Review



# Disinfection of Water by Chlorine, Peracetic Acid, Ultraviolet and Solar Radiations: A Review

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**Abstract:** Disinfection is an essential step during water treatment to ensure the microbiological safety of water for human consumption, and over time, it has been improved and better understood. In this context, this review provides a compilation of information, new insights, and perspectives on the main microorganisms present in supply water, their basic structures, and mechanisms of disinfection via chlorine, peracetic acid (PAA), ultraviolet (UV) radiation and solar disinfection (SODIS). Chlorine is the most common chemical disinfectant, however, there is the formation of toxic by-products, which has stimulated the use of non-chlorinated disinfecting power, the non-formation of toxic/carcinogenic by-products, its ability to generate radicals, such as  $CH_3C(O)O^{\bullet}$ ,  $HO^{\bullet}$  and  $HOO^{\bullet}$  with or without the use of electromagnetic radiation or thermal energy. The generation of radicals is one of the most used mechanisms to explain the oxidation process during disinfection processes, such as UV irradiation and SODIS have received significant attention because, in addition to having the ability to damage the RNA (Ribonucleic Acid) and DNA (Deoxyribonucleic Acid) of microorganisms causing their inactivation, these processes also promote the formation of radicals through reactive species that are ubiquitous in natural water. Therefore, the review will be important for studies focused on the process of water disinfection by advanced oxidized processes, especially those that use PAA combined with UV or SODIS.

Keywords: water disinfection, pathogens, effluent, chlorine, peracetic acid, ultraviolet, solar radiations

# **1. Introduction**

The absence of adequate sanitation and/or its structural fragility is one of the main causes of pollution and contamination of water, especially destined for public consumption, leading to the spread of waterborne diseases.<sup>1-4</sup>

In 2015, targets were set by the 2030 Agenda for Sustainable Development Goals (SDGs), with the aim of encouraging countries to start new efforts to achieve the 17 SDGs in the next 15 years, including objective 6 of "ensuring

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the availability and sustainable management of water and sanitation for all". Although the percentage of people with access to sanitation has improved, the world has not yet achieved the SDG target.

Conventional wastewater treatment plants use primary, secondary, and tertiary processes to remove solids, organic matter, and microorganisms.<sup>5</sup> These processes consist of coagulation, flocculation, sedimentation, filtration, disinfection, and fluoridation.<sup>6-7</sup> Water treatment plants act as a very important barrier and can prevent the spread of viruses, fungi, bacteria, and other waterborne pathogens, thus minimizing the potential risks to human health.<sup>8</sup> In addition, they are responsible for managing and replenishing water resources, because they are limited and becoming increasingly scarce.

Although water treatment involves several steps with a high degree of rigor, the survival of potential pathogens in treated water remains a serious problem and raises questions about the efficiency of these processes.<sup>9</sup> In this context, the disinfection step is particularly important, as it is responsible for removing and limiting pathogens, thereby ensuring public health and environmental safety.<sup>10-11</sup> Some pathogens and bacteria survive and grow again after disinfection because of resistance to disinfectants, which can occur as a result of underdoses, leading to the selection and adaptation by target organisms.<sup>12</sup>

Chlorine is the most widely used disinfectant,<sup>5</sup> however, some microorganisms survive beyond the standard chlorine dose limits recommended by the WHO and regulatory agencies of each country.<sup>9,13</sup> These chlorine-tolerant pathogens are concerning and cast doubt on the biological safety of water treatment.<sup>5</sup> Another problem with the use of chlorine is the formation of by-products that can be harmful to health.<sup>14</sup> and the ecology, as they also affect aquatic life.<sup>5</sup> Other chemical disinfectants, such as peracetic acid (PAA), and physical processes that use radiation, such as ultraviolet (UV) irradiation and SODIS, are also used because of their high efficiencies.

The search for alternative methods, protocols, and products that can improve the water and sewage treatment system has a high degree of importance for society.<sup>11</sup> Therefore, it is necessary to know the mechanisms of action of existing disinfectants to solve current difficulties and avoid future problems. In this context, this review aims to address and evaluate important issues, such as identifying the limitations of current disinfection methods, evaluating the effectiveness of alternative disinfection approaches, and proposing recommendations for improving water treatment processes. Furthermore, this review highlights the compilation of chemical reactions that demonstrate the participation of radicals in the disinfection process, which represents a more real and current explanation of the reaction mechanism involved.

### 2. Pathogens in public water supply

It is important to highlight the diversity of waterborne diseases, which are categorized as follows: (1) diseases, such as cholera, typhoid fever, salmonellosis, gastroenteritis, meningitis, and diarrheal diseases caused by bacteria and protozoa; (2) diseases caused by contaminated water, such trachoma; (3) water-related diseases, such as malaria, yellow fever, and dengue; and (4) water-borne diseases, such as schistosomiasis, dracunculiasis, and ascariasis.<sup>15</sup> To prevent these pathologies, it is necessary to understand the etiology, epidemiology, and pathophysiology of the infection, as well as the environmental, social, and behavioral factors that can dramatically impact the incidence of the disease.<sup>2,10</sup> The behavior of SARS-CoV-2 (Severe Acute Respiratory Syndrome Coronavirus 2), the virus responsible for the recent pandemic, as a water pollutant remains to be studied. There is still no data in the literature on its epidemiology and pathophysiology as a waterborne disease. However, it has been reported that this virus circulates in sewers and wastewater.<sup>16-19</sup>

The presence of microorganisms in water treatment and distribution systems is a routine problem,<sup>20-22</sup> which must be remedied to ensure the safety of the final consumer.<sup>22</sup>

Water supply networks have a great diversity of microorganism species that form biofilms owing to environmental changes and hydraulic conditions in the system. Determining the full biodiversity of these biofilms is challenging, as they form with different compositions for each supply chain.<sup>23</sup>

Figure 1 shows some of the microorganisms responsible for the occurrence of waterborne diseases.

The phylum Proteus includes most pathogens as well as potential pathogens present in treated water.<sup>25</sup> In addition to the natural microbiota, biofilms also contain microorganisms, such as *Pseudomonas* sp. and *Escherichia coli* (*E. coli*), which use carbon sources unavailable to other organisms.<sup>23,26</sup>

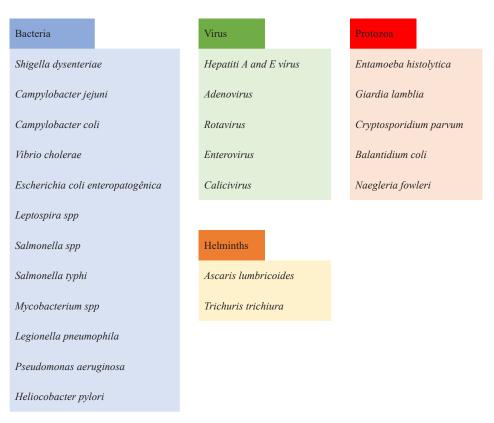


Figure 1. Reported pathogenic microorganisms in biofilms and water supplies<sup>24</sup>

Among the bacterial groups most frequently identified in drinking water are gram-negative bacteria and members of the phylum Proteobacteria, mainly of the alpha, beta, and gamma classes.<sup>21,22,27-29</sup> Other identified bacteria belong to the phylum Bacteroidetes.<sup>30-32</sup>

Microorganisms are structurally simple and classified into two markedly different cell groups: eukaryotic and prokaryotic.<sup>33</sup> Prokaryotic bacteria, which are the cause of several waterborne diseases, mostly range from 0.2 to 2  $\mu$ m in diameter and from 2 to 8  $\mu$ m in length. They have different shapes, such as spheres (cocci), rods (bacilli), and spirals (spirochetes) due to the cell wall. This is a taxonomic characteristic used to classify a bacterium, as well as the number of joined cells and their arrangement in the colony; for example, bacilli organized in rows/chains are called streptobacilli.<sup>21,27,34-36</sup>

Bacteria, although simple, have several structures that allow them to survive. Glycocalyces, flagella, axial filaments, fimbriae, and *pili* are external structures of the extracellular wall of prokaryotes.<sup>34</sup> The glycocalyx, secreted by prokaryotes on their surface, is a viscous gelatinous polymer that is located externally to the cell wall and is composed of polysaccharides, polypeptides, or both.<sup>37-39</sup> These structures are described as capsules, which protect the bacteria by preventing phagocytosis. Glycocalyces are also related to bacterial virulence and are a very important component of biofilms that helps attaching bacteria to the surface and other bacteria-forming colonies.<sup>37,38</sup> For example, *Vibrio cholerae*, which causes cholera, produces a glycocalyx that helps it adhere to the cells in the small intestine.<sup>40</sup>

Flagella and axial filaments are responsible for the movement of bacteria; bacteria that do not have these filaments are known as atrichia.<sup>34,41</sup> Motile bacteria contain receptors inside or outside their cell wall, which are responsible for recognizing stimuli from the environment. When the stimulus is positive, the bacterium moves towards it, and when it is negative, the bacterium does the opposite.<sup>34,42</sup>

Bacteria contain hair-like appendages or trichomes that facilitate communication between bacteria.<sup>35</sup> These structures are made up of a protein called pilin and are divided into two types: fimbriae and *pili*.<sup>35,43</sup> Fimbriae can be distributed throughout the bacterial cell and promote adhesion to other bacteria and different types of surfaces, in addition to being involved in biofilm formation.<sup>31,44-45</sup> The fimbriae of *Neisseria gonorrhoeae*, the causative agent of

gonorrhea, assist bacteria in colonization prior to causing the disease.<sup>46</sup>

*Pili* are also involved in bacterial cell motility; however, another important function of *pili* is to transfer genetic material,<sup>47-48</sup> through a process known as conjugation, in which a cell connects to the receptor on the surface of another bacterium of its own species or of different species. The two cells establish physical contact, followed by the transfer of genetic material.<sup>49</sup> This sharing can add new functions to the recipient cell, such as antibiotic resistance or other abilities.<sup>48</sup>

Among the structures that form a bacterial cell, the cell wall is the most complex.<sup>50</sup> It is responsible for shaping the cell and protecting the fragile plasma membrane, as in plants and fungi. However, its main function is to protect bacteria from environmental variations.<sup>51</sup> The bacterial cell wall is composed of a polymer known as peptidoglycan, which consists of a repetitive disaccharide linked by polypeptides.<sup>52</sup> The glycan moiety is formed by disaccharides that are composed of monosaccharides called *N*-acetylglucosamine and *N*-acetylmuramic acid, which are alternately linked in rows of 10 to 65 molecules to form a carbohydrate skeleton. The peptide portion forms rows adjacent to polypeptide-linked glycans.<sup>51</sup>

Understanding the bacterial cell wall and its structure is important, as the specificities of each bacterium and its possible sites of action allow the development of antibiotics and disinfecting agents.<sup>51</sup> Penicillin, for instance, interacts with peptidoglycan bonds, thereby weakening the cell wall and causing cell lysis.<sup>53</sup> Bacterial walls present different conformations and can be divided into two groups: gram-positive bacteria with a cell wall made up of multilayered peptidoglycans, and gram-negative bacteria with a cell wall containing only monolayered peptidoglycans though with an external plasma membrane that protects the cell wall.<sup>51,54</sup>

The proteobacterium *E. coli* was selected as a biological safety indicator for water treatment in the 1890s because of failures of the methods used to identify "fecal coliforms" and "total coliforms". With the advent of defined substrate technology in the late 1980s, it became possible to identify *E. coli* directly from drinking water and simultaneously analyze total coliforms in an economical and effective manner.<sup>55</sup>

Although *E. coli* is found in all mammalian feces at high concentrations, it does not multiply appreciably in the environment. The bacterium can survive in drinking water for 4-12 weeks, depending on environmental conditions, including temperature and local microbiota. In water distribution systems, *E. coli* has a much longer life; therefore, in most circumstances, a monitoring program that allows for the protection of public health at a low cost is necessary. Compared to other known methods of identifying fecal coliforms, analysis for *E. coli* has been shown to be much more effective.<sup>55</sup>

Protozoan parasites contaminate a variety of substrates, both in environmental and refrigerated storage conditions. They have been identified in food, water, and environmental systems. The main protozoa are from the genera *Giardia*, *Cryptosporidium*, and *Cycospora*, for which several treatments have already been tested and are currently in use.<sup>56</sup>

Viruses are more difficult to detect than bacteria in environmental samples, particularly in water, where these microorganisms are normally found in smaller numbers. The most common viruses found in water contaminated by human waste are poliomyelitis and infectious hepatitis. Being obligate intracellular parasites, viruses do not multiply in water. Therefore, the choice of concentration methods with high recovery efficiency for the detection of viruses requires large volumes of water.<sup>54</sup> Consequently, the quality of treated water is not always guaranteed in terms of virological safety because the current indicators of the coliform group only determine the bacteriological safety of the water.

In this context, water can be considered a potential health hazard, which makes it necessary to constantly monitor its quality, especially when the population is supplied with untreated water from alternative supply systems instead of sanitation companies.<sup>56</sup>

#### **3. Disinfection processes**

Water disinfection has been practiced for millennia, and there are indications about using boiled water for human consumption since earlier than 500 BC,<sup>57</sup> although the mechanisms through which the disinfection process occurred, as well as knowledge about pathogenic microorganisms, are not known. Disinfection can be defined as any physical or chemical process, or a combination of both, that aims to eliminate, destroy, or inactivate pathogens capable of inducing or producing diseases in another organism.<sup>58</sup>

The survival of microorganisms in water depends on several factors, such as temperature, pH, turbidity, oxygen,

nutrient availability, and intra-and/or interspecific competition.<sup>59-60</sup> Thus, disinfection promotes imbalance/disturbance in the ecological niche occupied by these microorganisms, which can cause their death, inactivation, or reduce their ability to reproduce.<sup>59</sup>

Although the sedimentation, coagulation, and filtration steps in water treatment processes remove some of the microorganisms, it is the disinfection step that neutralizes the microorganisms.<sup>58</sup> The disinfection of water can be achieved via several methods, which are classified as (1) physical treatment: heat application, ultraviolet irradiation, and other physical agents and (2) chemical treatment: silver, copper, iron, sodium hydroxide, ammonia, halogen, ozone, among others.<sup>59</sup> The mechanisms of the chemical and physical disinfection processes are different, as shown in Figure 2.

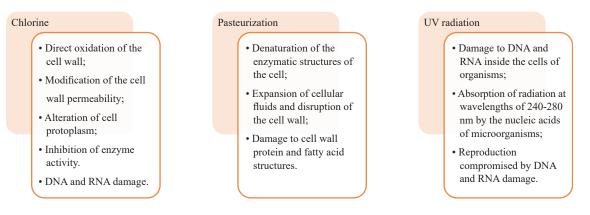


Figure 2. Mechanisms of disinfection via chlorine, UV radiation, and pasteurization<sup>5</sup>

The characteristics of the water to be treated also influence the disinfection process, as by-products can form or the presence of certain substances can lead to an inefficient disinfection process.<sup>60-61</sup>

Conventional disinfection technologies, such as chlorination, ozonation, and UV irradiation are efficient, operationally simple, and cost-effective. Additionally, they can be applied on a large scale.<sup>60</sup> Some challenges are encountered in disinfection processes, such as agglomeration of organisms, which can create a barrier to the penetration of the disinfectant. Previous studies have shown that the inactivation curve tends to exhibit a tail phenomenon when only a single disinfectant is used,<sup>62-64</sup> causing the microorganisms to reestablish themselves and replicate again, which can lead to the resistance of some species of microorganisms to certain disinfectant.<sup>65-67</sup> The Figure 3 show five characteristics of an ideal disinfectant.

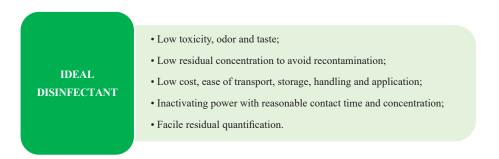


Figure 3. Characteristics of an ideal disinfectant.<sup>14</sup>

The propagation of microorganisms in water distribution systems manifests itself as a worrying problem because of the problems it can lead to, such as biofilms and odors, which compromise the water quality and generate a bad taste.

#### Fine Chemical Engineering

Therefore, it is essential to control microorganisms in water distribution systems.<sup>68-69</sup>

Some microorganisms can survive in water for several weeks at temperatures close to 21  $^{\circ}$ C or lower. Disinfection aims to eliminate or inactivate pathogenic or undesirable organisms but does not imply complete elimination, as is the case with sterilization.<sup>14,70</sup>

### 4. Chlorine

Chlorine disinfection is a key global public health strategy for the prevention and control of diseases. It is the most commonly used agent for general disinfection, is widely used for the inactivation of microorganisms.<sup>68-69</sup> Chlorine is more effective in treating viruses and bacteria compared to protozoa and is typically used in the form of elemental chlorine (Cl<sub>2</sub>), hypochlorite (ClO<sup>-</sup>), and chlorine dioxide (ClO<sub>2</sub>).<sup>71</sup>

The use of chlorine in water treatment and disinfection began with the application of sodium hypochlorite (NaClO), which is obtained by the igneous electrolytic decomposition of sodium chloride (NaCl).<sup>68</sup> Chlorine is the most used disinfectant to combat pathogens; however, it was initially used only in critical contamination situations, such as epidemics.<sup>58</sup> At the beginning of the 20th century, chlorine began to be used regularly for water treatment, and the term "chlorination" became synonymous with disinfection.<sup>72</sup> In addition to water treatment, chlorine is also used in hospitals, food and agriculture industries, and daily life.<sup>68</sup>

Species	$E^{0}(\mathbf{V})$	References		
Hydroxyl radical (HO <sup>•</sup> )	2.80	Legrini et al. <sup>76</sup>		
Ozone (O <sub>3</sub> )	2.07	Legrini et al. <sup>76</sup>		
Peracetic acid (CH <sub>3</sub> COOOH)	1.96	Luukkonen and Pehkonen <sup>77</sup>		
Hydrogen peroxide (H <sub>2</sub> O <sub>2</sub> )	1.78	Legrini et al. <sup>76</sup>		
Chlorine radical (Cl <sup>•</sup> )	2.55	Wardman <sup>78</sup>		
Chloro radical anion $(Cl_2^{\bullet})$	2.13	Laat et al. <sup>79</sup>		
Chlorine dioxide (ClO <sub>2</sub> )	1.5	Popescu <sup>80</sup>		
Hypochlorous acid (HClO)	1.49	Kurniawan et al. <sup>81</sup>		
Chlorine (Cl <sub>2</sub> )	1.36	Legrini et al. <sup>76</sup>		
Sulfate radical (SO <sub>4</sub> <sup>••</sup> )	2.6	Stefan <sup>82</sup>		
Persulfate (K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> )	2.0	Wang et al. <sup>83</sup>		
Peroxymonosulfate (KHSO <sub>5</sub> )	1.8	Wang et al. <sup>83</sup>		
Potassium permanganate (KMnO <sub>4</sub> )	1.7	Popescu <sup>80</sup>		
	1.78 at pH 7.0	Augusto et al. <sup>84</sup>		
Carbonate radical anion ( $CO_3^{\bullet}$ )	1.59 at pH 12.0	Arnold <sup>85</sup>		

Table 1. Oxidation potential of various chemical species

However, in recent years, the abusive use of disinfectants and antibiotics has triggered certain bacteria to become resistant to these agents, which is a grave concern as these bacteria pose a serious threat to human health and the ecological system.<sup>73</sup> The use of antimicrobial agents imposes selective pressure on commensal and pathogenic bacteria, thereby increasing their resistance to disinfectants.<sup>74</sup> Disinfectants and disinfection by-products can promote resistance gene transfer and induce multidrug resistance in bacteria.<sup>14,63,75</sup>

Chlorine and its compounds are strong oxidizing agents. Table 1 lists numerous oxidizing chemical species, such as chlorine radicals, chlorine oxide radicals, chlorine dioxide, hypochlorous acid, and chlorine that can react as molecules in the environment and form other reactive radical species such as HO<sup>•</sup>, HOO<sup>•</sup>, SO<sub>4</sub><sup>•-</sup>, and CO<sub>3</sub><sup>•-</sup>.

In general, the reactivity of chlorine decreases and increases with increasing pH and temperature, respectively<sup>68</sup> and its use leads to the emergence of various by-products.<sup>59,63</sup> Hypochlorous acid (HOCI) is a weak acid, which forms when chlorine is added to water. The acid controls disinfection, but like all chemical disinfectants, it needs to be evenly dispersed in the water to ensure a uniform concentration.<sup>75</sup> Therefore, agitation promotes disinfection, but the process does not occur instantly. In general, disinfection proceeds gradually, with physical, chemical, and biochemical steps that depend on the microorganism.<sup>86-87</sup>

Chlorine-based disinfectants can induce oxidative stress in bacteria owing to their strong oxidizing properties (Table 1) and lead to antibiotic and disinfectant resistance. Chlorine acts on the cells of microorganisms, causing oxidative damage to membranes, proteins, nucleic acids, amino acids, and cell walls, ultimately causing loss of viability. Four abiotic conditions can impair the efficiency of chlorine disinfection. These are free chlorine concentration, exposure time, temperature, and pH. The minimum CT value should be 15 mg·min·L<sup>-1</sup> during which the free chlorine concentration will be 0.5 mg·L<sup>-1</sup> with a residence time of 30 min for water with pH  $\leq 8$  and turbidity  $\leq 1$  NTU.<sup>68</sup>

In general, it takes a few hours for reactions to occur between chlorine and organic matter.<sup>19</sup> When added to chemically pure water, the following reaction occurs.

$$\operatorname{Cl}_{2(g)} + \operatorname{H}_{2}O_{(I)} \leftrightarrow \operatorname{HOCl}_{(aq)} + \operatorname{H}^{\dagger}_{(aq)} + \operatorname{CI}^{\dagger}_{(aq)} \tag{1}$$

The disinfecting action of chlorine is mediated by hypochlorous acid (HOCl). At  $pH \le 6$ , the undissociated form (HOCl) prevails. At  $pH \ge 6$ , hypochlorous acid rapidly dissociates to form hypochlorite ion (OCl<sup>-</sup>), as depicted by reaction 2:

$$HOCl_{(aq)} \leftrightarrow H^{+}_{(aq)} + OCl_{(aq)}$$
(2)

As the pH value in a water supply system usually ranges from 5 to 10, both forms (acid and ion) are present.<sup>14</sup>

When ammoniacal compounds are present in water, active chlorinated compounds, known as chloramines, are formed with the addition of chlorine. Chlorination and chloramination (usually with mono-chloramine) are commonly used disinfection methods because they are effective, inexpensive, and supply the necessary amount of residual disinfectant in the system. Despite the effective inactivation of pathogens, however, chlorine and chloramine react with organic and inorganic matter existing in water to form unintentional disinfection by-products (DBPs).<sup>14,88</sup>

The most common DBPs generated by chlorine are hypochlorous acid (HOCl), hypochlorite (OCl<sup>-</sup>), hydrochloric acid (HCl), and trihalomethanes (THMs). THMs are represented by four main chemical compounds: trichloromethane, bromodichloromethane, dibromochloromethane, and tribromomethane, <sup>45,89</sup> and the chemical structures are represented in Figure 4. THMs are formed by the interaction of chlorine with some compounds known as precursors.<sup>14</sup> THMs have been studied since the 1970s and pose serious health risks owing to their carcinogenic nature and also causes short-term effects on development and reproduction.<sup>14,90-94</sup> Therefore, chlorination must be performed with caution and the levels must not exceed the limits established by water quality control bodies.<sup>89,92</sup> Not all disinfection by-products can be identified, which makes it difficult to fully understand the effects of these contaminants.<sup>95</sup>

To reduce the formation of by-products, it is recommended that before chlorine disinfection, the organic precursors present in the water are removed. For this, physical treatments can be used, such as adsorption and filtration, this practice also helps to reduce the consumption of the disinfectant.<sup>96</sup>

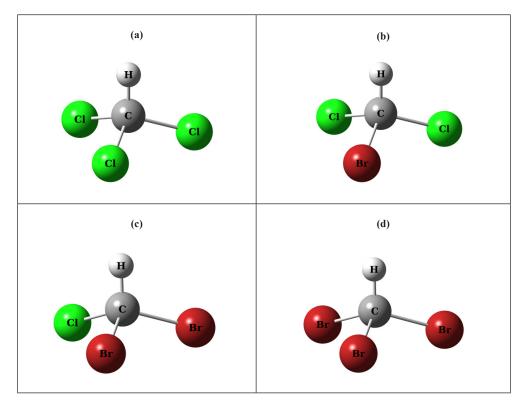


Figure 4. Chemical structure of (a) thichloromethane (CHCl<sub>3</sub>), (b) bromodichloromethane (CHBrCl<sub>2</sub>), (c) dibromochloromethane (CHClBr<sub>2</sub>) and (d) tribromomethane (CHBr<sub>3</sub>)

From 1974 onwards, a correlation between DBPs in drinking water and cancer was established, and in 1979, the US Environmental Protection Agency (EPA) regulated the maximum concentration of THMs in the public water supply to be 100  $\mu$ g·L<sup>-1.97</sup>

Although few studies have been conducted on the toxicity of chloramines, the potential adverse health effects of chloramines have been well-described. Chloramines can cause tissue, RNA, and DNA damage, leading to aging and cancer.<sup>88,98</sup> These factors, in combination with the need to control the parameters (pH, organic matter, temperature, and time) used in the chlorination process, have caused chlorination to lose credibility, and consequently, new alternative technologies have been developed.<sup>99</sup>

Chlorine is the most used water disinfectant due to its low cost, high efficacy and residual biocidal effect.<sup>11,71</sup> The antimicrobial activity of chlorine varies depending on concentration, temperature and pH, however, its effectiveness is directly related to the concentration of organic matter, which leads to the production of several harmful by-products.<sup>91</sup> Chlorine dioxide (ClO<sub>2</sub>) has recently been considered an alternative to chlorine as it does not react with humic substances to form halogenated by-products that limit the environmental safety of chlorine.<sup>100</sup> In addition, chlorine dioxide is highly effective against many microbial pathogens over a wide pH range (3-7).<sup>29</sup> Thus, these chemical disinfectants are practically and potentially useful for inactivating harmful water-borne microorganisms. Table 2 shows the effectiveness of disinfection of Cl<sub>2</sub> and ClO<sub>2</sub> against some microorganisms described in the literature.

From Table 2 it is possible to observe that the use of  $ClO_2$  is efficient using a lower concentration than  $Cl_2$  and used in many groups such as Bacteria, Virus, and Fungi.

Group	Species	ClO <sub>2</sub>		Cl <sub>2</sub>	References		
		Concentration	Reduction	Concentration	Reduction	- References	
Bacteria	<i>Legionela</i> spp	0.5 a 0.8 mg·L <sup>-1</sup>	2 log	-	-	Sidari et al. <sup>101</sup>	
	Escherichia coli O157:H7	$0.5 \text{ mg} \cdot \text{L}^{-1}$	0.85 log	$0.5 \text{ mg} \cdot \text{L}^{-1}$	3 log	Keskinen et al. <sup>102</sup> Abnavi et al. <sup>103</sup>	
	Total coliforms	2 a 3 mg·L <sup>-1</sup>	$\sim 4 \log$	$6.5 \text{ mg} \cdot \text{L}^{-1}$	$\sim 2 \log$	Ayyildiz et al <sup>104</sup>	
	Salmonella	4 a 5 mg $\cdot$ L <sup>-1</sup>	1.53 log	-	-	Tomás-Callejas et al. <sup>105</sup>	
Vírus	Rotavirus (HRV)	$0.05 \text{ a} 0.1 \text{ mg} \cdot \text{L}^{-1}$	$\sim 4 \log$	-	-	Xue et al. <sup>106</sup>	
	Norovirus (MNV)	$0.288 \text{ mg} \cdot \text{L}^{-1}$	$\sim 3.5 \log$	$0.193 \text{ mg} \cdot \text{L}^{-1}$	~3 log	Lim et al. <sup>107</sup>	
	Colifago MS2	$0.174 \text{ mg} \cdot \text{L}^{-1}$	$\sim 3.5 \log$	$0.174 \text{ mg} \cdot \text{L}^{-1}$	$\sim 4 \log$	Shin et al. <sup>108</sup>	
Fungi	Penicillium sp.	3 mg·L <sup>-1</sup>	1.182 log	1 mg·L <sup>-1</sup>	$\sim 2 \log$	Wen et al. <sup>109</sup>	
	Trichoderma sp.	3 mg·L <sup>-1</sup>	0.615 log	$1 \text{ mg} \cdot \text{L}^{-1}$	$\sim 2 \log$		
	Cladosporium sp.	3 mg·L <sup>-1</sup>	0.398 log	$1 \text{ mg} \cdot \text{L}^{-1}$	$\sim 2 \log$		
Protozoa	Giardia Cysts	-	-	$0.2 \text{ a} 0.5 \text{ mg} \cdot \text{L}^{-1}$	$\sim 3 \log$	Fernando <sup>110</sup>	

Table 2. Bacteria, Protozoa, Fungi and viruses' degradation using chlorine dioxide (ClO<sub>2</sub>) or Chlorine (Cl<sub>2</sub>)

#### 5. Peracetic acid

Peracetic acid ( $CH_3CO_3H$ ) (PAA) is an organic peroxyacid that is used in many formulations as a bleach, sterilant, oxidant, polymerization catalyst, and disinfectant.<sup>111</sup> PAA breaks down into oxygen and acetic acid ( $CH_3COOH$ ), which in turn breaks down into carbon dioxide and water.<sup>112</sup>

The history of PAA began in 1902 when was synthesized and studied by Freer and Novy as a disinfectant. In 1949, Hutchings and Xezones tested PAA and 23 other antimicrobial agents, in which PAA showed the best results against Bacillus thermoacidurans spores. In 1951, Greenspan and Mckellar proved the fungicidal, antimicrobial, and bactericidal action of PAA. Despite these studies, PAA was still considered as a bactericidal agent until 1955.<sup>113</sup> Soon after, there was a great acceptance of PAA in several industries, such as food, chemicals, health, pulp and paper, and water treatment.<sup>111</sup>

In the early 1970s, Chloroform, a by-product of chlorination, was discovered in drinking water. This led to a public health concern regarding the toxic DBPs and spurred the search for affordable alternatives with less environmental aggression.<sup>111</sup> Between the late 1970s and early 1980s, interest in PAA for water treatment emerged. The main reasons for using PAA as an alternative to chlorine were the limited formation of toxic DBPs, a similar sterilization spectrum, and a lower cost.<sup>111</sup> Disinfection with PAA in wastewater treatment was first adopted in Europe, followed by gradual adoption into North America.<sup>111</sup>

In 1985, PAA was registered by the USEPA (U.S. Environmental Protection Agency) as an antimicrobial agent for use on hard surfaces in hospitals. In 1999, the USEPA consented to the application of PAA in combined sewage disinfection, and in 2012 for the disinfection of wastewater.<sup>111</sup> Since then, water treatment using PAA has been extensively studied. When the keywords "disinfection and peracetic acid" are searched on Science Direct, several results are obtained, corresponding to the research in different domains related to the theme. The graph presented in Figure 5a demonstrates a clear increase in annual publications and underscores the importance of the disinfectant.

Figure 5b shows the domains in which the disinfection process and PAA are mostly used, with major application in the thematic areas: (i) medicine and dentistry (21%), (ii) agricultural and biological sciences (20%), (iii) environmental science (17%) and (iv) immunology and microbiology (15%).

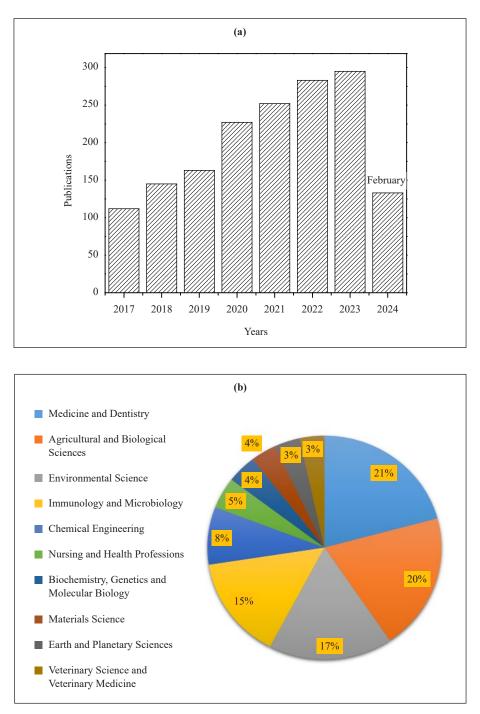


Figure 5. (a) Publications on "Disinfection and peracetic acid" from 2017 to February 2024, (b) main application domains of disinfection and peracetic acid

The efficiency of PAA is similar or superior to that of UV light, as it is a strong antioxidant with a redox potential of 1.385 V across the standard hydrogen electrode (pH 7, 25 °C, 101.325 Pa).<sup>114</sup>

Da Silva et al.<sup>115</sup> reported that the main advantage of using PAA to chlorination is the lower formation of toxic and carcinogenic by-products during contact with organic matter. However, PAA has other advantages too, such as no release of residues into the food and thus, no reduction in the quality of fruits and vegetables,<sup>99</sup> which has increased its use by small and large producers.

PAA exhibits a broad spectrum of disinfection, which allows it to eliminate various microorganisms such as bacteria (*E. coli, Pseudomonas spp., and Salmonella spp.*), fungi, viruses, and protozoa.<sup>115</sup> Moreover, PAA can also degrade organic micropollutants, such as pharmaceuticals, owing to its strong oxidation potential.<sup>111</sup>

PAA is a powerful organic peroxide and contains 25.8% reactive oxygen species. Peracids are thermodynamically unstable owing to their high-energy state, and therefore, safety precautions are necessary during handling.<sup>116</sup> Generally, PAA is marketed as a mixture of acetic acid, hydrogen peroxide, PAA, and water. The concentration of PAA in these formulations ranges from 5 to 15%, as solutions with higher concentrations are unstable and begin to exhibit reactive characteristics.<sup>117</sup> It is recommended that stabilized PAA (in its industrial form) should not be diluted before use, else it quickly starts to decompose. Even at low concentrations (up to 0.2%), approximately 50% of PAA undergoes a decomposition during its validity period, the product of which is acetic acid.<sup>118</sup>

PAA is formed by the reaction between acetic acid and hydrogen peroxide in the presence of a catalyst (1% sulfuric acid) (Reaction 3). Industrially, however, it is produced by the autoxidation of acetaldehyde is the most used.<sup>77</sup>

$$CH_{3}COOH_{(aq)} + H_{2}O_{2(aq)} \xrightarrow{H_{2}SO_{4}} CH_{3}CO_{3}H_{(aq)} + H_{2}O_{(1)}$$
(3)

PAA disinfection mechanisms are based on the release of highly reactive oxygen species (ROS) such as hydroxyl ('OH), alkoxyl ('OR), hydroperoxyl (HOO'), and superoxide ( $O_2^{-}$ ). These species are highly oxidative because of the unpaired electron, which provides an efficient antimicrobial effect.<sup>116</sup> In addition, organic radicals, such as CH<sub>3</sub>COO• and CH<sub>3</sub>CO• are also formed, which have a longer half-life than •OH radicals and are more effective in antimicrobial action.<sup>119</sup>

Specifically, PAA directly disrupts the bases of DNA molecules, inactivating the catalase, an enzyme capable of interfering with hydroxyl radicals. Owing to the oxidation of S-S (sulfhydryl) and S-H (sulfhydryl) bonds, the cell wall suffers from increased permeability, extravasation of cytoplasmic content and genetic material, which interfere with cellular survival and reproduction mechanisms.<sup>120,121</sup>

Being a strong disinfectant that acts on various microorganisms, PAA is bactericidal, sporicidal, fungicidal, and virucidal with several applications. The most common one is its use on thermosensitive surgical materials and surfaces and it is widely used as a food sanitizer in the food sector,<sup>99</sup> PAA also has a high potential for the degradation of aqueous organic micropollutants, such as pharmaceuticals,<sup>111</sup> as well as organic matter and body fluids, such as blood and fat.<sup>122</sup>

The advantages of PAA compared to conventional disinfectants in water disinfection are evident. PAA has a high sterilization effect, less pH dependence, facile application, forms less toxic by-products,<sup>111</sup> and is environmentally benign. Therefore, PAA is a suitable substitute for chlorinated disinfectants for water treatment.

Among its disadvantages are its higher cost, its ability to corrode and an increase in the organic content of the water. Furthermore, as it decomposes spontaneously, its residual concentration could not be guaranteed until its final distribution, as occurs with chlorine. Residual chlorine is necessary to ensure that there is no contamination of the water during distribution.<sup>115,123-124</sup>

#### 6. Ultraviolet radiation

Ultraviolet light has a wavelength of 100-400 nm, and it is estimated that approximately 9% of the sunlight that reaches Earth's surface is UV light. UV light is efficient in inactivating microorganisms contained in water and is increasingly being used for disinfection.<sup>125</sup>

UV light can be classified into UVA, UVB, and UVC. UVA rays with a wavelength of 320-400 nm have the highest incidence on Earth, as they are not absorbed by the ozone layer. UVB rays are partly absorbed by the ozone layer and have a wavelength of 280-320 nm. UVC rays have a wavelength of 100-280 nm and are fully absorbed by the oxygen

molecules in the atmosphere. The high-energy UVC rays are used to sterilize materials and disinfect water.<sup>99,125-126</sup>

UV light offers several advantages over conventional chemical disinfectants, such as non-requirement of additional chemicals, zero DBPs, and no increase in resistance of bacteria and other microorganisms. Thus, disinfection with UV light has been recommended as a replacement for chemical additives in surface water treatment.<sup>125</sup>

The mode of action of UV light consists of its absorption by the DNA and RNA of microorganisms, forming pyrimidine dimers, such as cyclobutane-pyrimidine and pyrimidine-pyrimidone.<sup>127-128</sup> These dimers block the transcription of nucleic acids, thereby compromising cell replication and leading to cell death.<sup>99,129</sup>

The control of microorganisms such as bacteria and viruses are two of the main concerns in water treatment. As seen earlier, the use of chlorine or its derivatives is a common approach to eliminate waterborne pathogens.<sup>130</sup> However, these products can generate problems, such as the formation of by-products, especially in the presence of organic matter in the water.<sup>14,131-132</sup> Therefore, ultraviolet (UV) disinfection is more convenient and safer, as it does not produce by-products and has broad-spectrum efficacy against various microorganisms, as described in Table 3.

Thus, UV disinfection has been considered a substitute for the use of chemical additives during water treatment or a great ally in combination with other disinfection methods, as they have the potential to increase the efficiency of disinfection or formation of •OH without addition of chemicals.<sup>99</sup> Table 3 shows results about the efficiency of using UV disinfection.

	Intensity of the radiation		<b>T</b> . (1 )		D.C.	
Species	UV intensity	λ	Time (hours)	Reduction %	References	
Legionella pneumophila	UVA	365 nm	0.60	99.9	Allahyari et al. <sup>133</sup>	
Legionella dumoffii	UVA	365 nm	0.60	99.1	Allahyari et al. <sup>133</sup>	
SAR-CoV	UVC	260 a 265 nm	< 0.1	88.5 a 99.7	Darnell et al.; <sup>134</sup> Kariwa et al.; <sup>135</sup> Hebling e al.; <sup>136</sup> Kitagawa et al.; <sup>137</sup> Heilingloh et al.; <sup>13</sup>	

Table 3. Efficacy of ultraviolet light against pathogenic microorganisms

As can be seen in Table 3, the use of radiation promotes a high reduction in microorganisms > 80% and this reduction occurs because damage occurs in structural molecules such as DNA and RNA of microorganisms.<sup>36,56,139</sup> Another important point to note is that the longer the time of irradiation, the greater the intensity, thus, the more severe the damage to the nucleic acid.<sup>140</sup>

As a disadvantage, the process presents high cost and electricity consumption, lower efficiency in the presence of suspended solids and absence of residual concentration. Regrowth by photoreactivation or regrowth in the dark and incomplete inactivation of some viruses, spores and cysts is also reported at low doses.<sup>141</sup>

#### 7. Solar water disinfection

Solar water disinfection (SODIS) is an effective and inexpensive method of providing potable water that can significantly reduce waterborne diseases.<sup>142</sup> Another advantage of SODIS is that it can be implemented in communities that do not have access to centralized water treatment, such as rural, semi-urban, and isolated populations. Access to safe and pathogen-free water is a fundamental and urgent issue; therefore, pathogen-free water it falls under the Millennium Development Goals and Sustainable Development. Therefore, the development of water treatment technologies, such as SODIS, which aim to make water treatment accessible and/or improve its quality, is important.<sup>142-143</sup>

SODIS is highly effective in inactivating waterborne pathogens, including chlorine-resistant microorganisms.<sup>144-145</sup> The disinfection through SODIS occurs because of a series of irreversible cellular damages, which result in the

inactivation of microorganisms and affect photosensitive regions that absorb the rays, causing physicochemical changes.<sup>146-147</sup>

The modeling and photoinactivation mechanisms of bacteria and viruses through visible and UV radiation were studied by Nelson and co-workers.<sup>147</sup> The inactivation of microorganisms using SODIS occurs essentially via two mechanisms: (1) direct mechanisms, in which solar energy (photon) is absorbed by photosensitive structures, such as genetic material, proteins, or other biomolecules that are located inside the microorganism, causing a change that compromises the chemical structure and consequently, the function of the organism, which can cause mutations or denaturation of essential proteins or substances and possibly impair the development of the microorganism; (2) indirect mechanisms, in which photosensitive or sensitizing structures, whether endogenous or exogenous, absorb energy and trigger the generation of photon-generated reactive products (PGRPs) using ozone, hydrogen peroxide among other compounds and form hydroxyl radicals (HO<sup>•</sup>), hydroperoxyl radicals (<sup>•</sup>OOH), and carbonate radical anions (CO<sub>3</sub><sup>•</sup>) in addition to singlet oxygen (<sup>1</sup>O<sub>2</sub>) and organic matter in the excited state.<sup>148</sup> Radicals oxidize cell components, which irreversibly damages different structures in the microorganism, compromising cell metabolism and causing apoptosis.<sup>142,147,149</sup>

It is noteworthy that all mechanisms can occur simultaneously or in contribution. For instance, direct damage to a bacterial enzyme, such as catalase, can lead to indirect inactivation, causing high levels of hydrogen peroxide to produce a photochemical reaction.<sup>142,147</sup>

Essentially, SODIS occurs through the synergy of the optical and thermal effects of solar radiation,<sup>150-151</sup> and the microbial inactivation accelerates proportionally to the increase in water temperature in a range of 30-50 °C and with a wavelength variation between 280 nm (UV) and 1,400 nm (infrared).<sup>142,152-156</sup> Infrared rays (760-1,400 nm) induce denaturation of structural proteins belonging to the cytoskeleton or bacterial cell wall, as well as functional proteins, such as enzymes. The damage caused to these proteins compromises the physical and chemical integrity of microorganisms and, therefore, affects their metabolism.<sup>142,152-153,156</sup> Photons in the UVB range directly damage different photosensitive molecules (e.g., the genome, proteins, and NADH), compromising their chemical structure and function. The UVA rays are responsible for direct and indirect cell damage and the production of PGRPs, which damage various components of the microbial cell.<sup>126,157</sup> Solar radiation in the visible spectrum (400-700 nm) is also involved in the indirect damage to cells.<sup>147,157</sup>

Treatment via SODIS usually involves the use of poly(ethylene terephthalate) (PET) bottles,<sup>142,153,158</sup> which makes this method inexpensive and sustainable, as it provides a new application for this material. As solar radiation penetrates the container and water, it undergoes spectral changes due to wavelength-dependent attenuation by water. Therefore, parameters, such as turbidity and depth also exert a significant influence on the rate of disinfection. The sunlight-mediated inactivation of microorganisms, in addition to water treatment, is subject to all kinds of wavelengths.<sup>146,159-160</sup>

Despite being an inexpensive, efficient, and very advantageous method, SODIS has its own limitations. Long exposure time (3-8 h) is required for disinfection to occur, which also varies depending on location and weather.<sup>153,158,160</sup> The turbidity of the water also influences the penetration of solar radiation, as suspended particles reduce the penetration of radiation. Therefore, the turbidity must be less than 30 NTU.<sup>161</sup> Another limitation is that after disinfection, which is usually conducted in 2-liter PET bottles, the water must be kept in closed containers until consumption. Owing to this, it is practically difficult to treat large volumes of water for the day.<sup>142,155</sup> Therefore, many studies have focused on combining SODIS with other techniques/products to expand its applicability on a large scale, as shown in Table 4.

Several studies have combined SODIS with other methods with the objective of improving their efficacy. Those listed in Table 4 were selected for conducting experiments with fecal coliforms and *E. coli*. One of the most important processes of SODIS is the increasing of water temperature in pasteurization. Therefore, heat concentrators are an interesting alternative to improve this technique, as concentrators with a larger capacity to conduct heat can increase the efficiency and reduce the exposure time of bottles.<sup>156</sup> However, the combination of SODIS with  $H_2O_2$  (Hydrogen Peroxide) resulted in a more satisfactory performance with 100% inactivation of microorganisms in 30 min at a temperature greater than 47 °C.<sup>163</sup>

Favorable results of combining  $H_2O_2$  with SODIS were also observed by Spuhler et al.,<sup>164</sup> who comparatively analyzed two methods. The first method (SODIS +  $H_2O_2$ ) presented similar results to those of other studies.<sup>162-163</sup> The second method was photo-Fenton (SODIS +  $Fe^{2+} + H_2O_2$ ) and was found to be more effective than the first method. Diez et al.<sup>162</sup> observed good results with the SODIS +  $Fe^{2+} + H_2O_2$  combination, confirming the observations made by Spuhler

et al.<sup>164</sup> However, the best results were obtained when  $H_2O_2$  was replaced with peroxymonosulfate. Therefore, the more oxidizing the medium, the greater the ability to inactivate microorganisms.<sup>162</sup>

	Inactivation		Time	Temperature	
Combined methods	Log.	%	(hours)	(°C)	References
SODIS + $Fe^{2+}$ + $H_2O_2$ (Photo-Fenton)	0.21	100	3	< 36	Diez et al. <sup>162</sup>
${\rm SODIS} + {\rm Peroxymonosulfate} + {\rm Fe}^{2+}$	0.27	116	3	< 36	
${\rm SODIS} + {\rm H_2O_2}$	0.69	100	0.5	< 47	Sciacca et al. <sup>163</sup>
SODIS + $Fe^{2+}$ + $H_2O_2$ (Photo-Fenton)	0.16	-	0.6	< 45	Spuhler et al. <sup>164</sup>
SODIS + metal heat concentrator	0.61	100	6	< 45	Vivar et al. <sup>156</sup>
SODIS + bamboo heat concentrator	0.5	90	8	< 40	

Table 4. Combinations used to improve the efficacy of SODIS in inactivating fecal coliform and E. coli.

The combined study of SODIS in the presence of carbonate and bicarbonate ions did not demonstrate promising results, which was justified by the fact that carbonaceous species act as a hydroxyl radical scavenger.<sup>165</sup>

Solar radiation, which is a natural process, can cause damage to all living beings.<sup>166-168</sup> Thus, several mechanisms are available in a cell to minimize this damage.<sup>169</sup> Sciacca et al.<sup>163</sup> provided an important warning about the SODIS process. The endophytic bacteria, such as fecal coliforms and *E. coli*, which live in the partial presence or absence of light, are more sensitive to sunlight exposure, and according to the authors may not be good bioindicators of SODIS, as they require lesser exposure time for inactivation compared to microorganisms that are more tolerant to sunlight. Therefore, endophytic microorganisms are more sensitive to sunlight than organisms that are more exposed to light, and their sensitivity or resistance may vary according to their physiology and the biological niche they occupy.<sup>170</sup> Therefore, understanding the biology and physiology of microorganisms is crucial for determining the best disinfection method.<sup>33</sup>

# 8. Formation of radicals

As future perspectives, understanding the mechanisms of radical formation represents new possibilities for the inactivation of pathogens and justifies the use of catalyzed or photocatalyzed processes in disinfection. For example, the disinfection of water supplies with PAA combined with  $Fe^{3+}$  demonstrated that the presence of ferric ions contributes to the decomposition of PAA, but its disinfectant capacity does not decrease, this was explained by the formation of radicals that also have the capacity to inactivate microorganisms.<sup>171</sup>

Electromagnetic radiation can be combined with PAA and chlorine disinfectants to generate numerous with different radicals and oxidation potentials.<sup>172-177</sup> While forming radicals using PAA, its quaternary composition, which is composed of peracetic acid, acetic acid, hydrogen peroxide, and water, must be considered. As the reaction rate increases, numerous radicals formed can cause damage to microorganisms. The formation of radicals by PAA and chlorine in combination with UV-Visible radiation is represented in reactions 4-33.

$$\mathrm{H}_{2}\mathrm{O}_{2(\mathrm{aq})} + hv \to 2 \,^{\bullet}\mathrm{OH}_{(\mathrm{aq})} \tag{4}$$

$$CH_{3}C(O)OOH_{(aq)} + h\nu \rightarrow CH_{3}C(O)O_{(aq)} + OH_{(aq)}$$
(5)

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$$CH_{3}C(O)OOH_{(aq)} + CH_{3}C(O)O\bullet_{(aq)} \rightarrow CH_{3}C(O)OO\bullet_{(aq)} + CH_{3}C(O)OH_{(aq)}$$
(6)

$$H_2O_{2(aq)} + CH_3C(O)O_{(aq)} \rightarrow HO_2_{(aq)} + CH_3C(O)OH_{(aq)}$$

$$\tag{7}$$

$$CH_{3}C(O)OOH_{(aq)} + \bullet OH_{(aq)} \rightarrow CH_{3}C(O)OO\bullet_{(aq)} + H_{2}O_{(l)}$$
(8)

$$CH_{3}C(O)OOH_{(aq)} + \bullet OH_{(aq)} \rightarrow CH_{3}C(O)\bullet_{(aq)} + H_{2}O_{(l)} + O_{2(g)}$$

$$\tag{9}$$

$$CH_{3}C(O)OOH_{(aq)} + \bullet OH_{(aq)} \rightarrow CH_{3}C(O)OH_{(aq)} + HOO\bullet_{(aq)}$$
(10)

$$H_2O_{2(aq)} + \bullet OH_{(aq)} \rightarrow HOO_{(aq)} + H_2O_{(l)}$$
(11)

$$CH_{3}C(O)O_{(aq)} \rightarrow CH_{3(aq)} + CO_{2(g)}$$
(12)

$$\bullet CH_{3(aq)} + O_{2(g)} \longrightarrow CH_3OO_{(aq)}$$
(13)

$$Cl_{2(g)} + H_2O_{(l)} \rightarrow HOCl_{(aq)} + HCl_{(aq)}$$
(14)

$$\operatorname{HOCl}_{(\operatorname{aq})} \leftrightarrow \operatorname{H}^{+}_{(\operatorname{aq})} + \operatorname{OCl}^{-}_{(\operatorname{aq})}$$
(15)

$$\mathrm{HOCl}_{(\mathrm{aq})} + hv \to {}^{\bullet}\mathrm{OH}_{(\mathrm{aq})} + \mathrm{Cl}^{\bullet}_{(\mathrm{aq})}$$
(16)

$$OCl_{(aq)}^{-} + H_2O_{(l)} + h\nu \rightarrow {}^{\bullet}OH_{(aq)} + Cl_{(aq)}^{\bullet} + OH_{(aq)}^{-}$$
(17)

$$OCl_{(aq)}^{\bullet} + hv \rightarrow {}^{\bullet}O_{(aq)}^{\bullet} + Cl_{(aq)}^{\bullet}$$
(18)

$${}^{\bullet}\mathrm{O}^{-}_{(\mathrm{aq})} + \mathrm{H}_{2}\mathrm{O}_{(\mathrm{l})} \rightarrow {}^{\bullet}\mathrm{OH}_{(\mathrm{aq})} + \mathrm{OH}^{-}_{(\mathrm{aq})}$$
(19)

$${}^{\bullet}\mathrm{O}_{(\mathrm{aq})}^{-} + \mathrm{H}_{(\mathrm{aq})}^{+} \to {}^{\bullet}\mathrm{OH}_{(\mathrm{aq})}$$

$$\tag{20}$$

$$\operatorname{Cl}^{\bullet}_{(\operatorname{aq})} + \operatorname{OH}^{-}_{(\operatorname{aq})} \leftrightarrow \operatorname{ClOH}^{\bullet}_{(\operatorname{aq})}$$
(21)

$$Cl^{\bullet}_{(aq)} + H_2O_{(l)} \leftrightarrow ClOH^{\bullet}_{(l)} + H^+_{(aq)}$$
(22)

$$ClOH \stackrel{\bullet}{}_{(aq)} \leftrightarrow \stackrel{\bullet}{}OH_{(aq)} + Cl_{(aq)}$$
(23)

$$HOCl_{(aq)} + HO^{\bullet}_{(aq)} \rightarrow ClO^{\bullet}_{(aq)} + H_2O_{(l)}$$
(24)

$$Cl^{\bullet}_{(aq)} + HOCl_{(aq)} \rightarrow H^{+}_{(aq)} + Cl^{-}_{(aq)} + ClO^{\bullet}_{(aq)}$$
(25)

$$\operatorname{Cl}_{(aq)}^{\bullet} + \operatorname{Cl}_{(aq)}^{\bullet} \to \operatorname{Cl}_{2}^{\bullet}_{(aq)}$$

$$\tag{26}$$

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$$Cl_{2}^{\bullet-}_{(aq)} + H_2O_{(l)} \rightarrow Cl_{(aq)}^{-} + HClO^{\bullet-}_{(aq)} + H^+_{(aq)}$$
 (27)

$$\operatorname{Cl}_{2}^{\bullet}{}_{(\operatorname{aq})}^{\bullet} + \operatorname{OH}^{-}_{(\operatorname{aq})}^{\bullet} \to \operatorname{Cl}^{-}_{(\operatorname{aq})}^{\bullet} + \operatorname{HClO}^{\bullet}_{(\operatorname{aq})}$$
(28)

$$OH_{(aq)}^{-} \rightleftharpoons O^{\bullet}_{(aq)} + H_{(aq)}^{+}$$
<sup>(29)</sup>

$$O^{\bullet}_{(aq)} + H_2 O_{(l)} \rightleftharpoons {}^{\bullet}OH_{(aq)} + OH_{(aq)}$$
(30)

$$Cl^{\bullet}_{(aq)} + Cl^{\bullet}_{(aq)} \rightarrow Cl_{2(l)}$$
(31)

$$\operatorname{Cl}_{2^{\bullet}(aq)}^{\bullet} + \operatorname{Cl}_{(aq)}^{\bullet} \to \operatorname{Cl}_{2(g)} + \operatorname{Cl}_{(aq)}^{\bullet}$$
(32)

$$ClO^{\bullet}_{(aq)} + Cl^{\bullet}_{(aq)} \rightarrow HCl_{(aq)} + HClO_{3(aq)}$$
(33)

Radicals initially generated by radiation can also combine with  $HCO_3^-$  or  $SO_4^{2-}$  and form other radicals, such as the carbonate radical anion  $(CO_3^{\bullet-})$  (Reactions 34-40) and sulfate radical anion  $(SO_4^{\bullet-})$  (Reactions 36-37) with different oxidation potentials.<sup>178-179</sup>

$$\mathrm{HO}^{\bullet}_{(\mathrm{aq})} + \mathrm{HCO}_{3}^{-}_{(\mathrm{aq})} \longrightarrow \mathrm{H}_{2}\mathrm{O}_{(\mathrm{l})} + \mathrm{CO}_{3}^{\bullet-}_{(\mathrm{aq})}$$
(34)

$$Cl^{\bullet}_{(aq)} + HCO_{3}_{(aq)} \rightarrow HCl_{(aq)} + CO_{3}^{\bullet}_{(aq)}$$
(35)

$$\operatorname{CO}_{3}^{2^{-}}_{(aq)} + \operatorname{CH}_{3}\operatorname{C}(O)\operatorname{O}_{(aq)} \to \operatorname{CO}_{3}^{\bullet}_{(aq)} + \operatorname{CH}_{3}\operatorname{C}(O)\operatorname{O}_{(aq)}^{\bullet}$$
(36)

$$\operatorname{CO}_{3}^{2^{\circ}}_{(aq)} + \operatorname{CH}_{3}C(O)OO_{(aq)} \to \operatorname{CO}_{3}^{\bullet}_{(aq)} + \operatorname{CH}_{3}C(O)OO_{(aq)}^{\bullet}$$
(37)

$$\operatorname{Cl}_{2^{\bullet}(aq)}^{\bullet} + \operatorname{HCO}_{3^{\bullet}(aq)}^{\bullet} \to \operatorname{H}^{+}_{(aq)}^{\bullet} + 2\operatorname{Cl}^{-}_{(aq)}^{\bullet} + \operatorname{CO}_{3^{\bullet}(aq)}^{\bullet^{\bullet}}$$
(38)

$$\mathrm{HO}^{\bullet}_{(\mathrm{aq})} + \mathrm{SO}_{4}^{2^{-}}_{(\mathrm{aq})} \to \mathrm{HO}_{(\mathrm{aq})}^{-} + \mathrm{SO}_{4}^{\bullet^{-}}_{(\mathrm{aq})}$$
(39)

$$\operatorname{Cl}_{(\operatorname{aq})}^{\bullet} + \operatorname{SO}_{4}^{2^{\circ}}_{(\operatorname{aq})} \longrightarrow \operatorname{Cl}_{(\operatorname{aq})}^{\bullet} + \operatorname{SO}_{4}^{\bullet^{\circ}}_{(\operatorname{aq})}$$
(40)

Carbonate, bicarbonate, and sulfate anions are naturally present in raw water that is supplied to water treatment systems. Therefore, the formation of these radicals in the disinfection process should not be ignored. In addition, the use of coagulants such as aluminum sulfate and alkalizing agents such as sodium carbonate should be considered as sources of these anions in the water treatment process.

# 9. Conclusion

In this review, disinfection using chlorine, peracetic acid, UV radiation, and SODIS was discussed. This information is important because it allows for the association of advanced oxidative processes (AOPs) with disinfection. From an environmental perspective, although AOPs are considered efficient for the degradation of complex contaminants and the disinfection process occurs simultaneously. As most of the generated radicals are non-selective,

the competition between chemical degradation and microbiological inactivation can increase the consumption rate of these radicals and decrease the residual concentration of reagents. Moreover, the generated by-products can be toxic to the population.

Chlorination remains the most widely used method. However, this process has disadvantages because it generates harmful by-products. Therefore, it is important to compare it with other alternative disinfection methods to achieve a gradual replacement. Moreover, it is imperative that their substituents are thoroughly studied to identify an ideal disinfectant.

This review discussed the individual mechanisms of disinfectants and demonstrated that there is a growing tendency to use disinfection processes in a combined manner, primarily in relation to the use of SODIS and chemical oxidants.

Finally, it is important to highlight that disinfection processes and their contributions need to be constantly monitored, studied, and reviewed for better applicability and efficiency.

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## **Author contributions**

All authors contributed to the study conception and design. Juliana Paggiaro performed the literature survey and the writing of the manuscript. Aline Karla Nolberto de Souza performed the literature survey and the writing of the manuscript. Murielly Fernanda Ribeiro Bihain performed the literature survey and the writing of the manuscript. Anna Karla dos Santos Pereira helped in the revision of manuscript. Grasiele Soares Cavallini gave the idea for review article and revised the manuscript. Douglas Henrique Pereira revised the manuscript.

# **Conflict of interest**

The authors declare no competing financial interest.

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