

UV dosimetry for solar water disinfection (SODIS) carried out in different plastic bottles and bags

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Abstract

Solar water disinfection (SODIS) is a well-established inexpensive means of water disinfection in developing countries, but lacks an indicator to illustrate its end-point. A study of the solar UV dosage required for SODIS, in order to achieve a bacteria concentration below the detection limit for: *E. coli*, *Enterococcus spp.* and *C. perfringens*, in water in PET bottles, PE and PE/EVA bags showed disinfection to be most efficient in PE bags, with a solar UV (290-385 nm) dose of 389 kJ m⁻² required. In parallel to the disinfection experiments, a range of polyoxometalate, semiconductor photocatalysis and photodegradable dye-based solar UV dosimeter indicators were tested under the same solar UV irradiation conditions. All three types of dosimeter produced indicators that largely and significantly change colour upon exposure to 389 kJ m⁻² solar UV; further indicators are reported which change colour at higher doses and hence would be suitable for the less efficient SODIS containers tested. All indicators tested were robust, easy to use and inexpensive so as not to add significantly to the attractive low cost of SODIS. Furthermore, whilst semiconductor photocatalyst and photodegradable dye based indicators are disposable, one-use systems, the polyoxometalate based indicators recover colour in the dark overnight, allowing them to be reused, and hence further decreasing the cost of using indicators during the implementation of the SODIS method.

Keywords: polyoxometalate; semiconductor photocatalysis; dye photodegradation; solar water disinfection; UV dosimeter

1 Introduction

Of the global population, around 35% lack access to clean water [1], with the main problem being microbial contamination [2] in developing countries across South America, Africa and Asia. This lack of safe drinking water leads to a high risk of waterborne diseases, such as cholera, typhoid fever, hepatitis A and dysentery, as well as other diarrhoeal diseases [2]. Recent figures [3,4] suggest 0.6 million deaths of children under the age of 5 were as a result of diarrhoea in 2012. Household water treatments, the most common of which is boiling, can result in as much as 35-44% reduction [5] in diarrhoeal disease. However, to those most in need of household water treatment, i.e. low-income families in rural and semi-urban areas, the unavailability or high cost of fuel is a barrier to boiling water, with an annual estimated cost in India of US\$ 2.11 per person [6]. Solar water disinfection (SODIS) is the process by which plastic bottles, generally made with polyethylene terephthalate (PET), are filled with water and exposed to sunlight for around 6 hours under clear to 50% cloudy skies [7] to disinfect the water from diarrhoea-causing pathogens (dose of 2000 kJ m^{-2} [8] of solar radiation in the 350-450 nm wavelength range). The SODIS process costs over three times less, at an estimated annual global cost of US\$ 0.63 per person [6], based on the purchase of the necessary number of plastic bottles. Several studies have shown that children under the age of 6 years who used the SODIS technique are less likely to contract cholera, dysentery and other types of diarrhoeal disease than non-SODIS users of the same age group [9-12].

Lab based studies have shown that SODIS effectively disinfects faecal bacteria (such as *Escherichia coli* (*E. coli*)) [13] as well as other waterborne pathogens such as viruses, protozoa and fungi. For the SODIS method, there is little difference in bacterial disinfection times for water temperatures of 12-40 °C [8], but the time taken for total bacterial disinfection is highly dependent upon the UV irradiance from the sun, which in turn is dependent upon latitude, altitude, weather and season [14]. Hence, at low solar UV levels ($\text{UVI} < 5$), 6 hours may not provide a sufficient UV dose for bacterial disinfection, whereas at high sunlight irradiance ($\text{UVI} > 10$), less than 6 hours in the sun is likely to be sufficient. According to the World Health Organization (WHO) [6], this uncertainty with regard to the

point at which solar disinfection is achieved is the main drawback of the SODIS method, as it leads to confusion, apparent failure (on cloudy days) and subsequent concern amongst consumers. Obviously it would be better to have a visual measure of UV dosage which would provide reassurance of complete UV disinfection, rather than relying on the current method of using an average time in the sun. Thus, an inexpensive, effective optical UV dosimeter indicator could play a useful role in facilitating the promotion and diffusion of the SODIS method.

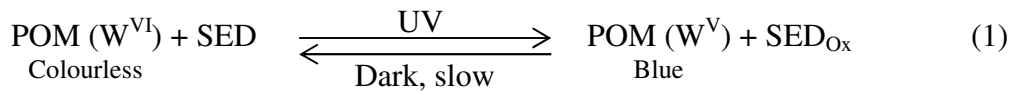
Current UV dosimetry technology is largely limited to electronic devices [15,16] which are still too expensive for assessing water purification in developing countries. Although some UV dosimetry labels are commercially available (e.g. SolarSafe [17], utilising photochromic dyes for sunburn warning) they are also too expensive (\$1.20 per label) to make a significant impact on the market, and are primarily designed as sunburn warning indicators and so are unable to measure the much higher solar UV dosage, received over a long period of time, needed for SODIS. Photochromic inks [18] and UV-cured security seals [19] have been patented for application with regard to SODIS but none have led to a realistic commercial product for global utilisation by the SODIS scheme; a key stumbling block is cost as such a UV dosimeter needs to be very inexpensive, especially if it is only single use.

Despite the current lack of an appropriate solar UV dosimeter to compliment the SODIS method, over 5.8 million people in about 30 countries [7] utilise the SODIS technique, but with 748 million people relying on unimproved water supplies [20], it follows that a UV dosage indicator for SODIS technology would help to improve the trust in, and hence a widespread global uptake of, the SODIS method by millions of people, significantly improving their quality of lives.

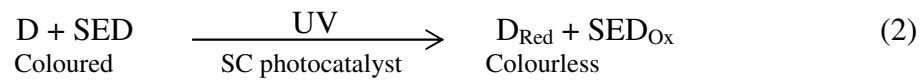
The UV dosimeters tested in this work for use with SODIS can be classified under three broad categories of UV absorber: polyoxometalate (POM), semiconductor (SC) photocatalyst and photodegradable dye (D). Each is dispersed in an ink and functions via the overall processes given below.

Thus, in the presence of a sacrificial electron donor (SED), such as glycerol, the POM, in a POM based ink, is reduced upon irradiation with UV light, as summarised in equation (1). The POM changes colour upon reduction making it a suitable UV dosimeter, although, in the

example tested, it can recover its colour in the dark as the photo-reduced metal is air-oxidised back to its colourless form overnight.



In a SC photocatalyst-based UV dosimeter, a coloured dye is irreversibly reduced to its colourless form, and a SED oxidised upon excitation of a SC photocatalyst with UV light, i.e.



Finally in the third type of UV dosimeter, dyes with poor photostability are oxidatively degraded with UV light, thereby losing their colour, as summarised by equation (3), and hence working as an indicator of UV irradiation.



These types of UV dosimeter, which function via the photo-induced reactions summarised by equations (1-3), are inexpensive, easy to use and robust. In this work these indicators were tested under real-sun conditions, in order to determine their potential as indicators for the SODIS scheme. Thus, in a first set of experiments, the colour response of the indicators coupled with the solar UV doses required to achieve a bacteria concentration below the detection limit for *E. coli*, *Enterococcus spp.* and *C. perfringens*, in water contained in PET bottles, PE bags and PE/EVA bags, were investigated.

2 Materials and Methods

2.1 Bacterial disinfection

In order to simulate a natural contaminated water and to avoid a weakening of bacterial cells natural well-water (Puerto Real, Spain) was used during the experiments with initial faecal contamination of 20-30 colony forming units, CFU/100 mL. The well-water was inoculated with urban wastewater (0.1% v/v), from a primary clarifier of a conventional urban wastewater treatment plant (Puerto Real, Spain), giving a final concentration in the order of

10^3 CFU/100 mL for *E. coli* and *Enterococcus spp.* and 10^2 CFU/100 mL for *C. perfringens*, corresponding with WHO guidelines [21] for bacterial counts in high risk contaminated water.

The membrane filtration technique [22] was employed for the detection of bacterial concentration. The growth media (Scharlau, Spain) for each microorganism were: Cromogenic Colinstant agar for *E. coli*, Slanetz & Bartley agar base for *Enterococcus spp.* and mCP for *C. perfringens*. Enumeration of bacteria contained in the SODIS containers exposed to sunlight was conducted through the standard plate count method [22], each sample was analysed in triplicate, with a detection limit of 2 CFU/100 mL. The experimental data were fitted using the GInaFit (Geeraerd and Van Impe Inactivation Model Fitting) tool [23], with the biphasic model [24] giving the best fit for *E. coli* and the log-linear model [25] for *Enterococcus spp.* and *C. perfringens*. For each case, the theoretical value of dose at which bacteria reduction below the detection limit is achieved ($Q_{UV, LD}$), namely “theoretical lethal dose”, was calculated.

2.2 SODIS containers

SODIS is traditionally carried out using PET bottles, but PET is quite brittle and not transparent to UVB radiation, and over time becomes a white milky colour due to scratches and general wear and tear. Instead, plastic bags have been found to work a little better than bottles, due to the reduced solar UV path length and higher surface area they offer in comparison. Furthermore, bags have been made from other polymers, such as PE/EVA or PE which are softer and more flexible, with a higher transmittance of UVB irradiation than PET bottles, as illustrated in Fig. 1. As a consequence the three SODIS containers used in this work were as follows:

- (i) **PE bag.** Polyethylene (PE) bag with a wall thickness of 0.23 mm, a maximum capacity of 6 L and a water layer thickness of 5 cm. This bag was designed especially for solar disinfection application, is easy to fill through a wide entrance.
- (ii) **PE/EVA bag.** This bag was made from two colourless layers of PE and an intermediate blue-tinted layer of ethyl vinyl acetate (EVA), which improves its flexibility and scratch resistance. The maximum capacity of this bag was 4 L, with a total wall thickness of 0.37 mm and water layer thickness of 9 cm.

- (iii) **PET bottle.** A typical polyethylene terephthalate (PET) bottle of 2 L capacity, 0.24 mm wall thickness and a water layer thickness of 8 cm. This is currently the typical form of a SODIS container.

All containers were placed in an area free from shadows, oriented on the North-south axis.

2.3 Radiation measurements

All solar UV experiments were performed under natural solar radiation on the rooftop of the Environmental Sciences Faculty at the University of Cádiz (36N 31' 43.38'', 6W 12' 49.36''), unless otherwise stated, in trials conducted in June 2013. Solar UV irradiance was measured with a UV radiometer (290–385 nm, Model CUV5, Kipp & Zonen, Netherlands) placed next to the SODIS containers, logging measurements at 10 second intervals. The solar UV dose delivered to the system (Q_{UV} , kJ m⁻²), was obtained by integrating the solar UV irradiance (I_{UV} , W m⁻²) over a given period of time ($\Delta t = t_2 - t_1$, s):

$$Q_{UV} = \int_{t_1}^{t_2} I_{UV} dt \quad (4)$$

2.4 UV dosimeters

As noted earlier the indicators tested and suited for use with SODIS can be classified under three broad categories of indicator ink, the formulations of which are as follows:

POM indicators, where 0.25g 30 wt% sulfonated polystyrene (SPS) were dissolved in 3 g ethanol, and to which 3 g phosphotungstic acid (PWA) and 500 mg glycerol (the SED) were added;

SC photocatalyst indicators, in which a quantity of dye (methylene blue, dichloroindophenol, acid violet 7, acid blue 9 or methyl orange) was dissolved in 2 g of an aqueous 5% hydroxyethyl cellulose (HEC) solution with addition of 50 mg of a SC photocatalyst (ZnO, SnO₂ or Ta₂O₅) and 100 mg glycerol;

Photodegradable dye indicators, in which a quantity of dye (brilliant green, ethyl violet, crystal violet, new methylene blue, thioflavin T or light green SF yellowish) was dissolved in

2.5 g aqueous polymer solution (14% polyvinyl propylene (PVP), 10% polyvinyl alcohol (PVA) or 5% HEC).

All materials were obtained from Aldrich, except SPS, the preparation of which is detailed elsewhere [26]. The spectra and structures of all dyes used are detailed in Figs S1-11 [27] of the supplementary material.

Each indicator ink was cast on polypropylene film and, once dry, a sticky plastic coating with UV cut-off of 250 nm was placed over the indicator film to act as a waterproof coating. UV dosimeters were tested in parallel with the study of the water disinfection efficacy of the different SODIS containers. Indicators were exposed to direct sunlight as well as being placed underneath, and hence irradiated through, a water-filled PE bag, with little difference in results. Unless otherwise stated, results presented are from indicators exposed to direct sunlight in June 2013. Work was also conducted under direct sunlight in December 2013, with no significant change in response found for the same UV dose at lower temperature. The indicators were photographed and scanned, and the RGB colour data then extracted from the images in order to provide a more accurate measure of the observed solar UV driven colour changes associated with the UV dosimeters under test. The typical error associated with all RGB measurements was $\pm 10\%$.

3 Results and Discussion

3.1 The SODIS method using different containers

Filled SODIS containers were exposed to sunlight from 11:00 to 17:00 hours. The UV irradiance measured in June over this time period can be seen in Fig. 2, illustrating typical data for the period of testing. The total UV dose (290-385 nm) measured over this 6 hour period was 950 kJ m^{-2} . Water temperature was monitored throughout the experiments, and never reached 40°C , suggesting that bacterial disinfection was due to solar radiation alone [8].

The observed changes for each SODIS container as a measure of $\log_{10}(N/N_0)$, where N_0 is the initial bacterial count, can be seen in Fig. 3 for *C. perfringens*, measured June 2013, with the

detection limit highlighted by the dashed line. Figs S12 and S13 in the supplementary material contain similar plots for *E. coli* and *Enterococcus spp.*, respectively. From these plots, the calculated theoretical lethal doses ($Q_{UV, LD}$) to achieve disinfection below the detection limit of the bacterial types in each SODIS container were estimated and are reported in Table 1.

Table 1

Estimated theoretical lethal dose required for bacteria reduction below the detection limit.

Bacteria	Initial bacteria concentration, CFU/100 mL	$Q_{UV, LD}$ (kJ m ⁻²)		
		PE bag	PE/EVA bag	PET bottle
<i>E. coli</i>	10 ³	245	219	227
<i>Enterococcus spp.</i>	10 ³	370	1140	520
<i>C. perfringens</i>	10 ²	389	847	1610

As noted earlier, and seen in Table 1, different bacteria types are disinfected at different rates, with *C. perfringens* generally found to be the most resistant microorganism of those tested to SODIS treatment. From Table 1 it can be seen that PE bags were the most effective SODIS container tested, which can be explained by their higher transmittance to UVB light (Fig. 1). Consequently, the focus of this work was to identify UV dosimeters which largely and significantly change colour upon exposure to a solar UV dose of 389 kJ m⁻², predicted for the disinfection of *C. perfringens* in PE bags, with some reference to those that are appropriate for PET bottles.

3.2 Different UV dosimeters

Three different types of UV dosimeters, based on (i) POM, (ii) SC and (iii) dye- bleaching were studied alongside the work on SODIS plastic containers and the results of this work are described below.

3.2.1 Polyoxometalate-based UV dosimeter indicators

Polyoxometalates (POMs) have great chemical and structural versatility, hence are increasingly being utilised for several important industrial processes [28]. They have found

application for dye degradation [29-32], removal of organic pollutants [33], as coatings, analytical reagents, membranes, dopants, gas sensors and in radioactive processing [28].

POMs are a class of materials, often colourless, which can be photo-reduced whilst keeping their structure intact, and upon irradiation with UV (and sometimes visible) light, they become powerful oxidizing agents with the ability to oxidise a great variety of organic compounds. Upon UV irradiation, the POM (phosphotungstic acid, PWA) used in this work, is photoreduced as its electronically excited state effects the oxidation of the SED in the ink, i.e. glycerol in this case, producing a characteristic blue colour (cf. its original colourless form), and making an ideal UV dosimeter. Furthermore, in the absence of UV light the photoreduced blue PWA reverts overnight back to its initial colourless state due to oxidation by ambient O₂. The photochemistry of PWA as a reversible UV dosimeter is summarised by equation (1).

Photochromic films comprising a variety of POMs as self-assembled layers [29,34] or dissolved in a variety of polymer matrices, (e.g. bisvinyl-A/N-vinylpyrrolidone crosslinked polymer [35] or polyacrylamide [36,37]) have been reported previously by others. However, their specific use in UV dosimeter indicator films has not been investigated and hence their study here.

Several polymer supports for a PWA UV dosimeter were studied initially and it was found that indicators based on the POM, PWA, made up in PVA (aq) or polyvinyl butyral (EtOH) were too fast to respond, i.e. too sensitive towards UV light, and so reached their fullest blue colour upon exposure to a modest dose of solar UV, i.e. 67 and 140 kJ m⁻² (corresponding to ca. 30 min and 1h in June in Cadiz), respectively. However, PWA and glycerol in an ethanol based ink containing sulfonated polystyrene, SPS, as the polymer, appeared much more useful as a UV dosimeter indicator, achieving a deep blue colour after exposure to 390 kJ m⁻² solar UV (2.5 hours in June). These results suggest that this UV dosimeter is suitable for identifying the point at which microbiologically contaminated water is solar-disinfected, as described in Table 1, in a PE bag, since this is typically achieved using a solar UV dose of 389 kJ m⁻². In contrast a POM-based indicator able to operate at the high UV dosages associated with the traditional PET SODIS bottle was not identified. As mentioned previously, an extra advantage of this UV dosimeter is that it is reversible in the absence of light, and although a naked indicator recovers to its colourless form in less than one hour,

when used with the sticky plastic waterproof barrier here, which slows the diffusion of oxygen into the film, the recovery process is slowed significantly, so that the indicator recovers overnight, ready for use the following day. The potential to re-use UV dosimeter indicators is an attractive feature which helps lower their cost, and this feature is illustrated by the results presented in Fig. 4 through fast activation with a UVB lamp (3.85 mWcm^{-2}) for 30 minutes, and overnight recovery, repeated 3 times.

3.2.2 Semiconductor photocatalysis-based UV dosimeter indicators

In recent papers colorimetric UV dosimeters that utilise a semiconductor photocatalyst for use as sunburn warning indicators [38,39] have been reported. The UVA indicators comprised a polymer film containing: a redox dye (D), SED and SC photocatalyst. A general reaction for such UV dosimeters is given in equation (2) whereby the SC absorbs the UV light and photo-oxidises the SED, allowing trapped photogenerated electrons to reduce the redox dye from its highly coloured oxidised form, to produce its colourless leuco form.

Since these UV dosimeters [38,39] are designed for sunburn warning they are far too UV sensitive to be appropriate as UV dosimeters for SODIS. The use of titania and SnO_2 as photocatalysts for sunburn indicators which absorb UVA and UVB light [38] and the UVB component only [39], respectively, have been previously reported. The latter system is much less solar UV sensitive due to the higher band-gap of SnO_2 which does not respond to the highly abundant UVA component in the solar spectrum. Other UVB-absorbing SCs, such as ZnO and Ta_2O_5 , were also investigated here as possible SC-based UV dosimeters. Another component of these systems which can alter the timescale of colour change is the redox dye and so a number of redox dyes which are less readily reduced, as those dyes used in the sunburn warning indicators were also investigated. The dyes tested include: methylene blue (MB), dichloroindophenol (DCIP), acid violet 7 (AV7), acid blue 9 (AB9), and methyl orange (MO). Table 2 shows the results for a number of SC-based UV dosimeters using various dyes, dye quantities (parts per hundred resin – pphr) and SC photocatalysts, and the dose of solar UV required to bleach the indicator. These results demonstrate that the 5 pphr AB9/ ZnO system is appropriate for identifying the solar UV dosage associated with water disinfection (390 kJ m^{-2}) using the new PE bags, whereas a 1 pphr AB9/ SnO_2 indicator was appropriate when using the more traditional PET bottles, which requires nearer 1600 kJ m^{-2} (see Table 1).

Table 2

A sample of semiconductor photocatalysis-based UV dosimeters tested with the indicators ink formulation in terms of dye, dye quantity (pphr) and SC photocatalyst, the dose of solar UV required to bleach the indicator, and therefore the SODIS container which the UV dosimeter could be used with to highlight bacterial disinfection.

Dye (pphr)	SC	Solar UV dose required to fully bleach (kJ m^{-2})	Appropriate SODIS container for use with UV dosimeter
AB9 (5)	ZnO	390	PE bag
DCIP (2.5)	Ta ₂ O ₅	455	PE bag
MO (2.5)	SnO ₂	892	PE/EVA bag
MB (2.5)	SnO ₂	955	PE/EVA bag
AV7 (2.5)	SnO ₂	1020	PE/EVA bag
MO (10)	ZnO	1020	PE/EVA bag
AB9 (10)	ZnO	1240	PE/EVA bag
AB9 (1)	SnO ₂	1785	PET bottle

An example of the 5 pphr AB9/ZnO UV dosimeter working is illustrated in Fig. 5 with the ‘R’ (i.e. red) component of the RGB data as a function of solar UV exposure time (i.e. UV dose; units: kJ m^{-2}). The photographs from which the RGB data was extracted are also shown, next to the R vs UV dose points.

3.2.3 Photodegradable dye-based UV dosimeter indicators

Some dyes are more prone to photodegradation by light than others with the photostability of dyes described by their lightfastness [40], *i.e.* their ability to resist fading upon exposure to light. Dyes are given a lightfastness grading on a scale of 1-8, with 1 being the most likely to fade, and 8 being the most resistant to fading.

The photodegradation of several commercial dyes [41-44] by sunlight and artificial light have been investigated by several groups as this is important to the textile industry, as a route to treating dye-polluted water systems. However, in such work often additional reagents, such as titania, are required to speed up the dye photodegradation process [45,46]. Little, if any,

work appears to have been conducted on the dye degradation process as an indicator for SODIS.

Basic dyes, such as brilliant green (BG), ethyl violet (EV), crystal violet (CV), new methylene blue (NMB) and thioflavin T (TT), are known to be light-sensitive [40], and were tested here as SODIS UV dosimeter indicators along with some others that are also known to not be very photostable [27]. Of the 19 dyes tested in the lab for solar dosimetry using solar simulated light (150 W xenon arc lamp (Oriel) with UG5 and WG20 filters inline [47]), 12 of these dyes were identified as showing potential as solar UV dosimeters, with just 6 of these dyes – BG, EV, CV, NMB, TT (basic dyes) and Light green SF yellowish (LGSFY) (an acid dye) – bleaching under the dosage ($389 - 1610 \text{ kJ m}^{-2}$) of relevance to SODIS. Table 3 lists the measured solar UV dosage required to bleach a range of photodegradable dye-based UV dosimeters in a variety of different polymers.

Table 3

Solar UV dosage required to bleach a range of indicators tested, in terms of the indicators ink formulation, given as dye and quantity (pphr) and polymer resin (polyvinyl propylene (PVP, hydroxyethyl cellulose (HEC), or polyvinyl alcohol (PVA)), and therefore the SODIS container which the UV dosimeter could be used with to highlight bacterial disinfection.

Dye (pphr)	Polymer	Solar UV dose required to fully bleach (kJ m^{-2})	Appropriate SODIS container for use with UV dosimeter
NMB (0.75)	PVP	396	PE bag
BG (0.25)	PVP	396	PE bag
TT (8)	HEC	482	PE bag
CV (0.3)	PVP	955	PE/EVA bag
LGSFY (2)	PVP	955	PE/EVA bag
BG (1.1)	PVP	1020	PE/EVA bag
EV (0.3)	PVP	1100	PE/EVA bag
TT (0.8)	PVP	1100	PE/EVA bag
BG (2)	PVA	1530	PET bottle

As seen from the data in Table 3, a number of the photodegradable dye-based indicators can be used to provide an indicator of the correct solar UV dosage associated with the

disinfection of a specific microbial species (see Table 1). Fig. 6 illustrates one of the promising photodegradable dye-based UV dosimeters, based on NMB in PVP, being utilised alongside SODIS in a PE bag. Fig. 7 illustrates a longer lasting UV dosimeter, more suitable for use with a PET bottle, where the 'R' component of the RGB data was plotted against UV dose (kJ m^{-2}), and the photographs from which the RGB data were extracted are also shown.

4 Conclusions

The solar UV dosages required for SODIS in order to achieve a bacteria concentration below the detection limit of *E. coli*, *Enterococcus spp.* and *C. perfringens* in PET bottles, PE and PE/EVA bags were determined by exposing containers to the sun from 11:00 to 17:00 hours in Cádiz in June 2013. Bacterial disinfection was found to be most efficient in PE bags, and a solar UV (290-385 nm) dose of 389 kJ m^{-2} was able to lower the concentration of all the bacteria tested to below the detection limit.

In parallel to the disinfection experiments, a range of polyoxometalate, semiconductor photocatalysis and photodegradable dye-based indicators were all tested under solar UV irradiation to determine their use as SODIS indicators. All indicators tested were robust, easy to use and inexpensive so as not to add significantly to the attractive low cost of SODIS. The semiconductor photocatalyst and photodegradable dye based UV dosimeters are disposable, one-use systems, while the polyoxometalate based indicator recovered its colour in the dark overnight, allowing it to be reused, and hence decreasing its cost to the SODIS scheme. A POM indicator consisting of PWA and glycerol in a SPS resin, a SC photocatalyst indicator utilising 5 pphr AB9 and ZnO in a HEC resin, and photodegradable dye indicators containing BG or NMB in a PVP resin were demonstrated to largely and significantly change colour upon exposure to 389 kJ m^{-2} solar UV. These indicators therefore are suitable to indicate the complete disinfection of *E. coli*, *Enterococcus spp.* and *C. perfringens* in a PE bag.

Other indicators, such as a SC photocatalyst indicator utilising 1 pphr AB9 and SnO_2 in a HEC resin, and a photodegradable dye indicator containing BG in a PVA resin, were reported which changed colour at higher solar UV doses and hence were appropriate as indicators for the less efficient, more traditional, SODIS container, i.e. the PET bottle.

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Figures

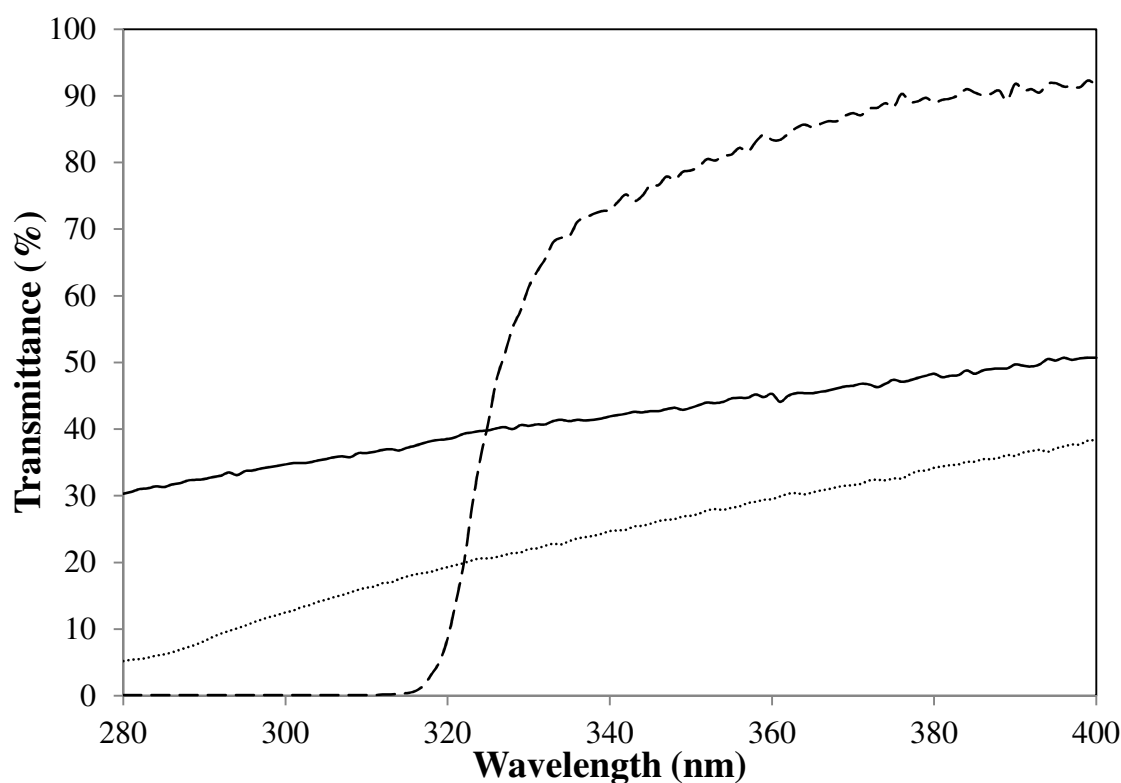


Fig. 1. %Transmittance of light through the walls of various SODIS containers; PE bag (—), PE/EVA bag (.....) and PET bottle (— —).

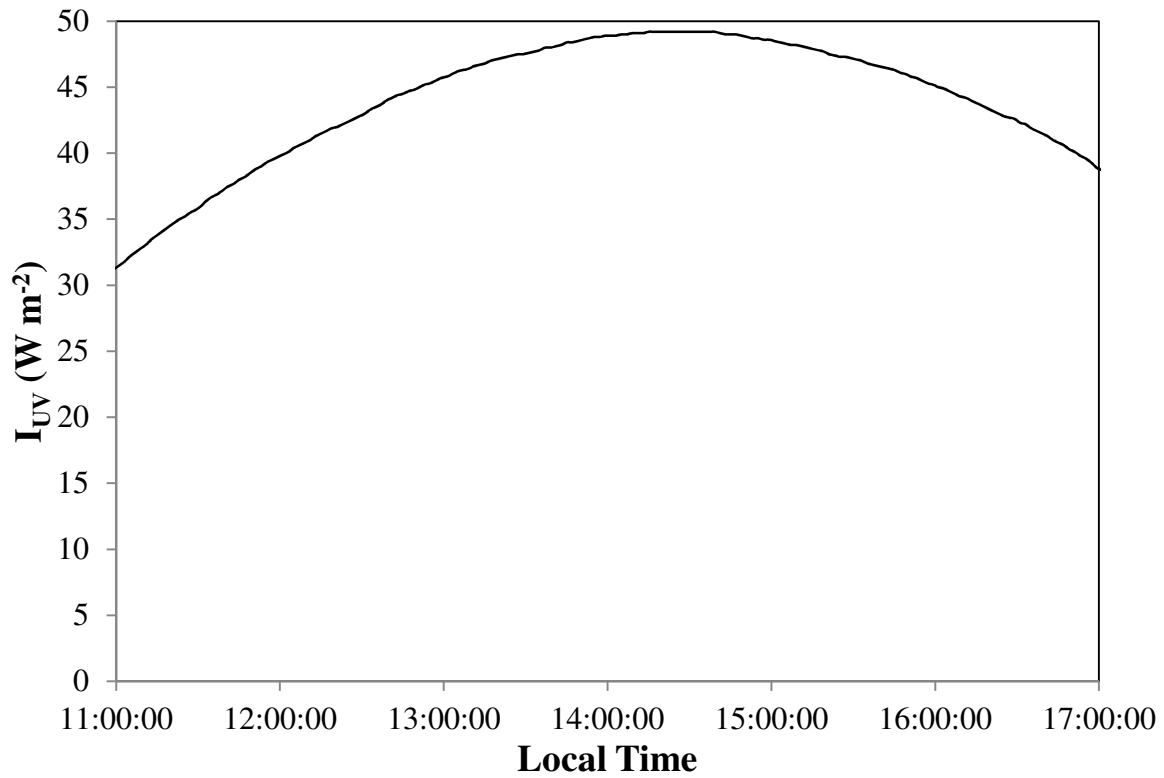


Fig. 2. UV Irradiance (290 – 385 nm) measured in June 2013.

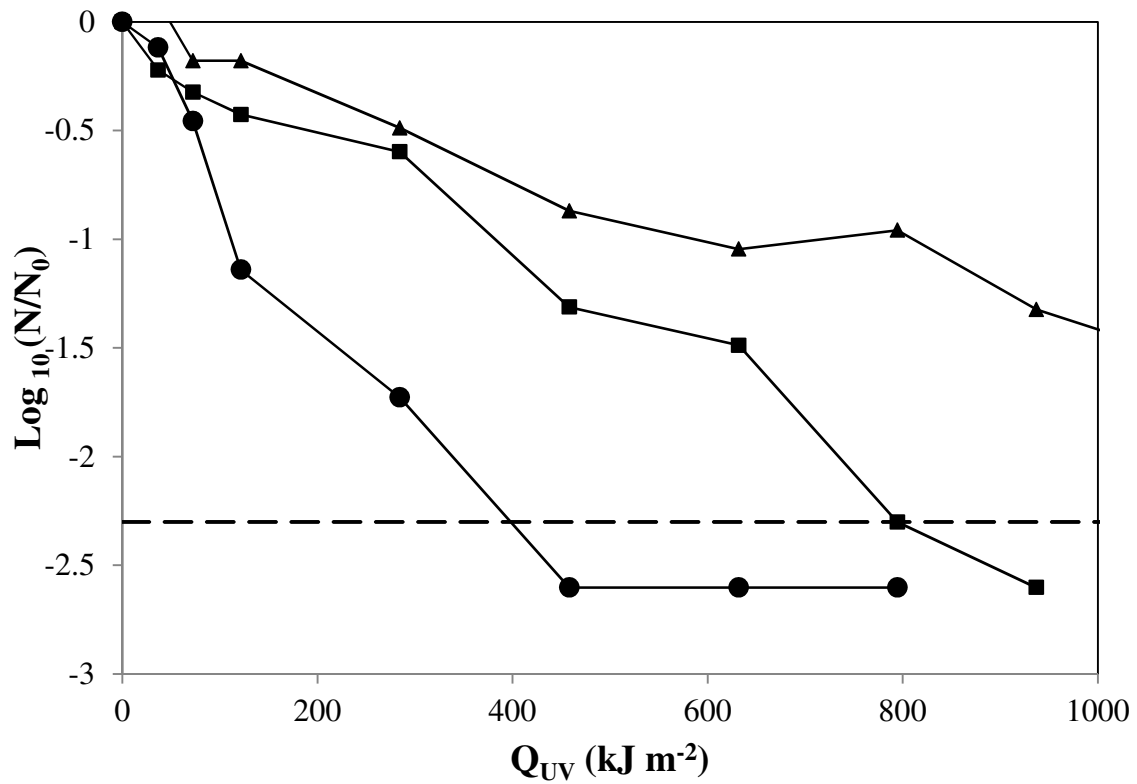


Fig. 3. Bacterial count as a function of UV dose for a PE bag (\bullet), PE/EVA bag (\blacksquare) and PET bottle (\blacktriangle), for *C. perfringens*, analysed in triplicate, with errors of <10%. The dashed line represents the detection limit (2 CFU/100 mL i.e. $Log_{10}(2/N_0)$).

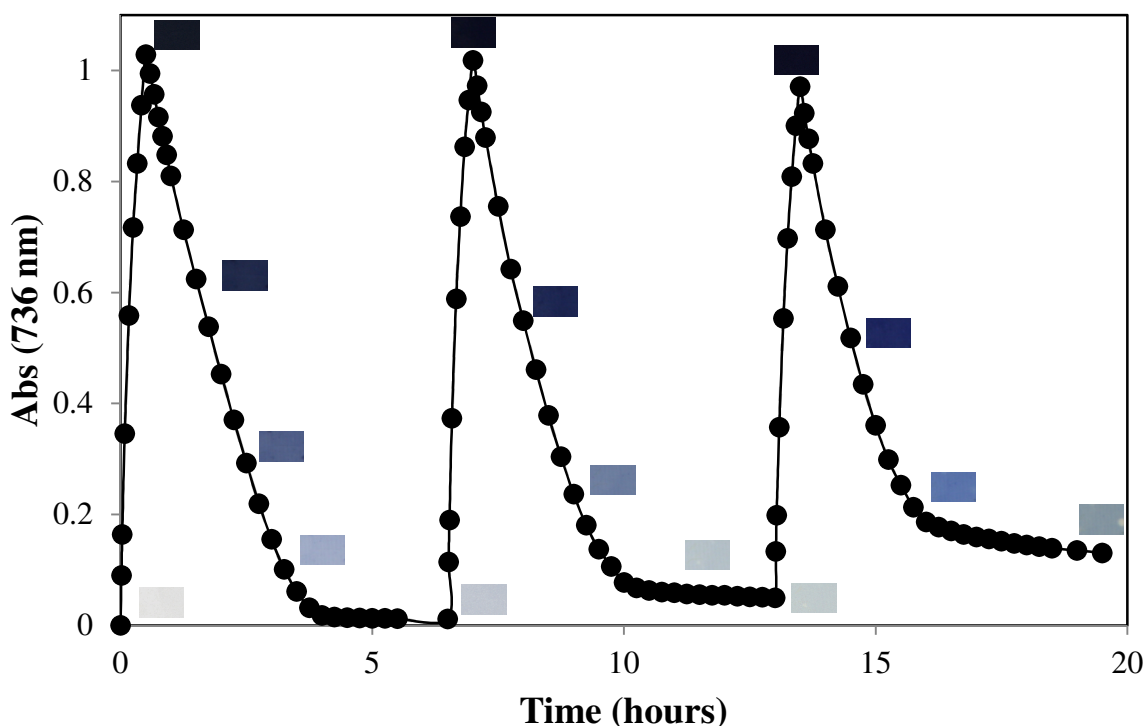


Fig. 4. PWA/SPS(EtOH) indicator, reaching full blue colour after fast activation with a UVB lamp (3.85 mWcm^{-2}) for 30 minutes, and overnight recovery, repeated 3 times.

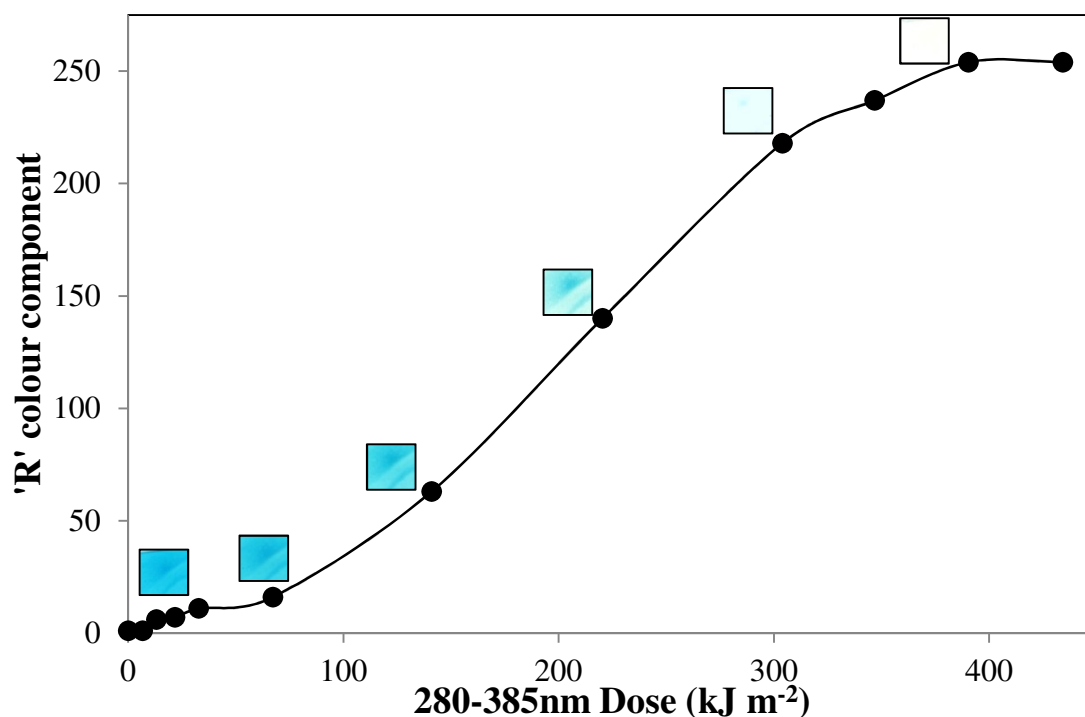


Fig. 5. 'R' component of the RGB data extracted from photographs (shown) of a UV-dosimeter which contained ZnO and 5 pphr AB9 in the ink formulation. As a consequence this indicator would be suitable for highlighting that a bacteria concentration below the detection limit in a PE bag (requiring a dose of 389 kJ m^{-2}) had been achieved.

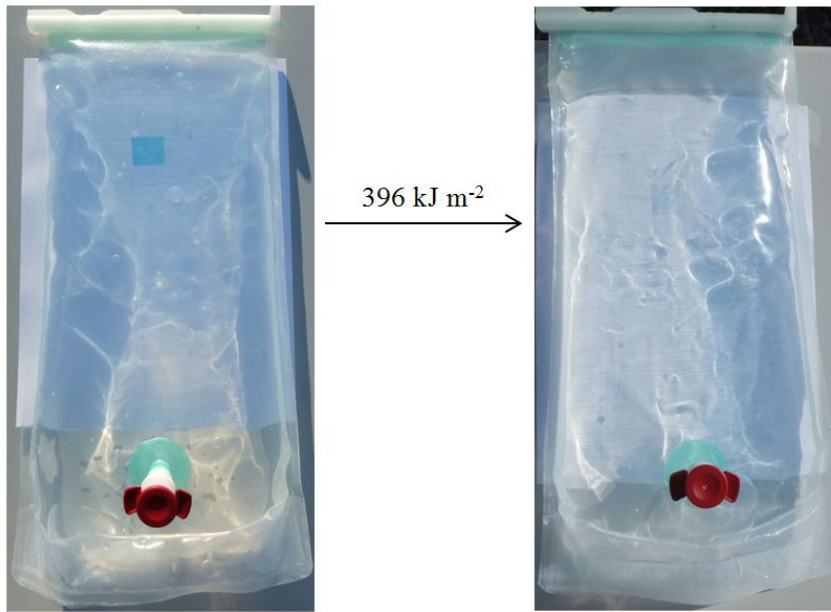


Fig. 6. NMB (0.75 pphr) in PVP indicator attached to a PE SODIS bag, bleaching after the required dosage for disinfection.

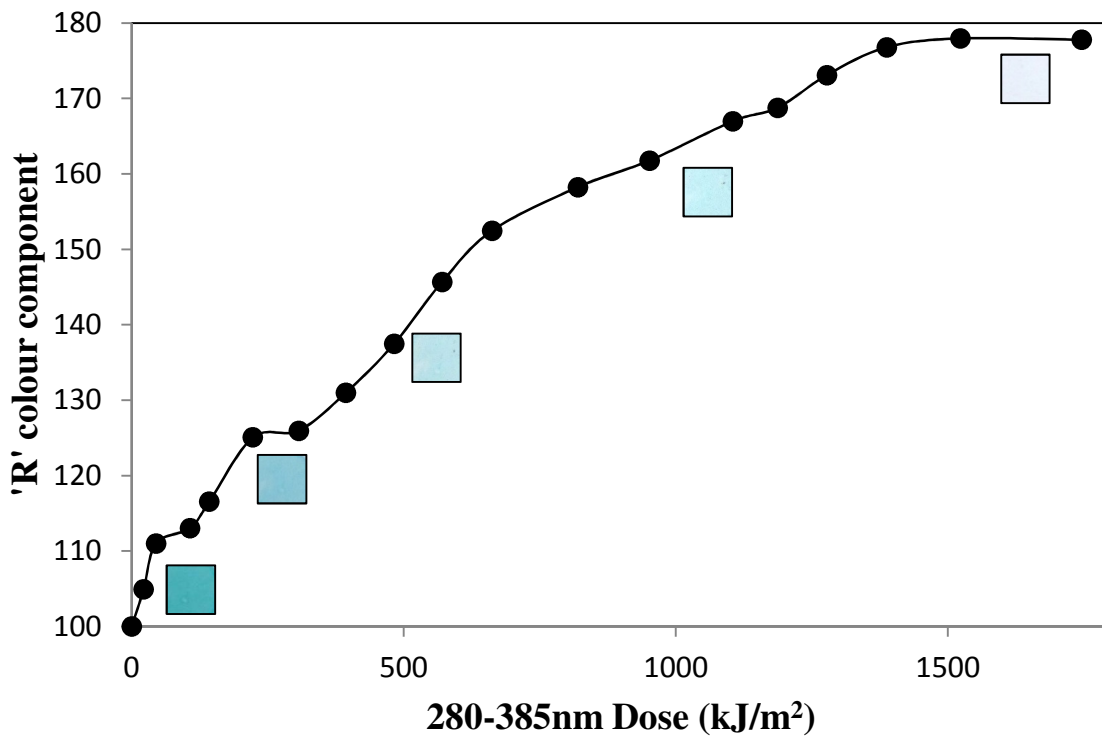


Fig. 7. 'R' component of the RGB data extracted from photographs (shown) of a UV-dosimeter which contained 2 pphr BG in PVA in the ink formulation. This indicator would be suitable for indicating when a PET bottle had received sufficient solar UV as to ensure the disinfection of any water contaminated therein.

Supplementary material

1 Materials

Figs S1-11 [1] illustrate the spectra and structure of each of the dyes used in this work.

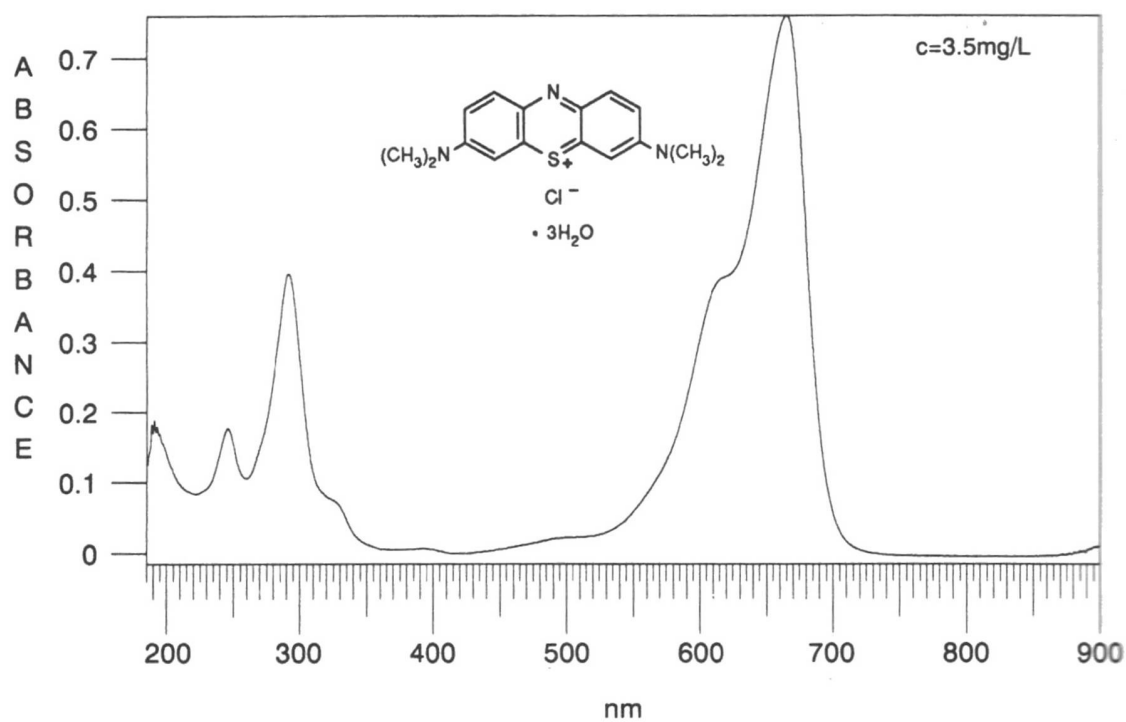


Fig. S1. Spectra and structure of methylene blue.

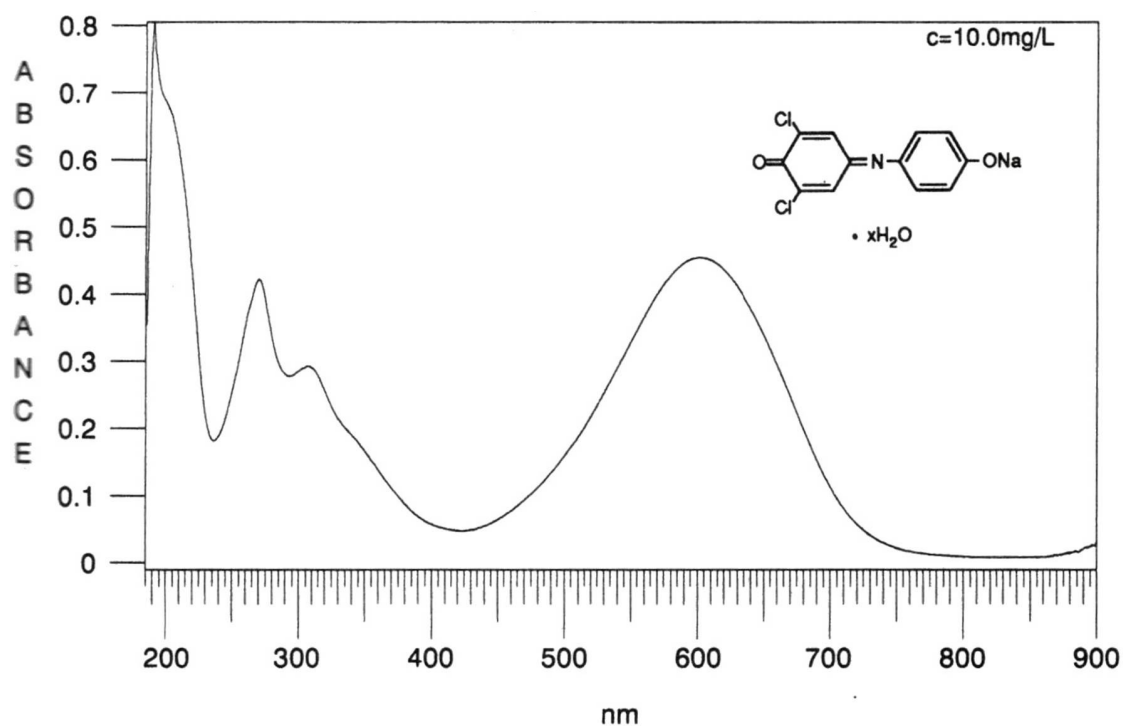


Fig. S2. Spectra and structure of dichloroindophenol.

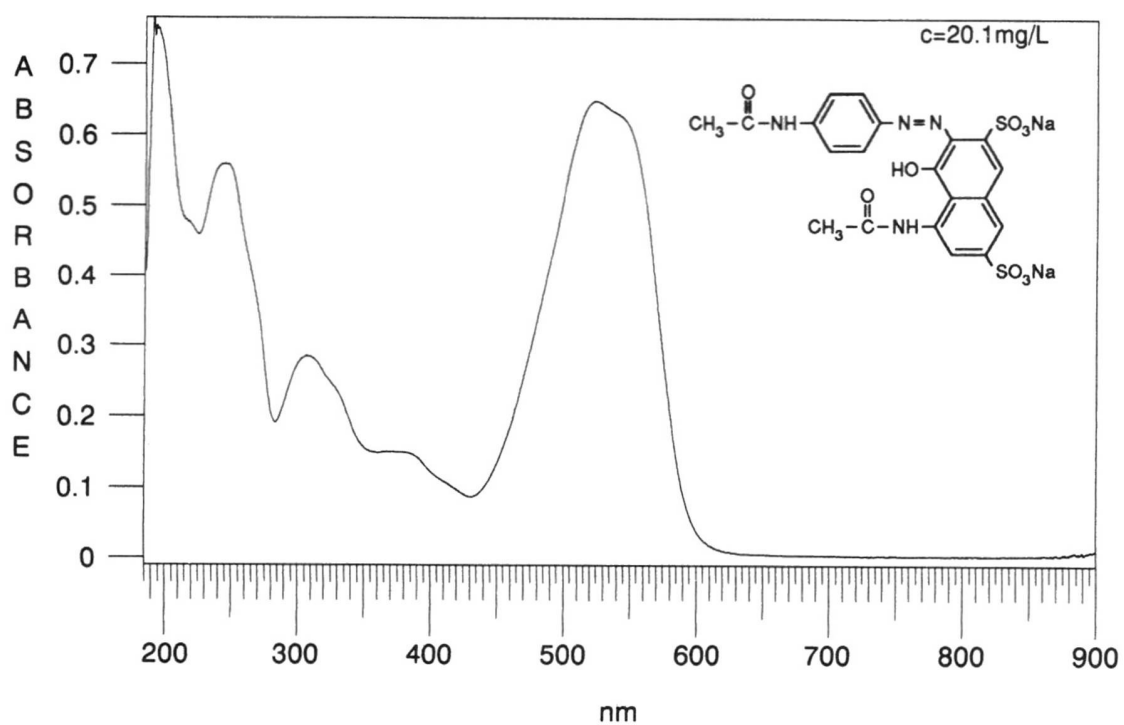


Fig. S3. Spectra and structure of acid violet 7.

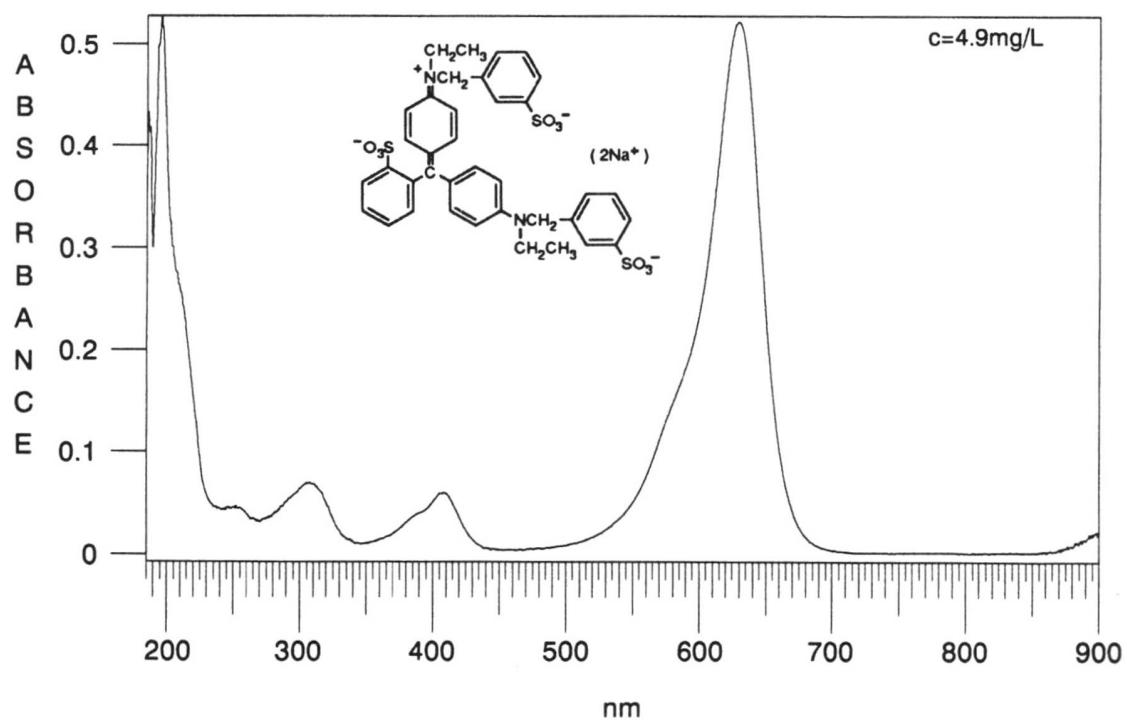


Fig. S4. Spectra and structure of acid blue 9.

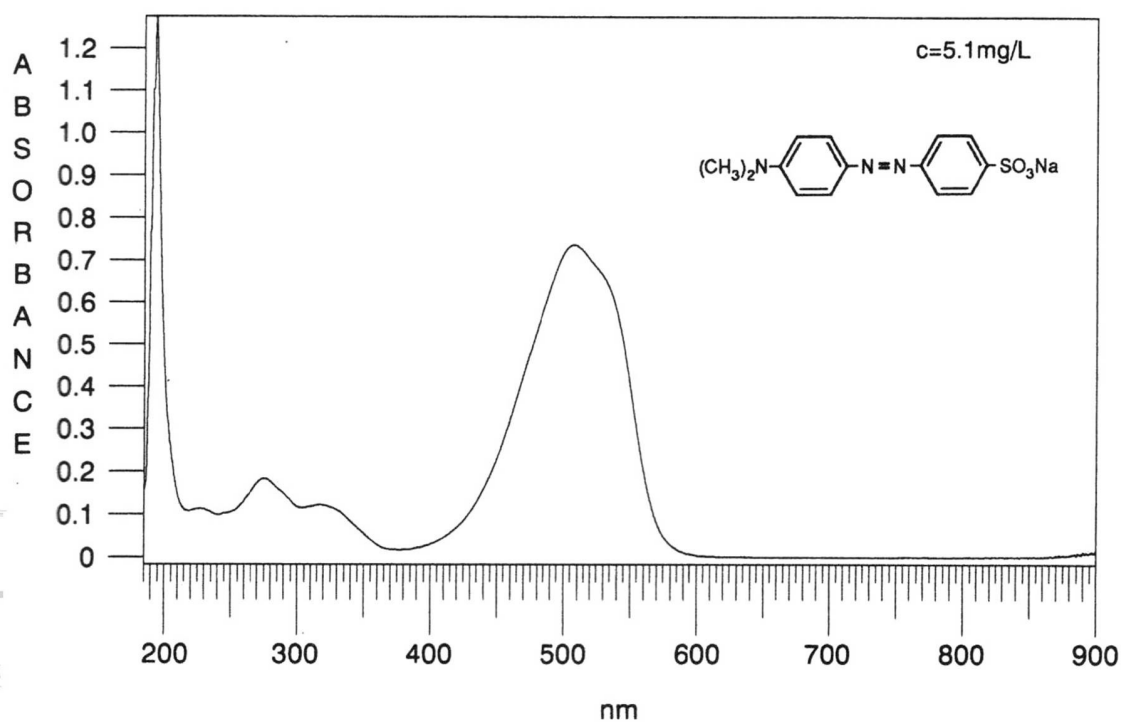


Fig. S5. Spectra and structure of methyl orange.

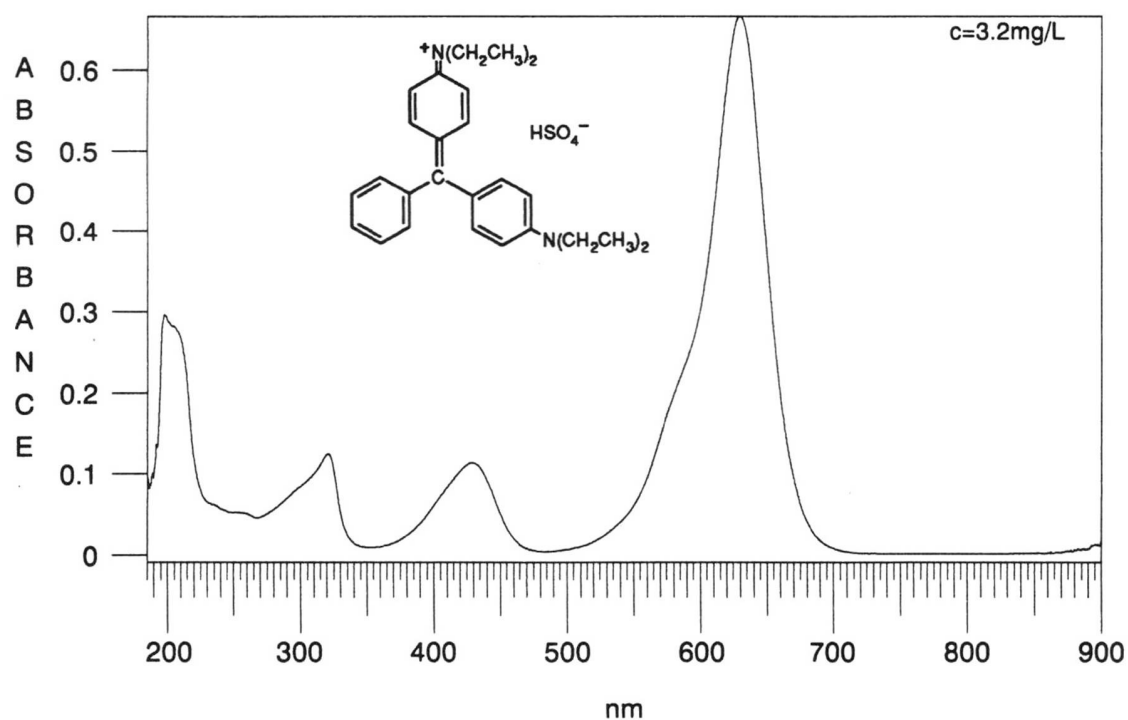


Fig. S6. Spectra and structure of brilliant green.

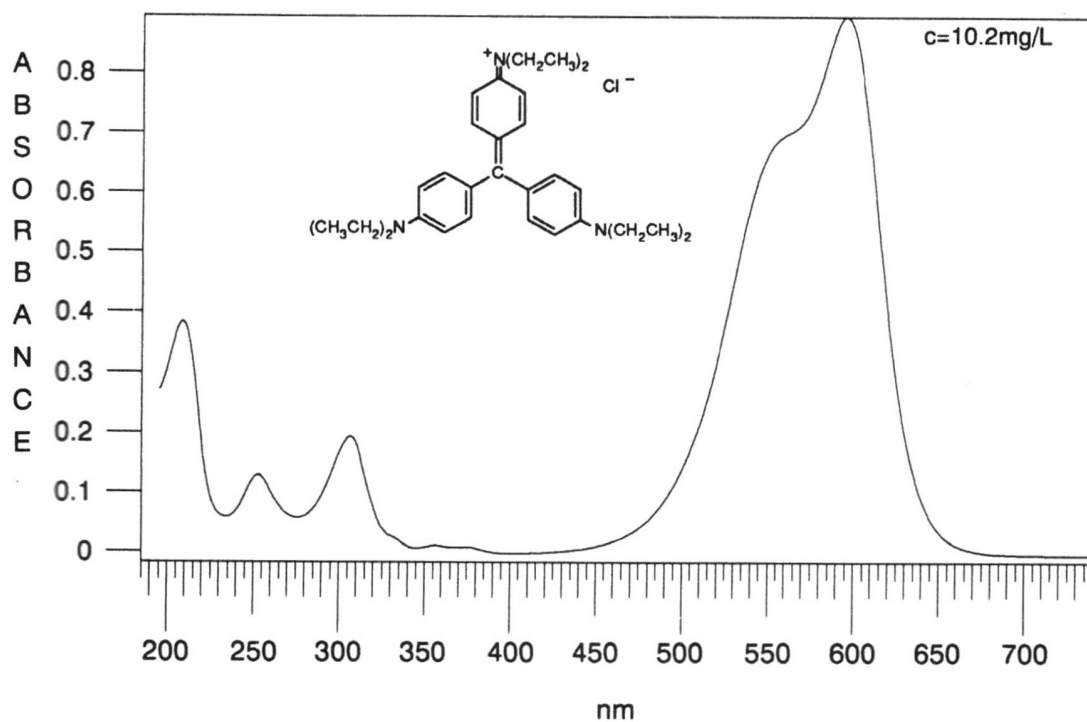


Fig. S7. Spectra and structure of ethyl violet.

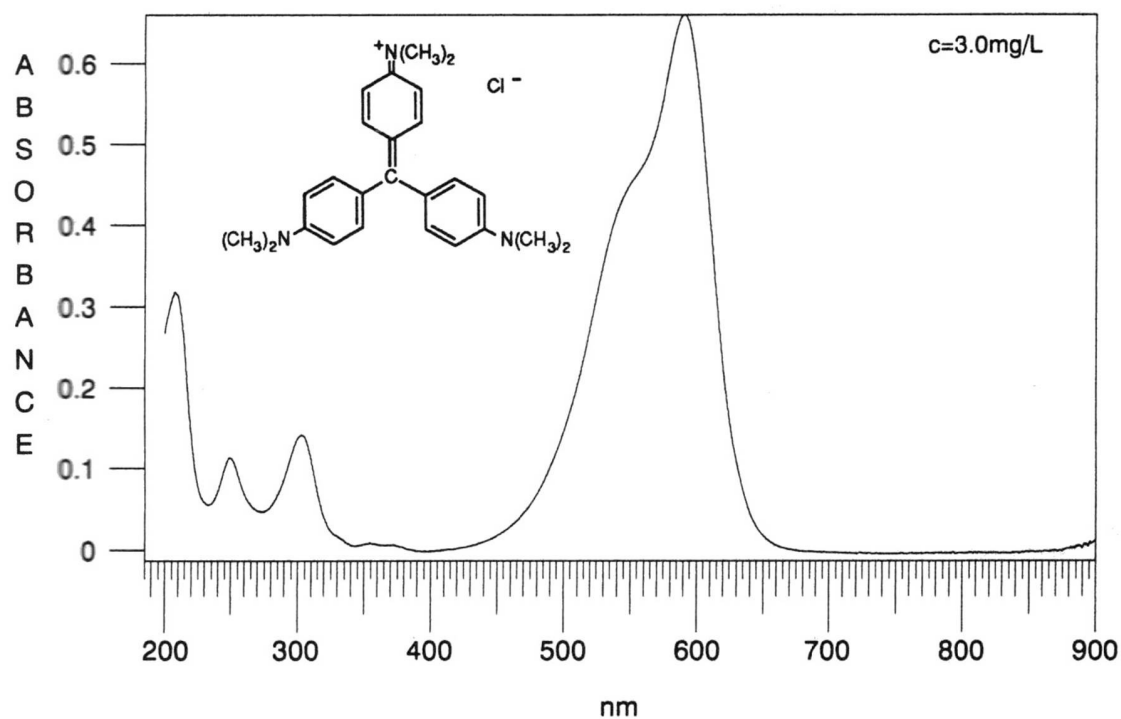


Fig. S8. Spectra and structure of crystal violet.

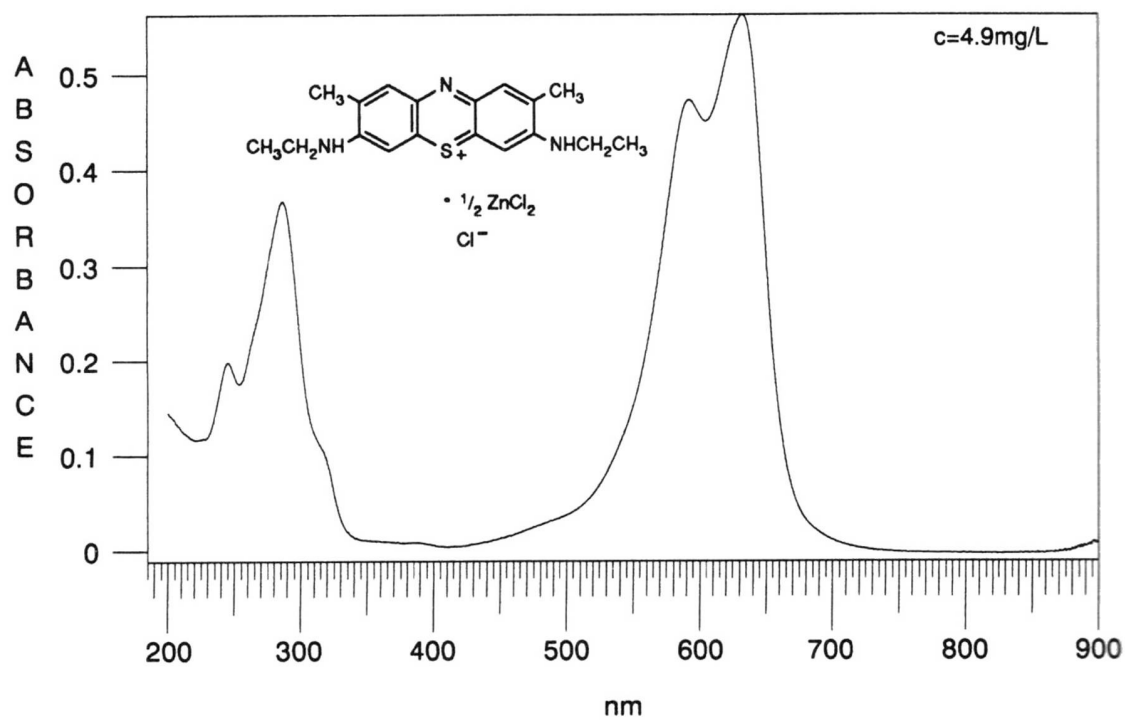


Fig. S9. Spectra and structure of new methylene blue.

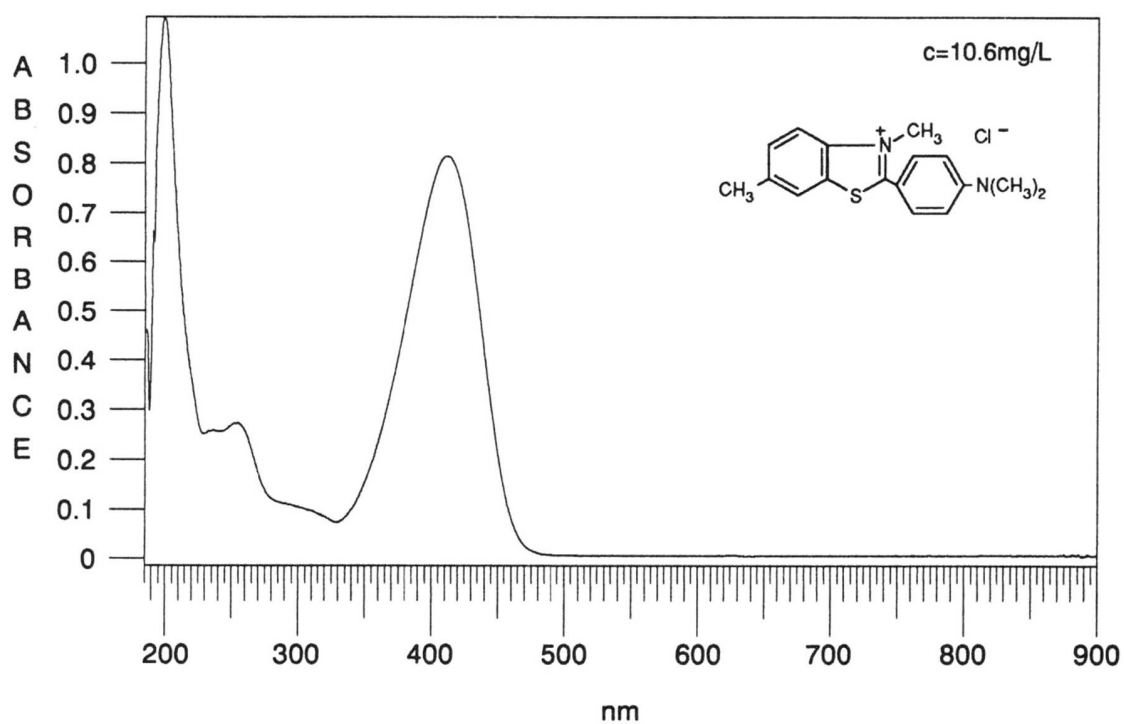


Fig. S10. Spectra and structure of thioflavin T.

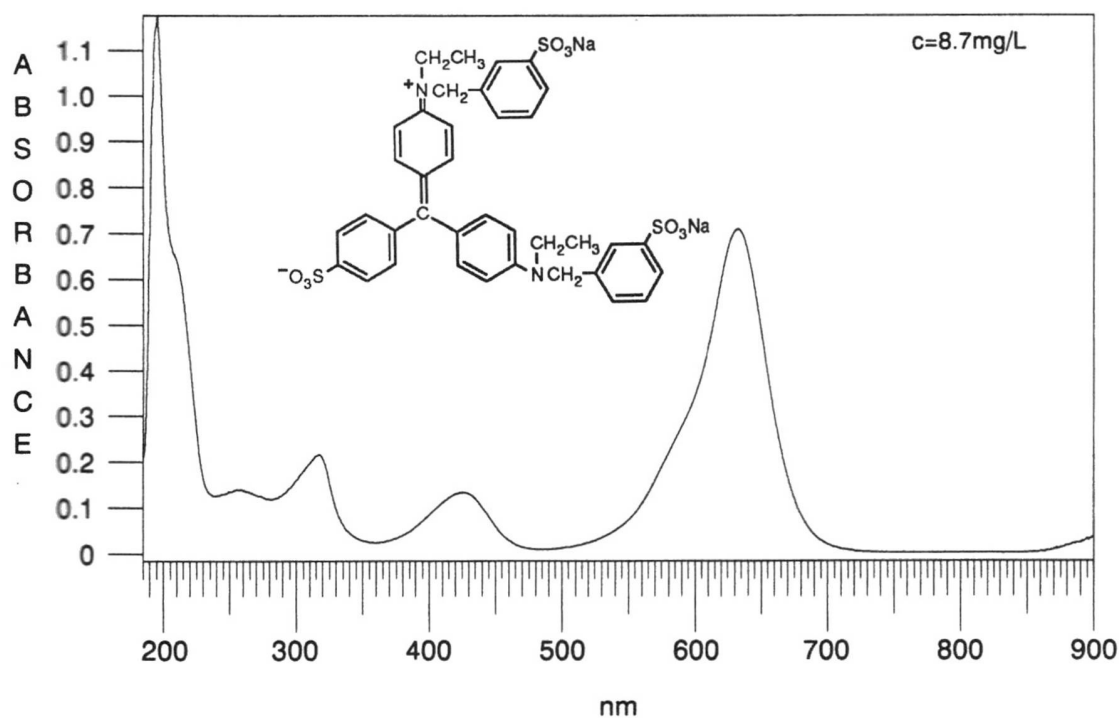


Fig. S11. Spectra and structure of light green SF yellowish.

2 Results

The observed changes for each SODIS container as a measure of $\log_{10}(N/N_0)$, where N_0 is the initial bacterial count, can be seen in Figs S12 and S13 for *E. coli* and *Enterococcus spp* respectively, measured June 2013, with the detection limit highlighted by the dashed line.

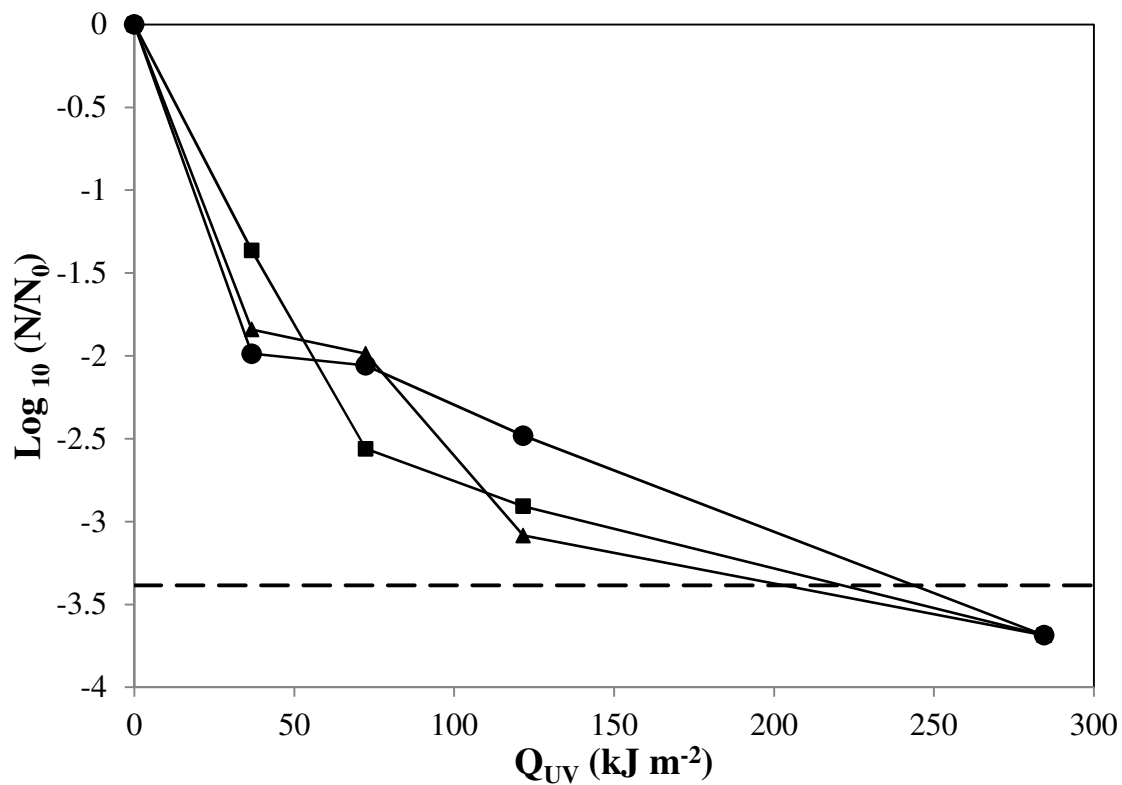


Fig. S12. Bacterial count as a function of UV dose for a PE bag (●), PE/EVA bag (■) and PET bottle (▲), for *E. coli*, analysed in triplicate, with errors of <10%. The dashed line represents the detection limit (2 CFU/100 mL i.e. $\log_{10}(2/N_0)$).

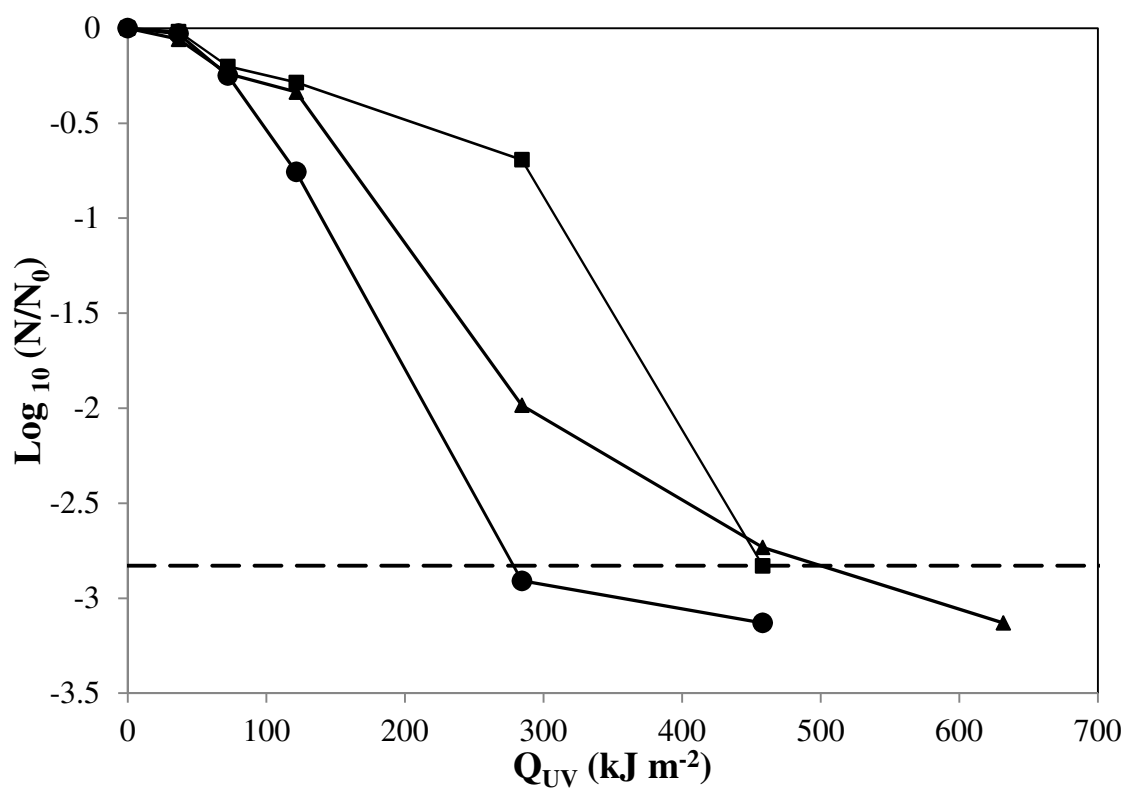


Fig. S13. Bacterial count as a function of UV dose for a PE bag (\bullet), PE/EVA bag (\blacksquare) and PET bottle (\blacktriangle), for *Enterococcus spp.*, analysed in triplicate, with errors of <10%. The dashed line represents the detection limit (2 CFU/100 mL i.e. $\text{Log}_{10}(2/N_0)$).

Author Biographies

Katherine Lawrie graduated from University of Strathclyde with an MSci degree in 2008, and gained her PhD on ‘Novel, UV-activated intelligent inks for food packaging’ from Queen’s University, Belfast in 2012. She is currently based at Queen’s University, Belfast, with the focus of her research on optical sensors, dye photochemistry and semiconductor photocatalysis.

Professor Andrew Mills graduated from the University of London (Westfield College) in 1979 and gained his PhD on ‘Water-splitting Photosystems’ in 1983. In 1986 he was awarded the RSC Meldola Medal and Prize. In 1982 he took up a lectureship at Swansea University and moved to University of Strathclyde in 1999, where he was the James Young Chair of Chemistry. In 2011 he took up a position as Professor of Materials Chemistry at Queen’s University, Belfast. His research interests include: photochemistry, semiconductor photocatalysis, redox catalysis and optical and electrochemical indicators.

Manuel Figueredo Fernández graduated in Marine Science from the University of Cádiz in 2011 and gained an MSc degree on water management from the same university in 2012. He is currently carrying out his PhD studies on solar treatments for drinking water at the University of Cádiz.

Sergio Gutiérrez Alfaro graduated in Chemical Engineering from the Complutense University of Madrid in 2008 and with an MSc degree on ‘Integrated water management’ from University of Cadiz in 2010. He is currently carrying out his PhD on ‘Solar disinfection of natural water for human consumption and waste water for reuse’ at University of Cadiz.

Professor Manuel Manzano graduated from University of Cádiz (Faculty of Science) in 1988 and PhD in Chemical Engineering (1999). He specialized in application of advanced oxidation processes to industrial wastewater for regeneration and solar disinfection of natural water for human consumption in developing countries, receiving the following awards: 1st - CEPSA award for innovation in the field of energy, petroleum and natural environment (2013), 1st - Foundation 3M "Innovation to improve the lives of people: The Water" (2012) and 1st - social entrepreneurship to human development and poverty reduction (Commitment and Development Program ONGAWA NGO, Engineering for Human Development (2013)).

Matthias Saladin graduated in Environmental Sciences from ETH Zurich in 1998 and gained an MSc in Environmental Engineering from Imperial College in 2000. He has extensive experience in the investigation, promotion and diffusion of the SODIS method at global scale and is involved in the development of innovations related to the SODIS method.