An integrated drinking water production system to remove chemical and microbiological pollution from natural groundwater by a coupled prototype helio-photochemical/H$_2$O$_2$/rapid sand filtration/chlorination powered by photovoltaic cell

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ABSTRACT

This study evaluates the simultaneous removal of 2,4-dichlorophenoxyacetic acid acid-2,4-D at $70 \,\mu g \, L^{-1}$ and the viability decreasing of *Escherichia coli* and *Klebsiella pneumoniae* from real groundwater samples containing natural amounts of iron ($0.39 \, mg \, L^{-1}$) and natural pH (7.31) in a coupled prototype system powered by a photovoltaic cell (SPh + LPh + H$_2$O$_2$ + RSF + Cl) consisting of photochemical (using both natural sunlight (SPh) and UV-B + A + Visible lamp (LPh) and a 30-L Compound Parabolic Collector-CPC reactor), rapid sand filtration (RSF) and chlorination (Cl, adding of Ca(OCl)$_2$ to get residual chlorine ranging between 0.2 and $0.6 \, mg \, Cl \, L^{-1}$) to drinking water production. Results showed that simple addition of H$_2$O$_2$ $10 \, mg \, L^{-1}$ and both natural sunlight and artificial light irradiation could enhance several natural photo-induced processes among them photocatalytic and photo-Fenton. These radicals could be responsible for both bacteria inactivation and 2,4-D removal from natural groundwater diminishing the addition of substantial amounts of chemicals into water samples. Coupling of photochemical processes with conventional treatments to drinking water production as RSF and Cl at high solar energy dose ($150,000 \, J \, m^{-2}$), led to the efficient removal 2,4-D and bacteria from natural groundwater without a significative trihalomethanes production. These results strongly suggest that coupling of helio-photochemical/H$_2$O$_2$ systems with RSF and chlorination treatments seems to be a promising approach to remove chronic and acute risk from groundwater obtaining drinking water with high chemical and microbiological quality. However, despite these encouraging results, bacteria inactivation underwent a detrimental effect when low solar energy doses ($75,000 \, J \, m^{-2}$) were tested.

1. Introduction

Although access to water and sanitation is considered as a human right, it is estimated that around 748 million and 2.8 billion of people around the world do not use an improved source of drinking water and sanitation facility respectively (UN water report, 2015; WWAP, 2015). Furthermore, Bain et al. (2014) have reported that about 1.8 billion of people could drink water contaminated with *E. coli,* an indicator of fecal pollution in water.

In Latin America, 30% of rural communities use groundwater as the main drinking water supply (UNEP-GEO, 2010). Unfortunately, most of these communities have not neither suitable sanitation facilities nor disinfection treatments and their main economic activity is frequently associated to agricultural production where agrochemicals, sometimes badly handled, are often used. Thus, microbiological and chemical quality of aquifers could be threatened by agrochemicals (chronic risk) and pathogen bacteria (acute risk). Chlorination (Cl) is an effective method to produce drinking water since removes efficiently acute risk by inactivating a wide spectrum of bacteria cells. However, it is not always available in remote and small rural communities in developing countries. Moreover, if these well waters are already polluted with pesticides and/or domestic wastewater, chorine application to drinking

water production could be unsafe since there would be a substantial risk to yield trihalomethanes (THMs) (Nikolaou et al., 2004; Bond et al., 2011; Hao et al., 2017) which are chemical substances often associated to cancer in humans (Plewa et al., 2008) increasing chronic risk in drinking water.

On the other hand, sand filtration is a very well-known and uncomplicated process to remove effectively acute risk (Bilardi et al., 2013; Urfer, 2017) in drinking water. However, it is not suitable to remove chemical pollutants and it does not exhibit residual effect as chlorination which could allow further bacteria regrowth. In this way, the finding of novel and simple drinking water production systems which can be easily applied in rural communities and grant high chemical and microbiological quality is a critical issue.

In the last years, the study of solar disinfection systems such as SODIS (solar disinfection) has been extensively reported in the literature (Figueredo-Fernández et al., 2017; Fisher et al., 2012; Keogh et al., 2015; McGuigan et al., 2012; Rodrigues Marques et al., 2013; Oates et al., 2003; Vivar et al., 2017; Wegelin et al., 1994). This is a simple and inexpensive technology which seems to be promising to produce drinking water in rural and isolated communities in developing countries. SODIS is based on the combined effect of UV-light and water heating (T > 45 °C) to inactivate waterborne bacteria. However, SODIS has several limitations such as the low water volume produced (~2 L) and incapacity to remove chemical pollutants (chronic risk).

Photo-Fenton process, which consists in the photo-induced reaction of iron aqua-complexes and H_2O_2 at acid pH to lead the formation of ˙OH radicals, have been studied recently as a water disinfection treatment (Fiorentino et al., 2015; García-Fernández et al., 2012; Ortega-Gómez et al., 2014; Polo-López et al., 2013; Rodríguez-Chueca et al., 2012). This process seems to be suitable to inactivate several bacteria strains, however, the most part of studies have been performed using considerable amounts of iron salts (2.5–50 mg L^{-1}) and in water disinfection treatments, these concentrations should not be allowable since its maximum concentration suggested in drinking water is around 0.3 mg L^{-1} (WHO, 2011).

Different natural photochemical events induced by sunlight could be responsible in a minor extent of chemical pollutants degradation in surface waters (Vione et al., 2014; Gligorovski et al., 2015). NO_3^-, NO_2^- and dissolved organic matter (DOM) irradiated with UV-B-A/visible light are able to photo-induce reactive oxygen species (ROS) such as ˙OH radicals among others, with high oxidation potential (2.8 v vs NHE) (Cheng and Li, 2007). Moreover, it has also been found that Fenton and photo-Fenton reactions could also be photo-induced in natural waters containing natural amounts of dissolved or colloidal iron and low concentrations of H_2O_2, this latter produced by different biotic processes (Nakatani et al., 2007; Miller et al., 2012). An interesting question arises about the possibility to enhance these natural photo-induced processes in order to promote high ˙OH radical production in natural waters increasing their capacity to remove organic pollutants and inactivate bacteria, especially addressed to drinking water production where considerable amounts of foreign chemical substances (i.e. iron or hydrogen peroxide) addition is not recommended.

A possible response was provided by Sciacca et al. (2010, 2011) and Ndounla et al. (2013) who found that different bacteria cells underwent a strong loss of culturability by the simple addition of 10 mg L^{-1} of H_2O_2 to natural surface or well waters irradiated by sunlight in Sahelian regions. They argued that H_2O_2 and sunlight irradiation promoted photo-Fenton processes with dissolved and/or colloidal natural iron (~0.1–0.3 mg L^{-1}) present in water samples, photo-inducing the formation of ˙OH radicals. Moreover, Moncayo-Lasso et al. (2009) studied the simultaneous inactivation of spiked laboratory strain *E. coli* cells (followed by culturability) and the removal of natural organic matter (NOM, which could be DBPs precursor) in CPC reactors by addition of H_2O_2 10 mg L^{-1} onto natural surface waters (containing natural iron)

previously treated by slow sand filter (SSF). Authors found that both bacteria and NOM were efficiently removed probably by helio-photo-Fenton processes involving natural iron; however, there was not coupling between photochemical treatment and SSF.

Recently, Gutierrez-Zapata et al. (2017a) found that in real groundwater samples with low turbidity irradiated with a solar simulator and containing natural amounts of iron (~0.3 mg L^{-1}), the addition of 10 mg L^{-1} of H_2O_2 led to the complete inactivation of *E. coli* cells after 6 h, but this time viability was followed instead of culturability by direct viable counting combined with fluorescent in situ hybridization (DVC-FISH).

Regarding the removing of chemical substances, these same authors reported degradation of 2,4-D, a highly used and water-soluble herbicide and its main degradation metabolite: 2,4-dichlorophenol (DCP), from natural groundwater at natural pH by the simple addition of 10 mg L^{-1} hydrogen peroxide upon solar simulator irradiation (Gutierrez-Zapata et al., 2017b). Both studies of Gutierrez-Zapata et al. (2017a, 2017b) found an interesting result, the presence of fluoride and carbonates in these natural groundwater samples could positively affect the photochemical events responsible of 2,4-D removal and bacteria inactivation.

Simultaneous removal of chemical and microbiological pollution from simulated groundwater by these "natural enhanced" processes was also explored but this time using real solar light and CPC reactors with a total volume of 30-L (Gutierrez-Zapata et al., 2017c; Alvear-Daza et al., 2018). Results showed that 90% of 2,4-D at an initial concentration of 70 µg L^{-1} was efficiently removed after the addition of H_2O_2 10 mg L^{-1} and 6 h of sunlight irradiation while DVC-FISH viability of *E. coli* laboratory strain was totally reduced after the same irradiation time. However, total viability reduction of *Klebsiella pneumoniae* laboratory strain, a highly resistant bacterium, was not achieved. This latter demonstrated that evaluation of water disinfection by these photo-induced process using a single bacterium is not suitable since bacteria strains seem to exhibit different response to the treatment.

Herein, it is reported for the first time the using a prototype powered by a photovoltaic cell consisting of a 30-L CPC reactor modified with a UV-B + A + Visible lamp coupled with rapid sand filtration (RSF) and chlorination (Cl) to the simultaneous removal of microbiological pollution (laboratory bacteria strains of *Klebsiella pneumoniae* and *E. coli* at initial concentrations of 10^5 and 10^6 cells mL^{-1} respectively followed by DVC-FISH) and chemical pollution (2,4-D 70 µg L^{-1}) in real groundwater containing already natural iron concentrations and neutral pH upon different solar energy doses (low and high). Production of THMs was also evaluated after the entire process. CPC reactor was equipped with a UV-B + A + Visible lamp in order to enhance photo-induced processes since as it was previously mentioned, studies reported by us showed that *K. pneumoniae* cells exhibited low inactivation rates; thus, addition of large chemicals amounts such as hydrogen peroxide and iron salts could be avoided.

2. Materials and methods

2.1. Well water samples

Natural groundwater was sampled in wells located in a small rural community (3°21′03.38″ N, 76°26′24.51″) near to the municipality of Candelaria (southwest of Colombia). The samples were stored at 4 °C in plastic bottles and physical-chemical analysis following standard procedures were performed in order to evaluate the presence of nitrates (NO_3^-), fluoride (F$^-$), total iron, phosphate (PO_4^{3-}), bicarbonate ($CO_3^=$), chloride (Cl$^-$). The pH in the samples was around 7.3. Results of physical-chemical characterization is shown in Table 1 (supplementary information).
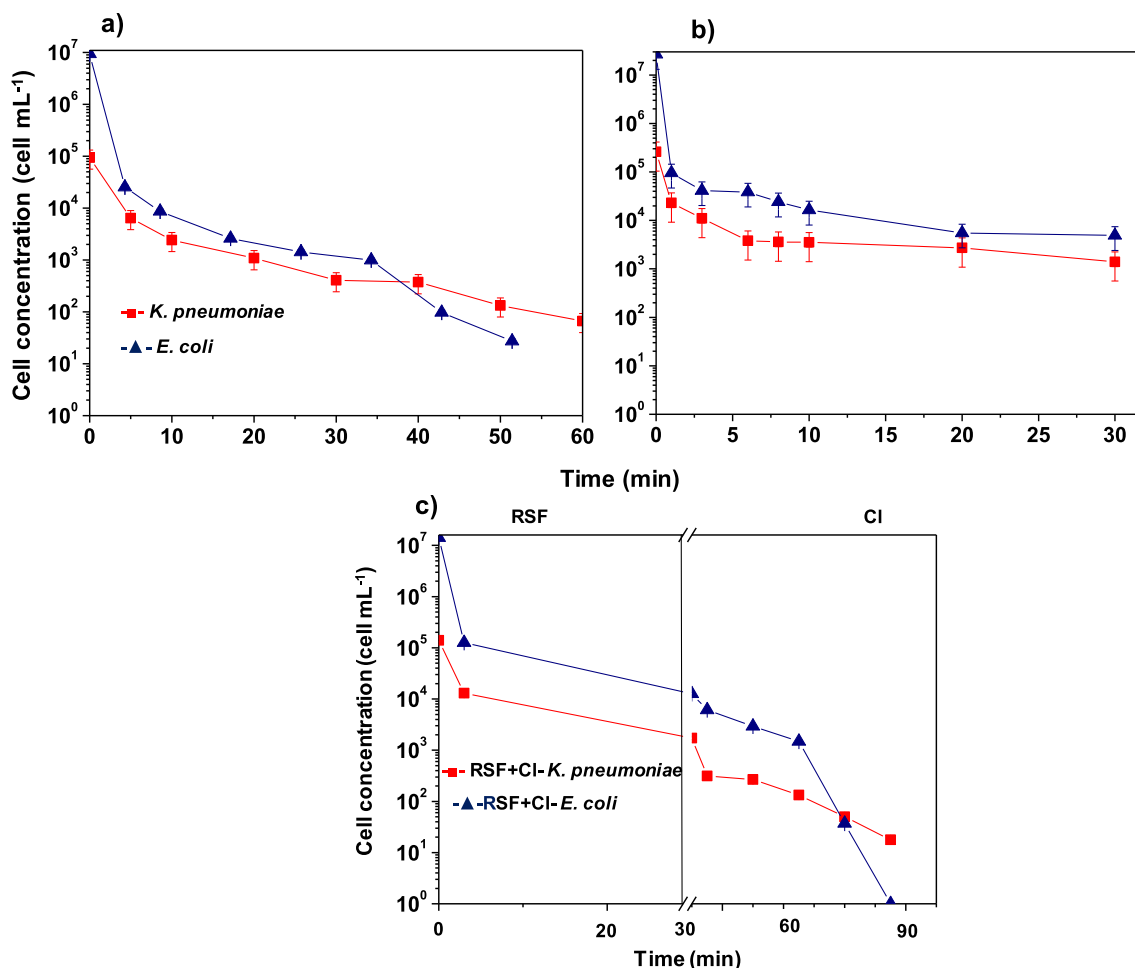
Fig. 1. *Klebsiella pneumoniae* and *E. coli* laboratory strains viability on natural groundwater samples during (a) chlorination (Cl) by addition of Ca(ClO)$_2$ 6.5 mg L^{-1} (residual chlorine of 0.5 mg L^{-1}) and (b) slow sand filtration (SSF) treatments (21 cycles at filtration rate of 0.0011 m s^{-1}). Initial pH: 7.31. (c) coupled chlorination (Cl) and slow sand filtration (SSF) treatment. [Ca(OCl)$_2$]: 6.2 mg L^{-1} (Residual chlorine 0.6 mg L^{-1}). SSF was performed during 21 cycles at filtration rate of 0.0011 m s^{-1}. Initial pH 7.2.

2.2. Reagents

Hydrogen peroxide (H$_2$O$_2$) (Carlo Erba), 2,4-D (Sigma-Aldrich), 2,4-Dichlorophenol (2,4-DCP), formaldehyde (Carlo Erba), ethanol (Merck), sodium chloride (Sigma-Aldrich), EDTA (Merck), calcium hypochlorite (Sigma-Aldrich), SDS (Fisher), Tris/HCl (Amresco), FISH probe ES-445 (Microsynth GmbH), nalidixic acid (Acros Organics), nutrient broth (Difco), yeast extract (Oxoid), peptone (Difco), and Milli-Q water. FISH probes Kpn (5'-CCT ACA CAC CAG CGT GCC-3') (Microsynth GmbH) and ES-445 (5'-CTT TAC TCC CTT CCT CCC-3') (Microsynth GmbH). All the reagents were used without further purification.

2.3. Viability analysis of laboratory strain bacteria

Viability of *E. coli* K12 (ATCC 23716) and *K. pneumoniae* (ATCCBAA-1705) was evaluated using direct viable count by fluorescent in situ hybridization (DVC–FISH). Samples were incubated in the dark for 18 h at 37 °C ± 2 °C in a nutrient broth solution, yeast extract and nalidixic acid (40 mg mL^{-1}) (Gutierrez-Zapata et al., 2017a). The DVC-FISH detection limit was around 30 cells mL^{-1} for both *E. coli* and *K. pneumoniae*. Quantification of cells was performed with the epifluorescence microscope Nikon-90i (Cy3 filter), using the software NIS element AR. Each sample was measured by triplicate and its average was reported

2.4. Determination of 2,4-D and trihalomethanes (THMs)

Concentrations of 2,4-D and its main degradation byproduct 2,4-Dichlorophenol (2,4-DCP) were monitored by HPLC following the method previously described (Gutierrez-Zapata et al., 2017b, 2017c). Concentrations of 2,4-D and 2,4-Dichlorophenol (2,4-DCP) were followed by HPLC (LC20AT- Shimadzu) using as mobile phase acetonitrile (55%), aqueous solution of acetic acid at pH 3.0 (30%) and Milli-Q water (15%) and a HPLC column C-18 Nucleosil 100–5. An isocratic flow of 0.8 mL min^{-1} and a UV detector at 280 nm were used. Solid-phase extraction clean-up with C-18 was performed previously (activation and elution with ethyl acetate). Limits of quantification (LOQ) of the chromatographic methods were 6 μg L^{-1} and 5 μg L^{-1} for 2,4-D and 2,4-DCP, respectively.

In addition, THMs concentration was monitored by gas chromatography-ECD using a Shimadzu GC-14. The carrier gas was N$_2$ (58–60 psi) and a semi-capillary column AT-1 (30 m length and i.d 0.53 mm) was used. Two temperature ramps were used, the first one initiating at 6 °C min^{-1} until reaching finally 95 °C and a second one of 40 °C min^{-1} until reach 220 °C. Injector and detector temperatures were 200 and 250 °C respectively. This method allows the detection of some THMs such as CCl$_4$, CHCl$_3$ and some chlorinated aliphatic acids. However, the only molecule detected in the samples was CHCl$_3$ and its LOQ was around 1 μg L^{-1}.

In all chromatographic methods each sample was injected three times and its average was reported.

Total organic carbon measurements (TOC) were performed using a TOC-V (Shimadzu).

2.5. Photochemical, rapid sand filtration (RSF) and chlorination (Cl) treatments

The system (Fig. S1a, supplementary information) includes a 30-L compound parabolic collector (CPC) reactor (SPh) equipped with UV-B + A + visible lamps (LPh) and coupled with rapid sand filter (RSF) and chlorination (Cl) systems. 30 L of water were pumped by a centrifugal pump through the system passing firstly by the CPC reactor and then to the RSF and Cl system respectively. Magnetic coupling centrifugal pump and UV-B + A + Visible lamp was electrically powered by a photovoltaic cell (AMPA ASM-250P24 solar pv module with dimensions of $1485 \times 668 \times 35$ mm) with a maximum power of 250 W and maximum system open circuit voltage of 2000 V DC. An inverter INTI IIP 24,600 (maximum power 1200 W; input and output voltage 24 V-DC and 110-AC respectively) was also used.

Experiments were conducted using a compound parabolic collector (CPC) under sunlight irradiation and/or UV-B + A + Visible irradiation (SPh and LPh) either in absence or in presence of $10 \, \mathrm{mg \, L^{-1}}$ of H_2O_2 (SPh + H_2O_2 and LPh + H_2O_2). The CPC was made of Pyrex® glass tubes (32 mm o.d.) placed over a reflective surface consisting of an alloy of anodized aluminum (99.85%) Almeco™ with a total reflectance of 86% and inclined to 3°, corresponding to the latitude of the location site (Cali, Colombia), with an irradiated volume of 10.77 L. A flow rate of $30 \, \mathrm{L \, min^{-1}}$ was used. Experiments were performed in Cali Colombia (coordinates: 3.22′38.27″N, 76.31 56.97″W).

A 14 W UV-B + A + Visible lamp (ReptiGlo 10.0 PT2169 Exo-Terra Lighting Germany) was coupled to the CPC reactor. This lamp illuminated a volume of 1.36 L and exhibits an emission spectrum between 280 nm and 700 nm, with maximum UV-B in 310 nm, UV-A in 365 nm, and Vis in 430 nm and 540 nm (Fig. S1b supplementary information). UV-B and UV-A intensities were measured by using an UV photo-radiometer A Delta OHM constituted of UV-B (280–315) and UV-A (315–400 nm) probes at 0.6 cm which corresponds to the reactor radius (Fig. 1a). The UV-B and UV-A intensities were 0.74 and $6.47 \, \mathrm{W \, m^{-2}}$ respectively.

RSF system was constituted of a PVC tube (I.D. 0.232 m and length 1.4 m) which was filled with anthracite and quartz sand following the recommendations of Spellman (2012). The filtration rate was $0.011 \, \mathrm{m \, s^{-1}}$ achieving a total of 21 cycles in 30 min of treatment.

Chlorination treatment was performed using calcium hypochlorite $(Ca(OCl)_2)$. Chlorine demand (CD) was determined by the standard method 2350B. $Ca(OCl)_2$ was used at a concentration oscillating between 4.0 and $6.1 \, \mathrm{mg \, L^{-1}}$ (residual chlorine between 0.2 and $0.6 \, \mathrm{mg \, Cl \, L^{-1}}$) with a contact time of 60 min. The Residual chlorine was evaluated by using kits HI 38,017 (HANNA).

2.6. Assay conditions

In natural groundwater samples was added 2,4-di-chlorophenoxyacetic acid $(70 \, \mathrm{\mu g \, L^{-1}})$ and the laboratory strains of *E. coli* and *K. pneumoniae* cells (at initial concentrations of 10^7 and $10^5 \, \mathrm{cells \, mL^{-1}}$ respectively). Assays were performed at circumneutral pH upon high $(150.000 \, \mathrm{J \, m^{-2}})$ and low $(75.000 \, \mathrm{J \, m^{-2}})$ solar energy doses (monitored using a Photo-radiometer HD 2102.2 - Delta Ohm with a radiometric probe UV-A (315–400 nm)). Experiments were not done by triplicate since physical-chemical features of groundwater samples and sunlight irradiation were not constants.

3. Results

3.1. Disinfection studies by using rapid sand filtration (RSF) and chlorination (Cl) of laboratory bacteria strains in natural groundwater samples followed by cell viability (DVC-FISH)

Fig. 1a shows the bacteria viability (followed by DVC-FISH) of *E. coli* and *K. pneumoniae* after 60 min of chlorination treatment (Cl) with a residual chlorine of $0.5 \, \mathrm{mg \, Cl \, L^{-1}}$ (addition of $Ca(ClO)_2 \, 6.5 \, \mathrm{mg \, L^{-1}}$). *E. coli* and *K. pneumoniae* underwent a viability dropping of 5 and 4 logs respectively.

Rapid sand filtration (RSF) results (Fig. 1b) exhibited viability reduction of 3 and 2 log for *E. coli* and *K. pneumoniae* respectively after 30 min of treatment.

Combining both treatments (Fig. 1c), viability reduction was strongly enhanced only to *E. coli* cells since its viability reached the lower limit of the detection method ($< 30 \, \mathrm{cell \, mL^{-1}}$) while *K. pneumoniae* showed similar results to those obtained for chlorination, where its viability dropped almost 4 logs. Residual chlorine was around 0.6 mg $Cl \, L^{-1}$ which is an acceptable value recommended by the World Health Organization (WHO, 2011). Monitoring trihalomethane concentrations (THM) such as CCl_4, $CHCl_3$ after coupled RSF-Cl system, revealed that only chloroform $(CHCl_3)$ was detected at concentrations of $8.72 \, \mathrm{\mu g \, L^{-1}}$, which is lower than the value recommended for drinking water $(300 \, \mathrm{\mu g \, L^{-1}}$ for chloroform) for the WHO (WHO, 2011) and USEPA $(70 \, \mathrm{\mu g \, L^{-1}})$.
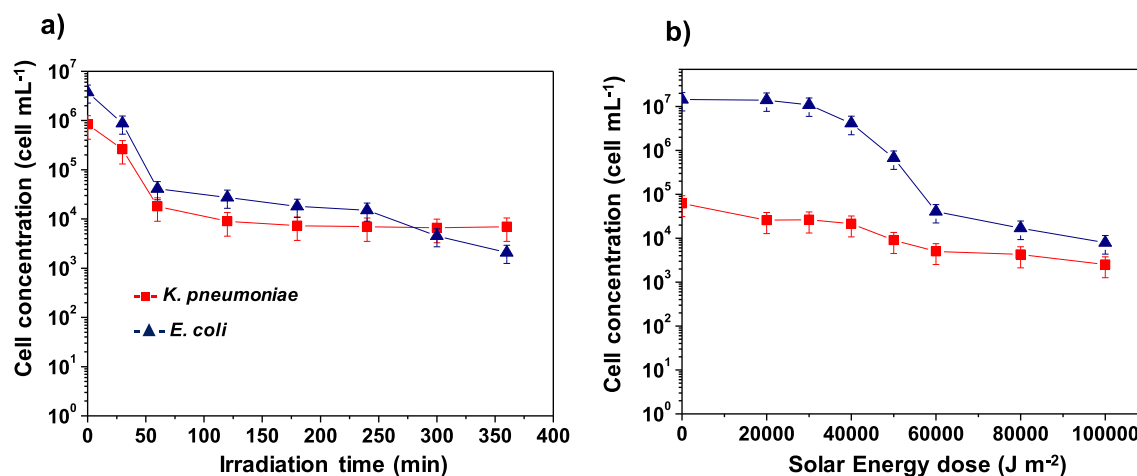

Fig. 2. Viability reduction of *Klebsiella pneumoniae* and *E. coli* laboratory strains under (a) 14 W UV-B + A + Visible lamp (LPh) (UV-B irradiation: $0.74 \, \mathrm{W \, m^{-2}}$ and UV-A irradiation: $6.47 \, \mathrm{W \, m^{-2}}$) and (b) natural sunlight irradiation (SPh) (cumulated irradiation $100,000 \, \mathrm{J \, m^{-2}}$).
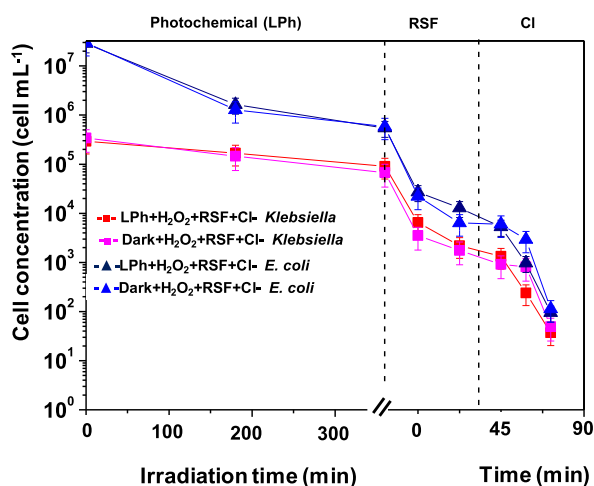
Fig. 3. Viability reduction of *Klebsiella pneumoniae* and *E. coli* laboratory strains under coupled 14 W UV-B + A + Visible lamp irradiation (LPh) (UV-B irradiation: 0.74 W m^{-2} and UV-A irradiation: 6.47 W m^{-2}), slow sand filtration (SSF) (21 cycles at filtration rate of 0.0011 m s^{-1}). and chlorination (Cl) ([Ca (OCl)$_2$]: 4.8 mg L^{-1} (Residual chlorine 0.2 mg L^{-1}). [H$_2$O$_2$]: 10 mg L^{-1} and initial pH 7.2.

3.2. Photochemical viability reduction of bacteria and 2,4-D degradation in natural groundwater samples without H$_2$O$_2$ addition

Photochemical experiments without H$_2$O$_2$ addition either with sunlight (SPh, solar energy dose: 100,000 J m^{-2}) or UV-B + A + visible (LPh) irradiation (UV-B irradiation: 0.74 W m^{-2} and UV-A irradiation: 6.47 W m^{-2}) (Fig. 2a and b) exhibited a poor viability decreasing for both *E. coli* and *K. pneumoniae*. On the other hand, simultaneous 2,4-D degradation showed values of 55.2 and 24% respectively when SPh and LPh experiments were performed respectively.

3.3. Coupling of helio-photochemical processes (SPh and LPh), rapid sand filtration (RSF) and chlorination (Cl) for simultaneous groundwater disinfection and detoxification by H$_2$O$_2$ addition

When the coupled prototype using only the UV-B + A + Visible lamp (LPh) (without sunlight irradiation), rapid sand filtration (RSF) and chlorination (Cl) (a solution of Ca(OCl)$_2$ 4.8 mg L^{-1} leading to a residual chlorine of 0.2 mg Cl L^{-1}) was evaluated in presence of 10 mg L^{-1} of H$_2$O$_2$ (Fig. 3), LPh + H$_2$O$_2$ + RSF + Cl, bacteria were not completely inactivated (viability reductions of 3 and 5logs for *K. pneumoniae* and *E. coli* respectively). Simultaneous 2,4-D degradation and dissolved organic carbon (DOC) reduction were around 89 and 65% respectively. Chloroform concentration was below the LOQ (1 µg L^{-1}).

Disinfection experiments under dark conditions Dark + H$_2$O$_2$ + RSF + Cl (Fig. 3) (where groundwater containing H$_2$O$_2$ 10 mg L^{-1} was recirculated into the fully coupled reactor without neither sunlight nor UV-B + A + Visible lamp irradiation) exhibited a similar behavior than those performed under LPh irradiation where viability of *E. coli* and *K. pneumoniae* laboratory strains was not strongly affected. Concentration of added Ca(OCl)$_2$ was 6.1 mg L^{-1} producing residual chlorine around 0.36 mg Cl L^{-1}. 2,4-D degradation and DOC removal exhibited values around 57 and 48.2% respectively and the monitoring of chloroform gave concentrations of 1.49 µg L^{-1}.

Regarding the bacteria inactivation by H$_2$O$_2$ (10 mg L^{-1}) helio-photochemical processes coupled with RSF and Cl (Ca(OCl)$_2$: 4.7 mg L^{-1} and residual chlorine 0.4 mg Cl L^{-1}) treatments (Fig. 4), SPh + H$_2$O$_2$ + RSF + Cl, results at low solar energy dose (75,000 J m^{-2}) (Fig. 4a) revealed that strong bacteria inactivation was not reached. Helio-photochemical treatment achieved viability reduction of 3 and 2 logs for *K. pneumoniae* and *E. coli* while RSF and Cl

reached 2 logs of viability reduction for both bacteria strains. The coupling of UV-B + A + Visible irradiation from lamp in the treatment SPh + LPh + H$_2$O$_2$ + RSF + Cl did not enhance bacteria inactivation. Chloroform was not detected (concentration below LOQ). Experiments SPh + H$_2$O$_2$ + RSF + Cl revealed 2,4-D and DOC removal of 68 and 46% respectively while SPh + LPh + H$_2$O$_2$ + RSF + Cl exhibited 2,4-D and DOC removals of 98 and 54.1% respectively.

However, at high solar energy dose (150,000 J m^{-2}) (Fig. 4b), SPh + H$_2$O$_2$ + RSF + Cl (Ca(OCl)$_2$: 5.4 mg L^{-1} and residual chlorine 0.6 mg Cl L^{-1}) showed viability reductions for *K. pneumoniae* and *E. coli* around 4 and 5 logs respectively. Experiments with the entire prototype (SPh + LPh + H$_2$O$_2$ + RSF + Cl (Ca(OCl)$_2$: 5.0 mg L^{-1} and residual chlorine 0.2 mg Cl L^{-1}) were able to reduce viability of both bacteria strains to the lower limit of the detection method (< 30 cell mL^{-1}). Furthermore, chloroform was not detected. Simultaneous 2,4-D and DOC removal in SPh + H$_2$O$_2$ + RSF + Cl treatments was around 77 and 61% respectively while the same parameters in SPh + LPh + H$_2$O$_2$ + RSF + Cl treatment were 100 and 83% respectively.

On the other hand, monitoring 2,4-dichlorophenol (2,4-DCP) in all experiments exhibited concentrations below to its LOQ (5 µg L^{-1}).

Water temperature during the treatments was also followed. At high sunlight dose, final temperatures oscillated between 24 and 38 °C. This latter was obtained in experiments performed with all the combined treatments. Temperature results suggest that this parameter should not be a key factor since water heating at T > 45 °C are necessary to inactivate bacteria (McGuigan et al., 2012; Wegelin et al., 1994). Furthermore, under these conditions, H$_2$O$_2$ does not undergo thermal degradation. Moreover, after the photochemical treatment either with SPh or LPh, pH increased from 7.3 to values around 8.5. RSF reduced slightly the pH until 8.2 and after chlorination was constant.

Regarding the H$_2$O$_2$ concentration during the process, this was monitored during the coupled helio-photochemical, RSF and Cl treatments. For instance, dark experiments in presence of 10 mg L^{-1} of H$_2$O$_2$ and coupled with RSF and Cl exhibited a hydrogen peroxide reduction of 60% (final concentration 4.1 mg L^{-1}).

On the other hand, LPh + H$_2$O$_2$ + RSF + Cl, SPh + H$_2$O$_2$ + RSF + Cl (high/low sunlight dose), SPh + LPh + H$_2$O$_2$ + RSF + Cl (high/low solar light dose) experiments showed H$_2$O$_2$ reductions of 64, 70/58, 80/54% respectively.

4. Discussion

Although chlorine and rapid sand filtration treatments separately were not efficient inactivating bacteria cells, combination of both processes achieved the total *E. coli* inactivation; however, *K. pneumoniae* viability was not fully reduced. This latter microorganism has exhibited some resistance to chlorination. For instance, Goel and Bouwer (2004) reported culturability reductions of this bacterium (initial concentration 10^6 CFU mL^{-1}) around 4 logs using chlorination at residual chlorine doses ranging from 0.46 to 0.67 mg L^{-1} and pH 7.0. Power et al. (1997) have also found chlorine resistance of *Klebsiella oxytoca*. Although chloroform concentration was below the WHO recommended value, combined RSF and Cl treatment led to the highest CHCl$_3$ concentrations.

Helio-, UV-B + A + Visible-photochemical and H$_2$O$_2$-dark treatments alone did not reduce strongly the bacteria viability and 2,4-D concentration. It is well known that UV light, specifically UV-C is lethal to bacteria, however, under our experimental conditions, there was not presence of this UV component. Regarding UV light, which is around 4–7% of total sunlight on the terrestrial surface), sunlight hitting the planet's surface is specifically composed of UV-B (in lesser extent) and UV-A. Both wavelengths cause damages on nucleic acids, antioxidant enzymes (catalase and superoxide dismutase) and proteins. 2,4-D molecule is not sensitive to UV-B or UV-A irradiation. Furthermore, H$_2$O$_2$ can also contribute to bacteria inactivation since it can induce
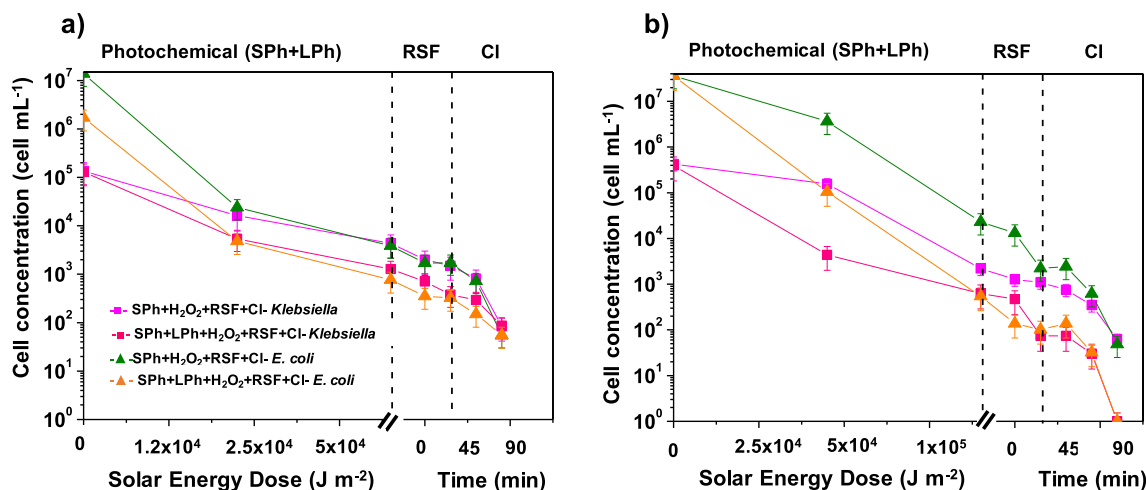
Fig. 4. Viability reduction of *Klebsiella pneumoniae* and *E. coli* laboratory strains under coupled solar light irradiation (SPh) (a) low (75,000 J m^{-2}) and (b) high (150,000 J m^{-2}) intensities, UV-B + A + Visible lamp irradiation (LPh) (UV-B irradiation: 0.74 W m^{-2} and UV-A irradiation: 6.47 W m^{-2}), slow sand filtration (SSF) (21 cycles at filtration rate of 0.0011 m s^{-1}) and chlorination (Cl) (At high sunlight intensities [Ca(OCl)$_2$]: 5.4 mg L^{-1} (Residual chlorine 0.6 mg L^{-1}) and low sunlight intensities: [Ca(OCl)$_2$]: 4.8 mg L^{-1} (Residual chlorine 0.2 mg L^{-1})). [H$_2$O$_2$]: 10 mg L^{-1} and initial pH 7.3.

detrimental effects on the cell membrane by increasing its permeability (Santos et al., 2013; Giannakis et al., 2016a, 2016b, 2017). In addition, groundwater samples contain also low amounts of iron (0.39 mg L^{-1}) which could be as dissolved or colloidal form (Appelo and Postma, 2005). H$_2$O$_2$ could induce dark Fenton reactions with dissolved or colloidal iron leading to the formation of ·OH radicals which could be responsible of low bacteria viability reduction and 2,4-D removal (Lipczynska-Kochany and Kochany, 2008; Ruales-Lonfat et al., 2014; Giannakis et al., 2016b).

As it was already mentioned, sunlight can induce photochemical events on natural surface waters leading to the formation of ·OH radicals in a lesser extent, since it has been reported ·OH concentrations around 10^{-12} M on natural surface waters (Nakatani et al., 2007).

Among these photochemical events, NO$_3^-$ (which were found in groundwater samples at concentrations around 1.77 mg L^{-1} (Table 1 supplementary information)) can undergo photochemical reactions by UV-B (present in natural sunlight and UV-B + A + Visible lamp) light leading to the generation of ·OH radicals (Eqs. (1) and (2)) (De Laurentiis et al., 2014; Vione et al., 2014; Gligorovski et al., 2015). These radicals with high oxidation potential can lead to the oxidative attack of organic molecules or cause oxidative stress on microorganisms (Giannakis et al., 2016a).

$$NO_3^- + hv \rightarrow ·NO_2 + O^{-·} \ (O^{-·} + H_2O \leftrightarrow ·OH + OH^-) \tag{1}$$

$$NO_3^- + hv \rightarrow NO_2 + O^· \tag{2}$$
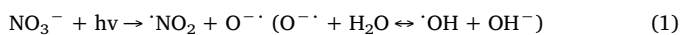
On the other hand, dissolved organic matter (DOM) (concentration of dissolved organic carbon (DOC) in groundwater samples was around 1.13 mg L^{-1}) can also lead to the photo-generation of reactive oxygen species (ROS) such as ·OH radicals and/or singlet oxygen (^{1}O$_2$), since UV-A or visible light (both present in our experimental conditions) are able to produce excited states of DOM which can be quenched by molecular oxygen through two processes: (i) electron transfer leading the production of ·OH radicals and (ii) energy transfer producing singlet oxygen (De Laurentiis et al., 2014; Gligorovski et al., 2015; McNeill and Canonica, 2016; Vione et al., 2014).

$$DOM + hv \rightarrow DOM^* + O_2 \rightarrow {}^1O_2 + ·OH \tag{3}$$
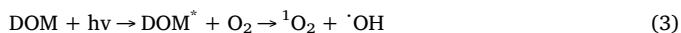
Thus, both UV-B-A and H$_2$O$_2$, and natural abiotic photo-induced processes could produce bacteria weakening and 2,4-D degradation which could contribute partially to simultaneous bacteria inactivation and herbicide removal.

Added H$_2$O$_2$ could also play a key role on ·OH production. Although

this molecule absorbs light principally in the UV-C region (which does not hit the CPC reactor and it is not emitted by UV-B + A + visible lamp) inducing H$_2$O$_2$ photolysis and producing ·OH radicals (Eq. (4)), the possible participation of UV-B light (which can be partially filtered by Pyrex glass) could not be neglected since despite that UV-B absorption by H$_2$O$_2$ molecules is lower than UV-C, some reports on the literature have claimed about UV-B could also induce H$_2$O$_2$ photolysis (Rojas et al., 2011; De Laurentiis et al., 2014; Vione et al., 2014; Gligorovski et al., 2015).

$$H_2O_2 + hv \rightarrow 2·OH \tag{4}$$

H$_2$O$_2$ in presence of dissolved or colloidal natural iron and upon sunlight or artificial UV-B + A light may induce photo-Fenton or photocatalytic processes yielding also ROS such as ·OH radicals. It was clear that hydrogen peroxide enhanced the natural production of ROS since removal of 2,4-D and bacteria viability reduction increased. Moreover, rapid sand filtration can contribute to the removal of bacteria and solids in suspension from water and chlorination exerts an important disinfectant role especially granting residual effect and inhibiting further bacteria regrowth.

An important finding was that photochemical processes coupled with conventional drinking water treatments did not lead to the considerable amounts of THMs. Some reports have argued that conventional photochemical processes to drinking water production such as UV-C irradiation could induce chemical modification on dissolved organic matter allowing that chlorine can easily react with modified molecules. This fact could lead to the production of THMs at important concentrations (Shah et al., 2011; Spiliotopoulou et al., 2015).

As it was already described by Gutierrez-Zapata et al. (2017a, 2017b), the presence of anions such as carbonates (CO$_3^=$), bicarbonates (HCO$_3^-$) and fluoride (F$^-$) which are in groundwater samples at concentrations of 366 and 1.0 mg L^{-1} respectively, may exert an important influence on the photo-induced processes. Carbonates and bicarbonates can react with ·OH producing CO$_3^{-·}$ radicals having an interesting oxidation potential (E° (CO$_3^{-·}$/CO$_3$=) = 1.78 V vs NHE) able to oxidize organics (Dell'Arciprete et al., 2012; De Laurentiis et al., 2014) and inactivate bacteria (Wolcott et al., 1994) increasing the water pH (Eqs. (5)–(7)). On the other hand, F$^-$ could modify the surface of iron (hydr) oxides increasing the production of ·OH radicals (Du et al., 2008).

$$HCO_3^- + ·OH \rightarrow CO_3^{-·} + H_2O \tag{5}$$

$$CO_3^{2-} + ·OH \rightarrow CO_3^{-·} + OH^- \tag{6}$$

$$CO_3^{-\cdot} + OM \rightarrow OM_{ox} \qquad (7)$$

In summary, H_2O_2/photochemical systems using both sunlight and artificial UV-B + A + visible light could enhance natural abiotic processes (especially at high solar irradiation) increasing the production of reactive oxygen species (ROS). Their coupling with conventional drinking water systems such as rapid sand filtration and chlorination lead to the production of drinking water with high microbiological and chemical quality. Moreover, this procedure did not exhibit the production of THMs.

It was found that residual H_2O_2 can remain on the groundwater samples. However, full coupled systems (SPH + LPh + H_2O_2 + RSF + Cl) at high sunlight doses showed the lowest residual H_2O_2 amount. Wang et al. (2016) reported the fate of H_2O_2 coming from advanced oxidation processes for drinking water production using a slow sand filter. They found that biotic (biomass) and abiotic processes (some Mg-oxides present on sand) could help to destroy residual H_2O_2. It is possible that photochemical induced processes such as photo-Fenton, photocatalytic and H_2O_2-photolysis together with biotic and abiotic processes mentioned by Wang et al. (2016) contribute to the H_2O_2 degradation observed. Furthermore, the same authors (Wang et al., 2017) have recently pointed-out that the guideline of allowable residual concentrations of H_2O_2 coming from advanced oxidation processes must be carefully evaluated since there are not recommended values.

However, despite this coupled system showed interesting potential to be applied in drinking water production from well waters, it is necessary to continue the research to find suitable conditions where a complete inactivating process can be achieved since it was found that at low solar energy dose, total bacteria inactivation was not reached. Issues such as coupling of more UV-B + A + visible lamps, and mechanism to decrease the residual H_2O_2 concentrations must be systematically studied to find the best conditions where it is possible to grant total bacteria inactivation either upon high or low solar energy doses without risk.

Results reported herein demonstrate that although there was chemical modification of organic matter (2,4-D oxidation and DOC reduction), remaining organic byproducts did not react strongly to chlorine and THMs were not highly produced.

5. Conclusions

Coupled helio-photochemical processes with artificial UVB + A + Visible light in presence of $10 \, mg \, L^{-1}$ of H_2O_2 with rapid slow filtration and chlorination demonstrated an interesting potential to simultaneous removal of organics (2,4-D) and total reduction of *E. coli* and *K. pneumoniae* viability only at high solar energy dose ($150,000 \, J \, m^{-2}$). However, despite bacteria inactivation was affected when experiments were carried out at low solar energy dose ($75,000 \, J \, m^{-2}$ accumulated), 2,4-D degradation did not undergo detrimental effects.

These coupled systems showed an interesting potential to be applied in drinking water production, but systematic studies must be performed in order to gain a better understanding and enhance its performance especially when low solar energy dose takes place.

Acknowledgement

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.solener.2018.10.070.

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