First results on the purification performance of LaVie system

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1-Introduction

The quality of tap water is of great concern and LaVie system answers a double issue provides pure, high-quality water, ideal for health and enjoyable to drink, and for people in developing countries, clean drinking water makes a large difference. This system purifies chlorine-containing network water while killing bacteria and viruses in all types of water. However, the processes implied in LaVie system is not well-known as well as its performance to remove other compounds such as organic pollutants.

Beyond UV-A irradiations that allow the improvement of tap water, one can suppose that other induced processes could take place. As, the tap water generally contains cations (magnesium, sodium, potassium, aluminium, iron), anions (bicarbonate, nitrate, sulphate, chloride, fluoride) and traces of organic compounds, its irradiation could produce reactive species such as singlet oxygen, hydroxyl, chloride or carbonate radicals (Desbiolles, 2018). Such radicals could oxidize organic compounds presents in the solution. In addition, like water treatment is generally based on the use of sodium hypochlorite to form hypochlorous acid (HOCl) and hypochlorite (ClO^-), other species could be generated under irradiation through the following reactions (Remucal and Manley, 2016):

If the pH < 6.5: $HOCl + h\nu \rightarrow {}^{\bullet}OH + Cl^{\bullet}$ $\Phi({}^{\bullet}OH)_{UV\text{-}A}$ = no data available

If the pH > 8.5: $ClO^- + h\nu \rightarrow Cl^- + O(^3P)$ $\Phi(O(^3P))_{UV\text{-}A} = 0.28$

$ClO^- + h\nu \rightarrow Cl^- + O(^1D)$ $\Phi(O(^1D))_{UV\text{-}A} = 0$

$ClO^- + h\nu \rightarrow Cl^{\bullet} + O^{-\bullet}$ $\Phi({}^{\bullet}OH)_{UV\text{-}A} = 0.08$

where $O(^3P)$ is the ground triplet state of O atom and $O(^1D)$ is the excited singlet state of O atom.

As LaVie system emits in UV-A region, the primary species formed just after irradiation are ${}^{\bullet}OH$, $Cl^{\bullet}$ and $O(^3P)$. In water, these species could evolve as follow:

$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet -}$ $k = 6.5 \times 10^9 - 2.1 \times 10^{10}\ M^{-1}\ s^{-1}$

$O(^3P) + O_2 \rightarrow O_3$ $k = 4 \times 10^9\ M^{-1}\ s^{-1}$

$O_3 + h\nu \rightarrow O(^1D) + O_2$ $\lambda < 411$ nm

$O(^1D) + H_2O \rightarrow 2.\,{}^{\bullet}OH$ $k = 1.2 \times 10^{11}\ M^{-1}\ s^{-1}$

${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2$

In the presence of hypochlorite ion, hydrogen peroxide could react as follow:

$H_2O_2 + ClO^- \rightarrow {}^1O_2 + H_2O + Cl^-$ with ${}^1O_2$ the excited singlet state of O_2

These reactive species ($^1O_2$, $^{\bullet}OH$, O_3, $Cl_2^{\bullet -}$) could also induce the degradation of organic compounds in tap water. The other chlorine radical species have not been considered because it has been proved that the concentration of the thee main chlorine radicals increased in the order $Cl_2^{\bullet -}$ > $ClOH^{\bullet -}$ > $Cl^{\bullet}$ (Yuan et al., 2012).

2-Aims

The objectives of this work is to assess the ability of LaVie System to eliminate organic pollutants potentially present in tap water. Two pharmaceutical products were selected as reference (carbamazepine and diclofenac) because of their detection in low amount (ng/L) in tap water (C.G. Daughton, 2010).

To reach this goal, LaVie system was tested with different water (ultrapure water, tap water and tap water spiked with Javel water). Kinetics experiments were undertaken, as well as the identification of the potential transformation products, and specific experiments were carried out to understand the degradation mechanism using chemical probe or specific scavenger.

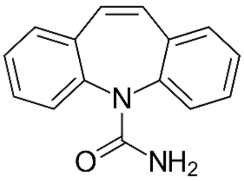
3- Material and analytical methods

3-1- Products and reagents

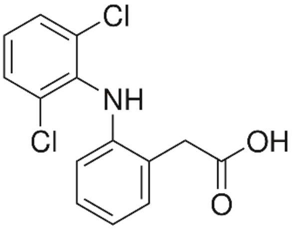
Carbamazepine, CBZ (99% purity), diclofenac, DCF (98% purity), hydroxyterephthalic acid, TAOH (97% purity) were purchased from Sigma Aldrich and terephthalic acid, TA (98% purity) and furfuryl alcohol, FFA (98% purity) from Alfa Aesar. Javel water (3.6% active chlorine) was provided by La Croix and isopropanol, IPA (99.7% purity) by Fluka AG Chem Fabrik. Acetonitrile Hipersolv Chromanorm and formic acid (LC/MS grade) were provided by VWR Chemicals and acetonitrile Optima LC-MS and Optima LC-MS water by Fisher Chemical.

3-2- Preparation of the solutions:

Stock solutions of CBZ and DCF were prepared with ultra-pure water (Direct-Q 5UV, Milipore) at 20 mg.L^{-1} after 2 days stirring at 25°C. Solutions were stocked in dark at 4°C since no degradation were observed after 2 months.



CBZ



DCF

Aqueous TA and TAOH stock solutions (8.2 and 9.5 mg L^{-1} respectively) were prepared with ultra-pure water from a Direct-Q 5UV Millipore device. Homogeneous solutions of TA and TAOH were obtained after 2 days stirring at room temperature in the dark, adjusting pH at 8 (with a KOH solution) to improve the dissolution.

1 L of water (ultrapure and tap) was spiked with CBZ and DCF stock solution to obtain a final concentration of 1.0 and 0.5 mg.L^{-1} in CBZ and DCF, respectively. These concentrations are about 10^{6} times more important than those measured in tap water (C.G. Daughton, 2010). In a second approach, 1 L of tap water spiked with Javel water (0.25 µL in 1 L of water) was used to obtain a concentration of free chloride between 0.5-0.6 mg/L.

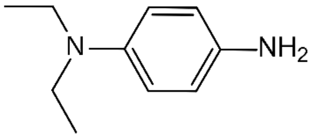
3-3- Purification system LaVie:

The system is equipped with ten LEDs purchased by Shenzeng Refond Optoelectronics corporation and the reactor is a glass bottle of 1 L. The programmed duration of the exposure is 15 min.

3-2-Analytical methods:

3-1-1- Measurement of free chloride:

To estimate the concentration of free chloride, which correspond to chlorine present in aqueous solution as hypochlorous acid ($HOCl$) and hypochlorite ion (ClO^-) (Jolley and Carpenter, 1982), AQUALYTIC AL450 photometer was used based on the formation of a coloured compound. This was realized with DPD powder (diethyl-p-phenylenediamine), represented below, as described in the litterature by Moberg and Karlberg (2000).



DPD

The oxydation of the tertiary amine function in the presence of free chlorine leads to the formation of the coloured DPD cation which absorbs in the UV-visible region (515 and 324 nm).

The test method allows to measure the free chlorine concentration in the range 0.01 to 6 mg/L with a limit of quantification equal to 0.01 mg/L with an error of ± 0.01 mg/L

3-1-2- Abatement of selected organic compounds by HPLC

In order to follow the concentration of CBZ and DCF, LC experiments using a PerkinElmer Flexar FX 10 UHPLC® system, including an A-30 solvent module (quaternary pump), a sample and column module (Perkin Elmer, Shelton, CT, USA) was used. was used with a flow rate of 0.5 mL/min and the injected volume was equal to 2 µL. The separation was obtained using a mixture of acetonitrile (A)/ water with 0.1% (v/v) formic acid (B) and an oven temperature of 30°C as described previously ((Meribout, 2016; Desbiolles, 2018).

3-1-3- Identification of transformation products by LC/ESI-MS

LC–MS analyses were performed using an Agilent 1290 Infinity. A reversed-phase column (Zorbax Eclipse Plus C18, 2.1 mm, 50 mm, 1.8 mm) distributed by Agilent was used at a flow rate of 0.4 mL min^{-1}. The mobile phase was composed of acetonitrile and water acidified with 0.1%v formic acid. To ensure a better separation, specific gradient program was used. Under these conditions, many photoproducts should be separated as previously observed (Meribout, 2016; Desbiolles, 2018).

An Agilent 6530 Q-TOF tandem mass spectrometer equipped with an Agilent jet stream (AJS) ion source was used. Instrument control, data analysis and processing were performed using Mass Hunter workstation software B4.00. The irradiated solution was introduced into the atmospheric pressure ionization source after LC separation, and ionized by ESI in positive ion mode leading to the formation of the $[M + H]^+$ ions of the various products. Mass calibration was first performed pre-acquisition using ESI-L low concentration tuning mix, provided by Agilent technologies and mass correction was performed by continuous calibration with hexakis(1H, 1H, 3H, tetrafluoropropoxy) phosphazine and purine at m/z 922.0098 and m/z 121.0509 amu. Source parameters were set as follows: fragmentor 160 V, capillary 3000 V, skimmer 65 V, and nitrogen was used as the drying (350°C, 10 L min^{-1}), nebulizing (30 psi) and sheath (400°C, 8 L min^{-1}) gas. Scanning was performed from m/z 50–700 amu with 10 000 transient per spectrum. A screening of the transformation products was performed by working in MS mode in order to determine molecular selected ions m/z. The list of the potential transformation products is presented in appendices (Table 1) and has been established gathering the results on the degradation products of CBZ and DCF by photooxidation from our previous works and the literature.

3-1-4- Evidence of the involvement of reactive species

The formation rate and steady-state concentration of photogenerated hydroxyl radicals were estimating using terephthalic acid (TA) (Page et al., 2010). TA reacts selectively with $^{\bullet}OH$ radicals to give hydroxyterephtalic acid (TAOH) assuming that the reaction of TA with $^{\bullet}OH$ radicals occurs with a rate constant, $k_{OH,TA} = (4.4 \pm 0.1) \times 10^9\ M^{-1}.s^{-1}$ (Page et al., 2010). Specific concentration of TA was determined to favour the specific reactivity of generated hydroxyl radicals with the probe and limit their further reaction with TAOH ($k_{OH,\ TAOH} = (6,3 \pm 0,1) \times 10^9\ M^{-1}.s^{-1}$ (Page et al., 2010) and with any constituents present in water samples.

In order to follow the concentration of TA and TAOH, LC experiments using a PerkinElmer Flexar FX 10 UHPLC® system, including an A-30 solvent module (quaternary pump), a sample and column module (Perkin Elmer, Shelton, CT, USA) was used. The column for CBZ analysis was used with a flow rate of 0.5 mL/min and the injected volume was equal to 2 µL. The separation was obtained using a mixture of acetonitrile (A)/ water with 0.1% (v/v) formic acid (B) and an oven temperature of 30°C.

Specific scavengers were used to react specifically and efficiently with reactive species such as singlet oxygen and hydroxyl radicals. Thus, water was spiked with FFA (0.01% v/v), which is a very efficient and well-known scavenger of singlet oxygen ($k = 1.2 \times 10^8\ M^{-1}\ s^{-1}$ (Haag et al., 1984)), and with isopropanol (0.01% v/v) which is a well-known hydroxyl radical quencher ($k = = 1,9 \times 10^9\ M^{-1}.s^{-1}$ (Asmus et al., 1973; Buxton et al., 1988; Rosario-Ortiz et Canonica, 2016).

4- Results

4-1- LaVie irradiation setup

The emission spectrum of LaVie irradiation set up was recorded with a radiometer provided by LOT-Oriel (model SR-051) and is presented on figure 1.

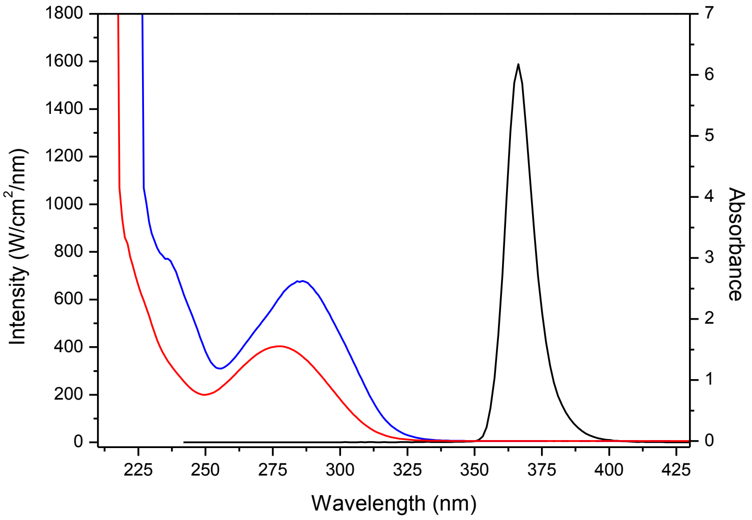


Figure 1: Emission spectrum of LaVie irradiation set up (black), of CBZ (blue) and DCF (red) solutions at 50 mg/L and pH around 8.

As shown in figure &, LaVie system emits in the range 350 to 405 nm with a maximum around 365 nm, in agreement with the purchase specifications (Shenzeng Refond Optoelectronics corporation, 2016). The measured irradiance (not the optimised measurement) between 300 and 450 nm was equal to around 204 W/m^2. This value is about three times more important than the solar light (Commission Internationale de l'Eclairage, 1989).

4-2- Elimination of organic compounds

The elimination of CBZ and DCF in the aqueous phase was undertaken in ultrapure and tap water. As it has been demonstrated that DCF could be degraded under irradiation (degradation quantum yield under solar light irradiation equal to 0.094-0.18 (Meite et al., 2010; Packer et al., 2003)) and in a lesser extent CBZ (degradation quantum yield under solar light irradiation equal to 4,77 x 10^{-5} (Andreozzi et al., 2003)), the results will give information about the involvement contribution of photolysis and photoinduced process in the degradation of the selected compounds.

4-2-1- Elimination study in ultrapure water

The study of CBZ and DCF behaviour in ultrapure water (pH = 6.1) was realised with concentration in the range equal to 8.5×10^{-6} to 2.1×10^{-4} M (or 2 to 50 mg/L) and 1.7×10^{-6} to 6.7×10^{-5} M (or 0.5 to 20 mg/L), respectively. Their concentrations were determined by HPLC analysis based on previous calibration as presented on Figure 2, with satisfied correlation coefficients and large linear response on the concentration scale:

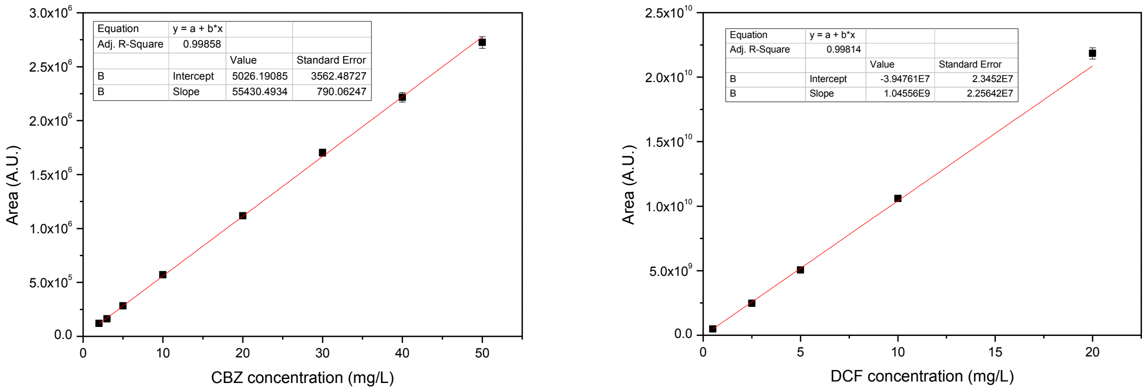


Figure 2: Calibration curve of CBZ (left) and DCF (right) in ultrapure water by HPLC

No degradation was observed for DCF after the exposure in LaVie system in ultrapure water (cf Figure 3 and Table 1S). The results agree with the UV-spectrum of CBZ and DCF, presented in Figure 1, with no overlap with the emission spectrum of LaVie irradiation system, even at very high concentration of pharmaceuticals, restrained thereby any photolysis process. For CBZ, no degradation was observed in ultrapure water in agreement with its UV-spectrum and its very low quantum yield as previously mentioned (cf. Figure 3 and Table 1S). This implies that any observed degradation of CBZ or DCF in tap water will be exclusively attributed to induced processes.

4-2-2- Elimination study in tap water

Tap water not spiked with Javel water. The concentration of free chlorine was systematically determined just after the tap water sampling (pH = 8.0). The measured concentrations are in the range 0.06 ±0.03 mg/L and below the concentration limit of 0.1 mg/L.

Irradiation experiments (Exp) in tap water were undertaken with CBZ and DCF concentration around 1.0 and 0.5 mg/L, respectively, and the results are presented in Figure 3 and in Table 1S in appendices.

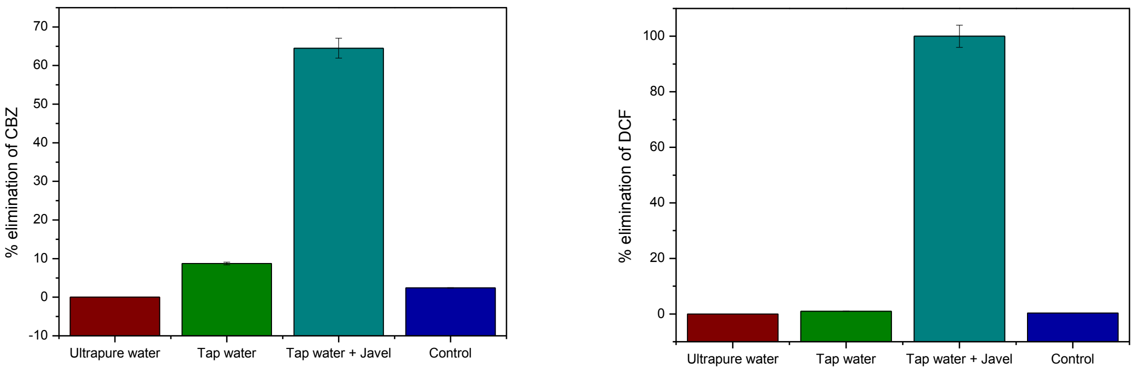


Figure 3: Elimination percentage of CBZ (left) and DCF (right) in different water after irradiation in LaVie system

The results show that DCF concentrations remain constant within the experimental errors (standard deviation lower than 2%). This implies that no degradation was observed for DCF after the exposure in LaVie system in tap water and no induced process takes place. For CBZ, a weak but significant degradation (upper than the experimental errors) of around 9% is observed, implying photoinduced processes and the involvement of reactive species.

Tap water spiked with Javel water. After the addition of Javel water, the measured concentrations are around 0.56 ± 0.1 mg/L and about 6 times higher than the concentration limit of 0.1 mg/L. The concentration of free chlorine was systematically determined just after the spiking and sometimes after the irradiation step as well as CBZ and DCF concentration. In addition, the same experiments were undertaken in dark conditions during 15 min. All the results are gathered in Table 2S and presented in Figure 3 and 4.

The results confirm the efficient removal of free chlorine during the irradiation in LaVie system with more than 70% of decrease as described in Figure 4. In parallel, CBZ photodegradation highly increases to reach an elimination percentage around 65% while in dark conditions (control) almost no transformation occurs within the experimental errors (cf. Figure 3).

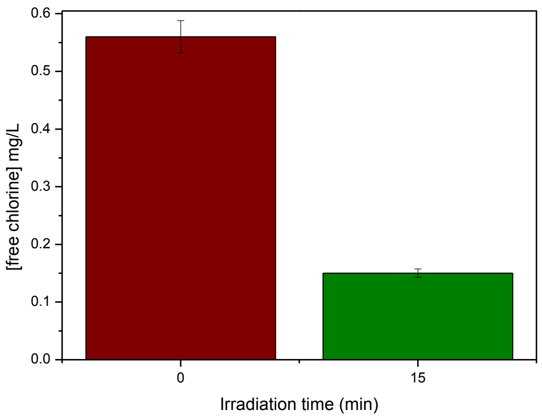


Figure 4: Free chlorine concentration in tap water spiked with Javel water before and after irradiation in LaVie system

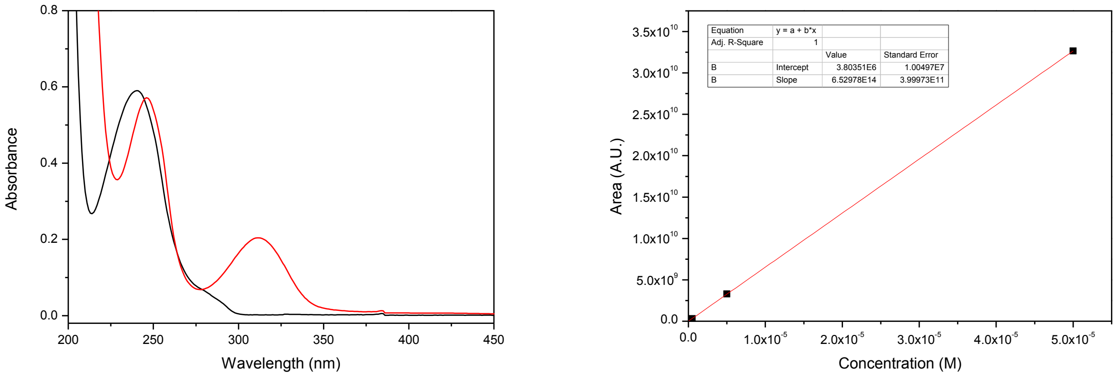
For DCF, its total elimination is observed in tap water spiked with Javel water while in dark conditions no degradation happens. This means that photoinduced process are exclusively implied in the degradation of CBZ and DCF, and that the addition of Javel water largely improves the elimination of the pharmaceuticals, around 7 times for CBZ. The results agrees with the literature (Sichel et al., 2011).

4-3- Involvement of reactive species

Many reactive species could be photogenerated from tap water (cf. introduction). Among them, hydroxyl radicals, other reactive oxygen species (ozone, singlet oxygen), carbonate radical, hydrogen peroxide… could be formed under irradiation. In the presence of Javel water, it has been clearly demonstrated that $^{\bullet}$OH radicals are mainly produced from the excitation of hypochlorite ions but also ozone, chloride dimer radical anion and hydrogen peroxide in a lesser extent. In a first approach, terephthalic acid (TA) was used as a probe to demonstrate the formation of hydroxyl radicals and furfuryl alcohol (FFA) as a specific trapping agent of singlet oxygen ($^1O_2$) and isopropanol (IPA) as $^{\bullet}$OH scavenger in a second approach.

4-3-1- Use of specific chemical probe TA

TAOH study in ultrapure water. TAOH was studied in ultrapure water to validate our HPLC conditions and to evaluate its stability in LaVie system under irradiation. In a second approach, similar experiments were realised in tap water before the exposure of TA in tap water to LaVie system and the measurement of TAOH formation. The UV-spectrum of TA and TAOH are given in Figure 4. LC calibration curve ranged from 5.0×10^{-9} to 5.0×10^{-5} M for TAOH presented in Figure 5 was obtained by HPLC analysis. One can see the very good correlation coefficient and the linear response on the concentration scale that validate the rigorous TAOH concentration determination.



Equation	y = a + b*x		
Adj. R-Square	1		
		Value	Standard Error
B	Intercept	3.80351E6	1.00497E7
B	Slope	6.52978E14	3.99973E11

Figure : (left) UV-spectrum of TA (black) and TAOH (red) in ultrapure water. [TA] = 4.9×10^{-5} M and [TAOH] = 5.2×10^{-5} M, cell length = 1 cm, and (right) calibration curve of TAOH in ultrapure water by HPLC

The stability of TA was not investigated assuming that no degradation should occur considering that no overlap exists between its UV-spectrum and the emission spectrum of LaVie system.

4-3-2- TA study in tap water

Tap water not spiked with Javel water. In this part, TA was added in tap water at two concentrations 7.8×10^{-8} M (2 mL of the stock solution of TA (8.2 mg L^{-1} or 3.9×10^{-5} M) in 1 L of tap water) and 1.95×10^{-5} M (500 mL of the stock solution of TA (8.2 mg L^{-1} or 3.9×10^{-5} M) in 1 L of tap water). In these conditions, no TAOH formation was observed whatever TA concentration. This means that the formation of hydroxyl radicals is very low (in agreement with low DCF and CBZ degradation) or that our experimental conditions should be improved to favour TA reaction with $^{\bullet}$OH and limit TAOH degradation (with higher concentration of TA, for example).

Tap water spiked with Javel water. The same set of experiments realised on tap water were undertaken in the presence of Javel water. Surprisingly, no TAOH formation was observed even with high concentration in TA.

To understand the unexpected results, further experiments were undertaken on TAOH (1.0×10^{-7} and 5.0×10^{-7} M) analysis in tap water and its behaviour under irradiation. The results showed that the fluorescent emission of TAOH by HPLC was scavenged by species present in tap water with a response of TAOH 20% lower than in ultrapure water. This could be attributed to the presence of dissolved organic matter (confirmed by the detection of fluorescent species emitted in our experimental conditions) which can allow deactivation pathways from TAOH excited state leading to the decrease of TAOH fluorescence. Moreover, the irradiation of TAOH in LaVie system showed that TAOH was degraded in tap water (free chloride = 0.07 mg/L) with disappearance equal to 2.3 and 23% with initial TAOH concentration equal to 1.0×10^{-7} and 5.0×10^{-7} M, respectively. Both results explain that no TAOH was observed in our experimental conditions and suggest that the evidence of $^{\bullet}$OH radicals with TA chemical probe should be improved.

4-3-3- Use of radical scavengers

Two approaches were developed to understand the degradation mechanism using two specific quenchers: isopropanol and furfuryl alcohol. The concentration of CBZ in tap water and tap water spiked with Javel water was followed in these experimental conditions and the results are presented below.

The values gathered in Table 3S (in appendices) and presented in Figure 6 showed that the presence of the scavengers always decreases CBZ elimination but in different way depending of the water.

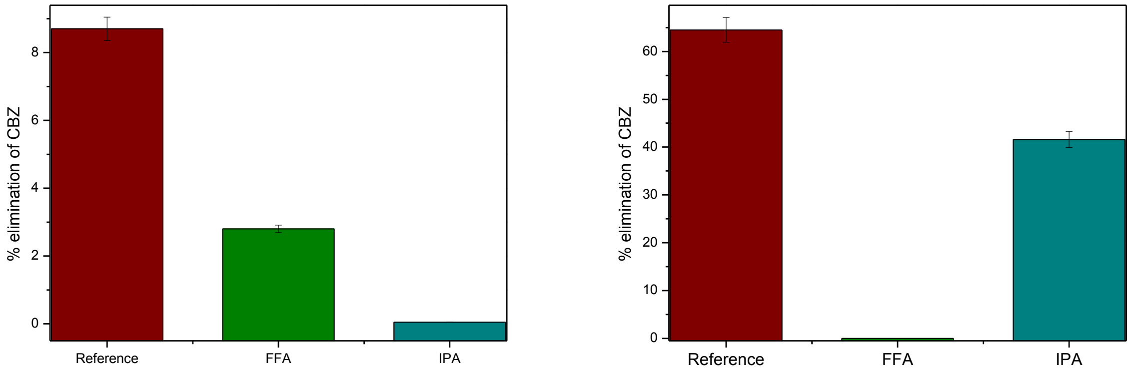


Figure 6: Elimination percentage of CBZ in the absence (reference) and in the presence of FFA and IPA in tap water (left) and in tap water spiked with Javel water (right)

Moreover, one can notice that the effect of FFA and IPA on CBZ transformation differs in the presence and in the absence of Javel water: total inhibition with IPA in tap water and total inhibition with FFA in tap water spiked with Javel water. This seems to indicate that different processes or reactive species are implied in both conditions. In addition, the results obtained in the presence of FFA seems to indicate that singlet oxygen is involved, previous studies have proved that FFA could react more efficiently with $^{\bullet}$OH radicals ($k = 1.5 \times 10^{10}$ M^{-1} s^{-1} (Richard et al. 1990)) than $^{1}O_2$. Consequently, we supposed that $^{\bullet}$OH scavenging occurs in the presence of FFA leading to the partial inhibition of CBZ degradation, if FFA did not react with chlorine radical species (no data found in the literature).

In tap water spiked with Javel water, CBZ degradation is partially inhibited in the presence of IPA and totally with FFA even if the scavengers were added in comparable amount (1.3×10^{-4} and 1.1×10^{-4} M, respectively). This suggests the improvement of $^{\bullet}$OH scavenging in the presence of FFA (by a factor of 7.5 comparing the rate constants) which leads to the total inhibition of CBZ degradation.

The preliminary results with radical scavengers seem to indicate that $^{\bullet}$OH radicals are responsible of CBZ degradation. Nevertheless, additional experiments should be undertaken to validate this hypothesis.

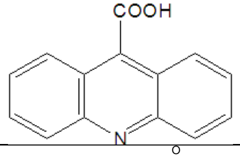
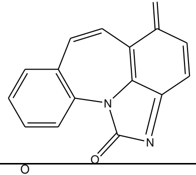
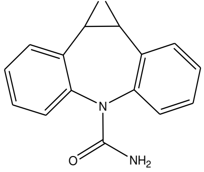
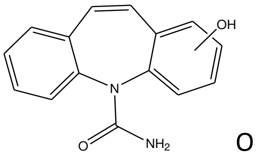
4-4- Detection of the transformation products

The detection of the transformation products of selected pharmaceuticals by ESI^{+}-LC-MS was undertaken on irradiated CBZ and DCF solutions in tap water spiked with Javel water, these experimental conditions allowing efficient degradation.

The identified transformation compounds are presented in the Table 1 for CBZ. The identification was based on the exact mass of the compounds and previous results obtained on the photodegradation of CBZ (Desbiolles, 2008). For DCF, no product was detected.

Among the compounds resulting from CBZ degradation, 9-CAA and the cyclised CBZ compound were identified. For the compound with a retention time of 4.42 min, two different structures are proposed: CBZ epoxide derivative and hydroxylated CBZ (OH-CBZ). The presence of hydroxylated and epoxide CBZ tend to prove the involvement of hydroxyl radicals in the degradation process of CBZ. No chlorinated derivative compound of CBZ was put in evidence suggesting that $Cl_2^{\bullet -}$ radicals are not involved in CBZ degradation as described previously for other compounds (Yuan et al., 2012).

Table 1: Retention time (t_{ret}), measured exact mass ($[M+H]^+$), elementary formula and proposed structure of transformation compounds in solution of CBZ irradiated 15 min in tap water spiked with Javel water with LaVie system

t_{ret} (min)	$[M+H]^+$ (measured m/z)	Formula	Proposed structure
1.2	224.0706	$C_{14}H_9NO_2$	9 carboxylic acridine acid (9-CAA) 
3.88	251.0820	$C_{15}H_{10}N_2O_2$	
4.42	253.0977	$C_{15}H_{12}N_2O_2$	 CBZ epoxide  OH-CBZ

For DCF, no transformation product was detected perhaps because of their low concentration or induced or direct degradation to lead to undetectable compounds in our experimental conditions.

5- Conclusion

The study of LaVie system allows to demonstrate the efficiency of the system to degrade organic compound by photolysis, *i.e.* by the direct absorption of light. This implies that organic compounds absorbing the wavelengths in the range 350 to 405 nm could be eliminate, depending on their absorption spectrum and degradation quantum yield. In addition, the LaVie system has proved its abilities to degrade pharmaceutical compounds present in tap water (even with concentrations 10^6 times more important than real ones) with an improved efficiency in the presence of traces of Javel water. These results clearly demonstrate that Lavie system appears to be a powerful system to eliminate traces of pharmaceuticals in these experimental conditions (concentration of pharmaceuticals around mg/L and concentration of free chlorine around 0.6 mg/L).

The involvement of reactive species such as $^{\bullet}OH$ radicals was demonstrated using chemical scavengers and by the identification of by-products, but other species such as O_3, $Cl_2^{\bullet -}$ or $Cl^{\bullet}$ could be also implied in the degradation process. Further experiments should be undertaken to validate the performance of LaVie system to degrade efficiently other organic compounds and to understand and/or improve all processes implied in the elimination of the organic pollution.

6- Perspective

The preliminary study allows to evidence the performance of LaVie system through the study of CBZ and DCF degradation in tap water and in tap water spiked with Javel water. However, to understand, the reactions and the reactive species involved in their transformation, additional experiments should be undertaken, among others: (*i*) the characterization of tap water (ions content, DOM…); (*ii*) the determination of oxidative species involved in the degradation process through the kinetic studies on the formation and disappearance of $Cl_2^{\bullet -}$ by laser flash photolysis to prove the involvement of chloride radical species in the degradation process or addition of N_3^-, as $Cl_2^{\bullet -}$ scavenger ($k = 1.2 \times 10^9$ $M^{-1}.s^{-1}$), the removal of oxygen to demonstrate the involvement on ozone, the effect of various concentration in Javel water, in IPA, FFA….; (*iii*) the exhaustive identification of the transformation products by LC-MS/MS as a function of irradiation time or amount of Javel water.

7-References

Andreozzi, R., Raffaele, M., Nicklas, P., 2003. Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment. Chemosphere 50, 1319–1330.

Asmus, K.D., Moeckel, H., Henglein, A., 1973. Pulse radiolytic study of the site of hydroxyl radical attack on aliphatic alcohols in aqueous solution. J. Phys. Chem. 77, 1218–1221.

Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B., 1988. Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O− in Aqueous Solution. J. Phys. Chem. Ref. Data 17, 513–886.

Commission Internationale de l'Eclairage (1989), N°85, Solar spectral irradiance, Technical report

Daughton C.G., 2010. Pharmaceutical Ingredients in Drinking Water: Overview of Occurrence and Significance of Human Exposure

Décret 61-859 du 1er Août 1961 et la Circulaire du 15 mars 1962

De Laurentiis, E., Chiron, S., Kouras-Hadef, S., Richard, C., Minella, M., Maurino, V., Minero, C., Vione, D., 2012a. Photochemical Fate of Carbamazepine in Surface Freshwaters: Laboratory Measures and Modeling. Environ. Sci. Technol. 46, 8164–8173.

Desbiolles F., 2018. Thèse de doctorat. Devenir photochimique de la carbamazépine et sous-produits dans des eaux naturelles et écotoxicologie à doses environnementales. Aix-Marseille université.

Haag W.R., Hoigné J., Gassman E., Braun A.M., 1984. Singlet oxygen in surface waters- Part I: Furfuryl alcohol as a trapping agent. Chemosphere 13, 631-640.

Jolley R.L. and Carpenter J.H., 1982. Aqueous chemistry of chlorine: chemistry, analysis, and environmental fate of reactive oxidant species. Chemical Technology Division, W-7405-eng-26.

Meite, L., Szabo, R., Mazellier, P., De Laat, J., 2010. Cinetique de phototransformation de polluants organiques emergents en solution aqueuse diluee. Rev. Sci. Eau 23, 31.

Meribout R., 2016. Thèse de doctorat. Dégradation de produits pharmaceutiques photoinduite par les oxychlorures de bismuth et par les ions persulfate dans le compartiment aquatique : Action de AgCl et Bi2MoO6 sur l'efficacité de BiOCl et activation des ions persulfate par le fer(II). Université des Frères Mentouri, Constantine, Algérie.

Moberg L., Karlberg B. (2000). An improved N,N'-diethyl-p-phenylenediamine (DPD) method for the determination of free chlorine based on multiple wavelength detection. Analytica Chimica Acta 407, 127–133

Packer, J.L., Werner, J.J., Latch, D.E., McNeill, K., Arnold, W.A., 2003. Photochemical fate of pharmaceuticals in the environment: Naproxen, diclofenac, clofibric acid, and ibuprofen. Aquat. Sci. 65, 342–351.

Page, S.E., Arnold, W.A., McNeill, K., 2010. Terephthalate as a probe for photochemically generated hydroxyl radical. J. Environ. Monit. 12, 1658–1665.

Page S. E., Arnold W. A. and McNeil K., 2011. Assessing the contribution of free hydroxyl radical in organic matter-sensitized photohydroxylation reactions. Environ. Sci. Technol. 45, 2818-2825.

Richard C. and Lemaire J., 1990. Analytical and kinetic study of the phototransformation of furfuryl alcohol in aqueous ZnO suspensions, Journal of Photochemistry and Photobiology A: Chemistry 55, 127-134.

Reisz E., Clemens von Sonntag C., Tekle-Röttering A., Sergej Naumov, Schmidt W., Schmidt T.C., 2018 Reaction of 2-propanol with ozone in aqueous media, Water Research 128, 171-182

Remucal C.K. and Manley D., 2016. Emerging investigators series: the efficacy of chlorine photolysis as an advanced oxidation process for drinking water treatment. Environ. Sci.: Water Res. Technol. 2, 565

Rosario-Ortiz, F.L., Canonica, S., 2016. Probe Compounds to Assess the Photochemical Activity of Dissolved Organic Matter. Environ. Sci. Technol. 50, 12532–12547.

Sichel C., Garcia C., Andre K., 2011, Feasibility studies: UV/chlorine advanced oxidation treatment for the removal of emerging contaminants, Water Research, 45, 6371-6380.

Yuan R., Ramjaun S.N., Wang Z., Jianshe Liu J., 2012 Concentration profiles of chlorine radicals and their significances in $^{\bullet}$OH-induced dye degradation: Kinetic modeling and reaction pathways, Chemical Engineering Journal 209, 38–45.

8-Appendices

Table 1S: CBZ and DCF elimination percentage in tap water after irradiation

	[CBZ] (mg/L)			[DCF] (mg/L)	
Elimination %	- 9.04	- 9.67	-7.50	+ 0.89	+ 1.04

Table 2S: Concentration of free chlorine, CBZ and DCF before and after irradiation and in dark conditions

	Free chlorine (mg/L)	**[CBZ] (mg/L)**			**[DCF] (mg/L)**		
		Irradiation		Dark			
		Exp 1	Exp 2	Exp 1	Exp 1	Exp 2	Dark
t = 0 min	0.56	0.833	0.836	0.984	1.09	0.66	0.604
t = 15 min	0.15	0.265	0.327	0.960	0	0	0.602
Elimination %	-73.2	- 68.2	- 60.9	- 2.4	- 100	- 100	- 0.33

Table 3S: Elimination percentage of CBZ in tap water (spiked or not with Javel water) and in the presence of FFA and IPA

	Tap water			Tap water + Javel water		
	Alone	With FFA	With IPA	Alone	With FFA	With IPA
Elimination %	8.7	2.8	0.05	64.5	0.01	41.6