



Sunshine and a pinch of tropical soils: A natural, low-cost photo-Fenton variation for safer water, assisted by H₂O₂ or percarbonate

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ABSTRACT

Clean water is essential for human survival, but access to safe drinking water remains a challenge in resource-limited regions. Herein, we explored a low-cost but effective solution for water potabilization using natural iron sources from soils along with sunlight to remove coliforms from water. We evaluated 30 soil samples from tropical regions and among them, we found that soils from Colombia and Cameroon with high clay content and low carbon levels were the most effective catalysts. Their combination with H₂O₂ enhanced the solar disinfection (SODIS) yield and induced a heterogeneous photo-Fenton process with secondary homogeneous contribution and/or photocatalytic action. We also found that storing soils in acidic conditions increased the concentration of soluble iron species, leading to enhanced *E. coli* removal due to homogeneous Fenton and Fenton-like processes. The addition of citrate as a ligand further improved the performance of the system, by facilitating the regeneration of dissolved iron, through metal chelation, thanks to the formation of photo-active complexes. Moreover, we explored the possibility of using sodium percarbonate as a substitute for H₂O₂ and found it to be a successful alternative, even over alkaline lake water samples. We discuss the mechanism behind the improved activity of sodium percarbonate and suggest that ferruginous soils, when combined with any form of H₂O₂, can induce the photo-Fenton process over a wide pH range and at low mg/L concentrations. Our study provides valuable insights into the potential of using natural iron sources to enhance solar disinfection, making clean water more accessible to communities in need.

1. Introduction

Nowadays, finding solutions to the water crisis is more important than ever. Providing at least improved drinking water sources in areas where there is no safe water supply has been prioritized by the Sustainable Development Goals (SDG6). Under this scope, solar disinfection (SODIS) as a water treatment technology has been widely accepted,

because of its high positive human health impact, proven reduction of viruses, bacteria and protozoa in water, simplicity and low cost [1]. Nevertheless, the length of time required to treat water is one of the most important drawbacks because a minimum of 6 h is required on sunny days to ensure the total disinfection of water [2].

The photo-Fenton process has emerged as a viable and safe alternative to increase the speed and efficacy of SODIS treatment [3]. In solar

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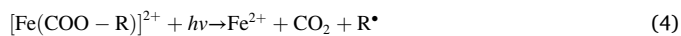
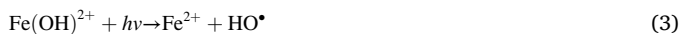
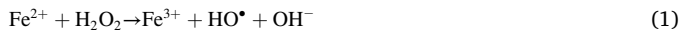
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photo-Fenton, the process is driven by sunlight and it plays the role of iron regenerator, or in other words, the enhancement of the Fenton process itself [4]. The main reactions occurring in (homogeneous) solar photo-Fenton are as follows (Eqs. (1)–(4)):



As observed in Eqs. (1)–(4), the photo-Fenton process requires the use of an oxidizing agent, such as hydrogen peroxide (H_2O_2), and a metal catalyst like iron (Fe), which makes its application in developing countries operationally complex for two reasons: (1) the operation can be performed by people with minimal training, to ensure the safe handling and storage of the reagents, despite the obvious simplicity of the treatment; (2) the increased cost of the treatment (compared to SODIS), despite the low concentrations of hydrogen peroxide and iron used. Therefore, it is necessary to search for innovative solutions to minimize the disadvantages of the application of the photo-Fenton process in low-income countries.

The use of metal oxides has been successfully reported, especially hematite (Fe_2O_3), not only as an iron source to promote Fenton's reaction but also because of their action as semiconductor photocatalysts [5–9]. These two modes of action run in parallel as opposed to one of them being a prior mechanism [1,10,11], occurring on the surface of the oxides [12], apart from equations 1–2 when a photon with an energy greater than the band gap gets absorbed by the iron oxide, a hole-electron pair is generated. These pairs can lead to redox reactions that can produce reactive oxygen species (ROS) or reduce surface Fe^{3+} to Fe^{2+} . Recombination of these pairs is also a possibility.



Besides, as mentioned before, iron oxides can also drive a heterogeneous photo-Fenton [13,14], similar to the bulk, but occurring on the oxide–water interface. Hence, their implementation in a SODIS enhancement seems a desirable modification, and acquiring this resource remains the question at hand.

In nature, iron in soil is a result of primary rock weathering, a process that dismantles rocks and minerals such as pyrite. The weathering process results in “secondary” iron - containing minerals, with the most important being iron-containing silicate clays and iron oxides. The iron oxides encountered in soil will most likely be goethite, hematite and lepidocrocite, with goethite and hematite being the dominant forms due to their high thermodynamic stability. For this reason, the use of mineral soils and/or clays as iron sources is considered as a low-cost alternative to iron salts [15,16]; iron-rich soil can be a free source, while (commercial) iron oxides have a cost of 0.75\$/kg [17]. Some authors have reported the use of raw or modified natural clays to improve the efficiency of the photo-Fenton process [15,18–22], but there is limited research on their use focused on water disinfection by improving the SODIS process through a heterogeneous solar photo-Fenton process.

Finally, in order to make solar photo-Fenton a viable method for drinking water treatment in low- or middle-income countries (LMICs), it is important to study alternatives to concentrated liquid hydrogen

peroxide because of their relative difficulty of transporting, handling and storing a liquid due to its instability. A more practical H_2O_2 source for the implementation of solar photo-Fenton is the use of sodium percarbonate. Percarbonate is significantly easier to implement on site, being in solid form, and dissolves in water yielding H_2O_2 . However, the use of sodium percarbonate is not without disadvantages, such as the unavoidable addition of carbonate to the aqueous matrix, i.e. a scavenging substance that traps hydroxyl radicals and thus inhibits the photo-Fenton process, especially when encountered in high concentrations [23,24]. Furthermore, its use leads to an increase in pH which is also clearly a disadvantage for the photo-Fenton process due to iron precipitation. Nevertheless, different authors have studied and compared sodium percarbonate as an alternative to hydrogen peroxide along with iron species to degrade chemical pollutants alone or activated [25–28], hence its use may be beneficial in SODIS enhancement and photo-Fenton induction.

As made clear from the above considerations, the main goal of this research is to study the SODIS enhancement by the photo-Fenton reaction by natural iron sources and alternative hydrogen peroxide sources to facilitate its implementation in LMICs, isolated or rural areas. Under this scope, this research studies the catalytic efficiency of tropical soils as a natural iron source under the action of heterogeneous photocatalytic phenomena take place. Special focus has been given in providing easily determinable characteristics that are correlated with an expected activity (e.g., clay and C content) apart from their iron content. In addition, in order to provide practical recommendations for the application of this process in small- but field-scale, we study the effect of acidic storage of iron/soil and the influence of co-storage with iron complexing ligand (i.e., citrate). This strategy may reuse food wastes (i.e., lemon or orange peels) to decrease the pH and facilitate the decrease. Finally, to overcome some of the costs related with the use of liquid H_2O_2 , the use of sodium percarbonate as an alternative source has been studied as a SODIS enhancement to facilitate the solar photo-Fenton process. To validate the aforementioned tests, assays have been performed in natural surface water (Leman Lake water, Switzerland) with highly encouraging results on the applicability of the process.

2. Material and methods

2.1. Chemical and reagents

Chemicals and reagents were used as received. Hydrogen peroxide (30% H_2O_2 ; Sigma-Aldrich) and sodium percarbonate (20–30% $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$; Sigma-Aldrich) were used as oxidant in different concentrations. Iron (II) sulfate heptahydrate (97% $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$; Sigma-Aldrich) was used as iron source for the (homogeneous) photo-Fenton reaction. Stock solutions were prepared with ultrapure water, i.e., purified milli-Q® water (15.8 MΩ·cm) using an Elix 3 Millipore system, equipped with a Progard filter (Millipore AG, Switzerland). The pH was measured with a Mettler Toledo S220 Seven Compact™ pH/Ion meter.

2.2. Natural iron and water sources

This work has tested different soils as natural iron sources for SODIS enhancement and photo-Fenton induction. Table 1 summarizes the characteristics and origin of the different soils tested. These samples have been collected from different soil types of Colombia and Cameroon (Inceptisols, Ferralsols) [29,30]. As observed in the table, the composition of clay and carbon content is different in all the soil samples. An iron-containing soil from a mine in Colombia (denominated CMS) was previously reported by Villegas-Guzmán et al. [16], with an iron content of the soil estimated in 81.26 %, predominantly $\alpha\text{-Fe}_2\text{O}_3$, determined by X-ray fluorescence analysis, a size of $< 1 \mu\text{m}$ as defined by HR-TEM, a band gap of 1.1 eV, and a specific surface area of 19.79 m^2/g [16]. Different soil stock solutions were prepared in milli-Q® water. Besides, acidic soil stock solutions were prepared with or without pH regulation,

Table 1

Summary of soil samples used as natural iron source in the catalytic activation of SODIS and heterogeneous solar photo-Fenton.

Soil code	Soil Origin	Soil depth (cm)	Clay content (%)	Carbon content (%)
CMS	Duitama (Colombia)			
P1	Piedmont (Colombia)	40	30	0.43
P2	Piedmont (Colombia)	40	44	0.50
A1	Altillanura (Colombia)	40	13	0.32
A2	Altillanura (Colombia)	60	14	0.26
A3	Altillanura (Colombia)	60	43	0.42
A4	Altillanura (Colombia)	60	60	0.83
C1	Bogso (Cameroon)	37.5	44	0.84
C2	Bogso (Cameroon)	52.5	44	0.78

or citrate solution (Sigma-Aldrich) was added, when mentioned. Prior to adding the soil to the solution, it was crushed with mortar and pestle.

Lake Lemán water was sampled from the pier in St. Sulpice, Switzerland, and the characteristics of the water are provided in Supplementary Table S1.

2.3. Experimental setup

Cylindrical Pyrex reactors (with 9 cm height, 7.5 cm outer diameter and 6.5 cm inner diameter), that filter most of the UV-B radiation, were used to perform the inactivation experiments. Reactors were acid cleaned after each experiment with 0.1 N H₂SO₄ or 0.1 M HNO₃ to prevent potential iron cross-contamination, then dried overnight in a Heraeus oven held at 120 °C.

Simulated solar light was delivered by a Heraeus CPS Suntest apparatus, equipped with an air-cooled Xenon lamp. 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 7% in the UV-A region, the photons profile emitted between 400 and 800 nm following the solar spectrum. The total irradiation intensity was periodically monitored with a pyranometer and amounted to approximately 840 W/m². A cooling system consisting of a rectangular vessel with a continuous cooling water flow was used to regulate the temperature inside the reactors. The temperature inside the reactors thus never exceeded 25 °C. A graphical representation of the setup is given in Scheme S1 of the Supplementary Material.

2.4. Preparation and enumeration of *Escherichia coli* K12

All the experiments were performed with an *Escherichia coli* K12 strain (DSMZ, No. 498; Deutsche Sammlung von Mikroorganismen und Zellkulturen). This non-pathogenic strain is especially suited for this study as it approximates wild-type *E. coli*, a common host of the intestinal flora of warm-blooded animals [31]. The detailed protocol for the preparation of the strain is provided in detail elsewhere [32]. Briefly, this strain was grown to its stationary phase by overnight aerobic cultivation in 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 water). Finally, the bacterial pellet was re-suspended in saline solution, and the concentration was enumerated around 10⁹ CFU/mL, from which water spiking to an initial concentration of 10⁶ CFU/mL was done.

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 is 10 CFU/mL.

2.5. H₂O₂ and metals' measurements

H₂O₂ was measured according to the DIN 38 409 Method, H15 DEV-18. Briefly, 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 and quantification was performed by calibration curves from standard concentrations (0–20 ppm).

Energy-Dispersive X-Ray Fluorescence spectrometry (EDXRF) was employed for the determination of the metal contents of the soils. 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 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 aqueous 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. SODIS enhancement and solar heterogeneous photo-Fenton

During a first approach, the catalytic enhancement of SODIS and the solar heterogeneous photo-Fenton with natural iron sources were tested on the disinfection of ultrapure (milli-Q®) and Lake Lemán water samples spiked with *Escherichia coli*. Fig. 1 shows the baseline results corresponding to the application of control experiments (SODIS, H₂O₂/SODIS and solar photo-Fenton with Fe²⁺). As expected, the differences between both water matrices are clear, with a reduction of kinetic disinfection in lake water samples requiring 180 min to reduce the *E. coli* population to 3-logU. The presence of organic matter, inorganic substances as carbonates and bicarbonates among others, significantly limited the efficiency of reactive oxygen species formed during the Fenton reaction as well as the penetration of solar radiation in the water samples [3,33,34].

Following, the catalytic enhancement of SODIS through the application of a Colombian mine soil was tested, denominated in Table 2 as CMS. The efficiency of this material in heterogeneous photo-Fenton treatment of wastewaters was successfully reported by Villegas-Guzman et al. [16]. As observed in Fig. 2, the solar exposure of 10 ppm of CMS (equivalent to a theoretical Fe²⁺ of 1 ppm; 10 ppm of CMS in an acidic solution was determined to contain 1 ppm soluble Fe) enhanced the *E. coli* inactivation efficiency obtained by SODIS treatment, reaching total inactivation in 30 min less than the plain SODIS reaction.

Normally, Fe²⁺ as a starting enhancement can increase the inactivation kinetics in pure water [35–37]. Here CMS shows milder but significant improvement. The observed enhancement can be attributed to the possible semiconductor action mode of CMS since adsorption was negligible (data not shown). CMS has a measured isoelectric point of 6.2, hence at pH = 6.5 (ultrapure water) its surface is slightly negative and

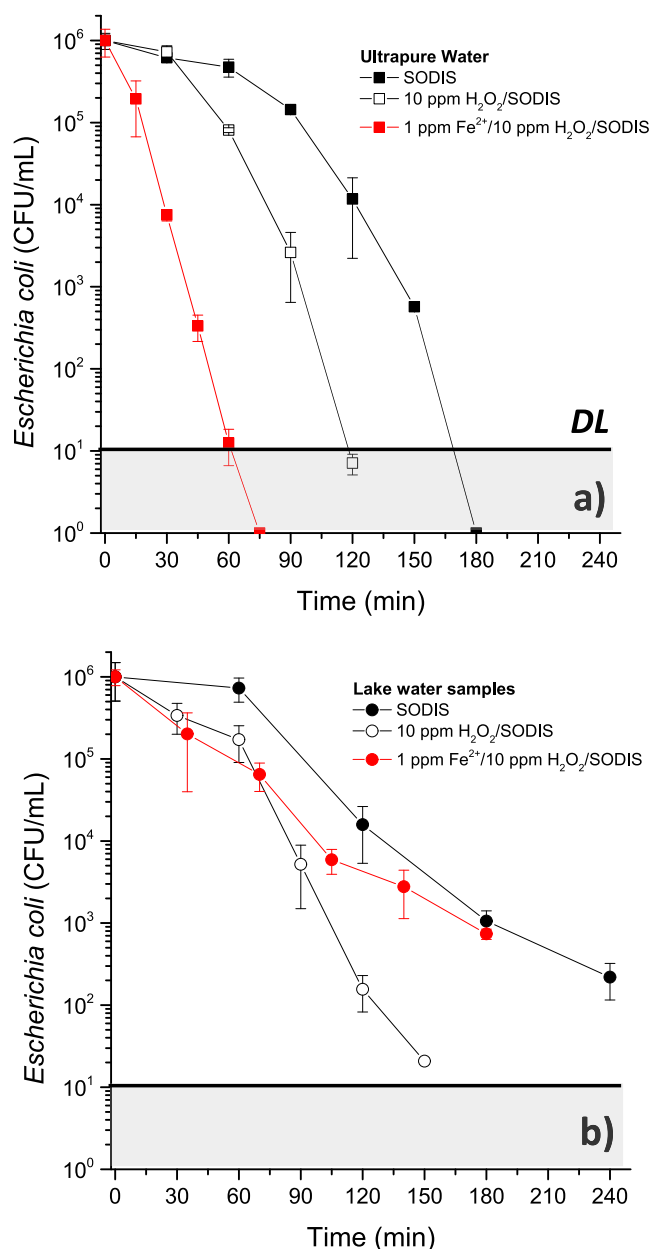


Fig. 1. Baseline *E. coli* inactivation by SODIS, H₂O₂/SODIS and solar photo-Fenton (using Fe²⁺ as an iron source), in experiments with (a) ultrapure and (b) lake water samples.

Table 2
ICP-MS results of CMS found for *E. coli* inactivation by heterogeneous photo-Fenton systems.

Sample	Al [ppb]	Cu [ppb]	Fe [ppb]	Mn [ppb]	Co [ppb]
5 ppm CMS – 2 h	6.53	1.12	3.52	–	0.27
10 ppm CMS – 2 h	6.52	1.23	3.58	–	0.26
20 ppm CMS – 2 h	7.97	2.33	3.97	–	0.27

will not have favorable interaction with the negatively charged bacteria to induce strong adsorption. At the pH of the pure water matrix tested, leaching and homogeneous diffusion of iron is not expected. Ruales-Lonfat et al. [36] reported that certain iron oxides such as hematite, goethite or wüstite possessed semiconductor capabilities against bacterial inactivation, as expected in the case of magnetite (which need H₂O₂

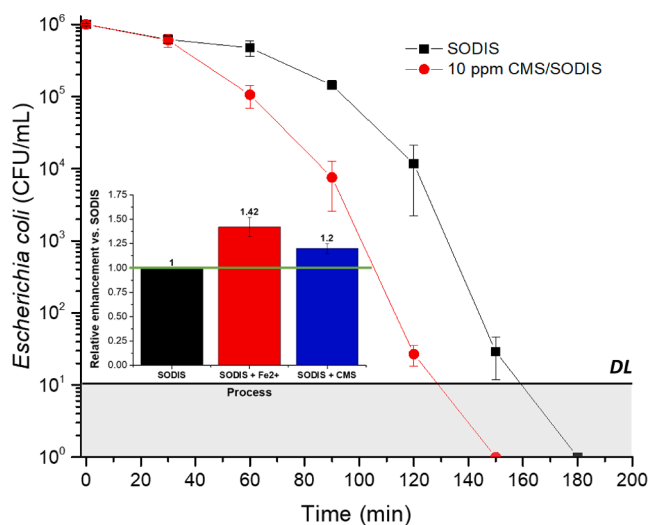


Fig. 2. Catalytic SODIS enhancement by 10 ppm of Colombian mine soil (CMS; [Fe²⁺]_{theoretical} = 1 ppm). Inset: relative enhancement of solar disinfection by iron: plain SODIS, SODIS + Fe²⁺, and SODIS + CMS.

as electron acceptor). Since its iron is mainly Hematite, some activity may not be excluded. The obtained results are better than the ones described by Villegas-Guzman, where using a mineral iron soil along with solar radiation in wastewater did not reach total inactivation of *E. coli* after 180 min, reaching approximately a reduction of 2-log units [16] due to the lack of competition with the effluent organic matter present in that matrix.

Having assessed the catalytic activity of sole CMS, the kinetics of photo-Fenton process were assessed as a function of the CMS concentration. Fig. 3 plots the kinetic rates (min⁻¹) vs. the concentration of CMS in solar photo-Fenton reaction using 10 ppm of H₂O₂ under standard and acidic iron stock solution storage conditions. As clearly observed in the Figure, the inactivation kinetics increased when the concentration of CMS was increased under standard pH conditions (regulated at pH = 6), but until a maximum concentration between 10 and 20 ppm. For concentrations higher than 20 ppm, inactivation rates decreased due to an increase in turbidity as observed by Giannakis et al. [5] for wüstite and maghemite oxides. However, under acidic conditions

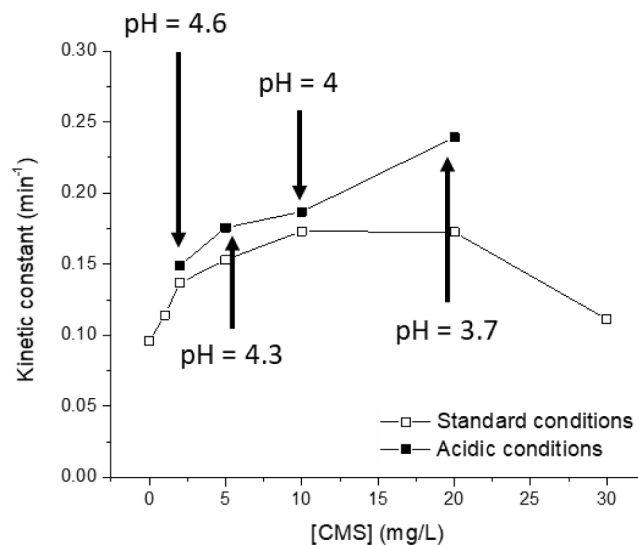


Fig. 3. Evolution of kinetic rate for *E. coli* inactivation under different concentrations of CMS and solar heterogeneous photo-Fenton with 10 ppm of H₂O₂. The value of the pH reached after the addition of CMS is denoted.

the inactivation rates of the photo-Fenton reaction with CMS as iron catalyst increases, not necessarily due to the acid effect on bacteria (differences are low till pH 3.7) but due to a higher leaching of iron occurring in the stock solution and lower precipitation; the measured dissolved iron concentration was twice as high as under standard conditions (0.1 vs. 0.05 ppm). This leads to higher Fe stoichiometric availability to react with hydrogen peroxide and therefore a higher fraction of homogeneous photo-Fenton occurring compared to the previous conditions. The other mechanism proposed in the literature is the higher Fe transport in the cell that aggravates the intracellular photo-Fenton occurring naturally under solar light [38,39].

Therefore, beyond the semiconductor action mode of CMS, it is proven that the addition of CMS provokes both the heterogeneous and homogeneous photo-Fenton reactions, by the presence of metals in the CMS at $t = 0$. In addition to dissolved iron, other metals with the ability to promote the (homogeneous) Fenton reaction have leached into water [40]. The ICP-MS results summarized in Table 2 show that the final dissolved iron concentration is around 4 ppb, while other metals such as Al, Cu and Co were detected in concentrations ranging from 0.2 to approx. 8 ppb. The dissolved metals can be coming from leaching of material through the actions of light during the experiments [41]. In any case, the final dissolved total iron concentration is below 0.3 ppm, the limit advised by WHO [42], and generally the concentrations do not exceed the limits imposed by legislation around the world [43], which may allow considering the process as potabilization. The consumption of the water from the end-user with the particles present will suppose the ingestion of 10 ppm of CMS, but simple decantation will ensure that the only metals left are the leached concentrations, which, as mentioned, do not present risks. Also, an application of acidifying the catalyst should be accompanied by an indication to store it in a plastic or glass bottle to avoid leaching from metallic containers.

After the positive results obtained with CMS as an iron source in the solar heterogeneous photo-Fenton reaction, the efficacy of other soils from Colombia and Cameroon was assessed, as previously reported in Table 1. For all the experiments, the previously determined (from the CMS) soil concentration of 10 ppm was employed and the H_2O_2 concentration was kept at 10 ppm throughout the experiments.

Fig. 4 shows the results obtained and their comparison with the baseline experiments (a detailed version is presented in the Supplementary Figure S1). Almost all the tested soils lead to faster inactivation kinetics than the solar/ H_2O_2 experiments (except A1, which is marginally similar), which constitutes a very positive result considering the heterogeneity of the soils tested; practically it means that if a soil

contained iron, it promoted the photo-Fenton reaction, improving the kinetic rate of H_2O_2 /SODIS treatment. The silver lining, however, is found in the equilibrium of added soils and the turbidity they may cause. Generally, turbidity due to inorganic particles is a hindering factor for solar-mediated processes [44-47]. However, even if the particle may be beneficial, as shown in Fig. 3, higher amounts of CMS actually delayed the bacterial inactivation. Even if in all cases the obtained efficiencies were significantly lower than the one obtained with homogeneous solar photo-Fenton (1:10 ppm Fe^{2+} : H_2O_2). If H_2O_2 is provided/available, then the addition of a ferruginous material at low concentration can lead to enhanced and permanent bacterial inactivation, i.e., without regrowth, as has previously been found in relevant literature for waters treated by the photo-Fenton process [16,48-51].

Among the different soils, the fastest *E. coli* inactivation was reached through the use of CMS, reaching the total inactivation after 90 min, only 15 min longer than homogeneous photo-Fenton. As it can be shown in Table 3 and previously commented, this soil presented notably concentration of different dissolved metals able to promote Fenton reaction and is considered as an iron source for this mine. CMS is tailed by a group of soils with a similar yield reaching the total inactivation in 120 min, namely the C2, P2 and A4 soil samples. The rest of the soils has similar efficiency to H_2O_2 /SODIS treatment. The most likely reason for the moderate enhancement is the balance between the iron content and the increase in turbidity caused by their addition. The higher efficiency of C2, P2 and A4 is likely related with the higher content of clay (Table 1), meaning it may contain more iron just enough to compensate for their light blocking.

To verify the source of enhancement, XRF was performed on the available samples. Table 3 shows the percentage of metals contained in the most catalytically active soils. Notably, a high percentage of iron content is observed especially for C2, hence their leaching is important to assess whether a homogeneous photo-Fenton process also occurs.

Table 4 shows the concentration of dissolved metals of soils A4 and C2 as determined by ICP-MS at the end of the treatment process. The concentration of dissolved iron is slightly lower than that obtained for CMS (Table 2). Other interesting observations include the absence of dissolved Mn as compared to Co, despite the lower percentage of the latter. Besides, the influence of clay can be clearly observed in four soils of the same region (Altillanura, Colombia). The clay contents for the A2, A3 and A4 samples were 13.8, 42.8 and 60.0 % respectively. All soils came from a depth of 60 cm. The carbon contents of the soils analyzed was 0.26, 0.42, and 0.83 % for A2, A3, and A4 respectively.

Apart from the clay content, literature suggests that an important variable to determine the final efficiency of the reaction is the carbon content, affecting the availability of active catalytic sites to react [52]. The carbon content of the soils was low, 0.26 and 0.83 % for A2 and A4, respectively. Although *E. coli* inactivation is slightly enhanced after the calcination process for soil A2 and sample A4 with 4 more carbon, kinetics was identical with the uncalcinated (Supplementary Figure S2), hence we found no correlation.

In addition, over the A2 and A4 samples, the photo-Fenton reaction in acidic storage conditions was tested (pH = 4.5), in order to promote the increase of the concentration of dissolved metals as a consequence of these acidic conditions. However, contrary to CMS, no enhancement was found (Supplementary Figure S3), and A3 with an intermediate clay content may not contain readily available minerals. Table 5 describes the main metals of apparently non-catalytic soils, and A3 apart from lower Fe content has more Zr, Y, Nb, Cr and Ga. Due to these low percentage of metals present, we believe that further parameters related to the soil composition or structure must be interfering such as silt and sand content, potential age of prior land use, soil pH and N content [29,30], and not only metals' content.

3.2. Influence of citrate addition during storage in photo-Fenton reaction

In order to increase the inactivation kinetics of *E. coli* in

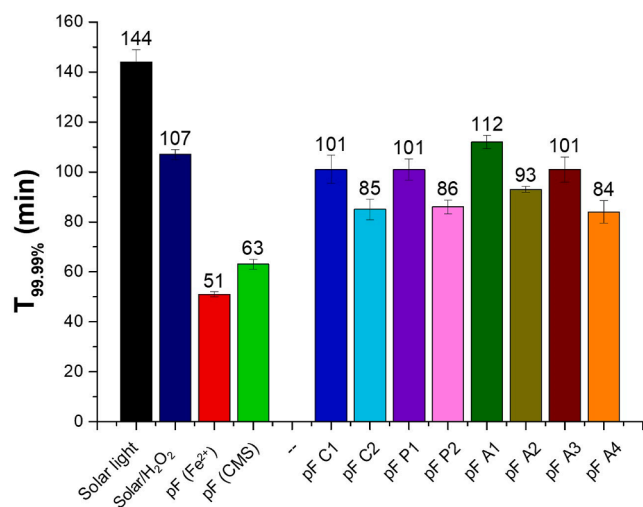


Fig. 4. Assessment of *E. coli* inactivation by solar heterogeneous photo-Fenton with different soil samples as natural iron source, comparing the time necessary to reach 4 logU inactivation ($T_{99.99\%}$). [soils] = 10 ppm; [H_2O_2] = 10 ppm.

Table 3
XRF analysis of CMS, A4 and C2 soils.

Soil	Element	Percentage	SD	Soil	Element	Percentage	SD	Soil	Element	Percentage	SD
CMS	Fe ₂ O ₃	81.26	± 0.55	A4	Fe ₂ O ₃	65.65	± 0.05	C2	Fe ₂ O ₃	80.24	± 0.23
	Al ₂ O ₃	6.68	± 0.45		SiO ₂	11.53	± 0.23		SiO ₂	7.10	± 0.16
	SiO ₂	4.29	± 0.34		ZrO ₂	9.61	± 0.43		TiO ₂	3.99	± 0.23
	P ₂ O ₅	2.78	± 0.38		TiO ₂	5.51	± 0.05		Al ₂ O ₃	3.72	± 0.16
	CaO	2.24	± 0.05		Al ₂ O ₃	5.10	± 0.18		ZrO ₂	2.31	± 0.16
	La ₂ O ₃	1.54	± 0.06		BaO	1.22	± 0.06		BaO	1.13	± 0.06
	SnO ₂	0.24	± 0.61		K ₂ O	0.36	± 0.08		K ₂ O	1.02	± 0.81
	MnO	0.24	± 0.09		Y ₂ O ₃	0.41	± 0.01		Cr ₂ O ₃	0.30	± 0.14
	TiO ₂	0.18	± 0.14		NbO	0.33	± 0.03		CuO	0.14	± 0.01
	ZnO	0.11	± 0.13		Cr ₂ O ₃	0.19	± 0.01		MnO	0.05	± 0.01
CuO	0.01	± 0.32	MnO	0.10	± 0.08	SO ₃	0.04	± 0.01			

Blue: Main elements. Green: Minor elements.

Table 4
ICP-MS results of A4 and C2 soil-driven for *E. coli* inactivation by heterogeneous photo-Fenton systems.

Sample	Al [ppb]	Cu [ppb]	Fe [ppb]	Mn [ppb]	Co [ppb]
10 ppm A4 – 2 h	6.18	1.41	2.86	–	0.24
10 ppm C2 – 2 h	8.19	1.32	3.85	–	0.26

heterogeneous photo-Fenton, the use of citrate as ligand to form photo-active complexes with leached iron during storage, which can facilitate the regeneration of dissolved ferrous iron, has been assessed. The influence of iron-to-citrate molar ratio was tested for three different ratios (1:1, 1:2, and 1:5). Fig. 5 presents the results of the inactivation tests obtained with 10 ppm of CMS, and H₂O₂ was kept at 10 ppm for all of the experiments (the Supplementary Figure S4 details the inactivation kinetics).

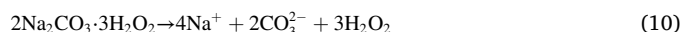
In Fig. 5, a progressive improvement of the efficiency of heterogeneous solar photo-Fenton is observed with the increase in the citrate concentration. The ratio CMS:citrate 1:1 did not seem to improve the inactivation compared with no addition of citrate. The molar ratio of 1:1 does not have a significant increase, but the 1:5 ratio improves the kinetics significantly, even though additional organic material was added to the reaction medium, lowering the T_{99,99%} to the times achieved by the homogeneous photo-Fenton. This is especially impressive since the influence of organic material on the form of citrate is mainly expected to be negative due to the scavenging of the produced ROS, this action is compensated by the complexing power of the chemical [53] keeping the metals in solution. The addition of citrate promotes the formation of soluble ferric complexes that drive homogeneous photo-Fenton reactions and the formation of photo-active complexes that can undergo ligand-to-metal charge transfer (LMCT) and regenerate ferrous iron species [16]. Besides, pH is another variable that might be influenced in the increase in the inactivation kinetics. We should note here that the addition of citrate decreases the pH of water. For the 1:1 M ratio, the pH of the reaction was 4, for the 1:2 M ratio 3.7, and 3.5 for the 1:5 ratio, which improved the pF process. For the 1:5 M ratio experiment, the observed *E. coli* inactivation curve is very similar to that of 1:2 M ratio, so the decrease of pH compensates the increased of organic content through the addition of higher citrate concentration and excessive pH decrease.

Thanks to the addition of citrate, the heterogeneous photo-Fenton process using natural soils allows yields similar to those obtained in a

conventional homogeneous photo-Fenton process. This fact points the way toward the viability of the treatment as a viable and low-cost alternative; WHO recommends pH 4 as minimum value, but commercial soft drinks have pH as low as 2.5, hence its consumption is not expected to be problematic.

3.3. Assessment of percarbonate as an alternative source of H₂O₂

In order to propose a low-cost treatment based on natural solutions that is easy to apply and handle for the local population in LMICs, an alternative to hydrogen peroxide is studied. Sodium percarbonate (2Na₂CO₃·3H₂O₂; SPC) is a stable solid, easy to handle and has lower risks than hydrogen peroxide. SPC dissolves in water (Eq. (10)):



However, the use of SPC has some clear disadvantages in comparison with H₂O₂, such as the addition of carbonates/bicarbonates to the water matrix, which may result in ROS scavenging or the increase of pH that may be affecting the photo-Fenton reaction in a negative way [9,54].

Fig. 6 compares the *E. coli* inactivation using H₂O₂ and SPC as oxidant in the treatments solar/oxidant and homogeneous solar photo-Fenton (with Fe²⁺) in pure water. The inactivation curves confirmed the the abovedisadvantages. As observed, the use of SPC reduced the efficiency in comparison with those treatments with H₂O₂, being more significant in solar photo-Fenton treatments. The main reason for this difference is that the solar/oxidant treatment is not a heavily pH-dependent process as it is the case for photo-Fenton.

Aside from the previously discussed inhibitory actions of carbonate/bicarbonate as a scavenger of hydroxyl radicals [24,55], the presence of these inorganic ions favors *E. coli* survival by reducing the energy requirements of bacteria to maintain the osmotic pressure [56]. Nevertheless, despite the disadvantages shown by SPC, this oxidant can promote the Fenton reaction, hence it cannot be discarded just yet; the advantages previously mentioned compared to H₂O₂ may allow to propose it as an alternative source of H₂O₂.

3.4. The influence of water matrix composition on the efficiency of the treatments

To make a proposal for a feasible treatment of drinking water in LMICs, it is important to assess the efficiency over real freshwater samples. In this section, treatments with CMS, A4, and C2 soil samples were tested as natural sources of iron to treat Lemna Lake water samples

Table 5
XRF analysis of the non-catalytic soils tested.

Soil	Element	Percentage	SD	Soil	Element	Percentage	SD	Soil	Element	Percentage	SD
A2	Fe ₂ O ₃	45.91	± 2.53	A3	Fe ₂ O ₃	57.80	± 0.80	C1	Fe ₂ O ₃	81.38	± 0.69
	SiO ₂	23.92	± 0.73		ZrO ₂	15.82	± 0.92		SiO ₂	6.87	± 0.43
	ZrO ₂	19.59	± 4.13		SiO ₂	11.03	± 0.64		TiO ₂	3.93	± 0.08
	TiO ₂	4.82	± 0.41		TiO ₂	7.47	± 0.23		Al ₂ O ₃	3.84	± 0.05
	Al ₂ O ₃	3.70	± 0.27		Al ₂ O ₃	4.54	± 0.17		ZrO ₂	2.04	± 0.18
	Y ₂ O ₃	0.47	± 0.03		Y ₂ O ₃	0.52	± 0.00		BaO	1.34	± 0.02
	Cr ₂ O ₃	0.45	± 0.01		NbO	0.36	± 0.01		Cr ₂ O ₃	0.25	± 0.03
	CuO	0.38	± 0.01		K ₂ O	0.19	± 0.01		CuO	0.17	± 0.02
	OsO ₄	0.30	± 0.06		Cr ₂ O ₃	0.19	± 0.01		MnO	0.10	± 0.04
	K ₂ O	0.24	± 0.02		Ga ₂ O ₃	0.11	± 0.00		SO ₃	0.09	± 0.01
Soil	Element	Percentage	SD	Soil	Element	Percentage	SD				
P1	Fe ₂ O ₃	64.29	± 0.23	P2	Fe ₂ O ₃	68.02	± 1.56				
	SiO ₂	15.60	± 0.48		SiO ₂	14.55	± 1.16				
	K ₂ O	5.52	± 0.06		K ₂ O	6.00	± 0.21				
	TiO ₂	3.74	± 0.69		Al ₂ O ₃	3.93	± 0.39				
	Al ₂ O ₃	3.91	± 0.06		TiO ₂	3.64	± 0.02				
	ZrO ₂	3.22	± 0.01		BaO	1.36	± 0.02				
	Rb ₂ O	0.76	± 0.04		Rb ₂ O	0.84	± 0.09				
	MnO	0.76	± 0.11		SrO	0.54	± 0.03				
	Y ₂ O ₃	0.36	± 0.00		MnO	0.50	± 0.00				

Blue: Main elements. Green: Minor elements.

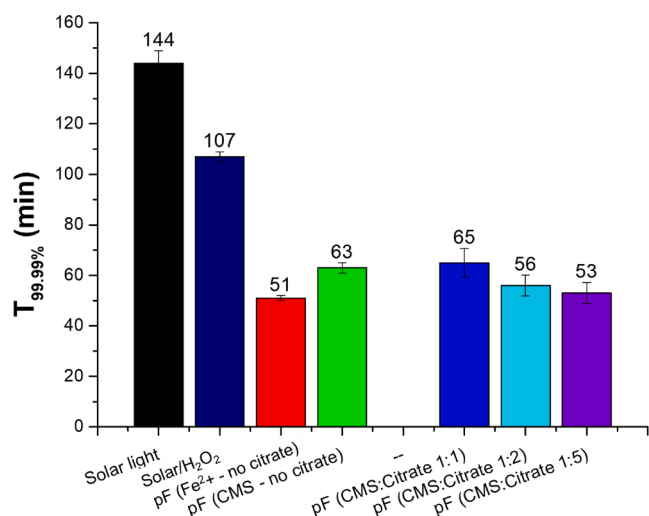


Fig. 5. Influence of CMS: citrate ratio on *E. coli* inactivation by solar heterogeneous photo-Fenton on the time necessary to induce 4 logU reduction. Conditions: [Fe_{theoretical}] = 1 ppm; [H₂O₂] = 10 ppm.

by a solar heterogeneous photo-Fenton reaction, fueled by H₂O₂ or SPC. Fig. 7 shows the time necessary for 99.99% *E. coli* inactivation using hydrogen peroxide or sodium percarbonate as the oxidant (detailed inactivation kinetics are presented in Supplementary Figure S5).

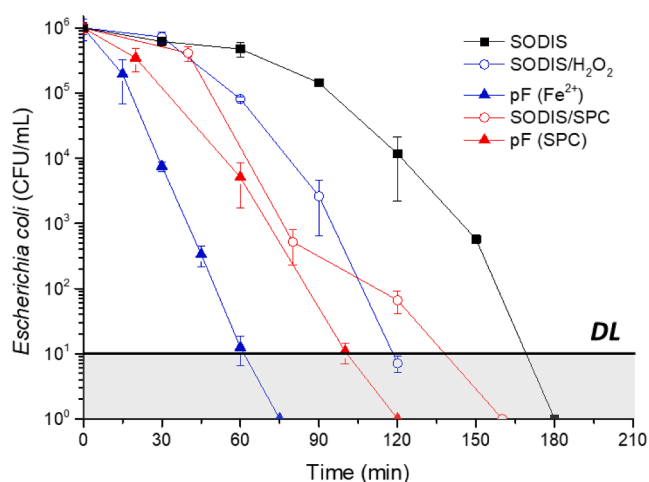


Fig. 6. Comparison of *E. coli* inactivation efficiency in ultrapure water using SPC as an alternative to H₂O₂. [Fe²⁺] = 1 ppm; [Oxidant] = 10 ppm.

As observed in Fig. 7, when a more complex water matrix is treated by photo-Fenton, the efficiency of the treatment is drastically reduced compared with the efficiency reported over milli-Q samples (Fig. 4). First, because hydroxyl radicals are not selective and could attack other substances different from *E. coli*, reducing the disinfection efficiency [57]. On the other hand, lake water contains organic matter and

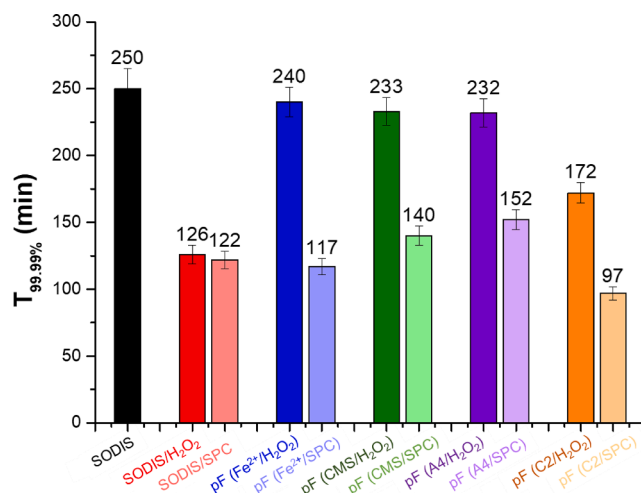


Fig. 7. Comparison of $T_{99.99\%}$ for *E. coli* inactivation efficiency in Lemna Lake water samples by solar photo-Fenton using H₂O₂ (dark-colored bars) or SPC (light-colored bars) as oxidants. Conditions: [Fe²⁺] = 1 ppm; [soil Fe_{theoretical}] = 1 ppm; [Oxidant] = 10 ppm.

inorganic ions responsible for reducing the filtration of radiation in water and scavenging hydroxyl radicals formed [58]. Interestingly enough, conventional photo-Fenton yielded slower inactivation kinetics than solar/H₂O₂, due to the formation of iron precipitates [3,59], when it yielded at least similar inactivation kinetics.

A similar result is observed in the case of the use of soils as iron source, in this case the results are slightly better than conventional photo-Fenton, which constitutes a very positive result regarding substituting Fe salts with ferruginous soils but with inactivation kinetics similar or lower than solar/H₂O₂. This kinetics is slower than the results obtained over milli-Q samples, a main reason most likely is the difference in pH in the two water matrices [60,61]. In fact, at the end of the heterogeneous photo-Fenton in lake water, the pH was measured to be 8.2 as opposed to 6.5 measured for Milli-Q water. This increase in pH decreases the availability of iron in solution and therefore has a negative impact on the photo-Fenton process. Walte and Morel [62] studied the photoactivity of iron oxides at pH levels of 6.5 and 8.2 and proposed that at pH 8.2, as opposed to pH 6.5, the concentration of photoactive ferric oxide species was too low to have effective reduction of ferric iron species. Hence, in our process, the effectiveness is expected to be diminished too.

On the other hand, when SPC is used as an oxidant, the addition of soils as an iron source does not have a positive influence on the homogeneous solar photo-Fenton. Almost all soils lead to slower photo-Fenton process. In the case of using C2 as the iron source, a yield similar to the SPC-driven homogeneous solar photo-Fenton is observed. This must be attributed to the high pH values of water matrix as mentioned before. The addition of SPC increased the pH of water matrix to 8.5 due to the addition of carbonates. This did not have a drastic effect as the pH of the lake water was already high to begin with.

However, our investigation led to an intriguing result. The substitution of H₂O₂ by SPC either restored the efficacy of the process or lead to further enhancement. Specifically, CMS and A4 ultimately lead to times close to Fe²⁺ reactions, but C2 leads to even faster bacterial inactivation. Most probably, the higher amount of Fe and Cu might have contributed to the heterogeneous photo-Fenton reaction in the surface of the oxide (details on the metals contained in the soils are given in Table S2).

Therefore, although under these operating conditions this type of treatment does not seem to be a great enhancement for increasing *E. coli* yields in strict chemical terms, we take as a positive point that there is no significant delay regardless of the iron source (natural Fe, CMS instead

of salt) and that the performance of the solar/oxidant treatment is acceptably enhanced, even better when using SPC than when using hydrogen peroxide in lake water. Recently, a similar behavior was found when using ashes as metal oxide sources to drive the photo-Fenton process, and SPC acted similarly [61]. Another possible explanation for this behavior is that the addition of 15 ppm of carbonate via SPC does not change significantly the composition of the water matrix in a drastic way. The composition of Lemna Lake water was determined [63], and the yearly average concentration of carbonates was 110.9 ppm (averaging 116 in the present tests). Therefore, 10% increase in carbonate concentration from adding SPC does not hinder the process.

Finally, in order to improve the performance of the heterogeneous photo-Fenton process using soils as a source of iron in lake water, either by SPC or H₂O₂, the addition of citrate was assessed. Villegas-Guzmán et al. [16] reported significant improvement of bacterial inactivation by homogeneous photo-Fenton when different organic acids, such as citric acid, were added to the reaction. This improvement was not attributed to pH but to the increase of the initial dissolved iron in the system facilitating Fe³⁺/Fe²⁺ exchange in the catalytic photo-Fenton reaction and consequently the production of hydroxyl radicals. In our tests, the use of 20 ppm of citrate in CMS, C2 and A4 did not lead to drastic enhancement, except when soil C2 was added in presence of H₂O₂ (Supplementary Figure S6). C2 was also the most effective with SPC or H₂O₂ without the addition of ligand, and among the sampled soils, was the one that led to the highest Al, Fe and Co presence in the water matrix, after CMS. Hence, the modification that citrate brings to the system, i.e., the availability of metals, is verified as the key factor, even at low concentrations.

3.5. Soils/SPC efficacy and natural water: Mechanism and environmental significance

Having presented the different parameters assessed in the study, in order to elucidate the driving force of inactivation in the soil-assisted photo-Fenton process, either with H₂O₂ or SPC, radical scavenger tests have been applied. The experiments consisted of acquiring the inactivation kinetics in absence of scavengers and Fenton reagents, homogeneous photo-Fenton (Fe²⁺/H₂O₂) in absence/presence of *tert*-Butanol (TBA) and methanol (MeOH) as quenching agents, heterogeneous photo-Fenton with CMS/H₂O₂ in absence/presence of scavengers and heterogeneous photo-Fenton with CMS/SPC, and are summarized in Fig. 8.. TBA and MeOH are both potent HO[•] radical scavengers, with rates of $6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [64] and $2.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [65] respectively. To compensate for the differences in the scavenging rates, MeOH was added at 24 mM and TBA at 10 mM; both concentrations were found harmless for bacteria (data not shown). Since a heterogeneous process was assayed, the use of both scavengers in parallel may assist in differentiating among bulk or bulk and surface bound radicals for TBA and MeOH, respectively. The pseudo-first order reaction rate of each process was calculated and compared in the presence/absence of the scavengers and the effect of each one was delineated.

The addition of the Fenton reagents brings a great enhancement in solar disinfection as seen before, and the addition of either scavenger significantly decreased the inactivation rates. As expected, the difference among the two quenching agents is negligible due to the Fe²⁺ salts added. However, when CMS was used as an iron source inducing the heterogeneous photo-Fenton process, TBA had a milder effect than MeOH (38% difference), indicating the presence of bulk and surface-bound radicals.

When CMS was used as heterogeneous Fe catalyst and SPC was employed as H₂O₂ source, the mechanism was modified. Firstly, in MQ water, lower photo-Fenton kinetics were observed (as indicated in the previous sections). The effect of TBA and MeOH was observable but much less than the corresponding changes observed in CMS/H₂O₂ process. This indicates that HO[•] is not the only species-driving inactivation. Considering that SPC adds 2 M of carbonates for each 3 M of H₂O₂

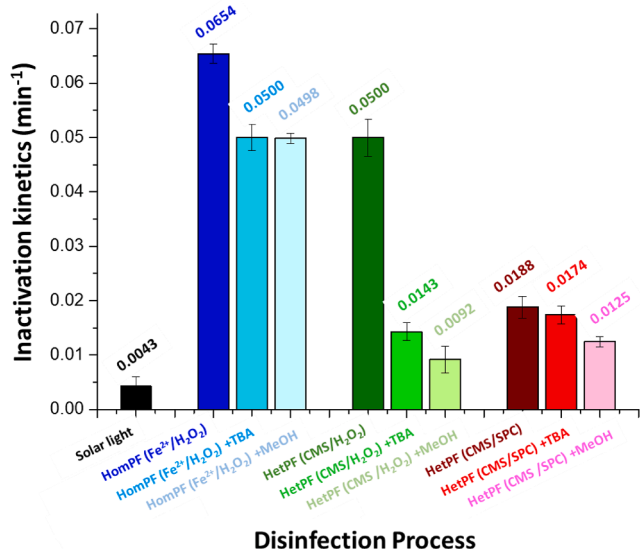


Fig. 8. Determination of the dominant mechanisms of bacterial inactivation via scavenger tests. Each family of bars depicts a distinct group of processes, namely homogeneous photo-Fenton (Fe²⁺/H₂O₂), heterogeneous photo-Fenton (CMS/H₂O₂) and heterogeneous photo-Fenton with percarbonate (CMS/SPC).

(stoichiometric ratio), it is rational to assume that scavenging of HO[•] was performed by CO₃²⁻, generating carbonate radicals (CO₃^{•-}) [52,66]. Also, it has been shown that among the most common (counter)ions, CO₃²⁻ has the lowest effect in catalyst passivation [67]. The reaction rates with bacteria have only been approximated [68], reaching 4.35 × 10¹⁰ M⁻¹ s⁻¹ for CO₃^{•-} vs. 10¹¹-10¹² M⁻¹ s⁻¹ for HO[•]. However, we caution the use of these rates because bacteria are higher order organisms than the typical organic molecule, so they can present significantly higher rates [24,69]. Nevertheless, carbonate radicals are known to react with

organic compounds, albeit at lower rates than HO[•] (~10⁶ M⁻¹ s⁻¹ for HCO₃^{•-} and ~10⁸ M⁻¹ s⁻¹ for CO₃^{•-}, in order of magnitude [69,70]) as they present a more selective behavior. Despite this obvious drawback, their higher lifetime (ns vs. μs, for HO[•] and CO₃^{•-}, respectively) may compensate for the decreased oxidative power (2.3 for vs. 1.78 V at pH = 7), for HO[•] and CO₃^{•-}, respectively [71,72].

Considering the above facts, our hypothesis is confirmed when comparing the reduction (%) in inactivation kinetics among CMS/H₂O₂ and CMS/SPC process: the reduction between CMS/H₂O₂, CMS/H₂O₂ + TBA or CMS/H₂O₂ + MeOH was 71.3 and 81.6% respectively, while the same systems with SPC had 7.4 and 33.7% reduction in k. The process is less affected by the presence of CO₃²⁻ that reacts in very low rates with alcohols (1.5 × 10⁴ M⁻¹ s⁻¹ with ethanol, 5 × 10³ M⁻¹ s⁻¹ with methanol, 5 × 10⁴ M⁻¹ s⁻¹ with isopropanol and < 1.6 × 10² M⁻¹ s⁻¹ with tert-Butanol [73,74]). Finally, the potential semiconductor effect cannot be completely excluded, however, with a band gap of only 1.1 V it may have a mild effect only against bacteria with 0.7 V membrane potential (direct oxidation via h⁺). In the presence of H₂O₂, a potent electron acceptor, electron excitation leads to further HO[•] generation, hence its contribution is reflected in the previously reported scavenger tests.

Finally, the disinfection results and the scavenger tests allow the formulation of an integrated mechanism for the solar-assisted inactivation of bacteria under the soil-peroxide-sun system is proposed in the various actions composing the process, summarized in Fig. 9.

First, the action of solar light (UVB, UVA and visible light) has known germicidal activity [59,75,76], based on thermal, optical and their synergistic actions [47,77,78]. The improved activity of solar light by H₂O₂ is also validated as an enhanced version of the solar activity, affecting the process in intracellular and extracellular damage (interested readers should refer to [46,79-82]). SPC has been recently highlighted as a good H₂O₂ replacement for UVC treatment enhancement for contaminants [83,84], and we further add that it acts as an adequate replacement for H₂O₂ under solar light for disinfection as well, besides UVC and/or VUV [55,83,85] (actions 1 and 2).

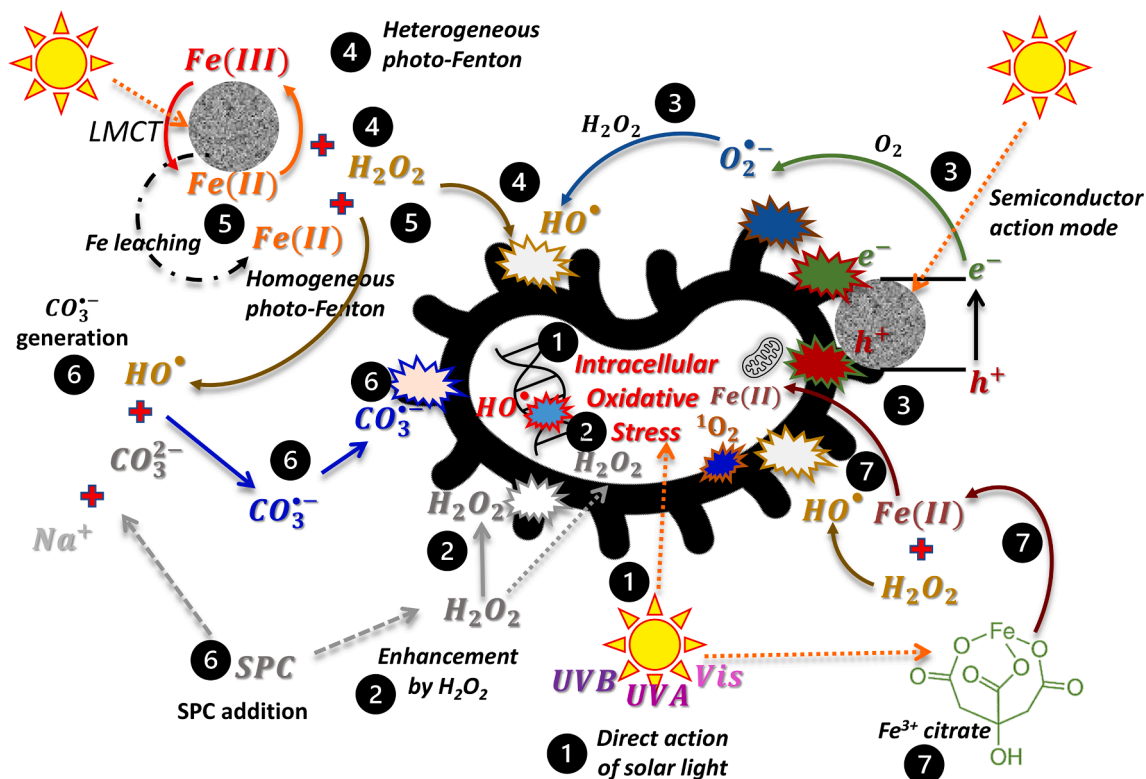


Fig. 9. Integrated bacterial inactivation mechanisms by soil- and peroxide-assisted photo-Fenton process. The numbers correspond to the actions described in text.

As far as the photo-Fenton process is concerned, we will separate the action of iron alone and the modes of inactivation it induces (homogeneous/heterogeneous). First, it is noteworthy that with simple changes in the standard SODIS procedure one can achieve notable enhancements. Considering that one of the key elements for the adoption of the SODIS technology is the availability of the materials [2], the use of soils as a catalyst may bring a notable enhancement. The higher the amount of iron and the purest the source, the semiconductor action mode can lead to inactivation, as shown by the CMS (action 3). Given that iron can induce both intracellular and extracellular damages, the regrowth of microorganisms and post-treatment re-contamination of water is not expected to occur [34,86]. Besides, in trace amounts our soils contained other semiconductors such as TiO_2 , which have long demonstrated germicidal activity; recently, natural minerals like ilmenite, which contain both Fe and Ti, have been shown to effectively and efficiently act as superior composite bactericidal semiconductor [87]. Similarly this mechanism is in our system but in a weaker effect. In the presence of a strong electron acceptor such as H_2O_2 , the electrons excited will lead to superoxide radical anion generation and with a quick reaction will enhance the HO^\bullet production, which is less selective and oxidative than the weak (but anyhow germicidal) superoxide. The main source of HO^\bullet production in this system, however, is the heterogeneous photo-Fenton process taking place on the surface of the oxide [88,89] (action 4). In a cascade similar to reactions 1–3, Fe^{2+} to Fe^{3+} oxidation takes place, producing HO^\bullet and reducing via ligand-to-metal charge transfer (LMCT) by the solar provided in the reaction is closing the catalytic cycle with further radical production [9]. We do not exclude the possibility that natural soils, which contain other catalytically active metals, such as Co or Cu, as our soils, may contribute to heterogeneous Fenton-like processes. The homogeneous action mode was amply demonstrated when the acidic storage of the soil was performed; higher leaching of metals occurred and the Fenton(like) process was enhanced (action 5).

It is interesting to note here that the replacement of (pure) H_2O_2 by SPC practically posed no issues in the photo-Fenton process. We used stoichiometrically the same amounts and although (bi)carbonates were added in the water (only 15 ppm) the reaction was not hindered (action 6); reports also presented enhancements by low carbonate presence [24,55]. By reaction of (bi)carbonate with HO^\bullet , the $\text{CO}_3^{\bullet-}$ is formed which has enough oxidation potential ($E_0 = 1.78$ at $\text{pH} = 7$) to oxidize the bacterial cell wall via electron transfer and hydrogen abstraction mechanisms at reaction rates that can reach up to $10^9 \text{ M}^{-1} \text{ s}^{-1}$ [90]. Its lifetime is in the order of milliseconds [91], which compared to HO^\bullet (μsec) highlights its importance for natural waters [92,93].

Finally, in natural waters such as Lake Lemnan water used in the study, the pH naturally leads to the precipitation of metals, limiting the catalytic activity and the homogeneous actions are expected to be hindered. The addition of citrate on the other hand has apparently created complexes with the metals that alleviated the issue; despite the expected complexation of citrate with naturally occurring elements or its reaction with the generated ROS in the system, its addition has facilitated the net effect of the homogenous photo-Fenton process. Previous works have detailed the reaction cascades occurring at alkaline pH values, which coincide well with our experimental conditions and importantly with the maximum Fe^{2+} stability constant [94]. This practically means more Fe^{2+} can be available, which leads to high superoxide and hydroxyl radical generation (action 7).

In summary, the SODIS process can be enhanced by hydrogen peroxide addition (either liquid or solid) and Fe-containing soil that has been stored in an acidic solution (preferably of citric origin). This strategy can be further generalized; other acids of vegetable and fruit origin that can be extracted from wastes have worked equally well for wastewater disinfection [41,95,96]. Hence in less contaminated matrix it is expected to work better and with significantly lower cost than conventional photo-Fenton, more water can be treated faster, thus reducing the financial burden and the environmental footprint.

4. Conclusions

In this work, we successfully explored low-cost soil-based photo-Fenton processes to enhance SODIS for the elimination of *E. coli* from water. Our findings revealed several crucial insights. First, SODIS can be effectively enhanced with very low concentrations of high-iron-containing samples, predominantly through heterogeneous photo-Fenton in the presence of H_2O_2 . The metal availability is the primary factor influencing bactericidal efficacy, while clay and carbon content had inconsistent effect on the photo-Fenton process.

The study also revealed that natural, non-contaminated soil samples containing metals such as Al, Fe and Co in such low concentrations are unlikely to present acute toxicity concerns and are beneficial for SODIS enhancement, although their potential bioaccumulation requires further investigation. Moreover, the generation of disinfection by-products cannot be excluded; they may be generated due to the presence of organic matter and inorganic ions in surface waters, which calls for validation of the produced water safety concerning human toxicity.

We also suggest that the heterogeneous process with percarbonate is competitive in surface waters where neutral-to-alkaline pH values prevail, organic matter is present, and anions interfere by scavenging generated radicals. Therefore, the use of SPC was approved as a potential replacement for H_2O_2 . However, further technoeconomic analysis is required to validate the economic viability proposed in this work or suggest proper adaptation, but these initial results provide a promising outlook.

Finally, the addition of any soil sample was found to be better than no addition at all as the photo-Fenton driven by soils and/or H_2O_2 /SPC was always better than SODIS. Although their use may increase the turbidity in water, a simple filtration step after sunlight exposure can easily solve this problem. Further work is necessary to investigate possible bio-incompatibilities, but the use of soil-based photo-Fenton processes is encouraged to be pondered upon, especially in low-income countries needing to accelerate the SODIS process in order to generate higher quantities of safe water faster.

CRediT authorship contribution statement

Jorge Rodríguez-Chueca: Methodology, Validation, Investigation, Visualization, Writing - original draft, Writing - review & editing. **Stefanos Giannakis:** Conceptualization, Methodology, Supervision, Funding acquisition, Investigation, Writing - original draft, Writing - review & editing. **Timur Senyuz:** Investigation, Visualization, Writing - original draft. **Jeremie Decker:** Investigation, Visualization, Validation, Writing - review & editing. **Paula Oulego:** Investigation, Visualization, Writing - original draft, Writing - review & editing. **Michaël Bensimon:** Investigation, Methodology, Resources. **Thomas Guillaume:** Resources, Writing - original draft, Writing - review & editing. **César Pulgarín:** Conceptualization, Resources, Project administration, Funding acquisition, Supervision, Validation, Writing - original draft, Writing - review & editing.

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 material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.seppur.2023.124221>.

References

- [1] S. Giannakis, M.I. Polo-López, D. Spuhler, J.A. Sánchez Pérez, P. Fernández Ibáñez, C. Pulgarin, Solar disinfection is an augmentable, in situ-generated photo-Fenton reaction—Part 1: A review of the mechanisms and the fundamental aspects of the process, *Appl. Catal. B Environ.* 199 (2016) 199–223, <https://doi.org/10.1016/j.apcatb.2016.06.009>.
- [2] K.G. McGuigan, R.M. Conroy, H.J. Mosler, M. du Preez, E. Ubomba-Jaswa, P. Fernandez-Ibanez, P. Fernandez-Ibanez, Solar water disinfection (SODIS): a review from bench-top to roof-top, *J. Hazard. Mater.* 235–236 (2012) 29–46, <https://doi.org/10.1016/j.jhazmat.2012.07.053>.
- [3] P. Ozores Diez, S. Giannakis, J. Rodríguez-Chueca, D. Wang, B. Quilty, R. Devery, K. McGuigan, C. Pulgarin, Enhancing solar disinfection (SODIS) with the photo-Fenton or the Fe²⁺/peroxymonosulfate-activation process in large-scale plastic bottles leads to toxicologically safe drinking water, *Water Res.* 186 (2020), 116387, <https://doi.org/10.1016/j.watres.2020.116387>.
- [4] S. Giannakis, M.I.P. López, D. Spuhler, J.A.S. Pérez, P.F. Ibáñez, C. Pulgarin, Solar disinfection is an augmentable, in situ-generated photo-Fenton reaction-Part 2: A review of the applications for drinking water and wastewater disinfection, *Appl. Catal. B Environ.* 198 (2016), <https://doi.org/10.1016/j.apcatb.2016.06.007>.
- [5] S. Giannakis, S. Liu, A. Carratalá, S. Rtimi, M. Talebi Amiri, M. Bensimon, C. Pulgarin, Iron oxide-mediated semiconductor photocatalysis vs. heterogeneous photo-Fenton treatment of viruses in wastewater. Impact of the oxide particle size, *J. Hazard. Mater.* (2017), <https://doi.org/10.1016/j.jhazmat.2017.06.037>.
- [6] C. Ruales-Lonfat, N. Benítez, A. Sienkiewicz, C. Pulgarin, Deleterious effect of homogeneous and heterogeneous near-neutral photo-Fenton system on *Escherichia coli*. Comparison with photo-catalytic action of TiO₂ during cell envelope disruption, *Appl. Catal. B Environ.* 160 (2014) 286–297.
- [7] G. Farinelli, M. Minella, M. Pazzi, S. Giannakis, C. Pulgarin, D. Vione, A. Tiraferri, Natural iron ligands promote a metal-based oxidation mechanism for the Fenton reaction in water environments, *J. Hazard. Mater.* 393 (2020), 122413, <https://doi.org/10.1016/j.jhazmat.2020.122413>.
- [8] L. Fernández, J. González-Rodríguez, G. Gamallo, T. Vargas-Osorio, C. Vázquez-Vázquez, Y. Piñeiro, J. Rivas, G. Feijoo, M.T. Moreira, Iron oxide-mediated photo-Fenton catalysis in the inactivation of enteric bacteria present in wastewater effluents at neutral pH, *Environ. Pollut.* 266 (2020), 115181, <https://doi.org/10.1016/j.envpol.2020.115181>.
- [9] I. de la Obra Jiménez, S. Giannakis, D. Grandjean, F. Breider, G. Grunauer, J. L. Casas López, J.A. Sánchez Pérez, C. Pulgarin, Unfolding the action mode of light and homogeneous vs. heterogeneous photo-Fenton in bacteria disinfection and concurrent elimination of micropollutants in urban wastewater, mediated by iron oxides in Raceway Pond Reactors, *Appl. Catal. B Environ.* 263 (2020), <https://doi.org/10.1016/j.apcatb.2019.118158>.
- [10] K. O'Dowd, S.C. Pillai, Photo-Fenton disinfection at near neutral pH: Process, parameter optimization and recent advances, *J. Environ. Chem. Eng.* 8 (2020), 104063, <https://doi.org/10.1016/j.jece.2020.104063>.
- [11] N. Thomas, D.D. Dionysiou, S.C. Pillai, Heterogeneous Fenton catalysts: A review of recent advances, *J. Hazard. Mater.* 404 (2021), 124082, <https://doi.org/10.1016/j.jhazmat.2020.124082>.
- [12] J. Xu, N. Sahai, C.M. Eggleston, M.A.A. Schoonen, Reactive oxygen species at the oxide/water interface: Formation mechanisms and implications for prebiotic chemistry and the origin of life, *Earth Planet. Sci. Lett.* 363 (2013) 156–167.
- [13] S.K. Han, T.-M.-M. Hwang, Y. Yoon, J.-W.-W. Kang, Evidence of singlet oxygen and hydroxyl radical formation in aqueous goethite suspension using spin-trapping electron paramagnetic resonance (EPR), *Chemosphere* 84 (2011) 1095–1101, <https://doi.org/10.1016/j.chemosphere.2011.04.051>.
- [14] H.G. Upritchard, J. Yang, P.J. Bremer, I.L. Lamont, A.J. McQuillan, Adsorption to metal oxides of the Pseudomonas aeruginosa siderophore pyoverdine and implications for bacterial biofilm formation on metals, *Langmuir* 23 (2007) 7189–7195.
- [15] M. Rodríguez, J. Bussi, M. Andrea De León, Application of pillared raw clay-based catalysts and natural solar radiation for water decontamination by the photo-Fenton process, *Sep. Purif. Technol.* 259 (2021), <https://doi.org/10.1016/j.seppur.2020.118167>.
- [16] P. Villegas-Guzman, S. Giannakis, S. Rtimi, D. Grandjean, M. Bensimon, L.F.L.F. De Alencastro, R. Torres-Palma, C. Pulgarin, A green solar photo-Fenton process for the elimination of bacteria and micropollutants in municipal wastewater treatment using mineral iron and natural organic acids, *Appl. Catal. B Environ.* 219 (2017) 538–549, <https://doi.org/10.1016/j.apcatb.2017.07.066>.
- [17] M. Garside, Iron oxide price in the United States from 2013 to 2022, Statista. (2023). <https://www.statista.com/statistics/881746/average-us-iron-oxide-price/>.
- [18] J. Herney-Ramirez, M.A. Vicente, L.M. Madeira, Heterogeneous photo-Fenton oxidation with pillared clay-based catalysts for wastewater treatment: A review, *Appl. Catal. B Environ.* 98 (2010) 10–26, <https://doi.org/10.1016/j.apcatb.2010.05.004>.
- [19] H. Bel Hadjtaief, A. Sdiri, W. Ltaief, P. Da Costa, M.E. Gálvez, M. Ben Zina, Efficient removal of cadmium and 2-chlorophenol in aqueous systems by natural clay: Adsorption and photo-Fenton degradation processes, *Comptes Rendus Chim.* 21 (2018) 253–262, <https://doi.org/10.1016/j.crci.2017.01.009>.
- [20] H.D. Rojas-Mantilla, S.C. Ayala-Duran, R.F. Pupo Nogueira, Nontronite mineral clay NAU-2 as support for hematite applied as catalyst for heterogeneous photo-Fenton processes, *Chemosphere* 277 (2021), <https://doi.org/10.1016/j.chemosphere.2021.130258>.
- [21] H.D. Rojas-Mantilla, S.C. Ayala-Duran, R.F. Pupo Nogueira, Modification of a Brazilian natural clay and catalytic activity in heterogeneous photo-Fenton process, *Chemosphere* 291 (2022), <https://doi.org/10.1016/j.chemosphere.2021.132966>.
- [22] Z. Redouane-Salah, M.A. Malouki, B. Khennaoui, J.A. Santaballa, M. Canle, Simulated sunlight photodegradation of 2-mercaptobenzothiazole by heterogeneous photo-Fenton using a natural clay powder, *J. Environ. Chem. Eng.* 6 (2018) 1783–1793, <https://doi.org/10.1016/j.jece.2018.02.011>.
- [23] R. Balachandran, M. Zhao, B. Dong, I. Brown, S. Raghavan, M. Keswani, Role of ammonia and carbonates in scavenging hydroxyl radicals generated during megasonic irradiation of wafer cleaning solutions, *Microelectron. Eng.* 130 (2014) 82–86, <https://doi.org/10.1016/j.mee.2014.10.022>.
- [24] E. Rommozzi, S. Giannakis, R. Giovannetti, D. Vione, C. Pulgarin, Detrimental vs. beneficial influence of ions during solar (SODIS) and photo-Fenton disinfection of *E. coli* in water: (Bi)carbonate, chloride, nitrate and nitrite effects, *Appl. Catal. B Environ.* 270 (2020), 118877, <https://doi.org/10.1016/j.apcatb.2020.118877>.
- [25] Y. Lyu, S. Lyu, P. Tang, W. Jiang, Y. Sun, M. Li, Q. Sui, Degradation of trichloroethylene in aqueous solution by sodium percarbonate activated with Fe(II)-citric acid complex in the presence of surfactant Tween-80, *Chemosphere* 257 (2020), 127223, <https://doi.org/10.1016/j.chemosphere.2020.127223>.
- [26] J.A.I. Pimentel, C. Di Dong, S. Garcia-Segura, R.R.M. Abarca, C.W. Chen, M.D.G. de Luna, Degradation of tetracycline antibiotics by Fe²⁺-catalyzed percarbonate oxidation, *Sci. Total Environ.* 781 (2021), 146411, <https://doi.org/10.1016/j.scitotenv.2021.146411>.
- [27] R. Yang, G. Zeng, Z. Xu, Z. Zhou, J. Huang, R. Fu, S. Lyu, Comparison of naphthalene removal performance using H₂O₂, sodium percarbonate and calcium peroxide oxidants activated by ferrous ions and degradation mechanism, *Chemosphere* 283 (2021), 131209, <https://doi.org/10.1016/j.chemosphere.2021.131209>.
- [28] X. Fu, X. Gu, S. Lu, Z. Miao, M. Xu, X. Zhang, Z. Qiu, Q. Sui, Benzene depletion by Fe²⁺-catalyzed sodium percarbonate in aqueous solution, *Chem. Eng. J.* 267 (2015) 25–33, <https://doi.org/10.1016/j.cej.2014.12.104>.
- [29] J.C. Quezada, T. Guillaume, C. Poeplau, J. Ghazoul, A. Buttler, Deforestation-free land-use change and organic matter-centered management improve the C footprint of oil palm expansion, *Glob. Chang. Biol.* 28 (2022) 2476–2490.
- [30] J.C. Quezada, A. Etter, J. Ghazoul, A. Buttler, T. Guillaume, Carbon neutral expansion of oil palm plantations in the Neotropics, *Sci. Adv.* 5 (2019) eaaw4418.
- [31] M. Madigan, J. Martinko, D. Stahl, D. Clark, Brock Biology of Microorganisms 13th ed, 2014. 10.1007/s13398-014-0173-7-2.
- [32] S. Giannakis, A. Gupta, C. Pulgarin, J. Imlay, Identifying the mediators of intracellular E. coli inactivation under UV-A light: The (photo) Fenton process and singlet oxygen, *Water Res.* 221 (2022), 118740, <https://doi.org/10.1016/j.watres.2022.118740>.
- [33] S. Shekoochian, S. Rtimi, G. Moussavi, S. Giannakis, C. Pulgarin, Enhancing solar disinfection of water in PET bottles by optimized in-situ formation of iron oxide films. From heterogeneous to homogeneous action modes with H₂O₂ vs. O₂ – Part 2: Direct use of (natural) iron oxides, *Chem. Eng. J.* 360 (2019) 1051–1062, <https://doi.org/10.1016/j.cej.2018.10.113>.
- [34] S. Shekoochian, S. Rtimi, G. Moussavi, S. Giannakis, C. Pulgarin, Enhancing solar disinfection of water in PET bottles by optimized in-situ formation of iron oxide films. From heterogeneous to homogeneous action modes with H₂O₂ vs. O₂ – Part 1: Iron salts as oxide precursors, *Chem. Eng. J.* 358 (2019), <https://doi.org/10.1016/j.cej.2018.09.219>.
- [35] D. Spuhler, J. Andrés Rengifo-Herrera, C. Pulgarin, The effect of Fe²⁺, Fe³⁺, H₂O₂ and the photo-Fenton reagent at near neutral pH on the solar disinfection (SODIS) at low temperatures of water containing *Escherichia coli* K12, *Appl. Catal. B Environ.* 96 (2010) 126–141, <https://doi.org/10.1016/j.apcatb.2010.02.010>.
- [36] C. Ruales-Lonfat, J.F. Barona, A. Sienkiewicz, M. Bensimon, J. Vélez-Colmenares, N. Benítez, C. Pulgarin, Iron oxides semiconductor are efficient for solar water disinfection: A comparison with photo-Fenton processes at neutral pH, *Appl. Catal. B Environ.* 166–167 (2015) 497–508, <https://doi.org/10.1016/j.apcatb.2014.12.007>.
- [37] I. García-Fernández, M.I. Polo-López, I. Oller, P. Fernández-Ibáñez, Bacteria and fungi inactivation using Fe³⁺/sunlight, H₂O₂/sunlight and near neutral photo-Fenton: A comparative study, *Appl. Catal. B Environ.* 121–122 (2012) 20–29, <https://doi.org/10.1016/j.apcatb.2012.03.012>.

- [38] L. Feng, C. Peillex-Delphe, C. Lü, D. Wang, S. Giannakis, C. Pulgarin, Employing bacterial mutations for the elucidation of photo-Fenton disinfection: Focus on the intracellular and extracellular inactivation mechanisms induced by UVA and H₂O₂, *Water Res.* 182 (2020), 116049, <https://doi.org/10.1016/j.watres.2020.116049>.
- [39] N. López-Vinent, A. Cruz-Alcalde, G. Moussavi, I. del Castillo Gonzalez, A. Hernandez Lehmann, J. Giménez, S. Giannakis, Improving ferrate disinfection and decontamination performance at neutral pH by activating peroxymonosulfate under solar light, *Chem. Eng. J.* 450 (2022), 137904, <https://doi.org/10.1016/j.cej.2022.137904>.
- [40] L. Zhang, B. Wu, G. Zhang, Y. Gan, S. Zhang, Enhanced decomplexation of Cu(II)-EDTA: The role of acetylacetone in Cu-mediated photo-Fenton reactions, *Chem. Eng. J.* (2019), <https://doi.org/10.1016/j.cej.2018.10.124>.
- [41] P. Villegas-Guzman, S. Giannakis, R.A.R.A. Torres-Palma, C. Pulgarin, Remarkable enhancement of bacterial inactivation in wastewater through promotion of solar photo-Fenton at near-neutral pH by natural organic acids, *Appl. Catal. B Environ.* 205 (2017), <https://doi.org/10.1016/j.apcatb.2016.12.021>.
- [42] WHO, Guidelines for drinking water quality: fourth edition incorporating the first addendum, 2017.
- [43] M. Kohantorabi, G. Moussavi, S. Giannakis, A review of the innovations in metal- and carbon-based catalysts explored for heterogeneous peroxymonosulfate (PMS) activation, with focus on radical vs. non-radical degradation pathways of organic contaminants, *Chem. Eng. J.* (2021), 127957, <https://doi.org/10.1016/j.cej.2020.127957>.
- [44] H. Haider, W. Ali, S. Haydar, S. Tesfamariam, R. Sadiq, Modeling exposure period for solar disinfection (SODIS) under varying turbidity and cloud cover conditions, *Clean Technol. Environ. Policy* 16 (2014) 861–874, <https://doi.org/10.1007/s10098-013-0677-4>.
- [45] M.I. Polo-López, P. Fernández-Ibáñez, E. Ubomba-Jaswa, C. Navntoft, I. García-Fernández, P.S.M. Dunlop, M. Schmid, J.A. Byrne, K.G. McGuigan, Elimination of water pathogens with solar radiation using an automated sequential batch CPC reactor, *J. Hazard Mater.* 196 (2011) 16–21, <https://doi.org/10.1016/j.jhazmat.2011.08.052>.
- [46] M. Castro-Alferez, M. Inmaculada Polo-López, J. Marugán, P. Fernández-Ibáñez, M. I. Polo-López, J. Marugán, P. Fernández-Ibáñez, Validation of a solar-thermal water disinfection model for *Escherichia coli* inactivation in pilot scale solar reactors and real conditions, *Chem. Eng. J.* 331 (2018) 831–840, <https://doi.org/10.1016/j.cej.2017.09.015>.
- [47] S.C. Kehoe, T.M. Joyce, P. Ibrahim, J.B. Gillespie, R.A. Shahar, K.G. McGuigan, Effect of agitation, turbidity, aluminium foil reflectors and container volume on the inactivation efficiency of batch-process solar disinfectors, *Water Res.* 35 (2001) 1061–1065.
- [48] P. Valero, S. Giannakis, R. Mosteo, M.P. Ormad, C. Pulgarin, Comparative effect of growth media on the monitoring of *E. coli* inactivation and regrowth after solar and photo-Fenton treatment, *Chem. Eng. J.* 313 (2017) 109–120, <https://doi.org/10.1016/j.cej.2016.11.126>.
- [49] Y. Ahmed, J. Lu, Z. Yuan, P.L. Bond, J. Guo, Efficient inactivation of antibiotic resistant bacteria and antibiotic resistance genes by photo-Fenton process under visible LED light and neutral pH, *Water Res.* 179 (2020), 115878, <https://doi.org/10.1016/j.watres.2020.115878>.
- [50] A. Fiorentino, G. Lofrano, R. Cucciniello, M. Carotenuto, O. Motta, A. Proto, L. Rizzo, Disinfection of roof harvested rainwater inoculated with *E. coli* and *Enterococcus* and post-treatment bacterial regrowth: Conventional vs solar driven advanced oxidation processes, *Sci. Total Environ.* 801 (2021), 149763, <https://doi.org/10.1016/j.scitotenv.2021.149763>.
- [51] M. Gmurek, E. Borowska, T. Schwartz, H. Horn, Does light-based tertiary treatment prevent the spread of antibiotic resistance genes? Performance, regrowth and future direction, *Sci. Total Environ.* 817 (2022), 153001, <https://doi.org/10.1016/j.scitotenv.2022.153001>.
- [52] M. Kohantorabi, G. Moussavi, P. Oulego, S. Giannakis, Heterogeneous catalytic ozonation and peroxone-mediated removal of Acetaminophen using natural and modified hematite-rich soil, as efficient and environmentally friendly catalysts, *Appl. Catal. B Environ.* 301 (2022), 120786, <https://doi.org/10.1016/j.apcatb.2021.120786>.
- [53] L. Clarizia, D. Russo, I. Di Somma, R. Marotta, R. Andreozzi, Homogeneous photo-Fenton processes at near neutral pH: a review, *Appl. Catal. B Environ.* 2017.
- [54] E. Ortega-Gómez, M.M. Ballesteros Martín, A. Carratalá, P. Fernández Ibáñez, J. A. Sánchez Pérez, C. Pulgarin, Principal parameters affecting virus inactivation by the solar photo-Fenton process at neutral pH and μM concentrations of H₂O₂ and Fe²⁺/³⁺, *Appl. Catal. B Environ.* 174–175 (2015) 395–402, <https://doi.org/10.1016/j.apcatb.2015.03.016>.
- [55] S. Mohammadi, G. Moussavi, P. Oulego, S. Giannakis, Development of a percarbonate-enhanced Vacuum UV process for simultaneous fluoroquinolone antibiotics removal and fecal bacteria inactivation under a continuous flow mode of operation, *Chem. Eng. J.* 431 (2022), 134064, <https://doi.org/10.1016/j.cej.2021.134064>.
- [56] D. Spuhler, J.A. Rengifo-Herrera, C. Pulgarin, The effect of Fe²⁺, Fe³⁺, H₂O₂ and the photo-Fenton reagent at near neutral pH on the solar disinfection (SODIS) at low temperatures of water containing *Escherichia coli* K12, *Appl. Catal. B* 96 (2010) 126–141, <https://doi.org/10.1016/j.apcatb.2010.02.010>.
- [57] R. Mosteo, A. Varon Lopez, D. Muzard, N. Benítez, S. Giannakis, C. Pulgarin, Visible light plays a significant role during bacterial inactivation by the photo-fenton process, even at sub-critical light intensities, *Water Res.* 174 (2020), 115636, <https://doi.org/10.1016/j.watres.2020.115636>.
- [58] D. Vione, G. Falletti, V. Maurino, C. Minero, E. Pelizzetti, M. Malandrino, R. Ajassa, R.-I.-I. Olariu, C. Arsene, Sources and sinks of hydroxyl radicals upon irradiation of natural water samples, *Environ. Sci. Technol.* 40 (2006) 3775, <https://doi.org/10.1021/es052206b>.
- [59] Á. García-Gil, R. Valverde, R.A. García-Muñoz, K.G. McGuigan, J. Marugán, Solar Water Disinfection in high-volume containers: Are naturally occurring substances attenuating factors of radiation? *Chem. Eng. J.* (2020), 125852 <https://doi.org/10.1016/j.cej.2020.125852>.
- [60] J.J. Pignatello, E. Oliveros, A. MacKay, Advanced Oxidation Processes for Organic Contaminant Destruction Based on the Fenton Reaction and Related Chemistry, *Crit. Rev. Environ. Sci. Technol.* 36 (2006) 1–84, <https://doi.org/10.1080/10643380500326564>.
- [61] J. Rodríguez-Chueca, S. Giannakis, M. Tranchant, P. Oulego, M. Bensimon, C. Pulgarin, Solar disinfection of drinking water at alkaline pH, assisted by ashes of spices and herbs containing catalytic metals, in a novel “phyto-Fenton” process, *Chem. Eng. J.* 464 (2023), 142598.
- [62] T.D. Waite, F.M.M. Morel, Photoreductive dissolution of colloidal iron oxides in natural waters, *Environ. Sci. Technol.* 18 (1984) 860–868.
- [63] S. Samoilii, G. Farinelli, J.Á. Moreno-SanSegundo, K.G. McGuigan, J. Marugán, C. Pulgarin, S. Giannakis, Predicting the bactericidal efficacy of solar disinfection (SODIS): from kinetic modeling of in vitro tests towards the in silico forecast of *E. coli* inactivation, *Chem. Eng. J.* 427 (2022), 130866, <https://doi.org/10.1016/j.cej.2021.130866>.
- [64] G.-X. Huang, C.-Y. Wang, C.-W. Yang, P.-C. Guo, H.-Q. Yu, Degradation of Bisphenol A by Peroxymonosulfate Catalytically Activated with Mn_{1.8}Fe_{1.2}O₄ Nanospheres: Synergism between Mn and Fe, *Environ. Sci. Technol.* 51 (2017) 12611–12618, <https://doi.org/10.1021/acs.est.7b03007>.
- [65] G. Yu, Y. Wang, H. Cao, H. Zhao, Y. Xie, Reactive Oxygen Species and Catalytic Active Sites in Heterogeneous Catalytic Ozonation for Water Purification, *Environ. Sci. Technol.* 54 (2020) 5931–5946, <https://doi.org/10.1021/acs.est.0c00575>.
- [66] M. Kohantorabi, G. Moussavi, S. Mohammadi, P. Oulego, S. Giannakis, Photocatalytic activation of peroxymonosulfate (PMS) by novel mesoporous Ag/ZnO@NiFe₂O₄ nanorods, inducing radical-mediated acetaminophen degradation under UVA irradiation, *Chemosphere* 277 (2021), 130271, <https://doi.org/10.1016/j.chemosphere.2021.130271>.
- [67] H. Mohebbi, G. Moussavi, M. Karimi, S. Giannakis, Development of a magnetic Ce-Zr bimetallic MOF as an efficient catalytic ozonation mediator: Preparation, characterization, and catalytic activity, *Sep. Purif. Technol.* 315 (2023), 123670, <https://doi.org/10.1016/j.seppur.2023.123670>.
- [68] P. Sun, C. Tyree, C.-H. Huang, Inactivation of *Escherichia coli*, bacteriophage MS2, and *Bacillus* spores under UV/H₂O₂ and UV/peroxydisulfate advanced disinfection conditions, *Environ. Sci. Technol.* 50 (2016) 4448–4458.
- [69] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\bullet\text{OH}/\bullet\text{O}^-$) in aqueous solution, *J. Phys. Chem. Ref. Data.* 17 (1988) 513.
- [70] E. Lipczynska-Kochany, G. Sprah, S. Harms, Influence of some groundwater and surface waters constituents on the degradation of 4-chlorophenol by the Fenton reaction, *Chemosphere* 30 (1995) 9–20, [https://doi.org/10.1016/0045-6535\(94\)00371-Z](https://doi.org/10.1016/0045-6535(94)00371-Z).
- [71] S. Fadaei, E. Taheri, A. Fatehizadeh, T.M. Aminabhavi, New combination of pulsed light and iron (II) for carbonate radical production to enhanced degradation of bisphenol A: Parameter optimization and degradation pathway, *J. Environ. Manage.* 322 (2022), 116059, <https://doi.org/10.1016/j.jenvman.2022.116059>.
- [72] P. Mazellier, C. Busset, A. Delmont, J. De Laat, A comparison of ferrous degradation by hydroxyl and carbonate radicals in aqueous solution, *Water Res.* 41 (2007) 4585–4594.
- [73] P. Neta, R.E. Huie, A.B. Ross, Rate constants for reactions of inorganic radicals in aqueous solution, *J. Phys. Chem. Ref. Data.* 17 (1988) 1027–1284.
- [74] Y. Liu, X. He, X. Duan, Y. Fu, D. Fatta-Kassinos, D.D. Dionysiou, Significant role of UV and carbonate radical on the degradation of oxytetracycline in UV-AOPs: Kinetics and mechanism, *Water Res.* 95 (2016) 195–204, <https://doi.org/10.1016/j.watres.2016.03.011>.
- [75] S. Moles, R. Mosteo, J. Gómez, J. Szpunar, S. Gozzo, J.R. Castillo, M.P. Ormad, Towards the Removal of Antibiotics Detected in Wastewaters in the POCTEFA Territory: Occurrence and TiO₂ Photocatalytic Pilot-Scale Plant Performance, *Water* 12 (2020), <https://doi.org/10.3390/w12051453>.
- [76] A. Martínez-García, M. Vincent, V. Rubiolo, M. Domingos, M. Cristina Canela, I. Oller, P. Fernández-Ibáñez, M.I. Polo-López, Assessment of a pilot solar V-through reactor for solar water disinfection, *Chem. Eng. J.* (2020), 125719, <https://doi.org/10.1016/j.cej.2020.125719>.
- [77] K.G. McGuigan, T.M. Joyce, R.M. Conroy, J.B. Gillespie, M. Elmore-Meehan, Solar disinfection of drinking water contained in transparent plastic bottles: characterizing the bacterial inactivation process, *J. Appl. Microbiol.* 84 (1998) 1138–1148.
- [78] R. Nalwanga, B. Quilty, C. Muanja, P. Fernandez-Ibáñez, K.G. McGuigan, Evaluation of solar disinfection of *E. coli* under Sub-Saharan field conditions using a 25L borosilicate glass batch reactor fitted with a compound parabolic collector, *Sol. Energy* 100 (2014) 195–202, <https://doi.org/10.1016/j.solener.2013.12.011>.
- [79] Á. García-Gil, L. Feng, J. Moreno-SanSegundo, S. Giannakis, C. Pulgarin, J. Marugán, Mechanistic modelling of solar disinfection (SODIS) kinetics of *Escherichia coli*, enhanced with H₂O₂ – part 1: The dark side of peroxide, *Chem. Eng. J.* 439 (2022), 135709, <https://doi.org/10.1016/j.cej.2022.135709>.
- [80] Á. García-Gil, L. Feng, J. Moreno-SanSegundo, S. Giannakis, C. Pulgarin, J. Marugán, Mechanistic modelling of solar disinfection (SODIS) kinetics of *Escherichia coli*, enhanced with H₂O₂ – Part 2: Shine on you, crazy peroxide, *Chem. Eng. J.* 439 (2022), 135783, <https://doi.org/10.1016/j.cej.2022.135783>.

- [81] E. Villar-Navarro, I. Levchuk, J.J. Rueda-Márquez, M. Manzano, Combination of solar disinfection (SODIS) with H₂O₂ for enhanced disinfection of marine aquaculture effluents, *Sol. Energy*. 177 (2019) 144–154.
- [82] L. Uhl, S. Dukan, Hydrogen Peroxide Induced Cell Death: The Major Defences Relative Roles and Consequences in *E. coli*, *PLoS One* 11 (2016) e0159706.
- [83] J. Gao, R.F. Nunes, K. O'Shea, G.L. Saylor, L. Bu, Y.-G. Kang, X. Duan, D. Dionysiou, S. Luo, UV/Sodium percarbonate for bisphenol A treatment in water: Impact of water quality parameters on the formation of reactive radicals, *Water Res.* 219 (2022), 118457, <https://doi.org/10.1016/j.watres.2022.118457>.
- [84] L. Li, R. Guo, S. Zhang, Y. Yuan, Sustainable and effective degradation of aniline by sodium percarbonate activated with UV in aqueous solution: Kinetics, mechanism and identification of reactive species, *Environ. Res.* 207 (2022), 112176, <https://doi.org/10.1016/j.envres.2021.112176>.
- [85] F.J. Rivas, O. Gimeno, T. Borralho, M. Carbajo, UV-C radiation based methods for aqueous metoprolol elimination, *J. Hazard. Mater.* 179 (2010) 357–362, <https://doi.org/10.1016/j.jhazmat.2010.03.013>.
- [86] S. Shekoohiyan, S. Rtimi, G. Moussavi, S. Giannakis, C. Pulgarin, Enhancing solar disinfection of water in PET bottles by optimized in-situ formation of iron oxide films. From heterogeneous to homogeneous action modes with H₂O₂ vs. O₂ – Part 1: Iron salts as oxide precursors, *Chem. Eng. J.* 360 (2019) 211–224, <https://doi.org/10.1016/j.cej.2018.10.113>.
- [87] P. García-Muñoz, C. López-Maxías, S. Guerra-Rodríguez, J. Carbajo, J.A. Casas, J. Rodríguez-Chueca, Photocatalytic activation of peroxymonosulfate using ilmenite (FeTiO₃) for *Enterococcus faecalis* inactivation, *J. Environ. Chem. Eng.* 10 (2022), 108231, <https://doi.org/10.1016/j.jece.2022.108231>.
- [88] L. Demarchis, M. Minella, R. Nisticò, V. Maurino, C. Minero, D. Vione, Photo-Fenton reaction in the presence of morphologically controlled hematite as iron source, *J. Photochem. Photobiol. A Chem.* 307 (2015) 99–107.
- [89] J.Y.T. Chan, S.Y. Ang, E.Y. Ye, M. Sullivan, J. Zhang, M. Lin, Heterogeneous photo-Fenton reaction on hematite (α -Fe₂O₃{104},{113} and 001 surface facets, *Phys. Chem. Chem. Phys.* 17 (2015) 25333–25341.
- [90] O. Augusto, M.G. Bonini, A.M. Amanso, E. Linares, C.C.X. Santos, S.L. De Menezes, Nitrogen dioxide and carbonate radical anion: two emerging radicals in biology, *Free Radic. Biol. Med.* 32 (2002) 841–859.
- [91] R.A. Larson, R.G. Zepp, Reactivity of the carbonate radical with aniline derivatives, *Environ. Toxicol. Chem.* 7 (1988) 265.
- [92] S. Canonica, T. Kohn, M. Mac, F.J. Real, J. Wirz, U. von Gunten, Photosensitizer method to determine rate constants for the reaction of carbonate radical with organic compounds, *Environ. Sci. Technol.* 39 (2005) 9182.
- [93] M. Bodrato, D. Vione, APEX (Aqueous Photochemistry of Environmentally occurring Xenobiotics): a free software tool to predict the kinetics of photochemical processes in surface waters, *Environ. Sci. Process. Impacts.* 16 (2014) 732–740, <https://doi.org/10.1039/C3EM00541K>.
- [94] C. Ruales-Lonfat, J.F. Barona, A. Sienkiewicz, J. Vélez, L.N. Benítez, C. Pulgarin, Bacterial inactivation with iron citrate complex: A new source of dissolved iron in solar photo-Fenton process at near-neutral and alkaline pH, *Appl. Catal. B Environ.* 180 (2016) 379–390, <https://doi.org/10.1016/j.apcatb.2015.06.030>.
- [95] L. Manrique-Losada, H.L. Santanilla-Calderón, E.A. Serna-Galvis, R.A. Torres-Palma, Improvement of solar photo-Fenton by extracts of amazonian fruits for the degradation of pharmaceuticals in municipal wastewater, *Environ. Sci. Pollut. Res.* 29 (2022) 42146–42156, <https://doi.org/10.1007/s11356-021-15377-1>.
- [96] U.J. Ahile, R.A. Wuana, A.U. Itodo, R. Sha'Ato, J.A. Malvestiti, R.F. Dantas, Are iron chelates suitable to perform photo-Fenton at neutral pH for secondary effluent treatment?, *J. Environ. Manage.* 278 (2021) 111566. [10.1016/j.jenvman.2020.111566](https://doi.org/10.1016/j.jenvman.2020.111566).