Fe vs. TiO$_2$ Photo-assisted Processes for Enhancing the Solar Inactivation of Bacteria in Water

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Abstract: Batch solar water disinfection (SODIS) is a known, simple and low-cost water treatment technology. SODIS is based on the synergistic action of temperature increase and light-assisted generation of Reactive Oxygen Species (ROS) on bacteria. ROS are generated *via* the action of solar photons on i) Natural Organic Matter (NOM), ii) some mineral components of water (Fe oxides or Fe-organic complexes, nitrogen compounds) and iii) endogenous bacteria photosensitizers (*e.g.* cytochrome). SODIS has proven its effectiveness for remote settlements or urban slums in regions with high incident solar radiation. All of the internal and external simultaneous processes are often driven by photoactive Fe-species present in the cell, as well as in the natural water sources. In SODIS, a temperature of 50 °C is required and due to this temperature dependence, only 1–2 L can be treated at a time. As required exposure time strongly depends on irradiation intensity and temperature, some SODIS households could be overburdened, leading to inadequate treatment and probable bacterial re-growth. This is why TiO$_2$ photocatalysis and Fe photo-assisted systems (*i.e.* photo-Fenton reactants) have been considered to enhance the photo-catalytic processes already present in natural water sources when exposed to solar light. Both TiO$_2$ and Fe-photoassisted processes, when applied to water disinfection aim to improve the performance of solar bacteria inactivation systems by i) enhancing ROS production, ii) making the process independent from the rise in temperature and as a consequence iii) allowing the treatment of larger volumes than 1–2 L of water and iv) prevent bacterial (re)growth, sometimes observed after sole solar treatment.

Keywords: Bacteria inactivation · Neutral photo-Fenton · Solar disinfection · TiO$_2$ photo-catalysis

Solar Disinfection of Water is an *in situ*-Generated Photocatalytic Process

Solar bacteria inactivation in natural water is a photocatalytic process promoted *in situ* by solar light, which attacks inside and outside the cell envelope. Indeed, the internal action of photons is related to the UV disruption of the H$_2$O$_2$ regulation system present in bacteria and especially catalase and dismutase enzymes.[1] Hence, accumulated inner metabolic H$_2$O$_2$ reacts with Fe^{2+} produced by the UV degradation of inner bacteria components containing iron as ferritin or iron-sulfur cluster components.[2] Thus a photo-Fenton reactant (H$_2$O$_2$, Fe^{2+}, light), which leads to the production of powerful oxidative ·OH radical, is generated in the bacteria (Fig. 1). In addition, internal components of bacteria such as cytochromes, tryptophan and flavins, are very efficient photosensitizers able to generate photo-excited triplet

forms which, in contact with oxygen, lead to reactive oxygen species (ROS) as ^{1}O$_2$.[3] Therefore, ·OH and other reactive oxygen species (ROS) generated by this internal Fenton, photo-Fenton and internal photo-

sensitization processes are mainly responsible for the cytoplasmic protein and DNA double helix damage in the bacteria. The UV-B part of the solar light directly attacks bacterial DNA but its contribution has gen-
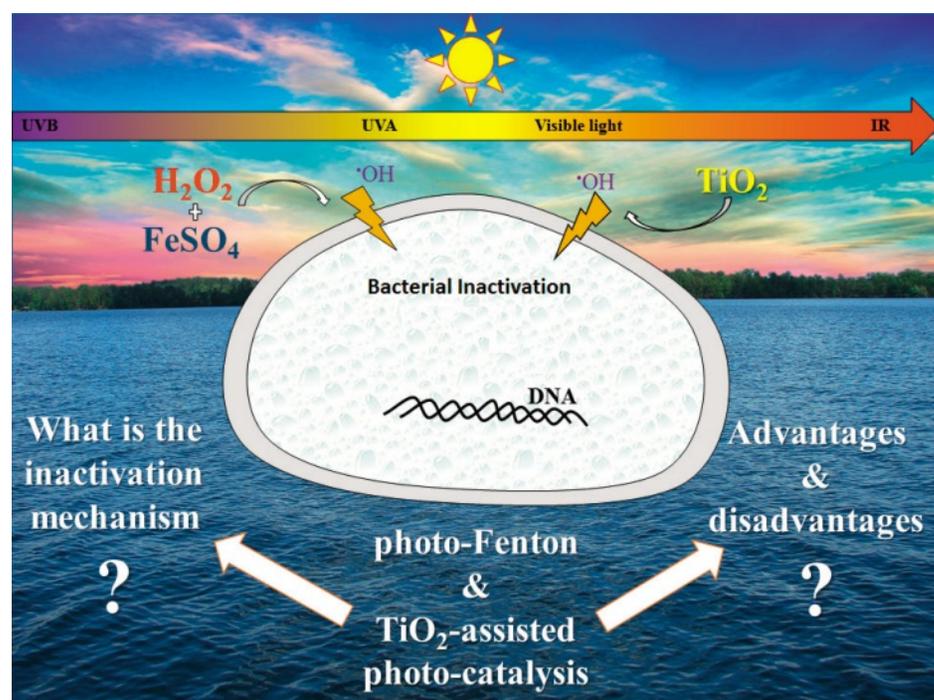
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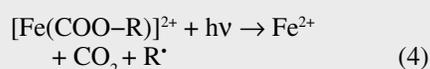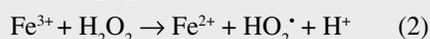Tel: +41 21 693 47 20
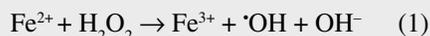E-mail: cesar.pulgarin@epfl.ch

Fig. 1. Fe- and TiO$_2$-photoassisted processes enhance the photo-catalytic processes already present in natural waters when exposed to solar light.

erally not been considered as receptacles used for disinfection on the field (PET or glass) filter most UV-B photons.

In addition to internal degradation, there is also external attack by photo-excited components of the natural organic matter (NOM) present in water. NOM, belonging to the humid acid family, generates under solar light photo excited triplet forms which, in presence of O_2, lead to ROS as H_2O_2, $^{.}OH$, $^1O_2$.[4] In natural waters, a part of the total iron content is composed of solid iron oxides.[5] Interesting bacterial inactivation rates have been obtained in the laboratory with iron oxides,[6] because of the capability of bacteria to solubilize Fe with the help of siderophores.[7] Siderophores produced by bacteria (enterobactin, aerobactin, and ferrichrome) can chelate iron to manage the Fe^{3+} transport inside the cell for its delivery into the cell as Fe^{2+}.[8,9] If Fe^{2+} is present in water (outside the cell), it can diffuse across the outer membrane and is transported by specific proteins *via* a Feo (ferrous iron-transport) system across the cytoplasmic membrane.[10] This increases the Fe^{2+} internal concentration, which in turn enhances the photo-Fenton initiated production of $^{.}OH$ and consequently the degradation rate of internal cell components. Other iron species present in natural waters are semiconductor iron oxides,[5] which have demonstrated capabilities to generate bactericidal ROS under visible solar light.[11] The energy of this part of the solar spectrum is enough to promote electrons from valence (VB) to the conduction band (CB) of most of the iron oxides existing in natural water sources. In this case, ROS (*i.e.* $O^{.-}_2$) are generated *via* the CB electron trapping by O_2 dissolved in water.[5] In contrast, the created holes (h^+), by visible light electron promotion, do not have the required oxidative potential to generate $^{.}OH$ in water.

Enhancement of Solar Bacteria Inactivation by Addition of Photo-Fenton Reactants

Fenton's reagent action is based on the reaction of H_2O_2 with Fe^{2+}, thus resulting in the formation of the powerful bactericide $^{.}OH$ and other highly oxidative species in aqueous media (reactions (1) and (2)). However, the Fenton process is limited by the Fe^{2+} regeneration of Fe^{3+} (reaction (2)). This drawback is partially countered by photo-Fenton reactions. In fact, Fe^{3+}-hydroxy complexes undergo photo-reduction under ultraviolet A (UV-A) and visible radiation, thus regenerating Fe^{2+} *via* ligand-to-metal charge transfer (LMCT) and contributing to an additional pathway of $^{.}OH$ production (reaction (3)).[12]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {^{.}OH} + OH^- \quad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{.} + H^+ \quad (2)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {^{.}OH} \quad (3)$$

$$[Fe(COO{-}R)]^{2+} + h\nu \rightarrow Fe^{2+}$$
$$+ CO_2 + R^{.} \quad (4)$$

However reactions (1) to (3) occur only at acidic pH that favors the formation of photoactive Fe^{3+} aqua-hydroxy complexes which are capable of generating, under solar light, bactericide $^{.}OH$.[13,14]

In 2006 the seminal publication demonstrating the enhancing effect of photo-Fenton reactant addition during solar disinfection of water appeared.[15] Since natural water sources have a near neutral pH, most iron precipitates as iron oxides and under these conditions only reaction (4) could occur in the homogeneous phase. Indeed, a part of NOM can complex Fe^{3+} maintaining it in solution in a homogeneous photo-Fenton cycle.[15–17] In addition, the photolysis of these Fe^{3+}-organo complexes, which generally have a high molar absorption coefficient in UV-A and visible light, not only leads to the regeneration of Fe^{2+} required for reaction (1) but also to the formation of a ligand radical[18] (reaction (4)). Byproducts, generated during bacteria inactivation, can also play the role of complex (R) for the reaction (4). The most recent research in my team (not yet published), inspired by the NOM action mode, exhibited efficient bacterial inactivation by the photo-Fenton process at near-neutral and alkaline pH with added iron citrate complexes. These complexes drive the photo-reduction of Fe^{3+} to Fe^{2+} by a LMCT mechanism and assure high $Fe^{2+,3+}$ catalytic turnover and fast $^{.}OH$ production, which is typical of a homogeneous photocatalytic Fenton cycle.[18]

In the above-mentioned processes, the bacterial inactivation rate depends on the amounts of the photo-Fenton reactants ($Fe^{2+,3+}$, H_2O_2, photons)[19,20] and the organic complexes present. As the light source is in this case the sun, this parameter cannot be voluntarily modified and only Fe^{2+}, Fe^{3+}, H_2O_2 and organic complex addition can be considered to enhance the solar assisted photo-Fenton disinfection. However, when $Fe^{2+,3+}$ salts are added to the water at neutral pH in the absence of organic complexes such as citrate, most of the iron rapidly precipitates as Fe^{3+} (hydr) oxides under the oxidative action of O_2 and H_2O_2.[6] In the presence of solar light, Fe^{3+} oxides (naturally present, or formed from added Fe salts) can act as i) Fe^{3+} source for siderophores, ii) semiconductors able to generate ROS in presence of O_2 and under visible light[5,6] and iii) heterogeneous photocatalyst for photo-Fenton process when

H_2O_2 is added. Rivers, lakes and wells have generally near-neutral pH and the iron oxides are under these conditions the most abundant iron species. Therefore, when exposed to solar light, these solid iron forms also play the role of photocatalyst that assures a bactericidal heterogeneous photo-Fenton cycle where the limiting reactant is the added H_2O_2. The heterogeneous photo-Fenton action is based, as for the homogeneous one, on the generation under light of ROS (especially $^{.}OH$) *via* the oxidation of Fe^{2+} by H_2O_2 and the LMCT of some photoactive Fe^{3+}-aqua-hydroxy-complexes at the surface of the iron oxide, which regenerate Fe^{2+}. In the heterogeneous system, this cycle takes place on the surface of the iron oxide particle whereas, in the homogeneous one, the same cyclic reaction occurs in the solution. In the latter system, as mentioned above, the $Fe^{2+,3+}$ is held in solution thanks to the formation of iron-NOM complexes or by the formation of iron complexes with byproducts resulting from bacterial degradation.[21]

It is worth mentioning that added H_2O_2 is also able to penetrate into the bacteria cell thus increasing the damage provoked by the internal photo-Fenton reaction.[21] Finally, we have also to consider that when Fe^{3+} is poured into neutral water, one part of it forms photoactive complexes with membrane components which are additional sites of bacterial attack as, under solar light, Fe^{3+}-bacteria complexes can suffer a LMCT leading to oxidation of bacteria wall components.[5]
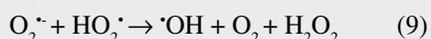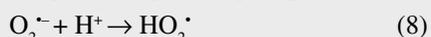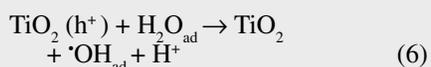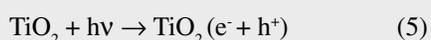
In addition to the detrimental action of solar light alone that leads to the formation and accumulation of internal photo-Fenton reactants ($Fe^{2+} + H_2O_2$ + light) that degrade internal constituents of the bacteria cell, all the other external processes often produce ROS (*i.e.* $^{.}OH$) that attack the cell envelope, provoking damage in the cell wall proteins and undergoing membrane peroxidation and an increase in permeability.[22]

The standard neutral photo-Fenton disinfection process presented above has been demonstrated to be efficient in field applications with 1-liters bottles and 40–50 liter solar reactors in Switzerland,[15,16] Colombia[17] and Burkina Faso.[19,20,23,24]

Enhancement of Solar Disinfection by TiO_2 Photocatalysis

In 1985, Matsunaga *et al.*[25] reported the first use of heterogeneous photocatalysis by TiO_2 as a sterilization process to inactivate bacterial cells. Heterogeneous photocatalysis consists in the irradiation of TiO_2 nanoparticles by UV light leading to the production of reactive oxygen species (ROS) such as hydroxyl ($^{.}OH$) and superoxide anion ($^{.}O_2^-$) radicals, singlet oxygen

($^1O_2$), and hydrogen peroxide (H_2O_2). The first event, after absorption of radiation, is the generation of electron/hole pairs (reaction (5)) separated between the conductance band (CB) and valence band (VB). The most relevant redox processes, which take place after the photo-generation of electrons (e^-_{CB}) and holes (h^+_{VB}) in aqueous medium, are summarized in reactions (5)–(9).

$$TiO_2 + h\nu \rightarrow TiO_2\,(e^- + h^+) \qquad (5)$$

$$TiO_2\,(h^+) + H_2O_{ad} \rightarrow TiO_2 \\ + {}^{\bullet}OH_{ad} + H^+ \qquad (6)$$

$$TiO_2\,(e^-) + O_2 \rightarrow TiO_2 + O_2^{\bullet-} \qquad (7)$$

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet} \qquad (8)$$

$$O_2^{\bullet-} + HO_2^{\bullet} \rightarrow {}^{\bullet}OH + O_2 + H_2O_2 \qquad (9)$$

The photo-produced ROS are highly oxidative species, able to inactivate/abate microorganisms.[26] These species are able to oxidize the cell constituents: proteins, lipids and nucleic acids. Photocatalytic inactivation of waterborne *E. coli* cells is influenced to a larger extent by the presence of dissolved organic matter and inorganic ions.[27] Both substance classes can compete for ROS and some inorganic ions could block the TiO_2 surface, causing a detrimental effect on the inactivation process. Dioxygen (O_2) concentration[28] and pH also play an important role. The former acts as an electron trap, decreasing the electron-hole recombination and the latter causes changes on the TiO_2 surface charge, allowing or hindering the physical contact between TiO_2 nanoparticles and cells.

Physical chemical properties inherent to TiO_2 materials can also affect the process. For instance, the TiO_2 isoelectric point plays an important role since depending on this feature, the photocatalyst can take on a positive or negative surface charge at neutral pH values affecting positive or negatively the inactivation process.[29,30] The use of non-metallic doped (with nitrogen and sulfur) TiO_2 materials with visible light absorption in the abatement of waterborne *E. coli* cells has also been demonstrated.[31,32] Although some of these doped materials did not show good photocatalytic performance towards oxidation of organic substances, inactivation of *E. coli* cells was made possible. Under visible light irradiation, N,S co-doped commercial TiO_2 powders did not produce highly oxidative ROS such as $^{\bullet}OH$ radicals; however it was observed that under these irradiation conditions, co-doped TiO_2 powders were able to generate singlet oxygen ($^1O_2$), a ROS with low oxidation potential to destroy organic matter, but also very toxic to cells.[31]

Provisional Conclusion

At the present state of the author's understanding, the neutral photo-Fenton process appears to be a more promising technology than TiO_2 photocatalysis for drinking water treatment. Indeed, due to the accelerated bacterial inactivation, temperature independence, non-existent controversy about nanomaterial presence in drinking water, easy application, and the presence in many water sources of natural iron forms, iron-catalyzed solar processes could be developed more intensively. This could be in particular with regard to the shape and volume of reactors, thus limiting the risk for post-irradiation regrowth, facilitate the acceptance among target populations and allow a larger dissemination of this sustainable low-cost technology.

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