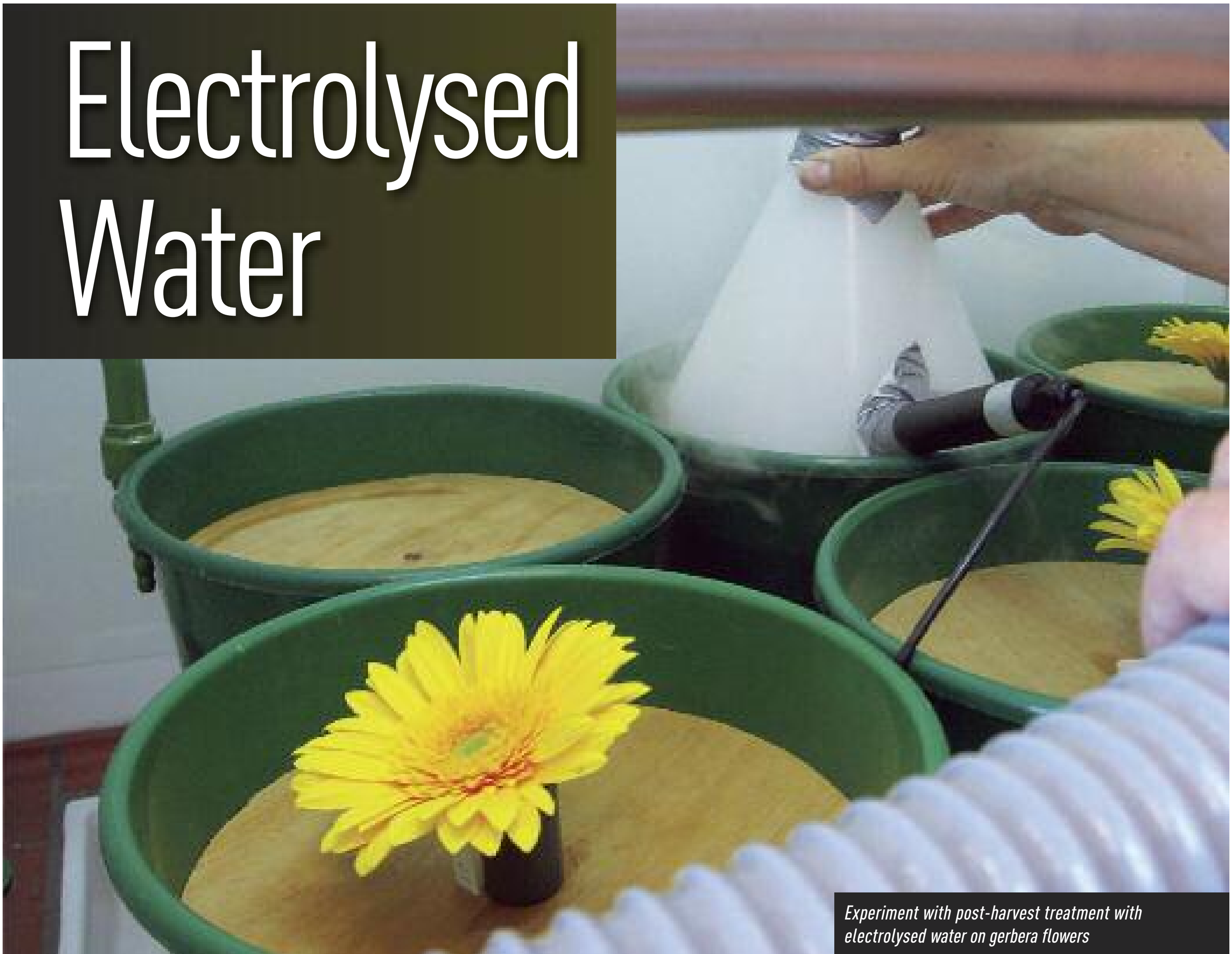
Electrolysed Water



Experiment with post-harvest treatment with electrolysed water on gerbera flowers

Electrochemical disinfection and disease control with electrolysed water

Electrolysed water is making headlines in the greenhouse industry in the Netherlands. It is effective for disinfection and has potential for disease control, as reported by ELLY NEDERHOFF, JANTINEKE HOFLAND-ZIJLSTRA, ROZEMARIJN DE VRIES and HARRY BRUNING.

Introduction

An electrical current running through salty water creates a powerful mixture of chemicals that kills microbes such as bacteria, fungi and viruses. The mixture is called 'electrolysed water'. The official term for this process is Anodic Oxidation (AO), and the machine that makes electrolysed water is an AO-unit. There are many other names for electrolysed water, including EW, hydrolysed water, electrically activated water, electrochemically produced water, activated water, active water (and more). Dutch suppliers of AO-units have chosen brand names such as ECA-water, Aquanox, Aqua-ox and Hortinox. Sterilising water using the AO technology is called electrochemical disinfection.

This is a promising technology for disinfection and disease control. It is already used successfully in many industries. In horticulture, the main application of electrolysed water so far is as a 'biocide', meaning 'life-killing' agent. It is used to break down the slimy build-up in hydroponic lines that often contains bacteria, fungal spores and other microbes. It is also used successfully for disinfection of seeds, flowers, fruits, vegetables, equipment and packing materials. In the near future it may be used for disease control in greenhouses.

History and new developments

The principle of Electrochemical Disinfection and Anodic Oxidation was discovered centuries ago. Around 1900 already, the technology was used on a large scale in Russia for disinfecting drinking water. Modern research started in the 1970s in Russia. Since then new applications have been found in many fields all over the world, for instance, in health care, dentistry, food and beverages industry, animal husbandry and agriculture.

The Dutch greenhouse industry got interested because there is a strong need for new technologies to replace fading-out agrichemicals. Electrochemical disinfection appeared to overcome residue problems and other shortcomings of conventional disinfection methods.

Horticultural applications started to be developed in the US and the Netherlands in the 1990s. Practical tests followed and gave promising results. This led to a permit being issued in 2009 for on-site production of electrolysed water for use as a biocide in horticulture in the Netherlands.

Now growers are eagerly waiting to see if electrolysed water can safely control diseases in greenhouse and hydroponic systems. The most promising development is where electrolysed water is dispersed by 'Ultrasonic Atomisation' which creates 'dry fog'. Tests with dry fog on flower crops in greenhouses showed good control of fungal diseases, without crop damage or residues. But what stands in the way is that electrolysed water has a corrosive nature and can damage materials. Further refinements are needed and are underway.

Principle

Electrolysed water is produced in an AO-unit also known as Electrochemical Disinfection Device. This is basically a tank with a salt solution, with two electrodes placed in the tank on opposite sides. One electrode (called the anode) is positively charged, while the other (the cathode) is negatively charged. A voltage put on these electrodes sends a current through the water. This current splits molecules into smaller particles and creates new chemicals. The principle is demonstrated in *Figure 1* with a simple reactor. This has one chamber holding both electrodes. It is filled with clear water only instead of salty water. The electric current produces hydrogen and oxygen gas, which simply bubble out. This mixture made from pure water has no disinfecting properties. At best it may bring oxygen in the water.

Two-chamber reactor

Most Anodic Oxidation units (Electrochemical Disinfection devices) consist of two chambers, separated by a membrane *(Figure 2)*. The membrane lets certain particles pass, which is essential for the working of the system. One chamber holds the anode (positive electrode) and the other holds the cathode (negative electrode). This system is filled with salty water so that the effective chemicals can be created.

Figure 1.

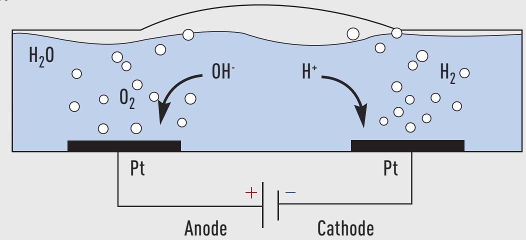
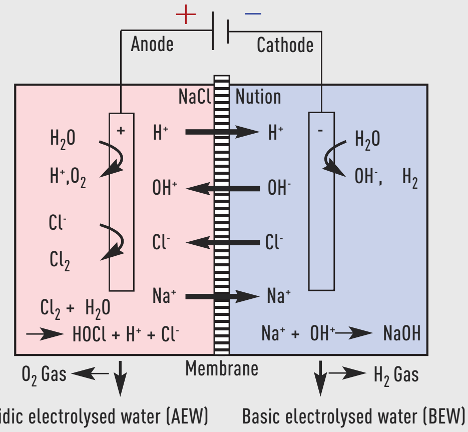


Figure 2.



Salts

Figure 1 explained the principle of Anodic Oxidation (AO) using just pure water. But in order to create effective chemicals, it is necessary to add a bit of salt, usually just table salt. Most systems use 3-10 gram salt per litre, but manufacturers are working to reduce this amount. Table salt (sodium chloride, NaCl) releases chlorine, which then forms new chlorine-containing chemicals, in particular chlorine gas, hypochlorous acid and hypochlorite (see the chemicals in *Figure 2*).

Simple table salt works well and has advantages. But it adds a small amount of sodium to the nutrient solution, which is sometimes undesirable in hydroponics. In that case other salts can be used such as potassium chloride (KCl) and magnesium chloride ($MgCl_2$). In a test, all three salts produced electrolysed water of similar strength and with similar effects against a fungal disease. Magnesium salt gave slightly more damage to plants in one test.

Biocide (life-killing) agent

Some of the particles produced by Anodic Oxidation are electrically charged and are very aggressive in themselves. Some other newly formed compounds are 'oxidants' that can 'burn' germs. (Also some innocent gases such as oxygen and hydrogen are formed and they simply escape). The remaining mixture contains water, charged particles and active chemicals, especially free chlorine. This mixture is the actual 'electrolysed water' that destroys organic matter. It also destroys living creatures including bacteria, fungi, viruses, viroids, algae, protozoa and nematodes, and is therefore called biocide (life-killing). In medical applications, electrolysed water is used to assist wound healing by killing bacteria and damaged tissue.

Control of bacteria has been investigated a lot in the medical world and food industry. Laboratory tests showed that control of different bacteria requires different concentrations of free chlorine (varying from 10 to 90 ppm) as well as different exposure times (varying from 1 to 30 seconds). Electrochemical disinfection can meet these requirements. Bacteria in horticulture are killed in much the same way.

ORP and pH

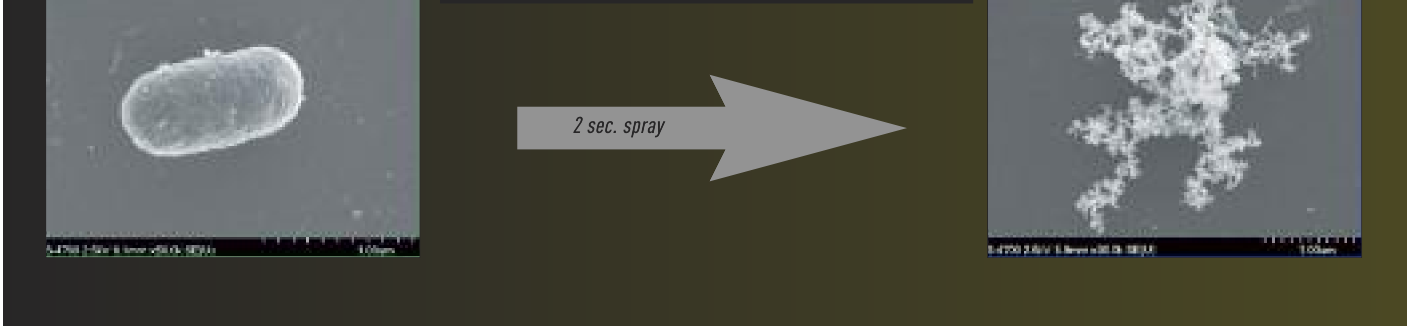
Electrolysed water varies in chemical composition, e.g. in amount of free chlorine, acidity (pH), and strength. These traits all depend on the amount of salt used, the power of the current and the efficacy of electrodes in the AO-unit.

The strength of electrolysed water is indicated by a number, called ORP or REDOX (meaning oxidation-reduction potential). ORP is expressed in millivolt (mV). ORP indicates how aggressive something is against organic matter including microbes. Water itself has an ORP up to 250 mV, water with salt up to 450 mV, electrolysed water 700-1200 mV. ORP above 750 mV is very much stronger than ORP up to 450 mV.

Acidity or pH is measured on a scale of 0 to 14. A solution with pH of 7 is neutral, and everything below 7 indicates acidic, while everything over 7 indicates alkaline or basic. We will see that electrolysed water can have a pH as low as 2 or 3.

AO, AEW, BEW and NEW mixtures

Most AO-units have a two-chamber reactor as shown in *Figure 2*. The water mixtures in both chambers are very different. The water in the anode room is acidic, and is called Acidic Electrolysed Water (AEW). This is the most aggressive of the two solutions. Amongst other ingredients it contains hypochlorous acid. The pH is 2 or 3 (very low); the ORP value is over 1100 mV (very high); the content of active (free) chlorine is



Electrolysed water 'burns' away a bacteria
Source: Tennent Company Group (spray with Oribio-4 technology)

Examples of where electrolysed water can be useful as a biocide

Electrolysed water extends the vase-life of gerbera
(Van Os, E.A., et al, 2010. Wageningen University Glastuinbouw, Netherlands)

10-90 ppm (very potent). It has a strong chlorine smell and a corrosive effect on metals, even on some stainless steels.

The other chamber, the cathode chamber, produces a totally different water mixture. This is alkaline (basic) and is therefore called Basic Electrolysed Water (BEW). The pH is typically 10-13 and the ORP is between -800 and -900 mV (negative ORP values). This type of mixture is a detergent (dissolves fats) and surfactant (causing lower surface tension and foaming). It has no smell and is less corrosive, but still not risk-free for use on stainless steel.

The two mixtures (AEW and BEW) can be mixed, resulting in a neutral pH of around 7-8 and a moderate ORP of 750 mV. This water is called Neutral Electrolysed Water (NEW). The same mixture can also be produced in a single chamber reactor. Surprisingly, NEW is as effective as AEW.

What influences the working of electrolysed water?

The efficacy of electrolysed water depends on the concentration of free chlorine and other substances, and also on ORP, EC, pH, exposure time, temperature, stirring and the presence of organic matter.

- Higher temperature during the disinfection process increases the working.
- However, higher temperature during storage reduces the life span of an AO mixture.
- Presence of organic matter in the solution reduces the working, because free chlorine molecules bind with organic molecules, and thus are lost for killing microbes.
- Being in an open tank reduces the working, because chlorine gas escapes.
- Agitation (movement, stirring) reduces the working, because it speeds up the loss of chlorine gas and the break-down of other chlorine compounds.
- Light reduces the working, because (diffuse) light breaks down chlorine compounds.
- If electrolysed water is stored it should be in dark bottles, at low temperature (4°C).

Available disinfection methods

So far two principles of water treatment were used in horticulture: physical disinfection and chemical disinfection. Electrochemical disinfection is now the third group.

Physical disinfection is eliminating microbes by radiation, heating, ultrasound or filtration. These methods have no after-effect, as will be explained later.

Chemical disinfection kills microbes by substances such as chlorine, hydrogen peroxide, bromide, hypochlorite or chlorine dioxide. These are dangerous chemicals that pose a risk during transport and handling. Moreover, they may produce dangerous (cancer-causing) substances as by-products. Chemical disinfection methods usually do have an after-effect.

Electrochemical disinfection has many advantages over the two alternative methods.

Advantages of electrochemical disinfection

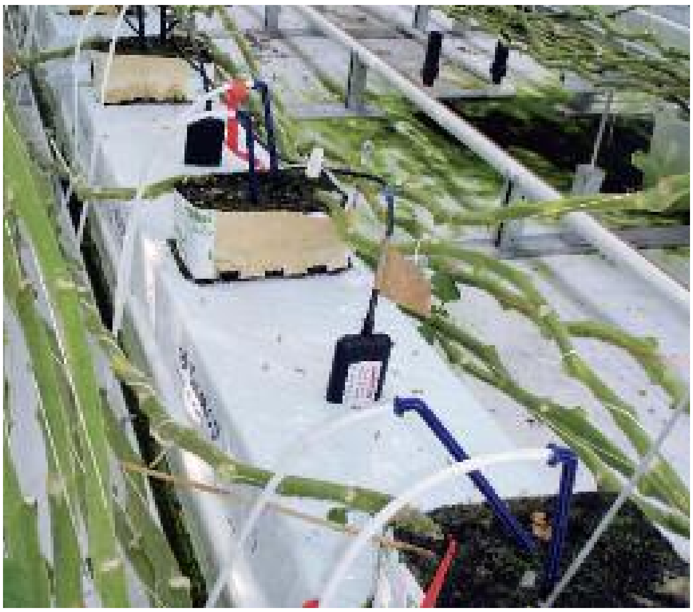
- Effective against a wide range of micro-organisms
- Produced on-site and on-demand from simple ingredients, thus always available
- Produced from cheap ingredients (pure water and salt)
- No transport, storage and dosage of dangerous chemicals needed
- Electrolysed water contains free chlorine, which is much stronger than bleach (sodium hypochlorite) or chlorine dioxide (OCl_2), and stronger than hydrogen peroxide (H_2O_2)
- Can be combined with many surfactants, fungicides or insecticides (details see further)
- Leaves no residues (only small amount of chlorine gas is produced)
- Low chance of bacteria becoming resistant
- Environmentally friendly, especially from machines with limited catholyte (by-product)
- Ultrasonic atomisation to make 'dry fog' of electrolysed water is promising for disease control
- Costs are low after initial investment in the AO-unit
- Limited maintenance required
- Can run on solar cells far from the power grid, e.g. drinking water in isolated places.

Limitations of electrochemical disinfection

- Corrosive properties of electrolysed water can harm metals and some plastics
- Droplets of electrolysed water can cause crop damage (but dry fog is safe)
- Electrolysed water based on sodium salt adds a bit of sodium to the hydroponic system
- Some machines need regular attention
- AO and electrochemical disinfection require care and knowledge to operate
- Risks for operators: skin irritation after contact with electrolysed water, and lung irritation after inhaling chlorine gas escaping from the AO-unit
- By-product (catholyte) formed at the cathode (can be used as detergent though)

Aquaox system

ECA-system



An ultrasonic unit is being tested for spreading electrolysed water into a greenhouse


Electrolysed water (from Aquanox system) used on cymbidium orchids via ultrasonic dispersion ('dry fog')

- Storage leads to loss of strength in electrolysed water
- Machines are not allowed to go off-site and electrolysed water is not allowed to be transported (under current law in the Netherlands)
- Ultrasonic atomisation (dry fog) needs 5 - 15 minutes for good coverage, depending on the treatment area.

After-effect

Water treatments differ in the amount of after-effect. No after-effect means that a treatment only works inside the machine (e.g. inside an UV installation). An after-effect does exist with chemical disinfection. The action happens at the machine that injects the chemical (e.g. hydrogen peroxide), but the effect remains in the water as it flows through the growing system. The chemicals kill bacteria everywhere in the hydroponic system, including on the roots.

In hydroponics an after-effect can be an advantage and disadvantage. The good thing is that remaining chemicals in water kill pathogens that hide in the system e.g. in the slimy layer inside lines, pumps, filters, tanks. But not good is that remaining chemicals can possibly damage the plant roots, too. However, some people say that a mild stress on the roots can increase the plants' immune response.

Ultrasonic dispersion or 'dry fog'

Ultrasonic technology is being developed as a method for more effective dispersion of water. This technology creates very fine droplets, also known as 'dry mist', and uses a fraction of the energy that normal humidifiers use. Electrolysed water can be dispersed ultrasonically. This creates fine droplets of active water that penetrates the crop well. This technology saves water, substances and energy.

The capacity of the ultrasonic systems is relatively small, but large enough for post-harvest disinfection. It would need to be scaled-up for use in multi-hectare greenhouses. Also, a protocol must be developed with regard to droplet size, density of the dry fog, application technology, way to control, time of the day for treatment, etc.

Ultrasonic dispersion of electrolysed water for crop treatment in greenhouses is not permitted yet. Before that can happen, the corrosive action of electrolysed water must be minimised.

Corrosion and damage

A problem is that electrolysed water oxides ('burns') many materials. It causes corrosion in metals, even in some types of stainless steel, and makes some plastics brittle. Apparently some materials are not sensitive to electrolysed water, such as galvanised aluminium, PVC and polyethylene. The extent of the corrosion depends on amount of free chlorine, exposure time, pH and temperature. Corrosion is less at lower concentration, shorter exposure time, and also at lower temperature.

Electrolysed water may cause plant damage too on some crops such as young cucumber plants, or if electrolysed water sits on the leaves for some time.

A lot of work is done on testing the effect of adding anti-corrosion substances, such as phosphates, sulphates, azoles (nitrogen), and more. The anti-corrosion effects and side-effects vary a lot. The good thing is that, in a test, the anti-corrosion additives did not reduce the bacteria-killing effect of electrolysed water.

Combining electrolysed water with pesticides

It was tested in a laboratory if electrolysed water can be mixed with surfactants, fungicides or insecticides, without electrolysed water losing its potency. The test was done on fungal spores (conidia of *Botrytis*, grey mould). The literature reports that some surfactants reduced the working of electrolysed water (e.g. Triton-X-100 and Tween-20). Research by WUR found that the addition of 'Finish' to electrolysed water had no such effect.

Many fungicides and insecticides that were added to electrolysed water had no effect on its efficacy, but a few did impede the working. In summary, electrolysed water does not necessarily lose its potency when mixed with surfactants or pesticides. It is recommended to check this before mixing a particular agent into electrolysed water.

Horticultural applications

Electrolysed water (water from Anodic Oxidation) is used in horticulture in many ways, for instance:

- Seed treatment: surface of seeds are sanitised, without compromising seed vitality
- Sterilisation of packing material and tools; smooth surfaces are easiest to sterilise
- Removing of biofilm in hydroponic pipes: built-up organic matter with bacteria are dissolved
- Post-harvest disinfection of fruit: killing fungal spores and bacteria without deteriorating the fruit
- Post-harvest disinfection of vegetables: treatment of spinach (at pH 7) improved shelf-life and left no residue
- Post-harvest disinfection of flowers; ultrasonic dispersion (dry-fogging) on loose unwrapped flowers was successful
- Prolonged shelf-life of flowers is achieved in South-Africa by using electrochemical disinfection of water in the crates

- Control of fungal diseases in irrigation systems in orchards: electrolysed water cleaned the irrigation lines and slightly reduced fungal infection of the soil
- Tests with spraying greenhouse crops: treatment with electrolysed water on vegetable or flower crops in a greenhouse reduced fungal infection (e.g. mildew), but leaf damage could occur depending on application frequency and product acidity.

Some examples

A rose grower bought an AO-unit for making electrolysed water and for controlling bacteria, fungi, viruses, and algae in the root-zone. He adds electrolysed water (1 - 1.5%) to the water entering the nutrient tank. It works so well that the grower switched his UV water disinfection machine off. It was not needed anymore, and was using power unnecessarily.

The same grower was looking for an alternative for sulphur against mildew, since sulphur is now regarded as environmentally unfriendly. Electrolysed water is environmentally friendly, as it breaks down to table salt in a number of weeks. Suppliers developed a fogging system with fans for dispersion of electrolysed water. Unfortunately, the results were disappointing. The grower was also put off by the risk of oxidation (rust) of metals that are in contact with electrolysed water. The grower is now supporting and awaiting research currently undertaken by WUR and by suppliers.

A grower is running a test using electrolysed water as a post-harvest treatment on cymbidium cut flowers to prevent spots caused by *Botrytis*. The electrolysed water is fogged on the flowers that are hanging up-side down in a tent. It is very effective but it takes time. Fogging itself lasts 8-10 minutes, and waiting time is about an hour.

Research

WUR ran an experiment where 8 of the 10 suppliers of AO-units submitted their electrolysed water for a comparative test. They all had to provide a mixture with certain characteristics. The test aimed to achieve 100% kill of bacteria *Erwinia chrysanthemi* in water within 5 minutes. All units achieved that goal, and it turned out the concentration of free chlorine had to be at least 45 ppm.

Suppliers are further developing Electrochemical Disinfection (Anodic Oxidation technology), and researchers are investigating further the effects on microbes. Also, Ultrasonic Atomisation ('dry fogging') is being developed further. In addition, work is underway to design protocols for safe and effective use of electrolysed water for disease control.

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