1. INTRODUCTION

1.1. Safe drinking water

1.1.1. Availability, distribution and problematic

Water is a precious but scarce resource that is essential for life. Only 3.5% of the Earth's water is freshwater and fit for human consumption. Of this freshwater, only 1% is free-flowing in rivers, lakes, or streams **(Fig. 1.1).** Even so, there is sufficient drinking water on the planet to meet the needs of the population. However, accessibility and availability of safe drinking water (free from pathogens and priority chemical contamination) at the household level is not equal for all. Ensuring these basic needs is one of the greatest challenges currently facing humanity.

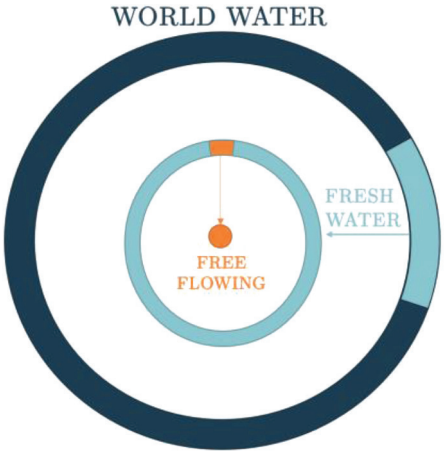

Fig. 1.1: Water distribution on Earth.

Over the years, global actions have been taken to satisfy basic water needs of the entire population **(Fig. 1.2).** On 28th July 2010, the United Nations (UN) General Assembly recognised the human right to water and sanitation, declaring that clean drinking water and sanitation are essential to fulfil all human rights (United Nations (UN), 2010). In September 2015, the same assembly announced the Sustainable Development Goals (SDGs) in the 2030 Agenda action plan. There are 17 SDGs, and all work towards "ending poverty in all its forms". They are the successors of the Millennium Development Goals (MDG) signed in 2000, but these new goals incorporate a specific 6th SDG on water. SDG6 aims to "Ensure availability and sustainable management of water and sanitation for all" and includes eight global targets related to the management

of natural water resources, wastewater, and the environment. The first target is to "Achieve access to safe and affordable drinking water" before 2030 since water accessibility is not guaranteed for a significant 29% of humanity. For example, 844 million people still lack access to safe drinking water, and approximately 1000 children die each day due to diseases related to unsafe drinking water or sanitation (United Nations (UN), 2018, 2015). Furthermore, the availability of water is becoming more unreliable and problematic due to the effects of the climate crisis (FAO, 2017; IPCC, 2018; UNU-INWEH/UNESCAP, 2013), the water demand of an ever-increasing population, the expansion of cities, and the developing economy (UNESCO/UN-Water, 2020; Wada *et al.,* 2014).

Fig. 1.2: Timeline of safe drinking water statements.

1.1.2. Household Water Treatments (HWT)

The lack of safe drinking water affects communities in low-to-medium-income countries most. The lack of financial and technological resources impedes the implementation of drinking water treatment plants in these regions. To deal with this situation, Household Water Treatments (HWT) are required since they tend to be (McGuigan *et al.,* 2012):

▸ *Low-cost:* the most impoverished communities are the most affected.

▸ *User-friendly:* everybody should easily produce safe drinking water.

▸ *Sustainable:* to avoid consumables that are expensive or hard to obtain.

Most HWT are small-scale adapted water treatments that anyone can use. They can also include pre-treatments to remove solids that negatively influence disinfection treatment. At the household level, very simple forms of pre-treatment can be provided, including filtration through fabric or sand,

flocculation-coagulation with natural substances, or sedimentation. However, these pre-treatments do not completely eliminate the pathogens (bacteria, viruses, and protozoa) responsible for waterborne diseases and other health risks (Gadgil, 1998; Pichel *et al.,* 2019).

The most widely adopted HWT for pathogen removal are the following (their characteristics are summarised in **Fig. 1.3):**

▸ *Boiling:*

This process is highly effective against all classes of microbial pathogens (World Health Organization (WHO), 2015). People universally accept that boiling makes water safer to drink, so they trust the treatment and adopt it readily. Boiling requires large amounts of fuel with estimated costs of up to $10.56 per person per year (Clasen *et al.,* 2008), unless it is freely collected. However, boiling causes health risks due to indoor air pollution and boiled water is very vulnerable to recontamination since it usually is cooled in open containers (Gadgil, 1998; Gilman and Skillicorn, 1985).

▸ *Chlorination:*

Chlorine can be added in liquid or tablet form, is also easy to apply at the household level, and is very inexpensive (estimated costs of $0.66 per person per year (Clasen *et al.,* 2007)). A particular strength of chlorine is that residual chlorine in the water can protect against bacterial regrowth. However, chlorine is less effective against some viruses and ineffective against common protozoa. Disinfection by-products can be formed due to reactions with naturally occurring substances. These by-products can change the smell and taste of the treated water and chlorination is sometimes rejected on these grounds. Also, intensive use requires consumables that must be replaced periodically, and, in general, the population that demands HWT is in difficult to access, remote areas (Pichel *et al.,* 2019; World Health Organization (WHO) Regional Office for South-East Asia, 2017).

▸ *Filtration:*

Generally, filters do not remove all pathogens since their filter pores are larger than the microorganisms. However, ceramic filters do retain protozoa, work well against bacteria and some of them have efficacy against viruses (the smallest pathogen). Users have confidence in filters since they tend to clarify the water, and ceramic filters can also evaporatively cool the water (Pichel *et al.,* 2019; World Health Organization (WHO), 2002). Nevertheless, ceramic filters are fragile and can be costly to maintain (estimated costs of $3.03 per person per year (Clasen et *al.,* 2007)).

▸ *SODIS:*

Solar water disinfection, or SODIS, is based on the germicidal effect of UV light and its synergistic effect with the rise in water temperature. The procedure is very user-friendly since it involves just filling a transparent container with water and placing it in direct sunlight for several hours. The treatment is economical because only a transparent container is required (estimated costs of $0.63 per person per year (Clasen *et al.,* 2007)). Solar UVA radiation is lethal against bacteria, as it is UVB radiation against bacteria, viruses, and protozoa. However, turbidity decreases the available solar radiation and prolongs treatment time. It is recommended that the water is treated and stored in the same container to avoid recontamination (Rufener et *al.,* 2010) and is consumed within the 24 h following exposure since bacteria can regrow in the dark while the water is stored and cooling.

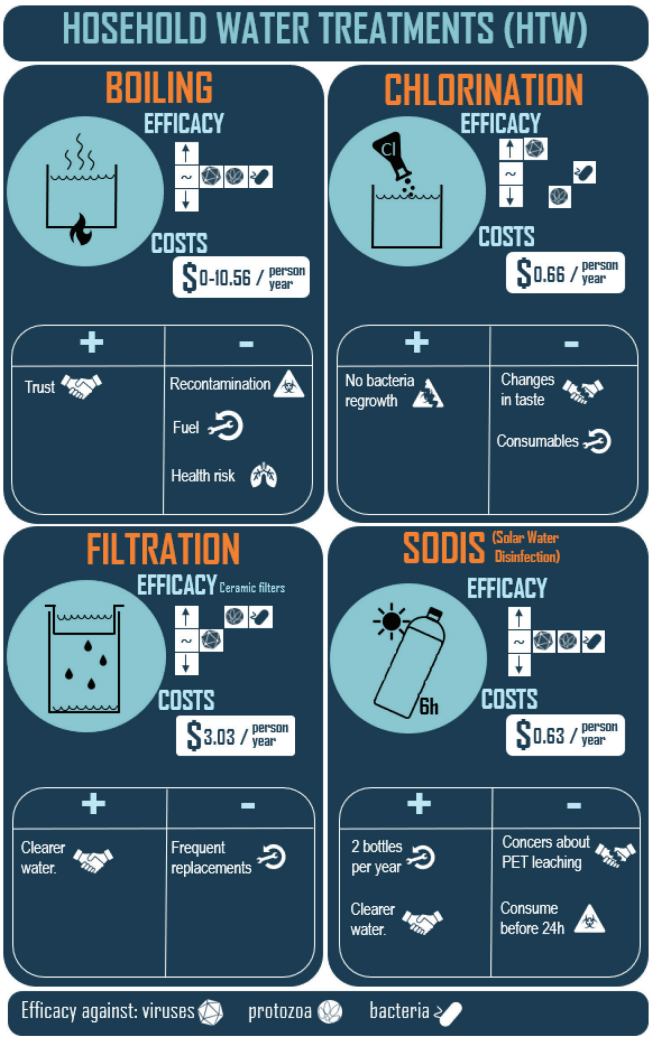

Fig. 1.3: Household water treatments.

1.1.3. Standard SODIS procedure

SODIS has been found to be one of the most appropriate treatments for producing safe drinking water, because it is inexpensive and not dependent on consumables. The SODIS process is driven entirely by solar energy, and its effectiveness for the removal of pathogens from water has been widely proved.

The most widely accepted procedure for this simple technology is described in detail in the *"SODIS manual: Guidance on solar water disinfection"* published by Luzi ***et al.*** (2016). Briefly, water with a maximum level of 30 NTU should be exposed to the sunlight in clean 2-litre polyethylene terephthalate (PET) bottles for 6 h on sunny days, 48 h on cloudy days, while on days of continuous rainfall SODIS should not be used. PET bottles are selected due to their low-cost and wide availability. Concerns about chemical contaminants from plastic migration have been addressed by previous studies (Ubomba-Jaswa ***et al.,*** 2010a; Wegelin ***et al.,*** 2001). SODIS has been accepted by the World Health Organisation (WHO) and has been recommended for low-income countries and in the aftermath of natural disasters or humanitarian crises (World Health Organization (WHO), 2011, 2005).

Implementing SODIS treatment requires behaviour changes that sometimes generate obstacles to uptake. In this sense, any new SODIS-based innovations should be user-friendly, supported by local community elders, and ergonomically designed for a favourable reception. Many studies have reported successful SODIS implementation under diverse field conditions in locations such as Kenya, Cameroon, India, Cambodia, and Latin America (Center for Desease Control and Prevention (CDC), 2011; Conroy ***et al.,*** 2001; Graf ***et al.,*** 2010; Rose ***et al.,*** 2006).

1.2. SODIS. Variables

The SODIS guidance has been published to facilitate a standard procedure for worldwide implementation. However, this general method has limitations. Several variables must be exhaustively studied since they interfere with radiation transfer from sunlight to the pathogen and, consequently, determine the treatment efficacy.

1.2.1. Radiation

It is well-known that the higher the radiation intensity, the higher the cell damage. However, the photoinactivation mechanism, and, consequently, the inactivation rate, varies strongly with wavelength.

Photoinactivation mechanisms

Microorganisms are photoinactivated when they suffer damage triggered by an excited chromophore (any substance capable of absorbing photons). Photoinactivation can be conducted via direct or indirect damage.

Direct damage:

An endogenous process that occurs when photon absorption by a chromophore induces changes to the chemical structure. The chromophore is generally a constituent of the microorganism's genome (e.g. nucleic acids, proteins, or other macromolecules). Since all pathogens have a genome, all of them are susceptible to this type of damage.

Indirect damage:

In this case, photon absorption by a chromophore generates photo-produced reactive intermediates (PPRI) that damage components of the microorganism. In this instance, the chromophore is called a sensitiser. Depending on the location of the sensitiser, indirect photoinactivation can be exogenous or endogenous (Nelson ***et al.,*** 2018):

- *Endogenous indirect inactivation* takes place when PPRI are generated from internal sensitisers. Examples of internal sensitisers are amino acids, coenzymes, vitamins, or metalloproteins that mainly produce reactive oxygen species (ROS) such as hydrogen peroxide, hydroxyl radicals, singlet oxygen, or superoxide radicals. Only microorganisms with sufficient internal sensitisers are subject to this type of damage.

- *Exogenous indirect inactivation* happens when the sensitiser is external, such as dissolved organic matter, nitrates, nitrites, or metal complexes. Depending on water quality, diverse PPRI can be externally formed: e.g. Check pdf, 2016), or reactive halogen species (RHS) in seawater (Parker and Mitch, 2016). This mechanism is only possible if the extra-cellular water matrix contains these sensitisers. Therefore, in pure water, exogenous indirect inactivation does not occur.

Solar spectrum

Different portions of the solar spectrum participate in the three mechanisms of photoinactivation. This wavelength dependence comes from the different chromophores with different sensitivities and absorption spectra that are involved (summarised in **Fig. 1.4**):

(Endogenous) direct damage:

Photons in the UVB range (280-320 nm) mainly contribute to the (endogenous) direct damage since RNA and DNA absorption spectra extend up to 320 nm (Busse *et al.,* 2019; Mattle *et al.,* 2015; Silverman *et al.,* 2019). UVB wavelengths are more energetic than UVA radiation. Despite the UVB radiation intensity at the Earth's surface is relatively low, it can trigger harmful damage, which is more than sufficient to kill biological cells.

Endogenous indirect damage:

This damage is primarily initiated by UVB and UVA photons, but also can be initiated by visible (400-700 nm) photons. Internal components of some microorganisms such as coenzymes, vitamins and metalloproteins can generate internal PPRI illuminated with UVA and UVB radiation. Flavins and porphyrins can also be activated with visible light.

Exogenous indirect damage:

This can involve photons in the UVB, UVA, and visible radiation ranges. Nitrites and nitrates are mainly activated by the UVB region. However, organic matter, the most common external sensitisers in fresh water, absorbs light in all three radiation ranges.

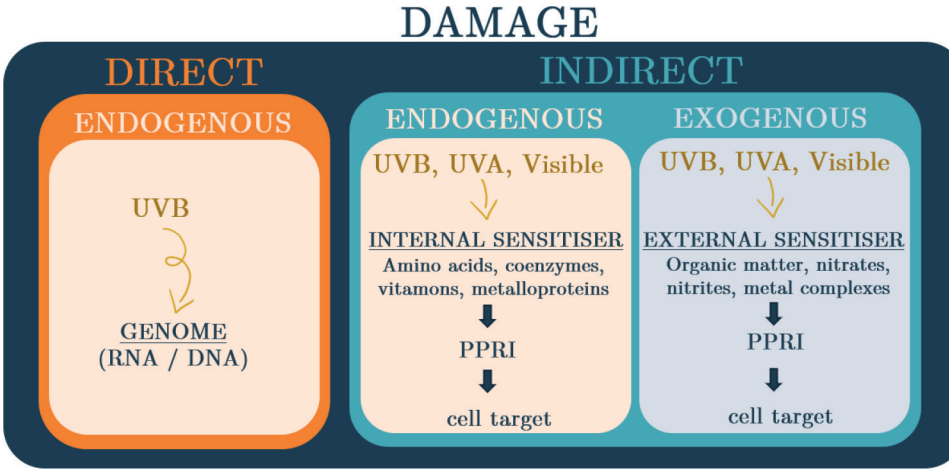

Fig. 1.4 Photoinactivation mechanisms and their spectral actions.

1.2.2. Container

The SODIS process requires a UV-transparent container or reactor since the solar radiation must penetrate through the material. The selection of mate-

rials for manufacturing of SODIS containers must take into account not only optical properties but also mechanical properties, their long-term durability, and material availability. These properties are evaluated in this section and the optimal properties of a SODIS container are summarised in **Fig. 1.5.**

Optical properties

SODIS mainly relies on the damage caused by solar UV radiation to microbial pathogens. However, the pathogen's susceptibility varies with wavelength. Thus, knowing the radiation distribution at the Earth's surface is not sufficient on its own. The wavelengths transmitted into the interior of the SODIS container is a critical factor for assessing disinfection performance.

PET bottles are the most frequently used containers for solar water disinfection. PET transmits UVA and visible light but is opaque to UVB (Fisher *et al.,* 2012), preventing the possibility of the most powerful type of direct cell damage caused by UVB radiation. Alternative containers and materials that transmit UVA and UVB radiation have been successfully evaluated, including: polypropylene (PP); polycarbonate (PC); polystyrene (PS) (Fisher *et al.,* 2012), polyethylene (PE) bags (Lawrie *et al.,* 2015), polymethylmethacrylate (PMMA) (Reyneke *et al.,* 2020; Ubomba-Jaswa *et al.,* 2010b) and glass reactors fitted with compound parabolic collectors (CPC) (García-Gil *et al.,* 2019; Kalt *et al.,* 2014; Mac Mahon and Gill, 2018).

Mechanical properties

Generally, SODIS containers are used to collect, treat, and store household drinking water which is an advantage since recontamination risk is reduced (Rufener *et al.,* 2010). For this reason, the containers should be manufactured from robust materials that can withstand frequent handling. Sometimes, as for polyvinyl chloride (PVC), additives are added to increase the elasticity of the plastic but, in high concentrations, these can diffuse out of the plastic and into the water, posing a health risk (Wegelin and Sommer, 1998). The key mechanical properties that potential materials must guarantee are:

- *Resistance:* measured as tensile strength and stiffness (before failing or becoming permanently deformed) and toughness (the energy required to fracture or scratch the material).

- *Lightweight:* since the container may be transported every day from the house to the water source.

On the other hand, non-transportable, static SODIS systems are also used to provide safe drinking water in larger communities, such as small schools or clinics

(McGuigan *et al.,* 2012; Reyneke *et al.,* 2020). In this sense, good mechanical properties for the materials are not essential since the containers are less subjected to falls and scratches that can decrease light transmission or cause breakages. In such circumstances, more fragile and/or more density materials, such as glass or PMMA, can be used (Fagan *et al.,* 2015; Martínez-García *et al.,* 2020).

Ageing material

The mechanical and optical properties of plastics can vary as a result of weathering. The harmful effect of weather exposure on plastics is primarily attributed to photo-degradation or photo-oxidation processes by UV light and the action of oxygen (Gillen and Celina, 2017). Furthermore, it is well-known that temperature and humidity can speed up the degradation process (Martin and Gardner, 1981; White, 2006).

From the viewpoint of photostability, plastics can be grouped as follows (Rånby, 1993):

- *Poorly photostable plastics:* The lifetime of these plastics is very short, usually less than one year. Some examples are PS, PVC, PP, and PE.

- *Moderately photostable plastics:* These polymers can be used for a few years outside. Examples are PET and PC.

- *Highly photostable plastics:* These have an outdoor life of many years. A typical example of such polymers is PMMA.

Degradation can be slowed if temperature, UV light, and contact with oxygen and water are controlled (Kircher, 1987). However, this is not possible for SODIS container materials for the following reasons:

- *Avoiding unnecessary thermal exposure:* The SODIS containers, by necessity, must be exposed to the sun, which heats it. In fact, the thermal effect has been shown to accelerate the disinfection rate. Therefore, natural heating is welcomed.

- *Removing oxygen and water contact as much as possible:* SODIS container walls are continuously in contact with water and oxygen. From inside because they are filled with untreated water and from outside because of the atmosphere, the wind, and the humidity.

- *Adding UV blockers to the plastic:* If UV blockers are incorporated into the plastic, the UV transmittance reduces and, consequently, the inactivation rate is also reduced.

Accessibility

Since solar water disinfection is designed for uptake in resource-poor environments, three more factors should be considered:

Affordability

SODIS is usually selected when insufficient finances are available to afford higher-price HWT. However, the selection of material must be evaluated not only in terms of efficacy (good and durable optical and mechanical properties) but also with regard to affordability. For example, PMMA is robust and highly UV transmissive, but costs twice that of PET (28.9 €/kg vs 13.9 €/kg - data from Database 2.0 Ecoinvent (Frischknecht ***et al.,*** 2005)). Plastic ageing sometimes offsets production costs: for example, PMMA is a highly photostable plastic with many years of predicted outdoor life, whereas PET should be replaced in one or two years. However, most of the households do not have the initial investment available. If they had the funds for the more expensive material, then they would have been able to afford alternative higher-price HWT in the first place. Thus, lower-cost materials are typically used in SODIS.

Availability

Regions without access to safe drinking water are generally isolated, located far from the industrial centres and at the end of very long supply routes. Often, the transport cost of the material makes them too expensive, and consequently, one cannot choose the material with the best transmission or lifetime characteristics. In this sense, it is always recommended to select a local container. In fact, the widespread availability of PET bottles containing bottled water or soft drinks is the main reason why PET bottles are the most frequently used SODIS containers.

Adoption

Another point to consider for optimal containers is the ease of social adoption (acceptability). Several obstacles have been found when introducing SODIS to communities. These include scepticism due to the simplicity of the procedure, concerns about leaching of harmful substances from the plastic into the water and the lack of promotion by bottle manufacturers (McGuigan ***et al.,*** 2012; Ozores Diez ***et al.,*** 2020). The design of the container can improve community uptake if the design is adapted in accordance with their usual practices. For instance, in Sub-Saharan Africa, 20 L to 25 L plastic jerrycan containers are already in widespread use collection and transport of water. Standard jerrycans are typically made of opaque PE plastic. The use of transparent jerrycans that also allows the application of SODIS has been used to increase implement HWT in this region (“WaterSPOUTT project,” 2022).

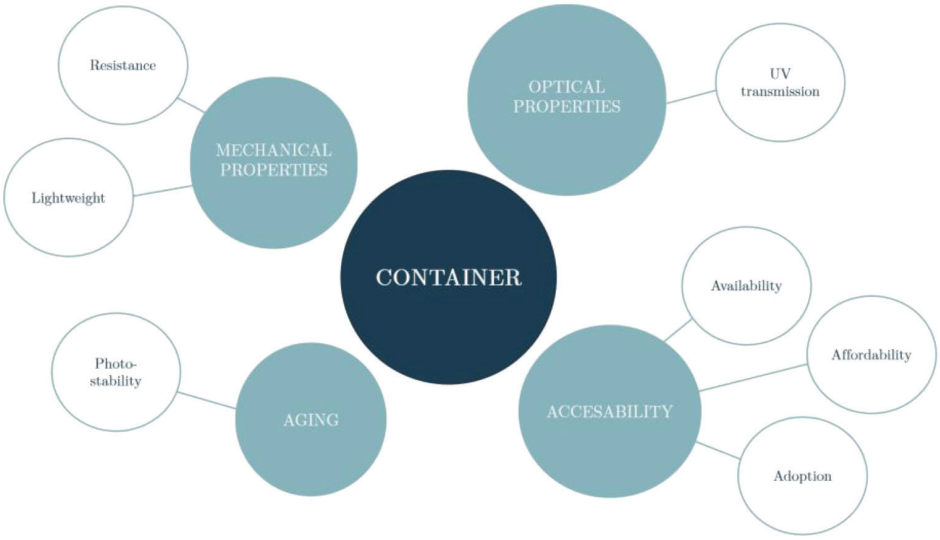

Fig. 1.5: Optimal properties for a SODIS container.

1.2.3. Water quality

Chemical composition

Freshwater can contain naturally occurring substances such as (bi)carbonates, carbohydrates, organic matters, solids, or even iron or hydrogen peroxide. Although the concentration of these substances is generally low, they can play two critical roles within the SODIS process: either as radiation attenuators and/or as sensitisers.

Radiation attenuators

Radiation is only slightly attenuated by pure water, which absorbs some wavelengths more than others resulting in preferential radiation concentration in the blue-visible window near the attenuation minimum (Gall ***et al.,*** 2013), giving water its blue colour. However, most other substances within fresh water tend to attenuate radiation at shorter wavelengths (UV range). Water can contain suspended or dissolved natural substances. Suspended substances, such as solids, usually scatter radiation. In contrast, dissolved substances generally absorb radiation. Dissolved organic matter is the main substance that absorbs radiation, especially coloured dissolved organic matter (CDOM). Scattering and absorbance increase exponentially with declining wavelengths, resulting in yellow/orange-coloured waters. Therefore, UV wavelengths tend to be strongly attenuated by naturally occurring substances (Nelson ***et al.,***

2018). As the concentration of attenuating substances is usually very low, its role can be irrelevant for small-volume containers (i.e., 1 L bottle). However, if the SODIS process is carried out in large-volume containers, the water quality and increased absorption path length significantly influence the disinfection rates.

Sensitisers

Naturally occurring substances such as Check pdf excited by photons which induce reactions with biomolecules through a sensitised process. In these situations, such substances are termed sensitisers. The excited chromophore can act as an oxidant or promote the formation of PPRI, such as carbonate radicals ($CO_3^{\bullet-}$), the excited triplet state of CDOM ($^3CDOM^*$) or ROS in fresh water. Among ROS, singlet oxygen ($^1O_2$) is formed by energy transfer to dissolved oxygen, superoxide radical ($O_2^{\bullet-}$) and hydrogen peroxide (H_2O_2) are formed by electron and proton transfer to dissolved oxygen, and hydroxyl radicals ($HO^\bullet$) are formed by Fenton reactions (hydrogen peroxide and dissolved iron), photolysis of nitrate or nitrite, or other processes involving excited chromophores (Foote et ***al.,*** 1995; Hoigné ***et al.,*** 1988; McNeill and Canonica, 2016; Vione ***et al.,*** 2014; Zafiriou, 1974). Depending on the water composition, the PPRI concentrations can vary by several orders of magnitude (Bodrato and Vione, 2014; Foote ***et al.,*** 1995). In addition, chromophore absorption is wavelength dependent. Thus, the PPRI concentrations and the resultant exogenous damage depends on the available radiation spectrum. Standard concentration ranges of PPRI in sunlit water are 10^{-17} to 10^{-15} M for $HO^\bullet$, 10^{-14} to 10^{-12} M forCheck pdf. The concentrations of PPRI for a specific water matrix and the photoreactions involved, can be calculated using the APEX freeware as a function of water chemistry and the optical path length (and water depth) of sunlight in water (Bodrato and Vione, 2014; Vione, 2020). The most likely reactions of PPRI with individual biomolecules have been intensively studied and are associated with electron-rich sites on biomolecules. For example, in nucleic acids, PPRI usually react with guanine (Smit, 1989), and in proteins, with electron-rich amino acids such as tryptophan, tyrosine, histidine, methionine, and cystine (Boreen ***et al.,*** 2008; Davies, 2003; Lundeen ***et al.,*** 2014; Michaeli and Feitelson, 1994). However, the reactions that happen with the pathogen as a whole are unknown. In addition, PPRI attacks do not necessarily result in pathogen inactivation since they are site-specific, and many microorganisms have repair mechanisms, especially complex pathogens such as bacteria (Nelson et ***al.,*** 2018).

Pathogens

The most important pathogens which cause waterborne diseases are bacteria, viruses, and protozoa. Their sensitivities to the different types of damage differ because of their distinct morphologies **(Fig. 1.6):**

Viruses

Viruses are the smallest pathogens, usually in the range of 0.1 µm in size. Viruses need a host cell to live, grow, and reproduce since they do not have an independent metabolism. Many viruses are host-specific, causing disease in only humans or particular animals. Rotaviruses and hepatitis A and E viruses are the most widespread waterborne viruses affecting humans. In 2004, rotavirus was estimated to cause over 500.000 deaths each year, with more than 85% of these occurring in low-income countries (Parashar ***et al.,*** 2009). Another example is the coliphage MS2, a single-stranded RNA virus that infects ***Escherichia coli*** bacteria and other Enterobacteriaceae, and is commonly used as an indicator of photoinactivation due to its higher resistance in comparison to other viruses or bacteria (Love ***et al.,*** 2010; Theitler ***et al.,*** 2012).

Photodamage: Endogenous photoinactivation occurs mainly via direct damage when the genome is exposed to UVB radiation. Indeed, the action spectra of photoinactivation closely mirror the absorption spectra of RNA/DNA (Lytle and Sagripanti, 2005). Due to their simple structure, consisting of a genome surrounded by a protein capsid, indirect endogenous damage is usually negligible. Regarding exogenous direct damage, external PPRI within the water matrix can inactivate viruses. Examples of harmful PPRI are singlet oxygen (Kohn ***et al.,*** 2007; Kohn and Nelson, 2007; Michaeli and Feitelson, 1994), hydroxyl radicals (Mattle ***et al.,*** 2015; Romero-Maraccini ***et al.,*** 2013), carbonate radicals (Mattle ***et al.,*** 2015) or excited state organic matter (Rosado-Lausell ***et al.,*** 2013). Although all of these PPRI can inactivate viruses in isolation, their relative significance depends on the specific water characteristics and the contribution of direct inactivation (sometimes, the larger contribution of direct inactivation overshadows the exogenous inactivation) (Nelson et ***al.,*** 2018).

Bacteria

Bacteria are prokaryotic cells, typically of micrometre dimensions. They can live without any host since they are more complex microorganisms than viruses. Although most bacteria are harmless or even beneficial to humans, some can cause diseases such as cholera, trachoma, or salmonellosis. ***E. coli*** is globally found in human and animal faeces and is a universally recognised faecal indicator. Most ***E. coli*** strains are not pathogenic; however, some strains, such as enterotoxigenic ***E. coli*** (ETEC), do cause disease. The Global Enteric Multicenter Study (GEMS) found ETEC among the top 5 pathogens most likely to produce diarrhoeal disease in children.

Photodamage: Bacteria can be photoinactivated by all three damage mechanisms. As bacteria have a genome, they are sensitive to direct photoinactivation by solar UVB radiation (Jagger, 1985). As bacteria are complex microorganisms, they contain several chromophores that produce endogenous

indirect damage. In fact, even in dark conditions, bacteria can generate PPRI originating from metabolic processes. To generate energy, bacteria carry out cell respiration, involving electron transport. A small portion of free electrons interacts with the oxygen in the cell interior to produce superoxide radicals and hydrogen peroxide. The latter substance can interact with internal iron by the Fenton reaction to generate hydroxyl radicals. Superoxide and hydroxyl radicals indiscriminately attack several cell targets (Nelson *et al.,* 2018). When cells are illuminated with UVA radiation, the photosensitiser NADH coenzyme, promotes superoxide formation from oxygen molecules (Chen and Schopfer, 1999). However, bacteria have their own defence mechanisms, such as: superoxide dismutase enzyme (SOD) that converts this radical to hydrogen peroxide; the catalase enzyme (CAT); and alkyl hydroperoxide reductase enzyme (Ahp) that neutralises the hydrogen peroxide (Seaver and Imlay, 2001a). These enzymes are also inactivated by UVB and UVA radiation. Furthermore, bacteria have mechanisms that repair damage caused by radical attacks and photodamage, and often recover and regrow in darkness after light exposure (Giannakis *et al.,* 2015; Sinha and Häder, 2002). External sensitisers found in water also can damage bacteria via exogenous indirect photoinactivation under UVA radiation, specifically in Gram-positive cells: Enterococci (Gram-positive bacteria) are susceptible to indirect exogenous damage, but *E. coli* (Gram-negative bacteria) does not show noticeable inactivation (P.A. Maraccini *et al.,* 2016; Peter A Maraccini *et al.,* 2016).

Protozoa

Protozoa are the largest class of pathogens by size, usually about 10 to 50 μm. Protozoa are single-celled eukaryotes. Some form cysts to survive unfavourable conditions (exposure to unusual temperatures or chemicals). Many protozoa are parasites that can cause diseases such as malaria and giardiasis. In low-income countries, *Cryptosporidium parvum* protozoon is one of the top three pathogens causing diarrheal disease in children under two years old, being responsible for 30-50% of childhood mortality (Kotloff *et al.,* 2013). Many conventional water treatments, including chlorination, are ineffective against *C. parvum,* although the risk of infection through drinking water can be reduced by UV radiation and temperature, thus it is amenable to SODIS (Gómez-Couso *et al.,* 2012b).

Photodamage: Solar inactivation of *C. parvum* is dominated by direct endogenous damage caused by the absorption of UVB radiation within the genome. Indirect endogenous damage is negligible since the action spectrum of *C. parvum* closely resembles that of the DNA absorption (Busse et *al.,* 2019; Liu *et al.,* 2015). This similarity also confirms the wavelength dependence for the photoinactivation of *C. parvum* (Beck *et al.,* 2015; Busse *et al.,* 2019; Linden *et al.,* 2001). Exogenous damage is generally negligible since the presence of natural organic matter (NOM), one of the most important external sensitisers,

does not cause any effect on *C. parvum* viability, most likely due to its highly resistant thick oocyst wall (Liu et *al.,* 2015).

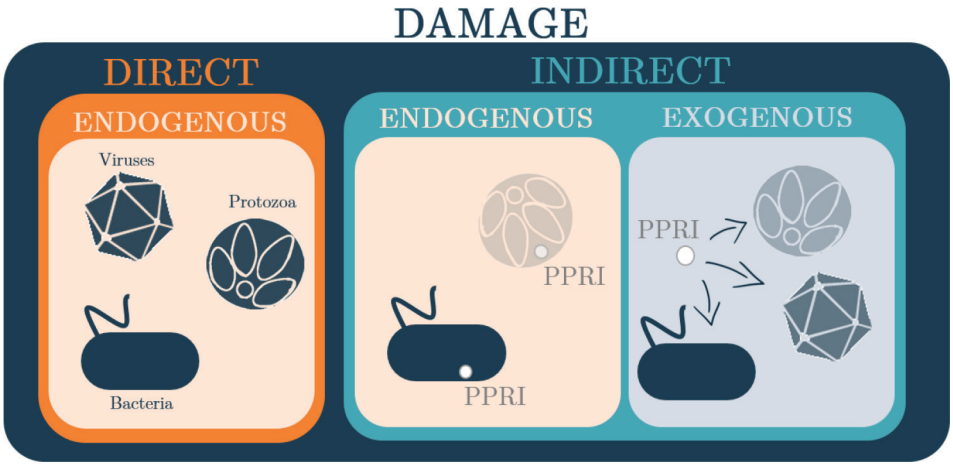

Fig. 1.6: Sensitivity of bacteria, viruses, and protozoa to types of damage. The more transparent, the less sensitive.

1.2.4. Temperature

Inactivation effects

Above a certain temperature, most microorganisms' cells collapse and die. The explanation for this lack of heat resistance is that high temperatures denature those proteins essential for life in microorganisms. During solar exposure, water temperature can increase significantly up to 30-50°C. Therefore, if the pathogen contains essential proteins which are sensitive in this temperature range, it will be thermally inactivated, and these proteins will establish the thermal threshold for the pathogen. For example, cellular function in *E. coli* begins to be disrupted at 40°C because of the melting point of the lipid membranes, whereas *T. thermophilus* bacteria proteins are unaffected up to 70°C (Leuenberger *et al.,* 2017; Mackey *et al.,* 1991). Some investigations have found that the viability of *C. parvum* protozoa progressively drops for temperatures in the range from 30 to 50°C due to the increase in the metabolic activity and the melting point of fatty acids and hydrocarbons present in its oocyst wall (Fayer and Nerad, 1996; Jenkins *et al.,* 2010; King *et al.,* 2005; Peng *et al.,* 2008). Temperatures above 37°C can induce spontaneous excystation of *C. parvum* oocysts, making their survival impossible in the absence of a host (Gómez-Couso *et al.,* 2009; Smith *et al.,* 2005). In the case of viruses, thermal inactivation at SODIS temperatures is usually more complicated since the virus contains fewer components than other microorganisms with more complex structures. MS2 virus shows noticeable thermal inactivation above 50°C (Seo *et al.,* 2012).

Inactivation synergistic effect

In 1992, Šolić and Krstulović, (1992) confirmed significant separate effects of temperature and solar radiation on the survival of faecal coliforms using analysis of variance (ANOVA), but also the dependence of the effect of one factor on the level of another. The results indicated that temperature and solar radiation effects are not merely additive but are synergistic. In 1998, under experimental conditions, synergistic temperature-radiation effects were found to be significant for all types of pathogens in the temperature ranges of SODIS treatment (K. G. McGuigan *et al.,* 1998; McGuigan *et al.,* 2012). This synergistic effect results from the simultaneous action of the temperature (distributed damage caused by denaturation of components) and the UV radiation (targeted damage triggered by absorption by chromophores). The temperature threshold and the inactivation trend vary with pathogenic species. MS2 virus, and *rotavirus* show a strongly temperature-dependent above 40°C (Romero *et al.,* 2011), whereas *E. coli* bacteria is susceptible above 30°C (Castro-Alférez *et al.,* 2017a).

Enhancements

Various modifications to SODIS containers have been investigated in an effort to enhance temperature effects:

- *Painting the bottom of the container black* or *placing the bottles on a black surface.* The non-absorbed radiation by pathogens is absorbed by the black surface, increasing water temperature by black-body radiation (Mani *et al.,* 2006).

- *Using* reflectors. The main aim of using reflectors in the SODIS process is the concentration of sunlight. However, temperature also can be slightly increased as a secondary effect. CPCs are largely used as solar collectors, although they are considered to be prohibitively expensive for adoption at the household level (Casado *et al.,* 2019; Kehoe *et al.,* 2001; Rijal and Fujioka, 2004). However, high-performance low-cost solar collectors fabricated with recycled materials, open-source hardware, and 3D-printing technologies have been developed (Martín-Sómer *et al.,* 2021).

1.3. SODIS. Kinetic modelling

Standard SODIS guidance recommends an exposure time of 6 h on sunny days and 48 h on cloudy days. However, this is a general statement, based only on experimental results, that often overestimates the required solar exposure time. Kinetic models of the SODIS process are needed to answer the

questions such as how long should the container be exposed to the sun? Reported solar disinfection rates vary over several orders of magnitude even for the same microorganisms since the kinetic models do not consider all the variables that contribute to inactivation. An accurate model should account for all the variables and parameters described in the previous section, especially for comparing of the inactivation rates from different models or predicting the required solar exposure time under field conditions.

To model the SODIS process, the most critical parameters to be considered are temperature and spectral irradiance, which are variable and unpredictable. First, precise quantitative values of these parameters must be confirmed. Then, models need to predict how both variables affect the inactivation, especially considering the potential existence of a synergistic interaction between irradiance and temperature.

Summing up, the steps for the accurate modelling of the SODIS process are listed below:

- *Actual irradiance and temperature:* Before modelling the kinetics, the temperature and spectral irradiance experienced by the pathogens must be determined. For the latter, the solar radiation at the container wall and the irradiance losses caused by absorption and scattering by both the container material and the water matrix, must be studied. **Fig. 1.7** schematically shows the pathway that the radiation follows in the SODIS process before producing damage to the microorganisms.

- *Modelling photonic inactivation:* Identification of the photo-activated processes, the participant chromophores, the type of damage produced, and the reactions involved.

- *Modelling thermal inactivation:* Assessment of the thermal contribution to the inactivation.

- *Synergy:* Study of the possible synergistic effects by the joint action of irradiance and temperature.

- *Assembling the pieces:* The combination of the different submodels results in the comprehensive global kinetic model.

Inactivation rates can be influenced by additional factors such as abnormal pH, dissolved oxygen concentration, physiological state of microorganisms, or changes in the water matrix (for example, increased concentrations of harmful substances such as hydrogen peroxide or iron). These additional processes should be considered within the kinetic model.

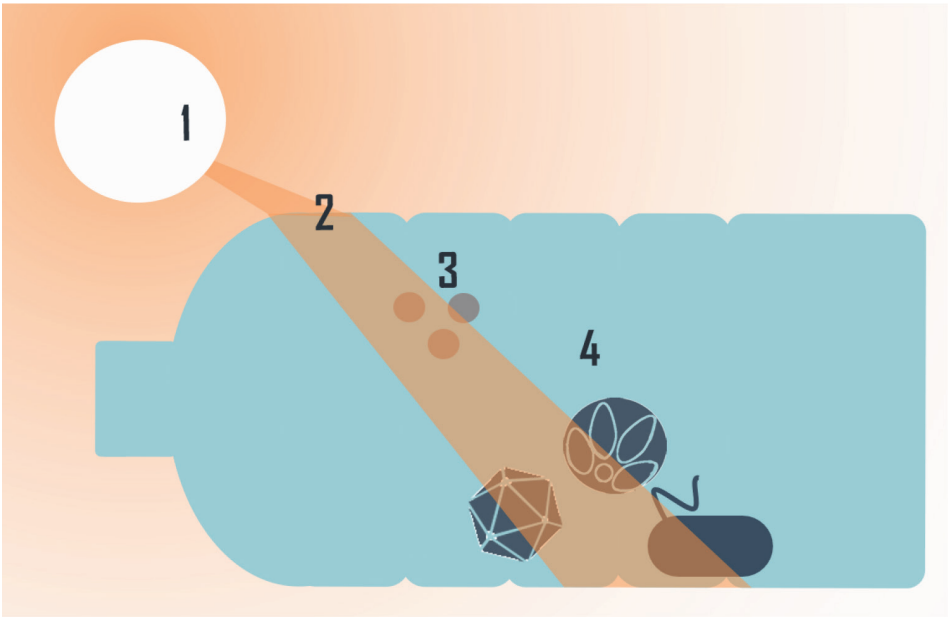

Fig. 1.7: The path the radiation travels from the sun to the pathogen in the SODIS process. #1: Radiation source; #2: Crossing through the container; #3: Crossing through the water; #4 Radiation that reaches pathogens.

1.3.1. Actual irradiance and temperature

Spectral irradiance values

Radiation source

Solar radiation intensity and its spectral distribution that reaches at the Earth surface vary with solar zenith angle (a function of latitude, time of day, and time of year) and weather conditions (García-Gil ***et al.,*** 2019):

▶ *Solar zenith angle*

Solar radiation passes through the atmosphere to the Earth's surface and is attenuated by the air mass. The path length of the air mass depends on the relative sun position (zenith angle). The longer the path length, the higher the radiation loss. The solar zenith angle, the angle between the sun's rays and the normal to a plane tangent to the surface of the Earth, varies with latitude, time of day, and time of year (season). Knowing this angle, the theoretical solar spectrum for any point on the Earth's surface can be estimated.

▸ *Weather conditions*

Changes in meteorological conditions do not imply a proportional change to the spectral radiation delivery. Visible and UVA spectral distributions are stable regardless of cloud-cover and atmospheric ozone concentrations. UVB radiation is particularly attenuated by atmospheric ozone concentration and consequently with increasing path length. This effect varies with the time of day and the season. For example, between summer and winter at mid-latitudes, UVA and visible radiation intensities vary by a factor of two, while UVB intensity varies by a factor of four (Nelson et ***al.,*** 2018).

Several tools can be used to estimate the theoretic sunlight spectrum as a function of zenith angle, such as the Simple Model of the Atmospheric Radiative Transfer of Sunshine (SMARTS) (Gueymard, 2005), the Tropospheric Ultraviolet and Visible Radiation Model (TUV) (Kohn et al., 2016; National Center for Atmospheric Research, 2022), or the solar calculator tool developed by Moreno-SanSegundo ***et al.*** (2021) (Moreno-SanSegundo ***et al.,*** 2021). The latter estimates both diffuse and direct irradiation from AM 0.0, introducing atmospheric extinction (atmosphere depth calculated from solar vector and elevation), absorption and scattering due to cloud coverage, and other minor contributions from temperature or humidity. Also, these tools are available in software form, such as the Solar Calculator from ANSYS Fluent®, based on an algorithm from the National Renewable Energy Laboratory (NREL, USA) database ("National Renewable Energy Laboratory, Solar Position Algorithm|NREL.," 2022). These predictive tools usually offer an option to include a cloud-cover factor or forecast the cloud-coverage from historical data (Moreno-SanSegundo ***et al.,*** 2021). However, climate conditions such as the cloud cover are unpredictable and very influential in the spectral distribution. Thus, radiation intensity and its spectral distribution should ideally be measured in real-time during the treatment. In this sense, the use of a spectroradiometer is highly recommended in order to save the wavelength-specific irradiance over the desired range. However, the accuracy of spectroradiometer or predicting models is critical, especially in the UVB range, since kinetic rates are very sensitive to these wavelengths (Nelson ***et al.,*** 2018).

Material container

As SODIS is usually performed in a transparent container, the solar radiation that reaches the Earth's surface is further modified when it passes through the container wall. The radiation is attenuated since containers walls absorb the radiation as a function of thickness and type of material. These variables can be easily related by the well-known Beer-Lambert law in which the absorbance is directly proportional to the path length and the extinction coefficient (Beer, 1852; Lambert, 1760). The path length is determined by the thick-

ness of the wall, and the extinction coefficient is specific and characteristic for each material and wavelength. Note that extinction coefficients of the materials are wavelength-dependent. Therefore, each plastic has extinction coefficient spectrum and, consequently, the radiation attenuation is different for each wavelength.

It should also be noted that the characteristic extinction coefficient spectrum of each material will change as the container ages due to weathering. For this reason, it is necessary to analyse the potential changes in transmission of the containers during their lifetime.

Water composition

Radiation is also attenuated by water. For low volume containers (1-2 L bottles) and clear water, radiation losses related to absorption and scattering can be neglected. For natural water with low extinction, a volume-average irradiance value can be estimated from the attenuation provided by the Lamber-Beer law using the extinction coefficient of the water matrix. However, for large dimension, high-volume containers, the radiation profiles within the water must be carefully considered. The downward irradiance over a depth interval in a water column can be approximately estimated using the vertical attenuation coefficient in the downward direction (Kirk, 1994). This is an empirical parameter that must be measured for each particular water matrix. However, this does not account for transmission losses caused by scattering off solid particles. In this case, numerical simulation can be used to determine the irradiance distribution inside the container as a function of both absorption and scattering properties (discussed in depth in **Section 1.3.5. Assembling the pieces**).

Temperature

The temperature of water bodies changes depending on the solar radiation over the day and the season. Radiation transmission into water bodies is highly sensitive to the clarity of the water. Water bodies often experience thermal stratification in which shallower layers are brighter and warmer than the deeper layers (Boyd, 2020). However, due to the relatively low volume of SODIS containers, the temperature gradient can be neglected.

Water temperature can be estimated by a heat balance of the water volume in the SODIS container as a function of the date using the solar altitude (Brutsaert, 1979). Several authors have used this method to estimate the water temperature even in water flowing in the shade (Rutherford *et al.*, 1997). However, to achieve accurate data, experimental measurements are recommended.

1.3.2. Modelling photonic inactivation

The earliest model for the inactivation of microorganisms by disinfectants derives from the Chick-Watson Law (Chick, 1908; Watson, 1908). This law states that the rate of microorganism destruction (*dC/dt*) is directly proportional to the number of organisms remaining at any time (*C*). This relation implies a uniform susceptibility of all species at a constant concentration of disinfectant — irradiance value in the case of the SODIS process — and is quantified by the kinetic constant (*k*). This model is based on a first-order kinetic in which the slope of the linear equation is the kinetic constant:

$$\frac{dC}{dt} = -k \cdot C = -k' \cdot E \cdot C \qquad \text{Eq. 1.1}$$

Many modifications of the Chick-Watson Law have been proposed to account for deviations from the simple first-order kinetics. For example, in 1972, Hom introduced an empirical generalisation to reproduce frequently observed curvilinear functions (Hom, 1972). In 1978, for cases where the radiation is not constant, Chamberlin and Mitchell redefined the kinetic constant expression as the product of the kinetic constant with downward irradiance (Chamberlin and Mitchell, 1978). Yet another example is the series-event model proposed by Severin in 1982 that is based on the fact that microorganisms have multiple targets, all of which must be inactivated before cell death, or that a single site within the microorganisms must be hit several times before inactivation (Severin ***et al.,*** 1982).

All these models are based on empirical results. Empirical models are non-selective and straightforward, so they can be adapted to other pathogens relatively easily. However, for complex systems, these models do not accurately reproduce the actual results and do not respond well to situations outside the range of the operational conditions studied (interpolation is only recommended). In contrast, mechanistic models can account for such reactions and processes. Due to their accuracy and rigour, mechanistic models can handle any operational conditions (interpolation and extrapolation) and behaviours such as synergies. However, they are more specific and more complex. A rigorous description of all involved biochemical routes is far from reality. Therefore, mechanistic models capture the essential steps of the global process and are considered an optimal compromise between the fundamental description of the process and the simplicity of the model's requirements for engineering purposes (Castro-Alférez ***et al.,*** 2017b).

To develop kinetic models, contributions from all three types of damage (exogenous damage, direct endogenous damage, and indirect endogenous damage) should be contemplated. However, many kinetic models focus only on

general endogenous damage since it is difficult to separate direct and indirect endogenous damage.

Endogenous damage

As the importance of the action spectrum of light in SODIS has been demonstrated previously (McGuigan *et al.,* 2012; Nelson *et al.,* 2018), many authors have developed kinetic models of endogenous photoinactivation considering the irradiance distribution.

Kinetic models usually assume that all photons in a radiation range contribute to the photoinactivation in the same way. For example, Silverman *et al.* (2015) assumed that only UVB radiation took part in the photoinactivation of MS2 virus and, therefore, only this range of radiation should account as an input parameter (*E* from **Eq. 1.1)** for modelling. Castro-Alférez *et al.* (2017b) studied the significant importance of UVA radiation in *E. coli* disinfection (ignoring direct damage caused by UVB radiation). They developed a mechanistic kinetic model only considering this range and defined the ROS reactions involved in the bacteria inactivation. These models fitted well to the experimental results obtained with the same radiation emission spectrum. However, they do not consider radiation distribution and cannot respond appropriately to changes in the emission spectra caused when SODIS is performed with different container materials, times of the year, or atmospheric conditions.

Some authors obtained the spectral action of light for photoinactivation of microorganisms using monochromatic radiation sources (via LEDs or cut-off filters). In this sense, they empirically defined a biological weighting function (*P*) that describes the microorganism's sensitivity to sunlight as a function of wavelength (λ)

$$\frac{dC}{dt} = -k \cdot C = -\int_{\lambda} P(\lambda) \cdot E(\lambda) \cdot d\lambda \qquad \text{Eq. 1.2}$$

Fisher *et al.* (2011) defined this function for MS2 and PRDI viruses, and Silverman and Nelson (2016) and Lui *et al.* (2016) for different strains of *E. coli* and enterococci bacteria. However, these models are empirical and tell us nothing about how and why the damage occurs.

As we know now, endogenous damage is produced when the internal chromophores (*CHROM*) are excited (*CHROM**) by the sun and, consequently, they can directly damage the microorganism (*MO*) or promote several harmful reactions (with PPRI as intermediates), and return to their original ground-state by emitting energy in the form of heat (infrared photons):

$$CHROM + hv \rightarrow \begin{vmatrix} CHROM^{*} + MO \rightarrow MO_{damaged} \\ CHROM^{*} + X \rightarrow PPRI \,/\, PPRI + MO \rightarrow MO_{damaged} \\ CHROM^{*} \rightarrow CHROM + heat \end{vmatrix}$$

Chromophore activation is determined by its absorption spectrum and the reaction rate depends on the number of absorbed photons. Since the rate-determining step (RTD) is chromophore activation, the kinetic constant (*k*) can be expressed as follows:

$$k = \int_{\lambda} \phi(\lambda) \cdot \varepsilon_{CHROM}(\lambda) \cdot CHROM \cdot E(\lambda) \cdot d\lambda \qquad \text{Eq. 1.3}$$

where ϕ is the quantum yield of the reaction (microorganisms damaged per photon) or (PPRI formed per photon), $\varepsilon(\lambda)$ is the specific spectral extinction coefficient of the chromophore (mL • cromophore^{-1} • cm^{-1}), ***CHROM*** is the concentration of the chromophore (cromophore • mL^{-1}), and ***E(λ)*** is the irradiance that reaches the chromophore (Einstein • s^{-1} • cm^{-2}).

For simple microorganisms, the action spectra of photoinactivation closely mirror the absorption spectra of the RNA/DNA of many viruses as also of the absorption spectrum of the DNA of the protozoon *C. parvum* (Busse ***et al.,*** 2019; Fisher ***et al.,*** 2011; Liu ***et al.,*** 2015; Lytle and Sagripanti, 2005). In these cases, the RNA/DNA is assumed to be the unique significant chromophore and, therefore, endogenous direct damage response is the only photoinactivation path. In this sense, **Eq. 1.3** can be rewritten for the endogenous photoinactivation of the microorganisms as:

$$k_{endo} = \phi \cdot \int_{\lambda} \varepsilon_{DNA/RNA}(\lambda) \cdot C_{DNA/RNA} \cdot E(\lambda) \cdot d\lambda \qquad \text{Eq. 1.4}$$

This method was proposed by Mattle ***et al.*** (2015) to model the solar inactivation of the MS2 virus from a mechanistic perspective. The same procedure can be adapted to model other microorganisms inactivated via direct damage. It would be only necessary to know the genome type and size to obtain the microorganism's absorption spectrum (the product of multiplying the DNA/RNA absorption spectrum ($\varepsilon_{dna/rna}$) by its concentration ($C_{dna/rna}$)).

For complex microorganisms such as bacteria, many chromophores involved in the inactivation mechanisms should be considered. So far, no model has been developed to combine the action spectra with the internal reactions of the inactivation mechanisms.

To simplify the modelling calculations, Vione (2021) published a new approach based on a monochromatic approximation to the polychromatic problem, introducing the concept of equivalent monochromatic wavelengths (EMWs). The EMW is the single wavelength that reproduces the behaviour of the polychromatic system, using a monochromatic (Lambert-Beer based) equation. Following this approach, **Eq. 1.3** is transformed into:

$$k = \int_{\lambda} \phi_{app} \cdot \varepsilon_{CHROM}(\lambda_{eq}) \cdot CHROM \cdot E(\lambda_{eq}) \cdot d\lambda \qquad \text{Eq. 1.5}$$

where ϕ_{app} is the apparent quantum yield, $\varepsilon_{CHROM}(\lambda_{eq})$ and $E(\lambda_{eq})$ are the specific spectral extinction coefficients of the chromophore and the irradiance that reaches the chromophore at the equivalent wavelength (λ_{eq}), respectively. Note that ϕ_{app} is not exactly a quantum yield since it is the ratio between the reaction rate of a polychromatic process and the absorption of monochromatic radiation at λeq. For this reason, ϕ_{app} can take values up to 1. This is what happens in surface waters illuminated with the complete solar spectrum. However, for SODIS, the range of wavelengths that reach the water can vary greatly depending on the container material and may even absorb at the equivalent wavelength. In this sense, a new equivalent wavelength should be estimated for each new material.

Exogenous damage

Exogenous inactivation is usually modelled as a sum of the inactivation contributions generated by the PPRI detected in the water matrix. The general form to express the kinetic rates uses a second-order kinetic equation as a function of the PPRI and microorganism concentrations as follows:

$$\frac{dc}{dt} = -k_{PPRRI} \cdot C \cdot PPRI \qquad \text{Eq. 1.6}$$

However, determining the PPRI concentrations in the water matrix is difficult since they depend on the water composition and the spectral irradiance. To define the mechanistic pathway to produce PPRI, a detailed characterisation of the water composition (concentrations and action spectrum) would be required. To avoid this, the steady-state PPRI concentrations are directly measured in the water body. However, another limitation should be noted since the PPRI concentrations can vary spatially within the volume of the container due to the differences in the irradiance distribution. Freely available APEX software can be applied to address this (Bodrato and Vione, 2014; Vione, 2020). The kinetic model of APEX predicts photochemical reactions and pollutant/microorganisms phototransformation as a function of water

chemistry, for the optical path length (and water depth) of sunlight in water and its spectral distribution. The model applies **Eq. 1.5** for each water substance to calculate the PPRI concentration and, later uses **Eq. 1.6** to calculate the disinfection rate for the exogenous damage. However, key input data on pollutant/microorganism photoreactivity parameters such as the direct photolysis quantum yield and the second-order reaction rate constants with HO•, $\mathbf{CO_3}$•, $\mathbf{^1O_2}$ and ^{3}CDOM* are required. Second-order rate constants have been reported in the literature for different viruses (MS2, PhiiX174, HadV, and rotavirus) and PPRI (singlet oxygen, hydroxyl radical, carbonate radicals, and excited dissolved organic matter) (Kohn and Nelson, 2007; Mattle ***et al.,*** 2015; Rosado-Lausell ***et al.,*** 2013; Silverman ***et al.,*** 2015). However, in some cases, different values of kinetic constant are reported for the same reaction. For example, the second-order kinetic constant for MS2 inactivation with the singlet oxygen PPRI was reported as $3.1 \cdot 10^9$ $M^{-1}s^{-1}$ by Mattle ***et al.*** (2015) and as $3.8 \cdot 10^8$ $M^{-1}s^{-1}$ by Silverman ***et al.*** (2015). These discrepancies can be caused by overstated assumptions or differences between the sensitiser-virus association that depends on the water matrix (Nelson et ***al.,*** 2018). In addition, as PPRI promotion depends on the excitation of the chromophores within the body of water, the water composition and the spectral irradiance can play important roles. For these reasons, it is recommended to obtain the specific kinetic constants for each specific water.

1.3.3. Modelling thermal inactivation

Other modifications derived from the Chick-Watson Law have been used to model thermal inactivation. In 1978, Mancini defined the kinetic constant by an exponential function depending on the temperature (Mancini, 1978). Later, this thermal inactivation model was adopted by Peng ***et al.*** (2008) for the modelling of the *C. parvum* protozoa inactivation as well as Kevin G. McGuigan ***et al.*** (1998) for the modelling of the *E. coli* bacteria die-off. In fact, this publication was the first kinetics considering the radiation-temperature synergistic effect. They reported a synergy parameter that multiplied the sum of the light and temperature kinetic constants. Values of this parameter larger than 1 indicate that synergy happens.

All the previous approaches are very close to the well-known Arrhenius equation which has been widely used for modelling the temperature dependence of reaction rates (complex reactions as well as elementary reactions) as follows:

$$k_T = k_o \cdot \exp\left(-\frac{Ea}{R \cdot T}\right) \qquad \text{Eq. 1.7}$$

This equation is seen as an empirical relation since the preexponential factor (k_o) and the activation energy (*Ea*) are temperature-independent constants experimentally determined for each reaction. Despite this consideration, Arrhenius explained that the activation energy concept indicates the minimum amount of energy acquired by substances to react. This term justifies the exponential nature of the relationship and can be calculated from statistical methods.

For reactions in which the relation between the kinetic rate and temperature are larger than exponential, the variant Modified Arrhenius equation **(Eq. 1.8)** can be used:

$$k_T = k_o' \cdot T^n \cdot \exp\left(-\frac{Ea}{R \cdot T}\right) \qquad \text{Eq. 1.8}$$

where the pre-exponential factor is proportional to T_n being *T* the temperature and *n* a constant. If n takes the value 1.0, this variant becomes in the original Arrhenius Equation.

The Arrhenius-like equation can be rewritten by introducing a threshold temperature (T_0) as follows:

$$k_T = k_o \cdot \exp\left(-\frac{Ea}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \qquad \text{Eq. 1.9}$$

As Peleg *et al.* (2012) demonstrated, the threshold temperature can be suppressed, which involves a different value of k_0 for the same value of *k*. However, the temperature threshold can be kept as a conceptual threshold to account for the temperature above which the thermal effect is observed.

1.3.4. Synergy

The Arrhenius equation approach was used by Castro-Alférez *et al.* (2017a) to include the inactivation of *E. coli* bacteria in the dark as well as the UV-T synergistic effect, including this temperature dependence in the photoinactivation kinetic constant of their mechanistic model. However, this kinetic model does not consider the action spectral (the reactions are described like **Eq. 1.1).** The integration of both action spectral and synergistic effect can be possible if the reactions are described as **Eq. 1.3** and the quantum yield is expressed as temperature-dependent.

1.3.5. Assembling the pieces

A comprehensive kinetic model must consider all significant factors affecting the microorganism inactivation. Once all the significant photo-activated processes and thermal effects are identified and kinetically described following the approaches above-mentioned, the microorganisms' inactivation balance can be solved. For that, the microorganism die-off depends on all the reactions related to endogenous damage (endogenous chromophores), synergistic effect, exogenous damage (external PPRI), and dark inactivation (usually thermal inactivation):

$$\frac{dC}{dt} = -\left(k_{endo} + k_{exo} + k_{dark}\right) \cdot C \qquad \text{Eq. 1.10}$$

where:

$$k_{endo} = \sum \int_{\lambda} \phi(\lambda, T) \cdot \varepsilon_{CHROM}(\lambda) \cdot CHROM \cdot E\left(\lambda\right) \cdot d\lambda$$
$$k_{exo} = \sum k_{PPRRI} \cdot PPRI$$
$$k_{dark} = k_T$$

However, some reactions rates can depend on other non-constant substances. Thus, the mass balance of these substances must also be taken into account.

If irradiance is homogenous inside the SODIS device, **Eq. 1.10** can be easily solved because $E(\lambda)$ is constant. If irradiance is not homogenous but the water is well-mixed, **Eq. 1.10** can be solved using a unique value of $E(\lambda)$ that represents the average incident radiation in the total volume. This value can be obtained by actinometry or numerical simulation. If the irradiance is not homogeneous and the system is not well-mixed, **Eq. 1.10** must be simultaneously solved in each differential volume and this is only possible using numerical simulation.

Numerical simulation

Solving numerical equations *in silico* offers great benefits in the system design, optimisation, and scaling-up since it saves time, costs, and effort. It is based on dividing the space into numerous discrete cells and solving the equations in each cell for all the phenomena involved. Its main advantage in photoactivated processes resides in the possibility of coupling rigorous calculations of the radiative transport equation (RTE), with hydrodynamics, radiation transfer, mass transport, and chemical reaction rate within the system.

The RTE is an integro-differential equation that describes the journey of photonic rays through the volume with their corresponding energy loss due to

absorption and out-scattering, and energy gain due to inscattering. In the case of the SODIS process, the water matrix can be considered pseudohomogeneous, and the radiation emission can be neglected due to the operational temperatures. The solution of the RTE allows the evaluation of the radiation field at any point (differential space) inside the reactor volume, and takes the following form (Cassano and Alfano, 2000):

$$\frac{dI_{\lambda,\underline{\Omega}}}{ds} = -k_{\lambda} I_{\lambda,\underline{\Omega}} - \sigma_{\lambda} I_{\lambda,\underline{\Omega}} + \frac{\sigma\lambda}{4\pi} \int_{\Omega'=4\pi} p\left(\underline{\Omega'} \rightarrow \underline{\Omega}\right) I_{\lambda,\underline{\Omega'}} d\Omega' \qquad \text{Eq. 1.11}$$

where $I_{\lambda,\Omega}$ is the intensity of photons with wavelength λ propagated along direction Ω, ***s*** is the differential space, k_{λ} is the volumetric absorption coefficient, σ_{λ} is the volumetric scattering coefficient and $p(\underline{\Omega'}\ \underline{\Omega})$ is the phase function that describes the directional distribution of scattered radiation.

Solving the RTE can be accomplished using different approaches. The Discrete Ordinate Method (DOM) solves the radiation field at any point inside the geometry for a finite number of discrete solid angles, each one associated with a direction vector. This method is the most versatile and rigorous, since it allows consideration of the wavelength the emission, absorption, and scattering properties of surfaces and volumes. It is also valid for the whole range of optical thicknesses and the solution or radiation transport through semitransparent walls. When the DOM is used, the spatial discretisation of the computational region is taken directly from the mesh grid topology. However, the directional discretisation for the RTE is explicitly specified using an angular discretisation of the sphere octant in ***Nθ*x*Nϕ*** solid angles, also called control angles, conforming to the directions in which the RTE is solved. The selection of the angular discretisation and the meshing must be carefully studied to guarantee independent results from the complexity of angular and space discretisation. However, the higher the number of divisions, the higher the computational costs. Thus, a balance must be found.

Once the distribution of incident radiation is known, the average can be obtained by integrating over the volume or surface of interest, or the value of each cell can be considered to solve differentially for other phenomena such as the reaction rate.

1.4. SODIS. Challenges

1.4.1. Challenges and possible solutions

The standard SODIS methodology presents some drawbacks that limit its widespread adoption:

- **Bottle volume:** the low volume (2L) of the bottles usually employed means that a family requires several containers to ensure the provision of safe drinking water, a significant part of the daily water requirement estimated by the World Health Organization (WHO) (50–100 L per person and day). The recontamination risk increases with the number of bottles in use. In this sense, scaling-up the process using large-volume containers is a good alternative to reduce the number of devices. However, increasing the volume of the SODIS containers must be carefully addressed to ensure that the effect of water characteristics on the radiation distribution (absorption and scattering) is considered to make an in-depth appraisal of the radiation that reaches pathogens.

- **Limited effectiveness against viruses and protozoa:** while the effectiveness of SODIS against waterborne bacterial pathogens is excellent, it is limited against some viruses and protozoa. PET plastic does not transmit UVB radiation, so the inactivation of viruses and protozoa significantly slows down or is, in some cases, negligible. In this regard, the study of other potential plastic materials for manufacturing SODIS devices is a key point to ensure disinfection or to reduce the required solar exposure time.

- **Overestimated exposure time:** The variability of weather conditions and the water characteristics requires the incorporation of a safety factor into the standard recommended exposure time from 6 h on sunny days to up to 48 h in cloudy conditions. The reason is that the irradiance and its spectral distribution, the temperature, the container material, the water composition, and the type of pathogen drastically modify the inactivation efficacy. In this sense, the kinetic models that forecast the required solar exposure time must consider all the variables just commented. The improvement of the kinetic models is crucial for maximising the production of safe drinking water.

1.4.2. Objectives of the PhD Thesis

This thesis aims to develop a comprehensive kinetic model that accurately estimates the required solar exposure time in large-volume containers that overcome the current challenges and limitations of the SODIS process. To achieve this goal, the spectral solar irradiance, the material of the container, the water composition and the temperature of the water have been considered as part of the following specific objectives:

- **SOLAR RADIATION:** Development of a simple algorithm to predict the actual daily dose depending on the latitude and the day of the year.

- **CONTAINER:** Development of a calculator tool that determines the spectral irradiance inside the SODIS container as a function of the thickness and the

type of plastic used its manufacture. Evaluation of alternative plastic materials for the manufacture of SODIS containers considering mechanical and optical properties as well as ageing due to weathering, including the impact on disinfection efficacy, durability of the container and economic viability.

- **WATER COMPOSITION:** Development of a procedure to calculate the effective incident radiation in large-volume SODIS containers as a function of the concentration of naturally occurring substances found in water.

- **KINETIC MODEL:** Development of a set of mechanistic kinetic models of the synergistic thermal and spectral actions on the inactivation of viruses, protozoa, and bacteria in water by the SODIS process.

The relation between the objectives, the chapters of results, and scientific publications is schematised in **Fig. 1.8.**

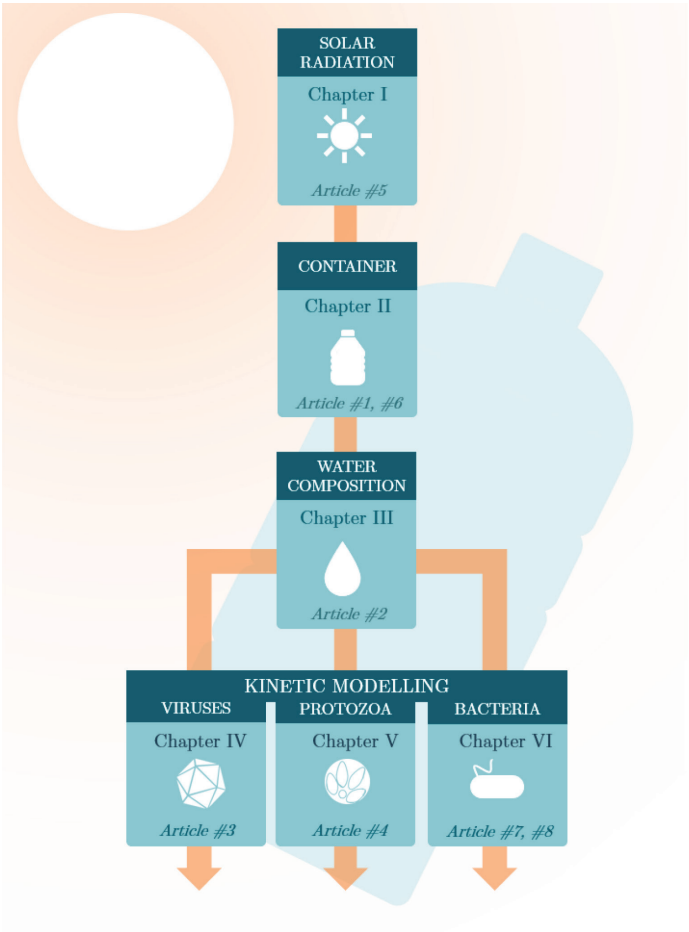

Fig. 1.8: Objectives, chapters, and publications.