



Solar disinfection of drinking water at alkaline pH, assisted by ashes of spices and herbs containing catalytic metals, in a novel “phyto-Fenton” process

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ABSTRACT

In this manuscript, the improvement of solar disinfection (SODIS) for water treatment through the photo-Fenton reaction using iron replacements, namely calcined herbs and spices (thyme, cumin, cinnamon, ginger, and cocoa), naturally containing high content of metals. The bactericidal performance of SODIS, H₂O₂/light and solar photo-Fenton (light/H₂O₂/Fe²⁺) were assessed in pure and Lake Lemán water. Sodium percarbonate (SPC) and ashes were successfully employed as substitutes of H₂O₂ and Fe²⁺, respectively. Low spices/herbs' addition improved the H₂O₂/light process, especially when ginger, cumin, thyme, or cocoa were used, inducing effective heterogeneous photo-Fenton process even at alkaline pH. In ultrapure water, solar photo-Fenton with ashes was only slightly slower than the corresponding Fe²⁺-driven reaction, while in lake water total bacterial inactivation was achieved by cumin, thyme or ginger ashes. SPC enhanced SODIS performance, while the addition of ashes resulted in faster kinetics than light/SPC only. Overall, this work succeeded in converting the classic photo-Fenton process into a low-cost variant, the “phyto-Fenton” process, driven by the metals contained in the organic-free ashes and the H₂O₂ content of SPC.

1. Introduction

According to the World Health Organization (WHO) and the United Nations International Children's Emergency Fund (UNICEF), nearly 844 million of people lack access to an improved source for drinking water [1]. This lack of access poses a serious threat to human health, due to consumption from polluted water sources. As a result, millions of people suffer from related diseases, such as diarrhea, cholera, typhoid fever or polio, which are responsible for thousands of deaths each year [2].

Hence, fresh water supply and access to treated water for a community has to be cheap, safe, efficient, easy to use and maintain. Due to these reasons, Solar Disinfection (SODIS) has gained popularity over the past decades and shows an interesting potential in response to the aforementioned needs [3,4].

SODIS is a low-cost method and is thereby especially suited for low-income countries. This technology is characterized by its effectiveness against pathogenic microorganisms and its independence of costly energy sources and complex supply chains [5]. Its function is simple, as it

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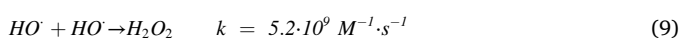
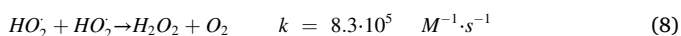
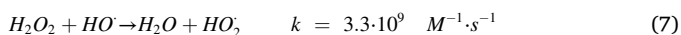
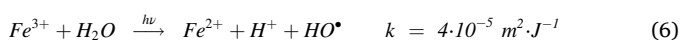
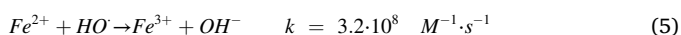
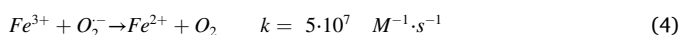
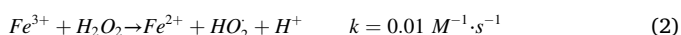
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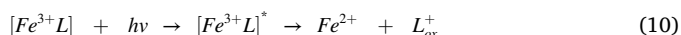
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kills microorganisms via thermal and UV stress [6]. Nevertheless, the SODIS treatment has some limitations, such as the dependency on sunlight irradiation or the long treatment times and microbial regrowth associated with leftover live cells [7]. These limitations could be overcome by the application of Advanced Oxidation Processes (AOPs), such as the photo-Fenton process. The efficiency of photo-Fenton process has been largely reported in literature for the disinfection of water and wastewater [8–12]. The Fenton's reagent is based on the decomposition of hydrogen peroxide by metals in order to generate highly reactive radical species [13].

In natural waters, one of the main mechanisms taking place under with UV-A radiation is the intracellular induction of oxidative stress [14], as well as the excitation of photo-sensitizers, which react with surrounding biomolecules and oxygen species, leading to the generation of Photo-Produced Reactive Intermediates (PPRIs) [15]; these can be either free radicals such as O_2^- , HO^* , or non-radicals like 1O_2 or H_2O_2 [16–18]. Their action is often non-selective and could lead to permanent cell inactivation, and in addition can act complementarily with the (photo-)Fenton process; solar light will facilitate the otherwise iron photo-catalytic regeneration. Eqs. (1) through (9) describe the main initiation, propagation, recycling and termination reactions in the (photo-)Fenton process [18–20]:



Of special interest, we highlight that the complexed iron can be regenerated as shown by Eq. (5), or via a Ligand-to-Metal Charge Transfer (LMCT), leading to Fe^{3+} reduction to Fe^{2+} and it's re-participation in the Fenton reaction (Eq. (10)):



Despite the high efficiency of the photo-Fenton process against microorganisms, there are some limitations, such as the generation of iron sludge at the end of the process [21,22]. Besides, the technology is hard to manage, with high operation and capital investment costs in a possible large-scale application, so it is not suitable to be applied in countries with emerging economies or isolated communities; besides, handling of some chemicals such as liquid H_2O_2 may require constant supervision and storage conditions incompatible with these special contexts. As such, alternatives to perform a low-cost photo-Fenton treatment without many restrictions in these contexts is required.

An alternative for iron supply would be the use of different locally available iron-rich spices or herbs, which could be used after calcination, as a substitute for the use of iron salts or heterogeneous iron catalysts. Using iron oxides and in extension, the heterogeneous photo-Fenton process, may overcome some limitations of the homogeneous photo-Fenton, including a simple physical step to separate and recover the catalyst [23–25], as well problems about iron acquisition. Also, liquid solutions of H_2O_2 can be substituted by sodium percarbonate [26] (SPC, $Na_2CO_3 \cdot 1.5H_2O_2$) avoiding the problems related with its

instability and safety precautions. Sodium percarbonate is a solid, making it easier to transport, more stable and safer to use than hydrogen peroxide [27]. Besides, its properties in aqueous solution are substantially similar to those of liquid H_2O_2 solutions [28]. A potential drawback, though, could come from the formation of (bi)carbonate ions, depending on the pH, reducing the efficiency of Fenton reaction as consequence of their scavenging of hydroxyl radicals [29].

Taking into account the above considerations, the main objective of this research is the assessment of alternative, available food-related materials as iron sources, allowing to enhance SODIS treatment through photo-Fenton reaction in resource-poor environments, namely the "phyto-Fenton" process (*phyto-* = Greek for "plant", herein: "pertaining to plants" or "of plant origin"). These materials could reduce the costs of photo-Fenton reaction application, enhancing the kinetic of SODIS treatment, and thus being able to treat water faster. More specifically, this research will focus on i) employing the iron compounds (and other catalytic metals) present in some commercially available foods and spices, namely, herbs and spices found around the globe, ii) investigating the influence of mineral ashes addition on solar disinfection processes and comparing it to conventional solar and photo-Fenton process and iii) evaluating the catalysts' efficiency alongside the substitution of hydrogen peroxide with sodium percarbonate. The use of these materials in Lake Leman water disinfection will act as a proxy for the possible success in the field.

2. Material and methods

2.1. Chemical and reagents

Chemicals and reagents were used as received. Hydrogen peroxide (H_2O_2 ; Sigma-Aldrich) and sodium percarbonate ($Na_2CO_3 \cdot 1.5H_2O_2$; Sigma-Aldrich) were used as oxidants in different concentrations. Iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$; Sigma-Aldrich) was used as Fe^{2+} source for the photo-Fenton reaction. Ultrapure (Milli-Q) water (Millipore Elix Advantage 3, Merck) was used for aqueous solutions' preparation (15.8 $M\Omega \cdot cm$) and experimentation in controlled conditions.

2.2. Natural iron sources: herbs and spices

The natural iron materials available for this project consisted of a set of herbs and spices commercially available, from foods with high Fe content. Table 1 shows the content in different metals of different herbs and spices commercially available, according to the product label or, in its absence, our measured values.

Herbs and species were subjected to a calcination process to extract the content of iron (and other metals) removing the organic part. Different combustion temperatures and times, namely 500 and 600 °C (no gas purging, rate 2 °C/min), while 2, 4 and 6 h have been assessed in the optimization step [32–34]. Crucibles were acid-cleaned with 0.1 N H_2SO_4 after each run, and the ashes' stock solutions were prepared with (theoretical) iron concentrations of 125 and 250 ppm (based on Table 1), from which Fe was added to the reactors during experimentation.

Table 1
Metals content in herbs and spices commercially available [30,31].

Name	Iron content (mg/100 g)	Copper content (mg/100 g)	Manganese content (mg/100 g)
Spirulina	123	6.10	1.90
Thyme	82.4	0.86	7.87
Cumin	66.4	0.87	3.33
Curry ^{28,29}	29.7	1.20	8.30
Ginger ^{28,29}	19.8	0.48	33.3
Cinnamon	18.2	0.34	17.5
Cocoa	14.0	3.60	2.50

2.3. Experimental setup

Cylindrical, 100-mL Pyrex batch reactors were used to perform the inactivation experiments. Reactors were acid cleaned after each experiment with 0.1 N H₂SO₄ to prevent potential iron cross contamination, and dried overnight in a Heraeus oven at 120 °C.

Simulated solar light was delivered by a Heraeus SUNTEST CPS solar simulator equipped with an air-cooled Xenon lamp (1500 W, with irradiance regulation system). The emitted spectrum was in the range of 250–800 nm, with 0.5% of the total photons emitted in the UV-B region, approximately 5% in the UV-A region, the photons profile emitted between 400 and 800 nm following the solar spectrum. The global irradiance was monitored with a pyranometer (Th. Friedrichs & Co. Datalogger Combilog 1020) and amounted to approximately 840 W·m⁻². A cooling system consisting of a rectangular vessel with a continuous water flow was used to regulate the temperature inside the reactors; this configuration allowed to discard any temperature changes due to heating and ambient variations. The temperature inside the reactors thus did never exceed 35 °C (exception: temperature influence experiments). A representative image can be found in the Supplementary Scheme S1.

2.4. Preparation and enumeration of *Escherichia coli* K-12

All the experiments were performed with a wild-type *Escherichia coli* K-12 strain (Deutsche Sammlung von Mikroorganismen und Zellkulturen-DSMZ, No. 498). This non-pathogenic strain was selected to approximate the common strains of the intestinal flora of warm-blooded animals [35]. The detailed protocols and growth procedure can be found elsewhere [36]; briefly, this strain was grown to stationary phase by creating overnight aerobic cultures in spiked LB medium at 37 °C. The bacterial suspension was centrifuged, and the solid phase was washed three times by a sterile saline solution (8 g NaCl/0.8 g KCl in 1 L of water). Finally, the bacterial pellet was re-suspended in saline solution, and the concentration was enumerated around 10⁹ CFU/mL.

The samples taken during the experiments were enumerated using the standard plate counting method, through a serial 10-fold dilutions in sterile saline solution; diluted samples of 100 µL were plated on plate count agar (PCA). Colonies were counted after incubation for 24 h at 37 °C. The detection limit (DL) of this experimental method was 10 CFU/mL.

2.5. H₂O₂ and metals' measurements

H₂O₂ was measured according to the DIN 38 409 Method, H15 DEV-18: 20 µL of titanium(IV) oxysulfate (1.9–2.1%, Sigma-Aldrich, Switzerland) were mixed with 1 mL filtered (0.45 µm) sample. The absorbance of the solution was measured at 410 nm with a Shimadzu UV-1800 spectrophotometer.

Energy-Dispersive X-Ray Fluorescence spectrometry (EDXRF) was employed for the determination of the metal contents of the herbs, spices, and their ashes. A Shimadzu EDX-720 spectrometer (Shimadzu Corporation, Japan) was used, equipped with an Rh target X-ray tube (50 W) and a Si (Li) detector using a voltage of 50 kV and auto-tunable current in order to obtain a detector date time of 25%. The equipment was calibrated according to manufacturer's instructions using an aluminum alloy (A750 calibration standard). The analyses were performed in triplicate under vacuum in a polyethylene cell for powder samples with a polypropylene film (suitable for the trace analysis of light elements) and without filter. The measurement diameter and acquisition time were 10 mm and 50 s, respectively. The processing of X-ray spectra was performed using the EDX-720 software package provided by Shimadzu.

For the determination of metals in the media after reaction, inductively coupled plasma mass spectrometry (ICP-MS) was employed to measure trace Al, Cu, Fe and Mn amounts during experiments. A

Finnigan™ ICP-MS 7-238-NU1700 (Nu Instruments, Wrexham, UK) was used, equipped with a double focusing reverse geometry mass spectrometer, with low background signal and high ion-transmission coefficient.

3. Results and discussion

3.1. Selection of reference materials (herbs and spices), calcination conditions and Fe addition levels

Firstly, we assessed the volatilization of the organic matter from the herbs and spices, in order to keep only the inorganic part containing the catalytic metals. The mass loss of the different herbs and spices under study with the different conditions was studied (Fig. S1 of the Supplementary Material details the TGA analysis and cumin as a further example for conventional calcination). After 2 h of calcination the low mass loss indicated insufficient removal of organic compounds, rejecting this calcination time. Beyond that point, no differences were observed between 4 and 6 h of calcination in terms of mass loss (≈ 92%) at both calcination temperatures, confirming the selection of 500 °C and 4 h as the best calcination conditions. Table 2 shows the mass loss and appearance after the calcination of six different spices and herbs at 500 °C for 4 h, except in the case of spirulina, with a calcination temperature of 300 °C (its calcination at 500 °C exerted a pressure that spilled it out of the crucible). As a consequence, and due to the poor catalytic effects material has (probably still containing organic carbon), we have discarded spirulina from the disinfection tests.

Following, the photo-Fenton conditions that would be applied in the next steps were selected, namely the level of Fe addition (0.5 to 2 ppm), the operational pH, and temperature conditions. Briefly, we have encountered negligible differences when the initial Fe addition was varied from 0.5 to 2 ppm; as the increase was rarely accompanied by an enhancement in kinetics, and 0.5 ppm was always slower, 1 ppm was selected for the rest of the tests (see supplementary Fig. S2).

The influence of pH in the final efficiency of the heterogeneous photo-Fenton treatments was tested. Any ash contains high concentrations of K₂O and CaO (Supplementary Table S1 details cumin calcined 4 h at 500 °C as an example), hence the pH of the water increases significantly; a pH ~ 9.4 was obtained. The addition of ashes in ultrapure water resulted in high initial pH; 9.4, 9.6, 9.7 and 9.9 were measured for cumin, thyme, cinnamon, and ginger ashes, respectively. This high increase is attributed to the lack of buffer effect of the ultrapure water.

Basic pH is considered an inhibitory factor for the success of the (photo)Fenton process, hence three different working pH levels were applied (6.3, 7.1 and 9.4) considering a concentration of Fe in the ashes of 1 ppm. Cumin ashes exerted the fastest inactivation (see supplementary Fig. S3) and will be further used for the optimization of the process, but since the differences with the other materials were small (Fig. S2), no other material was discarded yet, besides spirulina. The possible reasons for this apparent contradiction, i.e., the higher efficacy at higher pH, may be related i) to the heterogeneous metal content of the ashes and the varied speciation as a function of the pH as compared to the typical Fe-driven Fenton, and ii) the possible side-effects in bacterial susceptibility to handle oxidative stress in the long run. The bacteria

Table 2
Mass loss (%) after the calcination step of the spices and herbs at 500 °C after 4 h.

Name	Mass loss (%)	Final appearance
Cumin	91.30 ± 0.04	Fine gray powder
Thyme	90.32 ± 0.15	Heterogeneous gray powder
Cinnamon	94.82 ± 0.19	Fine gray powder
Ginger	95.24 ± 0.04	Agglomerated brownish powder
Cocoa	90.18 ± 0.08	Agglomerated gray powder
Spirulina*	44.27 ± 1.96	Very fine black powder

*Calcination temperature up to 300 °C was only achieved.

were previously grown in stationary phase, and suspended in ultrapure water, hence they are metabolically inactive (starvation induced survival mode). The possibility of them being affected by pH directly (e.g., structurally), or indirectly, by other naturally occurring substances, cannot be excluded. It is possible, though, that in a potential field application, rinsing the ashes may alleviate the influence of pH change resulting from the dissolution of the alkaline and alkaline earth metal oxides.

Finally, the influence of temperature was studied, by the application (or absence) of a water-cooling system. Although the temperatures in the field can reach levels similar to our simulation, for the sake of simplifying solar photo-Fenton, an already complex photo-chemical process, we kept temperatures at levels lower than 35 °C, to avoid thermal inactivation of bacteria (see [supplementary Fig. S4](#)), since temperatures above 40 °C may synergistically inactivate *E. coli* [37,38]. Under these conditions, the bacteria are more vulnerable to oxidative stress [39,40]. For this reason, in order to focus just on the enhancement of the optical part of SODIS by the addition of ashes as iron source, hereon, all the experiments show were performed with the cooling system activated.

3.2. Catalytic enhancement of SODIS and photo-Fenton reaction in ultrapure water samples

After the optimization of calcination conditions, ashes from spices and herbs were tested in catalytic enhancement of SODIS and as iron source in heterogeneous photo-Fenton reaction for *Escherichia coli* inactivation. Firstly, the efficiency of ashes as photocatalysts was assessed. A dark control experiments performed with cumin ashes discarded the bactericidal effect, the pH influence within 2 h or the adsorption of bacteria on the ashes. [Fig. 1](#) shows the inactivation results after the combination of solar light with cumin, thyme, or ginger ashes with a theoretical Fe concentration of 1 ppm; SODIS treatment was performed as benchmark. Ashes of thyme and cumin had a photocatalytic effect, clearly enhancing the efficiency reached just for SODIS treatment, contrary to of ginger ashes. Cumin and thyme ashes

combined with an exposition to solar radiation reached a bacterial reduction of 5 logU after 140 min, with kinetic constant rates of 0.077 and 0.074 min⁻¹ respectively, slightly faster than SODIS treatment, 0.066 min⁻¹. The lower efficiency of ginger ashes could be related with the lower iron content in this material, hence the necessary higher addition of ashes to reach the target 1 ppm iron concentration, and the subsequent reduction of the transmittance or in other words, the blocking of sunlight irradiation. Besides, the addition of the ashes raised the pH of water samples from 6.76 observed in SODIS treatment, until values in the range of 9 to 10; that allows to discard the pH influence in inactivation. A summary of the modifications with respect to SODIS kinetics is given at [Supplementary Fig. S5](#).

[Fig. 2](#) shows the *E. coli* inactivation results for heterogeneous photo-Fenton treatments (“phyto-Fenton”) using the ashes of five different spices and herbs (cumin, thyme, cinnamon, ginger, and cocoa). We induced the reaction using 1 ppm of Fe from ashes and 10 ppm of H₂O₂, while control experiments, namely SODIS, 10 ppm H₂O₂/light and solar photo-Fenton with ferrous sulfate (1 ppm Fe²⁺/10 ppm H₂O₂) were also performed.

Cinnamon ashes did not contribute to inducing the photo-Fenton reaction. The inactivation efficiency is similar to the one obtained with SODIS treatment, showing a similar kinetic, and lower than H₂O₂/light treatment. Hence, no enhancement takes place. A low transmittance of radiation in the water samples was measured ([Supplementary Fig. S6](#)) and a significantly higher consumption of H₂O₂ in side-reactions other than ROS generation ([Supplementary Fig. S7](#)). This higher consumption did not lead to a faster *E. coli* inactivation, most probably because H₂O₂ was taking part in secondary reactions occurring at a faster rate compared to the photo-induced reactions leading in cellular damages. As such, cinnamon ashes were discarded as potential metal sources.

Successful use of ashes in solar-assisted process enhancement occurred with thyme, ginger, and cumin. The addition of their ashes in presence of H₂O₂ significantly increased the bacterial inactivation efficiency under light, when compared by the H₂O₂/light treatment

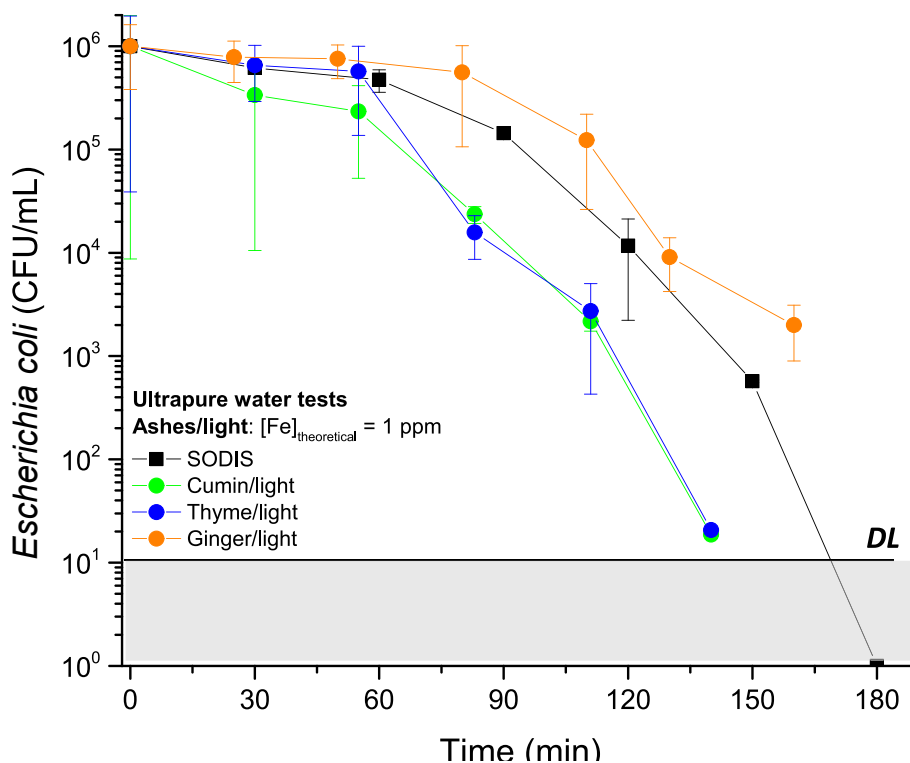


Fig. 1. *E. coli* inactivation efficiency by catalytic enhancement of SODIS in ultrapure water without H₂O₂, using ashes of (●) Cumin; (●) Thyme; (●) Ginger. [Fe_{theoretical}] = 1 ppm.

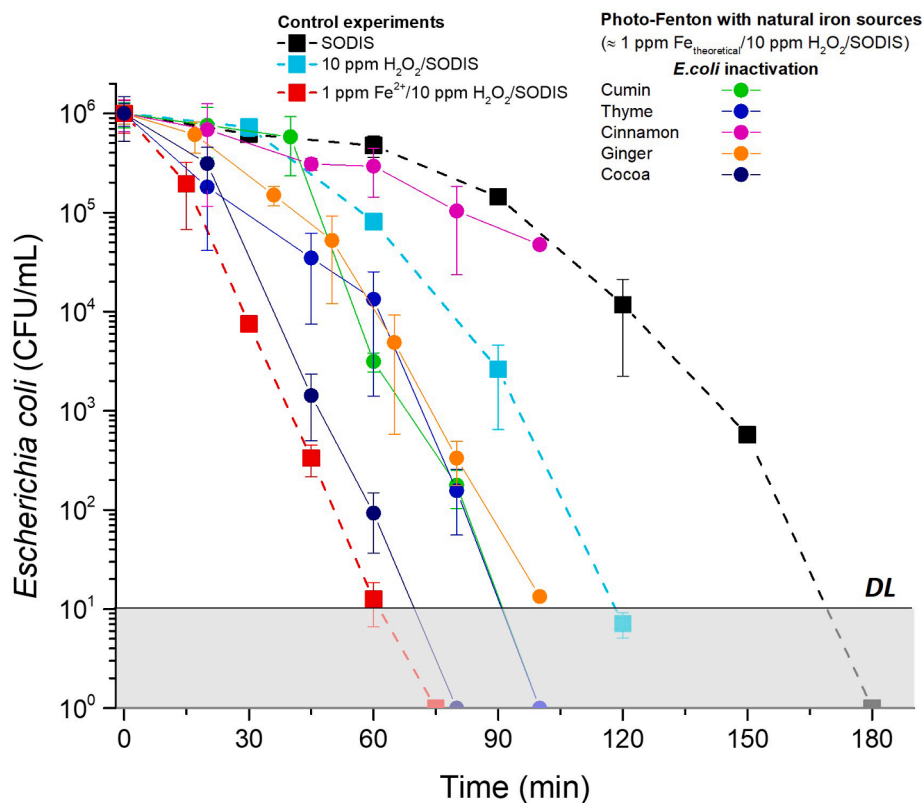


Fig. 2. *E. coli* inactivation efficiency by solar heterogeneous photo-Fenton using different herbs and spices ashes in ultrapure water samples: (●) Cumin; (●) Thyme; (●) Cinnamon; (●) Ginger; (●) Cocoa; (●) Spirulina. [Fe_{theoretical}] = 1 ppm; [H₂O₂] = 10 ppm.

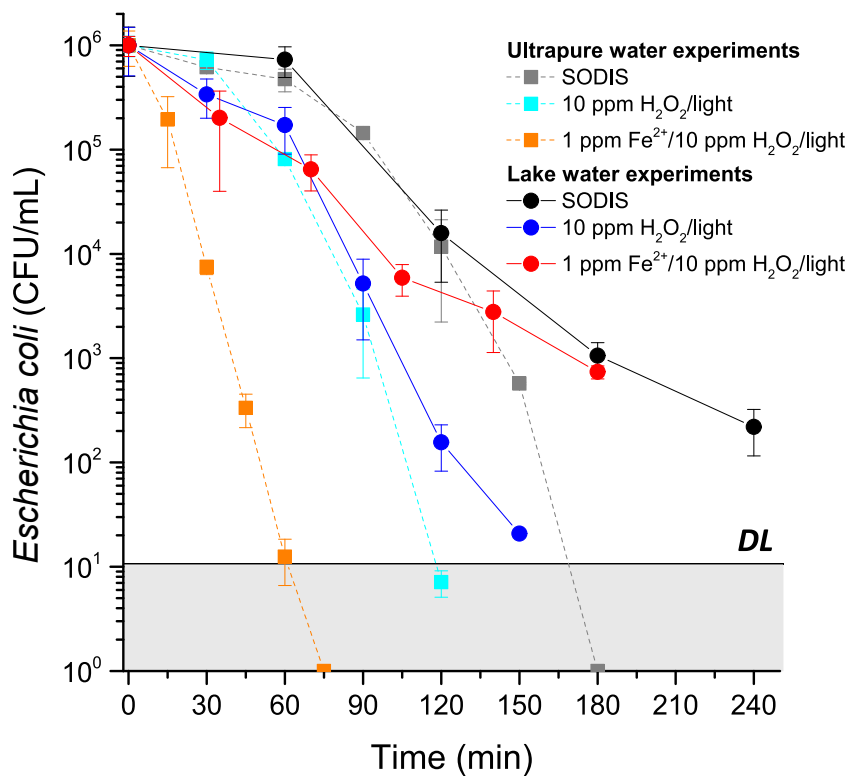


Fig. 3. Effect of water matrix on *E. coli* inactivation with SODIS, H₂O₂/light and conventional photo-Fenton. [Fe²⁺] = 1 ppm; [H₂O₂] = 10 ppm.

(without Fe). Under these operating conditions, total inactivation of bacteria was reached after 105 min, faster than $\text{H}_2\text{O}_2/\text{light}$, and with slightly slower kinetics than $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{light}$. We would like to highlight here that this result is especially remarkable, considering that addition of Fe^{2+} and H_2O_2 in ultrapure water decreased the initial pH to 4.1 while addition of the ashes led to alkaline initial pH. Hydrogen peroxide was consumed in a similar pattern; hence we could suggest that this is an effective application of a basic-pH photo-Fenton. We should note that the fastest *E. coli* inactivation was reached using cocoa as iron source, with total removal after 80 min, or in other words, close to the efficiency of conventional (acidic) photo-Fenton using Fe^{2+} (total inactivation at 75 min). However, the high pH values measured with cocoa ashes addition (10.5–10.6) make it incompatible with direct human consumption, hence we discarded it from the list of candidates and subsequent experiments.

3.3. Application of heterogeneous photo-Fenton reaction with ashes (“phyto-Fenton”) in ultrapure and lake water samples

After the application of heterogeneous photo-Fenton in ultrapure water samples, the efficiency was tested in a more complex and realistic matrix, in order to assess its applicability to water potabilization. We decided to use surface water, because the potential users in developing countries would use similar sources for drinking water consumption. In this case, water from Lake Lemman (Lausanne, Switzerland) was collected and used. Table S2 (Supplementary Material) summarizes the physico-chemical properties of Lemman Lake samples (average from 3 sample campaigns).

Fig. 3 shows the effect that the water matrix brings on the photo-Fenton mediated inactivation of *Escherichia coli*, comparing its conventional form ($\text{Fe}^{2+} + \text{H}_2\text{O}_2$) over ultrapure and lake water samples. Similarly to the existing literature [6], the experiments carried out in ultrapure water samples showed a faster *E. coli* inactivation regarding to lake water samples. These results could be explained by the presence of both organic and inorganic matter in lake water. Organic matter can absorb solar irradiation, producing a light screening effect that limit light absorption of photo-active species (Supplementary Fig. S8). Furthermore, the dissolved organic matter can act as scavenger, quenching reactive oxygen species, and inhibit *E. coli* inactivation. In addition, previous research [41] showed that Lemman lake water presents bicarbonates ions to a concentration as high as 100 mg/L (which is in accordance with our carbonates measurements), which slower the reaction; only low amounts of HCO_3^- have shown not to inhibit the photo-Fenton process or to act synergistically [42]. Hence, while total inactivation was obtained in 75 min in ultrapure water, only 3-logU reduction was reached after 180 min when lake water was treated.

The baseline control experiments and constituents of the photo-Fenton process also helped elucidate the process. Specifically, in the case of $\text{H}_2\text{O}_2/\text{SODIS}$ system very low differences in the consumption are observed (50 and 48% in ultrapure and lake water samples respectively), following the trend of the small differences observed on the *E. coli* inactivation independently of the water matrix by this process. However, contrary to the $\text{H}_2\text{O}_2/\text{SODIS}$ process, the photo-Fenton systems showed significant differences in the H_2O_2 consumption (91 and 64% in ultrapure and lake water samples, respectively). Firstly, the presence of inorganic ions reduces the osmotic stress for *E. coli*, hence a possible physical effect is prevented. Besides, pH is another critical variable in this comparison; ultrapure water samples have a pH around 6.5, while the lake water had an average pH value of 7.9. At this pH, the dominant iron (II) species in lake water is $\text{Fe}(\text{OH})_2$, and Fe^{2+} precipitates reduce the efficiency of the treatment [43]. The amount of generated hydroxyl radicals and other reactive species is decreased, thus limiting the capability of the process to reach high inactivation levels. On the other hand, the addition of iron for the photo-Fenton reaction in ultrapure water samples reduced the initial pH to 4, a pH where the Fenton reaction still proceeds in a radical mechanism [44] and hence is expected

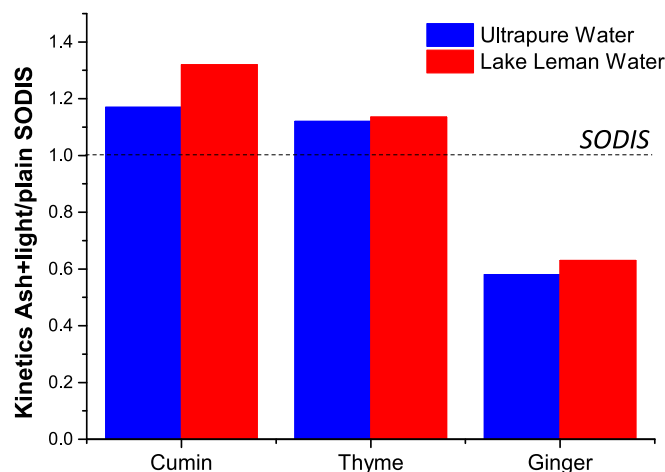


Fig. 4. *E. coli* inactivation efficiency enhancement by ashes addition under sunlight radiation: comparison of ratio Ash + light with plain SODIS in ultrapure vs. lake water samples.

to be very effective against bacteria.

After the assessment of the water matrix influence, we assessed the substitution of Fe^{2+} by iron from the ashes of burnt spices and herbs. As a control test, we performed the experiments in absence of H_2O_2 ; Fig. 4 shows the results corresponding to the utilization of ashes (1 ppm theoretical Fe) to sunlight radiation, compared to the SODIS (without ashes) in either ultrapure or lake water (Supplementary Fig. S9 shows the detailed ash/light kinetics in lake water). We report that all ashes, namely cumin, thyme, and ginger (Ash + light process) enhanced inactivation even more than the respective experiments in ultrapure water. In the case of ginger though, the net result remains inhibitory (ratio Ash + light/SODIS less than 1). We postulate that the addition of Fe from the ashes brings the enhancement in a similar manner to ultrapure water experiments, but in lake water tests, the pH increase due to the ashes addition is smaller. Specifically, from an initial 7.9 pH (lake water) the final pH of the experiment did not surpass 9.14, 8.96 and 8.65 for cumin, thyme, and ginger, respectively; this is attributed more to the buffer effect of the lake water matrix and less to the presence of dissolved organic matter which can complex the metals contained in the ashes. As such, the metals/metal oxides possibly stay dissolved for a longer time, and effectively participate in a ligand-to-metal charge transfer (LMCT) process with the bacterial cell wall and/or semiconductor-type photo-killing, resulting to faster inactivation.

Fig. 5 shows the disinfection results after the application of heterogeneous photo-Fenton (“phyto-Fenton”) with cumin, thyme and ginger ashes as iron source. Under these operating conditions and judging from the observed kinetics, homogeneous photo-Fenton reaction most likely did not take place, reaching less than 3.5 logU inactivation after 180 min of treatment. On the other hand, experiments involving cumin and thyme ashes were significantly enhanced, compared to $\text{H}_2\text{O}_2/\text{light}$ and homogeneous photo-Fenton. It appears that the metals in the ashes are not equally susceptible to precipitation due to the alkaline pH as the Fe^{2+} salts and permit a photo-Fenton process.

The results presented in Fig. 5 indicate that addition of any of the prepared ashes in lake water and in presence of H_2O_2 , namely the “phyto-Fenton” process, can effectively enhance bacterial inactivation. Chemically speaking, literature reporting effective photo-Fenton process at alkaline pH is scarce [45,46] and at values that high has not been demonstrated before, so further investigation on the possible steps have to be performed. As far as a treatment of a surface water is concerned, the addition of either ash, or ash/ H_2O_2 leads to higher bacterial removal than SODIS and light/ H_2O_2 processes and that ashes of iron-containing vegetables could play the role of the photocatalyst in situations of Fe^{2+} salt shortage or difficulty of storage.

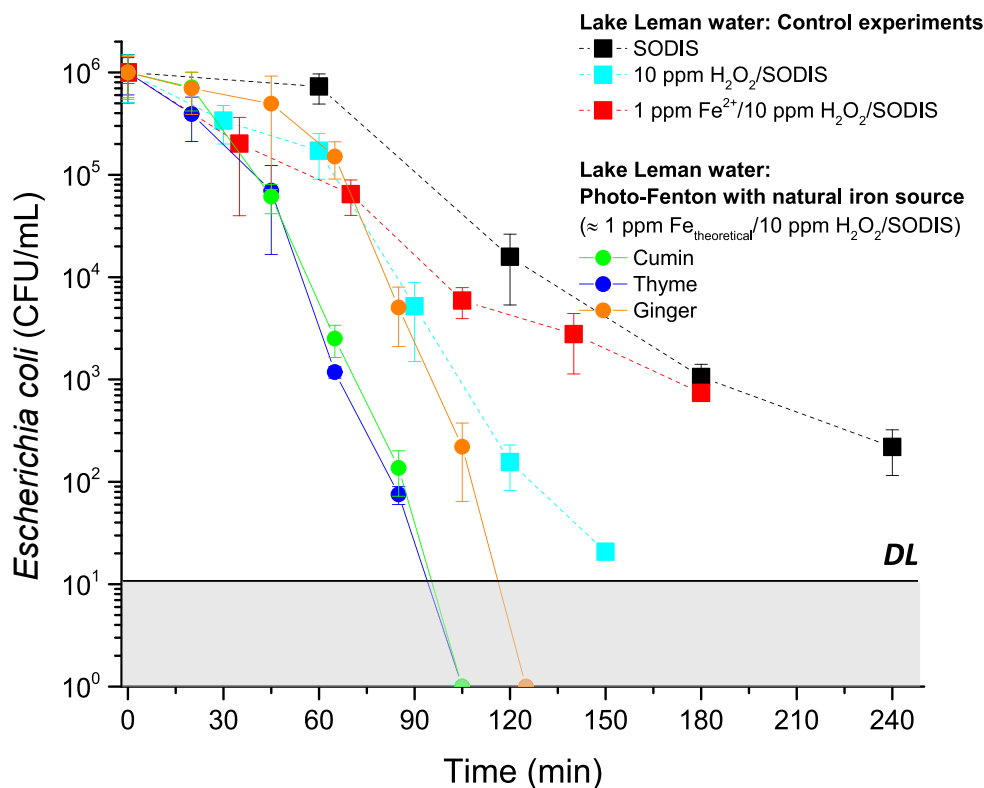


Fig. 5. *E. coli* inactivation efficiency by solar heterogeneous photo-Fenton using different herbs and spices ashes in lake Lemman water: (●) Cumin; (●) Thyme; (●) Ginger. [Fe_{theoretical}] = 1 ppm; [H₂O₂] = 10 ppm.

3.4. Sodium percarbonate (SPC) as an alternative source of H₂O₂ for the Fenton reaction in lake water

The efficiency of alternative oxidants to H₂O₂ was assessed. Fig. 6a shows the *E. coli* inactivation results after the substitution of hydrogen peroxide with sodium percarbonate (SPC) in experiments that took place in Lake Lemman water. The treatments with H₂O₂ and solar light showed very similar results, reaching 4 logU in approximately 120 min of reaction independently of the kind of oxidant, i.e. H₂O₂ of solid or aqueous origin. However, in Lake Lemman water the addition of Fe²⁺ to induce the photo-Fenton process is not very effective; as shown in the control experiment (Fe²⁺/H₂O₂/light), the addition of Fe does not enhance bacterial inactivation. If SPC is used as a precursor of H₂O₂, the process is slightly faster than in absence of Fe. Hence, we can suggest that SPC could replace H₂O₂ in solar processes even if it induces a pH increase; we note that the addition of SPC increases the Lake Lemman water from 7.9 to 9.37.

Replacing iron salts with ashes did not reach a significant enhancement, except for the use of cumin ashes. As observed in the Fig. 6b, thyme and ginger ashes did not improve the efficiency of photo-Fenton treatment with SPC. The inhibition observed for the experiments involving the three ashes, which are supported by hydrogen peroxide consumptions, might probably be due to the scavenger effect associated with (bi)carbonate ions; an additional increase takes place due to the Na₂CO₃ salt in the SPC molecule. However, although the use of SPC presented slightly lower inactivation efficiency compared to the use of hydrogen peroxide, it allows an effective treatment, with or without the addition of Fe²⁺; the advantages of using SPC in terms of handling, storage, and use, make it attractive and a serious alternative in challenging contexts.

3.5. Mechanistic interpretation: proposition of an integrated inactivation pathway

The experiments that took place in the previous sections have intended to assess the possibility of SODIS enhancement in a resource-poor context, hence alternative, low-cost additives were sought. Table 3 summarizes the previous experiments, in ultrapure or Lake Lemman water, with three types of ashes, from a kinetic standpoint.

The fastest kinetics were obtained at acidic pH in ultrapure water, where H₂O₂ was apparently employed for bacterial inactivation (~91% utilization) and not for side-reactions. Addition of ashes converted the media to alkaline, hence the iron precipitation and less effective “phyto-Fenton” is obvious from the H₂O₂ consumption; even less H₂O₂ than in the absence of ashes was used. Nevertheless, faster kinetics were observed in the ash/H₂O₂/light system, and thus, we postulate that the iron added had an effect on bacteria. The pH 9.4 is consequence of the ashes addition to water, and although it exceeds 8.5, the maximum recommended by the World Health Organization for drinking water, the WHO indicates that this pH is based on aesthetic considerations and a broader pH range could be acceptable [2]. Therefore, the ashes could be used as a natural iron source to enhance SODIS treatment by the photo-Fenton reaction.

In lake water, the (homogeneous) photo-Fenton is significantly hampered, demonstrated by the slow kinetics and the lower H₂O₂ consumption. However, in presence of ashes the pH increase was lower, which is more favorable for post-treatment consumption. Furthermore, although the H₂O₂ consumption was similar to ultrapure water, the effectiveness of the heterogeneous reaction was multiple times higher than the homogeneous, and twice as fast than H₂O₂/light. Despite the presence of Natural Organic Matter (NOM), (bi)carbonates and other substances which can scavenge radicals, the photo-Fenton process still takes place. The comparison is still between a neutral pH process with alkaline pH, without efficacy loss; as such, if H₂O₂ is available, we propose that the ashes can drive an effective photo-catalytic

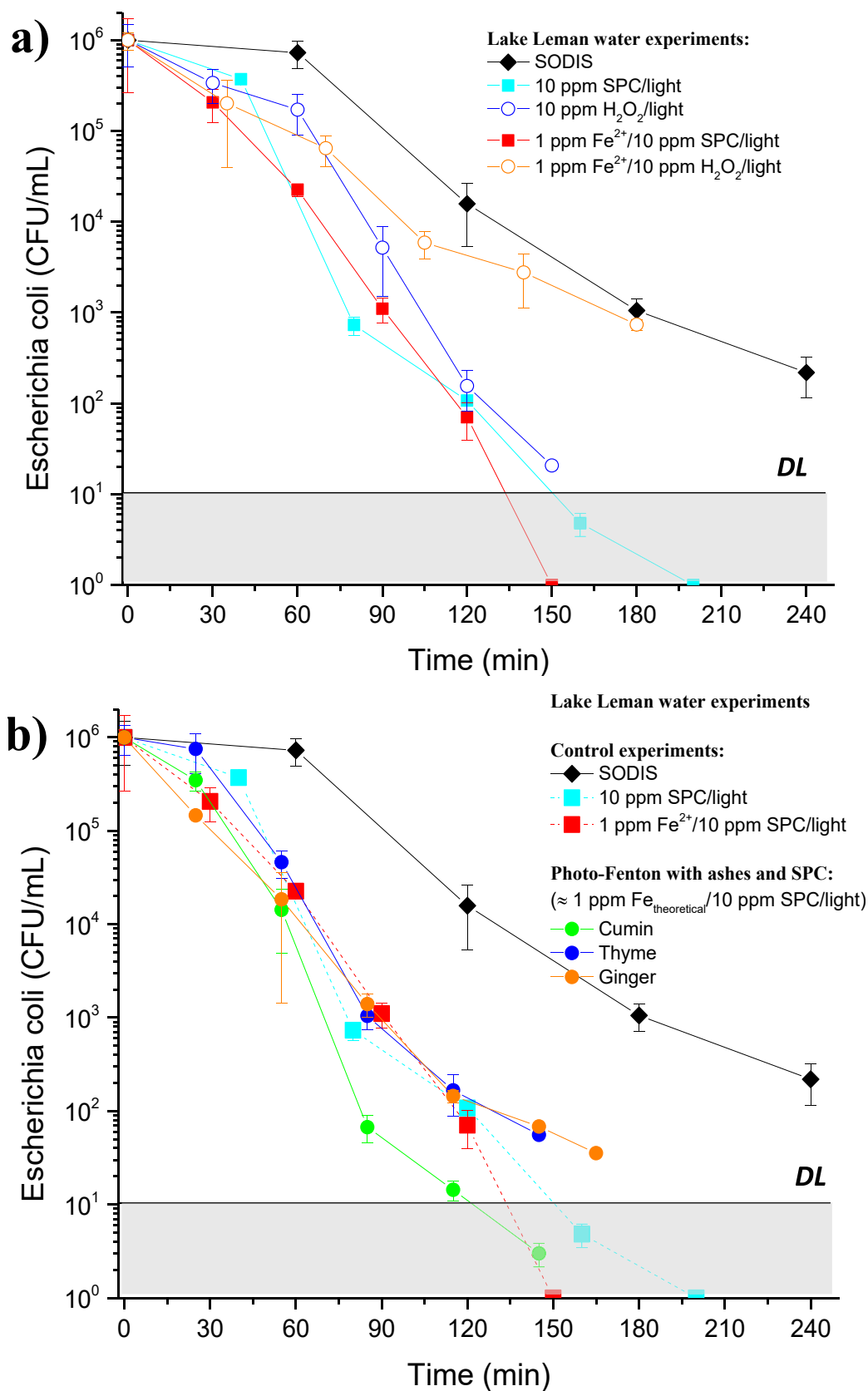


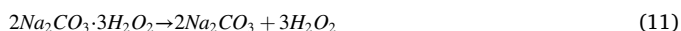
Fig. 6. A) Comparison between the application of SPC and H₂O₂ as oxidant in *E. coli* inactivation in lake Leman water. b) *E. coli* inactivation efficiency by solar heterogeneous photo-Fenton using different herbs and spices ashes in lake Leman water (● Cumin; ● Thyme; ● Ginger, and SPC as oxidant. [Fe_{theoretical}] = 1 ppm; [SPC] = 10 ppm.

Table 3Summary of the results associated with *E. coli* inactivation in different water matrices and sources of the Fenton reagents.

		(Heterogeneous) "phyto-Fenton" (i.e. Fe from ashes/light/H ₂ O ₂)			Homogeneous photo-Fenton	H ₂ O ₂ /light
		Cumin	Thyme	Ginger	(i.e. Fe ²⁺ /light/H ₂ O ₂)	
Ultrapure water	<i>k</i> _{obs} (min ⁻¹)	0.107	0.102	0.101	0.192	0.089
	H ₂ O ₂ consumption (%)	41.6	38.7	28.7	90.7	50.1
	Initial pH	9.39	9.59	9.89	4.11	6.76
Lake Leman water		Fe from ashes/light/H ₂ O ₂			Fe ²⁺ /light/H ₂ O ₂	H ₂ O ₂ /light
	<i>k</i> _{obs} (min ⁻¹)	0.125	0.123	0.097	0.041	0.060
	H ₂ O ₂ consumption (%)	42	39	29	63.8	47.7
Lake Leman water		Fe from ashes/light/SPC			Fe ²⁺ /light/SPC	SPC/light
	<i>k</i> _{obs} (min ⁻¹)	0.091	0.07	0.064	0.094	0.068
	H ₂ O ₂ consumption (%)	67.1	66.5	66.1	30.1	68
	Initial pH	9.57	9.54	9.43	9.23	9.37

enhancement of bacterial inactivation in surface water.

The use of SPC as an H₂O₂ source led to a good SODIS enhancement, and a better photo-Fenton process with Fe²⁺. The overall "phyto-Fenton" process is decreased by SPC but maintains comparable kinetics to Fe²⁺ and higher than the SPC/light. The inhibition observed for the experiments involving the three ashes, which are supported by hydrogen peroxide consumptions, might probably be due to the scavenger effect associated with carbonates and bicarbonates ions, as illustrated in reactions 11–13. The presence of these ions indeed inhibits the oxidative attack of hydroxyl radicals, thereby offering a protective effect on bacteria. In addition, it is worth noticing that bicarbonate ions predominate over carbonates in the pH ranges indicated in Table 3, since the pKa associated to the dissociation of bicarbonates ions into carbonates ions is 10.33.



Hence, we propose that SPC is a viable alternative, and the SPC/ashes Fenton process is an effective SODIS enhancement. As we have previously mentioned on several occasions, this enhancement of SODIS would have as target consumer users in challenging contexts, but still in the need of an efficient and safe, but simple technology. For these reasons, the search of reagents easily to use and to handle is recommended in these treatments. Ashes of spices and herbs are the alternative to conventional iron reagents, leading to the novel "phyto-Fenton" modification, while the sodium percarbonate (Na₂CO₃·1.5 H₂O₂) would be the alternative to hydrogen peroxide.

However, despite the apparent influence of ashes in the induction of the photo-Fenton process, the exact inactivation mechanism of "phyto-Fenton" is not evident. In this part, we attempt to dissociate the various actions and propose an integrated mechanism for the SODIS enhancement.

Firstly, in all cases, SODIS is the baseline damage, and regardless of the H₂O₂ precursor, the type of damage is similar. Hence these two actions will be assessed first:

i) **Solar light only:** the UVB, UVA and visible light have documented efficacy against *E. coli*, hence the typical shouldered inactivation (linear with lag phase) is expected and observed here. The matrix influences SODIS, bringing a decrease in kinetics, since the transmittance is lower; the presence of organic matter is screening light, decreasing its transmission. Besides, the presence of (low) suspended solids may cause shielding and aggregation and deter the inactivation rates (for more details, interested readers should refer to [12,42,47,48]).

ii) **Addition of H₂O₂:** the addition of 10 mg/L H₂O₂ enhances inactivation due to the increased presence of H₂O₂ inside the cell [49]; H₂O₂ mediates towards an intracellular Fenton-type damage for bacteria [50–52]. The extracellular damage is negligible, or at least non-lethal at this short timeframe of experiments. The use of liquid or solid H₂O₂ precursor does not directly affect bacteria, although from Table 3 we report a higher H₂O₂ loss for similar inactivation, probably due to side-reactions with the matrix.

However, when ashes are introduced in the bulk, there are new pathways that occur, in absence or presence of H₂O₂. In absence of H₂O₂, the metals contained in ashes may induce a semiconductor photocatalytic effect, while in presence of H₂O₂, the heterogeneous photocatalytic effects of the "phyto-Fenton" process are predominant.

1) Addition of ashes (without H₂O₂): Semiconductor action mode

Table 4 details the content of the main metal oxides with possible photo-catalytic activity in the different calcinated herbs and spices. The use of herbs and spices ashes present a great variety of different metal oxides as it is shown in Table 4, with the hematite iron oxide form being the main one. However, the presence of other metal oxides, such as ZnO, MgO, TiO₂, or CuO among others, can contribute to *E. coli* inactivation as it has been previously reported [53–56]. Other semiconductors (e.g. NiO) may not result in effective generation of transient species below sunlight due to their wide band gap [57]. In this sense, and although their degree of participation may be minor compared to the influence that iron exerts on the reaction, the proposed "phyto-Fenton" mechanism should include the action of different metal oxides as photocatalysts that generate reactive oxygen species.

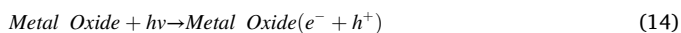
In the semiconductor action mode, the metal oxides absorb sunlight radiation that promotes the excitation of electrons to the conduction band (CB) generating holes in the valence band (VB). When the CB of photosensitizer shows a more negative potential than that of O₂/O₂^{•-} (-0.33 eV/NHE), the e⁻ at the CB will take advantage of the O₂ to

Table 4

Appearance of metal oxides with possible catalytic activity in the results of the XRF analysis of the ashes from different herbs and spices (the complete list is given in the Table S3).

Metal oxide (%)	Herbs and spices ashes					
	Cumin	Thyme	Cocoa	Ginger	Cinnamon	Curry
Fe ₂ O ₃	3.08	1.57	0.97	4.95	3.58	4.19
CuO	0.20	0.12	0.43	0.21	0.17	0.30
MnO	0.37	0.07	0.29	4.53	3.50	0.57
SrO	2.88	0.47	0.23	0.26	1.31	1.18
ZnO	0.51	0.22	0.65	0.44	0.27	0.46
MgO	0.53	0.31	0.52	0.57	0.11	0.51
TiO ₂	–	0.11	–	0.12	0.08	–

generate O_2^- ; this depends on the position of the CB and it is verified in iron or copper oxides and TiO_2 . Furthermore, $\bullet OH$ can be generated by O_2^- . Besides, h^+ on VB would exploit the OH^- (especially at the basic pH of operation) or H_2O in the aqueous phase to generate $\bullet OH$, when the VB is more positive than 2.4 eV/NHE or 2.72 eV/NHE ($OH^-/\bullet OH$, $H_2O/\bullet OH$) [58]. It has been demonstrated that the excitation and production of holes in the band gap oxidize bacterial membranes leading to bacterial inactivation. These band gap values normally encountered in iron oxides do not permit the oxidation of water to produce $\bullet OH$ [43], but do so e.g. in TiO_2 . There is however direct bacterial cell wall oxidation by the holes. Meanwhile, different Reactive Oxygen Species (ROS) as 1O_2 or O_2^- with demonstrated bactericidal action, can be generated through electrons using oxygen as electron acceptor [59]; a summary of the above mechanisms is provided in reactions 14–19:



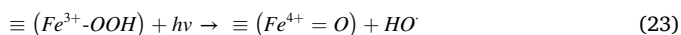
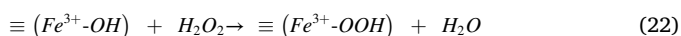
2) Addition of ashes in presence of H_2O_2

a) Heterogeneous photo-catalytic inactivation of bacteria.

As Table 4 details, a series of oxides are present in the bulk of the solution. Among these metals, many of them can participate in Fenton and Fenton-like reactions; besides iron (Fenton), copper, magnesium, manganese and zinc can generate hydroxyl radicals in the interface among bacteria and the oxides, enhancing their inactivation [60]. Some of the abovementioned can also regenerate via LMCT and re-participate in the catalytic process; an indicative set of reactions is provided below (reactions 20–21), “ \equiv ” indicates reactions on the surface of the oxide):



Besides, under light, iron oxides have demonstrated an additional hydroxyl radical generation pathway (22–23) [61]:



Nevertheless, according to the results summarized in Table 4, a correlation between the efficacy of the ash as a photocatalyst and the contents in iron cannot be directly made. Ginger, cinnamon, and curry contain more iron (%) but their overall efficacy is lower than cumin and thyme. Hence more pathways and more metals have to be involved.

b) Homogeneous photo-catalytic inactivation of bacteria.

Considering that illumination of metal oxides of ashes leads to metals leaching [40] which in turn can enhance bacterial inactivation, then the possibility of a homogeneous reaction in the bulk may take place. In this case, there are two likely pathways from the point of view of bacterial inactivation. The first one is related with the easy diffusion into the bacterial cell, promoting the internal oxidative processes, such as an intracellular photo-Fenton process [11,62], while the other is a bulk Fenton or Fenton-like process. ICP-MS analysis performed shows dissolved metals concentration in the range of ppb, as summarized in

Table 5

ICP-MS results of metal's leaching from herbs and spices ashes, found in the bulk of ultrapure water during the heterogeneous photo-Fenton inactivation of *E. coli* (the complete list can be found in Table S4).

		Cumin	Thyme	Ginger
Fe (ppb)	Initial	5,44	4,23	5,80
	Final	5,09	2,38	4,89
Cu (ppb)	Initial	0,64	0,75	1,89
	Final	1,03	1,05	1,09
Mn (ppb)	Initial	0,48	0,37	0,62
	Final	0,79	0,48	0,94

Table 5. The presence of other metals or metal oxides different to iron, for instance copper or manganese, could play an interesting role in the inactivation of *E. coli*. We observe a loss of Fe over the duration of the test, a further release of Mn, while Cu presents both behaviors. Nevertheless, if we take cumin for instance, we inserted the equivalent of 1 mg/L of Fe in form of ash, and only 5 ppb or 0.005 mg/L of Fe are in solution; the other metals are in even less quantities, hence the homogeneous pathway has minimal contribution or can practically even be ignored; the oxidation of Fe^{2+} is pH dependent, and is faster as pH gets higher [43]. Hence, the participation of a homogeneous pathway at pH > 9 is small.

In overall, considering the kinetic results, the initial metal contents of the ashes and the dissolved metals in solution, a direct chemical correlation with the bactericidal kinetics cannot be formulated. Most likely, the screening effect (absorbance) of the ashes mentioned before (Fig. S6), and the agglomeration of the ashes (Table 2) must dominate the photonic and catalytic aspects, respectively, resulting to a highly complex net action. Nevertheless, based on the mechanisms previously reported, Fig. 7 summarizes the general metal oxide-driven photo-catalytic bacterial inactivation via the “phyto-Fenton” process, integrating the aforementioned actions of light, extracellular oxidative stress, as well as the homogeneous and heterogeneous photo-Fenton actions.

4. Conclusions

The enhancement of SODIS in resource poor environments may rely in un-orthodox means. Although in laboratory settings the enhancement of SODIS with $Fe^{2+}+H_2O_2$, i.e., the photo-Fenton process is a relatively simple task, the means used in the field may vary significantly. As such, in this work we demonstrated that the ashes of various spices and herbs may be used to enhance SODIS. Firstly, we proved that ashes enhance bacterial disinfection in pure water and this process was always faster than plain SODIS. If the photo-Fenton process is intended to be induced, light/ H_2O_2 process was always enhanced by the addition of low ppm values of theoretical iron, or a very low amounts of ashes; although this process was slightly slower, kinetics-wise, than the addition of Fe^{2+} in salts form, the effective use of ashes opens the possibilities of further application of the “phyto-Fenton” process.

In lake water, adding ashes of cumin, thyme or ginger always brought an enhancement in inactivation, and in even higher amounts than in ultrapure water. This baseline enhancement led to an increase in the photo-Fenton efficacy, which was hampered in the Lake Leman water; replacing Fe^{2+} with ashes led to significantly faster kinetics of photo-Fenton and light/ H_2O_2 , even at the naturally occurring alkaline pH values of the lake water and the ashes addition. Finally, the use of sodium percarbonate (SPC) as a liquid H_2O_2 replacement was validated, and the ash/SPC photo-Fenton process was equally effective as the Fe^{2+}/H_2O_2 or in cases faster (e.g., cumin).

In overall, our recommendation for a field application would be to use ashes as SODIS enhancement and if H_2O_2 is commercially available, it would constitute a desirable enhancement. We must note here that although SPC is a viable alternative for H_2O_2 concerning storage and handling, the logistics of SPC distribution and vending in resource-

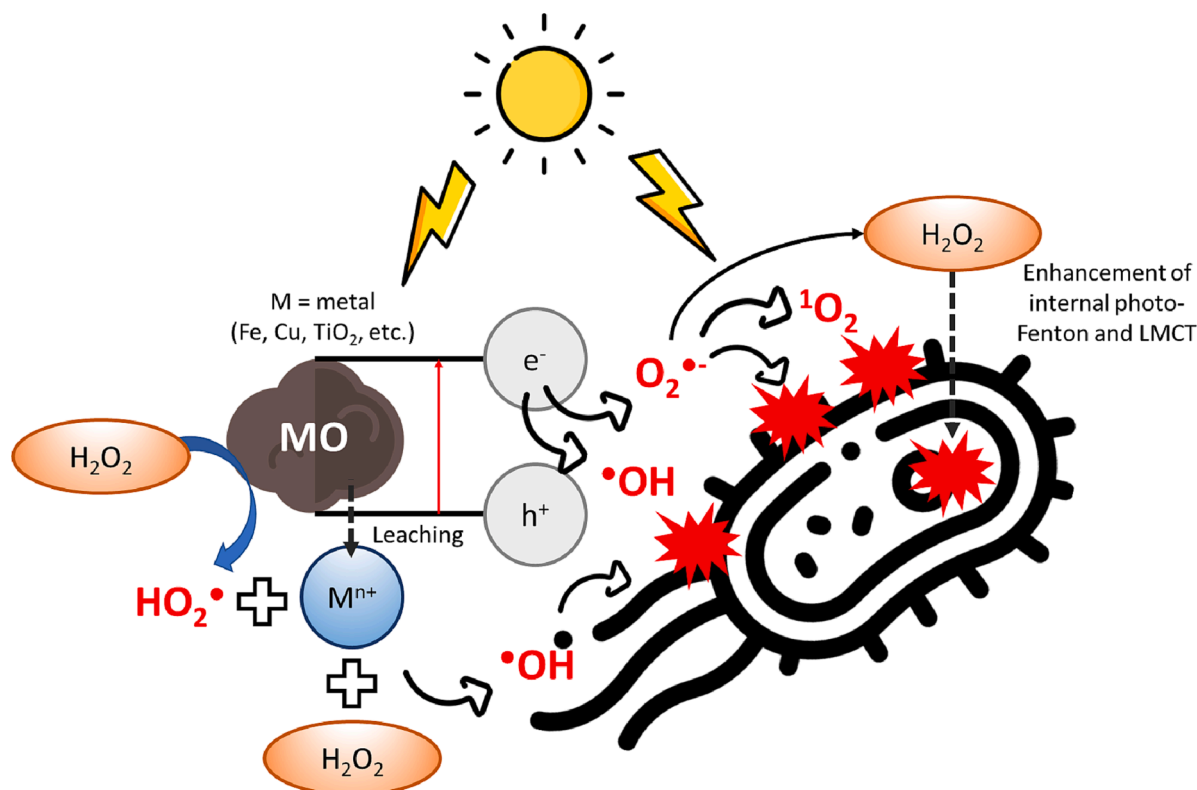


Fig. 7. Proposed integrated inactivation pathway through the use of herbs and spices ashes as substitute of iron salts.

challenged environments is still a caveat that may limit further divulgation of the “phyto-Fenton” towards the populations in need.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2023.142598>.

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