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Enhancing solar disinfection of water in PET bottles by optimized *in-situ* formation of iron oxide films. From heterogeneous to homogeneous action modes with H_2O_2 vs. O_2 – Part 1: Iron salts as oxide precursors

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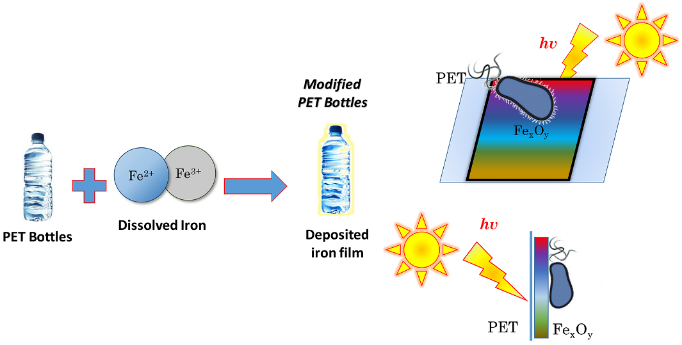
HIGHLIGHTS

- Solar disinfection in PET bottles was enhanced deposing iron by homogeneous precursor.
- The optimization parameters indicated a simple, fast and durable reactor for SODIS.
- Semiconductor action and ppb levels of iron leaching enhanced disinfection.
- Photo-Fenton process was effectively yielded with H_2O_2 addition.
- The process can be effective in slightly acidic natural waters, without regrowth.

GRAPHICAL ABSTRACT



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ABSTRACT

Solar disinfection (SODIS) is a WHO-accepted intervention method for improving water sources in developing countries. Despite its effectiveness, the limitations of long exposure and bacterial regrowth risk demand further improvement of the practice. In this work, we have generated an iron oxide film on the inner surface of PET bottles used in SODIS, to generate further pathways of solar-mediated inactivation, namely a semiconductor mode of action and controlled iron leaching in the system, which both have demonstrated bactericidal capacity. More specifically, in this Part 1, the deposition process using Fe salts has been scrutinized, assessing the use of various homogeneous Fe precursors ($FeCl_3$, $FeSO_4$ and $Fe_2(SO_4)_3$), amounts of iron (0.5–20 g/L) and deposition time (1–8 h) to find the delicate balance among deposition layer thickness and light penetration. At the optimal conditions (4 h deposition, 1 g/L $FeCl_3$) SODIS was enhanced, reducing 60% the exposure time; a simple washing step brought a further reduction (70%), while eliminating regrowth in volumes from 330 up to 1500 mL reactors. A robust process and reactor was attained, able to reuse its precursor solution almost 10 times and the reactor in 5 consecutive tests, without the need for re-deposition. The modification also proved to be an invaluable iron source to fuel the photo-Fenton process, when H_2O_2 as an electron acceptor was added to the system. The improvement induced by the heterogeneous photo-Fenton process was around 80% compared to the SODIS/H_2O_2 process in plain PET bottles and exceeded 85% when compared to SODIS, while being durable to the high

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oxidative conditions. Finally, in the view of application in drinking water treatment, the process performed well in the lightly acidic region, due to the physicochemical implications of natural waters' pH in iron cycling.

1. Introduction

Safe drinking water is one of the basic health fundamental rights around the globe. However, improper sanitation and compromised water sources have been associated with a series of health problems, such as increasing human mortality, due to gastrointestinal diseases related with enteric pathogens [1]. Over the last decades, research has shifted into developing a cost-effective and proper technology for water disinfection instead of chemical treatment processes, like chlorination, due to the production of dangerous disinfection by-products compounds [2]. Solar disinfection (SODIS) is one of the household water treatment methods that can be used extensively in isolated regions, developing countries or ones with sunny climate [3,4]. In this method, transparent bottles such as polyethylene terephthalate (PET) plastic are filled with the polluted water and exposed to sunlight for a specific time in order to inactivate the microorganisms [5,6]. This simple water disinfection procedure has been successfully used in different regions with illuminated days such as South Africa, Cameroon, Senegal and India [7].

The pathogen inactivation in this solar-driven treatment processes is caused by synergistic effect of UVA, UVB and temperature increase during light exposure [8]. Indeed, UVB at wavelengths around 280–320 nm can be absorbed directly by genetic material and lead to serious damage in DNA molecules and finally inactivation [9]. *E. coli* is a Gram-negative bacterium that is frequently used as a fecal pollution indicator in the majority of microbiological investigations. Additionally, the efficacy of this treatment method has been studied against diverse microorganisms such as bacteria, fungi, viruses, protozoa and helminths [3,10–12]. Specifically for bacteria, the effect of solar light can be related to the endogenous photosensitizers and their abilities for producing reactive oxygen species (ROS) when exposed to solar light which initiate a series of intracellular oxidative reactions, causing damage to key components in the cell [13–16].

The Advanced oxidation processes (AOPs) represent one of the promising options used for drinking water disinfection and simultaneous mineralization of organic compounds [17–19]. Among AOPs, the photo-assisted Fenton process combines Fe^{2+}, H_2O_2 and light in order to enhance the bacterial inactivation and this reaction can be considered for water disinfection under solar light irradiation [20–23]. The main effective agents in this process are ROS products especially non-selective $HO^{\cdot}$ that produced by consuming of H_2O_2. One of the main advantage of using solar irradiation or photon up to 580 nm in photo-Fenton process is accelerating photo-reduction of Fe^{3+} organo-complexes and increasing the $HO^{\cdot}$ production [24–26]. Consequently, if solar light is combined with other additives such as H_2O_2 and iron, it can produce reactive oxygen species such as $HO^{\cdot}$, superoxide radical anion ($O_2^{\cdot-}$) and singlet oxygen ($^1O_2$) [27] with potentials for severe damage in bacterial cells as well as regrowth elimination [20,21].

In the (homogeneous) photo-Fenton process, iron added to the solution and the interaction between oxidizing agents with organic pollutants or bacteria ensues as follows (Eqs. (1)–(3)):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^{\cdot} \ (k = 63\,\mathrm{M^{-1}\,s^{-1}}) \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^- + H^+ \ (\mathrm{k}=3.1 \times 10^{-3}\,\mathrm{M^{-1}s^{-1}}) \tag{2}$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + HO^{\cdot} + H^+ \ (\mathrm{k} = 2.9 \times 10^{-3}\,\mathrm{M^{-1}\,s^{-1}}) \tag{3}$$

The photo-Fenton process has an narrow optimal pH operating region (peak: 2.8) [21], hence many works have focused on enhancing its applicability by overcoming the iron-related limitations, i.e. precipitation [26]. Some propose the use of chelating ligands, such as EDDS or citrate [28,29], oxalate [30], natural products [18,31] or the support of the catalyst on proper substrates [32,33]. However, very few of these works have taken into account the cost factor, as it can be perceived in water-stressed isolated regions, which are already using SODIS or may be open to do so.

In this work, the effectiveness of iron oxide films as bacterial inactivation enhancers in water was assessed, after their deposition in the inner surface of a PET bottle-reactor. The idea lies in the effectiveness of SODIS and the induction of iron-related processes that lead to the enhancement of bacterial inactivation. Hence, iron was deposed, and bacterial inactivation in the bulk was assessed. The main factors under investigation were the operational parameters, such as the deposition iron precursor, the time for deposition, the concentration of the precursor, in the most economical way. Afterwards pre- and post-treatment of the reactor was performed to study the possible improvements in reaction kinetics, as well as the addition of H_2O_2 for further disinfection enhancement with the induction of a supported photo-Fenton reaction. The mechanical and surface properties were followed by different surface science methods and finally, application of the modified reactors towards drinking water treatment was assessed. For each step, a proposition for the mechanism of inactivation was suggested.

2. Material and methods

2.1. Chemicals and reagents

Ferric chloride ($FeCl_3{\cdot}6H_2O$) (Sigma-Aldrich); Ferrous sulfate ($FeSO_4{\cdot}7H_2O$) (Sigma-Aldrich); Ferric sulfate ($Fe_2\,(SO_4)_3{\cdot}xH_2O$) (Sigma-Aldrich); Hydroxylamine Hydrochloride; Ferrozine (Sigma-Aldrich); Sodium hydroxide (98% Sigma-Aldrich); Ammonium hydroxide (28–30%) (ACROS); Ammonium acetate (Sigma-Aldrich); Hydrogen peroxide (H_2O_2) 30% w/w (Sigma-Aldrich) and Titanium (IV) oxysulfate ($TiOSO_4$) (Fluka) were purchased from Sigma-Aldrich, Switzerland. The plate count agar (PCA) media was purchased from Merck GmbH, Microbiology division KGaA, under the catalogue N° 1.05463.0500. All of chemicals were in analytical grade. All solutions were prepared with Milli-Q water (18.2 MΩ.cm). Also, the natural water from Lake Geneva with physicochemical properties showed in Table 1 was used to suspend bacteria and inactivation test.

2.2. Bacterial stock preparation and microorganism enumeration

The *E. coli* strain K12 (DSMZ No. 498) was purchased from Deutsche Sammlung von Mikro-organismen and Zellkulturen GmbH. *E. coli* K12 is a non-pathogenic and used as a typical surrogate for enteric bacterial pathogens. The preparation has been published elsewhere [34,35].

Table 1

The physicochemical properties of Lake Geneva water.

Parameter	Milli-Q water	Lake Geneva water
Conductivity at 20 °C (μS/cm)	< 0.055	252
Transmittance at 254 nm (%)	100	96
pH	6–6.5	8.3
Total organic carbon (TOC) (mg/L)	< 0.005	0.8–1
Phosphates	–	0.019
Hydrogen carbonate (mg/L)	–	108
Chloride (mg/L)	–	8
Sulfate (mg/L)	–	48
Nitrate (mg/L)	–	2.7