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Postharvest Chlorination

Basic Properties and Key Points for Effective Disinfection

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Postharvest handling of many vegetables and fruits usually involves the use of flumes, water dump tanks, spray washers, or hydrocoolers. Most postharvest processes recirculate used water (process water) to conserve water and energy. Dirt, organic matter, and disease-causing pathogens can accumulate in process water during bin dumping, hydrocooling, and flume recirculation.

Disinfection is the treatment of process water to inactivate or destroy pathogenic bacteria, fungi, viruses, cysts, and other microorganisms. The goal of disinfection is to prevent the transfer of these organisms from process water to produce and from one produce item to another during postharvest handling, increasing the likelihood that the produce is microbiologically safe for human consumption. Disinfection may employ chemicals such as chlorine, iodine, ozone, or peroxide, or it may use physical processes such as microfiltration or ultraviolet illumination.

Disinfection is part of an overall sanitation and safety management program. Chlorination of process water is one of the primary elements of a properly managed postharvest sanitation program. In conjunction with an overall safety management program, chlorination is generally effective, comparatively inexpensive, and may be implemented in operations of any size.

Chlorination alone is not a sanitation program—it is best viewed as a way to minimize the transmission of pathogens from infested produce or debris to noninfested surfaces such as harvest or process cuts, wounds, or natural plant surface openings.

FORMS OF CHLORINE IN WATER

Chlorine (Cl) is a very potent disinfectant with powerful oxidizing properties. It is soluble in water, either by injection of chlorine gas or by the addition of hypochlorite salts (see fig. 1). This solution, called chlorine (or chlorinated) water, consists of a mixture of chlorine gas (Cl_2), hypochlorous acid (HOCl), and hypochlorite ions (OCl^-) in amounts that vary with the water pH. The terms *free chlorine*, *reactive chlorine*, and (more correctly) *available chlorine* are used to describe the amount of chlorine in any form available for oxidative reaction and disinfection. Available chlorine

$$NaOCl + H_2O \leftrightarrow NaOH + HOCl$$
$$HOCl \leftrightarrow H^+ + OCl^-$$
$$HOCl + HCl \leftrightarrow H_2O + Cl_2$$

Figure 1. Forms of chlorine in water.

does not include chlorine combined with ammonia or other less readily available forms of chlorine with weak antimicrobial activity such as chloramines.

Total chlorine refers to the total available and combined chlorine that is present in water and still available for disinfection and oxidation of organic matter. Although combined chlorine compounds are more stable than available chlorine forms, they are slower in disinfectant action. In process water, the desired form of chlorine is hypochlorous acid, which is a much more effective bactericide than the hypochlorite ion.

The degree of acidity or alkalinity of a solution as measured on a scale of 0 to 14 is known as pH. The midpoint of 7.0 on the pH scale represents neutrality; that is, a neutral solution is neither acid nor alkaline. Values below 7.0 indicate acidity; values greater than 7.0 indicate alkalinity. Although hypochlorous acid concentration is highest at pH 6.0 (table 1), the best compromise of activity and stability is achieved by maintaining a water pH between 6.5 and 7.5. At low pH, chlorine gas is released from water.

Table 1. Activity of chlorine forms in water of varying pH

pH of process water	Approx. % of chlorine as HOCl	Approx. % of chlorine as OCl^-
3.5	90	0
4.0	95	0
4.5	100	trace
5.0	100	trace
5.5	100	trace
6.0	98	2
6.5	95	5
7.0	78	22
7.5	50	50
8.0	22	78
8.5	15	85
9.0	4	96
9.5	2	98
10.0	0	100

Chlorine may incompletely oxidize organic materials to produce undesirable byproducts in process water, such as chloroform ($CHCl_3$) or other trihalomethanes, that have known or suspected carcinogenic potential. At high pH, chlorine reacts with organic nitrogen-based materials to produce chloramines. From a U.S. government regulatory perspective, the benefits of proper chlorination as a primary tool for sanitation outweigh concern for the potential presence of these byproducts. The use of chlorination for produce washing (chlorinated water in direct contact with produce) has been banned in a few countries other than the United States and may affect the export of chlorinated produce. Assistance and information on export regulations may be obtained from the FDA Center for Food Safety and Applied Nutrition (200 C St. SW, Washington, D.C. 20204).

WARNING
Never combine chlorine with ammonia or acetylene, as poisonous chlorine gas can be produced.

Concern for the potential hazards associated with chlorine reaction byproducts and wastewater disposal have heightened efforts to evaluate and register alternative water disinfection and surface sanitizer treatments for produce and postharvest handling. These are discussed briefly under “Other Disinfectants,” below.

REGISTERED PRODUCTS

Chlorine is commercially available in three forms that have been approved for use (registered) by the U.S. Environmental Protection Agency (EPA) and, for California, by the California Department of Pesticide Registration (DPR). For a discussion of other disinfectants, including some that may not be registered, see “Other Disinfectants,” below.

Chlorine Gas (Cl_2)

Chlorine gas is the least expensive but most demanding source of chlorine from a safety and monitoring standpoint. Generally restricted to use in very large operations, the use of chlorine gas requires automated, controlled injection systems with in-line pH monitoring. Chlorine gas reduces the pH of water to below 6.5.

Calcium Hypochlorite ($CaCl_2O_2$)

Calcium hypochlorite is the most common source of chlorine used for disinfecting produce and produce process water. Registered formulations are 65 percent or 68 percent active ingredient (a.i.). It is available as a granulated powder, compressed tablets, or large slow-release tablets. In dry storage, calcium hypochlorite is more stable than liquid sodium hypochlorite. Phytotoxicity (bleaching or burning) of produce can occur if calcium hypochlorite granules fail to dissolve in cool wash tank water or in a hydrocooler system. Always dissolve granules in a small volume of warm water before adding them to cooling or wash water. Calcium hypochlorite increases water pH to slightly above 7.5.

Sodium Hypochlorite (NaOCl)

Sodium hypochlorite is the source of chlorine commonly used in small-scale operations. It is generally used in concentrations of 5.25 percent or 12.75 percent a.i. in liquid form, because the solid forms readily absorb water from air and release chlorine gas. Only registered formulations are approved for use on produce (household bleach is not a registered material for produce). Sodium hypochlorite is generally more expensive than other forms of chlorine due to the added shipping cost of the water-based formulations. Excess sodium buildup from repeated applications of sodium hypochlorite to recirculating water may damage sensitive produce. Sodium hypochlorite increases water pH to above 7.5.

KEY POINTS FOR PROPER CHLORINE DISINFECTION

Water Source

Potable water should be used for all postharvest washing, grading, and cooling operations. Contaminated water used during postharvest operations can transmit diseases that decay the produce or adversely affect human health. Water taken and used directly from rivers or holding ponds should not be used for postharvest washing or cooling. Because some pathogens of concern to human safety are not easily killed by chlorination, even under optimal conditions, beginning with clean potable water is the best preventive step available. The effectiveness of other disinfectant options, such as ozonation and UV treatment of process water, is currently being evaluated against these chlorine-resistant microorganisms. When using a nondomestic water source, water quality evaluations should be performed by a certified analytical lab. For further information, see A. E. Greenberg, ed., *Standard Methods for the Examination of Water and Wastewater*, 19th ed. (Washington, D.C.: American Public Health Assn., 1995).

Temperature

Although chlorine activity slightly increases with temperature, some chlorine gas is lost to the atmosphere as warmer temperature increases the rate of volatilization. Low temperature and improper pH values in hydrocooling, for example, can greatly reduce disinfection efficiency. In general, the need for rapid cooling to optimize postharvest quality makes temperature adjustment of chlorinated process water for optimizing disinfection activity unavailable as a management option.

Organic Matter

Chlorine is highly reactive with leaves, soil, and any plant or vegetable matter whenever oxygen is present. Each chemical reaction reduces the amount of active chlorine in the water. Changing chlorinated water frequently or filtering out organic matter and debris is essential for effective sanitation. Also, prewashing very dirty produce can prolong the useful life of chlorinated cooling water.

Concentration and Length of Exposure

Disinfection is best accomplished by deriving contact (exposure) times and concentrations through direct experience for each type of produce and local conditions. Exposure times of 3 to 5 minutes at concentrations of 50 to 75 parts per million (ppm) or less (1 to 1.5 ounces of calcium hypochlorite at 65 percent a.i. per 100 gallons of water provides 50 to 75 ppm) maintained at pH 6.5 is generally adequate for controlling most postharvest pathogens suspended in water.

Microorganisms differ in their sensitivity to chlorine: bacteria are most sensitive, many fungal spores are less sensitive, and some spore-forming animal parasites are highly insensitive. In practice, total chlorine concentrations may need to exceed 300 ppm to sustain sufficient available chlorine activity in process water throughout the daily use cycle. The practical duration of contact exposure is generally 10 to 15 minutes. Caution must be used as some produce is sensitive to surface bleaching or pitting at high concentrations. For example, bell peppers are not affected by 250 ppm available chlorine but carrots may lose orange color intensity, and celery and asparagus may develop light-brown surface pits when exposed to chlorine concentrations exceeding 250 ppm.

Performance Enhancers

Chlorine kills only what it directly contacts. Water films that form on very small contours on plant surfaces may prevent the chlorinated water from directly contacting target microorganisms. Adding approved surfactants to process water reduces water surface tension and may increase the effectiveness of chlorination. Consult a postharvest chemical supplies dealer for available and approved materials. Examples of these materials are polysorbate 80, other sorbitan esters, and Chlorine Potentiator (Bonagra Technologies, Inc.).

Monitoring

The chlorine concentration and pH of chlorinated process water should be checked frequently using test paper strips, colorimetric kits, or electronic sensors. The optimal frequency of testing is best determined through on-site experience. In general, monitoring should increase as the concentration of suspended materials in the water increases. Different tests measure different forms of chlorine; some are accurate only at very low concentrations. Dilution of most process water with distilled or deionized water is required to obtain useful results from these tests. Select a chlorine test kit that is based on DPD (N, N diethyl-p-phenylenediamine) that specifically tests for available (reactive) chlorine. Become familiar with what is being measured and how water quality affects the results. Muriatic (hydrochloric) acid (HCl) or citric acid ($C_6H_8O_7$) is commonly used to maintain wash or cooling water at a pH of 6.5 to 7.5. Consult a postharvest management service for designing an effective and safe acid-injection system.

Some automated cooling systems monitor the oxidation reduction potential (ORP) of process water using probes that measure activity in millivolts (mV). The relationship between ORP, contact time, and microbial inactivation for chlorine-based oxidizers in laboratory tests and field confirmation tests are used to establish the setting for the system. For example, an ORP setpoint of 600 to 650 mV is commonly used in hydrocooling systems.

Table 2. Chlorine concentrations generally used on selected vegetables

Commodity	Treatment type	Available chlorine (ppm)
Artichokes	Sprayer over continuous belt	100–150
Asparagus	Sprayer over continuous belt	100–150
	Hydrocooler*	125–150
Bell peppers	Sprayer over continuous belt	150–200
	Dump tank	300–400
Broccoli	Sprayer over continuous belt	100–150
Brussels sprouts	Sprayer over continuous belt	100–150
Cabbage (shredded)†	Sprayer over continuous belt	100–150
Carrots	Sprayer over continuous belt	100–150
	Flume	150–200
Cauliflower	Sprayer over continuous belt	100–150
Celery	Hydrocooler*	100
	Sprayer over continuous belt	100–150
Corn	Sprayer over continuous belt	75–100
Cucumbers	Sprayer over continuous belt	100–150
Garlic (peeled)†	Sprayer over continuous belt	75–150
Greens, chopped leafy	Sprayer over continuous belt	100–150
Lettuce, butterhead	Sprayer over continuous belt	100–150
Lettuce, iceberg		
whole, shredded†	Sprayer over continuous belt	100–150
	Hydrovac cooler*	
Lettuce, romaine	Sprayer over continuous belt	100–150
Melons, all types	Sprayer over continuous belt	100–150
	Dump tank	100–150
Mushrooms‡	Sprayer over continuous belt	100–150
Onions, green	Sprayer over continuous belt	100–150
Peas, pod-type	Sprayer over continuous belt	50–100
Peppers, chili	Sprayer over continuous belt	300–400
Potatoes, brown or red	Flume	200–300
	Dump tank (prewashed)	30–100
	Sprayer over continuous belt	100–200
Potatoes, white	Dump tank (for bleaching)	500–600
Pumpkins	Sprayer over continuous belt	100–200
Radishes	Sprayer over continuous belt	100–150
	Dump tank	25–50
Spinach	Sprayer over continuous belt	75–150
Sweet potatoes	Dump tank (prewashed)	100–150
Squash, all types	Sprayer over continuous belt	75–100
Tomatoes	Flume	200–350
	Dump tank	200–350
Turnips	Dump tank	100–200
Yams	Dump tank	100–200

Note: This table represents the combined range of concentrations from the product labels and technical information of formulations currently registered in California. These concentrations are guidelines reflecting industry practice; always follow directions, use rates, and tolerances listed on approved product labels. Determine cultivar sensitivity within a given concentration range.

*For more information on hydrocooler chlorination see *UC Perishables Handling Newsletter* no. 84 (Nov. 1995) (special issue on hydrocooling), also available on the Internet at http://postharvest.ucdavis.edu.

† Residual water must be removed by centrifugation or some other dewatering process following treatment.

‡ Not a common treatment. When used, follow with an antioxidant to prevent browning. Ascorbic acid or erythorbic acid in combination with citric acid are examples of these antioxidants.

Wastewater Disposal

A disposal plan for chlorinated process water must be in place before any chlorination system is used. Although land application has been allowed, always determine if a local permit or other restrictions apply. The EPA Office of Wastewater Management sets federal policy and standards for disposal of chlorinated process water and the impacts of chlorinated byproducts in environmental water systems. State and local water resource management agencies, air quality management boards, and wastewater resource boards are responsible for regulatory oversight of disposal issues.

Worker Safety

As a concentrate, chlorine gas is extremely dangerous and should be used only in properly designed containment systems that are isolated from the processing plant area. Chlorine fumes released from treated water will cause worker discomfort and eye irritation. If a chlorine odor is even barely detectable by a worker just entering an area where a chlorinated processing and cooling water system is operating, it is likely that the maximum safe chlorine concentration has been reached. In addition to being a health hazard, excessive chlorine reaction odor (odors from interaction with organic amine compounds) or chlorine gas may also indicate improper pH adjustment. The Occupational Safety and Health Administration (OSHA) (see website http://www.osha-slc.gov) establishes and publishes the Threshold Limit Value (TLV) and Short-Term Exposure Limit (STEL) for worker exposure to chlorine, chlorine dioxide, ozone, and other hazardous materials.

OTHER DISINFECTANTS

In the search for effective disinfectant treatments for process water sanitation, the postharvest handling industry often operates within areas of regulatory uncertainty. Some produce handlers and processors use chlorine dioxide and ozone for sanitation and other postharvest applications, in part because of their characteristics in relation to registered materials (see fig. 2). For applications to whole or peeled produce, handlers and processors may be assuming that these materials have an approved Generally Regarded as Safe (GRAS) status. Recent expert advisory panel recommendations have made this determination, but, to date, the U.S. Food and Drug Administration (FDA) has not released an official determination on these materials. Unlike chlorine gas, calcium hypochlorite, and sodium hypochlorite, no postharvest uses of chlorine dioxide or ozone in contact with produce are currently registered by the U.S. EPA or the California DPR.

Figure 2. Disinfection efficiency and efficacy for chlorine forms.

$OCl < HOCl < ClO_2 < O_3$

Relative antimicrobial disinfection efficency

$HOCl$	O_3	ClO_2
Strong	Moderate	Low

Efficacy impacted by pH

Chlorine Dioxide (ClO_2)

A yellow to red gas with 2.5 times the oxidizing potential of chlorine gas, chlorine dioxide is explosive at concentrations above 10 percent a.i. or at temperatures above 130°C (266°F). It is normally diluted to less than 10 percent a.i. and shipped frozen for many industrial uses, including water treatment and sanitation of food processing contact surfaces. On-site generation of chlorine dioxide is also available by combining either chlorine gas and sodium chlorite or sodium hypochlorite, hydrochloric acid, and sodium chlorite. As with chlorine gas, the safety hazards associated with the use of chlorine dioxide demand detailed attention to proper engineering controls to prevent or reduce exposure. Violent explosions can occur when chlorine dioxide comes into contact with ammonia compounds.

The disinfecting power of chlorine dioxide is relatively constant within a pH of 6 to 10. It is effective against most microbes at concentrations of 3 to 5 ppm in clean water. The need for on-site generation, specialized worker safety programs, and closed injection systems for containment of concentrate leakage and fumes from volatilization make chlorine dioxide relatively expensive for produce applications.

Currently, chlorine dioxide is not registered (approved for use by the California DPR) as a postharvest treatment for direct contact with produce.

Ozone (O_3)

Ozone is another strong oxidizing agent used in disinfection of process water, drinking water, and swimming pools. In clean, potable water free of organic debris and soil particulates, ozone is a highly effective sanitizer at concentrations of 0.5 to 2 ppm. Ozone is almost insoluble in water (0.00003g/100mL at 20°C [68°F]); its disinfectant activity is unaffected in at a water pH from 6 to 8. Ozone is highly corrosive to equipment and lethal to humans with prolonged exposure at concentrations above 4 ppm. Ozone is readily detectable by human smell at 0.01 to 0.04 ppm. At 1 ppm ozone has a pungent, disagreeable odor and is irritating to eyes and throat.

Effective but safe ozone concentrations are difficult to maintain in process water because automated detection systems are not highly reliable. Electrode probes that measure the ORP of the water or colorimetric kits are used to monitor ozone concentrations. Ozone is also highly unstable in water and decomposes to oxygen in a very short time (less than half the activity remains after 20 minutes). In process water with suspended soil and organic matter, the half-life of ozone activity may be less than 1 minute. Maintaining effective concentrations for microbial disinfection by using remote ozone generation and injection into a centralized water system, as is done with chlorine, has proved difficult.

Currently, ozone is not registered by the California DPR as a postharvest treatment for direct contact with produce. The recent expert panel recommendation to the FDA supporting GRAS classification of ozone as a disinfectant for foods has opened the door for the produce industry to establish independent affirmation of safety when applied in a manner consistent with good manufacturing practices.

Peroxyacetic Acid (CH_3CO_3H)

Peroxyacetic acid has recently been approved for use on produce by the California DPR. For the treatment of fruit and vegetable surfaces, current formulations combine hydrogen peroxide 11 percent and peroxyacetic acid 15 percent a.i. The labeled rate for surface contact on produce is 80 ppm. After application of peroxyacetic acid for disinfection, produce must be rinsed with potable water. Peroxyacetic acid is a colorless liquid with an acrid odor; as a concentrate it is considered a hazardous substance and a severe irritant if breathed.

Sodium Hypophosphite (NaH_2PO_2)

Although sodium hypophosphite has been shown to be active against spore-forming microbes known to be resistant to standard levels of chlorine, it has had few performance tests in process water. Currently, it is not registered by the California DPR as a postharvest treatment of produce.

Sodium Sulfite (Na_2SO_3)

Sodium sulfite has been evaluated as a process water disinfectant. The U.S. FDA prohibits the use of sodium sulfite or any sulfite-generating materials as additives to process or cooling water at any concentration. No food residue or tolerance level is permitted.

Ultraviolet Illumination

An alternative to chemicals for disinfection of recycled or recirculating process water, ultraviolet light has germicidal activity in wavelengths from 250 to 275 nm (shortwave UV [UV-C]). The effectiveness of UV-C in disinfection depends on maintaining a clean water supply by filtration; high-intensity UV-C systems can kill microorganisms in only a few seconds.

RELATED WEBSITES OF INTEREST

National Food Safety Database http://www.foodsafety.org

UC Postharvest Outreach Program http://postharvest.ucdavis.edu

Water Quality Association http://www.wqa.org

Occupational Safety and Health Administration (OSHA) http://www.osha-slc.gov

The information in this publication should not be viewed as an authoritative source for current registration status or legal use recommendations of any product. For more information contact the California Department of Pesticide Registration Information Center at (916) 324-0399. To simplify information, trade names of products have been used. No endorsement of named or illustrated products is intended, nor is criticism implied of similar products that are not mentioned or illustrated.

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