Research on Chlorine Dioxide Gas Technology at Purdue University

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Outline

- Chlorine dioxide (ClO_2)
- ClO_2 research at Purdue
- Food Processing
- Food Safety
- Food Security
- Research on basic science
- Technology commercialization

Chlorine dioxide

Chlorine Dioxide (ClO_2)

- Properties

- Boiling point	11°C
- Solubility limit, aqueous, 25°C, 34.5 mm Hg	~ 3 g/L
- Solubility limit, aqueous, 0-5°C, 70-100mm Hg	~ 20 g/L
- Explosion velocity in air	50 m/s
- Explosion in air	> 10% or >130°C

- Broad and high biocidal effectiveness (bacteria, viruses, bacterial spores, and algae)

Chlorine Dioxide (ClO_2)

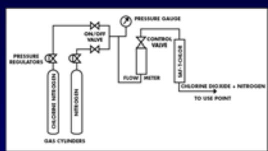
- Advantages over chlorine
  - 2.5 times oxidation capacity
  - Lack of harmful chloramine and THMs
  - Lower dosage
  - Lack of odor and taste (Elphick, 1998)
- Advantages over ozone
  - Lower dosage
  - More stable and higher generation yield
  - Higher solubility in water

Uses of ClO_2 in Food Industry

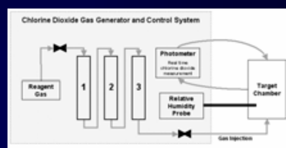
- Aqueous ClO_2
  - 1995 Approved by FDA for poultry processing water
  - 1998 Approved by FDA for washing produce (<3ppm)
- Gaseous ClO_2
  - 1996 Decontamination of food contact surfaces (aseptic juice storage tanks) and produce surfaces
  - 2001 Approved by EPA for emergency use in anthrax decontamination

Methods to generate ClO_2 gas

$2\ NaClO_2 + Cl_2 \rightarrow 2\ ClO_2 + 2\ NaCl$



CDG Technology, Inc.



ClorDiSys Solutions, Inc.

ClO_2 gas monitor systems

- Electrochemical gas detector

  Interscan Corp., Chatsworth, CA

- UV spectrophotometric detector

  Abs. max. at 359 nm

ClorDisys Solution, Inc.

ClO_2 research at Purdue

Research Grants

1996- Sterilization of bulk orange juice storage tanks using chlorine dioxide gas (Enerfab and Tropicana)

1997– 2000 Inactivation of microorganisms in minimally processed and refrigerated fruits and vegetables by ozone and chlorine dioxide gas (USDA)

2000-2003 Effect of different inoculation methods on determination of the efficacy of chlorine dioxide gas and chlorinated water to decontaminate produce (FDA)

Research Grants

2000-2005 Novel methods to sanitize fruits and vegetables using chlorine dioxide gas (USDA)

2002-2004 Efficacy of chlorine dioxide gas in reducing pathogens on meat products and poultry and its effects on meat quality (USDA)

2003-2004 Mechanisms of inactivation of bacteria and spores by chlorine dioxide (NSF)

2004-2007 Improving the safety of fresh fruits and vegetables with chlorine dioxide gas using a miniaturized industrial-size tunnel system (USDA)

Food Processing

- Sterilize food-contact surfaces

Sterilizing Aseptic Juice Storage Tank

- **Background**

  - Current sanitizer:

    25ppm iodine solution

  - 1 million gallon orange juice storage tanks – takes one week

  - > 6 log reduction of spoilage isolates from orange juice after 10 mg/l ClO2 gas, 30 min, > 90% RH, 9-28°C

Treatment conditions leading to complete inactivation on epoxy surfaces

Microbes	*Initial levels (log cfu)*	*ClO_2 gas sterilization conditions*
Lactobacillus buchneri	6.6	6 mg/l – 30 min, 25-26°C, 87% RH
	6.8	8 mg/l – 30 min, 10-11°C, 89% RH
Lactobacillus mesenteroides	6.4	8 mg/l – 30 min, 27°C, 75% RH
	6.5	8 mg/l – 30 min, 11°C, 93% RH
Candida spp. and *Saccharomyces cerevisiae*	5.6	10 mg/l –10 min, 26°C, 91% RH
	5.6	8 mg/l – 30 min, 11°C, 89% RH
Eurotium spp. and *Penicillium spp*	5.4	10 mg/l –10 min, 26°C, 91% RH
	5.4	8 mg/l – 30 min, 11°C, 89% RH

Sterilizing aseptic juice storage tank

A pilot scale chlorine dioxide gas treatment system for juice storage tank

Food Safety

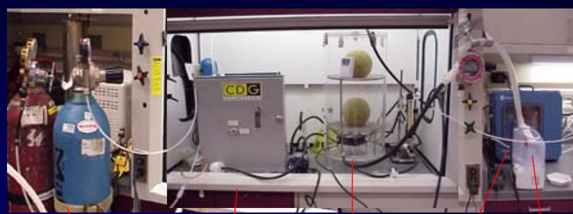
- Fruits and vegetables (focus)
- Meat surfaces
- Sprout seeds
- Almonds

Background

- **Current pathogen reduction method**
  - Washing with chlorinated water (50-200ppm chlorine)
  - Other aqueous sanitizers: H_2O_2, peroxyacetic acid, trisodium phosphate, ozone, chlorine dioxide, and their combinations
- **Limitations**
  - Less than 2 log reductions (Beuchat, 1992 and 1999; Cherry, 1999)

Batch ClO_2 gas treatment system

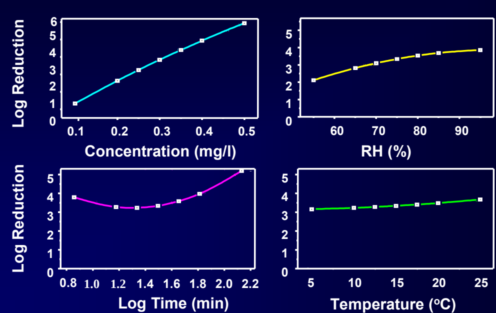
Continuous ClO_2 gas treatment **system**



Produce Overview : Efficacy of ClO_2 Gas

Microorganisms	Treatment conditions	Log Reduction	Surfaces
E. coli O157:H7 *L. monocytogenes*	0.6 mg/l - 30 min	7.3 6.3	Green peppers (Han et al. 2000, 2001)
E. coli O157:H7 *L. monocytogenes*	4.0 mg/l – 10 min 4.8 mg/l – 10 min	5.5 4.8	Apples (Du et al. 2002a and b)
E. coli O157:H7 *L. monocytogenes*	0.6 mg/l –15 min	5.6	Strawberries (Han and Linton 2002)
Salmonella spp. *E. coli* O157:H7	0.5-1 mg/l –10 min	3-5	Cantaloupes (Han et al.)
L. monocytogenes	0.2 mg/l - 30 min	2	Lettuce (Dlima and Linton 2002)

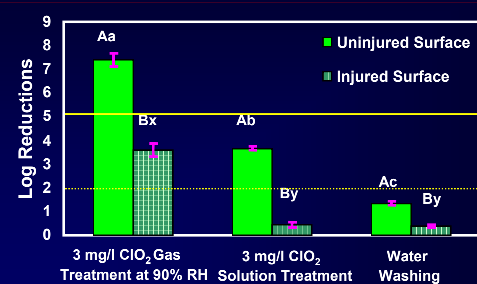
Factor Effects on ClO_2 gas treatment



Concentration > Time > RH > Temperature (p<0.01)

(Han et al., 2001)

Aqueous and Gaseous ClO_2 vs. Washing for Reducing *L. monocytogenes* on Peppers

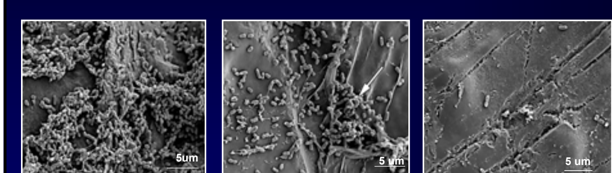


- All the treatments were for 10 min at 20°C.

(Han et al., 2001)

Washing vs. ClO_2 Gas Treatment *E. coli* O157:H7 on Injured Green Peppers

Injured peppers | Washing | 1.2 mg/l ClO_2 gas



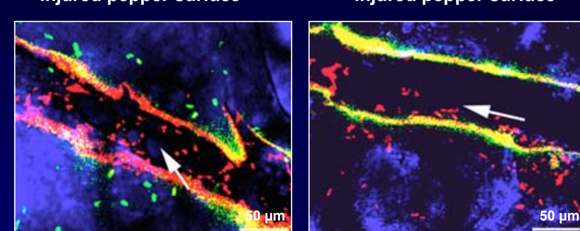
7.9 log cfu | 6.4 log cfu | 1.5 log cfu

1.5 log reduction | 6.4 log reduction

(Han et al., 2000)

Confocal Laser Scanning Microscopy for *L. monocytogenes* Inactivation by ClO_2 Gas

Injured pepper surface | Injured pepper surface



0.3 mg/l ClO_2 gas treatment for 10 min at 20°C and 90% RH

3 mg/l ClO_2 gas treatment for 10 min at 20°C and 90% RH

(Han et al., 2001)

Treatment of green peppers

Total aerobic plate count, residual ClO_2 and residual chlorite after a continuous 200 ppm ClO_2 treatment for 10 min.

Samples	*Total Aerobic Plate Count (TPC; log cfu/g)*	*ClO_2 (mg ClO_2/kg)*	*Chlorite (mg Cl_2/kg)*
Before treatment (day 0)	2.95±0.29	0±0	0.07±0.12
After treatment (day 0)	ND[b]	0.13±0.05	0.39±0.49
Untreated and stored for 4 weeks	7.60±0.22	NA[a]	NA[a]
Treated and stored for 4 weeks	ND[b]	0.02±0.04	0±0

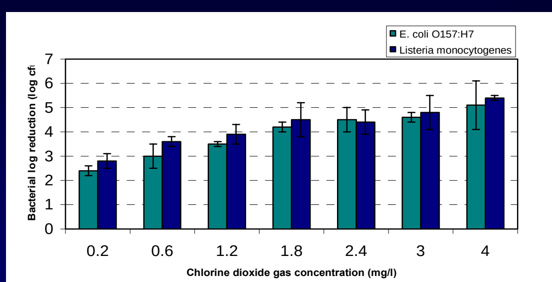
[a]NA=Data not available   [b]ND=No bacteria detected

Extension of Shelf-life

Untreated green peppers stored for 4 wks at 4°C

Green peppers treated with 200 ppm ClO_2 gas for 10 min and stored for 4 wks at 4°C

ClO_2 Gas Treatment on Strawberries



0.2-4 mg/l ClO_2 gas treatments for 30 min at 22°C and 90-95% relative humidity. Initial inoculation level 8.0±0.3 log cfu *L. monocytogenes* and 8.0±0.2 log cfu *E. coli* O157:H7.

Treatment of strawberries

Total aerobic plate count, residues of ClO_2, and residual chlorite after a continuous 1000 ppm ClO_2 gas treatment for 10 min.

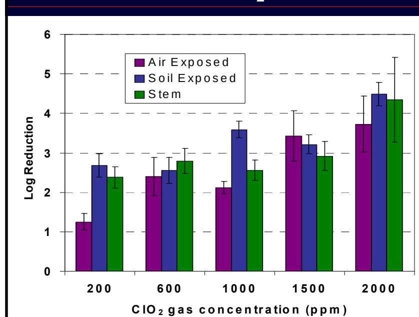
Samples	*Total Aerobic Plate Count (TPC; log cfu/g)*	*ClO_2 (mg ClO_2/kg)*	*Chlorite (mg Cl_2/kg)*
Before treatment (day 0)	2.22±0.22	0±0	0±0
After treatment (day 0)	ND[a]	0.19±0.33	1.17±2.02
Untreated and stored for 1 week	2.40±0.22	NA[b]	NA[b]
Treated and stored for 1 week	ND[a]	0±0	0.07±0.12

[a]ND=No bacteria detected   [b]NA=Data not available

Untreated and stored for 6 weeks at 4°C

Treated with 10 mg/l Chlorine dioxide gas for 10 min and stored for 6 weeks at 4°C

Reduction of *Salmonella* spp. on Cantaloupes after ClO_2 Gas for 10 min



Untreated and treated cantaloupes with 2000 ppm ClO_2 gas treatment for 10 min

Reducing *E. coli* O157:H7 on Apples by ClO_2 gas

Inoculation site	*ClO_2 concentration (mg/L)*	*Population after air drying (log cfu/site)[a]*	*Population after ClO_2 treatment (log cfu/site)[a]*	*Log reduction (log cfu/site)[a, b]*
Calyx cavity	1.1	7.6±0.0	5.0±0.8	2.6±0.74C
	3.3	7.5±0.1	3.6±0.5	4.0±0.4 B
	4.8	7.6±0.2	2.9±0.0	4.8±0.2 B
	7.2	7.4±0.2	0.9±0.8	6.5±0.7 A
Stem cavity	1.1	7.6±0.1	4.8±0.5	2.8±0.4 B
	3.3	7.5±0.2	3.3±0.7	3.9±0.3 A
	4.8	7.5±0.1	3.8±0.8	3.7±0.7 A
	7.2	7.5±0.2	3.4±0.3	4.1±0.2 A
Pulp skin	1.1	7.3±0.0	2.8±0.5	4.5±0.5 B
	3.3	7.3±0.1	0.4±0.7	6.9±0.7 A
	4.8	7.3 ±0.1	ND[c]	≥7.3±0.1 A
	7.2	7.3±0.0	ND	≥7.3±0.0 A

*1.1-7.2 mg/L ClO_2 gas treatments for 30 minutes (Du et al. 2002)

Reduction of *Salmonella* on Oranges by ClO_2 gas

INCREASE →

INCREASE ↓

50 ppm, 2 min	50 ppm, 12 min
SIDE 2.00 STEM 1.94 BOTTOM 1.74	SIDE 2.79 STEM 3.29 BOTTOM 2.55
150 ppm, 2 min	**150 ppm, 12 min**
SIDE 3.39 STEM 3.67 BOTTOM 2.33	SIDE 5.54 STEM 5.70 BOTTOM 5.60

Reducing *L. monocytogenes* on Lettuce by ClO_2 Gas

Untreated

0.2 mg/l, 30 min.
1.3 log reduction

0.2 mg/l, 10,20,30 min.
1.8 log reduction

A Pilot ClO_2 Gas Treatment System for Produce

A Laboratory ClO_2 Gas Treatment System for Meat

Efficacy of ClO_2 Gas in Reducing Microbes on Meat

Bacteria	Surface Type	ClO_2 gas Treatment Conditions (3-5°C)	Log Reduction
Generic *E. coli* k-12 *Salmonella* spp.	Pork lean, fat and skin Beef fat and skin Chicken lean and skin	500 or 2500 ppm for 10, 20, or 30 min	1-2
Generic *E. coli* k-12 *Salmonella* spp.	Pork fat and skin, Chicken skin	4500 ppm for 10 min	3-4
E. coli O157:H7	Beef fat	4500 ppm for 10 min	2.3
Campylobacter jejuni	Pork lean, beef fat, and chicken skin	4500 ppm for 10 min	1.7-2.2

Food Security

- Fight against biological weapons in food systems
- Decontaminate food processing plants

On-line monitoring efficacy of chlorine dioxide gas treatment using bioluminescent bacteria

Dr. Bruce Applegate

Basic Science

- Mechanism of inactivation of bacteria and bacteria spores by ClO_2 gas
- Standard methodology for determination of efficacy of ClO_2 gas treatment on surfaces
- Simulation and modeling of ClO_2 gas treatment…………

Technology commercialization

Barriers for Technology Transfer

- Regulations in food industry

  Aqueous chlorine dioxide

  - 1995, approved by FDA for poultry processing water
  - 1998, approved by FDA for washing produce

  Gaseous chlorine dioxide

  - 2000, GRAS by FDA for ClO_2-releasing LDPE film
  - 2002, Approved by EPA for stored potatoes
- Operation safety concerns

Acknowledgements

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Questions??