

# Effect of water constituents on the degradation of sulfaclozine in the three systems: UV/TiO<sub>2</sub>, UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and UV/TiO<sub>2</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>

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**Abstract** Bicarbonate, phosphate, chloride ions, and humic substances are among the constituents most widely present in natural waters. These non-target constituents can greatly affect the efficiency of advanced oxidation processes used for water decontamination due to their capacity to interfere with the adsorption of the target compounds on the surface of TiO<sub>2</sub>, absorb photons, scavenge hydroxyl radicals ( $\cdot\text{OH}$ ), and generate photochemical reactive intermediates. In this work, the effect of these constituents on the degradation of sulfaclozine (SCL) was monitored in three different AOPs systems: UV/TiO<sub>2</sub>, UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and UV/TiO<sub>2</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. It was shown that bicarbonate ( $\text{HCO}_3^-$ ) and phosphate ( $\text{HPO}_4^{2-}$ ) ions enhanced the degradation of SCL in UV/TiO<sub>2</sub> and UV/TiO<sub>2</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems whereas the addition of humic substances influenced these rates with a much smaller extent. On the other hand, the degradation rate of SCL in the UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system was not

affected by the presence of  $\text{HCO}_3^-$  and  $\text{HPO}_4^{2-}$  but was inhibited in the presence of humic substances. In addition, the different mechanisms that can take place in the presence of these constituents were discussed and the degradation rate enhancement in presence of  $\text{HCO}_3^-$  and  $\text{HPO}_4^{2-}$  was attributed to the formation of new reactive species such as carbonate ( $\text{CO}_3^{\cdot-}$ ) and hydroxyl ( $\cdot\text{OH}$ ) radicals activated by TiO<sub>2</sub> holes ( $h^+$ ). In the presence of chloride ( $\text{Cl}^-$ ) and nitrate ( $\text{NO}_3^-$ ) ions, an enhancement of SCL adsorption on the surface of TiO<sub>2</sub> was observed. Finally, a comparative study of the degradation of SCL in river water and ultrapure water was reported.

**Keywords** Sulfaclozine · Advanced oxidation processes · Sulfate radicals · Hydroxyl radicals · Bicarbonate · Phosphate

## Introduction

Sulfonamides are a group of broad-spectrum antibiotics widely used for clinical and veterinary purposes for the treatment of bacterial infections (Abdallah et al. 2014; Huertas-Pérez et al. 2016; Kools et al. 2008). Unfortunately, these compounds are not totally metabolized in the human and animal body and a fraction can be excreted unchanged in both urine and feces. Antibiotics, as biologically active molecules, are not effectively eliminated in the conventional wastewater treatment plants using biological treatments (Fabińska et al. 2014; Klavarioti et al. 2009; Kümmerer 2009), and their persistence in the environment can have health implications such as allergies, cancer, and also can induce bacterial resistance to antibiotics (Baran et al. 2011). Therefore, complimentary treatments such as the advanced oxidation processes (AOPs) that are based on the generation of reactive oxygen species (ROS), especially hydroxyl radicals ( $\cdot\text{OH}$ ) and sulfate radicals

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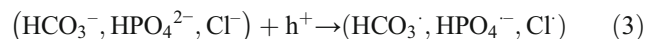
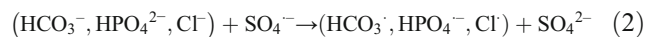
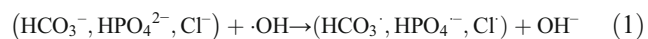
( $\text{SO}_4^{\cdot-}$ ) (Dirany et al. 2012; Guo et al. 2015; Ismail et al. 2017; Xu et al. 2014), were used. Among the different AOPs, heterogeneous photocatalysis using  $\text{TiO}_2$  as a catalyst has emerged as a promising process for eliminating antibiotics from water (Hu et al. 2007; Xekoukoulotakis et al. 2011). Photocatalysis is based on the generation of ( $e^-/h^+$ ) pair leading to the formation of reactive species, such as hydroxyl radicals ( $\cdot\text{OH}$ ) and superoxide radical anions ( $\text{O}_2^{\cdot-}$ ), when illuminated with photons whose energy is equal or greater than their band-gap energy (Andreozzi et al. 1999; Herrmann 1999; Malato et al. 2009).

Sulfate radicals ( $\text{SO}_4^{\cdot-}$ ) have also a strong oxidation-reduction potential (2.6 V/ENH) and could be applied for the degradation of organic contaminants (Leng et al. 2014; Li et al. 2016; Malato et al. 1998; Wang and Hong 1999) including sulfonamides (Ji et al. 2015, 2017a, b).  $\text{SO}_4^{\cdot-}$  can be generated from persulfate activated by UV, heat, base, transient metals, peroxide, or by the  $\text{TiO}_2$  photocatalytic system by trapping the photogenerated electrons in the conduction band (Ismail et al. 2017; Zhao et al. 2013). In the latter case, the photocatalytic degradation should be enhanced due to the fact that the  $e^-/h^+$  recombination rate will be reduced and further radical species will be produced.

When applying AOPs in real water, these processes can be inevitably affected by various water constituents such as  $\text{HCO}_3^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{Cl}^-$  as well as humic substances. However, the underlying mechanisms of the impacts of water constituents are poorly understood although degradation of various contaminants by different AOPs has been extensively studied.

Indeed, inorganic ions are usually assumed to decrease the efficiency of AOPs for the following reasons:

- 1) by scavenging the reactive species such as  $\cdot\text{OH}$ ,  $\text{SO}_4^{\cdot-}$ , and  $\text{TiO}_2$  valence-band holes ( $h^+$ ) to form less reactive species according to the following reactions:



For example, scavenging reactions of  $\cdot\text{OH}$  by carbonate ions, which are among the ions most widely present in water with environmentally relevant concentration ranging from 0.4 to 4 mM, can be presented as the following: (Bhatkhande et al. 2002; Haarstrick et al. 1996; Ji et al. 2013; Mehrvar et al. 2001)

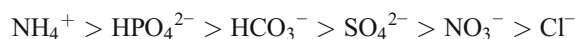


Moreover,  $\text{HCO}_3^-$  have been reported to scavenge as well  $h^+$  (Santiago et al. 2014):



- 2) by competing with organic molecules to adsorb on the surface of  $\text{TiO}_2$ . For example, Guillard et al. (2005) assumed that the decrease of the photocatalytic efficiency of methylene blue degradation in the presence of inorganic ions ( $\text{PO}_4^{3-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ) was due to the formation of an inorganic salt layer at the surface of  $\text{TiO}_2$  which inhibits the approach of methylene blue molecule and then reduces its adsorption on the surface of  $\text{TiO}_2$ .

Indeed, it is well known that inorganic ions are more or less adsorbed on the  $\text{TiO}_2$  surface and can be ranked according to their effect on the competitive adsorption as the following (Zhang et al. 2012):



It is noteworthy that the pH has an effect on the electrostatic charge of the  $\text{TiO}_2$  surface which determines the density of  $\text{TiOH}^{2+}$  groups, and at  $\text{pH} > \text{pH}_{\text{pzc}}$  ( $= 6.5$ ),  $\text{TiO}_2$  is negatively charged and a depressed adsorption of the anions is expected, nevertheless,  $\text{HPO}_4^{2-}$  and  $\text{HCO}_3^-$  were still adsorbed on the surface of  $\text{TiO}_2$  unlike  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$  (Zhang et al. 2012).

Moreover, Autin et al. (2013) have observed that in the presence of carbonate ions in the solution, the size of the  $\text{TiO}_2$  aggregates increased, possibly resulting from complexation reactions, thereby decreasing the interaction surface between the catalyst and the substrate and thus the effectiveness of the photocatalytic degradation.

A number of studies have examined the effect of various inorganic ions on the degradation of organic molecules in different AOPs. For example, Lair et al. (2008) observed an inhibition of the degradation of naphthalene by heterogeneous catalysis on  $\text{TiO}_2$  when carbonate ions were added, and they explained these findings by (1) the scavenging of  $\cdot\text{OH}$  by carbonate ions according to Eq. 4 and Eq. 5, and (2) by the adsorption competition between carbonate ions and naphthalene molecule.

Although most studies suggest that inorganic ions may be playing an inhibition role, other authors found that, on the contrary, the presence of inorganic ions enhanced some molecules degradation. For example, Hu et al. (2007) observed that the degradation of sulfamethoxazole, a sulfonamide, was actually enhanced by the presence of carbonate ions at pH 9, and the level of enhancement significantly increased at higher carbonate concentrations. They explained these results by the fact that, even though  $\text{CO}_3^{\cdot-}$  is less reactive than  $\cdot\text{OH}$ , it is

more selective towards organic compounds and has a high reactivity with the aniline group which is present in the structure of sulfonamides ( $k(\text{CO}_3^- + \text{aniline}) = 6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) (Larson and Zepp 1988).

Moreover, Ji et al. observed an enhancement in atenolol (ATL) degradation and explained these findings by considering that  $\text{HCO}_3^-$  were present in  $\text{TiO}_2$  suspensions at much higher concentration than ATL and these ions would interact more strongly with  $\text{Ti(IV)}$  than ATL. As a result,  $\text{HCO}_3^-$  ions might be able to scavenge adsorbed  $\cdot\text{OH}$  more efficiently than ATL and since  $\text{CO}_3^-$  is less reactive and has fairly longer life-time than  $\cdot\text{OH}$ , it could reach a much higher steady-state concentration on  $\text{TiO}_2$  surface, which enables them to diffuse into the bulk aqueous solution and react with ATL molecules (Ji et al. 2013).

Regarding to phosphate ions, Zhao et al. (2008) found that, for the molecules poorly adsorbed on  $\text{TiO}_2$  surface, the addition of phosphate ions can enhance the degradation rate in the photocatalytic system by promoting the generation of  $\cdot\text{OH}$  radicals.

Humic substances are ubiquitously present in aquatic systems as well, and may affect the photocatalytic process by competing with the target compound to adsorb on the surface of  $\text{TiO}_2$  and by scavenging  $\cdot\text{OH}$ . In addition, humic substances can absorb UV but in this case reactive species could be generated such as hydroxyl radical and singlet oxygen (Doll and Frimmel 2005; Epling and Lin 2002; Lin and Lin 2007).

Sulfaclozine (4-amino-N-(6-chloropyrazin-2-yl) benzenesulfonamide) is an antibiotic that belongs to the family of sulfonamides. It is widely used for the treatment of poultry diseases (Şentepe and Eraslan 2010). The elimination of sulfaclozine (SCL) in the three systems: UV/ $\text{TiO}_2$ , UV/ $\text{K}_2\text{S}_2\text{O}_8$ , and UV/ $\text{TiO}_2/\text{K}_2\text{S}_2\text{O}_8$  was studied in previous publications (Ismail et al. 2017; Ismail et al. 2016). It was found that SCL is weakly adsorbed on the surface of  $\text{TiO}_2$  at pH 7 (< 5%) but efficiently eliminated with the following three systems: UV/ $\text{TiO}_2$ , UV/ $\text{K}_2\text{S}_2\text{O}_8$ , and UV/ $\text{TiO}_2/\text{K}_2\text{S}_2\text{O}_8$  in ultra pure water. Moreover, 12 of SCL by-products were identified and reaction pathways showed that, in addition of  $\cdot\text{OH}$  and  $\text{SO}_4^-$  radicals, the conduction-band electrons were responsible for the formation of some main by-products either directly or by the formation of superoxide radicals according to the following reactions (Ismail et al. 2016, 2017):



On the other hand, the efficiency of the above-mentioned systems has just been examined in ultra pure water. Since their efficiency can always be affected by the presence of inorganic

ions and humic substances, the main objective of this study was to obtain an insight of the effect of water constituents on the degradation of SCL. Hence, we studied the effect of different concentrations of  $\text{HCO}_3^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{Cl}^-$ , and humic substances on the degradation of SCL in the three systems UV/ $\text{TiO}_2$ , UV/ $\text{K}_2\text{S}_2\text{O}_8$ , and UV/ $\text{TiO}_2/\text{K}_2\text{S}_2\text{O}_8$ . Moreover, the degradation of SCL in river water was conducted in the three systems and was compared to that in the ultra pure water.

## Materials and methods

### Chemicals and reagents

Sulfaclozine sodium (99% purity) was purchased from Sigma-Aldrich and used as received. Titanium dioxide AEROXIDE  $\text{TiO}_2$  P 25 was provided by Evonik Degussa with a specific BET area of  $50 \text{ m}^2 \text{ g}^{-1}$ , a mean particle size of 30 nm, and crystal distribution of 80% anatase and 20% rutile. Polyvinylidene fluoride (PVDF) filters ( $0.45 \mu\text{m}$ ) were purchased from Millipore. Potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ), acetonitrile, formic acid, potassium nitrate ( $\text{KNO}_3$ ), sodium nitrate ( $\text{NaNO}_3$ ), sodium chloride ( $\text{NaCl}$ ), sodium bicarbonate ( $\text{NaHCO}_3$ ), disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ), and the humic substances were purchased from Sigma-Aldrich. Ultra pure water was obtained from a Millipore Waters Milli-Q water purification system. Other reagents were at least of analytical grade.

### Experimental procedure

Experiments were performed in an open Pyrex glass reactor (cutoff at 295 nm) with an inner diameter of 4 cm and a height of 9 cm with a double-walled cooling water jacket to keep the temperature of the solutions constant throughout the experiments ( $20 \text{ }^\circ\text{C}$ ). An HPK 125-W Philips water-cooled mercury lamp with a maximum emission wavelength of 365 nm and in a lower emission wavelength of 312 nm was used as a light source. The radiant flux entering the irradiation cell was measured by a VLX-3W radiometer with a CX-365 detector (UV-A) and a value of  $4 \text{ mW cm}^{-2}$  was found at the walls of the reactor. Adequate persulfate doses were added into 25 mL of SCL solution ( $88 \mu\text{mol L}^{-1}$ ) and the reaction solution was mixed by a magnetic stirrer to ensure homogeneity during the reaction. When needed,  $2.5 \text{ g L}^{-1}$  of  $\text{TiO}_2$  was added 20 min before irradiation to reach the adsorption-desorption equilibrium. Inorganic ions and humic substances were added at the beginning of the experiments. The first sample was taken out at the end of the dark adsorption period just before turning on the irradiation, in order to determine the bulk SCL concentration. This value was taken as the initial concentration for the photocatalytic experiment. During irradiation, the samples were withdrawn regularly from the reactor and

filtered immediately through 0.45  $\mu\text{m}$  PVDF membrane filters to remove  $\text{TiO}_2$  particles.

It is noteworthy that absorption spectra of SCL at different pHs was provided in a previous publication (Ismail et al. 2016). Moreover, SCL photolysis was studied and it was found to be negligible (1% after 60 min of irradiation) due to (i) a low overlapping between sulfaclozine UV–vis absorbance spectrum and the filtered HPK lamp emission spectrum and (ii) a low quantum yield of degradation (Ismail et al. 2016).

SCL adsorption on  $\text{TiO}_2$  surface was also investigated at pH 7 and a weak adsorption was observed (3%) after the adsorption-desorption equilibrium (Ismail et al. 2016).

It should be noted that, in these systems, control experiments were carried out and the removal of the substrate was considered negligible and that the most of the measurements were repeated up to three times and the error for those repeated were less than 5%.

## Analytical methods

### HPLC-DAD

The concentration of SCL during the degradation was determined using Shimadzu VP series HPLC system equipped with a photodiode array detector (PDA). A 20  $\mu\text{L}$  of filtered irradiated samples (25  $\text{mg L}^{-1}$ ) was directly injected. Analytical separations were performed using an Interchim C18 column (125 mm  $\times$  4 mm, particle size 5  $\mu\text{m}$ ) with a mobile phase of 80% water at pH 3 (adjusted with formic acid) and 20% ACN at a flow rate of 0.5  $\text{mL min}^{-1}$ . The detection wavelength was 271 nm, corresponding to  $\lambda_{\text{max}}$  of SCL at pH 3.

### Total organic carbon analysis

After filtration through 0.45  $\mu\text{m}$  PVDF membrane filter, the organic carbon amount in the initial humic substances solution was determined by a TOC-L (Shimadzu) and calibration was achieved with potassium hydrogen phthalate standard.

## Results and discussion

### Effect of phosphate ions on SCL degradation

To study the effect of phosphate ( $\text{HPO}_4^{2-}$ ) ions on SCL degradation, different concentrations of  $\text{Na}_2\text{HPO}_4$  (0.05, 0.1, 0.2, and 1 mM) were added to the three systems viz. UV/ $\text{K}_2\text{S}_2\text{O}_8$ , UV/ $\text{TiO}_2$ , and UV/ $\text{TiO}_2/\text{K}_2\text{S}_2\text{O}_8$  (initial concentration of SCL = 25  $\text{mg L}^{-1}$  (88  $\mu\text{mol L}^{-1}$ )) and an additional experiment using just UV irradiation was performed as a control.

Figure 1 shows that in the UV system, there was no degradation regardless of  $\text{HPO}_4^{2-}$  concentration added, meaning

that no direct or photo-induced degradation took place under these experimental conditions.

The addition of  $\text{HPO}_4^{2-}$  on the UV/ $\text{K}_2\text{S}_2\text{O}_8$  system has no significant effect. This result can be explained by the fact that the kinetic rate constants of  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  radicals with phosphate ions are relatively low (respectively  $1.5 \times 10^5$  and  $1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  with  $\text{HPO}_4^{2-}$ ;  $2 \times 10^4$  and  $< 7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  with  $\text{H}_2\text{PO}_4^-$  (Maruthamuthu and Neta 1978)) and that the kinetic rate constants of SCL with these radicals are more than 1000 times higher ( $k(\cdot\text{OH}, \text{SCL}) = 5.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and  $k(\text{SO}_4^{\cdot-}, \text{SCL}) = 7.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) (Ismail et al. 2017).

Concerning the UV/ $\text{TiO}_2$  system, the increase of phosphate concentration from 0 to 0.1 mM accelerated the oxidation of SCL but for higher phosphate concentrations (0.2 and 1 mM) no further enhancement of SCL degradation was observed.

The enhancement of SCL degradation was less observed in the UV/ $\text{TiO}_2/\text{K}_2\text{S}_2\text{O}_8$  system than that in the UV/ $\text{TiO}_2$  system and a decrease is even observed from 0 to 0.05 mM.

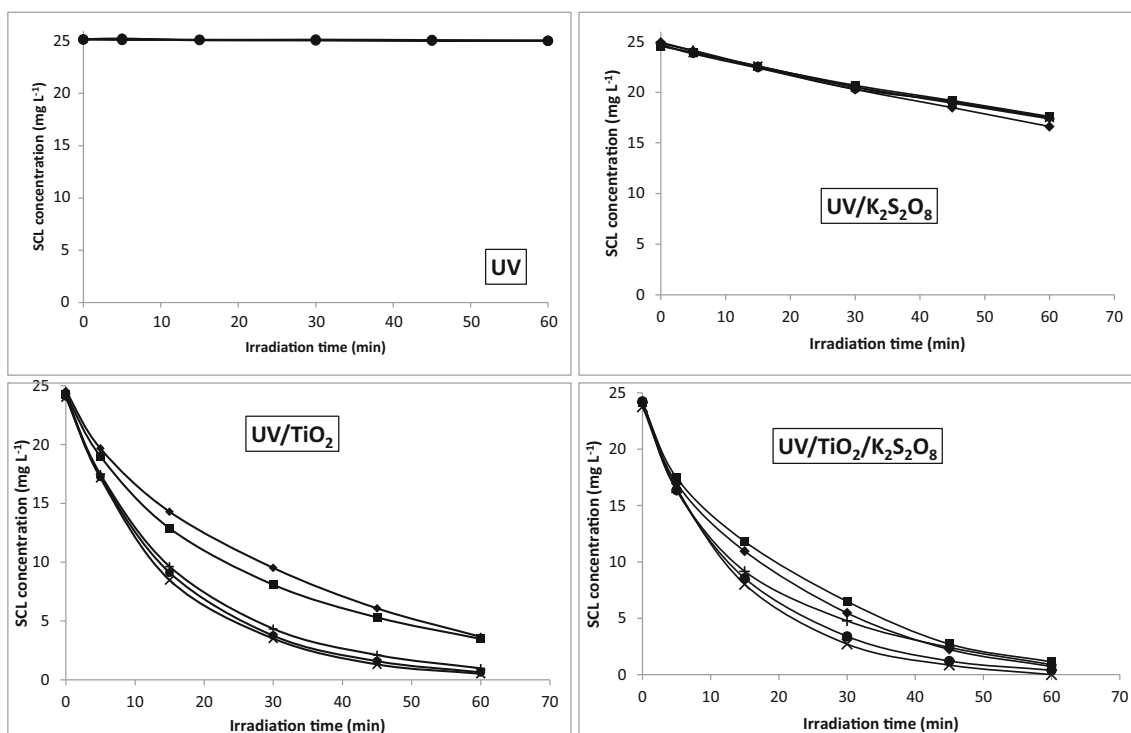
The enhancement was not expected and could be explained by considering an increase of ROS in solution coming both from  $\text{HPO}_4^{2-}$  and hydroxyl anions ( $\text{OH}^-$ ). For example, Brusa et al. (Brusa and Grella 2003) suggested that the trapping of  $\text{h}^+$  by phosphate ions adsorbed on the semi-conductor surface may be envisaged as adequate route to generate  $(\text{HO})_2\text{PO}_2^-$ . In this case, even if the reactivity of  $(\text{HO})_2\text{PO}_2^-$  is low, their great amount in solution can accumulate provoking an enhancement of the degradation.

Moreover, Zhao et al. (2008) and Liao and Reitberger (2013) suggested that phosphate ions, specifically adsorbed on  $\text{TiO}_2$  surface, make its surface negatively charged which enhances the separation of the photogenerated holes and electrons and thus allowing holes of the catalysis surface to react with water molecules adsorbed on its surface. Consequently, more free  $\cdot\text{OH}$  will be formed as it was observed by Sheng et al. (2013), so that the degradation of substrates with a weak adsorption on  $\text{TiO}_2$  and susceptible to hydroxyl radical attack will be accelerated by the addition of phosphate ions.

Concerning the lower enhancement obtained with UV/ $\text{TiO}_2/\text{K}_2\text{S}_2\text{O}_8$  system, we could suggest that since  $\text{TiO}_2$  surface is strongly negatively charged, the formation of  $\text{SO}_4^{\cdot-}$  by  $e_{\text{CB}}^-$  could not be achieved since  $\text{S}_2\text{O}_8^{2-}$  will no longer be adsorbed onto  $\text{TiO}_2$ . Of course such hypothesis should be confirmed.

### Effect of bicarbonate ions on SCL degradation

To investigate the effect of bicarbonate ions on the degradation of 25  $\text{mg L}^{-1}$  (88  $\mu\text{mol L}^{-1}$ ) of SCL in the UV, UV/ $\text{TiO}_2$ , UV/ $\text{K}_2\text{S}_2\text{O}_8$ , and UV/ $\text{TiO}_2/\text{K}_2\text{S}_2\text{O}_8$  systems, different sodium bicarbonate concentrations ranging from 0 to 10 mM were used. The pH of the solution after the addition of bicarbonate

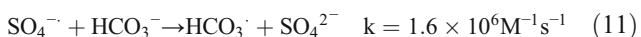
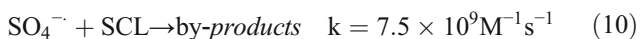


**Fig. 1** Effect of  $\text{HPO}_4^{2-}$  on SCL degradation in UV, UV/ $\text{K}_2\text{S}_2\text{O}_8$ , UV/ $\text{TiO}_2$ , and UV/ $\text{TiO}_2/\text{K}_2\text{S}_2\text{O}_8$  systems: (filled diamond) 0 mM  $\text{HPO}_4^{2-}$ , (filled square) 0.05 mM  $\text{HPO}_4^{2-}$ , (plus sign) 0.1 mM  $\text{HPO}_4^{2-}$ , (filled circle) 0.2 mM  $\text{HPO}_4^{2-}$ , and (multiplication sign) 1 mM  $\text{HPO}_4^{2-}$

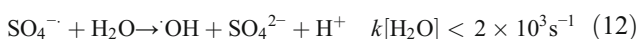
was 8.4. It is noteworthy that at this pH carbonate was mainly present as  $\text{HCO}_3^-$  ( $\text{pKa}(\text{HCO}_3^-/\text{CO}_3^{2-}) = 10.32$ ) and that SCL is poorly adsorbed on the surface of  $\text{TiO}_2$  (less than 5%) (Ismail et al. 2016).

Figure 2 shows that in the UV system, there was no degradation regardless of the concentration of bicarbonate added, meaning that no direct or photo-induced degradation took place under these experimental conditions.

In the UV/ $\text{K}_2\text{S}_2\text{O}_8$  system, the variation of bicarbonate concentration did not affect significantly the degradation rate of SCL. This observation can be explained by the fact that the reaction rate constant between  $\text{SO}_4^{\cdot-}$  radicals and SCL (Eq. 10) (Ismail et al. 2017) is much higher than that between  $\text{SO}_4^{\cdot-}$  radicals and  $\text{HCO}_3^-$  (Eq. 11) (Deng et al. 2013).



Since in the UV/ $\text{K}_2\text{S}_2\text{O}_8$  system, both  $\text{SO}_4^{\cdot-}$  radicals and  $\cdot\text{OH}$  radicals (which can be produced either from water molecules (Eq. 12) or from  $\cdot\text{OH}$  in alkaline conditions (Eq. 13)) were present in the solution, it seems that any of them interact significantly with  $\text{HCO}_3^-$ .

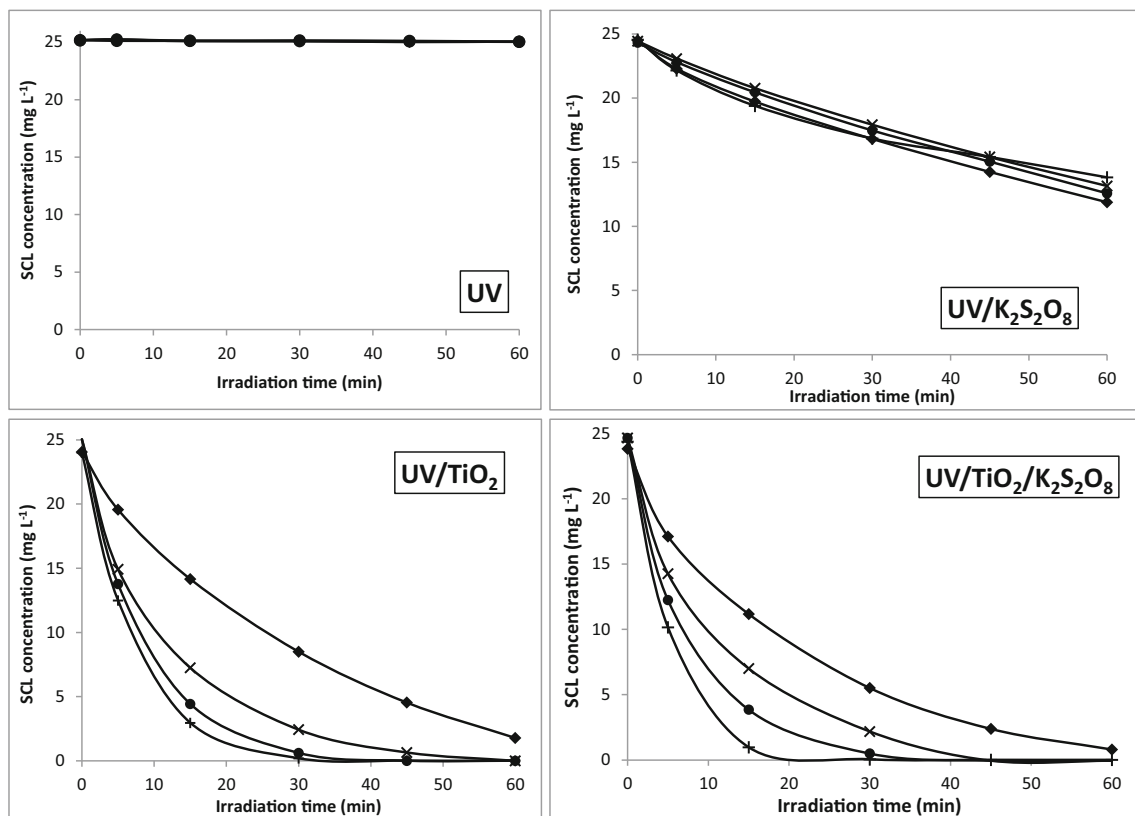


For the two following photocatalytic systems, viz. UV/ $\text{TiO}_2$  and UV/ $\text{TiO}_2/\text{K}_2\text{S}_2\text{O}_8$ , preliminary experiments were conducted to determine whether the addition of  $\text{HCO}_3^-$  affect the adsorption of SCL, but no significant modification was observed. However, SCL degradation was enhanced in the presence of  $\text{HCO}_3^-$ , and the level of enhancement increased in line with the increasing concentration of  $\text{HCO}_3^-$  (Fig. 2).

Since SCL is weakly adsorbed on the  $\text{TiO}_2$  surface and the addition of  $\text{HCO}_3^-$  did not modify its adsorption, we could also assume here that the increase in the reactivity is due to an increase of reactive species such as  $\text{CO}_3^{\cdot-}$ .

Since  $\text{CO}_3^{\cdot-}$  are less reactive than  $\cdot\text{OH}$ , it is unlikely that their formation comes from  $\cdot\text{OH}$  scavenging. On the contrary, this reaction should rather decrease the rate of the degradation. In this context we can assume their formation by holes scavenging since it is known that  $\text{HCO}_3^-$  can be well adsorbed on  $\text{TiO}_2$  surface (Chen et al. 1997; Zhang et al. 2012).

To confirm these hypotheses, two additional experiments were proposed. In the first one, a batch of experiments was conducted in an homogeneous system generating only  $\cdot\text{OH}$  (e.g., the UV/nitrate system) to see the effect of  $\text{HCO}_3^-$  on  $\cdot\text{OH}$  scavenging, while in the second one, experiments were conducted in the presence of hole scavengers (e.g.,  $\text{HPO}_4^{2-}$ ) in the UV/ $\text{TiO}_2$  system. Indeed,  $\text{HPO}_4^{2-}$  are well adsorbed on the  $\text{TiO}_2$  surface and thus can limit the availability of  $\text{h}^+$  for the oxidation of  $\text{HCO}_3^-$  as was shown in part 3.1.



**Fig. 2** Effect of  $\text{HCO}_3^-$  on SCL degradation in UV, UV/ $\text{K}_2\text{S}_2\text{O}_8$ , UV/ $\text{TiO}_2$ , and UV/ $\text{TiO}_2/\text{K}_2\text{S}_2\text{O}_8$  systems: (filled diamond) 0 mM  $\text{HCO}_3^-$ , (multiplication sign) 2 mM  $\text{HCO}_3^-$ , (filled circle) 5 mM  $\text{HCO}_3^-$ , and (plus sign) 10 mM  $\text{HCO}_3^-$

#### Effect of the addition of bicarbonate ions on SCL degradation in the UV/nitrate system

Nitrate ions irradiated with UV light are assumed to generate  $\cdot\text{OH}$  according to the following reactions (Warneck and Wurzinger 1988; Zepp et al. 1987):

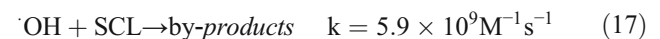


In this study, different concentrations of nitrate (1, 2, 5, and 10 mM) were used for the oxidation of SCL as shown in Fig. 3; thus, as expected, an increase of the degradation rate of SCL in line with nitrate concentrations was found, resulting from a higher generation of  $\cdot\text{OH}$  radicals.

Then, by choosing an initial nitrate concentration of 10 mM, different bicarbonate sodium concentrations were added in the UV/nitrate system, and Fig. 4 shows that in presence of low bicarbonate concentrations (e.g., 2 and 5 mM) a negligible effect on the degradation of SCL was found. On the other hand, a higher bicarbonate concentration (10 mM) inhibited SCL degradation which was likely due to a

scavenging of  $\cdot\text{OH}$  by  $\text{HCO}_3^-$  and not due to a pH change since the pH was almost the same with 2 and 10 mM of  $\text{HCO}_3^-$  (pH = 8.9 and pH = 9.3, respectively).

At low bicarbonate concentrations, no scavenging effect was found which can be explained by the fact that the reaction rate constant between  $\cdot\text{OH}$  radicals and SCL (Eq. 17) (Ismail et al. 2017) is much higher than that between  $\cdot\text{OH}$  and  $\text{HCO}_3^-$  (Eq. 18).



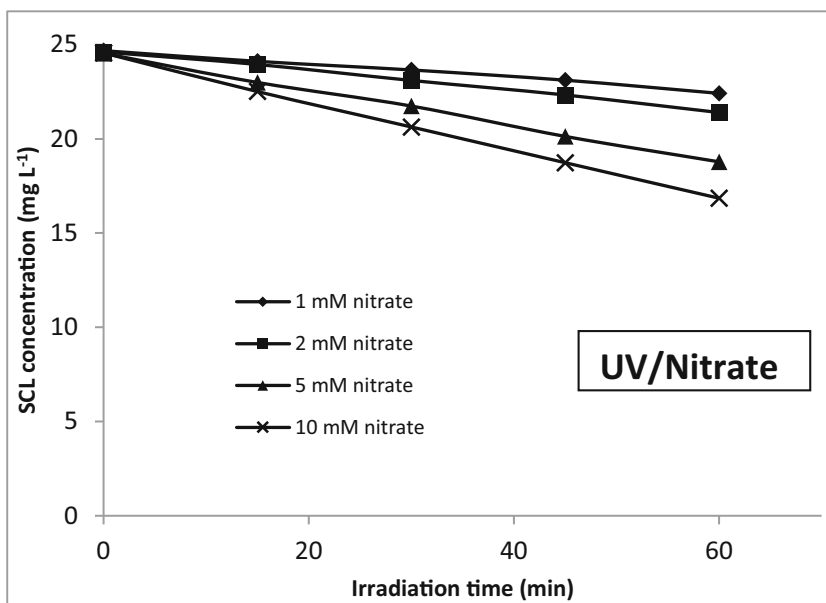
However, when the concentration of the latter increases, Eq. 18 can no longer be ignored and  $\cdot\text{OH}$  radicals can then be more scavenged.

To evaluate the rate of  $\cdot\text{OH}$  scavenged by  $\text{HCO}_3^-$  in the presence of SCL, the following equation was used:

$$\eta = \frac{k_{(\cdot\text{OH},\text{HCO}_3^-)}[\text{HCO}_3^-]}{k_{(\cdot\text{OH},\text{HCO}_3^-)}[\text{HCO}_3^-] + k_{(\cdot\text{OH},\text{SCL})}[\text{SCL}]} \quad (19)$$

Scavenging values of 3, 8, and 14% were found for bicarbonate concentrations of 2, 5, and 10 mM, respectively, which

**Fig. 3** Degradation of SCL in the UV/nitrate system with different nitrate concentrations



remains relatively low and hence allow us to conclude that this mechanism does not represent an important source of  $\text{CO}_3^{\cdot-}$  which is in agreement with the finding obtained with the UV/ $\text{K}_2\text{S}_2\text{O}_8$  system. In the same way, we assume that this reaction will not be able to reduce significantly the SCL degradation in the UV/ $\text{TiO}_2$ , and UV/ $\text{TiO}_2/\text{K}_2\text{S}_2\text{O}_8$  systems since we are in the same range of bicarbonate concentration.

*Effect of the addition of phosphate ions on SCL degradation in the UV/ $\text{TiO}_2$  in the presence of bicarbonate ions*

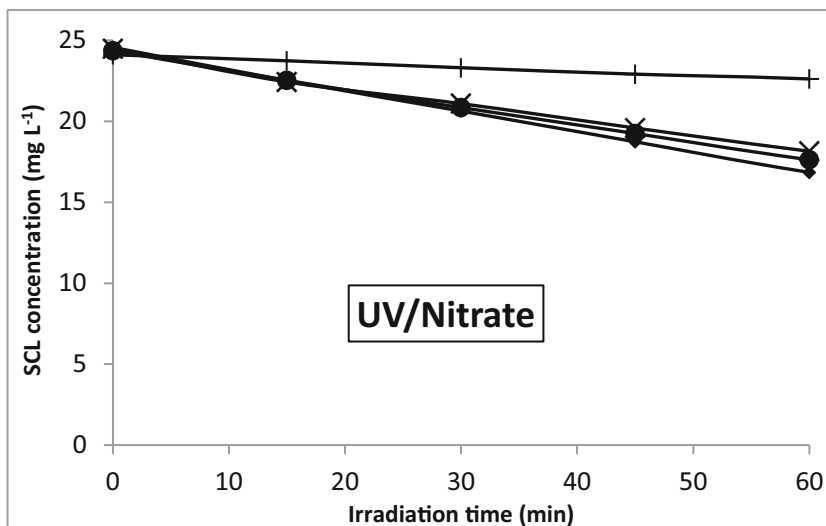
To evaluate the possibility of  $\text{CO}_3^{\cdot-}$  generation by  $\text{h}^+$ ,  $\text{h}^+$  scavengers such as  $\text{HPO}_4^{2-}$  were used. Therefore, different  $\text{HPO}_4^{2-}$  concentrations (0.05, 0.1, 0.2, and 1 mM) in the presence of 5 mM  $\text{HCO}_3^-$  were used during SCL photocatalytic degradation. From Fig. 5, we can see that the addition of  $\text{HPO}_4^{2-}$

reduced the promoting effect of  $\text{HCO}_3^-$  on SCL degradation that was observed in the previous part. Furthermore, the higher the phosphate concentration added, the lower the effect of  $\text{HCO}_3^-$ . This result can be explained by the fact that  $\text{HPO}_4^{2-}$  are more easily adsorbed on the surface of  $\text{TiO}_2$  than  $\text{HCO}_3^-$  and so hinder the direct hole oxidation of  $\text{HCO}_3^-$ .

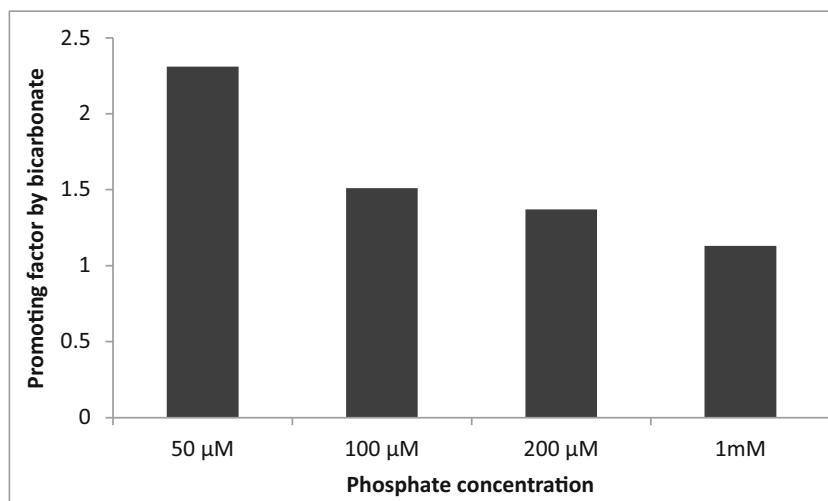
To conclude this part, we can propose that a part of  $\text{HCO}_3^-$  were adsorbed on  $\text{TiO}_2$  surface and  $\text{CO}_3^{\cdot-}$ , as a new reactive species, were generated. These species shall be additional to  $\cdot\text{OH}$  explaining the observed enhancement. It is noteworthy that  $\cdot\text{OH}$  scavenging by  $\text{HCO}_3^-$  could never explain an enhancement since  $\cdot\text{OH}$  remains more reactive than  $\text{CO}_3^{\cdot-}$ .

But why this finding is not always observed? Indeed, in our case and as was proposed by Hu et al. (2007),  $\text{CO}_3^{\cdot-}$  has a selectivity and a high reactivity with certain functional groups such as the aniline one which is present in the structure of

**Fig. 4** Effect of the addition of different concentrations of  $\text{HCO}_3^-$  on SCL degradation in the UV/nitrate system: (filled diamond) 0 mM  $\text{HCO}_3^-$ , (multiplication sign) 2 mM  $\text{HCO}_3^-$ , (filled circle) 5 mM  $\text{HCO}_3^-$ , and (plus sign) 10 mM  $\text{HCO}_3^-$



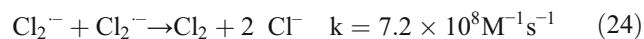
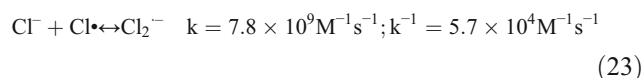
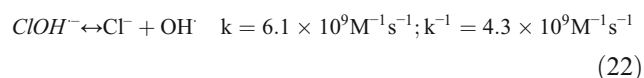
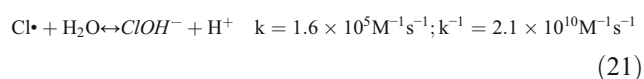
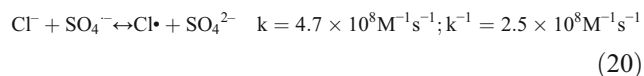
**Fig. 5** Effect of the addition of phosphate ( $\text{HPO}_4^{2-}$ ) ions on the degradation of SCL in presence of bicarbonate ( $\text{HCO}_3^-$ ) ions in the UV/ $\text{TiO}_2$  system;  $[\text{HCO}_3^-] = 5 \text{ mM}$



sulfonamides ( $k(\text{CO}_3^{2-} + \text{aniline}) = 6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) (Larson and Zepp 1988). In addition, here as SCL is poorly adsorbed on  $\text{TiO}_2$  surface, the role usually played by inorganic ions which desorb organic molecules from  $\text{TiO}_2$  surface and then decrease the rate of reaction cannot occur in our case.

### Effect of chloride ions on SCL degradation

Chloride ( $\text{Cl}^-$ ) ions are among the most abundant constituents of real waters and can greatly affect the degradation of SCL in water by reacting with the reactive species such as  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  radicals to generate less reactive radicals according to the following reactions (Deng et al. 2013; Mahdi Ahmed 2014; Zhang et al. 2015):



Thus, the effect of the  $\text{Cl}^-$  addition on UV/ $\text{TiO}_2$ , UV/ $\text{K}_2\text{S}_2\text{O}_8$ , and UV/ $\text{TiO}_2/\text{K}_2\text{S}_2\text{O}_8$  systems was investigated.

First of all, SCL adsorption on the surface of  $\text{TiO}_2$  in the presence of three different concentrations of  $\text{Cl}^-$  (0.2, 0.5, and 1 mM) was conducted. The results show a similar enhancement of the adsorption for the three concentrations

(adsorption of 48% of SCL after 90 min in the dark for all chloride concentrations).

This enhancement of SCL adsorption on  $\text{TiO}_2$  surface in the presence of  $\text{Cl}^-$  might be due to an increase of the ionic strength which would reduce the electrostatic repulsion and push SCL molecules towards the surface of  $\text{TiO}_2$ . It is noteworthy that this effect was not observed neither with  $\text{HPO}_4^{2-}$  nor with  $\text{HCO}_3^-$  probably because they exhibit a greater adsorption on the  $\text{TiO}_2$  surface. Indeed, Sheng et al. (2013) have shown that anions strongly adsorbed on  $\text{TiO}_2$  surface make its surface strongly negatively charged due to the replacement of surface adsorbed  $\text{H}_2\text{O}$  by the anionic species. To verify this hypothesis, they measured the point of zero charge (PZC) and observed that the PZC changed from 6.5 for naked  $\text{TiO}_2$  to 2.3 in the presence of phosphate. So since the pKa of SCL was found to be equal to 5.5 (Ismail et al. 2016), it means that at pH 8.4 it will be negatively charged which explains why its adsorption onto  $\text{TiO}_2$  in presence of  $\text{HCO}_3^-$  is unlikely.

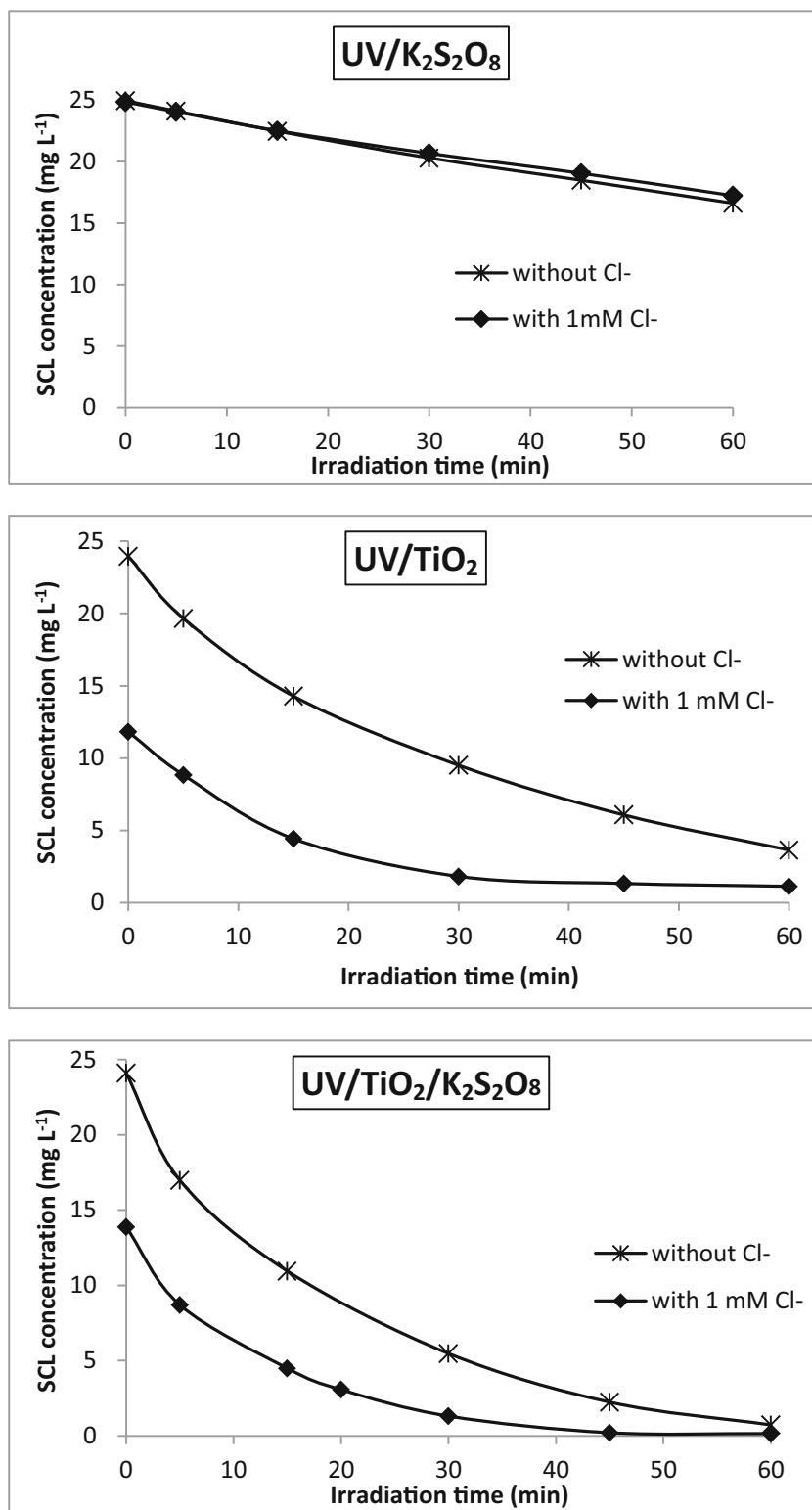
To confirm this hypothesis, additional experiments with nitrate ions for which the adsorption on  $\text{TiO}_2$  surface is low (Chen et al. 1997; Guillard et al. 2005) were carried out. Here also, an enhancement of SCL adsorption similar to the one obtained in the presence of chloride ions was observed, which agrees with the assumption in which molecules are pushed towards the  $\text{TiO}_2$  surface which is free (more or less) of inorganic ions.

SCL degradation in the presence of  $\text{Cl}^-$  in the three systems was then conducted and the results were shown in Fig. 6. Results showed that  $\text{Cl}^-$  had no significant effect on the degradation of SCL in UV/ $\text{K}_2\text{S}_2\text{O}_8$ .

Similar results were observed by Liang et al. who found that  $\text{Cl}^-$  levels below 0.2 M did not affect the degradation of trichloroethylene with persulfate (PS) (Liang et al. 2006). Furthermore, Monteagudo et al. found that in the presence of low concentrations of NaCl (up to  $50 \text{ mg L}^{-1} = 0.86 \text{ M}$ ), the mineralization rate of carbamazepine achieved in the



**Fig. 6** Effect of  $\text{Cl}^-$  on the degradation of SCL in three different systems UV/ $\text{K}_2\text{S}_2\text{O}_8$ , UV/ $\text{TiO}_2$ , and UV/ $\text{TiO}_2/\text{K}_2\text{S}_2\text{O}_8$



PS/ultrasound/UV/ $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  system was not affected (Monteagudo et al. 2015). These findings can be explained by the fact that even though  $\text{Cl}^-$  is an effective  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  scavenger since its reaction rate constant is high ( $4.3 \times 10^9$  and  $3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , respectively), its

effectiveness is offset by the reverse reaction with the rate constant being  $(6.1 \pm 0.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$  Eq. (26) at neutral and basic pH (Liao et al. 2001).



For the UV/TiO<sub>2</sub> and UV/TiO<sub>2</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems, and after the adsorption-desorption equilibrium, SCL degradation was carried out and a slight decrease in the initial rate was observed mainly due to the decrease of the initial concentration of SCL.

### Effect of humic substances on SCL degradation

Humic substances are ubiquitously present in aquatic systems and may affect the photocatalytic process by competing with the target compound to adsorb on the surface of TiO<sub>2</sub>. In addition, humic substances can scavenge ·OH radicals, absorb UV light but can also generate reactive species when exposed to the UV/visible light, such as superoxide anions (O<sub>2</sub><sup>·-</sup>), singlet oxygen, etc. (Doll and Frimmel 2005; Epling and Lin 2002; Lin and Lin 2007).

The effect of the addition of humic substances on the degradation of SCL (25 mg L<sup>-1</sup>) in the UV, UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, UV/TiO<sub>2</sub>, and UV/TiO<sub>2</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems was shown in Fig. 7. In the UV system, no degradation of SCL was observed and the addition of humic substances did not enhance the degradation, meaning that in our case, the degradation of SCL could not be carried out by reactive species generated from the excitation of the humic substances.

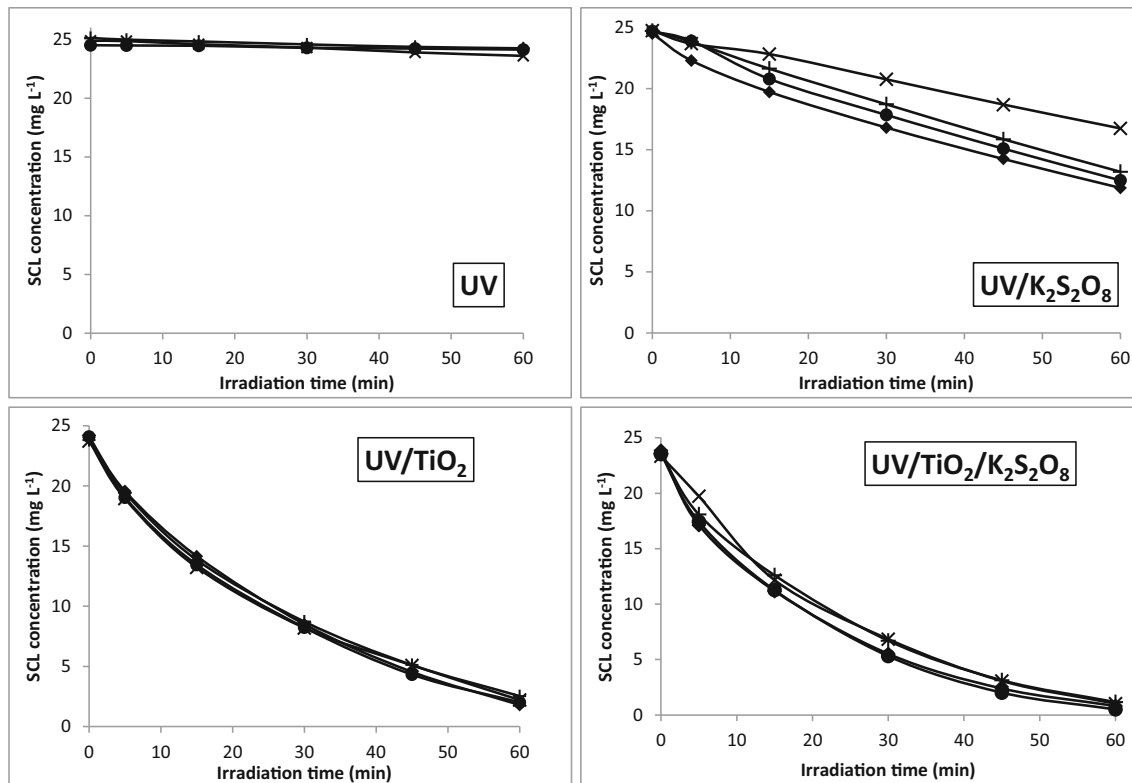
For UV/TiO<sub>2</sub> and UV/TiO<sub>2</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems, Fig. 7 shows that the addition of humic substances had no significant effect

on the degradation of SCL whereas a decrease of the rate of the degradation was observed in the UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system. Indeed it is known that the kinetic rate constant between humic substances and OH· is around ten times higher than that with SO<sub>4</sub><sup>-</sup> (Yang et al. 2015). Here if humic substances do not generate reactive species during irradiation it is difficult to understand why the reaction with UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> is more inhibited than the ones with TiO<sub>2</sub> generating more ·OH. Indeed, we have shown in a previous work about the photocatalytic degradation of SCL using TiO<sub>2</sub> as photocatalyst (Ismail et al. 2016) that in addition ·OH, O<sub>2</sub><sup>-</sup>, and electrons were involved in the degradation of SCL. Here since at pH 7, humic substances are weakly adsorbed on the TiO<sub>2</sub> surface (Li et al. 2002) the surface can continue to generate these reactive species towards SCL. This hypothesis should be confirmed in a future work.

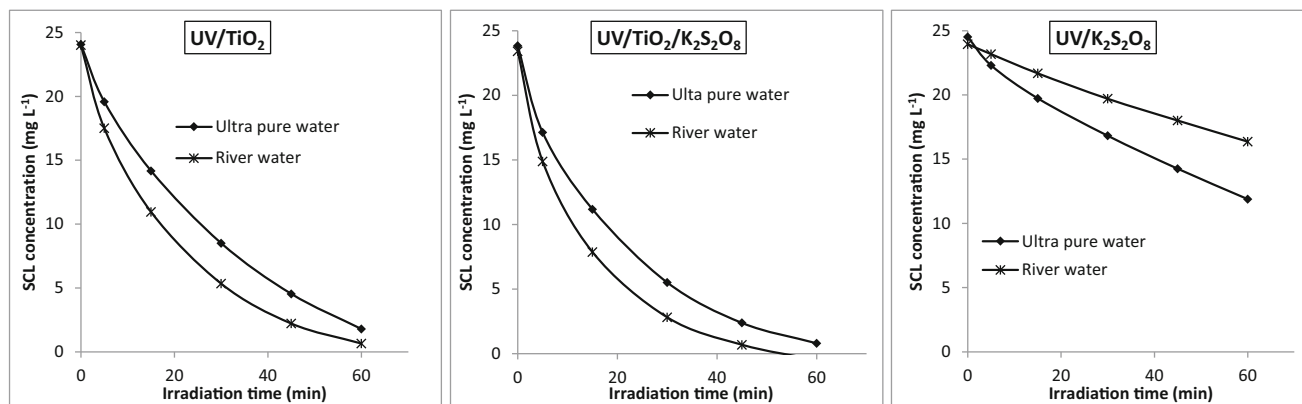
It is noteworthy that humic substances can also convert the radical cations of sulfonamides to their parent forms, thus inhibiting the degradation of sulfonamides (Ji et al. 2017b; Wenk and Canonica 2012; Wenk et al. 2011).

### Effect of river water constituents on SCL degradation

To obtain a further insight of water constituents on SCL degradation, the degradation of SCL in river water taken from the Rhône River (25 mg L<sup>-1</sup> spiked solution, cf. Table S1 for the



**Fig. 7** Effect of humic substances on SCL degradation in UV, UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, UV/TiO<sub>2</sub>, and UV/TiO<sub>2</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems: (filled diamond) 0 mg C L<sup>-1</sup>, (filled circle) 1.3 mg C L<sup>-1</sup>, (plus sign) 3.5 mg C L<sup>-1</sup>, and (multiplication sign) 7 mg C L<sup>-1</sup>



**Fig. 8** Effect of the Rhône river water matrix on the degradation of SCL in UV/TiO<sub>2</sub>, UV/TiO<sub>2</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems; pH = 8, [TiO<sub>2</sub>] = 2.5 g L<sup>-1</sup>, [SCL] = 88 μM (25 mg L<sup>-1</sup>), [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>]/[SCL] = 100

water composition in Supplementary Material) was compared to that in Milli-Q water matrix in the different systems. Figure 8 shows an enhancement of the degradation rate of SCL in UV/TiO<sub>2</sub> and UV/TiO<sub>2</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems while an inhibition is observed in the UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system. These findings confirm the assumptions made on the effect of the different inorganic ions on the degradation of SCL and especially the effect of HCO<sub>3</sub><sup>-</sup> which are present in the Rhône river water with a concentration of 2.23 mM.

### Conclusions

In the literature the role played by inorganic ions are sometimes contradictory, some findings proposing an enhancement whereas other propose a decrease. Indeed, we think that it is not possible to generalize the role played by inorganic ions as the findings will depend on several parameters such as the adsorption of molecules to be degraded, their molecular structure, the inorganic ion concentrations, the pH, etc.

In this work, the study of the effect of HCO<sub>3</sub><sup>-</sup>, HPO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, and humic substances on the degradation of SCL which is weakly adsorbed on the TiO<sub>2</sub> surface, in the following systems viz. UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, UV/TiO<sub>2</sub>, and UV/TiO<sub>2</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> revealed that HCO<sub>3</sub><sup>-</sup> and HPO<sub>4</sub><sup>2-</sup>, at environmental concentrations, promoted the degradation rate of SCL in the UV/TiO<sub>2</sub> and UV/TiO<sub>2</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems and had no effect on that in the UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system. Indeed, it was found that in presence of HCO<sub>3</sub><sup>-</sup> and HPO<sub>4</sub><sup>2-</sup>, new ROS activated by the holes of TiO<sub>2</sub> were formed. Moreover, it was observed that chloride and nitrate ions highly enhanced the adsorption of SCL on the surface of TiO<sub>2</sub>. Such results can occur with molecules weakly adsorbed on TiO<sub>2</sub> surface and containing reactive moieties towards CO<sub>3</sub><sup>2-</sup> such as aniline derivatives. Concerning humic substances, an inhibitory effect on the degradation rate of SCL in the UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system was observed whereas no significant effect on its degradation were found for the two other systems.

Eventually, the application of UV/TiO<sub>2</sub> and UV/TiO<sub>2</sub>/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> systems is still efficient for the application in real water while the UV/K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system is found to be more sensitive to the water matrix.

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