Photochemical & Photobiological Sciences

Dynamic Article Links

Cite this: *Photochem. Photobiol. Sci.*, 2012, **11**, 821

www.rsc.org/pps

PAPER

The detrimental influence of bacteria (*E. coli*, *Shigella* and *Salmonella*) on the degradation of organic compounds (and *vice versa*) in TiO_2 photocatalysis and near-neutral photo-Fenton processes under simulated solar light

Alejandro Moncayo-Lasso,†[a] Luis Enrique Mora-Arismendi,‡[a] Julián Andrés Rengifo-Herrera,[b] Janeth Sanabria,‡[a] Norberto Benítez†*[a] and César Pulgarin*[c]

Received 8th September 2011, Accepted 27th January 2012
DOI: 10.1039/c2pp05290c

TiO_2 photocatalytic and near-neutral photo-Fenton processes were tested under simulated solar light to degrade two models of natural organic matter – resorcinol (R) (which should interact strongly with TiO_2 surfaces) and hydroquinone (H) – separately or in the presence of bacteria. Under similar oxidative conditions, inactivation of *Escherichia coli*, *Shigella sonnei* and *Salmonella typhimurium* was carried out in the absence and in the presence of 10 mg L^{-1} of R and H. The 100% abatement of R and H by using a TiO_2 photocatalytic process in the absence of bacteria was observed in 90 min for R and in 120 min for H, while in the presence of microorganisms abatement was only of 55% and 35% for R and H, respectively. Photo-Fenton reagent at pH 5.0 completely removed R and H in 40 min, whereas in the presence of microorganisms their degradation was of 60% to 80%. On the other hand, 2 h of TiO_2 photocatalytic process inactivated *S. typhimurium* and *E. coli* cells in three and six orders of magnitude, respectively, while *S. sonnei* was completely inactivated in 10 min. In the presence of R or H, the bacterial inactivation *via* TiO_2 photocatalysis was significantly decreased. With photo-Fenton reagent at pH 5 all the microorganisms tested were completely inactivated in 40 min of simulated solar light irradiation in the absence of organics. When R and H were present, bacterial photo-Fenton inactivation was less affected. The obtained results suggest that in both TiO_2 and iron photo-assisted processes, there is competition between organic substances and bacteria simultaneously present for generated reactive oxygen species (ROS). This competition is most important in heterogeneous systems, mainly when there are strong organic–TiO_2 surface interactions, as in the resorcinol case, suggesting that bacteria–TiO_2 interactions could play a key role in photocatalytic cell inactivation processes.

1. Introduction

The development of alternative processes to eliminate pathogenic agents in water is a matter of growing interest especially for isolated populations not connected to a centralized drinking water treatment system. Indeed, conventional drinking water disinfection by chlorination can generate disinfection by-products (DBPs) with carcinogenic and mutagenic potential.[1] Phenolic compounds coming from humic acid degradation are considered as disinfection by-product precursors (DBPPs).[2] For these reasons, solar disinfection processes are of particular interest for water treatment mainly in sunny regions.

In addition, the evaluation of microbiological water quality has historically been based on the estimation of coliform microorganisms because of (a) high abundance with regard to other pathogens and (b) a similar response in natural and treatment conditions. Additionally, its relative simple and less expensive detection technique has converted it to a general reliable innocuous water indicator. However, the World Health Organization (WHO) and other authors have reported limitations in its application to detect health risks from relevant bacteria such as *Salmonella* sp.[3–5]

Recently, solar heterogeneous photocatalysis over TiO_2 and the photo-Fenton reaction have been successfully tested at laboratory and field scales to inactivate several types of microorganisms, including Gram-negative and positive bacteria and their spores, as well as viruses, fungi and protozoa.[6–16] Particularly interesting has been bacterial inactivation by a solar induced photo-Fenton process carried out at near-neutral pH.[6,15,16]

[a]*Universidad del Valle, Grupo de Investigación en Procesos Avanzados de Oxidación (GAOX), A. A. 25360, Cali, Colombia. E-mail: luis.benitez@correounivalle.edu.co; Fax: +57 2 3212148; Tel: +57 2 3212148*
[b]*Centro de Investigación y Desarrollo en Ciencias Aplicadas "Dr. J.J. Ronco" (CINDECA), Departamento de Química, Facultad de Ciencias Exactas, UNLP-CCT La Plata, CONICET, Calle 47 No. 257, 1900 La Plata, Buenos Aires, Argentina*
[c]*Ecole Polytechnique Fédérale de Lausanne (EPFL), Institute of Chemical Science and Engineering, GGEC, Station 6, CH-1015 Lausanne, Switzerland. E-mail: cesar.pulgarin@epfl.ch*
† Facultad de Ciencias Naturales y Exactas, Departamento de Química.
‡ Escuela de Ingeniería de Recursos Naturales y del Ambiente (EIDENAR).

Illumination of TiO_2 nanoparticles with light (typically below 400 nm) produces an electron–hole pair that initiates a series of chemical reactions in which ROS, such as hydroxyl ($^{\cdot}OH$), superoxide ($O_2^{\cdot-}$) radicals and singlet oxygen ($^1O_2$) are generated (eqn (1)–(4)). These photo-induced ROS on TiO_2 surfaces are toxic for bacteria and degrade organic pollutants also.[17–22]

$$TiO_2 + h\nu_{UV} \rightarrow TiO_2(e^- + h^+) \quad (1)$$

$$TiO_2(h_{VB}^+) + H_2O_{(ads)} \rightarrow {}^{\cdot}OH_{(ads)} + H^+ \quad (2)$$

$$TiO_2(e_{CB}^-) + O_2 \rightarrow O_2^{\cdot-}/HO_2^{\cdot} \ (pK_a = 4.5) \quad (3)$$

$$O_2^{\cdot-} + TiO_2(h_{VB}^+) \rightarrow {}^1O_2 \quad (4)$$

On the other hand, homogeneous Fenton (eqn (5) and (6)) and photo-Fenton processes (eqn (5) to (7)) in water produce $^{\cdot}OH$ and peroxyl ($HO_2^{\cdot}/O_2^{\cdot-}$) radicals. Those species, especially $^{\cdot}OH$, attack almost every organic compound.[23–25]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + {}^{\cdot}OH \quad (5)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \quad (6)$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\cdot}OH + H^+ \quad (7)$$

Eqn (7) shows the effect of light irradiation on Fe^{2+} formation by photo-reduction of aqua–Fe(III) complexes, leading to the additional production of $^{\cdot}OH$ radicals. An additional advantage of the photo-Fenton process is the light absorption up to 600 nm comprising 35% of the solar spectrum against 4–7% in the TiO_2 photo-assisted process. Additionally, the interaction between pollutant and oxidizing agent is enhanced in the homogeneous photo-Fenton process; the overall process is described in ref. 26 and 27. Photocatalytic TiO_2 and photo-Fenton processes could be negatively affected by the simultaneous presence of chemical and microbiological pollution since both bacteria cells and organic molecules could compete for the ROS yielded.

The aim of this work was to study the effect of the simultaneous presence of organic compounds – resorcinol (R) and hydroquinone (H) (DBP precursors) – and bacteria cells – *E. coli*, *S. typhimurium* and *S. sonnei* – on the degradation of organics and inactivation of bacteria in water by heterogeneous photocatalysis on TiO_2 and near-neutral photo-Fenton systems. The effect of the presence of chemical substances that interact strongly or weakly with TiO_2 surfaces, such as R and H, respectively, and those that can be found in natural waters, on the photocatalytic inactivation of bacteria cells was also evaluated.

2. Experimental details

2.1 Reagents

TiO_2 Degussa P-25 (Degussa-Evonik Germany) (70% anatase and 30% rutile with a specific surface area (SSA) of 50 g m^{-2}) slurries were used as photocatalyst to inactivate bacteria and degrade organic compounds. Ferric chloride ($FeCl_3{\cdot}6H_2O$) supplied by Fluka (Buchs, Switzerland) was used to run photo-Fenton experiments without further purification. Hydrogen peroxide (35%) was supplied by Riedel-de Haën (Germany). Photo-Fenton experiments were run adjusting the initial pH at 5.0 using HCl or NaOH. Hydroquinone and resorcinol solutions (Fluka < 99%) were prepared in Milli-Q water (18.2 MΩ cm at 25 °C), immediately prior to irradiation experiments.

2.2 Analytical methods

Hydroquinone (H) and resorcinol (R) degradation was followed by HPLC (Hewlett-Packard series 1100) with a column C-18 Nova-Pack with particle size 4 μm; 3.9 mm i.d. and 150 mm length. The mobile phase utilized was methanol–water (30 : 70 v/v) with a flow of 1.0 mL min^{-1}. The concentration of H_2O_2 was monitored by Merckoquant (Merck) peroxide analytical test strips. The pH was measured with a pH-meter Metrohm 827 pH-lab using a glass electrode. All the samples were filtered through 0.45 μm (pore size) membrane prior to the HPLC analysis.

2.3 Bacterial strain and growth media

The bacterial strains used were *Escherichia coli* K12 (ATCC 23716), *Salmonella typhimurium* (ATCC 15490) and *Shigella sonnei* (ATCC 25931) and were supplied by DSM, German Collection of Microorganisms and Cell Cultures. For reactivation of each bacteria, a vial was removed from a stock stored at −20 °C (with 15% of glycerol) and thawed to inoculate a tube with brain infusion hearth broth (Oxoid) pre-warmed, and then incubated at 35 °C for 18 h under constant agitation to assure aerobic conditions; this step was repeated twice. The bacterial cells were collected in a stationary phase, by centrifugation at 6000 rpm for 3 min at 4 °C, and the bacterial pellet was washed three times with a tryptone solution (1%, w/v). Finally, the bacterial pellet was resuspended in tryptone solution and diluted in deionized water to the required cell density corresponding to 10^4–10^7 colony forming units per milliliter (CFU mL^{-1}). Thereafter, the bacterial suspension was exposed to irradiation in the presence of TiO_2 or Fenton reagent. Samples were taken during the illumination period and were analyzed immediately; at the end of each experiment the reactors were wrapped with aluminum foil immediately and maintained in dark conditions with mechanical agitation for 24 h before sampling. To estimate the viable populations we used decimal dilutions and the superficial standard plate method on plate-count-agar (PCA, Merck) in triplicate and incubation at 35 ± 2 °C for 24 h; samples were not filtered prior to plating.

2.4 Photocatalytic procedures

A Pyrex glass bottle of 80 mL (3.5 cm in diameter and 10 cm high) was used as batch reactor. Solar irradiation was simulated by a Hanau Suntest (AM1) lamp having a wavelength spectral distribution with about 0.5% of emitted photons <300 nm (UV-C range) and about 7% between 300 and 400 nm (UV-B, A range). The emission spectrum between 400 and 800 nm follows the solar spectrum.[28] Light intensity in all experiments was 1000 W m^{-2} and it was monitored with a Kipp & Zonen (CM3) power meter (Omni instruments Ltd, Dundee, UK). The irradiation experiments were performed at room temperature (25 °C) and the temperature of the solution increased up to

approximately 30 °C during irradiation. All experiments were carried out in equilibrium with air agitation at 700 rpm. Control experiments in the dark were performed under similar conditions. A TiO_2 concentration of 1.0 g L^{-1}, which in previous studies[29] was found to be optimal for our experimental setup, was used and it was irradiated for 3 h. In the case of the photo-Fenton process, the Fe^{3+} and H_2O_2 concentrations were 1.0 mg L^{-1} and 60.0 mg L^{-1}, respectively. The initial bacterial concentration in TiO_2 and photo-Fenton experiments was of 10^6 CFU mL^{-1} and 10^7 CFU mL^{-1} respectively. The initial concentration of resorcinol and hydroquinone was 10 mg L^{-1}. The initial pH value was 5.0 and the run time was 1.0 h. The samples were taken from the reactor at different intervals and used for pH, H_2O_2 and HPLC measurements. The Fenton reaction was stopped with sodium bisulfite. Results represent the average of three experimental runs and their standard deviations were equal to or lower than 15% for the microbiological analysis and less than 5% for HPLC measurements.

3. Results and discussion

3.1 Effect of bacteria on resorcinol (R) and hydroquinone (H) degradation by TiO_2 photocatalysis and near-neutral photo-Fenton reactant

Photocatalytic degradations of R and H were carried out in the presence of *E. coli*, *S. typhimurium* and *S. sonnei* using 1 g L^{-1} of TiO_2 under simulated solar irradiation. Previously it was found that the sole presence of hydroquinone or resorcinol was not toxic for the microorganisms (data not shown) and that total abatement of R and H in the absence of bacteria was achieved in 90 and 120 min of photocatalytic treatment, respectively (Fig. 1). This difference could be due to the stronger interaction of R with TiO_2 surfaces by forming inner-sphere complexes, *i.e.* chemisorptions at acidic and neutral pH values.[30,31] Hence, the chemisorbed resorcinol can react rapidly with shallowly trapped holes[32] while hydroquinone, which has a weak interaction with TiO_2 surfaces, undergoes slower photocatalytic degradation *via* photo-induced ROS present on the solid/liquid interface.[33] On the other hand, the degradation rate of phenolic compounds can also be related to the ability of the substitutes to generate ring activating or deactivating positions for $^{\cdot}OH$ radical attack. This is determined by the Hammett constant where more negative values indicate larger ring activation and consequently a greater attack probability. The ability to generate aromatic ring activating positions in contact with TiO_2 surface is as follows: resorcinol > catechol > hydroquinone.[34]

Fig. 1a shows that TiO_2 photocatalytic R degradation decreased by around 55% in 90 min when bacteria were simultaneously present. In contrast, H degradation after 120 min of irradiation decreased by 70% in the presence of microorganisms. These results suggest (a) a competition between organics and cells for reactive oxygen species (ROS) generated under light-induced photocatalytic process and (b) a stronger R–TiO_2 surface interaction that could explain the lower detrimental effect of bacteria on its degradation with regard to H degradation.[35]

On the other hand, Fig. 1b shows that H and R, in the absence of bacterial cells, underwent a complete degradation in 40 min of simulated solar irradiation under photo-Fenton conditions at

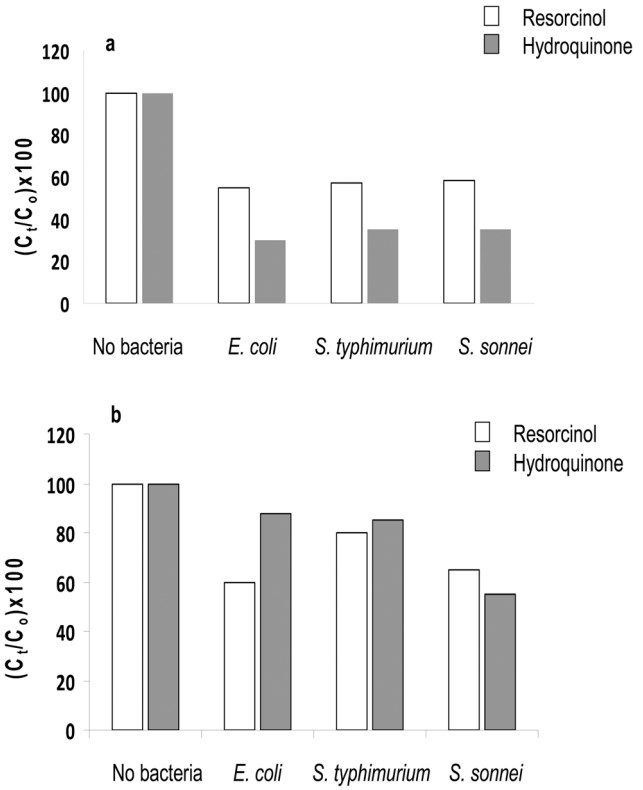

Fig. 1 Degradation percentage of resorcinol (R) and hydroquinone (H) in absence or presence of *E. coli*, *S. typhimurium* and *S. sonnei via* (a) TiO_2 photocatalytic process (irradiation time for complete R and H degradation: 90 and 120 min respectively, TiO_2 concentration: 1 g L^{-1}), (b) photo-Fenton reagent process at pH 5.0 (irradiation time for R and H degradation 40 min, Fe^{3+}: 1 mg L^{-1}, H_2O_2: 60 mg L^{-1}). For both (a) and (b) runs R and H concentration: 10 mg L^{-1} initial bacterial concentrations 10^6 CFU mL^{-1}. Solar simulator light intensity: 1000 W m^{-2}. Results represent the average of three experimental runs and their standard deviations were equal to or lower than 5%.

initial pH 5.0, and their degradation rates are not markedly different. As in the results obtained in photo-assisted TiO_2 processes, H and R photo-Fenton degradation was negatively affected by the presence of microorganisms; however, this negative effect was lower than in heterogeneous photocatalysis.

3.2 Effect of R and H on bacterial inactivation by TiO_2 photocatalysis and near-neutral photo-Fenton reactant

Fig. 2a and 2b show that in the absence of chemical substances, TiO_2 photocatalytic inactivation of *E. coli* was completely achieved (6 logs) in 120 min, while *S. typhimurium* showed inactivation of 3 logs. In contrast, *S. sonnei* was rapidly inactivated in just 10 min (data not shown). These differences in the inactivation rates are not easily explained since both cell strains belong to the same family (Enterobacteriaceae), have similar sizes, a well-conserved genetic map and a rather high degree of identity due to their common ancestor. However, some previous studies have found that *Salmonella* strains seem to be more resistant than *E. coli* using solar disinfection process (SODIS)[36] and SODIS enhanced by neutral photo-Fenton reactions.[15] This

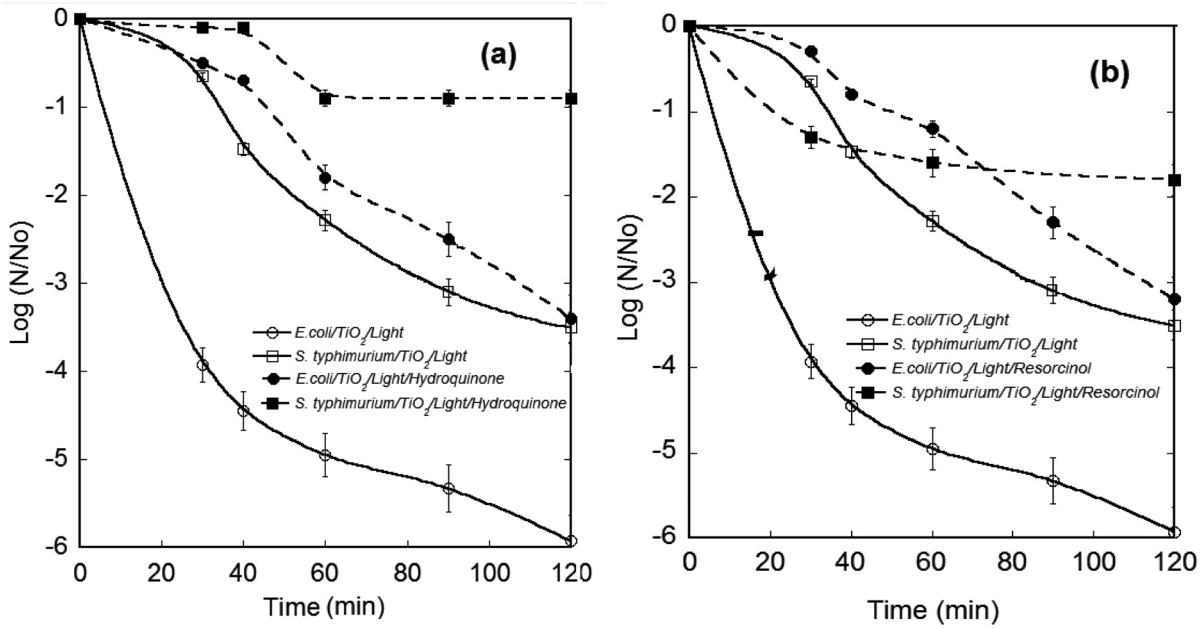

Fig. 2 Bacterial inactivation *via* photocatalytic TiO_2 process in presence of hydroquinone (a) and resorcinol (b): 10 mg L^{-1}, TiO_2 concentration: 1.0 g L^{-1}, initial bacteria concentration: 10^6 CFU mL^{-1}. Solar simulator light intensity: 1000 W m^{-2}. Results represent the average of three experimental runs and their standard deviations were equal to or lower than 15%.

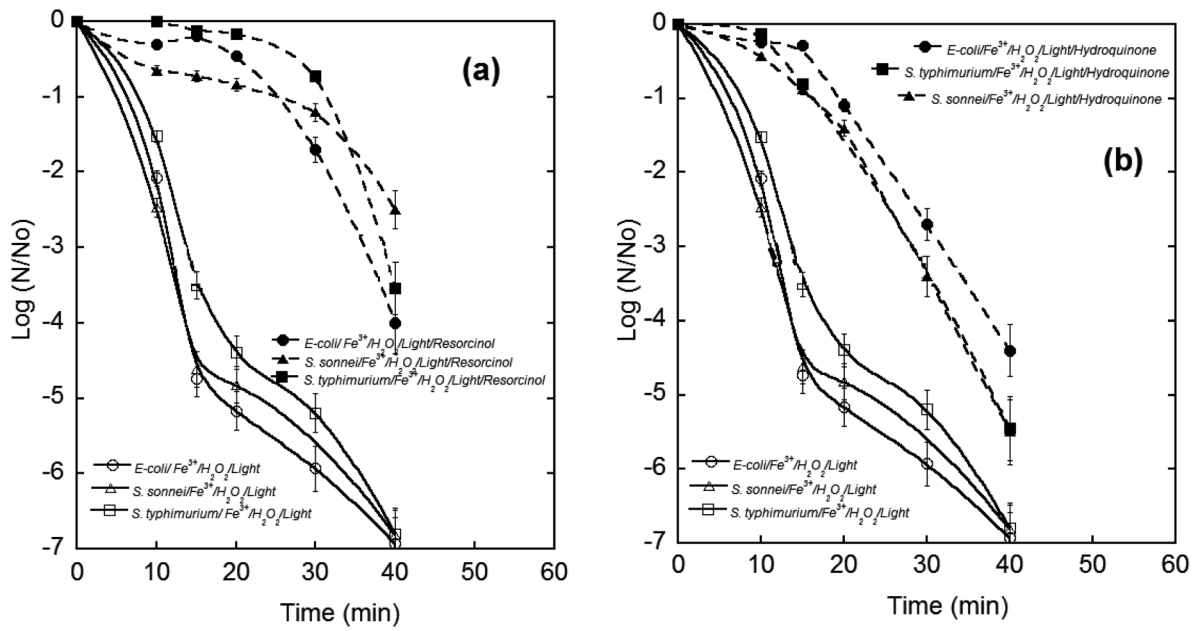

Fig. 3 Bacterial inactivation *via* photo-Fenton reagent in presence of (a) resorcinol and (b) hydroquinone at 10 mg L^{-1}, Fe^{3+}: 1 mg L^{-1}, and H_2O_2: 60 mg L^{-1}, initial pH = 5.0. Initial bacteria concentration: 10^6 CFU mL^{-1}. Solar simulator light intensity: 1000 W m^{-2}. Results represent the average of three experimental runs and their standard deviations were equal to or lower than 15%.

demonstrates the key importance of the bacterial indicator choice for assessing and monitoring this kind of disinfection treatment.

In the presence of R and H, TiO_2 photocatalytic inactivation of *E. coli* and *S. typhimurium* decreased (Fig. 2a and 2b). This detrimental effect could be due to the fact that chemical substances are 1000 times smaller than bacteria and undergo, to a lesser extent, diffusional limitations. Therefore, they are closer to the TiO_2 surface than the cells, being more exposed to the oxidation sites (*i.e.* for resorcinol) or ROS generated at the solid–liquid interface (*i.e.* for hydroquinone).

Bacterial inactivation by photo-Fenton processes at initial pH 5.0 (Fig. 3a and 3b) in the absence of organics revealed that all the tested microorganisms were completely inactivated (−7 logs) before 40 min of simulated solar light irradiation. Bacterial

inactivation by photo-Fenton processes was more strongly affected by R presence than H (Fig. 3a and 3b, respectively). A deep observation of Fig. 1a, 1b, 2 and 3 shows that organic degradation and bacterial inactivation by heterogeneous TiO_2 photocatalysis were generally more negatively affected by the competitive presence of bacteria and organics, respectively, than when the photo-Fenton process is applied.

However, if organics (as is the case for R) are close to the TiO_2 surface, they will compete efficiently either for photo-generated h_{VB}^+ or ROS. In contrast, photocatalytic degradation of organics will be negatively affected to a larger extent if chemical substances do not interact strongly with TiO_2 surfaces as is the case for H. Both observations suggest that surface-related phenomena represent a key factor when simultaneous organic degradation and bacterial inactivation are carried out by TiO_2 photocatalysis (Fig. 4). On the other hand, since the photo-Fenton reaction occurs in homogeneous media, the adsorption limitations can be neglected during both the bacterial inactivation and organic abatement. In addition, some authors have demonstrated that the photo-Fenton process absorbs solar radiation in a greater range of wavelengths, offering better $^{\cdot}OH$ generation yields from both aqua and organic photoactive iron complexes formed between organic degradation by-products such as organic acids and Fe^{3+} ions.[29]

Although a comparison between the heterogeneous photocatalytic and neutral photo-Fenton processes is not appropriate, it is remarkable to mention that the differences between the processes in inactivating bacteria cells could be due to size and interaction of the cell membrane with TiO_2 or ferric ions. At pH 5.0, Degussa P-25 particles are positively charged (*Z*-potential of P-25 around 6.0)[37] while *E. coli* cells would have a slightly negative charge (*Z*-potential of *E. coli* cells 4.3),[38] thus a possible interaction between TiO_2 particles and *E. coli* cells could be benefited.[39] However, ferric ions with positive charge can strongly interact with cell membranes, as was already reported by Spuhler *et al.*[16] This last fact could not be the only issue to explain our results. It is also necessary to take into account size considerations. In aqueous suspensions, Degussa P-25 particles can form aggregates with an average size around 370 nm[37] and the *E. coli* size is around 1.5 μm,[40] while ferric ions, with a positive charge and smaller size than TiO_2 aggregates, and bacteria could strongly interact with cell membranes or even penetrate into the cells.[16] Thus, ferric ions might attack on several points of the cell membrane or internal cell organelles *via* Fenton and photo-Fenton reactions, inactivating the microorganisms more efficiently. In contrast, contact between larger TiO_2 aggregates and the cell membrane would be limited to just a few points on the cell membrane, decreasing its inactivation capacity (Fig. 5).

In our work conditions (pH 5.0), the process showed good efficiency for organic compound degradation and bacterial inactivation confirming that a low pH is not necessarily required in photo-Fenton processes, as has been reported by some recent studies.[6,15,16]

Fe(III) exists as the hexaaquo ion, $Fe(H_2O)_6^{3+}$, in strongly acidic solution; as pH increases, this ion undergoes extensive hydrolysis (eqn (8)). Depending on the counterion, ionic strength, pH and total iron concentration, this Fe(III) complex can precipitate as amorphous ferric oxyhydroxides.[41]

$$Fe^{3+} \rightarrow FeOH^{2+} \rightarrow Fe(OH)_2^{+} \rightarrow Fe_2(OH)_2^{4+} \rightarrow \text{other polynuclear species} \rightarrow Fe_2O_3 \cdot nH_2O(s) \quad (8)$$

However, keeping the total iron in solution below 1×10^{-4} M, *i.e.* less than 10^{-2} M of H^+ (in this work the iron concentration is below 1 mg L^{-1}), avoids a fast hydrolysis of Fe^{3+} and therefore the precipitation of iron oxides is diminished.[26] At pH 5.0, species such as $Fe(OH)_2^+$ exist and carry out the photo-Fenton process even if other iron species such as $Fe(OH)^{2+}$ are less present.[42,43] However, a relatively high concentration of $Fe(OH)^{2+}$ has been reported in weakly acidic conditions.[44]

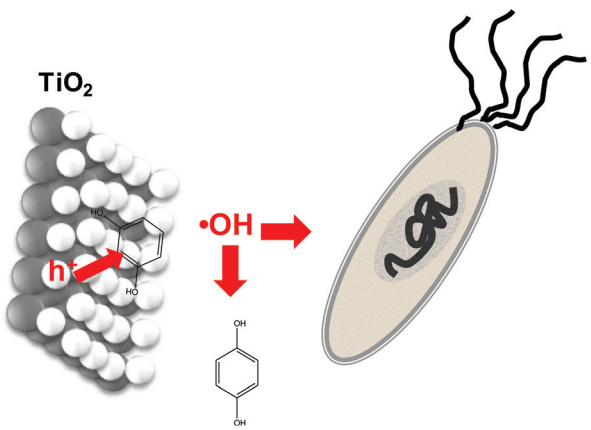

Fig. 4 Scheme of photocatalytic oxidation of organics and cells inactivation on TiO_2.

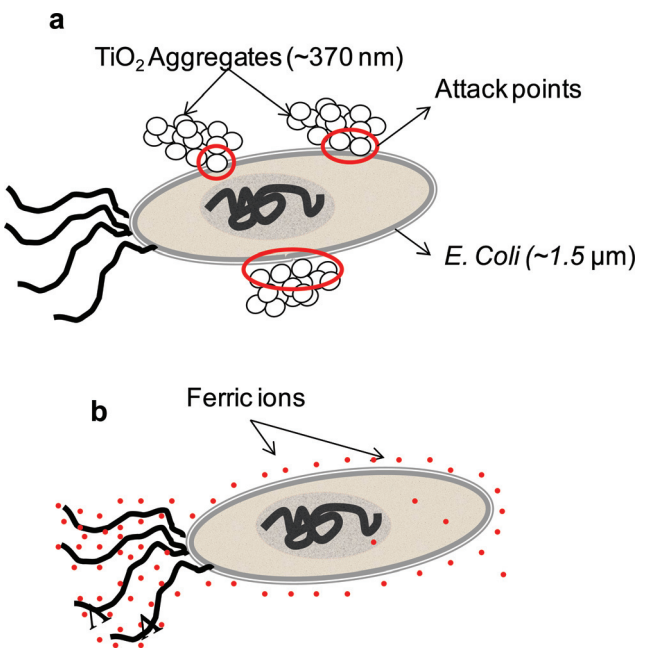

Fig. 5 Bacterial cells inactivation by (a) heterogeneous photocatalysis on TiO_2 and (b) photo-Fenton reactions.

4. Conclusions

Simultaneous degradation of H, R, and inactivation of *E. coli*, *S. typhimurium* and *Shigella sonnei* by TiO_2 photocatalytic treatment and photo-Fenton reactions was achieved. Homogeneous photo-Fenton reactions at near-neutral pH were less affected by the simultaneous presence of organics and bacteria than heterogeneous TiO_2 photocatalytic processes.

The results revealed competition for ROS between chemical substances and cells when they are simultaneously present in water. The presence of organics having different interactions with TiO_2 surfaces provoked a negative effect (mainly when R was present) on the photocatalytic inactivation of bacteria cells suggesting that the possible bacteria–TiO_2 interaction might play a key role in its inactivation, as already reported by other authors.

On the other hand, results show that near-neutral photo-Fenton processes are less sensitive than heterogeneous photocatalytic ones to the simultaneous presence of organics and bacteria. Therefore, near-neutral photo-Fenton processes might have a tremendous potential to be applied in water disinfection processes.

Acknowledgements

We gratefully acknowledge COLCIENCIAS-Colombia for the fellowship granted to Alejandro Moncayo. Our special thanks to UNIVALLE-EPFL cooperation program supported by the Cooperation@EPFL; J. A. Rengifo-Herrera gratefully thanks Cooperation@EPFL for its support to the Argentinean-Swiss cooperation Seed Money project: "Argentinean-Swiss cooperation action in based TiO_2 photo-active nano-materials for bacteria inactivation and pollutant oxidation in solid–gas and solid–water interfaces", CONICET-Argentina for the grant for his post-doctoral fellowship, and EPFL and the Swiss Agency for Development and Cooperation for its support to the Biosolar-Detox project. The authors are indebted to Luis David Lievano and Alejandro Valencia for their scientific and technical collaboration. C. Pulgarin acknowledges the Swiss-Hungarian cooperation program for the support to the project: "Sustainable fine chemical pharmaceutical industry".

References

1 S. D. Richardson and T. A. Ternes, Water analysis: emerging contaminants and current issues, *Anal. Chem.*, 2005, **77**, 3807–3838.
2 T. Bond, E. H. Goslan, S. A. Parsons and B. Jefferson, Treatment of disinfection by-products precursors, *Environ. Technol.*, 2011, **32**, 1–25.
3 K. Lemarchand and P. Lebaron, Occurrence of *Salmonella* spp. and *Cryptosporidium* spp. in a French coastal watershed: relationship with fecal indicators, *FEMS Microbiol. Lett.*, 2003, **218**, 203–209.
4 M. Woolhouse, D. T. Haydon and R. Antia, Emerging pathogens: the epidemiology and evolution of species jumps review, *Trends Ecol. Evol.*, 2005, **20**, 238–244.
5 WHO, Microbial fact sheets, in *Guidelines for Drinking-water Quality*, WHO, Geneva, 2006, pp. 221–294.
6 A. Moncayo-Lasso, C. Pulgarin and N. Benitez, Degradation of DBPs' precursors in river water before and after slow sand filtration by photo-Fenton process at pH 5 in a solar CPC reactor, *Water Res.*, 2008, **42**, 4125–4132.
7 A. Markowska-Szczupak, K. Ulfig and A. W. Morawski, The application of titanium dioxide for deactivation of bioparticulates: an overview, *Catal. Today*, 2011, **169**, 249–257.
8 J. A. Ibañez, M. I. Litter and R. A. Pizarro, Photocatalytic bactericidal effect of TiO_2 on Enterobacter cloacae comparative study with other Gram (-) bacteria, *J. Photochem. Photobiol., A*, 2003, **157**, 81–85.
9 M. Cho, H. Chung, W. Choi and J. Yoon, Linear correlation between inactivation of *E. coli* and OH radical concentration in TiO_2 photocatalytic disinfection, *Water Res.*, 2004, **38**, 1069–1077.
10 H. M. Coleman, C. P. Marquis, J. A. Scott, S.-S. Chin and R. Amal, Bactericidal effects of titanium dioxide-based photocatalysts, *Chem. Eng. J.*, 2005, **113**, 55–63.
11 M. Cho, Y. Lee and J. Yoon, Inactivation of *Escherichia coli* by photochemical reaction of ferrioxalate at slightly acidic and near-neutral pHs, *Appl. Environ. Microbiol.*, 2004, **70**, 1129–1134.
12 A. K. Bennabou, Z. Derriche, C. Felix, V. Moules, P. Lejeune and C. Guillard, Photocatalytic inactivation of *Escherichia coli*. Effect of concentration of TiO_2 and microorganism and intensity of UV irradiation, *Appl. Catal., B*, 2007, **76**, 257–263.
13 A. G. Rincon and C. Pulgarin, Comparative evaluation of Fe^{3+} and TiO_2 photoassisted processes in solar photocatalytic disinfection of water, *Appl. Catal., B*, 2006, **63**, 222–231.
14 J. A. Byrne, P. A. Fernández-Ibañez, P. S. M. Dunlop, D. M. A. Alrousan and J. W. J. Hamilton, Photocatalytic enhancement for solar disinfection of water: a review, *Int. J. Photoenergy*, 2011, 798051, DOI: 10.1155/2011/798051.
15 F. Sciacca, J. A. Rengifo-Herrera, J. Wéthé and C. Pulgarin, Dramatic enhancement of solar disinfection (SODIS) of wild *Salmonella* sp. in PET bottles by H_2O_2 addition on natural water of Burkina Faso containing dissolved iron, *Chemosphere*, 2010, **78**, 1186–1191.
16 D. Spuhler, J. A. Rengifo-Herrera and C. Pulgarin, The effect of Fe^{2+}, Fe^{3+}, H_2O_2 and the photo-Fenton reagent at near neutral pH on the solar disinfection (SODIS) at low temperatures of water containing *Escherichia coli* K-12, *Appl. Catal., B*, 2010, **96**, 126–141.
17 A. G. Rincon and C. Pulgarin, Fe^{3+} and TiO_2 solar-light-assisted inactivation of *E. coli* at field scale. Implications in solar disinfection at low temperature of large quantities of water, *Catal. Today*, 2007, **122**, 128–136.
18 A. L. Linsebigler, G. Lu and J. T. Yates, Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results, *Chem. Rev.*, 1995, **95**, 735–758.
19 M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, Environmental applications of semiconductor photocatalysis, *Chem. Rev.*, 1995, **95**, 69–69.
20 A. Mills, R. Davies and D. Worsley, Water purification by semiconductor photocatalysis, *Chem. Soc. Rev.*, 1993, **22**, 417–426.
21 A. Fujishima, X. Zhang and D. T. Tryk, TiO_2 photocatalysis and related surface phenomena, *Surf. Sci. Rep.*, 2008, **63**, 515–582.
22 J. Bandara, C. Pulgarin, J. Kiwi and P. Péringer, Chemical (photo-activated) coupled biological homogeneous degradation of p-nitro-toluene-sulfonic acid in flow reactor, *J. Photochem. Photobiol., A*, 1997, **111**, 253–263.
23 C. Pulgarin and J. Kiwi, Overview of photocatalytic and electrocatalytic pretreatment of industrial non-biodegradable pollutants and pesticides, *Chimia*, 1996, **50**, 50–56.
24 Y. Sun and T. L. Huang, Photochemical reactions involved in the total mineralization of 2, 4-D by $Fe^{3+}/H_2O_2/UV$, *Environ. Sci. Technol.*, 1993, **27**, 304–310.
25 H. Fallmann, T. Krutzler, R. Bauer, S. Malato and J. Blanco, Applicability of the photo-Fenton method for treating water containing pesticides, *Catal. Today*, 1999, **54**, 309–319.
26 J. J. Pignatello, E. Oliveros and A. MacKay, Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry, *Crit. Rev. Environ. Sci. Technol.*, 2006, **36**, 1–84.
27 F. Herrera, C. Pulgarin, V. Nadtochenko and J. Kiwi, Accelerated photooxidation of concentrated p-coumaric acid in homogeneous solution. Mechanistic studies, intermediates and precursors formed in the dark, *Appl. Catal., B*, 1998, **17**, 141–156.
28 T. Bond, E. H. Goslan, S. A. Parsons and B. Jefferson, Treatment of disinfection by-product precursors, *Environ. Technol.*, 2011, **32**, 1–25.
29 A. G. Rincón and C. Pulgarin, Effect of pH, inorganic ions, organic matter and H_2O_2 on *E. coli* K-12 photocatalytic inactivation by TiO_2: implications in solar water disinfection, *Appl. Catal., B*, 2004, **51**, 283–302.
30 H. Gulley-Stahl, P. A. Hogan II, W. L. Schmidt, S. J. Wall, A. Buhrlage and H. A. Bullen, Surface complexation of catechol to metal oxides: an ATR-FTIR adsorption and dissolution study, *Environ. Sci. Technol.*, 2010, **44**, 4116–4121.

31 J. Araña, J. M. Doña Rodriguez, O. Gonzales Díaz, J. A. Herrera-Melián, C. Fernández Rodríguez and J. Pérez Peña, The effect of acetic acid on the photocatalytic degradation of catechol and resorcinol, *Appl. Catal., A*, 2006, **299**, 274–284.
32 W. Xu and D. Raftery, Photocatalytic oxidation of 2-propanol on TiO_2 powder and TiO_2 monolayer catalysts studied by solid-state NMR, *J. Phys. Chem. B*, 2001, **105**, 4343–4349.
33 R. Enriquez and P. Pichat, Different net effect of TiO_2 sintering temperature on the photocatalytic removal rates of 4-chlorophenol, 4-chlorobenzoic acid, and dichloroacetic acid in water, *J. Environ. Sci. Health, Part A*, 2006, **41**, 955–966.
34 A. G. Rincon, C. Pulgarin, N. Adler and P. Peringer, Interaction between E. coli inactivation and DBP-precursors – dihydroxybenzene isomers – in the photocatalytic process of drinking-water disinfection with TiO_2, *J. Photochem. Photobiol., A*, 2001, **139**, 233–241.
35 D. M. A. Alrousan, P. S. M. Dunlop, T. A. McMurray and J. A. Byrne, Photocatalytic inactivation of *E. coli* in surface water using immobilized nanoparticle TiO_2 films, *Water Res.*, 2009, **43**, 47–54.
36 M. Berney, H-U. Weilenmann, A. Simonetti and T. Egli, Efficacy of solar disinfection of *Escherichia coli*, *Shigella flexneri*, *Salmonella typhimurium* and *Vibrio cholerae*, *J. Appl. Microbiol.*, 2006, **101**, 828–836.
37 D. Gumy, C. Morais, P. Bowen, C. Pulgarin, S. Giraldo, R. Hadju and J. Kiwi, Catalytic activity of commercial of TiO_2 powders for the abatement of the bacteria (*E. coli*) under solar simulated light: influence of isoelectric point, *Appl. Catal., B*, 2006, **63**, 76–84.
38 L. Fang, P. Cai, W. Chen, W. Liang, Z. Hong and Q. Huang, Impact of cell wall structure on the behaviour of bacterial cells in the binding of cooper and cadmium, *Colloids Surf., A*, 2009, **347**, 50–55.
39 G. Gogniat, M. Thyssen, M. Denis, C. Pulgarin and S. Dukan, The bactericidal effect of TiO_2 photocatalysis involves adsorption onto catalyst and the loss of membrane integrity, *FEMS Microbiol. Lett.*, 2006, **258**, 18–24.
40 C. Guillard, T.-H. Bui, C. Felix, V. Moules, B. Lina and P. Lejeune, Microbiological disinfection of water and air by photocatalysis, *C. R. Chim.*, 2008, **11**, 107–113.
41 R. N. Sylva, The hydrolysis of iron(III), *Rev. Pure Appl. Chem.*, 1972, **22**, 115–130.
42 S. Malato, P. Fernández-Ibáñez, M. I. Maldonado, J. Blanco and W. Gernjak, Decontamination and disinfection of water by solar photocatalysis: recent overview and trends, *Catal. Today*, 2009, **147**, 1–59.
43 H. Gallard, J. De Laat and B. Legube, Spectrophotometric study of the formation of iron(III)–hydroperoxy complexes in homogeneous aqueous solutions, *Water Res.*, 1999, **33**, 2929–2936.
44 C. Lee and J. Yoon, Determination of quantum yields for the photolysis of Fe(III)-hydroxo complexes in aqueous solution using a novel kinetic method, *Chemosphere*, 2004, **57**, 1449–1458.