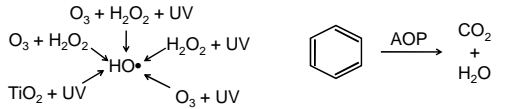


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## Advanced Oxidation Processes

Advanced Oxidation Processes (AOPs) are powerful tools that can be used to completely remove organic contaminants from water.

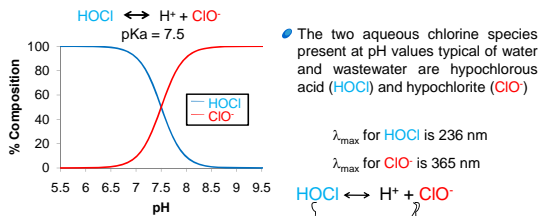


- AOPs work by combining chemical oxidants and UV light to generate hydroxyl radical (HO•), an extremely reactive oxidant species
- Hydroxyl radicals can fully mineralize organics during AOPs
- Traditional AOPs use hydrogen peroxide and/or ozone with 254 nm UV light
- While extremely useful in providing clean water through the removal of organic micro contaminants, AOPs are generally costly both in terms of chemical use as well as energy use (UV lamps)

## Use of Aqueous Chlorine in AOPs

Aqueous chlorine can also generate hydroxyl radicals during UV photolysis. This SBIR project aims to study, compare, and commercialize this AOP.

- Due to the acid/base disproportionation of hypochlorous acid, the photolysis of aqueous chlorine is highly dependant on solution pH

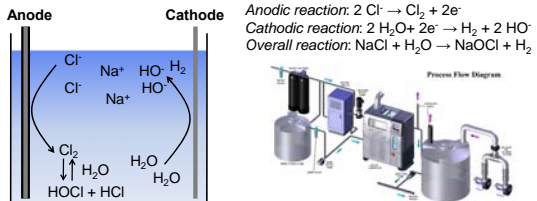


- Photolysis of both common forms of aqueous chlorine result in hydroxyl radicals, chlorine radicals, and other reactive species
- The quantum yield of hydroxyl radical generation is higher for aqueous chlorine than hydrogen peroxide

Feng, Y.; Smith, D. W.; Bolton, J. R., Jr. Environ. Eng. Sci. 2007, 6, 277-284

## On-Site Generation of Chlorine

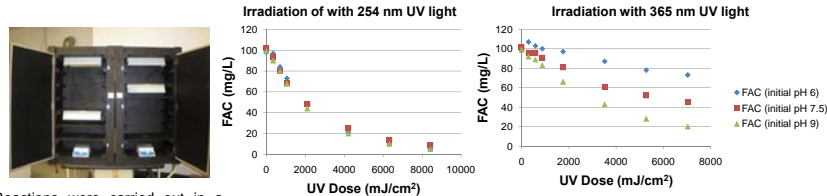
MIOX Corporation specializes in the electrochemical on-site generation of aqueous chlorine-based solutions



- By varying design and operational parameters during electrolysis, either hypochlorite or MIOX's unique Mixed Oxidant Solution (MOS), which is primarily hypochlorite but contains other oxidant species, can be generated.

## Photolysis of Aqueous Chlorine Solutions

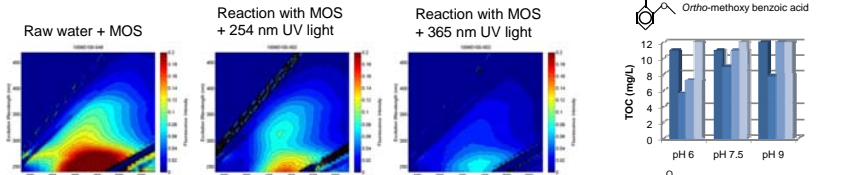
Photolysis reactions were conducted with both bleach and MOS over a range of initial free available chlorine (FAC) and solution pH conditions with both 254 and 365 nm UV light



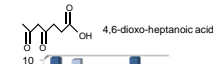
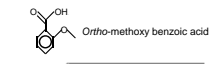
- Reactions were carried out in a custom built pseudo-collimated beam light cabinet with adjustable UV source and intensity
- Initial reaction solution pH had a greater impact on 365 nm reactions
- Substantial amounts of H<sup>+</sup> ions were generated during photolysis
- MOS and bleach behaved similarly during photolysis

## Removal of Organics During Aqueous Chlorine AOPs

Several tests examined the impact of aqueous chlorine-based AOPs on both natural organic matter (NOM) and synthetic chemicals in water

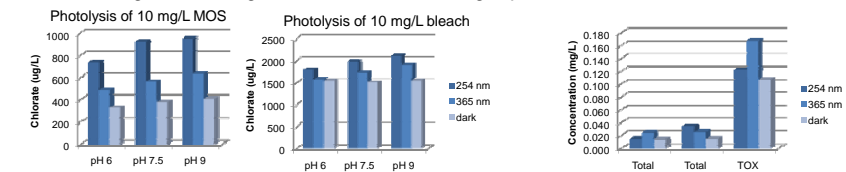


- Fluorescence Excitation-Emission Matrix images of Colorado River Water NOM demonstrate that aqueous chlorine based AOPs can alter the structure of NOM
- Aqueous chlorine-based AOPs could remove a number of common organic contaminants
- Irradiation with 254 nm UV light was more effective than 365 nm UV light
- Reactions performed at lower pH gave higher removal rates
- In all cases, MOS and bleach produced similar results
- High levels of tris (2-carboxyethyl) phosphine (TCEP) removal were observed
- TOC analysis indicated partial mineralization of the organics



## Disinfection Byproduct (DBP) Formation

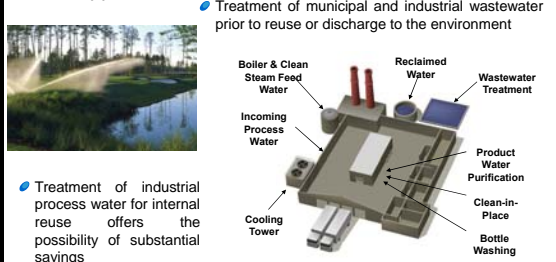
Levels of inorganic and organic DBPs formed during aqueous chlorine AOPs were measured



- UV photolysis leads to the production of chlorate (ClO<sub>3</sub><sup>-</sup>)
- Perchlorate production was undetectable at lower initial chlorine concentrations
- ClO<sub>2</sub><sup>-</sup> production levels were a function of UV wavelength and solution pH
- Lower concentrations of ClO<sub>2</sub><sup>-</sup> are expected to form in the presence of organics
- Organic DBP formation under UV irradiation was comparable to reactions between NOM and chlorine in the dark

## Reuse Applications for Aqueous Chlorine AOPs

Aqueous chlorine-based AOPs may provide an economical alternative to traditional AOPs with numerous reuse applications

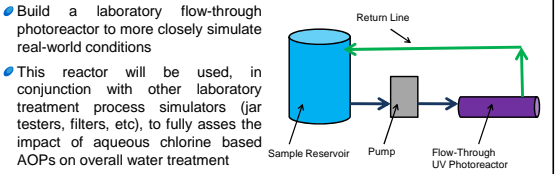


- Treatment of municipal and industrial wastewater prior to reuse or discharge to the environment
- Treatment of industrial process water for internal reuse offers the possibility of substantial savings
- Aqueous chlorine-based AOPs offer several potential advantages over traditional AOPs, including less energy usage, decreased chemical costs, and the ability to leave a chlorine residual if needed in a given application

## Continuing Research

The project team has submitted an NSF SBIR Phase II proposal to further study aqueous chlorine-based AOPs

- Initial testing will utilize the bench top pseudo-collimated beam reactor to further assess several aspects of the chlorine-based AOPs including:
  1. Optimization of chlorine and UV doses needed to remove and mineralize a variety of common organic contaminants and
  2. Competitive assessment of aqueous chlorine-based AOPs with AOPs using hydrogen peroxide and ozone
- Evaluation of disinfection capability: Several model organisms (bacteria spores, oocysts, and viruses) will be exposed to combinations of chlorine and UV light to determine if synergistic inactivation resulting from the formation of reactive oxygen species is possible



- Build a laboratory flow-through photoreactor to more closely simulate real-world conditions
- This reactor will be used, in conjunction with other laboratory treatment process simulators (jar testers, filters, etc), to fully assess the impact of aqueous chlorine based AOPs on overall water treatment

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