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Safe Drinking Water Generation by Solar-Driven Fenton-Like Processes

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1. Introduction

Around the world, it is estimated that 1.2 billion people have limited or no access to safe water for domestic use. As a result, the prevalence of water borne diseases affects not only the health of the inhabitants of these regions, but also their economic development (Gelover et al., 2006). It is clear that water resources management is becoming a critical issue worldwide, especially in regions with low rainfall and growing population (Bandala et al., 2010).

Just considering Africa, Latin America and the Caribbean, about one billion people have no access to safe water supplies resulting in serious human health effects, i.e. 1.5 million children died every year due to water borne diseases. Moreover, the lack of safe drinking water has been related to poverty and considerable limitations for sustainable development (Montgomery and Elimelech, 2007). In Mexico, for example, waterborne diseases affect over 6% of the total population, being rural communities with less than 2,500 inhabitants the most affected, since only 78% of this rural population has access to piped water (CONAGUA, 2011). Unfortunately, this situation is not limited to Mexico, but it is common in other developing countries in Latin America.

It is well known that human pathogens become sensitive to different environmental conditions once discharged into a water body. For example, some environmental conditions such as temperature and ultraviolet (UV) radiation are capable of inactivating waterborne pathogens. However, engineering processes are required if the goal is to assure the generation of safe drinking water for remote, poor, isolated regions in developing countries (Castillo-Ledezma et al., 2011).

Several different disinfecting processes have been tested in order to deactivate undesirable microorganisms in water. Within this variety of disinfectants, Advanced Oxidation Processes (AOPs) have been proven efficient and cost-effective for water treatment (Blanco et al., 2009). These physical-chemical processes have the potential of producing deep changes in the chemical structure of pollutants as a result of the action of hydroxyl radicals (HO•) (Orozco et al., 2008). Several scientific studies suggest that AOP's high efficiency is related to their thermodynamic viability and the increased rate of reaction produced by

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hydroxyl radicals. Among various AOPs, photocatalytic processes are very attractive for the mineralization (conversion to carbon dioxide, water, and other mineral species) of aqueous pollutants and inactivation of pathogenic microorganisms (Gelover et al., 1999; Bandala and Estrada, 2007; Bandala et al., 2007 & 2008). The use of AOPs for water disinfection, using solar radiation as the energy source, usually referred to as enhanced photocatalytic solar disinfection (ENPHOSODIS), has allowed the efficient deactivation of highly resistant microorganisms. Specifically, heterogeneous and homogeneous photocatalysis are the AOPs with the most technological applications because of their ability to remove organic pollutants and their capability to inactivate nuisance microorganisms. Regarding heterogeneous photocatalysis, the use of titanium dioxide (TiO₂) as a catalyst has been widely tested and proven effective for deactivating several microorganisms as well as carcinogen cells (Dunlop et al., 2008; Rincon and Pulgarin, 2003; Reginfo et al., 2008; Castillo-Ledezma et al., 2011). In comparison with the heterogeneous arrangement, homogeneous processes also rely on the generation of hydroxyl radicals. Nevertheless, it has been proposed that other highly oxidant species could be involved in pollutant degradation and microorganisms deactivation. Fenton and Fenton-like processes are among the most widely studied methodologies (Bandala et al., 2009; Guisar et al., 2007; Bandala et al., 2011). From the economic point of view, the possibility of using solar energy to promote both homogeneous and heterogeneous photocatalytic processes is an interesting alternative to the use of these technologies in developing countries (Bandala et al., 2011; Blanco et al., 2007).

The aim of this chapter is to review the state-of-the-art in the use of solar driven Fenton-like processes for the deactivating waterborne pathogens. It also the goal of this work to discuss the advantages and potential limitations of these treatment processes while analyzing the challenges and opportunities for the application of such technologies at real scale in poor, isolated regions in developing countries with no access to safe drinking water.

2. Chemical and biological mechanisms involved in homogeneous photocatalysis

2.1 Chemistry

The chemical mechanisms involved in the Fenton reaction are well known since early of the past century. The reactions of iron (II) salts with hydrogen peroxide have been widely studied for decades and the main reactions involved are summarized in Table 1 (Orozco et al., 2008; Gallard and De Laat, 2000; Gallard et al., 1999).

$Fe^{2+} +H_2O_2 \rightarrow Fe^{3+} +HO^{\bullet} + OH^-$	(1)
$Fe^{2+} +HO^{\bullet} \rightarrow Fe^{3+} +OH^{-}$	(2)
$Fe^{3+} +H_2O \leftrightarrow [FeOH]^{2+} +H^+$	(3)
$Fe^{3+} + H_2O_2 \leftrightarrow [FeHO_2]^{2+} + H^+$	(4)
$[FeOH]^{2+} + H_2O_2 \leftrightarrow [Fe(OH)(HO_2)]^+ + H^+$	(5)
$[FeOH]^{2+} \rightarrow Fe^{2+} + HO \bullet$	(6)
$[FeHO_2]^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet}$	(7)
$[Fe(OH)(HO_2)]^+ \rightarrow Fe^{2+} HO_2^{\bullet} + HO^-$	(8)
$RH + HO^{\bullet} \rightarrow R^{\bullet} + H_2O$	(9)

Table 1. Chemical reactions involved in the Fenton reaction (Fe (II) and H₂O₂).

When the process is carried out under radiation, called the photo-Fenton process, the influence of radiation increases the oxidation rate of the pollutant when compared to the conventional Fenton reaction (Bandala et al., 2007). Several possible reaction schemes for the photo-induced system have been proposed as well as the formation of different complexes studied by spectrophotometry. From these studies, the influence of iron oxidation state and the specific counter ion of the iron salt employed have been demonstrated to affect both the decomposition of H_2O_2 as well as the overall efficiency of the photo-Fenton process for the oxidation of some model pollutants.

$\begin{array}{c} Fe^{2+} + Cl^{-} \leftrightarrow FeCl^{+} & (10) \\ Fe^{3+} + Cl^{-} \leftrightarrow FeCl_{2}^{+} & (11) \\ Fe^{3+} + 2Cl^{-} \leftrightarrow FeCl_{2}^{+} & (12) \\ FeCl_{2}^{+} \rightarrow Fe^{2+} + Cl^{\bullet} & (13) \\ FeCl_{2}^{+} \rightarrow Fe^{2+} + Cl^{\bullet} ^{2-} & (14) \\ Fe^{2+} + Cl^{\bullet} \rightarrow Fe^{3+} + Cl^{-} & (15) \\ Fe^{2+} + Cl_{2}^{\bullet} \rightarrow FeCl_{2}^{+} + Cl^{-} & (16) \\ Cl^{-} + HO^{\bullet} \rightarrow [ClOH]^{\bullet-} & (17) \\ [ClOH]^{\bullet-} + H^{+} \rightarrow [HClOH]^{\bullet} & (18) \\ [HClOH]^{\bullet} \rightarrow Cl + H_{2}O & (19) \\ Cl^{\bullet} + H_{2}O_{2} \rightarrow HO_{2}^{\bullet} + 2Cl^{-} + H^{+} & (20) \\ Cl^{\bullet} + H_{2}O_{2} \rightarrow HO_{2}^{\bullet} + 2Cl^{-} + H^{+} & (21) \end{array}$		
$\begin{array}{cccc} Fe^{3+} + 2Cl^{-} \leftrightarrow FeCl_{2^{+}} & (12) \\ FeCl_{2^{+}} \rightarrow Fe^{2^{+}} + Cl^{\bullet} & (13) \\ FeCl^{2^{+}} \rightarrow Fe^{2^{+}} + Cl^{\bullet} & 2^{-} & (14) \\ Fe^{2^{+}} + Cl^{\bullet} \rightarrow Fe^{3^{+}} + Cl^{-} & (15) \\ Fe^{2^{+}} + Cl_{2^{\bullet}} \rightarrow FeCl_{2^{+}} + Cl^{-} & (16) \\ Cl^{-} + HO^{\bullet} \rightarrow [ClOH]^{\bullet-} & (17) \\ [ClOH]^{\bullet-} + H^{+} \rightarrow [HClOH]^{\bullet} & (18) \\ [HClOH]^{\bullet} \rightarrow Cl + H_{2}O & (19) \\ Cl^{\bullet} + H_{2}O_{2} \rightarrow HO_{2^{\bullet}} + Cl^{-} + H^{+} & (20) \end{array}$	$Fe^{2+} + Cl^{-} \leftrightarrow FeCl^{+}$	(10)
$FeCl_{2^+} \rightarrow Fe^{2^+} + Cl^{\bullet}$ (13) $FeCl^{2^+} \rightarrow Fe^{2^+} + Cl^{\bullet} 2^-$ (14) $Fe^{2^+} + Cl^{\bullet} \rightarrow Fe^{3^+} + Cl^-$ (15) $Fe^{2^+} + Cl_{2^{\bullet}} \rightarrow FeCl_{2^+} + Cl^-$ (16) $Cl^- + HO^{\bullet} \rightarrow [ClOH]^{\bullet -}$ (17) $[ClOH]^{\bullet -} + H^+ \rightarrow [HClOH]^{\bullet}$ (18) $[HClOH]^{\bullet} \rightarrow Cl + H_2O$ (19) $Cl^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + Cl^- + H^+$ (20)	$Fe^{3+} + Cl^- \leftrightarrow FeCl_2^+$	(11)
$\begin{array}{cccc} FeCl^{2+} \to Fe^{2+} + Cl^{\bullet} & 2^{-} & (14) \\ Fe^{2+} + Cl^{\bullet} \to Fe^{3+} + Cl^{-} & (15) \\ Fe^{2+} + Cl_{2}^{\bullet} \to FeCl_{2}^{+} + Cl^{-} & (16) \\ Cl^{-} + HO^{\bullet} \to [ClOH]^{\bullet-} & (17) \\ [ClOH]^{\bullet-} + H^{+} \to [HClOH]^{\bullet} & (18) \\ [HClOH]^{\bullet-} \to Cl + H_{2}O & (19) \\ Cl^{\bullet} + H_{2}O_{2} \to HO_{2}^{\bullet} + Cl^{-} + H^{+} & (20) \end{array}$	$Fe^{3+} + 2Cl^{-} \leftrightarrow FeCl_{2^{+}}$	(12)
$\begin{array}{ll} Fe^{2+} + Cl^{\bullet} \to Fe^{3+} + Cl^{-} & (15) \\ Fe^{2+} + Cl_{2}^{\bullet} \to FeCl_{2^{+}} + Cl^{-} & (16) \\ Cl^{-} + HO^{\bullet} \to [ClOH]^{\bullet -} & (17) \\ [ClOH]^{\bullet -} + H^{+} \to [HClOH]^{\bullet} & (18) \\ [HClOH]^{\bullet -} + Cl + H_{2}O & (19) \\ Cl^{\bullet} + H_{2}O_{2} \to HO_{2}^{\bullet} + Cl^{-} + H^{+} & (20) \end{array}$	$\operatorname{FeCl}_{2^{+}} \to \operatorname{Fe}^{2^{+}} + \operatorname{Cl}^{\bullet}$	(13)
$Fe^{2+} + Cl_{2} \rightarrow FeCl_{2^{+}} + Cl^{-} $ (16) $Cl^{-} + HO^{\bullet} \rightarrow [ClOH]^{\bullet -} $ (17) $[ClOH]^{\bullet -} + H^{+} \rightarrow [HClOH]^{\bullet} $ (18) $[HClOH]^{\bullet} \rightarrow Cl + H_{2}O $ (19) $Cl^{\bullet} + H_{2}O_{2} \rightarrow HO_{2^{\bullet}} + Cl^{-} + H^{+} $ (20)	$FeCl^{2+} \rightarrow Fe^{2+} + Cl^{\bullet} 2^{-}$	(14)
$Cl^{-} +HO^{\bullet} \rightarrow [ClOH]^{\bullet-} $ (17) $[ClOH]^{\bullet-} +H^{+} \rightarrow [HClOH]^{\bullet} $ (18) $[HClOH]^{\bullet} \rightarrow Cl + H_{2}O $ (19) $Cl^{\bullet} + H_{2}O_{2} \rightarrow HO_{2}^{\bullet} + Cl^{-} + H^{+} $ (20)	$Fe^{2+} + Cl^{\bullet} \rightarrow Fe^{3+} + Cl^{-}$	(15)
$[ClOH]^{\bullet-} +H^{+} \rightarrow [HClOH]^{\bullet} $ (18) $[HClOH]^{\bullet} \rightarrow Cl + H_2O $ (19) $Cl^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + Cl^{-} + H^{+} $ (20)	$Fe^{2+} + Cl_2^{\bullet} \rightarrow FeCl_2^{+} + Cl^{-}$	(16)
$[HClOH]^{\bullet} \rightarrow Cl + H_2O $ (19) $Cl^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + Cl^- + H^+ $ (20)	$Cl^- + HO^{\bullet} \rightarrow [ClOH]^{\bullet-}$	(17)
$Cl^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + Cl^- + H^+ $ (20)	[ClOH] ·- +H+→ [HClOH] ·	(18)
()	$[\text{HClOH}]^{\bullet} \rightarrow \text{Cl} + \text{H}_2\text{O}$	(19)
$Cl_{2} + H_{2}O_{2} \rightarrow HO_{2} + 2Cl_{2} + H_{1} $ (21)	$Cl^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + Cl^- + H^+$	(20)
(21)	$Cl_2^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + 2Cl^- + H^+$	(21)

Table 2. Suggested side reactions related with the iron salt counter ion during Fenton reaction.

2.2 Biological mechanisms

In general, photocatalytic processes, both homogeneous and heterogeneous, in the presence of iron and hydrogen peroxide have been demonstrated effective against a wide variety of resistant microorganism such as viruses (Kim et al., 2010), helminth eggs (Bandala et al., 2011a,b; Guisar et al., 2007), bacteria and spores (Dunlop *et al.*, 2008; Bandala *et al.*, 2009; Bandala et al., 2011c; Sichel *et al.*, 2009; Castillo-Ledezma et al., 2011).

The main mechanism involved in deactivating pathogenic microorganisms is suggested to be related with the cellular damage produced by so-called reactive oxygen species (ROS), mainly hydroxyl (HO•) and superoxide radical (O_2 •) as shown in Tables 1 and 2. According to different studies, these ROS are able to modify and eventually destroy the structure of the cell membrane (Alrousan *et al.*, 2009, Malato *et al.*, 2009), mainly as the result of lipid peroxidation (Dunlop *et al.*, 2008; Alrousan *et al.*, 2009). The initial damage is produced in the outer lipopolisaccarid and peptidoglycan walls, followed by lipid peroxidation and protein and polysaccarides oxidation (Malato *et al.*, 2009; Dalrymple *et al.*, 2010) affecting the regulatory function of the cell membrane for the internal and external interchange. The damage produced will further produce failure in the cell's respiratory activity and decrease its permeability, allowing the attack of inner cell components leading to its death (Alrousan *et al.*, 2009).

Some studies have also demonstrated that microorganism's deactivation is also improved by the presence of iron derivatives, which have been suggested to show an important inhibitory activity in important microbiological processes such as biofilm generation (Dunlop *et al.*, 2008). Cells are used to regulate iron adsorption as a defense mechanism against hydroxyl radical; however once hydroxyl radicals are generated in the intracellular media, as a result of the Fenton-like process by direct attack of the ROS, they are free for reacting with biomolecules (Darlymple *et al.*, 2009).

During cellular metabolism some ROS are produced, such as superoxide (O₂•), hydroxyl radical and hydrogen peroxide (H₂O₂), as a result of cell respiration. However, these oxidizing species are in equilibrium with the immune system defense mechanism through anti-oxidizing enzyme production related to superoxide dismutase (SODs), catalase (CAT) and glutathione peroxidase (GPX) families (Castillo-Ledezma et al., 2011). When microorganisms are exposed to a major oxidative stress, for example ROS produced during a photocatalytic process, enzyme production is no longer capable of eliminating excess radical allowing deep cell damage. In the same way, ROS may produce additional oxidative stress in the cells through Fenton and Heber-Weiss reaction (Dunlop et al., 2008) generating damage in all the cell components including proteins, lipids and DNA. In the case of DNA damage, produced by pyrimidine dimmers formation by the generation of covalent bonds among the bases in the same DNA chain (Sichel et al., 2009), it generates mutations that may lead to loss of functional capability and death of cell (Malato et al., 2009). At the same time, when microorganisms are exposed to ultraviolet radiation (UV, $\lambda \leq 400$ nm) during the photocatalytic reaction, DNA damage occurred directly through the radiation absorption by cell chromophores, which absorb radiation and produce heat. This interaction leads to an increase in ATP and RNA synthesis, jointly with the increase of ROS production. Microorganisms receiving a sub-lethal dose of UV radiation may become resistant to induced oxidative stress, partially recover their defense mechanisms and adapt to oxidative stress generated by exposure to UV radiation alone (tanning effect) (Bandala et al., 2011b).

3. Solar-driven Fenton and Fenton-like inactivation of pathogenic microorganisms

Homogeneous processes rely on the generation of hydroxyl radicals. Nevertheless, it has been proposed that other highly oxidant species could also be involved in pollutant degradation (Anipsitakis and Dionysiou, 2004). Fenton and Fenton-like processes are among the most widely studied methodologies. When a Fenton process uses ultraviolet (UV) radiation, visible light or a combination of both, the resulting process (known as photo-Fenton) has several advantages, including the increase of degradation rate and the flexibility of using alternative energy sources (i.e., solar radiation) for driving the process (Bandala et al., 2007; Bandala and Estrada, 2007; Fernandez et al., 2005). From the economic point of view, the possibility of using solar energy to promote both homogeneous and heterogeneous photocatalytic processes is an interesting alternative technology for use in developing countries (Bolton, 2001).

Several reports on the use of photo-Fenton process for deactivating pathogenic microorganisms have been published in the near past. In these studies, a wide variety of analysis have been conducted and reported, such as: the effects of the iron salt and pH on deactivating *E. coli* (Spuhler et al., 2010), the capability of solar driven photo-Fenton process to achieve simultaneous degradation of natural organic matter (NOM) and water disinfection (Moncayo-Lasso et al., 2009) as well as the effect of many other specific parameters as reported in a recent review by Malato et al. (2009).

In addition to the study of E. coli cells, many other microorganisms have been tested and used as indicators for evaluating the performance of photo-Fenton processes such as Salmonella spp. (Sciacca et al., 2011), Fusarium solani spores (Polo-Lopez et al., 2011), helminth eggs (Bandala et al., 2011a,b) and Bacillus subtilis spores (Bandala et al., 2011c). In a recent work, several different Fenton reagent concentrations were tested in combination with UV-A radiation (λ_{max} = 365 nm) to pursue deactivation of *B. subtilis* spores. The best spore deactivation conditions were found using [Fe(II)] = 2.5 mM and $[H_2O_2] = 100 \text{ mM}$ and UV-A radiation. As depicted in Figure 1, under these experimental conditions, over a 9-log reduction in spore viability was reached after 20 minutes of reaction. Interesting results were also observed from experiments conducted with low Fe(II) concentrations or even when no Fe(II) was added and only H₂O₂ and UV-A radiation were used. Under these experimental conditions, a lag phase -where no deactivation occurred- was observed during earlier stages of the disinfection process and much lower spore viability was determined after long time of irradiation. These results might suggest that microorganisms have the capability to generate defense mechanisms as a response to threatening environmental stresses. It is also suggested that the observed initial delays in the inactivation process may be due to the effect of defense mechanisms by the microorganisms against low ROS concentrations generated under these reaction conditions.

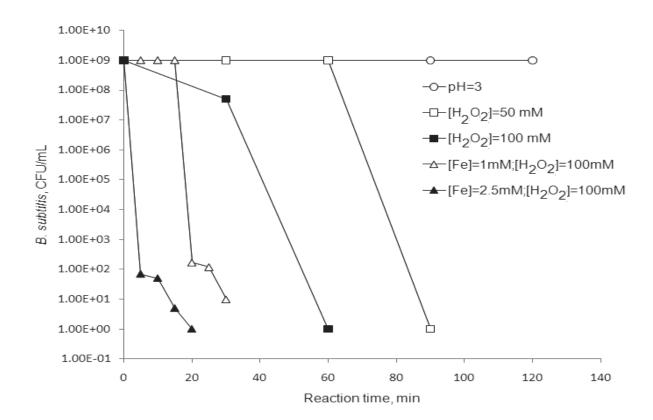


Fig. 1. Deactivation of Bacillus subtilis spores using photo-assisted Fenton reaction.

Furthermore, researchers have hypothesized that, when the iron salt is added to the reaction mixture, ROS generation increases dramatically and overwhelms the defense capability of the microorganisms leading to their immediate death without undergoing the lag phase observed previously.

The effects of ionic strength and natural organic matter (NOM) in spore deactivating kinetics have also tested and representative experimental results are illustrated in Figures 2 and 3, respectively. In both cases, an important decrease on the deactivating rate was observed when NOM concentration and ionic strength were increased. Experimental data has been modeled using a modification of the delayed Chick-Watson model, including the accumulated energy (Q_n), rather than the traditional C×t factor (disinfectant concentration times contact time) used for chemical disinfection (Bandala et al., 2009). Model fitting parameters, including deactivating rate constants for the different experimental conditions, are reported in Table 3.

$$\frac{N}{N_{0}} = \begin{cases} \frac{N}{N_{0}} if \ Q_{n} \leq Q_{nlag} = \frac{1}{k} \ln\left\{ \left(\frac{N_{1}}{N_{0}}\right) \left(\frac{N_{0}}{N}\right)_{c} \right\} \\ \frac{N_{1}}{N_{0}} e^{-k_{1}Q_{n}} \ if \ Q_{nlag} \leq Q_{n} \leq Q_{n2} \\ \frac{N_{2}}{N_{0}} e^{-k_{2}Q_{n}} \ if \ Q_{n} \geq Q_{n2} = \frac{1}{k_{2} - k_{1}} \ln\left(\frac{N_{2}}{N_{1}}\right) \end{cases}$$
(22)

It was demonstrated that the lag-phase described initially for spore deactivation was avoided by the use of photo-assisted Fenton reaction whereas very different results were obtained when natural organic matter was present in raw water.

As observed in the experimental results, the photo-assisted Fenton reaction might represent an interesting alternative to deactivate recalcitrant microorganisms in water. In this particular study, the photo-assisted process was used to kill *B. subtilis* spores, which are currently considered among the most resistant bacteria. It has been demonstrated that, if the photo-Fenton reaction is capable to deactivate *B. subtilis* spores, it could be able to eliminate other less resistant pathogenic microorganisms present in water under the same reaction conditions (Bandala et al., 2011a).

Experimental conditions	k2(min-1)	$\ln\left(\frac{N_1}{N_0}\right)$	$\ln\left(\frac{N_2}{N_0}\right)$
UV, pH = 3	/-())		-
$[H_2O_2] = 50 \text{ mM}$	-	2.45	_
$[H_2O_2] = 100 \text{ mM}$	0.39	0	2.99
$[Fe(II)] = 1mM; [H_2O_2] = 100 mM$	0.83	2.53	15.23
$[Fe(II)] = 2.5 \text{ mM}; [H_2O_2] = 100 \text{ mM}$	0.87	2.78	15.67
$[Fe(II)] = 2.5 \text{ mM}; [H_2O_2] = 100 \text{ mM}; [Cl-] = 25 \text{ mgL}^{-1}$	0.85	2.72	15.82
$[Fe(II)]=2.5 \text{ mM}; [H_2O_2] = 100 \text{ mM}; [Cl-] = 50 \text{ mgL}^{-1}$	0.02	2.77	16.61
$[Fe(II)] = 2.5 \text{ mM}; [H_2O_2] = 100 \text{ mM}; [Cl-] = 100 \text{ mgL}^{-1}$	0.02	2.69	16.11
$[Fe(II)] = 2.5 \text{ mM}; [H_2O_2] = 100 \text{ mM}; [SR-NOM] = 2.5 \text{ mgL}^{-1}$	0.74	2.53	17.05
$[Fe(II)] = 2.5 mM; [H_2O_2] = 100 mM; [SR-NOM] = 5.0 mgL^{-1}$	0.76	2.3	16.12

Table 3. Kinetic data obtained using Chick-Watson model for homogeneous photocatalytic disinfection.

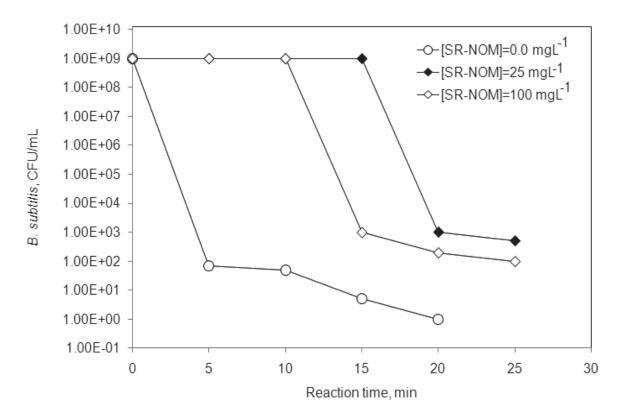


Fig. 2. Effect of natural organic matter (NOM) on the efficiency of photo-assisted deactivation of *B. subtilis* spores.

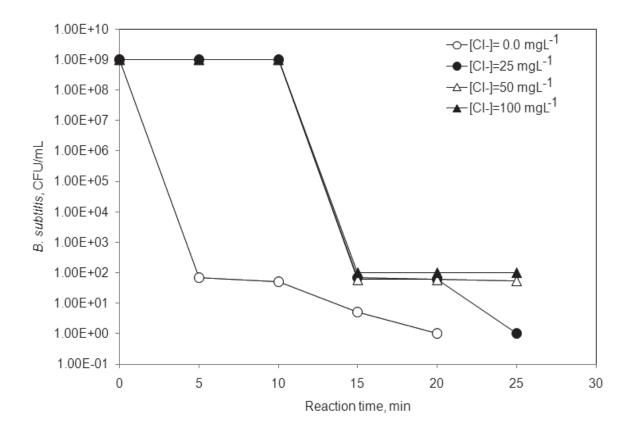


Fig. 3. Effect of ionic strength on the efficiency of photo-assisted deactivation of *B. subtilis* spores.

Spore deactivation using photo-Fenton reaction is considerably affected by the ionic strength and natural organic matter, mainly by delaying the beginning of actual deactivation process. As shown in Figure 2, an increase in the concentration of natural organic matter has an important slowing effect on spore deactivation since it increases the duration of the lag phase.

The experimental results presented in Figures 2 and 3 suggest that the efficiency of photo-Fenton processes used for disinfection depend largely on the quality of background water. Therefore, if these processes are to be cost-effective, they should be coupled with pretreatment and/or other conventional drinking water processes.

4. Sequential disinfection using Solar-driven Fenton-like processes

As proposed earlier, AOPs by themselves may not be capable enough to reach the desired level of pathogen deactivation as well as to assure quality of treated water because of their lack of disinfectant residual. In the past, different authors have suggested that the application of a strong oxidant (i.e. ozone) followed by a weaker oxidant (i.e. free or combined chlorine) could produce important synergistic effects on the deactivating kinetics of strong pathogens such as *Cryptosporidium parvum* oocysts (Rennecker et al., 2000; Driedger et al., 2000; 2001). The high efficiency demonstrated by sequential disinfection using the ozone-chlorine pair could be related to the generation of different reactive oxygen species (i.e. hydroxyl radicals) by the use of ozone which could synergically enhance the oxidative properties of chlorine, improving the overall inactivation rate. Considering this hypothesis, it could be possible that other methods producing hydroxyl radicals would be able to produce similar synergistic effects in similar sequential processes.

In a recent work, the efficiency of the sequential application of AOPs followed by free chlorine processes was investigated in order to deactivate helminth eggs, another highly resistant waterborne pathogen which is commonly found in surface waters contaminated with untreated domestic wastewater. Detailed information on the experimental matrix and methods used to perform these tests and to evaluate microorganism viability are described elsewhere (Bandala et al., 2011b). Figure 4 depicts the experimental results of sequential deactivation of *Ascaris suum* eggs using solar photocatalysis followed by free chlorine. For comparison purposes, notice that the inactivation results of *A. suum* eggs using free chlorine alone are also shown. It is important to mention that the reaction time, rather than the common *CT* value, is shown on the horizontal axis since the initial concentration of free chlorine (7.0 mg/L) was found to remain constant throughout the duration of the experiments. It is also important to mention that all deactivating tests were conducted in synthetic water at pH 7.0, at which hypochlorous acid (HOCl) was the predominant free chlorine species.

As shown in the experimental results of Figure 4, practically no effect on egg viability was observed when free chlorine alone was used as a single disinfectant. On the other hand, egg deactivation in the range of 25-30% was achieved when free chlorine was applied for 20 minutes after primary treatment with solar photocatalysis was applied. Experimental runs labeled as "Sequential 1" and "Sequential 2" are two different experiments carried out separately under the same reaction conditions ([Fe(II)]= 5mM; [H₂O₂]= 140 mM after 60 minutes of photo-assisted treatment). As mentioned, the effect of chlorine by itself on egg

viability is almost negligible. In a previous work, Bandala et al. (2011b), reported that comparing the effect of chlorine alone with the photo-assisted process alone, the sequential process shows a very close trend to the observed for the AOP. Nevertheless, after the initial 20 minutes of application of sequential chlorine deactivation, the eggs viability was observed remaining unchanged at 10%, whereas in the case of the photo-Fenton process, the helminth eggs deactivation continues until reaching almost 2-log deactivation.

The use of highly-resistant pathogens, such as helminth eggs, as a conservative surrogate for water disinfection is also a very interesting issue because the deactivation of the helminth eggs is a complex task, which was in agreement with previous results from our research group (Bandala et al., 2011b), achieving almost complete helminth eggs deactivation.

Any other less resistant pathogen microorganisms (i.e. bacteria) present in the raw water will be deactivated under the same reaction conditions and after providing the same solar radiation dose. It is reasonable then that the disinfection level reached using AOPs may be, as demonstrated here, improved by the further adding of free chlorine in the sequential process.

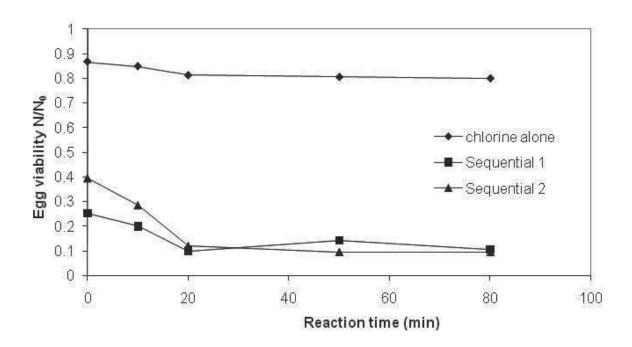


Fig. 4. Effect of sequential AOPs-chlorine processes on the deactivation of Ascaris suum eggs.

5. Conclusions and final comments

The use of solar radiation to catalyze Fenton-like processes has been proven to be effective to deactivate waterborne pathogens. Experimental results and reported deactivation parameters suggest that these processes could be an interesting alternative to conventional chlorine disinfection for developing countries. Furthermore, solar-driven Fenton-like processes is a more efficient alternative when compared to conventional solar disinfection (SODIS), since the required exposure times for both are significantly different and much lower for the photocatalytic arrangement. Nevertheless, it is well documented that for solar photocatalysis to perform at optimum conditions, a primary treatment of raw water might be needed in order to decrease the concentrations of interfering compounds such as natural organic matter. When considering the necessity to provide a disinfectant residual in order to protect water treated with AOPs, sequential disinfection using AOPs as a primary process coupled with secondary free chlorine also represents an interesting alternative for developing countries. Similar to the synergistic effects produced by ozone on secondary free chlorine deactivation of strong microorganisms such as C. parvum oocysts, preliminary studies conducted with AOPs used as primary disinfectant -instead of ozone- have reported to generate similar synergistic effects on the deactivation of conservative surrogates such as B. subtilis spores and helminth eggs. More comprehensive work needs to be conducted in order to fully characterize the magnitude and occurrence of this synergism under a wide range of experimental conditions of interest for drinking water treatment such as water pH and temperature. Finally, in order to fully understand the effectiveness of solar-driven Fenton-like processes when used for disinfection purposes, it is clear that more studies are required in order to elucidate the actual mechanism of cell deactivation when using such processes.

6. References

- Alrousan, D.M.A., Dunlop, P.S.M., McMurray, T.A., Byrne, A. Photocatalytic inactivation of *E. coli* in surface water using immobilised nanoparticle TiO₂ films. Water research 43 (2009) 47-54.
- Anipsitakis G.P., Dionysiou D.D. 2004. Transition metal/UV-based advanced oxidation technologies for water decontamination. Applied Catalysis B: Environmental, 54, 155-163.
- Bandala E.R., Pelaez M.A., Dionysiou D.D., Gelover S., García A.J., Macías D. 2007. Degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) using cobaltperoximonosulfate in Fenton-like process. Journal of Photochemistry and Photobiology A: Chemistry 186, 357–363.
- Bandala E.R., Estrada C. 2007. Comparison of solar collection geometries for application to photocatalytic degradation of organic contaminants. Journal of Solar Energy Engineering 129, 22–26.
- Bandala E.R., Pelaez M.A., Garcia-Lopez J., Salgado M.J., Moeller G. 2008. Photocatalytic decolourization of synthetic and real textile wastewater containing benzidine-based azo dyes. Chemical Engineering and Processing 47, 169–176.
- Bandala E.R., Corona-Vasquez B., Guisar R., Uscanga M. 2009. Deactivation of highly resistant microorganisms in water using solar driven photocatalytic processes. International Journal of Chemical Reactor Engineering 7, A7.
- Bandala E.R., González L., de la Hoz F., Pelaez M.A., Dionysiou D.D., Dunlop P.S.M., Byrne J.A., Sanchez J.L. 2011a. Application of azo dyes as dosimetric indicators for enhanced photocatalytic solar disinfection (ENPHOSODIS). Journal of Photochemistry and Photobiology A: Chemistry 218, 185-191.
- Bandala E.R., Gonzalez L., Sanchez-Salas J.L., Castillo J.H. 2011b. Inactivation of Ascaris eggs in water using sequential solar driven photo-Fenton and free chlorine. Journal of Water and Health, (In press).

- Bandala E.R., Duran J.A., Holland J.N. 2011c. Consequences of Global Climate Change for Water Quality and Community Sustainability along the U.S.-Mexico Trans-Border Region: Case Studies of Reynosa/McAllen and Laredo/Nuevo Laredo. Proceedings of the Puentes Consortium's Mexico-U.S. Higher Education Leadership Forum. March 2011 Rice University, Houston, Texas. Available online at http://www.puentesconsortium.org/papers/working-papers.
- Blanco J., Malato S., Fernandez-Ibañez P., Alarcon D., Gernjak W., Maldonado M.I. 2009. Review of feasible solar energy applications to water processes, Renew. Sustain. Energ. Rev. 13 (6–7), 1437–1445.
- Blanco J., Fernandez P., Malato S. 2007. Solar photocatalytic detoxification and disinfection of water: an overview. Journal of Solar Energy Engineering 129 (1), 4–15.
- Bolton J.R. 2001. Ultraviolet applications handbook. Bolton Photosciences Inc. Ontario, Canada.
- Castillo-Ledezma J.H., Sanchez-Salas J.L., Lopez-Malo A., Bandala E.R. 2011. Effect of pH, solar irradiation, and semiconductor concentration on the photocatalytic disinfection of Escherichia coli in water using nitrogen-doped TiO₂. European Food Research Technology 233, 825-834.
- Chacon J.M., Leal M.T., Sanchez M., Bandala E.R. 2006. Solar photocatalytic degradation of azo-dyes by photo-Fenton process. Dyes Pigments 69, 144–150.
- Comision Nacional del Agua (CONAGUA). 2011. Estadísticas del agua en Mexico. Secretaría de Medio Ambiente y Recursos Naturales (SEMARNAT), Mexico. March, 2011.
- Dalrymple, O.K., E. Stefanakos., M.A. Trotz., D.Y. Goswami. 2010. A review of the mechanisms and modeling of photocatalytic disinfection. Applied Catalysis B: Environmental 27-38.
- Driedger, A.M., Rennecker, J.L. & Mariñas, B.J. 2001. Inactivation of Cryptosporidium parvum oocysts with ozone and monochloramine at low temperature. Wat. Res. 35(1), 41-48.
- Driedger, A.M., Rennecker, J.L. & Mariñas, B.J. 2000. Sequential inactivation of Cryptosporidium parvum oocysts with ozone and free chlorine. Wat. Res. 34 (14), 3591-3597.
- Dunlop P.S.M., McMurray T.A., Hamilton J.W.J., Byrne J.A. 2008. Photocatalytic-inactivation of *Clostridium perfringens* spores on TiO₂ electrodes. Journal of Photochemistry and Photobiology A: Chemistry 196, 113–119.
- Fernandez P., Blanco J., Sichel C., Malato S. 2005. Water disinfection by solar photocatalysis using compound parabolic collectors. Catalysis Today 101, 345–352.
- Gelover S., Gomez L.A., Reyes K., Leal T. 2006. A practical demonstration of water disinfection using TiO₂ films and sunlight. Water Research, 40 (17), 3274–3280.
- Gelover S., Leal T., Bandala E.R., Román A., Jiménez A., Estrada C. 1999. Catalytic photodegradation of alkyl surfactants, Water Science and Technology 42 (5–6), 110–116.
- Gallard H., De Laat J. 2000. Kinetic modeling of Fe(III)/H₂O₂ oxidation reactions in dilute aqueous solutions using atrazine as a model organic compounds. Water Research 34, 3107 3116.

- Gallard H., De Laat J., Legube B. 1999. Spectrophotometric study of the formation of iron (III) hydroperoxy complexes in homogeneous aqueous solutions. Water Research 33, 2929 2936.
- Guisar R., Herrera M.I., Bandala E.R., García J.L., Corona B. 2007. Inactivation of waterborne pathogens using solar photocatalysis. Journal of Advanced Oxidation Technologies 10 (2), 1–4.
- Haber F., Weiss J. 1934. The catalytic decomposition of hydrogen peroxide by iron salts. Proceedings of the Royal Society A 134, 332 – 351.
- Kim, J.Y., Lee, Ch., Sedlak, D.L., Yoon, J., Nelson, K.L. 2010. Inactivation of MS2 coliphage by Fentons' reagent. Water Reserch 44, 2647-2653.
- Malato S., Fernández-Ibáñez P., Maldonado M.I., Blanco J., Gernjak W. 2009. Decontamination and disinfection of water by solar photocatalysis: Recent overview and trends. Catalysis Today 147(1), 1-59.
- Montgomery M.A., Elimelech M. 2007. Water and sanitation in developing countries: including health in the equation. Environmental Science and Technology 41 (1),17–24.
- Moncayo-Lasso A., Sanabria J., Pulgarin C., Benítez N. 2009. Simultaneous *E. coli* inactivation and NOM degradation in river water via photo-Fenton process at natural pH in solar CPC reactor. A new way for enhancing solar disinfection of natural water. Chemosphere 77(2), 296-300.
- Orozco S.L., Bandala E.R., Arancibia C.A., Serrano B., Suarez R., Hernández I. 2008. Effect of iron salt on the color removal of water containing the azo-dye reactive blue 69 using photo-assisted Fe(II)/H₂O₂ and Fe(III)/H₂O₂ systems, Journal of Photochemistry and Photobiology A: Chemistry 198, 144–149.
- Polo-López M.I., García-Fernández I., Oller I., Fernández-Ibáñez P. 2011. Solar disinfection of fungal spores in water aided by low concentrations of hydrogen peroxide. Photochemistry and Photobiology Sciences 10, 381-388.
- Reginfo-Herrera J.A., Mielczarski E., Mielczarski J., Castillo N.C., Kiwi J., Pulgarin C. 2008. *Escherichia coli* inactivation by N, S co-doped commercial TiO₂ powders under UV and visible light. Applied Catalysis B: Environmental 84 (3–4), 448–456.
- Rennecker, J.L., Driedger, A.M., Rubin, S.A. Mariñas, B.J. 2000. Synergy in sequential inactivation of *Cryptosporidium parvum* with ozone/free chlorine and ozone/monochloramine. Water Research 34(17), 4121-4130.
- Rincón A.G., Pulgarín C. 2003. Photocatalytical inactivation of *E. coli* effect of (continuousintermitent) light intensity and of (suspended-fixed) TiO₂ concentration. Applied Catalysis 44, 263–284.
- Sciacca F., Rengifo-Herrera J. A., Wéthé J., Pulgarin C. 2011. Solar disinfection of wild *Salmonella sp.* in natural water with a 18 L CPC photoreactor: Detrimental effect of non-sterile storage of treated water. Solar Energy 85(7), 1399-1408.
- Sichel, C., Fernández-Ibáñez, P., de Cara, M., Tello, J. 2009. Lethal synergy of solar UVradiation and H₂O₂ on wild *Fusarium solani* spores in distilled and natural water. Water Research 34, 1841-1850.
- Spuhler D., Rengifo-Herrera J.A., Pulgarin C. 2010. The effect of Fe²⁺, Fe³⁺, H₂O₂ and the photo-Fenton reagent at near neutral pH on the solar disinfection (SODIS) at low temperatures of water containing *Escherichia coli* K12. Applied Catalysis B: Environmental 96(1-2), 126-141.

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