PHOTOCATALYTIC PROCESSES FOR WATER TREATMENT

Martin V. Appleby,[a] Dylan Pritchard[a], and Julia A. Weinstein[a]

[a] Department of Chemistry, University of Sheffield, Sheffield S3 7HF, UK

e-mail: MVAppleby1@sheffield.ac.uk , Julia.Weinstein@sheffield.ac.uk

Definitions

Photocatalysis and photosensitisation processes use chemicals which absorb energy from light to undergo an interaction with another molecule(s). A photocatalyst is defined by International Union of Pure and Applied Chemistry (IUPAC) as follows: "the excited state of the photocatalyst repeatedly interacts with the reaction partners forming reaction intermediates and regenerates itself after each cycle of such interactions". (IUPAC, 2007) A photosensitiser is instead defined as a molecular entity which absorbs light to initiates a photochemical or photophysical change in another molecular entity, and is not consumed during the process. In this review, the systems discussed are split into photocatalysts and photosensitisers as described in the respective reference, and by the mechanism by which solar energy transfer occurs.

As an illustrative example, the photocatalysts discussed are mainly semiconductors that produce free radical reactive oxygen species (ROS), whereas the photosensitisers discussed rely on energy transfer to a triplet excited state of molecular oxygen which leads to the formation of a highly reactive singlet oxygen, $^1O_2$. The mechanisms by which the photosensitiser and photocatalyst work to kill microorganisms have been briefly described.

Introduction

2.1 billion people (25% of the global population) do not have access to a safely managed water source. 844 million people lack access to even a basic water source, which is defined as being protected from outside contamination and the travel to and from the source takes 30 minutes or less in a round trip (Goal 6, United Nations 2018). If this issue is not addressed it could escalate to a global crisis; an estimated 52% of the World's population will be put at risk by 2050 due to unsustainable pressures on water resources.

Lack of access to adequate water supplies often occurs in isolated and rural communities, hence efficient point-of-use solutions/household water treatments (POU/HWT) are needed (Hunter 2009; Loeb 2016). Many current solutions are either very inefficient, or power-hungry (Hunter 2009; WHO 2011a; Loeb 2016), and it is therefore vital to develop efficient and cost-effective antibacterial agents for water treatment.

Utilising sunlight for the disinfection of water is not a new concept, yet few technologies have emerged that enable its use and uptake. The most successful method so far has been 'solar water disinfection' (SODIS), which is classified as a protective treatment overall, and is highly protective against bacteria, Table 1 (Carratalà 2016; Loeb 2016).

Table 1 Minimum reduction of different pathogens necessary for an efficient water treatment. To be recommended by WHO as protective or highly protective, a treatment must meet the minimum reduction requirement for bacteria, viruses and protozoa. (WHO 2011b).

Pathogen	Protective	Highly Protective	SODIS
Bacteria	$2\log_{10}$	$4\log_{10}$	$3\log_{10}$ - $5.5\log_{10}$
Virus	$3\log_{10}$	$5\log_{10}$	$2\log_{10}$ - > $4\log_{10}$
Protozoa	$2\log_{10}$	$2\log_{10}$	$1\log_{10}$ - $3\log_{10}$

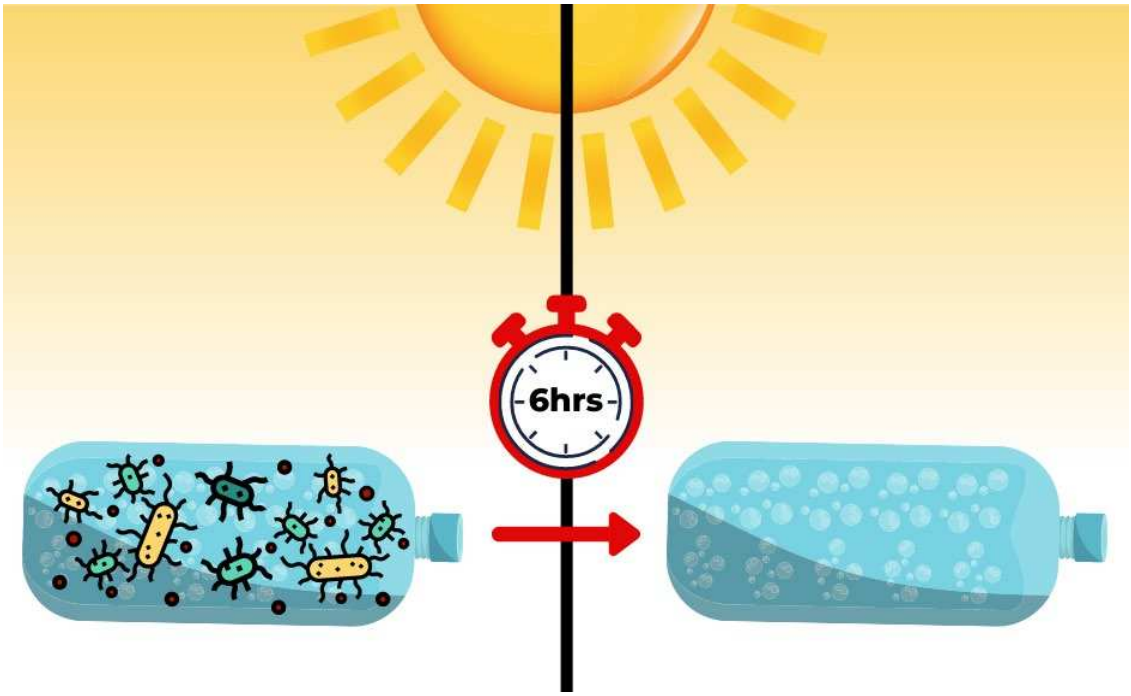

Fig. 1 Solar water disinfection: a bottle is exposed to 6 hours of sunlight (2 days under cloudy conditions) to achieve disinfection.

SODIS works by using a transparent container, such as plastic PET bottles or glass bottles, to purify water by exposing it to direct sunlight over a period of 6 hrs, Fig. 1. UV-light is absorbed by chromophores that naturally occur both inside microorganisms and in water (Heaselgrave and Kilvington 2011; Carratalà 2016; Alipour 2017). A detailed review on SODIS is given in another chapter in the encyclopedia (Marugán 2020).

A common approach to further improve SODIS is to use molecular photosensitisers such as $[Ru(bpy)_3]^{2+}$ (García-Fresnadillo 2018) or photocatalysts such as TiO_2 (Monteagudo 2017). These species absorb UV or visible light and then interact with oxygen molecules producing reactive oxygen species (ROS) that act as antibacterial agents. This approach can potentially achieve high reductions of micro-organisms in a shorter period than traditional SODIS.

This brief review will focus, from a view-point of chemists, on the use of photocatalysts and photosensitisers to improve SODIS effectiveness against bacteria, the advantages and disadvantages of each, and the types of technology that could be used to deliver these solutions for an effective water treatment. A comprehensive review of solar-powered waste-water treatments can be found in, for instance, (Sansaniwal 2019).

Solid-State Photocatalysts for water disinfection

Since the 1990s, photocatalytic semiconductors for water disinfection have become an increasingly popular research topic (Loeb 2019), as these semiconductors tend to be simple, robust, cheap, and reusable. However, many materials with reported high activity towards microorganisms are only at early stages of research. Research into photocatalytic inactivation of viruses is thoroughly covered by for example (Zhang 2019).

When semiconductors such as TiO_2 are irradiated with light with a photon of the energy equal to or greater than its band gap, the energy is absorbed causing the promotion of an electron from the valence band to the conduction band, producing

Mechanism of Photocatalysis

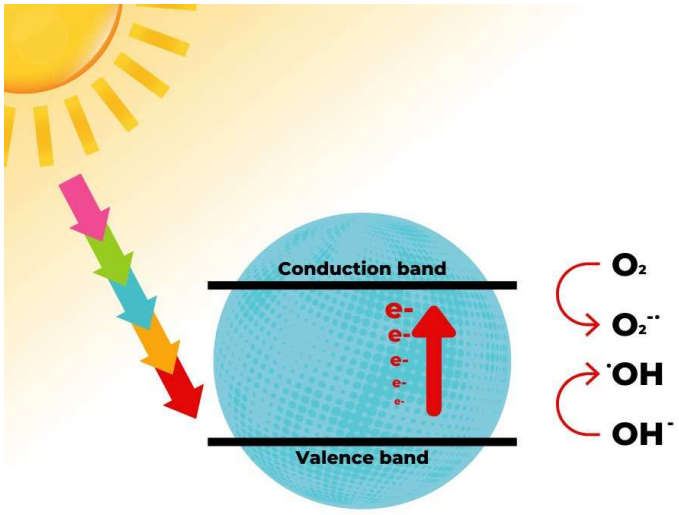

Fig. 2 Absorption of light by a semiconductor, and the resulting production of ROS in a typical photocatalytic water treatment.

an *electron-hole pair* (e^-_{cb} and h^+_{vb}). The excited state of the semiconductor then interacts with the oxygen in close vicinity, producing singlet oxygen ($^1O_2$), and ROS such as the hydroxide radical (•OH), or the superoxide anion (O_2^-), Fig. 2. These highly reactive species are strong oxidants, able to destroy numerous compounds and fatally damage water-borne microorganisms. A more in-depth description of these processes can be found in numerous reviews such as Malato 2009.

Promising Photocatalysts

Examples of early-stage research on photocatalysts for water disinfection that show high efficiencies in a short period of time, at low loading of active material, are given in Table 2. The reusability of the materials is also discussed. Hydrogen peroxide is the least damaging but longest-lived reactive oxygen species, with lifetimes in water of up to two days (Teng 2019). Hydrogen peroxide is a well-known bleach and disinfectant, which should not be added to drinking water. However, if produced in small amounts, close to the microorganism's surface, it can be effective at concentrations non-toxic to humans.

Edge-functionalised graphitic carbon nitride films that produce hydrogen peroxide (Teng 2019) reduced bacterial colonies of *E. coli* by $6\log_{10}$ (99.9999%) after 3 hrs of illumination (100 mW cm^{-2}). Another graphitic carbon nitride compound, functionalised with polyethylenimine PEI/C_3N_4 (Zeng 2020), has also been successfully employed for disinfection. The addition of polyethylenimine causes the bacteria to draw to the surface of the material, increasing the killing efficiency.

Fibrous red phosphorous, an abundant and recyclable material, has been efficient in disinfecting water containing *E. coli*, reducing colonies by $8\log_{10}$ in 30 min under illumination by direct sunlight (Roshith 2019). However, this excellent result comes at the price of a high material loading, 150 mg L^{-1}, and a complicated and lengthy synthesis.

Molybdenum sulfide (Mo_2S), another material which can easily be incorporated into existing SODIS containers, has displayed excellent bacteria killing ability ($5\log_{10}$) using just a 2 cm^2 film, equating to around 1.6 mg L^{-1} (Liu 2016).

Table 2 Examples of photocatalysts discussed

Sample	size/concentration	Irradiation Wavelength and Power Density	Bacteria Strain	Disinfection Efficiency	Disinfection time, min	Reference
g-C_3N_4	5 cm^2 film, 10 mg L^{-1}	>400 nm, 100 mW cm^{-2}	*E. coli, K-12, Salmonella ATCC 13076*	$6\log_{10}$	30	Teng 2019
PEI/C_3N_4	1 mg L^{-1}	solar simulator, 150 mW cm^{-2}	*E. coli* *E. faecalis*	$6.2\log_{10}$ $4.2\log_{10}$	45 60	Zeng 2020
FRP	150 mg L^{-1}	Sunlight	*E. coli*	$8\log_{10}$	30	Roshith 2019
AgBr-Ag-Bi_2WO_{63}	100 mg L^{-1}	> 400 nm, 190 mW cm^{-2}	*E. coli*	$7\log_{10}$	15	Zhang 2010
Cu-MoS_2	2 cm^2 film,1.6 mg L^{-1}	> 400 nm, 100 mW cm^{-2}	*E. coli, K-12*	$5\log_{10}$	20	Liu 2016

An AgBr-Ag-Bi_2WO_6 nanojunction (Zhang 2010) was utilised as a source of hydroxide radical for the eradication of *E. coli* in water through a semipermeable membrane. High levels of killing

were achieved ($7\log_{10}$) in just 15 min of exposure to visible light. Although a large amount of compound was used (100 mg L^{-1}) the use of a semi-permeable membrane permits the compound to be separate from the drinking water throughout disinfection. The design of various membrane materials is a separate important area of research.

Photosensitisers for Water disinfection

Photosensitisers for water purification share many properties with photocatalysts, but produce different type of ROS.

An ideal photosensitiser should be non-toxic to people, absorb a wide range of visible light efficiently, be photostable under many cycles of irradiation and have an excited state with a sufficiently long excited state lifetime to interact efficiently with dissolved molecular oxygen. The minimum excited state lifetime to efficiently produce ROS, through a bimolecular reaction between the sensitiser and dissolved oxygen, is of the order of 200 ns. This value has been estimated using Stern-Volmer equation (Appleby 2020). A comprehensive review of immobilised photosensitisers for antimicrobial applications can be found in for example (Spagnul 2015).

Mechanisms of action

Photosensitisers can produce ROS via two mechanisms: type I and type II (DeRosa and Crutchley 2002, Cieplik 2018), Fig. 3. In type I pathway, electron-transfer from excited state of the photosensitizer leads to formation of free radical ROS such as hydroperoxyl radical ($HO_2^{\cdot}$), superoxide anion ($O_2^{\cdot -}$), and hydroxyl radical ($HO^{\cdot}$). The more active species is $^1O_2$ which is formed in a type II pathway, where energy is transferred from the excited state of the photosensitiser to an oxygen molecule; the molecule of oxygen is excited from its triplet

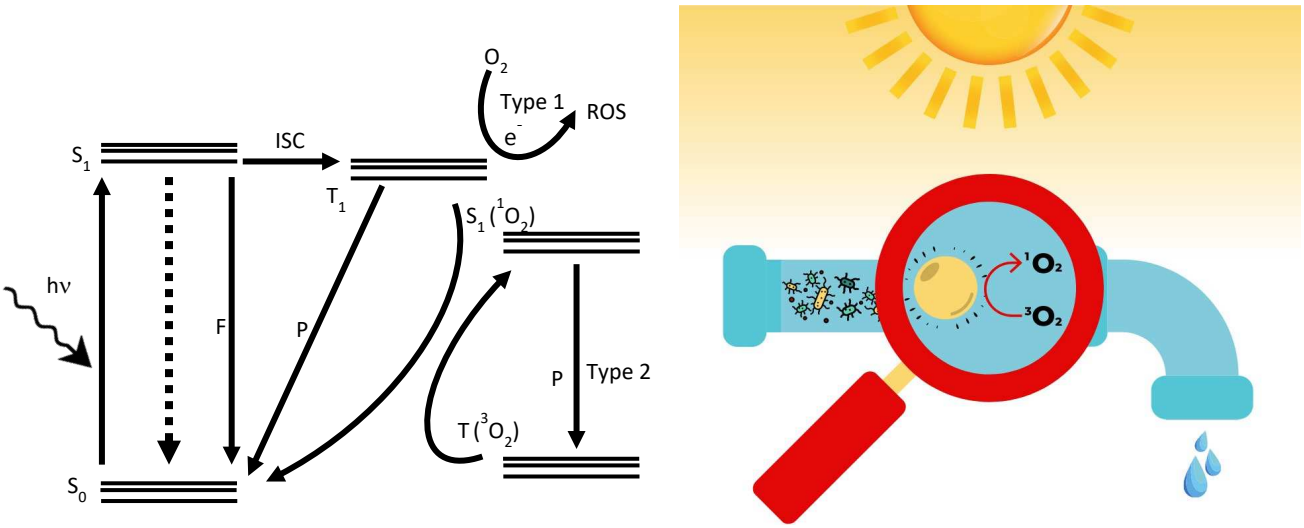

Fig. 3 Left**.** A typical Jablonski diagram showing the two reaction pathways between a photosensitiser and molecular oxygen. S_n, n^{th} singlet state; T_n, triplet state; F, fluorescence; P, phosphorescence; ISC, intersystem crossing. Right**.** A simplified diagram showing interaction of sunlight with a photosensitiser, leading to the excitation of oxygen. The excited oxygen molecule ($^1O_2$) then interacts with a microorganism, for example a bacterium, leading to its death.

ground state to a singlet excited state (Wilkinson 1995). The lowest singlet excited state in molecular oxygen has a lifetime of 3.5-7 µs in water and a diffusion distance of up to 0.1 µm from the source of generation (Bregnhøj 2016). This species is highly reactive when compared to the triplet ground state of molecular oxygen. A high yield of triplet excited states in a photosensitiser is essential for efficient interaction with triplet oxygen, generating $^1O_2$. The majority of molecules have a singlet ground state, which upon light absorption populates singlet excited states, S_n. The singlet-to-

triplet transition (intersystem crossing, ISC, Fig. 3 left) is spin-forbidden and usually cannot compete with the decay of S_n to the ground state (Archer 2012). The rate of ISC can be increased if mixing of singlet and triplet manifolds is promoted by an increase in spin-orbit coupling, induced by heavy atoms. Thus halogenated organic molecules, and transition metal complexes which often have ~100% yield of the triplet excited states are highly promising photosensitisers (McKenzie 2019).

Promising Photosensitisers

Examples of immobilised photosensitisers that show significant reduction of bacteria, are shown in Table 3. Several classes of molecular photosensitisers can be broadly identified (Fig. 4): small organic molecules including edible dyes; porphyrins and derivatives; and transition metal complexes. While an immobilised photosensitiser alone is unlikely to be used as a treatment without a delivery system such as a reactor, high reduction efficiency of a photosensitiser while immobilised shows that these treatments could see use in the future, see *Enhanced Containers for SODIS*.

Rose Bengal (RB) and Methylene Blue (MB) are commonly used organic photosensitisers which show favourable characteristics for water purification. For example, RB and MB immobilised on polyethylene (PE) beads, are photoactive against bacteria. When irradiated with white light (400-700 nm, 1.25 mw cm^{-2}), RB-PE (20 g L^{-1}) reduced *S. aureus* by $5\log_{10}$ in 1 hr, while *E. coli* was reduced by $5\log_{10}$ after 6 hrs. A reduction of 4 $\log_{10}$ of *S. aureus* was achieved after 30 min (Valkov 2018). Irradiation of the same white light on MB-PE (220 g L^{-1}) gave a reduction of $5\log_{10}$ *of S. aureus* and *E. coli* in 30 min, albeit at the loadings 10 times higher than those of RB-PE. It was shown that after 11 days of continuous irradiation the antibacterial properties of RB on polypropylene reduced, likely due to photobleaching (photodegradation of the dye).

Table 3 Examples of photosensitisers discussed. [a]60 min induction period before bacterial killing began.

Sample	concentration	Irradiation Wavelength and Power Density	Bacteria Strain	Disinfection Efficiency	Disinfection time	Reference
RB/PE suspension	(1% RB) 20 g L^{-1} (1% RB) 320 g L^{-1}	400-700 nm, 1.25 mW cm^{-2}	*S. aureus* *E. coli*	5 $\log_{10}$ 5 $\log_{10}$	1 hr 6 hr	Valkov 2018
MB/PE	(1% MB) 220g L^{-1} (1% MB) 220g L^{-1}	400-700 nm, 1.25 mW cm^{-2}	*S. aureus* *E. coli*	$5\log_{10}$ $5\log_{10}$	30 mins 30 mins	Valkov 2018
TMPyP/Chitosan	200 mM	Visible light, 32 mW cm^{-2}	*E. coli*	$3\log_{10}$	90 mins	Majiya 2019
ANT-SiO_2	2.5 g L^{-1}	365 nm, 3.85 mW cm^{-2}	*E. coli*	$6\log_{10}$	110 mins[a]	Benabbou 2011
(Ag NPs) –$[Ru(bpy)_3]^{2+}$	10^{10} NPs in 300 mL	430 nm, 9.76 mW cm^{-2}	*E. coli*	$3.93\log_{10}$	1 hour	An 2020
[Cu(Xant)(dmp)]tfpb-SiO_2	55 μM of complex, equiv. to 5 mg ml^{-1}	405 nm, 17.5 mW cm^{-2}	*S. aureus* *E. coli*	$6\log_{10}$ $6\log_{10}$	2 hr 3 hr	Appleby 2020
$[Mo_6I_8Ac_6]^{2-}$	40 g L^{-1}	460 nm, 13 mW cm^{-2}	*S. aureus* *P. aeruginosa*	$8\log_{10}$ $7\log_{10}$	2.4 hr 4.3 hr	Felip-León 2017

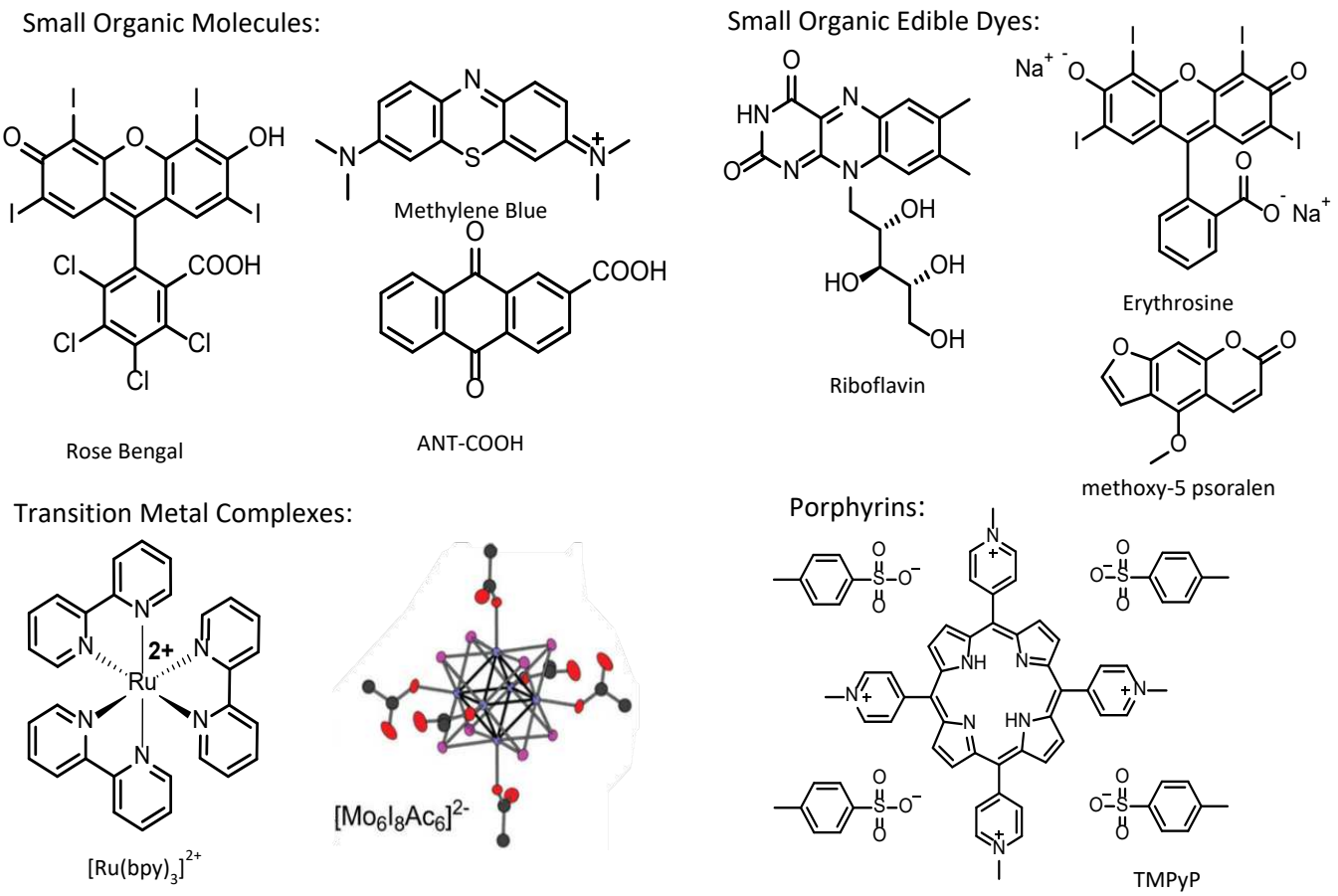

Fig. 4 Examples of different classes of molecular photosenstisers; and $[Mo_6I_8Ac_6]^{2-}$ as an example of a multimetallic cluster (Felip-León 2017).

Another example of an effective organic photosensitiser for water treatment is 9,10-Anthraquinone-2-carboxylic acid, immobilised on silica beads (ANT-SiO_2) (Benabbou 2011). Irradiation of 2.5 g L^{-1} (700 µmol L^{-1}) of the bound photosensitiser with 365nm light (3.85 mW cm^{-2}, 25.41 J cm^{-2}) achieved complete inactivation ($6log_{10}$) of *E. coli* after 110 min, with an induction period of 60 min. An induction period is typical in the treatment of Gram-negative bacteria, and is attributed, in very general terms, to their double cell wall, which makes penetration and damage more complicated. In comparison, 90 min irradiation of TiO_2 at 365nm, 3.85 mW cm^{-2}, led to a total inactivation of bacteria ($6log_{10}$), with no induction period. The difference between the treatment of *E. coli* using TiO_2 and ANT-SiO_2 was attributed to the difference in the type ROS generated by TiO_2 and ANT-SiO_2.

A future system could combine multiple compounds and structures to utilise inherent bactericidal properties, photoactivated generation of ROS, and the use of nanoparticles to enhance the properties of the photoagent. As an example, utilising the localised surface plasmon resonances of silver nanoparticles (AgNPs) in conjunction with a photosensitiser, $[Ru(bpy)_3]^{2+}$ has been shown to improve bacterial killing performance of the sensitizer (An 2020). Integrating the photocatalyst into a lipid membrane around the AgNP harnessed both the photoactivated killing by the complex and the bactericidal properties of Ag^+ ions. Exposure to 430 nm light, 9.76 mW cm^{-2}, for 1 hr led to a reduction of $3.93log_{10}$ of *E. coli* from a starting bacterial concentration of ~10^8 CFU and 10^{10} AgNPs in 300 µl. A flow reactor utilizing a Ru(II) photosensitiser is discussed in the section *Enhanced Containers for SODIS*.

Changing expensive and rare metals for more earth abundant and cheaper metals will make water treatment more sustainable, and more affordable. One such example is using the water

insoluble complex [Cu(xantphos)(dmp)]tfpb (xantphos - 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene, dmp – 2,9-dimethyl-1,10-phenanthroline or tfpb = tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) which was immobilized on silica particles, the first example of a 1st row transition metal complex used for water treatment. This system showed production of singlet oxygen and achieved a $6\log_{10}$ reduction of S. Aureus (2 hr) and E.Coli (3 hr) when irradiated with 405 nm, 17.5 mW cm^{-2}, demonstrating the potential of simple copper complexes for solar water treatment.

Another class of metal-containing photoactive compound are multimetallic clusters, such as $[Mo_6I_8Ac_6]^{2-}$ (Ac = acetate), which antibacterial properties were investigated on two types of support: a macroporous and gel-type resin polymer (Felip-León 2017). The results demonstrate the importance of the support used: the Mo-cluster on the macroporous polymer achieved a $8\log_{10}$ reduction of *S. aureus* when irradiated with 460 nm, 13 mW cm^{-2} whereas the cluster supported on a gel-type polymer only achieved a $4\log_{10}$ reduction at the same fluence. The difference in the activity has been attributed to the macroporous support enabling a higher rate of singlet oxygen production as the pores allow for oxygen diffusion; the cationic nature of the support may facilitate efficient killing of both Gram-positive and Gram-negative bacteria as the positive charge attracts the bacteria to the surface of the support (Manjón 2010), maximising exposure to ROS.

Another group of compounds often used as photosensitisers for ROS production are porphyrins, such as 5,10,15,20-tetrakis-(1-methyl-4-pyridinio)porphyrin tetra-*p*-toluene-sulfonate (TMPyP). TMPyP immobilised on a chitosan membrane caused a $3\log_{10}$ reduction of *E. coli* after 90 min of irradiation with visible light (32 mW cm^{-2}). TMPyP was also shown to cause significant killing of the bacteriophage MS2. One of the big advantages of this system is the chitosan membrane which is cheap, easy to make and biodegradable (Majiya 2019).

Enhanced Containers for SODIS

A common approach to enhance SODIS is to use containers already in use by communities which have favorable properties for light transmission, and coat them with a photocatalyst or a sensitiser. These containers, such as PET bottles, are portable, but are often fragile, have limited volume and need cleaning between each use.

One such portable system was created by casting edge-functionalised graphitic carbon nitride films ($g\text{-}C_3N_4$) onto the inside of a polyethylene bag for POU water disinfection through hydrogen peroxide production, Fig 5 (Teng 2019). The system achieved a $6\log_{10}$ reduction of *E. coli* in ~10L of water after 60 min under sunlight. After 40 cycles (60 hrs) the system showed no change in activity. 10L treatment is substantial and is on the scale of chlorination treatments.

A new vessel-style setup (Danwittayakul 2020) incorporates nano-structured Zinc Oxide (ZnO) into polyethylene bags. This simple setup shows an $6\log_{10}$ reduction in *E. coli* populations in just 15 min of exposure to sunlight. Additionally, this method showed consistent levels of bacteria killing across 5 days of use. The water volume of the polyethene bags was relatively low (0.2 L), and a bag with a large area would be needed to disinfect a large volume of water.

A field test in India using a co-catalyst system ($Bi_4Ti_3O_{12}$-TiO_2) coated soda-lime glass beads in

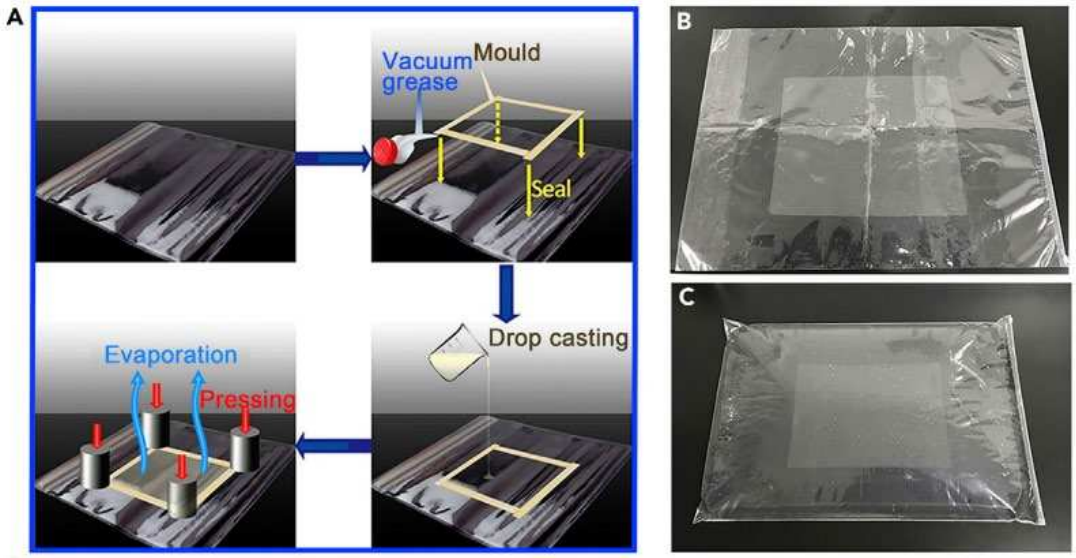

Fig. 5 (A) The coating process of the polyethylene bag with g-C_3N_4. (B) an empty F-g-C_3N_4-30-EP-coatd polyethylene bags; (C) the bag containing water. [Reprinted from Teng 2019 with permission from Elsevier.]

PET bottles showed efficient killing over SODIS (Porley 2020). The study showed the practicability of photocatalysis for water disinfection if further optimisations are made such as improving the efficiency of the catalyst in visible light and by turning the bottles regularly to counter the diffusion limit of the ROS.

Photocatalytic and photosensitiser enhanced reactors, Table 4, allow for higher volumes of water to be treated. Reactors are designed to increase the photon flux to the sample and the time the water is in contact with it, allowing for a practical and efficient application of the active material (Byrne 2011). For further details on CPC reactors consult Marugán 2020.

Natural magnetic spheralite (NMS), a promising material for photocatalytic reduction of bacteria due to its high durability and corrosion resistance, non-toxicity and high earth-abundance (Peng 2017), has been used in a small-scale reactor which was shown to reduce *E. coli* colonies by 5-$\log_{10}$ in 5 L of water after 100 min of exposure to sunlight. A distinctive advantage of NMS is the ability to be removed from solution using a simple magnet.

A TiO_2 CPC reactor was combined with a solar pasteuriser utilising sunlight to both produce ROS and to boil the water for treatment (Monteagudo 2017). 99.1% of the bacteria were inactivated in the CPC over 80 min with a catalyst load of 0.60 mg cm^{-2}. No bacteria were detectable in water after passing through the pasteuriser for 5 min. After 6 hrs the final volume treated was 38 L – a very promising result with a potential to scale-up. Using a pasteuriser, water extraction and flow can be controlled by a thermostat valve at the outlet, only extracting water when it is suitably purified.

Table 4 Examples of photoreactor systems. [a] Complete inhibition occurred after water from CPC reactor was flowed through a pasteuriser.

Reactor	Type of irradiation	Bacterial Strain	Water volume/L	Experiment time/hr	Disinfection Efficiency	Reference
NMS	Sunlight	*E. coli*	*5*	2	5 $\log_{10}$	Peng 2017
TiO_2-CPC[a]	Sunlight, 15 W m^{-2}	*E. coli*	38	6	2.05$\log_{10}$ in 80 min	Monteagudo 2017
RDP^{2+}- pSil	Sunlight, 400 ± 25 W m^{-2}	*E. coli / E. faecalis*	17.5	5	4.3$\log_{10}$ -6.3$\log_{10}$ hr^{-1} L^{-1}	García-Fresnadillo 2018

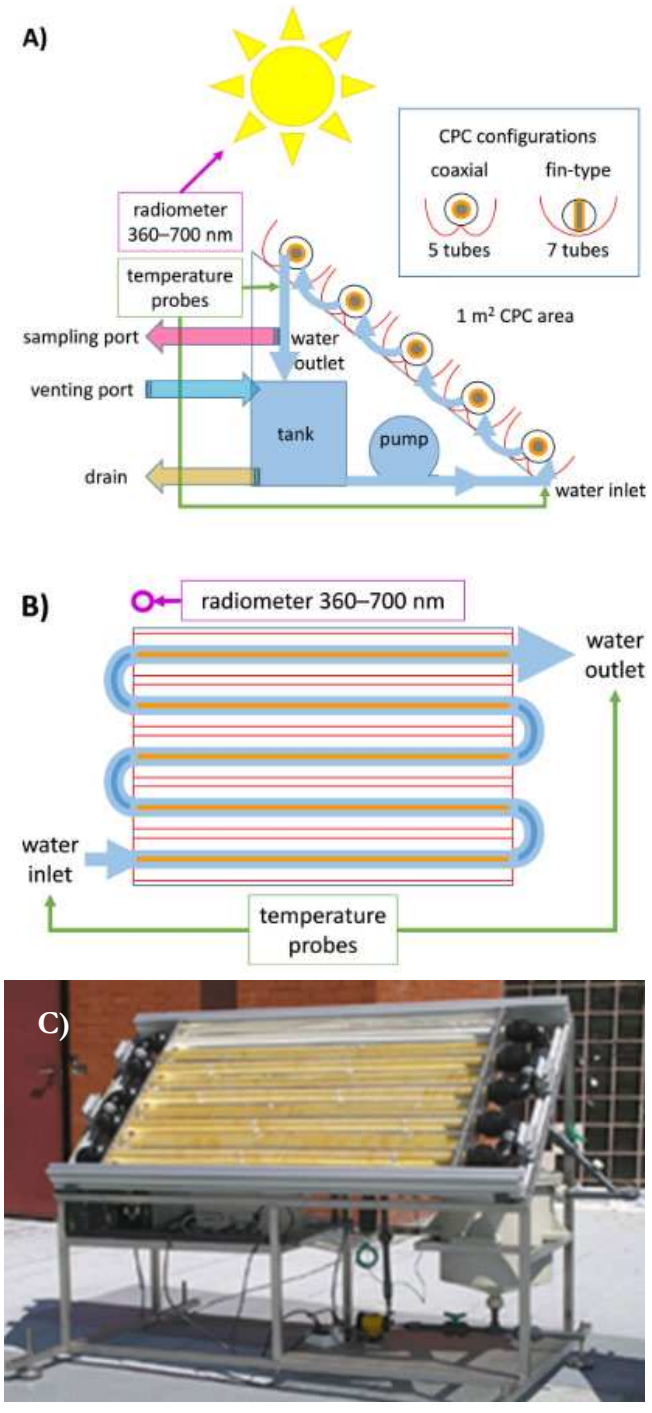

Fig. 6 Arrangement of the solar reactor prototypes. A) The lateral view of the prototype. The insert depicts the style of polypropylene support (grey) and $^1O_2$ photosensitising material (orange) used inside the borosilicate glass tubes (black); Al-mirror (red). B) The front view of the prototype with direction of waterflow. C) The front view of a solar reactor system [Reprinted from García-Fresnadillo 2018 with permission from Elsevier.]

An example of an immobilised transition metal photosensitiser is tris(4,7-diphenyl-1,10-phenanthroline)Ruthenium(II), RDP^{2+}bound to porous silicone (pSil) and loaded as rods in a flowed solar reactor prototype (García-Fresnadillo 2018, Fig. 6). The system at a flow rate of 2 L min^{-1} had inactivation rate of *E. coli* and *E. Faecalis* of 4.3log_{10}-6.3log_{10} hr^{-1} L^{-1} under a 12W solar simulator. The 5 hrs (720 J cm^{-2}) of irradiation treated 17.5 L of water. Importantly, it was shown that once the system has aged, the photosensitiser could be reloaded, and a similar disinfection rate achieved, providing reusability.

Edible dyes

There has been a rise in the study of dye-based water purification without support, such as "edible dyes", Table 5. For example, methoxy-5-psoralen, a photosensitiser extracted from bergamot (Sunda 2019), completely inhibits faecal coliforms after 60 min of exposure to a UV lamp (320-400 nm) at a concentration of 6 mg L^{-1}. Other examples include erythrosine (Ryberg 2018), an edible food colouring (FD&C red N3) and riboflavin, vitamin B2. Both of the dyes show high killing against viruses, and riboflavin has also shown to effectively reduce some strains of amoeba, protozoa and helminths (Heaselgrave 2011).

The principal benefit of an edible dye is the lack of toxicity to people, although consuming large amounts a dye could cause photosensitivity, as has been observed with bergamot oil (Navarra 2015).

Another benefit of using edible dyes in solution is that they may be taken up by bacteria allowing a more effective in-vitro killing. However, an obvious disadvantage of an edible dye is that the dye is consumed, requiring a continual supply. Immobilising the dye would allow its reuse, whilst leakage of an edible dye would likely be non-toxic. However, as previously mentioned many dyes become less effective photosensitisers once immobilized (Kim 2019).

Table 5 Examples of edible dyes

Sample	concentration	Wavelength, Irradiation power density	Pathogen Strain	Disinfection Efficiency	Disinfection time, min	Reference
Erythrosine	10 μM	400-700 nm, 100 mW cm^{-2}	MS2	6log10	20	Ryberg 2018
Riboflavin	100 μM		MS2	7log10	10	
Methoxy-5-psoralen	0.006 g L^{-1}	320-400 nm, UV lamp	Faecal Coliforms	4.5log10 (Complete inhibition)	60	Sunda 2019

Another benefit of using edible dyes in solution is that they may be taken up by bacteria allowing a more effective in-vitro killing. However, an obvious disadvantage of an edible dye is that the dye is consumed, requiring a continual supply. Immobilising the dye would allow its reuse, whilst leakage of an edible dye would likely be non-toxic. However, as previously mentioned many dyes become less effective photosensitisers once immobilized (Kim 2019).

Finally, a potential advantage of using coloured dye such as erythrosine is that it undergoes a colour change when photo-bleached, which could be used as an indicator of disinfection. This may build confidence in the user as they will know the water has been treated effectively. Lack of indication of disinfection is currently a disadvantage of the SODIS technique.

Discussion

The main advantage of photosensitisers is the use of ROS as an antibacterial agent. For example, the hydroxyl radical anion and $^1O_2$ can attack multiple sites on the pathogen, minimizing the potential for the pathogen to develop resistance to these treatments. Many photosensitisers work best in solution via *in vitro* killing where they pass through the membrane of bacteria and cause cellular death from ROS production inside the cell. However, for non-edible dyes the photosensitiser/catalyst needs to be immobilized, preventing in vitro interactions. Furthermore, immobilisation can also change the photophysical properties of a photosensitiser or catalyst, affecting its ability to produce ROS. Therefore systems that are effective at bacterial killing in solution are not guaranteed to provide efficient killing once immobilised.

Turbidity can cause significant reduction in the killing potential of photosensitisers /catalysts as debris can block sunlight and also react with ROS. Therefore, filtering water prior to treatment could greatly improve the efficiency of the disinfection, and also removes larger organisms such as protozoa. A combination of filtration and photo-sensitization or photocatalysis would be needed for an effective treatment for all types of pathogenic organisms.

The cost of using treatments is vitally important. While discussing the cost of early-stage research can be difficult, some estimates from the literature are given below. For RDP^{2+}/*p*-Sil reactor as described in the *Enhance containers* section, the cost would be ca \$160/m^2 (García-Fresnadillo 2018). This suggest an upfront reactor cost of \$160-200. The costs of reloading the photosensitiser/catalyst should also be compared. The sensitiser RDP^{2+} would add ca. \$15-20 to the cost of the reactor, approximately 2-3 times the cost of TiO_2. - it is clear that photosensitisers which do not contain expensive elements need to be developed.

A 25 L CPC batch reactor costs approximately \$200 to build for 10 years of operation, approximately \$0.2 per 100L of water (Keane 2014). According to Ryberg 2018, traditional SODIS treats water at an approximate cost of \$0.001/l whereas adding 5 μM of erythrosine can treat water at a cost of \$0.002−\$0.003/l. Over a reactor's lifetime, the cost per litre is comparable. However, the much higher upfront cost of a reactor could become a barrier against wider use of the treatment.

As well as reactors, a popular delivery mechanism is to coat a bottle with a catalyst or sensitiser, preferably in a method that can be done locally such as through a catalyst powder. While this could be a great way to provide the technology to

isolated communities, many barriers remain, including transport of glass and the toxicity of the catalysts. Some methods of immobilising the catalysts onto PET bottles have been shown to affect the properties of the bottles, potentially impacting their use. Sol-gel coatings could be mass-produced on glass bottles, but require laboratory preparation, potentially limiting their use in isolated communities (Keane 2014).

Coated bottles and edible dyes have the same limitation, the low volume of water that can be treated, but both methods have a low upfront cost and are simple to use. Reactors on the other hand allow a large amount of water to be purified in a reasonable amount of time, and can potentially be reused with only small effort from the user, but the upfront cost may hamper their uptake.

Suggestions for further research

Standardisation of water disinfection assays. Standardised testing of treatments need to be performed under sunlight, with the same strain of bacteria, same volume of water, and achieve the same level of disinfection (Keane 2014).

Optimisation of Photocatalyst and Photosensitizer. Many systems currently used only absorb small fractions of the solar spectrum or have other disadvantages such low photostability. Optimising the photoagents further will improve the functionality of any of the light-based treatments. As transition metal complexes are photosensitisers of $^1O_2$, and developing complexes of abundant metals such as Cu, Fe or Cr, instead of Ru or Ir would be highly beneficial.

Development of Dye-assisted SODIS. Development of a non-toxic dye or photo-active coating could vastly improve the efficiency of SODIS and may be the optimal future direction. Currently, whilst dye-assisted reactors are promising, they may seem less accessible due to the cost of initial setup, maintenance and training.

Community uptake. A lack of understanding and confidence in new technologies can reduce the likelihood of uptake. It is already known that SODIS retention can be quite low due to the minimal quantities of water treated and the labour required (Hunter 2009). Developing a delivery method which overcomes these barriers could lead to more effective uptake of the treatment.

Conclusion

Both photocatalysts and photosensitisers can provide new, affordable solutions for water disinfection. Whilst the aforementioned materials have shown very high levels of disinfection, far past the standard of $4\log_{10}$ 'highly protected' against bacteria (WHO 2011b), ultimately they must be incorporated into a delivery model for use in water disinfection technologies. The most promising of the materials discussed are those that have shown high levels of disinfection when used as films as it displays the ability to be easily deposited within a vessel, such as the PET bottles used for SODIS. Materials which can be loaded covalently or otherwise onto polymers also show promise for such a use. Whilst improvements can be made to the photosensitisers and photocatalysts themselves, without an effective delivery system they will not be sufficient for use. For any treatment to be fully considered for disinfection, optimisation of cost, usability and efficiency need to be made. Finally, a greater interaction between research communities from different disciplines – chemists, physicists, engineers, environmentalists, social scientists: working on various aspects of the problem is absolutely essential for success.

Acknowledgements

We thank the EPSRC (capital equipment award to Lord Porter Laser Laboratory), the Grantham Centre for Sustainable Futures (studentship to M.V.A.), and the University of Sheffield for support. Special thanks to Grace Appleby for the design and creation of Figures 1, 2 and 3b.

Cross-References

Marugán, J. Solar Disinfection as a Water Treatment Technology

Euzen, A. Water Uses and Global Change

Dickens, C., O'Brien, G. Water quality: Standard and Indicators

Lofrano, G. Water treatment

References

Alipour V, Rezaei L, Etesamirad MR (2017) Feasibility and applicability of solar disinfection (SODIS) for point-of-use water treatment in Bandar Abbas, South of Iran. Journal of Global Pharma Technology 9:40–46

An X, Naowarojna N, Liu P, Reinhard BM (2020) Hybrid Plasmonic Photoreactors as Visible Light-Mediated Bactericides. ACS Applied Materials and Interfaces 12:106–116. https://doi.org/10.1021/acsami.9b14834

Appleby M V., Walker PG, Pritchard D, et al (2020) Cu(I) diimine complexes as immobilised antibacterial photosensitisers operating in water under visible light. Material Advances, Advance Article. https://doi.org/10.1039/D0MA00642D

Archer S, Weinstein JA (2012) Charge-separated excited states in platinum(II) chromophores: Photophysics, formation, stabilization and utilization in solar energy conversion. Coordination Chemistry Reviews 256: 2530-2561. https://doi.org/10.1016/j.ccr.2012.07.010

Benabbou AK, Guillard C, Pigeot-Rémy S (2011) Water disinfection using photosensitizers supported on silica. Journal of Photochemistry and Photobiology A: Chemistry 219:101–108. https://doi.org/10.1016/j.jphotochem.2011.01.023

Bregnhøj M, Westberg M, Jensen F, Ogilby PR (2016) Solvent-dependent singlet oxygen lifetimes: Temperature effects implicate tunneling and charge-transfer interactions. Physical Chemistry Chemical Physics 18:22946–22961. https://doi.org/10.1039/c6cp01635a

Byrne JA, Fernandez-Ibañez PA, Dunlop PSM (2011) Photocatalytic enhancement for solar disinfection of water: A review. International Journal of Photoenergy 2011:. https://doi.org/10.1155/2011/798051

Carratalà A, Calado AD, Mattle MJ (2016) Solar disinfection of viruses in polyethylene terephthalate bottles. Applied and Environmental Microbiology 82:279–288. https://doi.org/10.1128/AEM.02897-15

Cieplik F, Deng D, Crielaard W (2018) Antimicrobial photodynamic therapy–what we know and what we don't. Critical Reviews in Microbiology, 44:571–589

Danwittayakul S, Songngam S, Sukkasi S (2020) Enhanced solar water disinfection using ZnO supported photocatalysts. Environmental Technology, 41:349–356. https://doi.org/10.1080/09593330.2018.1498921

DeRosa MC, Crutchley RJ (2002) Photosensitized singlet oxygen and its applications. Coordination Chemistry Reviews, 233–234:351–371. https://doi.org/10.1016/S0010-8545(02)00034-6

Felip-León C, Arnau Del Valle C, Pérez-Laguna V (2017) Superior performance of macroporous over gel type polystyrene as a support for the development of photo-bactericidal materials. Journal of Materials Chemistry B, 5:6058–6064. https://doi.org/10.1039/c7tb01478c

García-Fresnadillo D (2018) Singlet Oxygen Photosensitizing Materials for Point-of-Use Water Disinfection with Solar Reactors. ChemPhotoChem 2:512–534. https://doi.org/10.1002/cptc.201800062

Heaselgrave W, Kilvington S (2011) The efficacy of simulated solar disinfection (SODIS) against Ascaris, Giardia, Acanthamoeba, Naegleria, Entamoeba and Cryptosporidium. Acta Tropica 119:138–143. https://doi.org/10.1016/j.actatropica.2011.05.004

Hunter PR (2009) Household water treatment in developing countries: Comparing different intervention types using meta-regression. Environmental Science and Technology 43:8991–8997. https://doi.org/10.1021/es9028217

IUPAC (2007) Compendium of Chemical Terminology, 3rd ed. (the "Gold Book"), 79, 293:384. ISBN 0-9678550-9-8. https://doi.org/10.1351/goldbook.PT07446

Keane DA, McGuigan KG, Ibáñez PF (2014) Solar photocatalysis for water disinfection: Materials and reactor design. Catalysis Science and Technology 4:1211–1226. https://doi.org/10.1039/c4cy00006d

Kim HS, Cha EJ, Kang HJ (2019) Antibacterial application of covalently immobilized photosensitizers on a surface. Environmental Research 172:34–42. https://doi.org/10.1016/j.envres.2019.01.002

Liu C, Kong D, Hsu PC (2016) Rapid water disinfection using vertically aligned MoS2 nanofilms and visible light. Nature Nanotechnology 11:1098–1104. https://doi.org/10.1038/nnano.2016.138

Loeb S, Hofmann R, Kim JH (2016) Beyond the Pipeline: Assessing the Efficiency Limits of Advanced Technologies for Solar Water Disinfection. Environmental Science and Technology Letters 3:73–80

Loeb SK, Alvarez PJJ, Brame JA (2019) The Technology Horizon for Photocatalytic Water Treatment: Sunrise or Sunset? Environmental Science and Technology 53:2937–2947. https://doi.org/10.1021/acs.est.8b05041

Majiya H, Chowdhury KF, Stonehouse NJ, Millner P (2019) TMPyP functionalised chitosan membrane for efficient sunlight driven water disinfection. Journal of Water Process Engineering, 30:100475. https://doi.org/10.1016/j.jwpe.2017.08.013

Manjón F, Santana-Magaña M, García-Fresnadillo D, Orellana G (2010) Singlet oxygen sensitizing materials based on porous silicone: Photochemical characterization, effect of dye reloading and application to water disinfection with solar reactors. Photochemical and Photobiological Sciences 9:838–845. https://doi.org/10.1039/c0pp00026d

Marugán J, Giannakis S, McGuigan KG, Polo-López I (2020) Solar Disinfection as a Water Treatment Technology. In: Leal Filho W., Azul A.M., Brandli L., Lange Salvia A., Wall T. (eds) Clean Water and Sanitation. Encyclopedia of the UN Sustainable Development Goals. Springer, Cham. https://doi.org/10.1007/978-3-319-70061-8_125-1

McKenzie LK, Bryant HE, Weinstein JA (2019) Transition metal complexes as photosensitisers in one- and two-photon photodynamic therapy. Coordination Chemistry Reviews. 379:2–29

Monteagudo JM, Duran Segovia A, Israel SM, Acevedo AM (2017) A novel combined solar pasteurizer/TiO2continuous-flow reactor for decontamination and disinfection of drinking water. Chemosphere 168:1447–1456. https://doi.org/10.1016/j.chemosphere.2016.11.142

Navarra M, Mannucci C, Delbò M, Calapai G (2015) Citrus bergamia essential oil: From basic research to clinical application. Frontiers in Pharmacology 6

Peng X, Ng TW, Huang G (2017) Bacterial disinfection in a sunlight/visible-light-driven photocatalytic reactor by recyclable natural magnetic sphalerite. Chemosphere 166:521–527. https://doi.org/10.1016/j.chemosphere.2016.09.090

Porley V, Chatzisymeon E, Meikap BC (2020) Field testing of low-cost titania-based photocatalysts for enhanced solar disinfection (SODIS) in rural India. Environmental Science: Water Research and Technology, 6:809–816. https://doi.org/10.1039/c9ew01023h

Roshith M, Kumar MS, Nanda Kumar AK (2019) Urchin-like fibrous red phosphorus as an efficient photocatalyst for solar-light-driven disinfection of *E. coli*. Journal of Photochemistry and Photobiology A: Chemistry 384:112034. https://doi.org/10.1016/j.jphotochem.2019.112034

Ryberg EC, Chu C, Kim JH (2018) Edible Dye-Enhanced Solar Disinfection with Safety Indication. Environmental Science and Technology 52:13361–13369. https://doi.org/10.1021/acs.est.8b03866

Sansaniwal SK (2019) Advances and challenges in solar-powered wastewater treatment technologies for sustainable development: a comprehensive

review. International Journal of Ambient Energy, https://doi.org/10.1080/01430750.2019.1682038

Spagnul C, Turner LC, Boyle RW (2015) Immobilized photosensitizers for antimicrobial applications. Journal of Photochemistry and Photobiology B: Biology 150:11–30. https://doi.org/10.1016/j.jphotobiol.2015.04.021

Sunda MT, Rosillon F, Taba KMN, Wathelet B (2019) Contribution to the water disinfection study by photosensitization with plants extracts. International Journal of Innovation and Applied Studies 25:843–850. https://doi.org/10.1051/wqual/2008006

Teng Z, Yang N, Lv H (2019) Edge-Functionalized g-C3N4 Nanosheets as a Highly Efficient Metal-free Photocatalyst for Safe Drinking Water. Chem 5:664–680. https://doi.org/10.1016/j.chempr.2018.12.009

United Nations (2018) Sustainable Development Goal 6 Synthesis Report 2018 on Water and Sanitation

Valkov A, Raik KA, Mualem-Sinai Y (2018) Water disinfection by immobilized photosensitizers. Water (Switzerland) 11: https://doi.org/10.3390/w11010026

Wilkinson F, Helman WP, Ross AB (1995) Rate constant for the decay and reactions of the lowest electronically excited singlet-state of molecular-oxygen in solution - an expanded and revised compilation. Journal of Physical and Chemical Reference Data 24:663–1021. https://doi.org/10.1063/1.555965

World Health Organization (2011a) Guidelines for Drinking-water Quality 4th ed. 1–543

World Health Organization (2011b) Evaluating Household Water Treatment Options : Health-Based Targets and Microbiological Performance Specifications. 1–68

Zeng X, Liu Y, Xia Y (2020) Cooperatively modulating reactive oxygen species generation and bacteria-photocatalyst contact over graphitic carbon nitride by polyethylenimine for rapid water disinfection. Applied Catalysis B: Environmental 274:119095. https://doi.org/10.1016/j.apcatb.2020.119095

Zhang C, Li Y, Shuai D (2019) Progress and challenges in photocatalytic disinfection of waterborne Viruses: A review to fill current knowledge gaps. Chemical Engineering Journal 355:399–415

Zhang LS, Wong KH, Yip HY (2010) Effective photocatalytic disinfection of *E. coli* K-12 using AgBr-Ag-Bi 2WO6 nanojunction system irradiated by visible light: The role of diffusing hydroxyl radicals. Environmental Science and Technology, 44:1392–1398. https://doi.org/10.1021/es903087F