

Article

Overview of the Main Disinfection Processes for Wastewater and Drinking Water Treatment Plants

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Abstract: The use of water disinfection as a public health measure reduces the spread of diseases. Various disinfection technologies can be used to meet the pathogen inactivation demand in water. This work is an overview of the main disinfection technologies of wastewater and drinking water that reports for the conventional processes the action mechanism, the possible formation of by-products, the operative conditions, the advantages and disadvantages. For advanced and natural processes the action mechanisms are reported. Advanced technologies are interesting but are still in the research state, while conventional technologies are the most used. There is a tendency, especially in Italy, to use chlorine-based disinfectant, despite in some forms could lead to production of disinfection by-products.

Keywords: disinfection; toxicity; wastewater treatment; drinking water treatment

1. Introduction

The use of water disinfection as a public health measure reduces the spread of diseases. Various disinfection technologies can be used to meet the pathogen inactivation demand in water. Many of these chemical disinfectants if overdosed or used inappropriately can react with organic and inorganic precursors and bring the formation of disinfection by-products (DBPs) with adverse health effects.

The European Community's (EC) environmental regulations aim to set standards for drinking water and to protect public health from the adverse effects of any contamination (Council Directive 98/83/EC) [1], while for wastewater aim to reduce the pollution of surface water [2,3] caused by municipal wastewater discharge (Council Directive 98/15/EC) [4]. Italian legislation (Decree Italian Law 152/2006 and following modifications) provides that wastewater treatment plants with a capacity higher than 2000 PE (population equivalent), with the exclusion of treatment plants that apply natural technologies such as constructed wetlands or lagoons, must be equipped with a disinfection phase [5]. Disinfection is used in case of emergencies related to health risk situations or to ensure the achievement of the environmental quality objectives.

Drinking water regulations provide that drinking water treatment plants must be equipped with a disinfection phase when surface water is used [5,6].

With the use of chemical disinfectants, residues of the compounds used and/or their DBPs can be found in the treated water that may have a toxic effect on humans and the aquatic environment.

Aim of this work is exploring the disinfection technologies applied in drinking water treatment plants (DWTPs) and in wastewater treatment plants (WWTPs). This work consists of three parts: the first section reports the conventional processes applied on full scale; while the second one presents the advanced processes. In the third section the natural disinfection technologies are exposed. For conventional technologies, the following are examined: the action mechanisms; the possible formation of DBPs; the operative conditions, and; advantages and disadvantages. For advanced and natural processes the action mechanisms are reported.

2. Disinfection Treatment

To ensure microbiological quality disinfection treatment is of primary importance. Using disinfectants, pathogenic bacteria from the water can be killed and water made safe for the user [7].

The World Health Organization (WHO) provide the guidelines for drinking water quality in the protection of public health [8]. The guidelines provide the recommendations for managing the risk from hazards that may compromise the safety of drinking water and provide a scientific point of departure for national authorities to develop drinking water regulations and standards appropriate for the national situation. The guidelines are intended to support the development and implementation of risk management strategies that will ensure the safety of drinking water supplies through the control of hazardous constituents of water.

Securing the microbial safety of drinking-water supplies is based on the use of multiple barriers, from catchment to consumer, to prevent the contamination of drinking water or to reduce contamination to levels not injurious to health. Safety is increased if multiple barriers are in place, including protection of water resources, proper selection and operation of a series of treatment steps and management of distribution systems (piped or otherwise) to maintain and protect treated water quality. The preferred strategy is a management approach that places the primary emphasis on preventing or reducing the entry of pathogens into water sources and reducing reliance on treatment processes for removal of pathogens.

The Guidelines for Drinking Water Quality describe four distinct types of health-based targets, applicable to all types of hazards and water supplies:

- health outcome targets (e.g., tolerable burdens of disease);
- water quality targets (e.g., guideline values for chemical hazards);
- performance targets (e.g., log reductions of specific pathogens);
- specified technology targets (e.g., application of defined treatment processes) [8].

The quality assessment microbiological of water is based on the definition and the search for indicator organisms. In a quantitative microbial risk assessment it is not possible to consider all human enteric pathogens; therefore, reference pathogens are chosen that are of particular relevance to the exposure pathways and context of the individual risk assessment. Reference pathogens are intended to provide a conservative model for the risk assessment: if the reference pathogen is controlled, it is assumed that other important pathogens within each class would also be controlled.

When considering human enteric pathogens, at least one bacterium, one virus and one protozoan are typically recommended in order to cover the range of behaviors in the main enteric pathogen groups. Inclusion of a representative helminth (e.g., *Ascaris*) is recommended for wastewater reuse and sanitation-based scenarios.

Specific studies may require more detailed consideration of variability between pathogens within a particular group, in which case more than one reference organism should be selected (e.g., it may be relevant to model the highly chlorine-resistant oocysts from the parasitic protozoan *Cryptosporidium* alongside the less resistant but more numerous *Giardia* cysts in freshly contaminated waters). Both the GDWQ (Guidelines for Drinking Water Quality) [8] and the GWEG (Guidelines for the safe use of wastewater, excreta and greywater) [9] rely primarily on rotavirus, *Campylobacter* and *Cryptosporidium* as reference pathogens.

However, the guidelines recommend that local considerations need to be accounted for, including the following:

- the epidemiological information on disease prevalence and outbreaks via the local water pathway(s);
- scientific evidence on pathogen persistence and infectivity;
- severity of disease outcomes [10].

The choice of indicators is used to determine the microbiological quality of water environments. The use of indicator organisms doesn't allow a direct estimation of the presence of a pathogenic microorganisms in the aquatic environment; it allows, rather, the rating of the probability that it will be present.

The EPA (Environmental Protection Agency) RWQC (Recreational Water Quality Criteria) recommend using the bacteria *Enterococci* and *E. coli* as indicator organisms for freshwater. Interestingly, many of the states have used the EPA RWQC as the basis for the reuse of wastewater.

The reuse of wastewater has positive benefits such as: improved agricultural production; reduced energy consumption associated with production, treatment, and distribution of water; there are also significant environmental benefits, such as reduced nutrient loads to receiving waters due to reuse of the treated wastewater.

The key objective is to achieve a quality of reclaimed water that is appropriate for the intended use and is protective of human health and the environment [11]. Regarding the microbiological quality of drinking water, the standards currently in force in Italy take as indicator the *Enterococci* and *Escherichia coli* [6]. On the other hand, for wastewater the standards currently in force in Italy take as the single indicator of faecal pollution the *Escherichia coli* [5].

The factors to be considered in choosing the disinfection treatment are [12]:

- the water characteristics (type and concentration of microorganisms);
- the effluent final quality;
- the disinfectant agent toxicity;
- the disinfection by-products formation;
- plants characteristics (WWTPs and DWTPs);
- costs.

Moreover, the disinfection efficiency is affected by several interferences, such as ferrous and manganese ions, nitrites, sulphides and organic substances, that reduce the concentration of oxidizing disinfectants with the consequent reduction of microorganisms inactivation [13].

In order to evaluate the performance of the disinfection process is very important to consider the logarithmic removal rates. Table 1 shows the logarithmic removal rates for various human enteric pathogens with different disinfection processes.

Table 1. Indicative log₁₀ removals of enteric pathogens and indicator organism [14].

Treatment	<i>E. coli</i>	Bacterial Pathogens (Including <i>Campylobacter</i>)	Viruses (Including Adenoviruses, Rotaviruses and Enteroviruses)	<i>Giardia</i>	<i>Cryptosporidium</i>	<i>Clostridium</i> <i>Perfringens</i>
Chlorination	2.0–6.0	2.0–6.0	1.0–3.0	0.5–1.5	0.0–0.5	1.0–2.0
Ozonation	2.0–6.0	2.0–6.0	3.0–6.0	N/A	N/A	0–0.5
Ultraviolet (UV) radiation	2.0–>4.0	2.0–>4.0	>1.0 adenovirus; >3.0 enterovirus, hepatitis A virus	>3.0	>3.0	N/A
Membrane filtration	3.5–6.0	3.5–>6.0	2.5–>6.0	>6.0	>6.0	>6.0
Reverse osmosis	>6.0	>6.0	>6.0	>6.0	>6.0	>6.0
Lagoon storage	1.0–5.0	1.0–5.0	1.0–4.0	3.0–4.0	1.0–3.5	N/A
Wetlands-surface flow	1.5–2.5	1	N/A	0.5–1.5	0.5–1.0	1.5
Wetlands-subsurface flow	0.5–3.0	1.0–3.0	N/A	1.5–2.0	0.5–1.0	1.0–3.0

Note: N/A: not available.

In this work the disinfection treatments are divided in conventional, advanced and natural processes. The conventional technologies include chlorine, chlorine dioxide, ozone, peracetic acid and ultraviolet (UV) radiation. The advanced technologies include the combination of ozone and hydrogen peroxide, of ozone and UV radiation, of hydrogen peroxide and UV radiation, of UV radiation with titanium dioxide, membranes technologies, and processes that are being studied. Finally, the natural disinfection technologies (slow sand filtration, infiltration/percolation in the soil, wastewater stabilization ponds and constricted wetlands) are exposed.

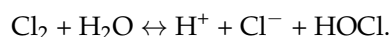
2.1. Conventional Technologies

Conventional technologies are the most widely used processes for disinfection of water. They are classified into chemical processes, including chlorine, chlorine dioxide, ozone and peracetic acid. In addition to chemical disinfectants, UV radiation has been used for many years for disinfection in wastewater treatment.

This section treats the different conventional disinfectants, their action mechanisms, the by-products formation and operative conditions.

2.1.1. Action Mechanisms

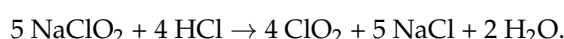
Chlorine is the most widely used disinfectant for the inactivation of waterborne pathogens in water treatment in the form of gaseous chlorine, chloramines and, above all, sodium hypochlorite [15]. The influencing factors are temperature, pH and organic content in the water. When chlorine gas is dissolved in water, it rapidly hydrolyzes to hydrochloric acid (HCl) and hypochlorous acid (HOCl) [16]:



Chlorine has a powerful bactericidal action through the “blockage” of vital activities, with rather complex mechanisms. The main action of chlorine is to modify the chemical structure of the enzymes that are the basis of the mechanisms of nutrition of bacteria, inactivating them and thus inhibiting their development and life.

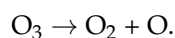
Chlorine dioxide is another bactericidal agent whose disinfectant power is equal to or higher than chlorine. Chlorine dioxide is a yellow-green gas with a pungent smell, water-soluble, but very unstable.

It is usually produced by sodium hypochlorite and hydrochloric acid according to the reaction:



Chlorine dioxide is characterized by high oxidizing power, which is the cause of its high germicidal potential. Due to the high oxidative power, possible bacterial elimination mechanisms may include inactivation of enzymatic systems or interruption of protein synthesis [17].

Ozone is an unstable gas produced by the dissociation of oxygen molecules in atomic oxygen. Ozone production can be done by electrolysis, photolytic reactions, and by radiochemical reaction induced by electric shocks. It is a highly unstable gas that, when produced, is rapidly discharged according to the reaction:



Ozone is an extremely reactive oxidizing agent characterized by disinfection efficiencies higher than the disinfection with chlorine [18]. The bactericidal power is generally attributed to the ability to destroy the cell wall of the microorganisms.

Ozonation also provides a significant reduction of UV absorbance and color, which can be an advantage for some reuse applications [19]. Furthermore ozonation is a promising technology for enhanced wastewater treatment to eliminate various organic micropollutants [20].

Peracetic acid is a feasible alternative to wastewater chlorination [21]. Peracetic acid (PAA) is produced by the reaction between hydrogen peroxide (H_2O_2) and acetic acid (CH_3COOH). During use the PAA decomposes, resulting the formation of acetic acid and oxygen.

The use of peracetic acid causes an increase of BOD (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand) on the final effluent resulting from the formation of acetic acid in solution.

The disinfecting action of PAA is due to the release of active oxygen or the production of reactive hydroxyl radicals that attack the bacterial cell causing cell wall and membrane destruction as well as certain enzymes and DNA [22–24].

Recently the combination between peracetic acid and UV radiation resulted very efficient [25,26].

The ultraviolet radiation (UV) includes electromagnetic radiations between the X-rays and visible light in the range of λ from 100 to 400 nm. The germicidal UV-ray portion falls in the range 220–320 nm. The generation of UV rays is carried out by means of lamps containing mercury vapors produced through an electric arc. The energy generated by the excitation of mercury vapors contained within the lamp results in the emission of UV radiation [27].

The radiation penetrates the cell wall of the microorganisms and is absorbed by the nucleic acids causing the inhibition of replication and the death of the cells [28].

The effectiveness of UV radiation for disinfecting high quality secondary or tertiary treated effluents has been demonstrated [29–31]. The efficiency of UV disinfection can be influenced by suspended particles, particle sizes, or concentrations of dispersed microorganisms [32].

UV disinfection technology results very effective against the (oo)cyst of *Cryptosporidium* and *Giardia*, two pathogenic microorganisms of major importance for the safety of drinking water [33].

2.1.2. By-Products Formation

Disinfection processes can result in the formation of both organic and inorganic disinfection by-products (DBPs) [34].

Chlorine, in presence of natural organic substances, produces trihalomethane and acetoacetic, known to be carcinogenic to humans [35–42].

The trihalomethanes (THMs) are generally the most prevalent. These are a volatile group of compounds, which comprises chloroform, bromodichloromethane (BDCM), chlorodibromomethane (CDBM), and bromoform.

Chlorine reacts with natural organic compounds (such as humic and fulvic acids) to form a wide range of unwanted halogenated organic compounds including THMs, haloacetic acids (HAAs), chlorophenols, chloral hydrate, and haloacetonitriles (HANs).

Chloroform is usually the most prevalent by-product formed, although brominated THMs can occur at high concentrations when waters with high bromide concentrations are chlorinated.

Most other DBPs occur at trace concentrations (usually $<1 \mu\text{g L}^{-1}$) [43].

The disinfection of water containing dimethylamine with chlorine leads to the formation of NDMA (N-nitrosodimethylamine). The concentration of NDMA is closely related to the ratio of chlorine, ammonia ions and dimethylamine [44].

During disinfection with chlorine dioxide, chlorite (ClO_2^-) and chlorate (ClO_3^-) are the major reaction by-products, potentially toxic. It is believed that the degradation of the residual chlorine dioxide and other final reaction products is faster than that observed in the case of chlorine and therefore these compounds should not represent a hazard to the aquatic environment [45].

During the disinfection with ozone, the formation of organic (e.g., aldehydes, carboxylic acids, and ketones) and inorganic (e.g., bromate) disinfection by-products has been well documented [46–53]. Ozone does not cause the formation of chlorinated by-products such as trihalomethane, but recent studies indicate that ozone induce the formation of NDMA [54–56].

The PAA dosage to the water causes the formation of aldehydes at very low concentrations ($<30 \text{ mg L}^{-1}$). The aldehyde formation is directly proportional to the peracetic acid dosage. The aldehydes formation varies with PAA/COD ratio, reaching a maximum around $0.3 \text{ mg PAA/mg COD}$ and then tending to vanish [57]. After initial increase ($<20 \text{ min}$), aldehydes formation starts to decrease and finally disappears in agreement with Chiang et al.'s two-step “formation and destruction” reaction mechanism [58].

The disinfection with UV radiation does not cause a formation of by-products [28].

Table 2 shown the advantages, the disadvantages, the actions spectrum and the applications of conventional disinfectants.

Table 2. Conventional disinfection technologies against different microbial groups [59,60].

Conventional Technologies	Advantages	Disadvantages	Application
Chlorine	Easy to handle and economical; Residual concentration; Technologies consolidated	High contact time; By-product formation; Residual toxicity of the effluent; Very corrosive	Drinking water; Wastewater
Chlorine dioxide	More effective than chlorine over short contact; Long residual	Residual toxicity of the effluent; By-product formation; Generation onsite; Medium-high management costs; Increase the concentration of solids in the effluent	Drinking water; Wastewater
Ozone	Short contact time	No residues of disinfectant; By-product formation; Generation onsite; High energy demand; High management costs	Wastewater
Peracetic acid	Simple solution; Residual concentration	Increase BOD and COD concentration in the effluent; By-product formation	Wastewater
UV radiation	No by-products formation; Short contact time; Inactivation of virus	No residues; High energy demand; High cost; Unsuitable for water with high levels of suspended solids, turbidity, color or soluble organic matter	Wastewater

Water disinfection is a treatment aimed at reducing the presence of pathogenic microorganisms in the water, with a variable removal rates, as shown in Table 3. In particular, the CT (CT value is the product of the concentration of disinfectant agent in the water and the time of contact) values for 99% (2-log) and 99.99% (4-log) inactivation of bacteria and viruses for various disinfectant agents are reported.

The concept of disinfectant concentration and contact time is important to the understanding of disinfection kinetics and the practical application of CT concept (which is defined as the product of the residual disinfectant concentration C , expressed in mg L^{-1} , and the contact time T , expressed in minutes, that residual disinfectant is in contact with water) is important. CT value represents an operative parameter and it is an indicator of the effectiveness of the disinfection process.

Table 3. Disinfectant dosage for bacteria and viruses inactivation [60].

Disinfectant Agent	Measurement Unit	Bacteria Inactivation		Viruses Inactivation	
		2-log	4-log	2-log	4-log
Chlorine	(mg min L ⁻¹)	0.1–0.2	10–12	2.5–3.5	6–7
Chlorine dioxide	(mg min L ⁻¹)	8–10	50–70	2–4	12–20
Ozone	(mg min L ⁻¹)	3–4	-	0.3–0.5	0.6–1.0
UV radiation	(mJ cm ⁻²)	30–60	80–100	20–30	70–90

2.1.3. Operative Conditions

The sodium hypochlorite dosing system consists of a pump and a storage tank. Adequate mixing and contact time must be provided after injection to ensure complete disinfection of pathogens. It may be necessary to control the pH of the water [61].

Chlorination with sodium hypochlorite is a relatively simple and cost effective process, which does not require extensive technical expertise and which is capable of dealing with supply systems of varying size by altering dosing systems or storage for chemical contact accordingly [62].

Sodium hypochlorite solution is diluted with water in a mixing/holding tank. The diluted solution is injected by a chemical pump into the water supply pipe at a controlled rate. Adequate mixing and contact time must be provided [61].

Chlorine dioxide is unstable and it not be stored, but must be produced directly on site and only after the production is added to water [63]. Chlorine dioxide can be produced by using sodium chlorine combined with hydrochloric acid or chlorine gas.

Ozone is unstable and therefore must be generated in situ. Ozonation equipment includes air preparation equipment (ozone generator, contactor, destruction unit), instrumentation and controls. The capital costs of ozonation systems are relatively high. Operation and maintenance are relatively complex. Electricity represents 26 to 43% of the total operating and maintenance costs for small systems [61].

In disinfection with PAA the plants are very simple, similar to the storage and dosing systems of sodium hypochlorite [63].

The effectiveness of UV radiation disinfection depends on the energy dose absorbed by the organism, measured as the product of the lamp's intensity (the rate at which photons are delivered to the target), the time of exposure, the color and turbidity of water. If the energy dose is not high enough, the organism's genetic material might only be damaged instead of destroyed. To provide a safety factor, the dose should be higher than needed to meet disinfection requirements.

Table 4 contains the operative conditions of conventional processes.

Table 4. Operative conditions of conventional technologies [63].

Conventional Technologies	Chlorine Gas	Sodium Hypochlorite	Chlorine Dioxide	Ozone	Peracetic Acid	UV Radiation
Capacity	all *	all	medium-high	medium-high	all *	all
Production and storage system	simple	-	complex (generation on site)	complex (generation on site)	simple	-
Maintenance	low	low	moderate	frequent	moderate	moderate/frequent
Staff risks/competence	high	low	low-medium	high	high	high
Investment costs	low	low	medium	very high	low	high
Management costs	low	low	medium	high	medium	medium

Note: * these chemical agents could be used for plant with all capacity, but the high risks for staff and the high competence required reduce the field of use.

2.1.4. Acute Toxicity

Wastewater treatment plants should maintain a certain residual in the wastewater to ensure bacterial die-off during chemical disinfection. Because disinfection is the last process in a WWTP before discharge, the residual gets transferred with the treated discharge. Residuals of the oxidizing disinfectants have long been known to be toxic to aquatic life in the receiving body of water [64].

A recent study demonstrates that chlorine and PAA residuals cause acute toxicity during disinfection. In particular, with values of residual disinfectant higher than 0.18 for free chlorine, and 2 mg L⁻¹ for PAA, acute toxicity on *Daphnia magna*, *Vibrio fischeri* and/or *Pseudokirchneriella subcapitata* has occurred [65].

2.2. Advanced Oxidation Processes

In this section, the advanced oxidation processes (AOPs) that can be used for the final phase of DWTPs or WWTPs are reported. Despite the AOPs are generally used for the oxidation of a wide range and variety of organic and inorganic compounds, they can be apply for the water disinfection.

2.2.1. Chemical Agents Combined with UV Radiation

Advanced oxidation processes (AOPs) are treatments that aim to chemically destroy a contaminant, with the formation of reaction reactants with high reactivity, such as OH• radicals, that can be obtained by simultaneously applying different oxidants: ozone; hydrogen peroxide; radiation UV, and; peracetic acid.

AOPs are a very effective treatment technology since they can simultaneously degrade recalcitrant organic compounds and biological contaminants [66].

There is a frequent debate on the role of OH• on pathogen disinfection. Some authors have stated that OH• are not effective against *Giardia muris*, while others have suggested that OH• play an important role in inactivation of *E. coli* and *Bacillus subtilis* spores. OH• produced in a photocatalytic disinfection process have been found to provide residual effects that repress the post-UV reactivation of coliform bacteria [67].

Traditional water disinfection treatment processes such as ozonation and UV disinfection can easily be retrofitted to accomplish advanced oxidation in both water and wastewater treatment plants.

The main applications in the treatment of water oxidation and disinfection are:

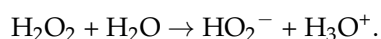
- ozone with hydrogen peroxide;
- ozone with UV radiation;
- hydrogen peroxide with UV radiation;
- UV radiation with titanium dioxide.

Advanced oxidation processes have advantages over conventional disinfection treatments such as, for example, not generating disinfection by-products [68]. Nevertheless, the common disadvantage shared between all AOPs is the high operating cost, which has somewhat limited large-scale application of this otherwise very powerful technology. However, with the introduction of higher efficiency UV lamps, visible light catalysts, and improved reactor design, with the help of computational fluid dynamics and energy modeling, both UV and solar-based photocatalysis have great potential for large-scale application [69].

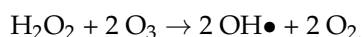
2.2.2. Ozone with Hydrogen Peroxide

The oxidation process combined with ozone and hydrogen peroxide (peroxone) is among the most used for water treatment.

Hydrogen peroxide decomposes according to the following reaction:



The HO_2^- reaction with ozone generates a sequence of chain reactions leading to the formation of $\text{OH}\bullet$ radicals. The overall reaction of the formation of $\text{OH}\bullet$ radicals is:



Disinfection efficiency can be given for peroxide/ozone systems depending on the ozone residual remaining in the effluent water; this residual will decrease as the peroxide to ozone ratio increases [70].

The key difference between ozone and peroxone is in the primary oxidation mode; that is, direct oxidation or hydroxyl radical oxidation. The reactivity of these compounds creates a different effect in the reactions with water constituents and, thus, disinfection effectiveness.

Several studies showed that peroxone was comparable to ozone, or slightly more powerful, when CTs were based on ozone residuals. These results suggest that free radicals provide little benefit in terms of microbial destruction [71].

When the combination of ozone and hydrogen peroxide is used, the primary cause for pathogen inactivation is attributed to ozone, specifically the mechanisms associated with the oxidation of pathogens by direct ozone reaction and hydroxyl radicals.

Studies using ozone-hydrogen peroxide have shown that disinfection of *E. coli* is less effective as the peroxide to ozone ratio increases to above approximately 0.2 mg mg^{-1} [71]. The decrease in disinfection was probably due to the lower ozone residuals associated with higher peroxide to ozone ratios, which indicates that direct ozone reaction is an important mechanism for pathogen inactivation.

The results of a work that studied the inactivation of *Giardia muris* cysts (Table 5) suggest that peroxone is slightly more powerful than ozone: the CT values for ozone are greater than for peroxone. However, because ozone decomposes more rapidly in the presence of hydrogen peroxide, higher ozone dosages may be necessary with peroxone to achieve comparable residuals. Moreover, the use of ozone residuals to calculate CT products for peroxone may not take into account other oxidizing species that may have disinfectant capabilities [71].

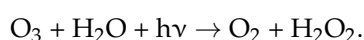
Table 5. Disinfectant dosage for *Giardia muris* inactivation [71].

Disinfectant Agent	Measurement Unit	<i>Giardia muris</i> Inactivation	
		1-log	2-log
Ozone	(mg min L ⁻¹)	1.6–2.8	3.4–5.4
Peroxone	(mg min L ⁻¹)	1.2–2.6	2.6–5.2

2.2.3. Ozone with UV Radiation

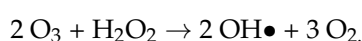
Combination of ozone with UV radiation leads to the formation of radical reactions triggered by photochemical reaction between UV radiation and ozone both in gaseous phase and aqueous solution. Radicals, thanks to their high redox and low selectivity potential, are able to trigger more effective processes than using ozone only.

The ozone photolysis reaction in aqueous phase is:

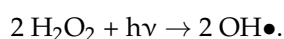


$h\nu$ indicates UV radiation.

The production of radicals result from secondary reactions taking up hydrogen peroxide:



From hydrogen peroxide photosynthesis:



As concerns the disinfection efficiency of this process, Fang et al., 2014 [67] showed that synergistic effects in *E. coli* inactivation were observed after the UV/ozone coexposure at ozone concentrations as low as 0.05 mg L⁻¹ in ultrapure water. This synergistic effect occurred particularly at the initial stage of the coexposure: this aspect could be explained by the enhanced production of OH• or other reactive especially during the initial coexposure but not at the later stage.

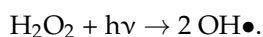
The UV/ozone coexposure achieved higher inactivation of *E. coli* than did the UV-ozone and ozone-UV sequential exposures, but the results of bacteriophage MS2 were the opposite. The synergistic effects were also found in tap water.

Moreover, Fang et al., 2014 [67] showed that combining UV with low-dose ozone can enhance disinfection efficiency and repress bacteria photoreactivation.

Other authors [72] report that the ozone/UV combination provides multiple barriers for *Cryptosporidium* and *Giardia*.

2.2.4. Hydrogen peroxide with UV radiation

The use of a low-pressure mercury lamp on water containing hydrogen peroxide leads to the H₂O₂ photolysis reaction; this reaction, essentially related to the absorption of a radiation emitted at 253.7 nm, is [73]:



The radicals, produced by the reaction, can start a series of radical-chain reactions. The main factors that limiting the process efficiency are:

- the low molar absorption coefficient of H₂O₂ which requires high concentrations of hydrogen peroxide to generate OH• radicals;
- H₂O₂ can function as a scavenger against OH• radicals (OH• + H₂O₂ → H₂O• + H₂O) so high concentrations of H₂O₂ can reduce process efficiency [74].

Despite many studies report that the H₂O₂/UV is effective for the destruction of various pollutants such as pesticides and pharmaceuticals, few available reports show the inactivation of microorganisms via OH radical oxidation.

Mamane et al. (2007) [75] showed that the addition of H₂O₂ (at 25 mg L⁻¹) in the presence of filtered UV irradiation over a 15 min reaction time did not result in any additional disinfection of bacteriophage T4, while an additional 1-log inactivation for bacteriophage T7 and 2.5-log for bacteriophage MS2 were obtained. As concerns the *E. coli* inactivation, only a slight additional effect was observed when H₂O₂/UV was applied.

Other authors [76] have investigated the H₂O₂/UV disinfection efficiency. They observed that the combined H₂O₂/UV disinfection only slightly influenced the microbial reductions compared to UV treatments and showed some antagonism and no synergies. In particular, the combined H₂O₂/UV treatments showed statistically significant antagonistic effects for *E. faecalis* and non-significant synergy for MS2 coliphage [76]. Furthermore, at a cost parity for PAA/UV advanced oxidation process has the same disinfectant action than H₂O₂/UV.

The efficiency of H₂O₂/UV depends on the microorganism and water type. These results indicate that for an UV based AOP process, the disinfection due to the presence of OH radicals is very small compared to the damage from the UV irradiation, although for viruses, there may be some oxidative enhancements that can assist disinfection efficacy [75].

Kruthof et al. (2007) [77] have studied H₂O₂/UV treatment for both primary disinfection and organic contaminant control in DWTPs. They proposed to apply this process before the GAC filtration in order to obtain a removal of residual H₂O₂.

Recently the combination with solar irradiation and H₂O₂ has been studied; it can produce cell inactivation due to the higher OH• generation caused by H₂O₂ photolysis at λ < 254 nm, cellular membrane attack and intracellular ROS (reactive oxygen species) formation [78].

2.2.5. UV Radiation with Titanium Dioxide

Titanium dioxide excited with UV radiation can produce $\text{OH}\bullet$ radicals through redox processes. The photocatalytic process most used ones include:

- the addition of powder catalyst in an aqueous solution;
- preparation of a catalyst-based film (sol-gel method), which is adhered to a support material.

The main parameters that influence the yield of the process are [79]:

- the amount of TiO_2 used (higher dosages are higher yields);
- lamp type (wavelengths less than 400 nm are generally sufficient for process activation);
- UV intensity (yield increases with increasing intensity);
- rotation speed (in rotating reactors the yield increases at the rate of increase);
- concentration of bicarbonate ions (increase in alkalinity decreases efficiency).

TiO_2 photocatalysis has been reported to kill microorganisms and is not expected to produce THMs when used to treat drinking water. A drawback to using TiO_2 photocatalysis as a disinfectant for drinking water is the lack of a residual disinfectant to maintain disinfection throughout a municipal distribution system. Because the hydroxyl radicals formed by TiO_2 photocatalysis are highly reactive and are short-lived in water, the DWTPs will probably need to use a secondary disinfectant, such as chlorine (in addition to TiO_2 /UV treatment), to maintain a residual disinfectant in the distribution system [80].

Many authors carried out studies to identify the effective disinfection factors, such as the TiO_2 concentration, light intensity, and pH.

Watts et al. (1995) [81] has investigated the photocatalytic inactivation of coliform bacteria and poliovirus I in secondary wastewater effluent. The results obtained with $0.25 \text{ g TiO}_2 \text{ L}^{-1}$ addition and the irradiation with a fluorescent light show that 150 and 30 min were required to achieve 2-log reduction of coliform bacteria and poliovirus I, respectively. Moreover, the photochemical removal of poliovirus I and coliform bacteria was unaffected by the pH of the solution (in the range tested: 5–8).

Chai et al. (2000) [82] showed that the disinfection capability in the aspect of time using both TiO_2 and UV light was more than 27 times as that by using only the UV. These authors have shown that the optimal TiO_2 concentration and UV light intensity were $0.1 \text{ gTiO}_2 \text{ L}^{-1}$ and 50 W m^{-2} ; in these conditions the time required for the complete disinfection of *E. coli* was 2–3 min.

Cho et al. (2002) [83] studied the effect of TiO_2 concentration on the survival ratio of *E. coli*: they showed that 0.1 wt % TiO_2 loading (equal to 0.1 g L^{-1}) is sufficient to harvest all of the incident light and that there is no advantage in going beyond this catalyst loading.

As concerns the inactivation behaviors of MS2 phage and *E. coli*, Cho et al. (2005) [84] showed that these aspects, which are mediated by the hydroxyl radicals generated on the illuminated TiO_2 surface, are quite different, depending on the kind of microorganism (MS2 phage or *E. coli*). It was found that the inactivation of MS2 phage was carried out predominantly through the action of the bulk phase free hydroxyl radical, but that *E. coli* was inactivated by both free and surface-bound hydroxyl radicals as a major path and by other ROS such $\text{O}_2^{\bullet-}$ and H_2O_2 as a minor path.

2.2.6. Membrane Filtration

The membrane technologies allow the separation through a physical barrier to the pollutants present in the water. With the passage through the membranes, there is almost complete remove of the bacteria, and partial viruses that however reach very high values in the case of ultrafiltration [85].

Membrane filtration is an effective method to remove particles, microorganisms and organic matter from drinking water and wastewaters. Compared with conventional treatment methods, membrane processes [86]:

- can provide better quality water;
- minimize disinfectant demand;
- are more compact;
- provide easier operational control and less maintenance;
- generate less sludge.

The most used technologies are (Table 6)

- microfiltration (0.1–10 μm) is able to ensure the removal of most bacteria and protozoa's cysts, while not providing adequate virus removal;
- ultrafiltration (0.01–0.1 μm) that allows complete removal of bacteria, viruses and protozoa;
- nanofiltration (0.001–0.01 μm) that is able to remove color, volatile organic compounds (VOC), pesticides, sulphates, phosphates and microcystins produced by many cyanobacteria species [87];
- reverse osmosis (<0.001 μm): it is necessary to provide some pre-treatment (flocculation, lime addition, sedimentation, rapid filtration or ultrafiltration) to reduce the content of colloidal substances, suspended solids and organic matter which may cause problems of fouling of membranes with consequent reduction of efficiency and operating flow [60].

Whereas nanofiltration and reverse osmosis processes are effective in removing protozoan (oo)cysts, microfiltration and ultrafiltration are the most commonly applied/used technologies for microbial removal because of their cost-effectiveness [88].

Table 6. Membrane technologies.

Technologies	Porosity (μm)	Pressure (bar)	Removal	Disinfection Efficiency (Log Reduction)		
				<i>E. coli</i> and <i>Fecal coliform</i>	<i>Giardia Muris</i>	<i>MS2 Coliphages</i>
Microfiltration MF	0.1–10	1–5	Suspended solids, macromolecules, bacteria	5.4–6	>4–6	0.3–2
Ultrafiltration UF	0.01–0.1	1–7	Macromolecules, viruses, humic acids, DBP precursors	5.5–>6	>4–6	0.4–2
Nanofiltration NF	0.001–0.1	5–10	Color, VOC, pesticides, MTBE (Methyl tert-butyl ether), sulphates, phosphates	N/A	N/A	2–3
Reverse osmosis RO	<0.001	15–70	Metal ions, metals (arsenic, lead)	N/A	N/A	3.5–4.5
References		[60,79,89]		[89]	[90]	[76,89,90]

Note: N/A: data not available. Disinfection by-product (DBP); volatile organic compound (VOC).

The efficiency of the membranes depends on the water quality, the load of solids and the formation of fouling during the treatment. To reduce this problem, we can use systems combined with a low pressures membrane filtration followed by high pressures membrane filtration.

2.2.7. Other Disinfectant: Research Experiences

Table 7 shows experiences of experiments of advanced disinfection processes reported in international scientific literature. These research experiences are very heterogeneous both for the type of disinfectant and the type of water treated.

Table 7. Other disinfectant [91–95].

Type of Disinfection	Action Mechanism	Type of Effluent	Operative Conditions	Experimental Scale	Results	Ref.
UV+Peracetic acid (PAA)	UV produces a homolytic rupture in the O–O bond of the PAA molecule, with the subsequent formation of the hydroxyl radical	Urban wastewater	PAA dosage: 2–8 mg L ^{−1} t: 10–30 min UV: 100–300 mJ cm ^{−2}	Pilot plant	<i>E. coli</i> : Total inactivation	[91]
Sonodisinfection	Production of free radicals in the bulk; shearing forces produced by US cavitation; breakage of bacteria agglomeration, that favours the disinfection	Urban wastewater	US: 200 W Irrad. time: 60 min	Bench scale	<i>E. coli</i> : 1-log	[92]
Electrodisinfection	Hypochlorite and chloramines production		Current density: 11.46 A m ^{−2}		<i>E. coli</i> : 3-log	
Sono-electrodisinfection	Hypochlorite and chloramines production		US: 200 W Current density: 8.91 A m ^{−2}		<i>E. coli</i> : 3-log	
Solar photolysis	Dimerization of DNA	Drinking water/wastewater	Irrad. time: 40 min	Lab scale	<i>E. coli</i> : 1-log	[93]
Solar photocatalytic (absence of HA)			Irrad. time: 60 min Dosage of dopants *		<i>E. coli</i> : 6-log	
Solar photocatalytic (presence of HA)			Irrad. time: 60 min Dosage of dopants **; Irrad. time: 90 min Dosage of dopant ***		<i>E. coli</i> : 6-log	
Combination of ultrasound (US) and UV radiation	Ultrasound destroys large suspended particles and the UV disinfection efficiency increases	Urban and industrial wastewater	US: 350 W UV: 1656 mJ cm ^{−2} t:15 min US: 1400 W UV: 1656 mJ cm ^{−2} t:15 min	Pilot plant	<i>E. coli</i> : 1.6-log Total coliform: 1.7-log <i>E. coli</i> : > 4-log Total coliform: 3.9-log	[94]
Comparison between UV continuous and UV pulsed	DNA damage	Wastewater	3 mJ cm ^{−2}	Bench scale	<i>E. coli</i> 1.75-log	[95]
					Phage T4 2.55-log	
					Phage T7 1.05-log	
					1.80-log	
					2.67-log	
					0.25-log	
					1.20-log	
					0.93-log	
					0.08-log	
					0.49-log	
					0.52-log	

Note: HA: humic acid; * 3 kinds of dopants are dosed: Se-doped TiO₂, N-doped TiO₂ and Se-N-co-doped TiO₂; ** 2 kinds of dopants are dosed: Se-doped TiO₂ and Se-N-co-doped TiO₂; *** 1 kind of dopant is dosed: N-doped TiO₂ t: contact time; Irrad. time: irradiation time; LP: low-pressure; MP: medium-pressure; PUV: pulsed UV.

2.3. Natural Disinfection

2.3.1. Slow sand Filtration

The slow sand filtration (filtration rate of $3\text{--}8\text{ m d}^{-1}$) utilizes the purifying action on a superficial biological film that forms on the filter medium, which can remove over 99% (2-log reduction) of the microorganisms present in the influent (previously decanted or subjected to secondary biological treatment) without the need for any further treatment [96].

Slow sand filtration is one of the oldest water treatment process used to produce microbiologically safe water. Additional research was conducted [97–100] to collect more quantitative information.

2.3.2. Porous Ceramic Water Filtration

The most used filters (at household level) are made of porous natural materials that are easily accessible, such as clay, or its blending with inorganic materials such as ceramic. A ceramic filter can be simply obtained by the mixing of dry clay with organic material (such as coffee, tea leaves or rice shells) with the addition of water to obtain a rigid mixture. Ceramic filters are being produced in many parts of the world. Some of them are manufactured in developed or emerging countries under strict quality control constraints.

The ceramic filters are extensively tested for efficacy in reducing various waterborne microbial contaminants. The disinfection performance of ceramic filters with a pore size equal to $0.2\text{ }\mu\text{m}$, in terms of log reduction, are the following [101]:

- *E. coli*: >7.9 ;
- *Shigella dysenteriae*: >6.9 ;
- *Vibrio cholera*: >4.0 ;
- *Giardia lamblia*: >6.5 ;
- *Cryptosporidium parvum*: >3.0 ;
- *Entamoeba histolytica*: >5.9 .

2.3.3. Infiltration/Percolation in the Soil

This technique is very similar to slow filtration and consists in periodically distributing the effluent from a secondary treatment over a sand filtration layer ($1.5\text{--}2\text{ m}$ thick). Periodic application makes filtration and percolation processes possible. As the effluent goes through the sand, the frequent presence of air in the sand layer maintains aerobic conditions.

With a sand filtration layer of 1.5 m and a hydraulic load between 0.15 and 0.35 m d^{-1} , the removal of *Fecal coliform* is equal to 5-log and the Helminth eggs are totally removed [96].

2.3.4. Managed Aquifer Recharge

Managed aquifer recharge (MAR) is used for treating water for potable use and storing water for future needs by recharging the natural groundwater source. There are several methods used for MAR: aquifer storage and recovery (ASR); aquifer storage; transfer and recovery (ASTR); infiltration ponds; infiltration galleries; soil aquifer treatment; percolation tanks or recharge weirs; rainwater harvesting for aquifer storage; recharge releases; dry wells; bank filtration; dune filtration; underground dams, and; sand dams [102]. The main principle being that surface water from a lake or a river is by artificial means made to percolate or flow through porous material such as sand to recharge the groundwater [103].

The MAR method by basin infiltration was shown to have a high pathogen removal capacity in regard to bacteria and viruses. The microbiological barrier regarding virus was efficient in 4 m of unsaturated zone, 3-log, comparable with both disinfection with chlorine and chemical precipitation. For viruses the efficiency was higher in unsaturated zone compared to saturated zone.

The microbiological barrier efficiency regarding bacteria was sufficient in 4 m of unsaturated zone, higher than 2.4-log, comparable to disinfection with chlorine and chemical precipitation. However, there was no obvious difference in efficiency between an unsaturated and a saturated condition.

The protozoa should be effectively removed because they are larger than bacteria; however, heterogeneity in the soil and the protozoan high survival suggests that this should not be taken for granted [103].

2.3.5. Wastewater Stabilization Ponds

This process consists of oxidation basins (depth $h = 1.5\text{--}2$ m and retention time of 10–50 d) working in series with an aerobic final stage ($h = 0.5\text{--}1$ m). Removal is due to different factors: food shortages, predation, algae adsorption, high pH values, solar radiation [96].

Elevated pH and dissolved oxygen concentrations, which are attributed to the presence of algae, are important factors for effective disinfection. Therefore, the presence of algae in natural wastewater treatment systems can contribute appreciably to disinfection. Consequently, based on algal concentrations, removal efficiencies of pathogenic microorganisms during wastewater treatment over the course of a year can be highly variable, where higher removal efficiencies would be expected in summer and fall seasons [104].

The reduction of bacteria helminth could reach 6-log and 3-log, respectively [96]. As concerns the virus, on average, 1-log reduction was achieved for every 14.5–20.9 days of retention [105].

2.3.6. Constructed Wetlands

The main factors responsible to reducing bacterial population are: physical processes such as mechanical filtration, sedimentation and adsorption; chemical processes such as the release of oxygen from plants and biological mechanisms such as natural death, predation and action of antibiotic substances released by macrophytes.

Gopal et al. (1993) [106] found that some acids such as tannic acid and Gallic acid are secreted from the roots of many aquatic plants and cause disinfection. In addition to this direct effect the development, in the rhizosphere, of populations of bacteria with antibiotic properties (e.g., *Pseudomonas*) may also contribute to the removal of *Escherichia coli* [96,107].

The removal efficiency of *Total and Fecal coliform* in different subsurface flow wetland (typically constructed as a bed or channel containing appropriate media) that receive secondary wastewater effluent can reach 3-log reduction especially with *Scirpus* and *Phragmites* macrophytes [96].

2.3.7. Solar Disinfection

Sunlight is known to be a pertinent factor governing the infectivity of waterborne viruses in the environment. Sunlight inactivates viruses via endogenous inactivation (promoted by absorption of solar light in the UVB range by the virus) and exogenous processes (promoted by adsorption of sunlight by external chromophores, which subsequently generate inactivating reactive species).

The extent of inactivation is still difficult to predict, as it depends on multiple parameters including virus characteristics, solution composition, season and geographical location.

Endogenous inactivation is mediated by virus-internal chromophores, such as the nucleic acid or aromatic amino acids in the protein coat, which absorb light in the solar range. Upon light excitation, these internal chromophores can degrade and cause the virus to become inactivated. This process is referred to as direct inactivation. Alternatively, endogenous inactivation can occur in an indirect fashion. Hereby, the excited chromophores transfer energy or electrons to dissolved oxygen or other solution constituents, which leads to the formation of a variety of transient reactive species (e.g., singlet oxygen). Along with the excited chromophores themselves, these reactive species can then oxidize surrounding virus constituents and thereby cause inactivation. In indirect exogenous inactivation, reactive species are produced by virus-independent chromophores present in solution [108].

Another method for water disinfection by means of solar energy is the use of solar ponds. Solar ponds are dug into the ground, filled with water and covered with glazing (sheets of plastic or glass). Within the solar pool, the temperature reaches 63 °C (very close to the pasteurization temperature of 65 °C), thanks to the greenhouse effect of the glazing cover [109].

With temperature between 55 and 65 °C, it is possible to obtain inactivation yields of 90% (1-log) for protozoa (*Giardia*, *Cryptosporidium*, *Entamoeba*), bacteria (*V. cholerae*, *E. coli*, *Shigella*, *Salmonella Typhi*) and viruses, with a 1 min exposure time. Instead, with 5 min exposure time, the inactivation yields can reach 99.99% (3-log).

In order to obtain an effective bacterial inactivation, it is important to maintain an optimal saline gradient in all solar pond surface. This value is still being studied, through the development and the implementation of different methodologies [109–111].

3. Conclusions

An overview of the main disinfection processes for wastewater and drinking water was presented in this work. Despite the availability of many disinfection processes based on different action mechanisms, the conventional processes, which are consolidated technologies, represent the most used treatments. Nowadays, chlorine-based disinfectants are commonly used in Italy (mainly due to their efficiency, low cost and easy use), despite the fact that they may bring by-products to the disinfection process.

The natural disinfection processes could represent valuable solutions, due in particular to the absence of chemical reagents. Moreover, the advanced technologies are very interesting but they are still in the research state. Several strategies aiming to avoid or reduce the use of chemical reagents (especially chlorine) have already been studied. Despite the advantages of these methods, several aspects (e.g., reliability and applicability to large-scale water treatment plant, costs, etc.) restrict the use of these technologies on an industrial scale.

In future perspectives, the role of disinfection treatment should be taken into account due to the control of emerging contaminants (i.e., protozoa, which are not currently regulated in Italy). Moreover, ongoing research will lead to a deeper knowledge in emerging contaminants and DBPs; thus, the use of alternative technologies, such as membrane filtration and UV-based processes, will increase.

Finally, the multi-step disinfection concept, that is, the application of disinfection process not only as final stage, could represent an interesting solution in order to reduce the production of DBPs and to improve the removal of microorganisms.

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