



Relevant impact of irradiance (vs. dose) and evolution of pH and mineral nitrogen compounds during natural water disinfection by photo-Fenton in a solar CPC reactor[☆]



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ABSTRACT

The inactivation of total coliforms/*E. coli* (10⁴ CFU/mL) and *Salmonella* spp. (10⁵ CFU/mL) in well water naturally containing dissolved (Fe^{2+/3+}) and solid iron forms (e.g. iron oxides) was carried out by photo-Fenton treatment (Fe²⁺·3+/H₂O₂/hv). In a preliminary run under simulated solar radiation, beyond 4 mg/L of added H₂O₂, the enteric bacteria were totally inactivated after 90 min. Thereafter, 25 L of well water were treated in the compound parabolic collector (CPC) under direct solar radiation. Three irradiation periods (i) 8 am to 2 pm (8–14 h), (ii) 10 am to 4 pm (10–16 h) and (iii) 12 pm to 6 pm (12–18 h) were evaluated for assessing the impact of different solar irradiances (W m⁻²) on the enteric bacterial inactivation rates. Both studied strains were totally inactivated under sole exposure to solar radiation in the CPC when the experiments were conducted from 8 to 14 h or 10 to 16 h. However, *Salmonella* spp. strains regrowth was noticed after the 24 h dark storage in all the samples previously treated with bare solar radiation. As the treated water contained Fe, the photo-Fenton disinfection at field scale in the CPC was carried out with the addition of H₂O₂ (10 mg/L). Significant enhancement of the enteric bacteria inactivation rate was therefore recorded comparatively to the one obtained under bare solar treatment. No regrowth was observed in water treated by photo-Fenton disinfection one week after the treatment. The comparative evaluation of photo-Fenton disinfection rate as a function of different irradiation periods was based on the monitoring of the effective disinfection time (EDT), or required time to acquire the total inactivation of targeted bacteria in defined conditions. Therefore, significant impact of the irradiance on the process was noticed. High average irradiance (AI) of 35 W m⁻² led to the total inactivation of *Salmonella* spp. in an EDT of 45 min and a dose of 26 Wh m⁻²; while low irradiance of 20 W m⁻² required an EDT of 180 min for a dose 60 Wh m⁻². Thus, the experiments revealed that lower irradiance level leads to higher doses to achieve the bacterial disinfection. pH, as well as nitrite and nitrate concentration, increased during the photo-disinfection processes, while depletion was recorded for aqueous ammonia concentration.

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1. Introduction

In Sub-Saharan Africa countries (e.g. Burkina Faso) as in most developing countries of the world, family well water and surface water in rural and sub-urban areas are used as drinking water by

several families. However, microbial contamination of these water sources by farming, breeding and/or domestic activities reduces the amount of potable drinking water and increases waterborne diseases outbreak such as dysentery, typhoid and cholera, as recorded in some of these countries [1]. Therefore, there is a need to develop low-cost water disinfection processes for rural and sub-urban areas. Many developing countries are situated in the latitude lines of 30°N and 30°S and receive about 2000 to 3000 h of solar illumination annually. This natural energy could be significantly used to disinfect such water sources by solar disinfection processes before consumption. Solar disinfection of water (SODIS) was first assessed in Beirut and afterwards in other tropical regions [2]. SODIS principles imply the synergistic effect of sunlight and temperature on

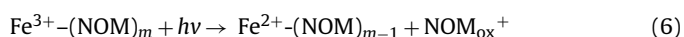
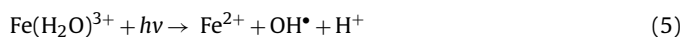
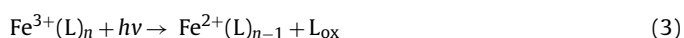
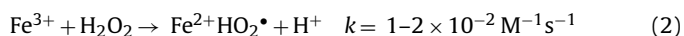
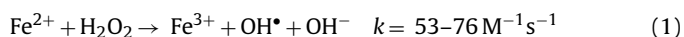
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enteric bacteria inactivation. SODIS treatment is used by more than 4.5 million people in more than 55 countries [2,3].

Researches on SODIS enhancement were focused on (i) the use of black back bottles to speed up increase of the temperature [4] either by using Pyrex bottles, instead of glass or polyethylene terephthalate (PET) bottles to increase UV-A radiation penetration, (ii) increase oxygenation of the system through the agitation of the bottles before exposition [4], (iii) the use of azo dyes as dosimetric indicators to enhance the photocatalytic process during the disinfection [5], (iv) the enhancement of production of highly oxidant hydroxyl radicals (OH[•]), which increases the inactivation rate by the addition of a photocatalyst, i.e. TiO₂, [6] or H₂O₂ and iron salts [7,8]. In order to enhance the solar disinfection process, a compound parabolic collector (CPC) solar reactor has been operated with the addition of catalyst (TiO₂ or iron salts) and/or oxidants (H₂O₂) [6,9,10]. Also, previous photo-disinfection treatment carried out under solar exposure in a CPC suggested that the accumulated radiation dose had a great influence on bacterial inactivation rate [11,12]. In the present work, since the natural water under treatment contains natural organic matter (NOM), dissolved and solid iron forms [7,13], it is likely that the addition of H₂O₂ will generate under solar light a homogeneous and heterogeneous photo-Fenton system. Therefore, no others chemical will be need for the enhancement of the photo-treatment. Photo-Fenton as well as dark Fenton reaction, was in the past considered to take place only within acidic pH values [14–16]. In these conditions the dark Fenton reaction (Eqs. (1) and (2)) is limited by the low kinetic of Fe²⁺ production (Eq. (3)) [14,17,18]. High production rates of additional Fe²⁺ and OH[•] are generated during the photoreduction of Fe³⁺-complexes in the solution (Eqs. (3)–(7)). The primary step of the photoreduction of dissolved ferric iron is a ligand-to-metal charge-transfer (LMCT) reaction. Fe³⁺-complexes undergo LMCT excitation to give Fe²⁺ and an oxidized ligand, L_{ox} (Eq. (3)). When a natural water sample containing Fe³⁺-NOM complexes is photo-irradiated, Fe³⁺ is reduced to Fe²⁺ and NOM is oxidized (Eq. (6)). For example, the photolysis of Fe³⁺-NOM carboxylate or Fe³⁺-polycarboxylate complexes through LMCT reaction, leads to the formation of Fe²⁺, which is introduced in the photo-Fenton cycle and the concomitant oxidation of the organic ligand (Eqs. (6) and (7)) [19–21].



where k is kinetic constants.

In the presence of iron oxides as is the case in the water study in this work, the heterogeneous photo-Fenton system could also be considered. This heterogeneous action could take advantage of the indiscriminant siderophore transport system present in bacteria. The siderophore is a molecular receptor that binds and transports iron [22,23]. Their impact on the heterogeneous photo-Fenton system could proceed from the fact that: (i) the siderophore and Fe³⁺ enter the bacterium together leading to internal Fenton reaction [8,22], (ii) a ligand exchange step occurs in the course of the transport and (iii) the implementation of the photo-Fenton reaction due

to the semiconductor action of some forms of iron oxides naturally present in water. [24].

Several studies on solar and photocatalytic disinfection efficiency have been reported using *E. coli* K12 in lab [8,12] and at field scale with natural water [6,11,25]. However, *E. coli* was determined to be not always an appropriate indicator for bacterial inactivation monitoring, due to its high sensitivity to photo-inactivation [7,26]. Recently, some authors have evaluated the efficiency of photo-Fenton on the inactivation of several microorganisms [21,27–30]. Sciacca et al. [27] have reported that photo-Fenton disinfection of wild total coliforms and *Salmonella* spp. in natural water containing NOM (turbidity: 800–1000 NTU (nephelometric turbidity units)) was not efficient. This inefficiency was due to the consumption of the H₂O₂ by the NOM. It is important before intending to address the photo-Fenton disinfection of drinking water to human consumption to evaluate its efficiency on disinfecting large volumes of natural clear water of turbidity less than 30 NTU, as recommended in SODIS references [2].

Most wells intended to drinking water collection are situated in agricultural areas in the Sahelian region (Sub-Saharan Africa region). Individual wells in agricultural areas throughout the world specifically contribute to nitrate-related toxicity problems and nitrate levels in the well water often exceed 50 mg/L [31]. The photochemical reduction of nitrite or nitrate and the chemical oxidation of ammonia are the most involved pathways during the interconversion of the nitrogen compounds in natural water. Some authors have reported that upon sunlight irradiation of natural waters in the presence of humic substances, nitrate and nitrite salts are produced and reactive oxygen species (ROS) are generated [32,33]. Nitrates in the soil are from various origins; it could be from humus degradation, fresh or composted natural organic matter that is used as fertilizer or from nitric nitrogen of chemical fertilizers. The infiltration of nitrates in wells' water can induce high concentrations, even greater than the restrictions of the World Health Organization (WHO) guidelines for drinking water (50 mg/L). The health risk related to excess nitrate in drinking water is mostly related to its transformation (oxido-reduction), which can lead to more toxic compounds, such as nitrite and nitrosamines. Most of them are classified as carcinogen by the WHO. The WHO guideline for nitrite in drinking water is less than 3 mg/L [31,34].

Moreover, the term ammonia includes the non-ionized (NH₃) and ionized (NH₄⁺) species. Ammonia in the environment originates from metabolic, agricultural and industrial processes and from disinfection with chloramine. Natural levels in groundwater and surface water are usually below 0.2 mg/L, while anaerobic groundwater may contain up to 3 mg/L. Farm animals' excreta lead to higher levels in surface water. Ammonia in water is an indicator of possible bacterial, sewage and animal waste pollution. Taste and odor problems, as well as decreased disinfection efficiency, are to be expected if drinking water containing more than 0.2 mg/L of ammonia. Ammonia in drinking water is not of immediate health relevance and therefore no health-based guideline value is proposed. [34–36].

The current study aims mainly to evaluate the contrasting effect of solar radiation parameters (irradiance vs. dose) on the efficiency of photo-disinfection of wild total coliforms/*E. coli* and *Salmonella* spp. under the addition of H₂O₂ in a natural drinking water source containing dissolved and solid iron forms. The evaluation of the impact of different irradiances and doses was carried out following several exposure sets of the water sample in a CPC solar reactor, during different day times. This evaluation could suggest a schedule of the most favorable day periods which could be proposed to the users, if the vulgarization of the processes is considered.

Considering the impact of the pH on the efficiency of the photo-disinfection and the proximity of the studied wells with agricultural areas, the monitoring of the variation of pH, NH₄⁺,

NO_3^- and NO_2^- during the photo-treatment will be followed in this study. This monitoring will lead to the evaluation of the impact of these parameters on the photo-disinfection treatment and vice-versa.

2. Materials and methods

2.1. Chemical reagents

Hydrogen peroxide, 30% (AnalaR Normapur, VWR) was used to prepare the Fenton reagent. Hydrochloric acid fuming (HCl), 37% (Fluka Analytical, Sigma-Aldrich®) was used for glass-reactor cleaning. HACH specific reagents were used for total iron, nitrite, nitrate and ammonia detection. Microbiology Chromocult® (Merck KGaA) was used for bacterial plating. Growth media was poured in pre-sterilized Petri Dishes; 92 × 16 mm (Sarstedt AG) for bacterial enumeration.

2.2. Analytical methods applied for measuring the physical parameters of water

A Universal meter WTW 340i equipped with a WTW SenTix 41-3 probe was used to measure the pH and temperature ($^{\circ}\text{C}$). The concentration of hydrogen peroxide (H_2O_2) was monitored during the experiments via Merckoquant peroxide analytical test strips (Test Peroxides, Merck Merckoquant), while detection limit was 0.5 mg/L.

The HACH DR/2000 spectrophotometer methodologies used in this study to characterize some physico-chemical properties of the water sample follow the guidelines of the Standard Methods for Examination of Water [37]. The water turbidity was evaluated with the program 750 (wavelength 450 nm) and the detection ranges were between 0 to 450 NTU/FTU (Nephelometric turbidity units/Formazin Turbidity Units). The nitrate (NO_3^-) contents was determined with the high range (HR) with the cadmium reduction method (NitroVer 5, Nitrate Reagent Powder Pillow, wavelength 500 nm) and the detection ranges were between 0 to 30.0 mg/L NO_3^- -N. The program gives the results as the concentration of (X) NO_3^- in N (nitrogen) contents of the sample (NO_3^- -N) and the exact concentration of NO_3^- in the water was calculated using the HACH species conversion factors (SCF) specific for each component and program. The SCF of NO_3^- -N is 4.427 mg/L, then $\text{NO}_3^- = X \times 4.427$ mg/L. The nitrite (NO_2^-) contents was determined with the low range diazotization method (LR) (NitriVer 3 Powder Pillows, detection ranges between: 0 and 0.300 mg/L NO_2^- -N), for wavelength 507 nm. As for the calculation of nitrate, nitrite is subject to a SCF number (3.284), then its exact determination was through the calculation $\text{NO}_2^- = X' \times 3.284$ mg/L. The ammonia (NH_4^+) concentration was evaluated with the Nessler Method at wavelength 425 nm and detection ranges were between (0 and 2.50 mg/L NH_3 -N). The result was of NH_4^+ concentration in N contents in the water was obtained after the calculation with the ammonia SCF (1.288), $\text{NH}_4^+ = X'' \times 1.288$ mg/L. X, X' and X'' was the number read on the spectrophotometer DR/2000 during each specific measure; the results presented in this paper are the average for each components recorded upon the experiments [37]. On site at the International Institute for Water and Environmental Engineering (2iE) of Ouagadougou, with the HACH process, the dissolved total iron content of the water sample was determined by the FerroVer Method (Powder Pillows), wavelength 510 nm and the detection ranges were between 0 and 3.00 mg/L. Further at École Polytechnique Fédérale de Lausanne (EPFL) the solid total iron (iron oxides) was evaluated with the ICP-MS spectrometry, with sensitive detection limit ranges (0.1–0.9 $\mu\text{g/L}$)

Table 1

Some characteristics of the wells water sample used during the experiments.

Parameters	Contents
Turbidity	5 ± 3 NTU
pH	5.4 ± 0.1
Temperature	29 ± 0.1 $^{\circ}\text{C}$
Total iron	0.07 ± 0.02 mg/L
Wild <i>E. coli</i>	10^4 CFU/mL
Wild <i>Salmonella</i> spp	10^5 CFU/mL

NTU = Nephelometric turbidity units, CFU/mL = Colony forming unit per milliliter, $^{\circ}\text{C}$ = Degree Celsius, mg/L = milligram per liter

2.3. Water sample characteristic

The experiments presented in this study were carried out from February to March 2011 (dry season) in Burkina Faso. The water samples were collected from a family well of Tanghin district of Ouagadougou. Ouagadougou is located at $12^{\circ}21'26''$ of Latitude North and $1^{\circ}32'7''$ of Longitude West and the experiments were conducted at the site of 2iE. This location is subject to approximately 2500 h of solar radiation per year [38]. Then it could be considered as a good place for the experimentation of solar and photo-Fenton disinfection of drinking water. Table 1 presents the initial concentration of some relevant physico-chemical parameters of the water and the microorganisms considered during the disinfection process. Sampling was performed one hour before the experiments. For the laboratory experiments, it was collected in 1.5 L PET bottles, while for field experiments; plastic jerricans of 20 L were used.

2.4. Laboratory experiments under simulated solar radiation

To evaluate the effect of H_2O_2 concentration on the photo-Fenton inactivating rate, 90 mL of the sample were introduced in eight glass reactors of 100 mL each containing different H_2O_2 concentrations (0, 2, 4, 5, 6, 7, 8 and 10 mg/L) and were irradiated in a solar simulator (Hanau Suntest). The radiation intensity applied for lab-scale experiments was 560 W m^{-2} (32 W m^{-2} in the UV-A) which is the average UV-A delivered by sun light in Ouagadougou during summer times [27,38].

To evaluate the bacterial inactivation rate, 1 mL of the sample was taken at time intervals (0, 10, 20, 30, 45, 60, 90, 120, 150, 180, 240, 300, 360 min) during the experiment (6 h) with a sterile 5 mL syringe connected to the reactor and placed in a sterile 1.5 mL Eppendorf microtube. From this 1 mL, 100 μL were sampled and poured in a Petri dish plate containing growth media (Chromocult agar). Plates were incubated for 18–24 h at 37°C and bacteria were counted with a colony counter (Stuart SC6 Colony Counter). Specification and use as well as plating and counting with Chromocult agar have been described before [9].

The final treated samples were kept in the dark for bacterial regrowth assessment after 24 h, 72 h and a week. To ensure the residual effect of the Fenton reaction in the treated water during the storage, the samples were kept in the dark without removing their remaining H_2O_2 . This residual content was measured every day during the storage for the evaluation of its decay in the water before its possible consumption. The experiments were repeated five times to ensure reproducibility.

2.5. Field experiments under direct solar radiation

Field experiments were conducted under solar radiation in a solar CPC with 25 L of well water at constant flow (2 L/min).

From the results of the determination of the optimized concentration of H_2O_2 to be used efficiently in drinking disinfection by photo-Fenton, evaluated at lab scale in the Suntest, the

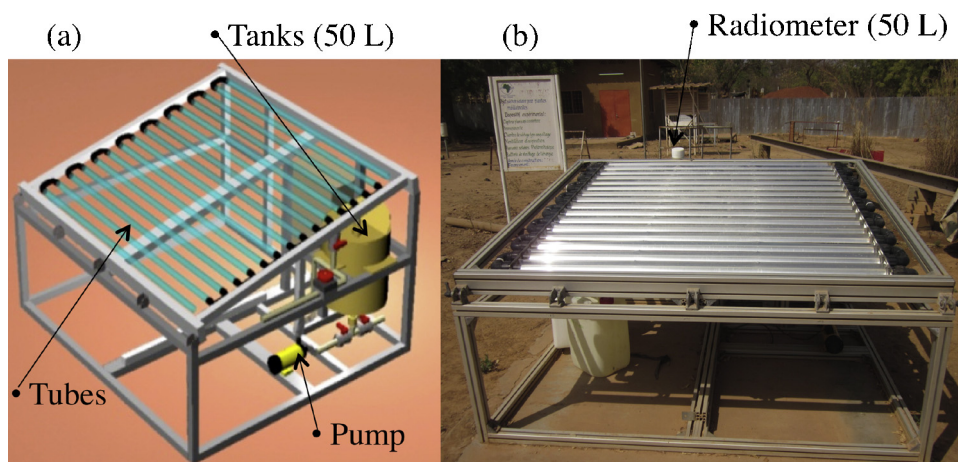


Fig. 1. The schematic (a) and physical (b) representation of the compound parabolic collector (CPC) solar reactor.

concentrations from 5 to 10 mg/L has shown approximately the same inactivation rate. Preliminary experiments were conducted at field scale with 5 mg/L of H_2O_2 added on the water sample. Unfortunately the H_2O_2 concentration in this case, in contrast to the stability noticed at lab scale, was degraded certainly due to high fluctuation of water in the CPC, which increased the oxygenation. This fast degradation has led to total consumption of H_2O_2 after only 3 to 4 h of exposure. In order to ensure that there is H_2O_2 left after the disinfection process (6 h), to ensure the residual effect of the Fenton treatment, the experiments presented in this paper were carried out with 10 mg/L of H_2O_2 . The remaining H_2O_2 in the treated water, when 10 mg/L was used, 2 to 3 mg/L; however the continuous evaluation of its persistence in the treated water has permitted to record that it was depleted totally after 48 h.

Control experiments were carried out on samples without added H_2O_2 . The efficiency of both photo-disinfection process (SODIS and photo-Fenton), was evaluated during three different time period of 6 h: (i) 8 am to 2 pm (8–14 h), (ii) 10 am to 4 pm (10–16 h) and (iii) 12 pm to 6 pm (12–18 h). The samples were subject to the variation of: (i) water temperature, (ii) instantaneous irradiation (irradiance) (W m^{-2}) and (iii) cumulated global radiation (dose) (Wh m^{-2}). Blank tests took place in the dark, a 100 mL samples also containing H_2O_2 . Experiments were repeated three times to ensure reproducibility.

The batch photoreactor (Fig. 1) used in this study was a compound parabolic collector (CPC): SOLARDETOX ACADUS-2003 device model delivered by Ecosystem SA, (Barcelona, Spain). It has a useful exposition surface of 2.12 m^2 , out of a total surface of 2.54 m^2 . The illuminated volume of the water during its flowing in the photoreactor is 15.1 L. Its minimum operating volume is 18 L and its total capacity is 50 L. It is made of 16 borosilicate cylindrical glass tubes of 32 mm diameter, 1.5 m length and 1.4 mm of width, through which water is circulating and exposed to solar irradiation. Tubes are disposed on aluminum cylindro-parabolic mirrors in such a way that the distribution of the UV irradiation by the mirrors is equal around the tube circumference. This configuration implies no light concentration, but allows working with diffuse light. A polypropylene stirring tank of 50 L is connected in series with the CPC module and constitutes a re-circulating tank. Hence, the pilot plant behaves as a plug-flow reactor in which water is circulating using a centrifugal pump with a flow of 24.2 L min^{-1} . The reactor is mounted on a two-position fixed platform inclinable at 10° and 35° allowing operating at the approximate local latitude of Ouagadougou-Burkina Faso (12.2°N), at 10° angle position for the most of the time. The solar UV radiation was reported during the experiments by a UV-A radiometer ACADUS 85 UV fixed on the CPC

photoreactor at the same inclination of 10° . Solar irradiance intensity per square meter (W m^{-2}) was then monitored between 300 and 400 nm.

2.6. Data analysis

The effective disinfection time (EDT), which is the time (h) required to get the total inactivation in water of a targeted bacteria in defined conditions [39] will be used for the comparative study on the influence of the irradiance on the bacteria inactivation rate.

$$\text{AI} : \text{Average irradiance during the EDT} (\text{W m}^{-2}). \quad (8)$$

$$\text{Dose for total inactivation} = \text{AI} * \text{EDT} (\text{Wh m}^{-2}). \quad (9)$$

The evaluation of the impact of the H_2O_2 concentration and the bacteria species on the efficiency of the enhanced-photo-disinfection was conducted by an analysis of variance (ANOVA). This analysis was carried out with the two-way ANOVA Package of the Wolfram Mathematica 8.0 program. The determination of the discriminating power (Fisher ratio (F)) of the H_2O_2 or the bacteria species on the inactivation rate will permit to point out the significance of each of these parameters on the photo-disinfection process. The accuracy of the results will be evaluated by the noise level (Probability (P)).

3. Results and discussion

3.1. Lab experiments in a solar simulator: Influence of H_2O_2 concentration on bacterial inactivation

The temperature of the water in the solar simulator (Suntest) increased from 28°C to 45°C during the experiments. It is well known that temperature above 45°C has a bactericidal effect [2]. According to this, it can be assumed that the bacterial inactivation obtained in the Suntest was not due to the thermal effect of IR irradiation. The studied well water already contained dissolved iron: $0.07 \pm 0.02 \text{ mg/L}$ of Fe^{2+} , $^{3+}$ and solid iron oxides: $0.23 \pm 0.01 \text{ mg/L}$, hence the additional reagent required to induce the photo-Fenton reaction is only H_2O_2 . Adsorption of bacteria to iron oxides was recorded in MilliQ water [8]. This adsorption favors the siderophore iron transport action [22]. In such conditions, heterogeneous photo-Fenton reaction can take place leading to bacterial inactivation [24,40]. To ensure the quality of treated water, H_2O_2 concentrations in the photo-Fenton process should be optimized for natural water source [19,27,38]. For this reason this part of the study aims to evaluate the minimal H_2O_2 concentration

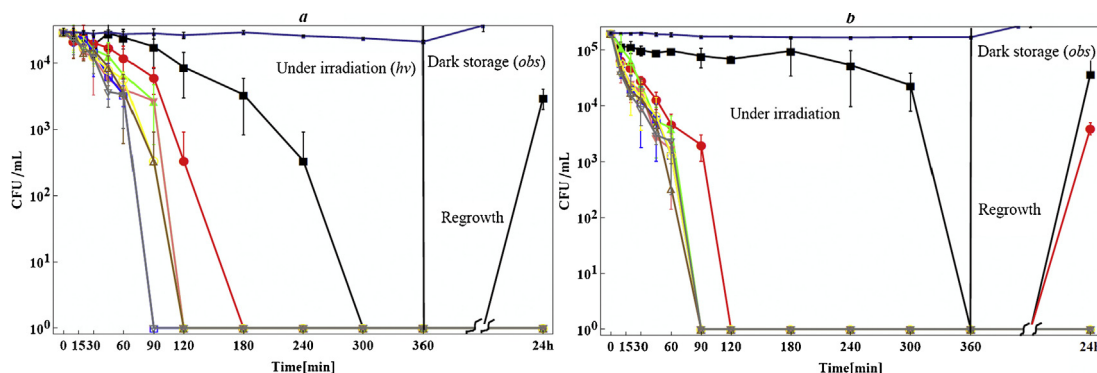


Fig. 2. Inactivation kinetics of the wild enteric bacteria of natural well water containing natural iron (dissolved: 0.07 ± 0.02 mg/L of Fe^{2+} , $^{3+}$ and solid iron oxides (0.23 ± 0.01 mg/L) treated with different concentrations of H_2O_2 . (a) Total coliforms/*E. coli*, (b) *Salmonella* spp. (■) 0 mg/L H_2O_2 , (●) 2 mg/L H_2O_2 , (▲) 4 mg/L H_2O_2 , (▼) 5 mg/L H_2O_2 , (□) 6 mg/L H_2O_2 , (○) 7 mg/L H_2O_2 , (△) 8 mg/L H_2O_2 , (▽) 10 mg/L H_2O_2 and (■) 10 mg/L Dark.

which could be used for significant drinking water disinfection by photo-Fenton.

The influence of H_2O_2 concentration on the photo-Fenton inactivation rate is presented in Fig. 2 Trace (■), representing the disinfection conducted without H_2O_2 , showed the lower inactivation rate for both enteric bacterial species (*Salmonella* spp., coliforms/*E. coli*). The inactivation rate constant k , presented in Table 2, confirmed the effect observed on the curves, with $k = -0.008 \pm 0.002$ and $-0.005 \pm 0.001 \text{ min}^{-1}$ for coliforms/*E. coli* and *Salmonella* spp., respectively. These inactivation rates have drastically increased in both cases in the presence of H_2O_2 . With only 2 mg/L of H_2O_2 (Trace (●)), more than 50% increase of the inactivation rate was noticed in both cases with, respectively $k = -0.016 \pm 0.003$ and $k = -0.083 \pm 0.002 \text{ min}^{-1}$ for coliforms/*E. coli* and *Salmonella* spp. Beyond 4 mg/L of H_2O_2 , the *Salmonella* spp. content of all the systems was totally inactivated in approximately 90 min. The inactivation rate of coliforms/*E. coli* and *Salmonella* spp., as presented in Table 2, underline that they were greater than the correspondent ones, under simulated solar light alone. The high sensitivity of *Salmonella* spp. here is in contrast with the report of several authors on treatment under direct solar radiation. Berney et al. [26] and Sciacca et al. [7] have noticed that *Salmonella* spp. was more resistant to photo-inactivation than *E. coli* and other enteric bacteria. The inactivation rate constant of coliforms/*E. coli* observed for 5 and 10 mg/L of H_2O_2 , were approximately the same, being $k = -0.032 \pm 0.001 \text{ min}^{-1}$ and $-0.034 \pm 0.001 \text{ min}^{-1}$. The first order kinetics decrease in CFU/mL was observed in the curves of both enteric bacteria treated by photo-Fenton with up to 4 mg/L of H_2O_2 , then k was calculated by linear regression [8]. Fig. 2 shows that control experiments (Trace (·)) that took place with 10 mg/L of H_2O_2 in dark did not lead to enteric bacteria inactivation. Post-irradiation evaluation after 24 hours of dark storage has revealed the regrowth of both enteric bacteria in the water, after their exposure to solar simulator, in the absence of H_2O_2 . Only *Salmonella* spp. regrowth was observed in the water illuminated in the presence of 2 mg/L of H_2O_2 . Beyond 4 mg/L of H_2O_2 , none of the enteric bacteria has shown regrowth after photo-treatment. It could be assumed that treated water under a solar simulator, with concentration of 4 mg/L of H_2O_2 , ensures not only efficient

inactivation of the enteric bacteria, but also prevents the subsequent regrowth.

The discrimination power (Fisher ratio (F)) obtained from ANOVA analysis for the evaluation of the impact of H_2O_2 concentration on the photo-Fenton inactivation rate is up to 51.5, leading to the evidence that this concentration has a strong impact on the process with a very small probability ($P < 0.001\%$) that the effect may be due to noise (Table 3). The bacteria species, either wild *E. coli* or *Salmonella* spp., did not significantly influence the inactivation rate under the photo-Fenton disinfection as shown by the low Fisher ratio ($F = 0.11$). The probability that this effect is due to noise is very large ($P = 74\%$). With an influence factor of 6.1, the interaction between the treatment and bacteria type seems to have just a slight impact on the photo-Fenton disinfection rate.

3.2. Field scale experiments in a CPC solar reactor

3.2.1. Treatment under solar irradiation alone

The photo-disinfection of both enteric bacteria under uniquely solar radiation from 8 to 14 h is presented in Fig. 3a. The total coliforms/*E. coli* strains (Fig. 3a, trace (○)) were totally inactivated after the first three hours of exposure when the average irradiance was 20 W m^{-2} (Fig. 3a' trace (–)) for a accumulated dose of 120 Wh m^{-2} (Fig. 3a- trace (+)). The *Salmonella* spp. strains (Fig. 3a, trace (●)) resisted till the fifth hour of exposure (dose of 250 Wh m^{-2}) with an average irradiance (AI) of 20 W m^{-2} and then were totally inactivated.

For the experiments conducted from 10 to 16 h, the exposure began when the sun irradiance (Fig. 3b' traces (–)) was three times higher than the one measured when started at 08:00. For *Salmonella* spp. (Fig. 3b, trace (●)) the fast temperature increase from 29°C to 45°C in less than one hour and half (Fig. 3b', trace (X)) coupled to average irradiance of 32 W m^{-2} (Fig. 3b' traces (–)) during the 3 h, required for total inactivation (EDT), led to a cumulated energy of 200 Wh m^{-2} . Compared to the previous period (5 h with a dose of 250 Wh m^{-2}), the *Salmonella* spp. were totally inactivated here in 3 h for a dose of 200 Wh m^{-2} , but at higher AI exposure. The total coliforms/*E. coli* (Fig. 3b, trace (○)) were completely inactivated in 30 min before the *Salmonella* spp. Regrowth of *Salmonella* spp. were

Table 2
Inactivation rate constant k (min^{-1}) of the enteric bacteria present in water treated by photo-Fenton with simulated solar radiation at different H_2O_2 (mg/L) concentrations.

Microorganisms	H_2O_2 (mg/L) and k (min^{-1})							
	0	2	4	5	6	7	8	10
<i>E. coli</i> and Coliforms	-0.008 ± 0.002	-0.016 ± 0.003	-0.022 ± 0.003	-0.032 ± 0.001	-0.028 ± 0.002	-0.029 ± 0.001	-0.029 ± 0.001	-0.034 ± 0.001
<i>Salmonella</i> spp.	-0.005 ± 0.001	-0.083 ± 0.002	-0.063 ± 0.002	-0.120 ± 0.002	-0.119 ± 0.001	-0.117 ± 0.003	-0.142 ± 0.003	-0.160 ± 0.003

Table 3
Results of the two way analysis of variance between treatment/bacteria species.

Parameters	DF	SS	MS	F	P
Treatment	7	399154	57022	51.51	0.001%
Bacteria species	1	119.83	119.83	0.11	74%
Treatment/Bacteria	7	47703.9	6814.84	6.1	0.01%
Error	76	84127.5	1106.94	-	-
Total	91	531105	-	-	-

DF: Degree of Freedom, SS: Sum of Square, MS: Mean Square, F: Fisher factor, P: probability.

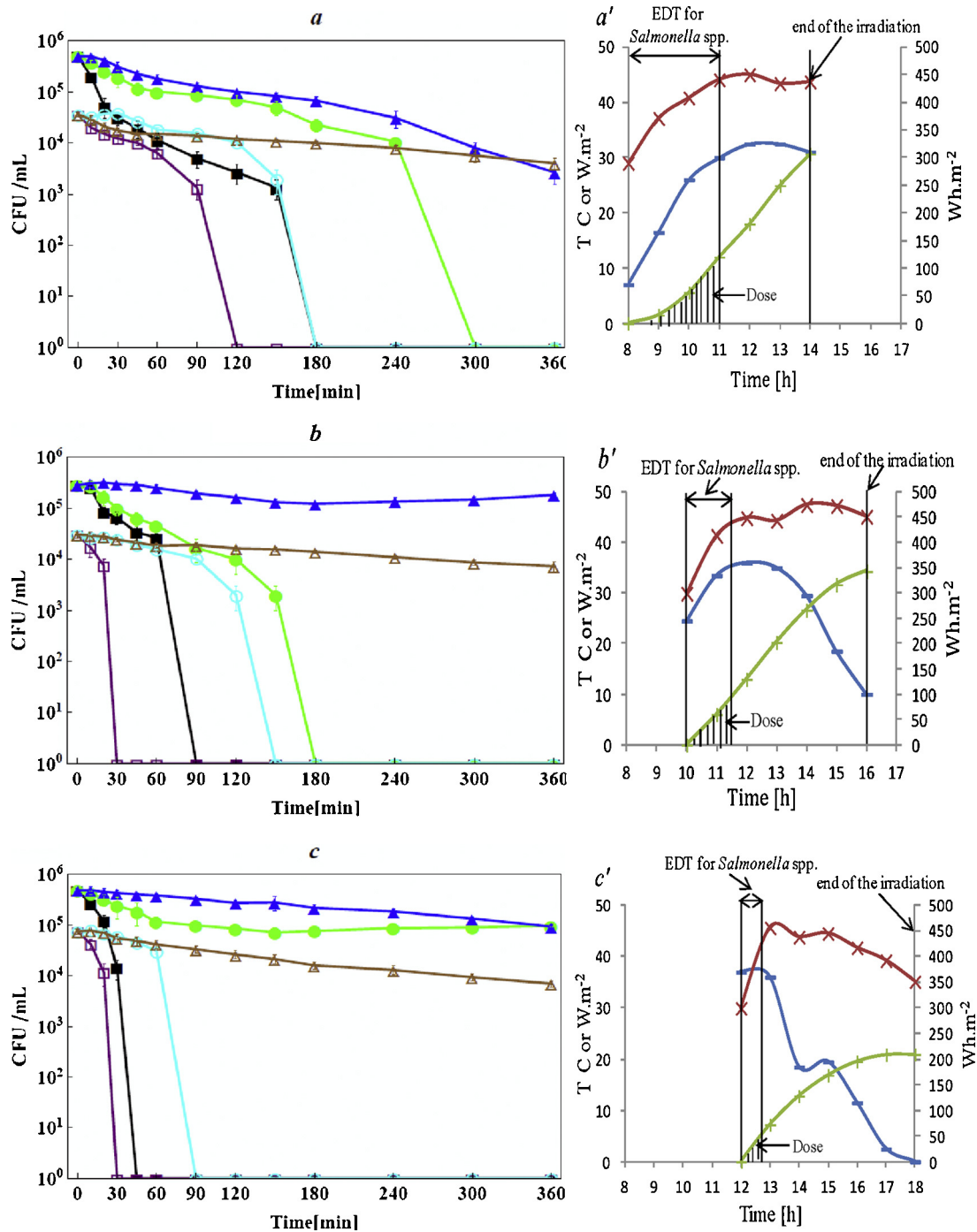


Fig. 3. Inactivation under different day periods (a, b, c) of the wild enteric bacteria of well water containing natural iron (dissolved: 0.07 ± 0.02 mg/L of Fe^{2+} , Fe^{3+} and solid iron oxides (0.23 ± 0.01 mg/L) and addition of 10 mg/l of H_2O_2). (a, b, c). Evolution of water temperature (T C), (X), Irradiance ($W \cdot m^{-2}$), (-) and cumulated total Dose ($Wh \cdot m^{-2}$), (+) during the Treatments. EDT (photo-Fenton): Effective Disinfection Time for *Salmonella* spp. (time required for the total inactivation of *Salmonella* spp. under photo-Fenton treatment). Day time periods (aa': 8–14 h), (bb': 10–16 h), (cc': 12–18 h). Total coliforms/*E. coli* (\square) and *Salmonella* spp. (\blacksquare) under photo-Fenton (natural Fe^{2+} , $Fe^{3+}/H_2O_2/h\nu$), total coliforms/*E. coli* (\circ) and *Salmonella* spp. (\bullet) under direct solar radiation (natural Fe^{2+} , $Fe^{3+}/h\nu$), total coliforms/*E. coli* (\triangle) and *Salmonella* spp. (\blacktriangle) in the dark Fenton (natural Fe^{2+} , $Fe^{3+}/H_2O_2/obs$).

also observed in this case as in the previous one during the post-irradiation tests (Table 5). Considering that the temperature level remained also below 50 °C here, the impact of temperature on the inactivation process was not significant.

In experiments carried out from 12 to 18 h, the average irradiance (37 W m⁻²) available at noon (Fig. 3c' trace (-)) together with a fast temperature increase from 29 °C to 44 °C in one hour (Fig. 3c' trace (X)) drastically affect the total coliforms/*E. coli* concentration, leading to their total inactivation in 90 min (Fig. 3c, trace (○)). However, the sudden decrease of irradiance to 18 W m⁻² after the first hour of exposure negatively affects the *Salmonella* spp. inactivation (Fig. 3c, trace (●)) even though the cumulative dose was still increasing (Fig. 3c' traces (+)). Indeed, after a slight decrease noticed at the beginning of the process, *Salmonella* spp. has remained stable at approximately 10⁵ CFU/mL till the end of the experiment (6 h). The resistance of *Salmonella* spp. to sole solar photo-disinfection, when the irradiance is low is significantly noticed here (Table 5) and confirmed the observation reported by Berney et al. [26] and Sciacca et al. [7]. These results point out that irradiance and temperature are more crucial for *Salmonella* spp. than for total coliforms/*E. coli* during solar treatment in a CPC.

The synergy between the irradiance (related to UV and visible part of sunlight) and thermal action (T°C) (related to infrared rays) has led to both enteric bacteria inactivation as already noticed by several authors [2]. However, *Salmonella* spp. regrowth occurred after 24 h of dark storage for all the illumination periods and for the samples taken at 90, 120, 150, 180, 240, 300 and 360 min. Therefore, it can be assumed that to ensure a lethal impact in solar disinfection of such resistant strains in a CPC reactor, temperature up to 50 °C is required, as recommended by SODIS reference for 1–2 L. However, the weather variation can't always ensure such conditions, even in the Sahelian region, as it can be observed with the irradiance fluctuations presented by the traces (-) of Fig. 3a–c'. The crucial impact of the available irradiance on the photo-Fenton disinfection of natural water will be addressed in the next part of this paper.

3.2.2. Enhanced photo-disinfection by addition of H₂O₂ in water containing naturally dissolved and solid iron forms

For this part of the study, the disinfection of natural well water in a CPC solar reactor was has been preliminary tested at field scale with 5 mg/L of H₂O₂ as explained in the methodology Section 2.5. However, it was noticed that during these preliminary runs that H₂O₂ was totally consumed after 3–4 h of irradiation. This consumption was probably due to intensive O₂ supply by water recirculation in the CPC into the solar simulator. Indeed, H₂O₂ degradation is favored by O₂ concentration. Oxygen associated to photosensitizers (i.e. NOM) present in water led to reactive oxygen species (ROS) generation [4,41], increasing H₂O₂ consumption, following the reaction presented in Eqs. (10)–(12) and the Haber–Weiss reaction (Eqs. (13) and (14)) [14,19]. In order to ensure that there is H₂O₂ left after the disinfection process, additional experiments were carried out with 10 mg/L of H₂O₂ initial concentration. The remaining H₂O₂ after the treatment was enough to ensure a residual effect during the dark storage (24 h). Experiments performed with 10 mg/L of H₂O₂ lead to a remaining H₂O₂ concentration of 3–4 mg/L after 6 h of irradiation. This residual H₂O₂ could possibly ensure the Fenton activity in the presence of the dissolved and solid iron of the water in the dark. Fig. 3a–c, shows the inactivation of wild enteric bacteria (open symbols for total coliforms/*E. coli* and full symbols for *Salmonella* spp.) contents of the natural wells water in the CPC during different periods of the day and different disinfection experimental trials. Direct solar radiation (hv) (○, ●), H₂O₂ enhanced photo-disinfection (Fe²⁺/H₂O₂/hv)

Table 4

Influence of irradiance on the efficient disinfection time and dose for the photo-Fenton treatment of *Salmonella* spp.

	^b AI (W m ⁻²)	^a EDT (h)	^c Dose (Wh m ⁻²)
8–14 h	20	3	60
10–16 h	28	1.5	42
12–18 h	35	0.75	26

^a Efficient disinfection Time (time required to achieve the total inactivation in water of a target bacteria (e.g *Salmonella* spp. in this case)).

^b Average irradiance during the EDT.

^c Solar cumulated energy during the EDT.

(□, ■) and the dark Fenton (Fe²⁺/H₂O₂/obs) (△, ▲). The initial concentration of the H₂O₂ added was 10 mg/L.



The decrease of both enteric bacteria under H₂O₂ enhanced photo-disinfection follows the first order kinetic while under the uniquely solar illumination the curves presented a shoulder leading to a concave shape [2,26]. Fig. 3a'–c', presents the evolution of water temperature (X) [T°C], solar irradiance (-) (W m⁻²) and cumulated total dose (+) (Wh m⁻²).

The *Salmonella* spp. Effective disinfection time (EDT), or in another words, the required time to achieve the total inactivation of *Salmonella* spp. in the water sample, was annotated on the graphs of (Fig. 3a'–c'). 10 mg/L of H₂O₂ was added to the water sample to initiate the photo-Fenton process, in the presence of its natural iron contains of (dissolved: 0.07 ± 0.02 mg/L of Fe²⁺, 3⁺ and solid iron oxides (0.23 ± 0.01 mg/L). We confirmed the meaningful contribution of the photo-Fenton process with the fact that when natural water is diluted, 2–3 folds of the bacteria inactivation rate significantly diminished event if the amount of added H₂O₂ is kept at 10 mg/L (results not shown). Despite the low average irradiance (AI) available, the photo-Fenton disinfection treatment conducted from 8 to 14 h led to an enhancement of the simple solar disinfection of 33% for total coliforms/*E. coli* strain (Fig. 3a, trace (□)) and of 40% for the *Salmonella* spp. (trace (■)). The EDT of 180 min (3 h) was noticed for the photo-Fenton inactivation of *Salmonella* spp., for an AI of 20 W m⁻² and a cumulated dose of 60 Wh m⁻² (Table 4). Temperature increased from 29 °C to 45 °C during the EDT (Fig. 3a' Trace (X)). The post-irradiation evaluation revealed that none of both enteric bacteria regrew during the subsequent 24 h of dark storage (Table 5). From these results it can be assumed that neutral photo-Fenton does not need temperatures higher than 50 °C to disinfect efficiently as it is required under sole solar illumination, in classical SODIS applications [2,10].

An important enhancement on the enteric bacteria inactivation rate of uniquely solar treatment (10–16 h) was observed, when the photo-Fenton treatment was applied. An increase of 50% and 80% was, respectively, noticed for *Salmonella* spp. (Fig. 3b, trace (■)) and total coliforms/*E. coli* (Fig. 3b, trace (□)). This increase in disinfection rates, compared to the one recorded in the experiments that took place from 8 to 14 h, is probably due to the higher AI available at the beginning of the process (28 W m⁻², Table 4). This leads us to suggest that AI and temperature increase have a greater impact on photo-Fenton than on solar irradiation only for enteric bacteria inactivation.

Table 5

Enteric bacterial regrowth evaluation (total coliforms bacteria/*E. coli* and *Salmonella* spp.), after the photo-disinfection and neutral photo-Fenton treatments of natural well water with or without H₂O₂ (10 mg/L) under direct solar light. The results were similar for all the illumination intervals (8–14 h; 10–16 h; 12–18 h).

Sampling periods (min)	Without H ₂ O ₂ (only direct solar radiation)		With H ₂ O ₂ (photo-Fenton)	
	Coliforms bacteria/ <i>E. coli</i>	<i>Salmonella</i> spp.	Coliforms bacteria/ <i>E. coli</i>	<i>Salmonella</i> spp.
90	–	+	–	–
120	–	+	–	–
150	–	+	–	–
180	–	+	–	–
240	–	+	–	–
300	–	+	–	–
360	–	+	–	–

– No regrowth of bacteria even after one week + regrowth of bacteria after 24 h.

The high AI (35 W m⁻²) recorded during the first 45 min (0.75 h) (EDT) in the experiments conducted from 12 to 18 h, has led to total inactivation of *Salmonella* spp. A dose of 26 Wh m⁻² was accumulated during this EDT (Table 4). From all the AI and doses recorded in Table 4 for *Salmonella* spp., it can be noticed that high irradiances, but not necessarily high doses, are needed to get an efficient achievement of inactivation (Fig. 3c, traces (□) and (■)) and durable lethal impact on enteric bacteria (Table 5) during the neutral photo-Fenton treatment. The enhancement of total coliforms/*E. coli* inactivation rate by neutral photo-Fenton compared to the one of the simple photo-disinfection by solar light, during the same illumination interval starting at 12 h, was of 67%. Rincon and Pulgarin [39] have reported a similar effect of the significant impact of the irradiance during the TiO₂ photocatalytic disinfection of *E. coli*. In contrast, Ubomba-Jaswa et al. [11] have reported the significant impact of the dose during the solar disinfection in the CPC reactor for effective *E. coli* K12 disinfection achievement. Nevertheless, solar disinfection of the wild enteric bacteria carried out in a similar reactor during this study reveals that the irradiance significantly influence the inactivation rate of the process (Fig. 3, traces (○), (●) and (–)). The lethal oxidative action of the neutral photo-Fenton on these enteric bacteria strains as reported previously by several authors [7–9,42] leads to the assumption that it could efficiently disinfect the *Salmonella* spp. and other resistant strains to ensure the sustainability of a CPC solar drinking water treatment of higher volumes of water.

The membrane peroxidation by external ROS attacks produced by photo-Fenton, due to natural dissolved and solid iron forms present in water and added H₂O₂, leads to an increased permeability and the disruption of the trans-membrane ion gradients [8]. The microorganism (*E. coli* or *Salmonella* spp.) death is related to the damages of their nuclear constituents (DNA) by intracellular highly ROS (H₂O₂, O₂^{•-}, OH[•]) generated after the inactivation of their antioxidant enzymes (catalases, superoxide dismutases, alkylhydroperoxidase and thiol peroxidase) by the thermal (temperature increase) and optical (UV A and B) effects [29,43,44]. The iron liberated from the iron sulfur clusters ([4Fe-4S]) after the inactivation by UV (A and B) of some clusters' enzymes induced the intracellular Fenton (Eq. (1)) in the presence of H₂O₂ leading to increase generation of highly reactive OH[•]. OH[•] attacks on cellular DNA lead to irreversible damages and consequently, to cell inactivation [8,45,46]. Additionally, the photo-degradation of humic substances and nitrogen compounds in both photo-disinfection treatments leads to the additional generation of OH[•] (Eqs. (13)–(15)) [32,33,47] which can contribute to the bacterial inactivation.

3.2.3. Fenton disinfection (dark experiments)

Enteric bacterial inactivation carried out in the dark (*obs*), shows a limited decrease of their contents during the whole experiment, as it could be observed in all graphs of Fig. 3, (traces (△) and (▲)), for total coliforms/*E. coli* and *Salmonella* spp. respectively. The Fenton (Fe/H₂O₂/*obs*) process was conducted in the dark simultaneously

with the photo-Fenton (Fe/H₂O₂/*hv*) ones. The significant effect of the illumination (*hv*) during the neutral photo-Fenton disinfection observed in this study is highlighted from these results.

3.2.4. Durability of the disinfection process: post-irradiation events

The evaluation of the sustainability of the photo-disinfection in the absence of H₂O₂ was carried out by the monitoring of post-irradiation events. The results presented in Table 5 pointed out that all the strains of total coliforms/*E. coli* have remained in their lethal state after 24 h of dark storage while that of *Salmonella* spp. have recovered their culturability as presented by their positive status. This *Salmonella* spp. regrowth could be due to the fact that the temperature did not rise up to 50 °C, as recommended for SODIS applications in bottles [2]. The results of the post-irradiation regrowth observed (+) or not (–) after the neutral photo-Fenton treatment are also shown in Table 5. No enteric bacterial regrowth was observed after 24 h of dark storage. This sustainability of the disinfection is highly significant, as some of the samples stocked in the dark for testing were collected before the total inactivation of their enteric bacterial content, (cf. sampling periods in Table 5 and graphics of Fig. 3). Notice that the absence of bacterial regrowth observed during the 24 h of dark storage, was maintained during the subsequent 72 and 168 h (one week). For water treated by simple direct solar radiation, only the total coliforms bacteria/*E. coli* did not show regrowth during the storage. Regrowth of *Salmonella* spp. was observed in all the samples (Table 5), after 24 h of dark storage. These results have confirmed the resistance of the *Salmonella* spp. strain to simple solar disinfection treatment as previously reported by some authors [7,26].

3.3. pH evolution during the irradiation process

The evaluation of the pH variation during the photo disinfection conducted in this study, showed an increase of 1.5 and 2.5 pH units range, respectively, for solar treatment (without H₂O₂) and neutral photo-Fenton as presented in Fig. 4, this pH increase follows the same tendency in all the times interval (8–14 h, 10–16 h, 12–18 h). The rising phase was recorded during the first two hours with an increase from 5.5 to 7.9 in almost all the photo-Fenton treatments and 5.5 to 6.8 or 7.2 for the solar treatment. This rising phase was followed by a stable phase in the new high pH values. This pH increase could be linked to several chemical pathways in action in the treated water during the photo-disinfection. Some of these pathways are (i) the degradation of bacterial nitrogen compounds, such as amino-acids and proteins, producing alkaline by-products, (ii) the shifting of the CO₂-carbonate equilibrium by water heating and CO₂ degassing, (iii) the photo-reduction of NO₂⁻ and NO₃⁻ in solution leading OH⁻ production (Eqs. (15) and (16)) [32,33] and (iv) the consumption of H⁺ or the generation of OH⁻ in the solution during, the Fenton and photo-Fenton process as described in Eqs. (1), (12), and (14) [14,18,19]. This last mechanism could be

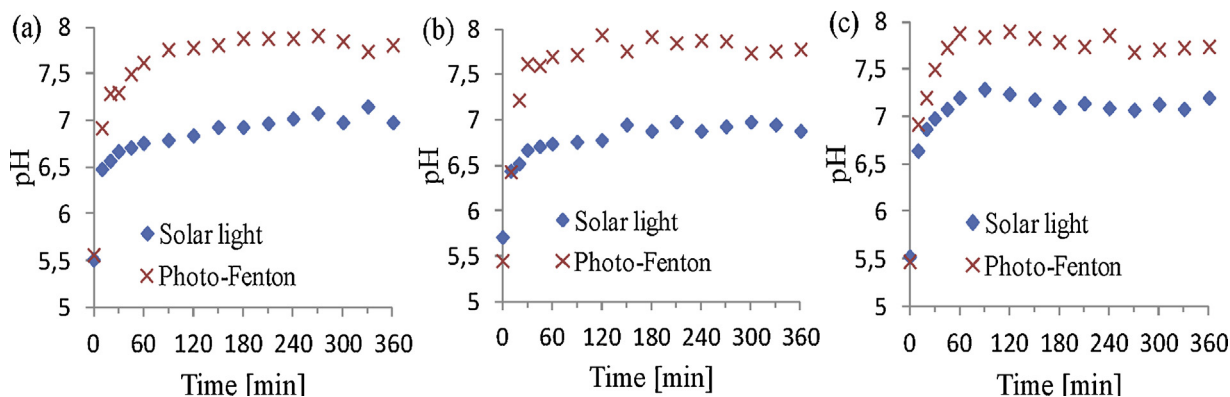
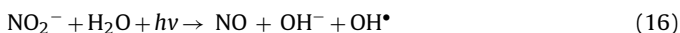
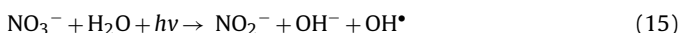


Fig. 4. Variations of pH during the disinfection by solar light exposure and neutral photo-Fenton of total coliforms bacteria/*E. coli* and *Salmonella* spp. recorded at different day time's intervals: (a) 8–14 h, (b) 10–16 h and (c) 12–18 h.

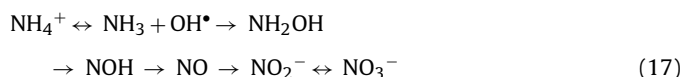
the one impacting the higher pH increase noticed in the neutral photo-Fenton process, with regards to the one observed in the uniquely solar treatment. The pH change to alkaline during the photo-disinfection could be useful to upgrade the one originally acidic groundwater in Sahelian region to the level 6.5–8 recommended for human consumption by the WHO [34].



3.4. Nitrite, nitrate and ammonia variation during the treatment

The concentration of nitrogen components was determined during both photo-disinfection treatment trials. As presented in Fig. 5, in the absence (solar treatment) or the presence of H_2O_2 (photo-Fenton), the rise in NO_2^- and NO_3^- concentration was recorded and concurrently the decrease in NH_4^+ concentration was also noticed. The photochemical reduction of NO_3^- in natural waters leads to NO_2^- , OH^- , and OH^\bullet , while that of NO_2^- leads to NO , OH^- and OH^\bullet (Eqs. (15) and (16)) [32,33]. However, the WHO report revealed that the presence of the ammonium cation in raw water may result in drinking-water containing nitrite as the result of catalytic action [35]. Brito et al. [47] have proposed a pathway of ammonia photo-oxidation by OH^\bullet leading to NO_2^- and NO_3^- generation (Eq. (17)). Hence, the variation recorded during the experiments could be attributed to these oxido-reduction interactions. The generation of the highly oxidant OH^\bullet will not certainly react only towards ammo-

nia oxidation but could also intervene on bacteria inactivation.



The World Health Organization (WHO) classifies ammonia as an esthetic quality component without a direct importance for health in the concentrations regularly recorded in natural drinking water. Therefore, no health-based guideline has been prescribed for it. The initial concentration of the nitrates followed in this study, was higher than that of the health-based guideline for drinking water recommended by the WHO (50 mg/L). During the applied photo-Fenton treatment, increased nitrite concentrations remain far below the health-based ones recommended for drinking water, (maximum 3 mg/L) [31,35]. When nitrate levels in drinking-water exceed 50 mg/L, drinking water will be the major source of total nitrate intake, especially for bottle-fed infants. The major biological effect of nitrite in humans is its involvement in the oxidation of normal hemoglobin (Hb) to methemoglobin (metHb), which is then unable to transport oxygen to the tissues. High nitrate concentration, above 100 mg/L, is an important cause of metHb formation [31]. Considering health risk relate to high nitrogen components presence in drinking water (methaemoglobinaemia or cancer) [36], further research should be conducted to intensively monitor and study the mechanism of its formation and persistence in the photo-treated water.

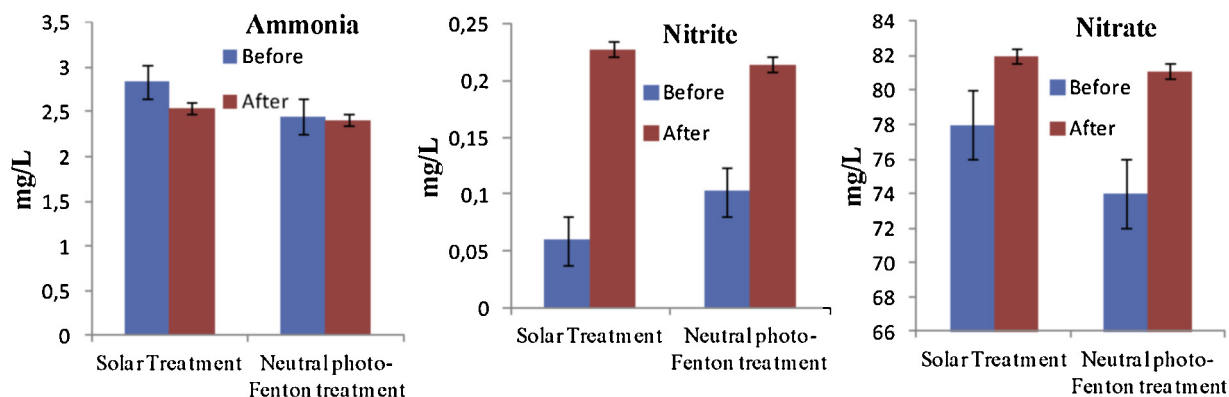


Fig. 5. Evolution of Ammonia, Nitrite and Nitrate concentration during the neutral photo-Fenton and sole solar treatment of natural well water. (Notice that the difference in the initial concentration of each chemical component in the results presented here are related to the fact that new water sample was collected and used for each new experiment).

4. Conclusions

The photo-disinfection of natural well water was successfully carried out at real scale in a solar CPC reactor under several time intervals of 6 h (8–14 h, 10–16 h, 12–18 h). 25 L of natural water were treated with H₂O₂ adding, which generate in-situ the photo-Fenton system (H₂O₂/natural Fe²⁺, 3⁺/hν) and by direct solar radiation exposure. All the samples treated without H₂O₂ addition showed *Salmonella* spp. regrowth after 24 h of dark storage. The resistance of the *Salmonella* spp. strain to direct solar disinfection treatment was recorded. The H₂O₂ addition has significantly enhanced the inactivation rate of the disinfection in all cases, without the need to reach 50 °C as required for classical SODIS bottles process. No enteric bacteria regrowth was noticed one week after the in-situ generated photo-Fenton treatment. Significant influence of the solar irradiance but not the dose was noticed during the process. The experiments revealed that higher irradiance level leads to lower EDT and dose to achieve bacterial disinfection. High average irradiance (AI) of 35 W m⁻² led to the total inactivation of *Salmonella* spp. with a dose of 26 Wh m⁻². In contrast, low irradiance of 20 W m⁻² required a dose of 60 Wh m⁻².

The pH becomes more alkaline during both neutral photo-Fenton and solar treatment. A rise of 1.5 and 2.5 in pH range was recorded respectively in solar treatment and neutral photo-Fenton. This pH increase was not detrimental to the photo-Fenton and bare solar disinfection, but could be beneficial for the Sahelian groundwater which are originally acidic and could then simultaneously be upgraded through photo-Fenton disinfection.

This study has revealed significant variation of the nitrogen compounds state during both photo-disinfection processes (Solar, Photo-Fenton). The recorded oxido-reduction of nitrates and nitrites and the oxidation of ammonia following the variation of their concentration during the treatments (increase of nitrates and nitrite and decrease of ammonia), has pointed out the importance of evaluating the sustainability of these disinfection processes before recommending them for human consumption. The WHO report on nitrate (NO₃⁻) in drinking water reveal that several wells water in the world naturally contain more than 50 mg/L of NO₃⁻, as the one found in this study. Considering this fact, it's a need to efficiently determine in further research project on photo-disinfection the nitrite (NO₂⁻) generation rate, produced through the reduction of nitrate or the oxidation of ammonia and evaluate if it eventually remains below 3 mg/L. The characterization of this nitrite and other nitrogen byproducts formation (such as nitrosamine), could help evaluate the health impact of the photo-disinfection of the drinking water before thinking the implementation of the photo-Fenton disinfection.

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