400 nm. The process in which the hydroxyl radical is formed is as follows:

$$HOCl + UV \rightarrow OH\cdot + Cl\cdot$$
$$OCl^- + UV \rightarrow O\cdot^- + Cl\cdot$$
$$O\cdot^- + H_2O \rightarrow OH\cdot + OH^-$$
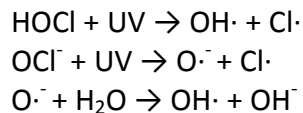
The research indicates that this type of AOP is successful at degrading microcontaminants and has a lower operational cost than other forms of AOP. (Sichel et al. 2011) (Zhao et al. 2011)

UV/ Titanium Dioxide

TiO_2 absorbs UV energy to promote electrons from the valence band to the conduction band. This action generates electron–hole pairs (e^-/h^+) where positive holes can directly oxidize contaminants and hydroxide, while electrons mainly reduce molecular oxygen to superoxide radical anions. The superoxide radical anion development will lead to production of the hydroxyl radical. The process in which the hydroxyl radical is formed is as follows:

$$TiO_2 + UV \rightarrow TiO_2 + e^- + h^+$$
$$TiO_2 + OH^- + h^+ \rightarrow TiO_2 + OH\cdot$$
$$TiO_2 + e^- + O_2 \rightarrow O_2\cdot^-$$
$$2O_2\cdot^- + 2H_2O \rightarrow 2OH\cdot + 2OH^- + O_2$$

(Cheng et al. 2016) (Vallejo et al. 2016)

Target Compounds

The performance of the AOP system shall be based on an individual or combination of the design surrogate performance for the following compound(s) as a minimum:

1. 1,4-Dioxane – Minimum 0.5 log (67%) removal of full-scale demonstrated performance
2. Methylisoborneol (MIB) – Minimum 1.0 log (90%) removal of full-scale demonstrated performance

The surrogate will be used to evaluate the performance of the following contaminants:

1.	Caffeine	26.	Sulfadimethozine
2.	1-Butanol	27.	Sulfamerazine
3.	2-Methoxyethanol	28.	Sulfamethazine
4.	Butylated hydroxyanisole	29.	Sulfathiazol
5.	Estradiol (17-beta estradiol)	30.	Sulfamethoxazole
6.	17alpha-estradiol	31.	Sulfametozazol
7.	Estrone	32.	Trimethoprim
8.	Estriol	33.	Bezafibrate
9.	Equilenin	34.	Carbamazepine
10.	Equilin	35.	Iopromide
11.	Testosterone	36.	Codein
12.	Androstenedione	37.	Ibuprofen
13.	Ethynylestradiol	38.	Acetylsalicylic acid
14.	Mestranol	39.	Diclofenac
15.	Acetaminophen (Paracetamol)	40.	Fenoprofen
16.	Hydrocodone	41.	Diazepam
17.	Trimethoprim	42.	Diclofenac
18.	Erythromycin	43.	Oxybenzone
19.	Roxithromycin	44.	Bisphenol A
20.	Amoxiline	45.	Phthalate
21.	Metronidazol		
22.	Amoxicillin		
23.	Clarithromycin		
24.	Carbadox		
25.	Sulfachlorpyridazine		

(Esplugas et al. 2007)

The manufacturer shall be required to provide a minimum one (1) year after start up performance warranty. The performance warranty shall meet the desired surrogate performance during challenge testing during the initial installation and eleven (11) months after installation. Challenge testing shall be completed over minimum, average, and maximum design flows and for a period not less than two (2) separate eight (8) hour periods. No less than three (3) surrogate samples shall be taken over the challenge testing period for a total of six (6) samples. Identified water quality indicator parameters shall be monitored at the same interval. The AOP system shall be operated by facility staff during all challenge testing. The manufacturer shall not operate the system at any time during challenge testing.

Approaches

The following is a generalized guidance approach to AOP selection and implementation
1. Select AOP technologies for evaluation
2. Obtain pilot protocol approval from DEQ

3. Conduct pilot testing
    a. Identify surrogate(s)
    b. Identify indicator parameters
    c. Identify statistics
    d. Conduct testing
    e. Conduct desktop model to confirm removal performance
4. Obtain Engineering Report approval from DEQ
5. Perform design of full-scale installation
    a. Include sufficient design correction for pilot to full-scale
6. Obtain Permit to Construct from DEQ
7. Construct full-scale AOP system
    a. Initial site specific challenge testing
    b. Submit results to DEQ
    c. Ten (10) month site specific challenge testing
    d. Submit results to DEQ
8. Obtain final AOP installation approval or take corrective actions

Pilot Testing

Pilot testing shall be completed in the proposed process locations. All pre-treatment or upstream processes must produce site specific water to be used for evaluation. The site specific parameters may be based on individual or a combination of 1,4-Dioxane and MIB. The full-scale design must be able to achieve the desired removal with 20% safety factor.

The user must describe and justify in the engineering report the following approvable indicator monitoring parameters:

1. Water quality monitoring parameters (UVT, DOC, etc.).
2. Dose-Response Process Performance (applied UV/ chemical dosage, chemical dosage, etc.).
3. Economic performance (electricity, consumables, maintenance, operational, etc.)

Pilot testing is important to consider when using AOP technologies. It is ultimately up to the user of the guidance document to develop a sufficient data set that is statistically representative of the variable water quality that can be experienced at wastewater treatment facilities. Once the data set has been developed, the user must select a 95 percent conservative confidence interval water quality design value (DV) using 1.96 times the standard deviation (SD) plus or minus the mean(x) (x+/-1.96(SD) = DV).

The pilot testing will ultimately lead to a site specific calibrated dose-response curve (Point Source Summation Method) or equivalent desktop model to be used to develop a relationship between the surrogate(s) and the contaminants of concern. The dose-response must show the

relationship between the surrogate and single, double, and triple bond contaminants of concern from the list identified in this document. The user must select at least three (3) single, three (3) double, and three (3) triple bond contaminants that each represent high, medium, and low molecular weights.

Full-scale Challenge Testing

The initial and ten (10) month full-scale challenge testing will be used to determine the overall performance of the AOP system. It is up to the user to select which compound will be used for full-scale challenge testing but at no time will any hazardous chemicals be allowed to be discharged to a public water supply or to the environment. The full-scale installation must meet the desired removal defined within this document. Conduct sufficient testing to confirm economic factors.

These post installation audits can be used to create more efficient designs for future installations or provide feedback to the regulating authority.

Finalized user-defined indicator monitoring parameters shall be published and submitted to DEQ.

Monitor full-scale water quality indicators and Dose-Response Process Performance parameters shall be recorded daily.

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