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# Heterogeneous photo-oxidation in microbial inactivation: A promising technology for seawater bio-securing?

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## ABSTRACT

This review is aimed at the actions of radical oxygen species (ROS) produced during the photocatalysis reaction on the different biomolecules composing the microorganisms, as well as the presentation and development of the key operational parameters influencing the efficiency of the photocatalytic treatment in the context of saltwater applications. Our study focuses on the case of heterogeneous photocatalysis, one of the advanced oxidation processes (AOP). This work highlights the importance of the analytical composition of the water (pH, salt, dissolved organic matter.) on the catalyst/target interactions. Similarly, the structural composition of microorganisms (cell wall biomolecules) also plays a key role in the sensitivity to the photocatalysis process, and to a lesser extent, their metabolism also has an impact on their resistance. Another important point of our work is that it highlights the fact that to date, there is no standardization in the way results from the literature are reported, making it extremely difficult to compare data for the purpose of evaluating different processes. Finally, our work underlines that photocatalysis is particularly promising for bio-securing applications like the decontamination of seawater in aquaculture via the treatment of tanks and closed aquariums, as well as for the shipping industry via the treatment of ballast water.

## KEYWORDS

AOPs ; Disinfection ; Seawater ; Photocatalysis ; Microbes

## 1. Introduction

Water is essential to life on Earth. Seawater, as opposed to freshwater, accounts for the vast majority of our planet's water, present within the oceans and seas, and represents 97.2 % of the total mass of water and 70 % of Earth's surface [1]. The quality of this seawater is critical to the health of ecosystems [2]. Further, marine organisms, such as algae, fish, molluscs..., can be negatively affected by contaminated water [3–6] and accumulated contaminants can impact human health. To prevent water contamination in the environment, wastewater treatment processes have been developed [7–9]. To date, the majority of these processes are dedicated to freshwater treatment and are used in either wastewater treatment plants [10] or in the production of fresh drinking water by removing microbial and chemical contaminants. Sometimes these contaminants can bypass treatment processes and end up in rivers, groundwater, and eventually in seawater. It can be cited that some cities still discharge their raw sewage into oceans or rivers to save on treatment, for one city alone this can amount to several billion liters of raw sewage per day [8].

On another hand, seawater invasions by non-native species are one of the most important environmental problems that can cause global economic losses up to tens of billions of dollars per year [11]. This invasion comes from globalization with an increase in shipping, between 5 [12] and 10 billion tons [13,14] of ballast water is exchanged annually and invasive species travel around the world through it. At the international level, the International Maritime Organization (IMO) regulates ballast water management (BMW). In 2004, IMO adopted the International Convention on the Control and Management of Ship's Ballast Water and Sediments. This convention requires all ships to comply with the D-2 standards, i.e. to install a ballast water treatment system before September 8, 2024. The ballast water treatment systems used must be approved by the water management systems (G8). 61 ballast water management systems using active substances received basic IMO approval in 2019 (45 of which received final approval) and 83 are compliant with the guidelines (G8) (resolutions MEPC.125(53) and MEPC.174(58)) [15]. In addition to the shipboard ballast water treatment system, port reception facilities are considered as a possible alternative for ships without treatment facilities, as stated in Regulation B-3.6 of the BMW Convention and in the Ballast Water Reception Facilities Guidelines (G5) (Resolution MEPC.153(55)). Most of the authorized/studied treatment methods can be grouped into mechanical or chemical treatments [13,16,17]. The mechanical treatments are not currently applied (hydrodynamic cavitation, ultrasounds, microwaves, electric pulse, heat treatment) except for Ultraviolet (UV) radiation whereas chemical treatments such as chlorine, peraclean biocide and sea kleen biocide are currently uses. Similarly, offshore wind turbines have been developed with the increase in demand for green energy, but these turbines are attached to the sea / ocean floor with large ballast water tanks. Like ship ballast water, these tanks accumulate microbes and must be treated to remove any microorganisms present before being released to the environment. In addition, economic losses caused by seawater contamination can also be related to aquaculture activity (pisciculture, shellfish farming...) or fishing activities. Economic losses related to fisheries are significant with approximately 60 millions dollars losses in 2014 [18], caused in particular by a decrease in fishing area with fewer fish due to seawater pollution from toxic runoff of chemicals. Today 40 % of the oceans are impacted by pollution [19]. With the increase in demand for seafood and the decrease in the number of fish in seawater, more intensive farms have been created, such as fish farms and/or aquaculture, in which the density of fish or shellfish is high and diseases frequently appear. For example, the mortality syndrome caused by the bacterial genus *Vibrio* induces a massive loss in shrimp production [20] and significant economic losses in oyster production [21]. To limit mortality events, antibiotics or genetic selection have been widely used. As a result of this massive use of antibiotic compounds, bacterial resistance phenomena have appeared [21]. Therefore, new disinfection processes must be developed for the biosecurity of farm influents and effluents. Moreover, economic losses in fisheries can also be attributed to algae, toxins and mycotoxins produced [22,23], or fungi [24]. Some organisms also produce toxin such as *Dinoflagellate* algae, which can produce phycotoxins (like Diarrhetic Shellfish Poisoning DSP toxin, Paralytic Shellfish Poisoning PSP toxin, and Amnesic Shellfish Poisoning ASP toxin). Only certain water treatment processes are capable of inactivating algal-derived toxins and, in particular, AOPs are known to effectively remove this class of biotic contaminants in water [25].

In this context, the objective of this review is i) to focus on the mechanisms of antimicrobial activity exerted by AOPs, ii) to detail in particular the heterogeneous photo-oxidation process using titanium dioxide ( $\text{TiO}_2$ ) described as the most widely used catalyst in this type of process- and iii) to discuss the relevance of the application of heterogeneous photo-oxidation for seawater treatment. In addition, given the increasing need to disinfect seawater in view of the elements described above, this review will present a detailed analysis of the influencing factors of heterogeneous photo-oxidation processes in order to evaluate its applicability to the microbial inactivation of seawater. Finally, a key point of this work is that we wanted to provide readers with a state of the art describing the operation of disinfection mechanisms in microbial inactivation in order to identify key technological parameters to be considered in the design of future photo-oxidation seawater disinfection processes.

## 2. Principle of heterogeneous photo-oxidation and effect on microorganisms

Heterogeneous photo-oxidation despite being under-studied has many advantages. As opposed to others AOPs, the heterogeneous photo-oxidation also named heterogeneous photocatalysis uses a solid catalyst instead of liquid catalyst to simultaneously degrade organic-matter and inactivate the microbial community present in seawater. The use of a solid catalyst allows for a limited operating cost since the catalyst can be separated and reused for the next treatments. Moreover, heterogeneous photo-oxidation operates under environmental temperatures and pH conditions, thus it is not necessary to adjust the experimental conditions over time such as in Fenton process. Another important advantage of the heterogeneous photo-oxidation for seawater treatment is that even if inorganic ions can reduce the treatment efficiency, no toxic subproducts are being generated [26]. Publications concerning seawater disinfection using photo-oxidation represent only 0.6 % of all AOP publications for seawater disinfection whereas its potential uses are important.

For information, the figure in [Supplementary 1](#) shows the effects of matrix components on the efficiency of the different AOPs.

### 2.1. ROS production during photo-oxidation

Heterogeneous photo-oxidation is an efficient AOP used for the degradation of persistent organic pollutants (biotic and abiotic) from water, wastewater, and seawater [27]. It is a proved process for freshwater disinfection [27,28] and also for water decontamination [29]. In general, AOP efficiency is based on redox reactions with a local of powerful oxidizing species (Reactive Oxygen Species, ROS) characterized by the non-selectivity of the target. The principal ROS produced in AOP is the hydroxyl radical ( $\cdot\text{OH}$ ), one of the most powerful oxidants. Other ROS may also be produced such as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), hydroperoxyl radicals ( $\text{HOO}\cdot$ ), superoxide radicals ( $\cdot\text{O}_2^-$ ), etc. [30]. All of these ROS are produced at a concentration which is sufficient to effectively remove pollutants. To generate these ROS, heterogeneous photo-oxidation uses a catalyst (mostly a semi-conductor [27]) as a catalytic active surface. Titanium dioxide ( $\text{TiO}_2$ ) is the most widely used catalyst. It has been studied for pharmaceutical, phytosanitary and PolyChloroBisphenyls degradation [31–34], as well as for bacterial disinfection. One of the main advantage of this AOP is that the solid catalyst is easily separable compared to a homogeneous catalyst, and thus can be recycled in further photo-oxidation reactions. Many supported catalysts are developed to improve catalyst separation and cancel the separation step after treatment.  $\text{TiO}_2$  has a maxima absorption lengthwave at 350 nm which correspond to UVA, and its activation only append below 400 nm [35]. Solar UV irradiation, composed mostly by UVA and B, represent 5 % of the total solar spectrum and can be an efficient UV source for photo-oxidation reactions. Only UVA and B can pass through the ozone layer (whereas UVC are filtered) and reach the earth surface.

Heterogeneous photo-oxidation uses solid particles in suspension into the treated matrix (water or air). After activation by UV photons, photocatalytic particles react with contaminants in their immediate proximity.

Heterogeneous photo-oxidation process can be separated into five steps, and photo-oxidation (ROS production) can be itself separated into three steps [36]:

Step 1: Matter transfer from the liquid phase to the catalyst surface through the boundary layer.

Step 2: Adsorption on the catalyst surface. Step 3: Photo-oxidation reaction (Fig. 1).

- a. Catalyst photoexcitation: when catalysts are exposed to sufficient energetic photons electron/hole pairs are produced (Eq. (1)) [37]



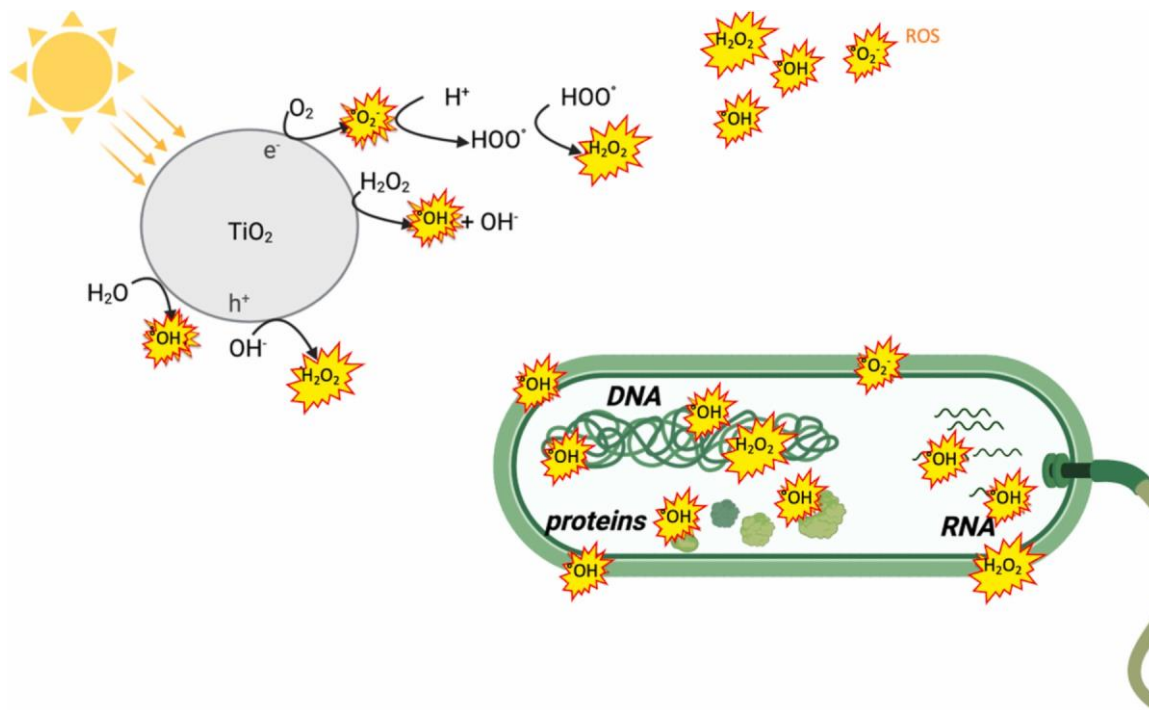
- b. Charge transfer into the catalyst: electrons and holes produced migrate to the catalyst surface and react with adsorbed species (electro-donor or electro-acceptor). During this step a recombination phenomenon can occur into electron/hole pairs [38,39].
- c. Free radical reactions: photo-oxidation and photo-reduction reactions occur when oxygen and water molecules adsorb into the catalyst surface to generate free radical species (Eqs. (2)–(6)) which can react with organic species close to the catalyst [37,40,41].



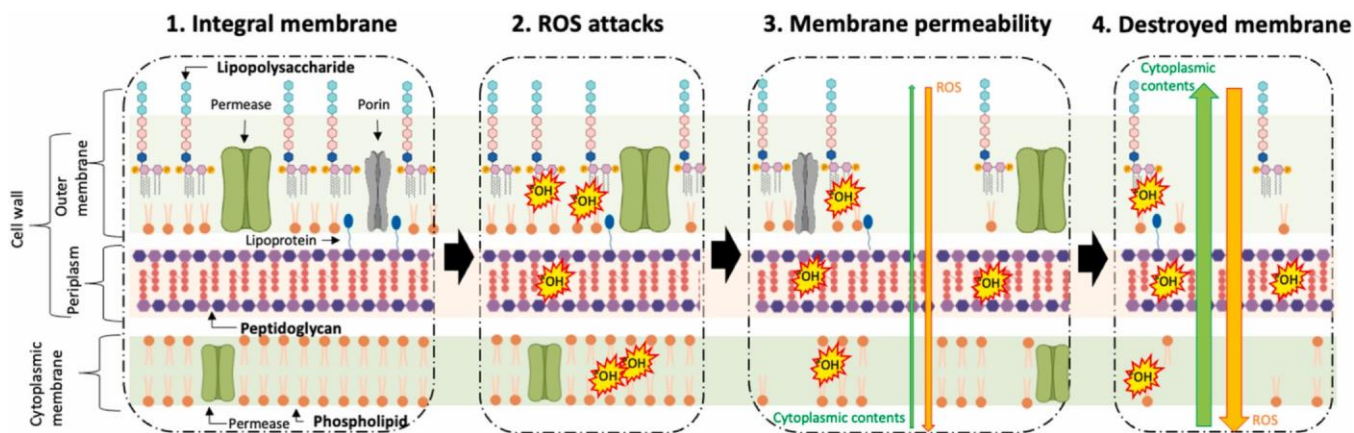
Step 4: Desorption of the catalyst surface.

Step 5: Transfer into the medium.

**Fig. 1.** ROS production in photo-oxidative process and targets for ROS in bacteria.



**Fig. 2.** Hydroxyl radical damage to cell envelope components of Gram-negative bacteria. Susceptibility to oxidative damages presents the following order: liposaccharide > phospholipids > peptidoglycan.



Heterogeneous photo-oxidation efficiency to remove contaminant relies on the ROS generation. ROS are known to efficiently degrade organic contaminant without specificity. In the case of microorganism disinfection, ROS efficiently damages many cellular compounds as presented below.

**2.2. ROS and UV target biomolecules**

Heterogenous photo-oxidation use both catalyst and UV radiation to generate ROS which are involved in microbial inactivation. Most studies show that ROS are responsible for the death of microbes. With another AOP, homogeneous photo-oxidation (UV chlorination), Wen et al. find, using *tert*-butyl alcohol (TBA) as a radical scavenger, that •OH were responsible for 20–30 % of the bacterial inactivation, UV- LEDs for a few percent and chlorine for 15–40 % [42]. The

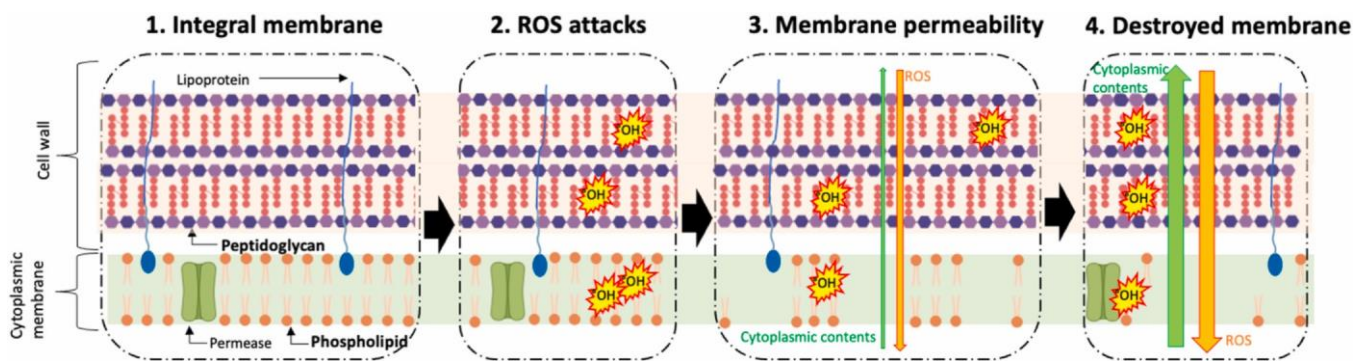


remaining percent of bacterial inactivation was due to other factors [42]. In the same way, in heterogeneous photo-oxidation,  $\cdot\text{OH}$  are not the only ROS produced molecules. Whereas  $\cdot\text{OH}$  are short-lived and very reactive species acting close to the  $\text{TiO}_2$  surface,  $\text{H}_2\text{O}_2$  is acting at a longer distance [43]. Nevertheless  $\cdot\text{OH}$  were shown to be the major ROS involved in bacteria killing [44]. The use of hydroxyl radical scavengers in inactivation studies revealed that other ROS such as  $\text{H}_2\text{O}_2$  and  $\cdot\text{O}_2^-$  may also play a role on the global disinfection process by UV/ $\text{TiO}_2$  treatment [45,46].

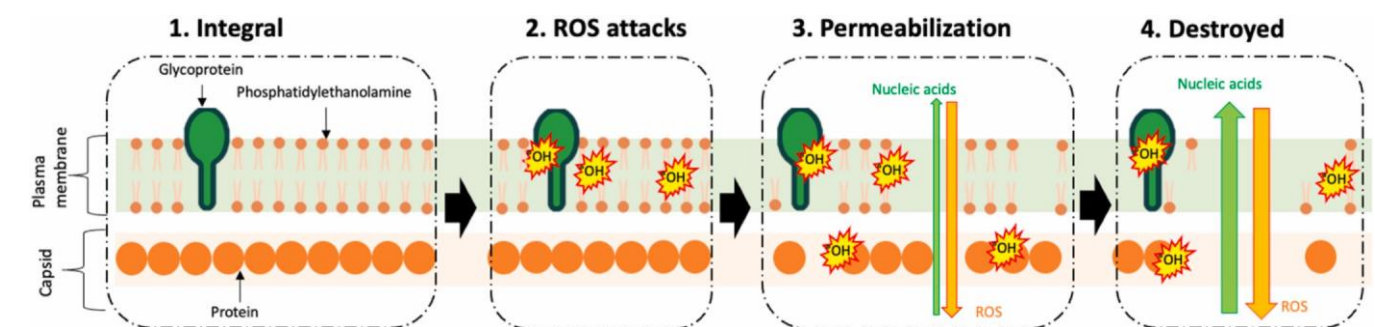
2.2.1. Damages to lipids

Lipids and phospholipids represent an important part of cell composition and especially membrane, constituting for example up to 10 % of bacteria biomass (Figs. 2–4) [47,48]. According to many authors, lipids are sensitive to UV and oxidative degradation by many ROS.  $\cdot\text{OH}$  can oxidize fatty acids such as linoleic acid and induce lipid peroxidation [25,49–51]. The lipid peroxidation by ROS during photo-oxidation experiment was demonstrated by monitoring the release of breakdown product, malondialdehyde (MDA) [52]. Other ROS such as  $\cdot\text{O}_2^-$  are known to induce lipid damages [53] but UV light alone can also induce lipid peroxidation by ROS generation with exogenous chromophores called sensitizers [54,55]. During this oxidation, carbonyl compounds (aldehydes, ketones and carboxylic acids) are formed and can be potentially toxic for bacteria [49,50].

**Fig. 3.** Hydroxyl radical damage to cell envelope components of Gram-positive bacteria. Susceptibility to oxidative damages presents the following order: phospholipids > peptidoglycan.



**Fig. 4.** Hydroxyl radical damage to cell envelope components of enveloped virus. Susceptibility to oxidative damages is almost identical (plasma membrane  $\approx$  capsid).



A detailed study conducted by Smith et al. examined the changes of lipid bilayer under UV oxidation by using neutron reflectometry. Unsaturated fatty acids deterioration seemed to be faster than for saturated fatty acids probably

because of double bonds that make them more susceptible to oxidative attack [56]. UV light can also cause phospholipid tail deterioration onto unsaturated lipids [57] which is responsible for bacterial membrane reorganization increasing membrane permeability.

### 2.2.2. Damages to protein into the cell

Proteins are the major component of cell biomass with around 50 % of total biomass of bacteria [47,48] making them one of the most abundant intracellular target for ROS [53]. Most reactions of amino acids, peptides and proteins with ROS occur via chemical reactions rather than physical ones (only Tryptophan is subjected to physical quenching) [53,58]. In proteins, some amino acids are more sensitive to oxidation (Table 1). Methionines (Met) and Cysteines (Cys) have a sulfur atom that makes them very sensitive to oxidation but their environment into the protein can make them more sensitive. For example, positively charged residues close to Cysteines increase its sensitivity to the deprotonation of the thiol group into thiolate ( $S^-$ ). For the Met, two oxidized forms exist, the first, Methionine sulfoxide (Met-O) is reversible, and the second, Methionine sulfone (Met-O<sub>2</sub>) is irreversible but less frequent [59]. Other authors also report a difference in susceptibility to oxidative stress for amino acids. Davies et al. report in a very detailed review that Tryptophan (Trp), Tyrosine (Tyr), Phenylalanine (Phe) and Histidine (His) are the more sensitive to UV light [53], probably because of double bonds. They also reported that proteins can suffer multiple damages as a consequence of  $^{\bullet}O_2^-$  oxidation. We can cite for instance peroxide formation that can occur within protein in the Trp, Tyr and His amino acids. Side chain changes at the Trp, Met and Cys amino acids are also observed in photooxidized proteins as well as the creation of cross-links disulfide bond between proteins and/or the aggregates formation (mostly from radical-radical termination reaction of Tyr-derived amino acids). All these chemical and physical changes drive modifications on protein properties and turnover [53] that can induce a decrease in enzymatic activity [51]. During UV irradiation or UV/TiO<sub>2</sub> photo-oxidation, surface protein degradation has been observed directly by microscopy (transmission electronic microscopy TEM or scanning electronic microscopy SEM) by Kim et al. [60] and Park et al. [61]. Moreover, Park et al. [61] have observed the diminution of total surface proteins by using electrophoresis SDS-PAGE (Sodium Dodecyl Sulfate – PolyAcrylamide Gel Electrophoresis).

### 2.2.3. Damages to peptidoglycans

Surprisingly, studies reported that peptidoglycan show the highest resistance to ROS [25,49,62]. In photocatalytic experiments, bacteria death occurs without visible degradation of peptidoglycan (Figs. 2 and 4). After exposure of *Staphylococcus aureus* to TiO<sub>2</sub>/UV treatment for 24 h, a frequent detachment of the cell wall from the cell membrane was observed by TEM [63]. In gram positive bacteria, the cell wall was mainly composed of a peptidoglycan layer (Fig. 3) and TEM imaging revealed no visible degradation [25,63]. The same observation was made using peptidoglycan dosage during bacteria death on TiO<sub>2</sub> film [62]. However, peptidoglycan alterations may not be obvious because of its highly cross-linked structure so damage can occur without destruction of its overall appearance [25]. In bacteria, peptidoglycan layers form 2 nm size pores thus ROS can penetrate into the cell and damage the other extracellular layer or cellular compounds [64].



**Table 1**

Rate constants for the interaction of ROS (singlet oxygen or hydroxyl radical) with cell component available in the literature.

Component	ROS	Constant rate (L mol <sup>-1</sup> s <sup>-1</sup> )	Refs./authors
<b>Amino acids</b>	1O <sub>2</sub>		
Alpha-alanine	1O <sub>2</sub>	2.0 × 10 <sup>6</sup>	
Methionine	1O <sub>2</sub>	5.06 × 10 <sup>6</sup> –8.4 × 10 <sup>7</sup>	[149]
Methionine	1O <sub>2</sub>	1.6 × 10 <sup>7</sup>	[149]
Arginine	1O <sub>2</sub>	< 1 × 10 <sup>6</sup>	[53]
Tyrosine	1O <sub>2</sub>	2.7 × 10 <sup>7</sup>	[149]
Tyramine	1O <sub>2</sub>	2.8 × 10 <sup>8</sup>	[149]
Histidine	1O <sub>2</sub>	3.2 × 10 <sup>7</sup> –5.43 × 10 <sup>9</sup>	[149]
Tryptophan	1O <sub>2</sub>	0.8 × 10 <sup>7</sup>	[149]
Tryptophan	1O <sub>2</sub>	2.5 × 10 <sup>8</sup>	[53]
Cysteine	1O <sub>2</sub>	8.9 × 10 <sup>6</sup>	[149] [53]
<b>Proteins</b>			
Superoxide dismutase	1O <sub>2</sub>	8.2 × 10 <sup>5</sup> –2.6 × 10 <sup>9</sup>	[149]
Carbonic anhydrase	1O <sub>2</sub>	6.5 × 10 <sup>8</sup> –8.0 × 10 <sup>8</sup>	[149]
Lysozyme	1O <sub>2</sub>	7.8 × 10 <sup>8</sup>	[149]
Trypsin	1O <sub>2</sub>	7.1 × 10 <sup>9</sup>	[149]
<b>Nucleosides (precursor of nucleotides)</b>			
Thymidine	•OH	4.8 × 10 <sup>9</sup>	[67]
Cytidine	•OH	4.8 × 10 <sup>9</sup>	[67]
Uridine	•OH	4.3 × 10 <sup>9</sup>	[67]
Adenosine	•OH	4.0 × 10 <sup>9</sup>	[67]
<b>Nucleotides</b>			
T	•OH	5.3 × 10 <sup>9</sup>	[67]
C	•OH	4.5 × 10 <sup>9</sup>	[67]
A	•OH	3.0 × 10 <sup>9</sup>	[67]
<b>Polynucleotides</b>			
Poly (C)	•OH	1.2 × 10 <sup>9</sup>	[67]
Poly (U)	•OH	1.25 × 10 <sup>9</sup>	[67]
Poly (A)	•OH	0.9 × 10 <sup>9</sup>	[67]
Poly (U + A)	•OH	0.5 × 10 <sup>9</sup>	[67]
DNA	•OH	0.3 × 10 <sup>9</sup> –0.8 × 10 <sup>9</sup>	[67]
<b>Polysaccharides</b>			
Glucose	•OH	1.0 × 10 <sup>9</sup>	[162]
Carboxymethylcellulose 2.2	•OH	1.0 × 10 <sup>9</sup>	[163]
Carboxymethylcellulose 1.3	•OH	9.8 × 10 <sup>8</sup>	[163]
Carboxymethylcellulose 0.86	•OH	× 10 <sup>8</sup> –9 × 10 <sup>8</sup>	[163]
Dextran	•OH		

#### 2.2.4. Damages to nucleic acid (DNA and RNA)

ROS can break the phosphodiester bonds between nucleotide chains of DNA and RNA, can induce changes in nitrogenous bases (T or C becoming U) or can enhance the formation of pyrimidine dimers by cross-linking [65–68]. DNA damages by UV radiation out of cell using specific ROS scavengers have been studied to dissociate damages caused by  $^1\text{O}_2$  and  $\cdot\text{OH}$  [69].  $^1\text{O}_2$  can induce oxidative DNA damages by reacting with guanine residues and cause few strand breaks. In contrast,  $\cdot\text{OH}$  attacks all four DNA bases and produce much more stand breaks and base loss [69]. Those structural damages conduct to the decreased of the concentration of the genomic DNA as treatment time progress [60]. Oxidative damages accumulated in RNA can also indirectly affect protein synthesis and may generate lack of cultivability [65]. The accumulation of oxidative damages in DNA can affect tridimensional structure, replication and transcription conducting to RNA and proteins modifications. All the nucleosides and nucleotides are not degradable by ROS at the same rate thus nucleic acids damages depends on its composition (Table 1).

#### 2.3. Effect of the heterogeneous photo-oxidation on microorganisms

Microorganisms include a variety of organisms such as viruses, bacteria, fungi and protists. Even if there are many functional differences between microorganisms (bacterial respiration, ATP production, antioxidant system...), the structural difference in the composition of the cell wall remains one of the most important factors for comparing the sensitivity of microorganisms to photocatalysis. However, the impact of functional difference will be discussed briefly in the case of bacteria. The cell wall is a complex structure that protects microorganisms from their environment. It is the first ROS target and is composed of proteins, lipids, and polysaccharides. Inside of a taxonomic group the membrane composition can be different, the difference around Gram-positive bacteria cell wall and Gram-negative bacterial cell wall can be cite as example [70] (Figs. 2 and 4). Other organisms have a different composition of their cell walls, such as fungi, which cell wall is composed by chitin, glucans, and proteins [70]. Moreover, some microorganisms have increased their resistance to biocides and as a result, also present a lower sensibility to AOP disinfection than other microorganisms. For example, several bacteria exhibit the capacity to limit ROS action in the cytoplasm by: *i*) decreasing biocide penetration by changing membrane composition and by porin regulation, *ii*) decreasing intracellular biocide concentration by activation of detoxifying superoxide dismutase and catalase enzymes [71], *iii*) changing metabolic pathways [72] and enhancing DNA repair mechanisms [73]. Bacteria can also promote cell aggregation (biofilm production) to decrease cell accessibility and improve cell protection. Moreover, it is important to underline that microorganism sensitivity also depend on operative conditions (see Section 5). Some authors have already reported that in freshwater, microbial disinfection by photo-oxidation depends on cell wall composition. Most of the time, virus and prions are the most susceptible organisms to AOPs disinfection. Additionally, gram-negative bacteria are generally more susceptible to disinfection than gram-positive bacteria [74,75]. There is an important diversity of composition within the same taxonomic group that can influence the general AOPs disinfection susceptibility and partly explain differences observed in the literature.

##### 2.3.1. Bacteria

The majority of photocatalytic antimicrobial studies have been performed with gram-negative bacteria (often with *Escherichia coli* in freshwater) but a few studies with Gram-positive are available. Probably ascribed to difference in cell wall structure, many authors have observed that Gram-positive bacteria are more resistant to photocatalytic disinfection than Gram-negative bacteria [25,76–78]. Gram-positive bacteria cell wall is composed by two parts, an inner membrane/cytoplasmic membrane composed by phospholipids and proteins and a cell wall composed by peptidoglycans and lipoproteins (Fig. 3). Whereas Gram-negative bacteria have much less peptidoglycans, but a second layer cell wall called outer membrane and composed by lipopolysaccharides, phospholipids, and proteins (Fig. 2). Conversely, other authors have reported a more efficient inactivation for Gram-positive bacteria [79] possibly because of experimental conditions. In their study, the catalyst surface charge was negatively charged, and Gram-negative bacteria are coated with lipopolysaccharide molecules, which carry a negative charge with can decrease

bacteria/catalyst interaction and enhance Gram-positive bacteria inactivation [80]. To understand inactivation mechanisms, many studies have followed bacteria integrity during photocatalytic treatment by electron or fluorescence microscopy to visualize membrane and damages to cell wall [81,82]. Detection of lipid peroxidation products, the leakage of intracellular components (RNA, protein, DNA...) has also been performed [31,61]. Interestingly, several authors have already proposed a process of bacteria killing during TiO<sub>2</sub> photocatalytic treatment [25,49,51,54,81]. First, the outer membrane is damaged, then the cytoplasmic membrane until complete degradation. Peptidoglycan being much more resistant, photocatalytic killing occurs without substantial visible degradation of periplasm but peptidoglycan were still damaged [25,62]. The cell wall permeabilization by photo-oxidation is progressive (Figs. 2–4). At the beginning of disinfection, small molecules such as ONPG (o-nitrophenyl-β-D-galactopyranoside) can go through the membrane and when cell wall damage/ permeability is sufficient, large molecules such as β-D-galactosidase may leak [83]. The membrane permeabilization occur soon after bacteria attach to catalyst particles [25,50].

In freshwater some authors have also attribute the difference in sensitivity between bacteria to metabolic differences or to the physiological state of the bacterial [84–86]. Indeed, Skorbe et al. [85] looked at the inactivation of *Pseudomonas fluorescens* (obligate aerobe gram negative bacteria) and *Lactococcus lactis ssp. Lactis* (facultative aerobe gram positive bacteria) by TiO<sub>2</sub> photocatalysis. During the photocatalysis, the damages induced by ROS increases the ion permeability of the cytoplasmic membrane and causes the loss of the proton gradient. *P. fluorescens* uses oxidative phosphorylation to store energy necessary for the respiratory functions which are therefore inhibited by photocatalysis whereas cytoplasmic membrane damages impact less for *Lc. Lactis* (facultative aerobe) which uses other energy storage mechanisms such as lactic acid fermentation. Similarly, some bacteria have endogenous antioxidant response systems to deal with ROS that are more effective with enzymes (such as catalase) with higher activity, which confers greater resistance to ROS produced during photocatalysis (such as H<sub>2</sub>O<sub>2</sub>) [87,88]. As Rincon et al. [89] shown the physiological state of bacteria during the inactivation experiment strongly impact the disinfection rate even if the inactivation is slower for bacteria in stationary state than for that on exponential state the inactivation by photocatalysis still remain efficient. During the exponential state bacteria are more sensitive to photocatalysis than that one on the stationary state. During the stationary state, bacterial metabolism change, for example, proteins expression can be modified influencing the regulation of genes involved in the protection against oxidants or in the reparation of oxidative damage [90,91].

The majority of studies have focused on the antimicrobial efficacy of photo-oxidation in freshwater, but there are few studies dedicated to microbial inactivation in seawater [28,74,75,79,92–98]. In those studies, the photocatalytic disinfection efficiency has been analyzed on one or more bacteria (Supplementary 2). Most of the time, bacteria inactivation is monitored by culture which limits the detection to viable and cultivable bacteria and does not allow an estimation of the effect of the process on viable but not cultivable bacteria. Sometimes bacteria can be so damaged by the treatment that they cannot grow back immediately but may regrow after some time (1 or 2 days after stopping the treatment). Despite what would seem to be a successful disinfection treatment, there can be a regrowth of treated bacteria [99,100]. Some studies have shown that AOP treatments can limit bacterial regrowth [96,101,102]. When Residual Oxidant (TRO), part of oxidant used for treatment, is still in solution at the end of the photocatalytic treatment, the bacterial regrowth is reduced for several days. The inhibition of bacterial regrowth after treatment occur as long as residual oxidant is in solution after heterogeneous photo-oxidation [103]. As highlighted by Rubio et al. [96] and Wu et al. [104], photo-oxidation has a stronger effect on bacterial regrowth compared to UVC treatment.

In addition, some studies have also shown that some microorganisms can develop a resistance to the photocatalytic process [95,103,105] which may be due to: (i) the genetic or morphologic heterogeneity of the population [106,107], (ii) the competition for photo-oxidation between viable bacteria and partially lysis bacteria (cytoplasmic compounds released when membrane became permeable) [80,108–110], or (iii) the bacteria agglomeration that protect a part of the population.

### 2.3.2. Viruses

Viruses with sizes from 20 to 300 nm have been recognized as important microbial targets to ensure water safety. For example, enteric viruses are listed as emerging biological contaminants on the United States Environmental Protection Agency Contaminant Candidate List [111]. Some research has been done to study virus disinfection by photo-oxidation in freshwater, but to our best knowledge no study has been performed in seawater. In freshwater, the viral disinfection is a complex process which depends on many parameters and in particular, virus sensibility to photo-oxidation is dependent on both the composition of the envelope, the capsid, the nature of the genetic material of the virus and the type of process applied [112]. The viral inactivation with photocatalytic process consists of three steps (Fig. 4): particle shape distortion, protein oxidation, and DNA leakage and damages on the genetic material [113]. Oxidizing disinfectants as  $\cdot\text{OH}$  primarily target amino acids of the protein capsid affecting the structure and the morphology of the virus [61]. For example, the abundance of Tyrosine amino acid (Tyr or Y) appears to be related to virus susceptibility to  $\cdot\text{OH}$ -based disinfection. UV disinfection efficiency is correlated to virus size both in terms of virion size as well as genome length and nature. For example, viruses with double strand DNA genomes (such as enteric viruses), are more resistant to UV disinfection because photorepair of UV damages after disinfection could be facilitated by dsDNA form. Virus capsid composition is also essential to predict virus resistance to disinfection processes. Moreover, high percentages of aromatic amino acids can reduce UV penetration which would then reduce viral nucleic acid damage and thereby increase UV resistance of the microbe [112]. Nakano et al. [114] reported that non-enveloped viruses are more resistant to UV/TiO<sub>2</sub> inactivation compared to enveloped viruses whereas according to Liga et al. [115], non-enveloped viruses are more susceptible to hydroxyl radicals than enveloped viruses. Other authors like Bogdan et al. [49] have demonstrated that the peroxidation of the phospholipidic membrane in the envelope promotes the oxidation of capsid proteins resulting in increased damages to the nucleic acid of the viruses.

Furthermore, it should be noted that protein oxidation might not be completely lethal to viruses because most of them can still stay infective and replicate again under proper conditions and the mechanisms responsible for these reparations are still largely unknown [113].

### 2.3.3. Protists

Protists constitute a very large and heterogenous group composed of mostly unicellular eukaryotes. This group includes algae, protozoa, and fungi. Seawater protists represent the second most important part of the seawater biomass after bacteria [116]. They play an important ecological role because of the photosynthetic activity of algae, or by helping to recycle nutrients [117]. To date, no publication related to fungus disinfection by heterogeneous photo-oxidation in seawater was found so the following part will focus on seawater algae disinfection.

Algae are a complex group of organisms with different sizes (from a few microns to few meters in length). Some algae are invasive species as *Dunaliella salina* that can affect ecosystems, while others can produce phycotoxins that can be harmful for other marine organisms and for humans when contaminated molluscs or crustaceans are consumed. For this reason, some algae are frequently measured in seawater. Most of the photo-oxidation seawater studies have focused on two algae: *Dunaliella salina*, an invasive unicellular green alga from ballast waters, and dinoflagellate algae, some of which can produce phycotoxins. Photocatalytic treatments have the advantage to efficiently inactivate toxins as well as microorganisms [25,118]. Algae disinfection such as for *D. salina* by photo-oxidation seems to be quick, and hydraulic residence time ranges from a few seconds to few minutes to achieve one log degradation [105,119]. After the end of the photo-oxidation treatment, gross photosynthesis by algae and chlorophyll quantity drastically decreases and after treatment by ZnO (another catalyst) no regrowth occurs even after 4 days [120]. Moreover, during treatment, ROS attack both the algal cell membrane and intracellular organelles. Algal organelles are degraded via lipid peroxidation, DNA damages and protein oxidation [121–123]. Interestingly, even if the majority of authors reported that algae are rapidly degraded in seawater by AOP (few minutes), because of the heterogeneity in this group some other authors studying the global plankton (zooplankton and phytoplankton) found that plankton seems to be more resistant to AOP than bacteria [95], [164].

### 3. Microbial inactivation modeling

Many studies have already been done to model the disinfection of fresh water by AOPs and many equations have been written. These models have been around for many years and over time have been modified to describe the process leading more accurately and rigorously to the inactivation of microorganisms. In the literature, bacterial disinfection follows a 3-step process [109]. In most studies, bacterial degradation is analyzed by viable and growable bacteria counts. At the beginning of the treatment, the bacteria are damaged but multiple damages are required to inhibit the growth process [109,124–126] leads to an initial shoulder in the disinfection kinetics. Once the process is initiated, the damage caused leads to microbial inactivation and the degradation can be modeled by first order kinetics. After a few hours, a stabilization of the concentration, linked to the development of bacteria resistant to the process, can be observed. In 2000, Lambert and Johnston divided inactivation models into two groups of assumptions used to describe them, namely, the mechanistic assumption or the vitalist assumption. For the latter, the model is built on the major principle that part of the microbial population is resistant to chemical disinfection, while in the second case, the models consider a degradation process similar to those described for the degradation of chemical compounds [127]. In freshwater, four kinetic models were frequently described in the literature [93,94]: *i*) Chick's model [128], *ii*) Watson and Chick's model [129], *iii*) Delayed Watson and Chick's model and *iv*) Hom's model [130]. Chick's model was the first to describe bacterial disinfection due to radical attack. It consisted in describing the degradation of bacteria according to a mechanistic approach, namely a chemical reaction. This approach has evolved to finally lead to the creation of the delayed model of Watson and Chick. This model allows to model either the shoulder or the tail in the disinfection curve. Another approach, particularly adapted to describe the whole process of bacterial disinfection during a radical attack, is the Hom model. It is based on a power law to model the three steps of disinfection (initial shoulder, exponential disinfection and final resistance). Other models have been written [92,93,131–133] since Watson and Chick's model and Hom's model to improve the representation of experimental data. These models often include too many empirical parameters, are particularly complex, and therefore are rarely applied. Watson and Chick's model and Hom's model remain the most frequently used models [93,94] and are often used as a starting point for the development of empirical models of kinetic power law models. Some studies have compared and validated the use of similar models between different water matrix by studying disinfection in fresh water, MQ water and artificial seawater, and showing that the same kinetic law is suitable to describe the kinetics in all three matrices [96]. As the reaction kinetics are of the same order, so it seems possible to consider applying the freshwater model to saltwater. The two simple and representative models, namely, the delayed Watson and Chick model and the Hom model, are detailed below as well as a more complex empirical model as an example of a recent model.

#### 3.1. First order models relative to the target concentration

##### 3.1.1. Delayed Watson and Chick's model

In 1908, the Chick's model [128] was the first model to compare bacterial inactivation to a chemical reaction. In this model individual bacteria were considered as molecules and the disinfection was modeled as a first order kinetics. Watson modified the Chick's model to introduce a concentration-time product to consider disinfectant concentration variation [129]. Thus, the delayed model of Watson and Chick, accounting for the initial time lag, was developed. It allows to represent the shoulder observed at the beginning of the disinfection process which translates the necessity to have multiple radical attacks on several sites before observing the inactivation of the bacteria. Then, this model considers that the disinfection process is of pseudo-first order (Eq. (7)) [94].

$$\ln \left( \frac{N}{N_0} \right) = -KC^nT \rightarrow \frac{N}{N_0} = \begin{cases} 1, & t \leq t_{lag} \\ e^{-k'(t-t_{lag})}, & t > t_{lag} \end{cases} \quad (7)$$

With  $N$  the bacterial concentration at time  $t$ ,  $N_0$  the initial bacterial concentration and  $t_{lag}$  the time at the end of the lag phase (initial shoulder),  $k=kC^n$  with  $k$  is directly related to irradiation  $I$ ,  $C$  the catalyst concentration at time  $t$  and  $T$  the needed time to achieve the wanted inactivation.

### 3.1.2. Hom's model

Hom's equation can model both the initial lag and the tailing off in the curve at the same time [130]. It is very similar to Watson and Chick's model but differs with the addition of a power factor  $m$  for time  $T$  (Eq. (8)). When  $m = 1$ , the equation corresponds to Watson and Chick's law,  $m > 1$  represents the initial shoulder in the kinetic curve and  $m < 1$  represents the tailing off [94].

$$\ln\left(\frac{N}{N_0}\right) = -KC^nT^m \rightarrow \frac{N}{N_0} = -K_1 \left[1 - e^{-K_2T}\right]^{K_3} \quad (8)$$

With  $N$  the bacterial concentration at time  $t$ ,  $N_0$  the initial bacterial concentration,  $C$  the catalyst concentration at time  $t$  and  $T$  the needed time to achieve the wanted inactivation and  $K_1$ ,  $K_2$  and  $K_3$  are empirical constant of the model.

### 3.2. Models based also on the flux density

As for the previous models, models with flux density have been developed for bacteria degradation in freshwater mostly using empirical approaches. For example, Kacem et al. [132] developed a photocatalytic inactivation model for *E. coli* in freshwater. This model considers the influence of flux density  $I$  as well as the variation of bacteria concentration  $C$  in the liquid phase. The variation of the bacterial concentration in the liquid phase is mainly due to two coupled phenomena which are the adhesion of the bacteria on the surface of the catalyst and the degradation by photo-oxidation. To be relevant, this approach is built on the writing of two mass balances respectively representative of the variation taking place in liquid phase and at the solid interface (catalyst) (Eqs. (9) and (10)).

$$\frac{dC}{dt} = -K_s \cdot S_{cat} \cdot (q_e - q) - \frac{V_r}{V_t} \cdot \alpha \cdot I_r^f \cdot C \quad (9)$$

$$\frac{dq}{dt} = K_s \cdot (q_e - q) - \frac{V_r}{V_t} \cdot \alpha' \cdot I_r^{f'} \cdot q \quad (10)$$

With  $C$  the bacterial concentration at time  $t$ ,  $q$  the bacteria density attached on the catalyst surface at time  $t$ ,  $q_e = F \cdot$

$\frac{1}{C_e^n}$  the bacteria density attached on the catalyst surface at the equilibria where  $F$  and  $n$  are model parameters,  $K_s$  the fluid film mass-transfer coefficient ( $s^{-1}$ ),  $S_{cat}$  the equivalent surface of catalyst per unit of total volume to be treated ( $m^2/L$ ),  $V_r$  the irradiated volume (L),  $V_t$  the total volume (L),  $I_r$  the average irradiation ( $W/m^3$ ), and  $\alpha$ ,  $\alpha'$ ,  $f$  and  $f'$  are kinetic parameters.

Thus, there are several types of models to represent bacterial inactivation by photo-oxidation. Nevertheless, all models have been established with a bacterial model target (*E. coli*) in fresh water. No model exists to describe the microbial disinfection process in seawater which is a more complex matrix due to its composition.



#### 4. Key operating parameters to be optimized for microbial inactivation by heterogeneous photo-oxidation processes

Microbial inactivation is induced by the coupling of two phenomena. The production of ROS which is mainly limited by the quantity of photons. The mass transfer in the medium which translates the microbial transfer from the liquid to the catalyst surface. This second phenomenon is partly based on the interaction between the catalyst particles and the microorganism. The production of ROS can be affected by different parameters such as the effect of pH, temperature, the presence of organic and inorganic matter. But, the influencing factors of photo-oxidation are finally classified into two groups: (1) those that govern the inactivation process such as flux density, target concentration and (2) those that have a direct impact on the microorganisms such as additional stress, heat, or change in the interaction with the catalyst with pH, organic and inorganic matter. As previously mentioned,  $\cdot\text{OH}$  are the main ROS involved in the destruction of microbes in heterogeneous photooxidation mechanisms, but these radicals being short-lived, are unlikely to diffuse far from the catalyst surface (no further than 1  $\mu\text{m}$ ) [25,43]. Kikuchi et al. showed that killing of *E. coli* still occurred even when bacteria are separated from the catalyst by porous membrane probably because of  $\text{H}_2\text{O}_2$ . On the other hand, bacteria membrane permeabilization occurs mostly when cells adhere to catalyst surfaces [25]. The interaction between the catalyst and the microorganisms is dependent on the experimental conditions such as pH or dissolved organic matter.

##### 4.1. Flux density

Majority of modeling written for bacteria disinfection by photo-oxidation process are based on flux density and initial concentration on bacteria as it was present previously (see Section 3.2). Therefore, flux density remains an important operating factor to photo-oxidation efficiency. Conversely, all the studies described in the literature reveal a strong dependence of the degradation rate on the flux density [108,132]. Consequently, the duration and intensity of the light flux are the key parameters to control the disinfection process. Kacem et al. [28] conducted disinfection experiments over a range of flux intensities while keeping the other operating conditions constant. This experiment highlighted that the kinetics of bacterial inactivation evolves nonlinearly with flux density. It also shows that the tail formed at the end of the kinetics appears in a more marked and premature way for the low density of flux. This characteristic, indicating the development of bacteria resistant to the treatment, seems to be favored at low flux density. It has been shown that the inactivation process of viruses and bacteria is dependent on the UV/TiO<sub>2</sub> treatment time [114].

##### 4.2. Temperature

Temperature plays a key role in the photo-oxidation process for microbial disinfection [99]. During the photo-oxidation period, oxidizing free radicals react with oxidizing microorganisms to oxidize organic biomass. Temperature can affect the global inactivation process in two ways: (1) at the ROS production step, and (2) on microorganism's physical condition (thermic stress).

Majority of studies on the temperature impact onto photocatalytic experiment have been performed with abiotic organic matter in freshwater. It results that over a range of 10–60 °C the temperature does not impact photocatalytic efficiency [134]. The increase in temperature favors the production of ROS but inhibits the adsorption process of the pollutants on the catalyst. These two phenomena having antagonistic effects, the influence of the temperature is not observed. On the other hand, high temperatures decrease the solubility of oxygen and negatively affect the production of superoxide radicals [135]. Recently, El Hakim et al. observed a photothermal effect onto the EDTA degradation by photo-oxidation. By performing EDTA photocatalytic experiments at three temperature (40 °C, 60 °C and 80 °C), they show that the EDTA degradation is raised at high temperature due to oxidizing radicals enhancement [136]. For disinfection, temperature plays a key role in the photo-oxidation process of bacteria. As shown in numerous studies, inactivation by free radical attack is significantly intensified when the temperature increases [46,94,137,138].

Cho et al. [46] justify the inactivation of *E. coli* at high temperature by the increase of ROS generated, while Evgenidou et al. [137] explain it by an increase of the collision frequency at high temperature.

With respect to microorganisms, temperature plays a very important role. Each organism has its optimal growth temperature and beyond this temperature heat stress occurs. During heat stress phenomena, vegetative cells have to face external damages onto cell wall components or onto the cytoplasmic membrane. On the other hand internal damage have been observed onto ribosomes, ribosomal RNA and onto tricarboxylic acid (TCA) enzymes (such as the enzyme found in the citric acid cycle which is involved in cellular metabolism) [104,139]. Liu et al. [138] demonstrated that temperature stress alters the composition of saturated fatty acids by forming unsaturated fatty acids. The increasing on the unsaturated fatty acid proportion made cell wall less rigid. Thus, during heat stress, some organisms develop thermal resistance while others die. Smelt and al. thus proposed a model to represent the inactivation of organisms in response to heat stress [140].

### 4.3. Seawater matrix complexity

Organic matter and inorganic matter are the two main components of seawater. This complex matrix is composed mostly of water and salts (2.5 % of salts, the most abundant ions of seawater are chloride  $\text{Cl}^-$ , sodium  $\text{Na}^+$ , sulfate  $\text{SO}_4^{2-}$ , magnesium  $\text{Mg}^{2+}$ , calcium  $\text{Ca}^{2+}$  and potassium  $\text{K}^+$ ), but there are also dissolved organic (such as carbohydrate and amino acids) and inorganic materials (mostly carbon, bromide, boron, strontium and fluoride), particulates and a few atmospheric gases such as oxygen, argon and carbon dioxide [141]. The salinity of seawater varies according to its location, the seasons, and the weather conditions. Heat, by promoting evaporation, increases salinity, while cold water and rainfall tend to limit the salinity level. Thus, the Atlantic and Pacific oceans have relatively low salt concentrations of about 35 g/L, while seas such as the Mediterranean reach values of 38 g/L, and up to 45 g/L for the most salty ones such as the Persian Gulf [142]. These compounds by modifying the conditions of photo-oxidation and the process of radical production can reduce the effectiveness of AOP disinfection (Supplementary 1).

The effect of inorganic ions on the photocatalytic disinfection is worth exploring. Indeed, many studies have found that the presence of inorganic ions can significantly influence the photocatalytic disinfection [95,96]. According to Liu et al. chloride ions, which are scavengers of hydroxyl radicals, have an effect on the microbial inactivation process, while sulfate does not seem to alter the disinfection process of *E. coli* [138]. Unlike ozonation, photo-oxidation do not produce toxic species by reacting with inorganic ions. Thus, the  $\text{H}_2\text{O}_2$  process is not recommended for seawater treatment due to the presence of dissolved bromide in seawater. More generally, the Fenton and ozonation processes, due to the inhibitory effects of inorganic matter, do not seem to be suitable technologies (Supplementary 1) [26]. When inorganic ions are present in large quantities, they interfere physically and chemically with the catalyst. Thus, the presence of inorganic ions, and in particular chlorides, is responsible for the loss of photoactivity of  $\text{TiO}_2$  due to two mechanisms: *i*) the scavenging effect where chlorine ions react with oxidizing radicals and *ii*) the fouling of the active site on the catalyst surface. For example, several authors demonstrated that a prolonged exposition period of  $\text{TiO}_2$  film to artificial seawater decreased catalyst activity by elimination of  $\text{TiO}_2$  (hydrodynamic stress) and by recovering the catalyst with a chemical or biological film [79].

The effect of organic matter, widely studied for photocatalytic disinfection of fresh and wastewaters, deserves to be explored in the case of saline waters [95,96]. Indeed, even if organic matters have not been identified as an inhibitor of the heterogeneous photocatalysis process, the efficiency of the process is limited in the presence of organic matter. This impact could have two origins. First, the presence of organic matter, by absorbing part of the radiation, limits the flux of photons transmitted in the medium to the surface of the catalyst. Thus, the high concentrations of ions and organic matter, particularly present in seawater, can potentially reduce significantly the available photons to initiate the photo-excitation process. [96]. The second reason is related to the presence of dissolved organic matter which can react with the ROS produced by the catalyst. Indeed, as the disinfection process takes place at the vicinity of the catalyst (ROS lifetime is short), the organic matter can consume part of the ROS intended for the degradation of microorganisms. This competition between the species presents by decreasing the number of ROS available, limits the efficiency of the disinfection process. Thus, when organic matter interact strongly with the catalyst, they slow down the disinfection rate either by competition or by covering the catalyst. These effects

were highlighted in the work of Reoyo-Prat et al. [34] on abiotic pollutants, using four pharmaceutical molecules. They have shown that one together into the matrix the degradation rate of each compound are reduce compared to those of molecule alone.

#### 4.4. pH

Even if we can consider that the pH is almost constant in all the seas of the world (around 8.2 [143,144]), his parameter significantly influences the disinfection process and has been studied under controlled conditions. The pH acts in different ways on the properties of the catalyst either by changing the number and nature of the charges on the surface of the catalyst, or by facilitating the formation of catalyst aggregates but also by modifying the position of the valence and conduction bands. Thus, the surface properties of the catalysts during heterogeneous photo-oxidation are sensitive to the pH variation. Indeed, the isoelectric point or point of zero charge (PZC) of the catalyst switches positively or negatively according to the pH. When the pH value is lower than the PZC, the positively charged surface of the catalyst increases the electrostatic attraction to the negatively charged contaminant. As the adsorption of negatively charged contaminants on the photocatalyst is improved, the disinfection process is facilitated. Above the PZC, the negatively charged catalyst surface, attracts the positively charged contaminants. At the PZC, the interactions between the catalyst and the targets are reduced because the electrostatic forces at the surface of the solid are negligible. For example, for TiO<sub>2</sub> catalyst, the PZC is around 7 and surface charge changing occurs according to Eqs. (11) and (12). Below pH 7, microorganisms that are negatively charged are attracted to the catalyst and those positively charged are repulsed, suggesting that negative microorganisms are more susceptible to disinfection. Now, in the opposite situation, positively charged microorganisms interacting more strongly with the catalyst surface and are more easily subjected to the disinfection process [75,145]. In seawater, whereby an immobilized TiO<sub>2</sub> at pH 7.8-8 (> PZC) renders gram-positive bacterium like *Corynebacterium stationis* more susceptible than gram-negative bacterium like *Alteromonas sp.* [79]. Kormann et al. [147] having studied the distribution of TiO<sub>2</sub> forms as a function of pH, report that, between 3 < pH < 10, the surface is mainly functionalized to TiOH, for pH > 10, TiO<sup>-</sup> is present at more than 20 %, while at pH < 3, TiOH<sub>2</sub><sup>+</sup> is present at more than 20 %. They also determined the equilibrium constant of the reaction at different pH values.:

$$pK_{TiOH_2^+} = 2.4 \text{ and } pK_{TiOH} = 8.0 \text{ [146,147].}$$



Bacterial adhesion on the catalyst surface clearly depends on the pH. Schwegmann et al. [145] observed by scanning electronic microscopy (SEM) that *E.coli* adhesion on solid catalysts are more efficient at low pH (pH at 4, thus below the PZC) than at high pH (pH at 10, thus above the PZC). In freshwater, Kacem et al. observed that bacterial adhesion to solid catalysts also depends on catalyst size. When the catalyst is micrometric i.e. the catalyst particles are larger than the bacteria, it has been observed (by SEM) that several bacteria adhere to the same catalyst particle. On the other hand, when the particles are nano-sized (smaller than the bacteria), several catalyst particles adhered to the same bacteria. However, the particles size can be influenced by pH, at PZC the neutral surface charge of the catalyst enhances the catalyst particles aggregation. Catalyst particles are unable to produce the interactive rejection for solid-liquid separation so catalyst particles start aggregate and particles become larger [27].

Interestingly, several authors have been demonstrated that the pH has an impact on reaction rate between ROS and cell component [53,148,149]. Matheson et al. [148] having studied the reaction rate constant of histidine with singlet oxygen, find that this reaction rate in a function of pH. The photo-oxidative disinfection being based on ROS attacks onto micro-organisms, so a change on the reaction rate between ROS and protein can impact the global inactivation rate.

## 5. Seawater bio-securing application of photo-oxidation processes

Over the past decade, seawater bio-securing has become an interesting field for AOPs disinfection processes applications with ballast seawater treatment or aquaculture. Most efficient AOPs treatment used UVC irradiations combined to hydroxide peroxide ( $\text{H}_2\text{O}_2$ ) which have a great disinfectant power on plankton and bacteria (both gram positive and negative) (Supplementary 2) [95,96,150–152]. The disadvantage is that using UVC requires an energy-consuming UV lamp, whereas the development of AOPs using UVA or UVB allows the use of solar UV, and the liquid catalyst remain in the seawater after the end of the treatment. Even if less efficient, in combination with catalyst (solid as  $\text{TiO}_2$  or  $\text{Cn-N-TiO}_2$  [79,95,153], or liquid as  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ ,  $\text{Fe}^{2+}$  or  $\text{HSO}_5^-$  [95,98,151]) UVA and UVB AOPs have a great disinfectant power in seawater. Photo-catalytic treatment applied for the seawater disinfection need to be choose carefully depending on the application. In seawater the used of  $\text{O}_3$  will generate bromide which is toxic so an adsorption process such as activated carbon (AC) need to be add at the end of the treatment. Once the bromide has been eliminated, the seawater can be re-used in aquaculture, as Poblete-Chavez et al. show with the rotifer culture (rotifer comprise one of the most used feeds in finfish aquaculture) [154]. The photo-Fenton treatment is strongly modified the seawater pH by acidifying it [155] so after or during the treatment the pH need to be adjust to avoid negative impact on fishes or mollusks if the treated seawater was used in aquaculture. Moreover, generator of radicals such as  $\text{H}_2\text{O}_2$  can reduce metabolisms of marine organisms and induce mortality. For example, mussel exposition to 10 mg/L of  $\text{H}_2\text{O}_2$  start inducing mortality after 200 h [156] whereas for the *Vibrio alginolyticus* inactivation Moreno-Andrés et al. used 5 mg/L of  $\text{H}_2\text{O}_2$  [151] which had a half-lives in seawater from 15 to 70 h [157]. Solid catalyst such as  $\text{TiO}_2$  can also impact marine organisms (mussel and oysters) [158–160] but as it is solid it can be separated from the treated seawater before it used in aquaculture that made UV/ $\text{TiO}_2$  disinfection processes an promising processes for seawater treatment.

## 6. Conclusion and future prospects

In this review, the focus was on disinfection of seawater by heterogeneous photooxidation. Operational factors (flux density, temperature, seawater composition, pH) and ROS-targeted biomolecules are considered to gain insight into the potential of seawater disinfection via this process. Despite the limited number of seawater disinfection studies available in the literature and the lack of knowledge, heterogeneous photocatalytic oxidation is positioned as a promising technology for microbial seawater disinfection applications, but in doing so, additional studies on viral seawater disinfection are however needed.

Heterogeneous photo-oxidation has four major advantages:

- efficient elimination of all microbes present in seawater as well as toxins.
- do not generate toxic subproducts.
- no need to add reagents during treatment and reused of catalyst.
- sustainable process (solar irradiation as UV source) applied under environmental condition (pH, temperature...).

In the years to come, the demand for seawater disinfection is expected to increase and heterogeneous photo-oxidation seems to be a promising disinfection process to apply. in:

### (1) Ballast water treatment:

With globalization, shipping has increased and with it invasives species dissemination around the world. Since 2004, the International Maritime Organization (IMO) who regulates ballast water management (BMW) have adopted the International Convention on the Control and Management of Ship's Ballast Water and Sediments. In addition, with the increase of green energy demand, offshore wind turbines have been developed. Those turbines are moored to sea floor with big ballast water tanks. Those tanks are accumulating microorganisms that can be released into the environment, and thus need to be treated to eliminate all microbes present.

(2) Aquaculture (and pisciculture) bio-securing:

With the increase in demand for seafood, intensive farming has developed. On these farms, the density of fish or molluscs is high, and diseases appear frequently. To limit mortality episodes, antibiotic treatments and/or genetic selection are widely used. An increasing number of antibiotic-resistant bacterial strains are emerging, and new disinfection methods need to be developed to bio-secure this type of effluent. Moreover, it has already been shown that water treatment processes using photocatalysis can achieve sufficient water quality to be applied in closed-loop aquariums containing coral reefs as well as fish and other invertebrates [161].

One of the undeniable advantages of photocatalysis is that it can act simultaneously on biotic and abiotic contaminants present in water (micro-organisms, microbial toxins, pesticides, pharmaceutical substances). However, the application of such a process still requires several methodological developments as highlighted in our review: firstly, no study was found in the literature devoted to the disinfection of viruses present in seawater by heterogeneous photocatalysis. Secondly, among the studies cited in this paper (Supplementary 2), we pointed out the lack of homogeneity in units of inactivation efficiency according to the microorganisms considered, which would allow researchers and professionals to compare the inactivation performance of AOP processes applied to seawater treatment. Indeed, the sensitivity of each microorganism to disinfection remains one of the key points to really predict the global disinfection of seawater.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.nxsust.2023.100003](https://doi.org/10.1016/j.nxsust.2023.100003).

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