The purification performance of LaVie system: effect of free chlorine and dissolved oxygen concentration

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1-Introduction and aims

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.

The first results obtained on the 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 (free chlorine). 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). However, some questions remained about the role of free chlorine and the mechanism involved in the elimination process of organic compounds

The objectives of this work is to demonstrate the major role of free chlorine in the elimination process of organic compounds and to have more knowledge in the mechanism involved. To reach this goal, LaVie system was tested with tap water spiked with different amount of Javel water and in aerated and dearated conditions. Diclofenac, a pharmaceutical product, was selected as reference compound and kinetics experiments were undertaken as well as dark control.

3- Material and analytical methods

3-1- Products and reagents

Diclofenac, DCF (98% purity) was purchased from Sigma Aldrich and Javel water (3.6% active chlorine) was provided by La Croix (Colgate-Palmolive Company). Acetonitrile Hipersolv Chromanorm and formic acid (LC/MS grade) were provided by VWR Chemicals.

3-2- Preparation of the solutions:

Stock solution of DCF were prepared with ultra-pure water (Direct-Q 5UV, Milipore) at 50 mg/L after 2 days stirring at 25°C in the dark. Solutions were stocked in dark at 4°C since no degradation were observed after 2 months.

1 L of tap water was spiked with DCF stock solution and Javel water to obtain DCF concentration between 0.5 to 2.5 mg/L in, and free chlorine concentration between 0.1 and 2.0 mg/L.

Deaeration of DCF aqueous solution (1 L) was realised by bubbling with nitrogen during 2h to mainly remove the dissolved oxygen present in the solution before adding Javel water.

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 and dissolved oxygen:

To estimate the concentration of free chloride, AQUALYTIC AL450 photometer was used based on the previous methodology described in the previous report.

The dissolved oxygen concentration was measured using specific electrode WTW oxygen CellOx 325 and a Multimeter WTW 340i.

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

In order to follow the concentration of 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 (Solable report April 2019).).

4- Results

4-1- Determination of experimental parameters

All experiments were undertaken in aerated solutions and preliminary studies were required to adjust DCF concentration to observe a significant degradation of this compound even with low concentration of free chlorine (around 0.1 mg/L) and to control the concentration of free chlorine by adding defined volume of Javel water. DCF concentration adjustment was investigated because in the previous report the total disappearance of DCF was observed with a DCF and free chlorine concentration of 0.5 and 0.6 mg/L, respectively.

Free chlorine concentration was measured as a function of Javel water volume in 1 L of tap water as presented on figure 1.

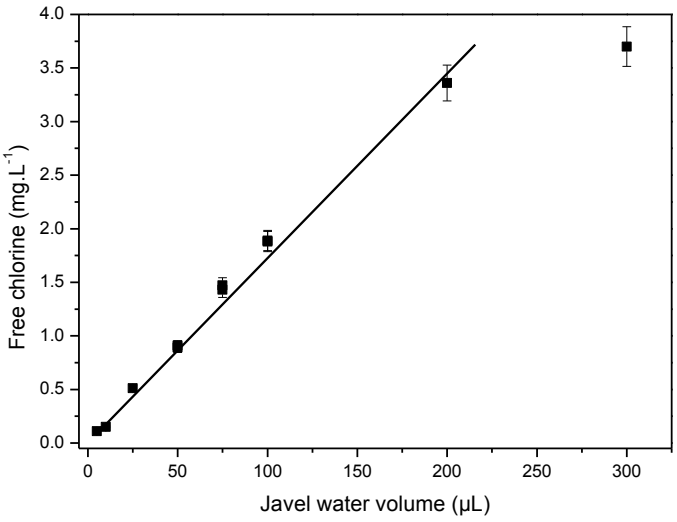

Figure 1: Free chlorine concentration as a function of Javel water volume in 1 L of tap water.

As shown in figure 1, the free chlorine concentration increases proportionally with the amount of Javel water volume until a volume of 200 µL from around 0.1 to 3.4 mg/L of free chlorine. This implies that the referred free chlorine range of 0.1 to 2.0 mg/L could be investigated. In addition, a relationship was established as presented in the following equation 1: : $Y = 0.01708 (\pm 5{,}44.10^{-4}) X + 0.08167 (\pm 0.04779)$ with a good correlation coefficient of 0.9909.

In addition, preliminary experiments were realised with low concentration of DCF (around 0.7 mg/L) in the presence of free chlorine (concentration around 0.1 mg/L). As a degradation around 5% of DCF was observed with the low concentration limit of free chlorine, we decided to work, in a first approach,

with a higher concentration of DCF, equal to 2.5 mg/L, in order to allow to measure its degradation with low and high amount of free chlorine.

4-2- Effect of free chlorine concentration on DCF degradation

Two approaches were investigated to correctly evaluate the effect of free chlorine concentration on DCF elimination. Conditions 1 with a quite high concentration of DCF (2.5 mg/L) and a large scale range of free chlorine concentration from 0.1 to 2.0 mg/L and conditions 2 with a low concentration of DCF (< 1 mg/L) and a scale range of free chlorine concentration from 0.05 to 0.5 mg/L.

4-2-1- Effect of free chlorine concentration on DCF degradation at "high" concentrations

DCF degradation (abatement in %) was investigated with different amount of free chlorine in triplicate and all the values obtained are presented in appendix (Table 1S to 3S). In addition to the measurement of DCF concentration before and after the irradiation step (T0 et T15), free chlorine concentrations were also determined after irradiation and DCF concentrations in mixtures of DCF and free chlorine in tap water were determined after 15 min in dark conditions (T15 blank).

By plotting DCF degradation percentage or DCF removed concentration as a function of free chlorine concentration, the following graph on figure 2 is obtained assuming that one set of values was not considered

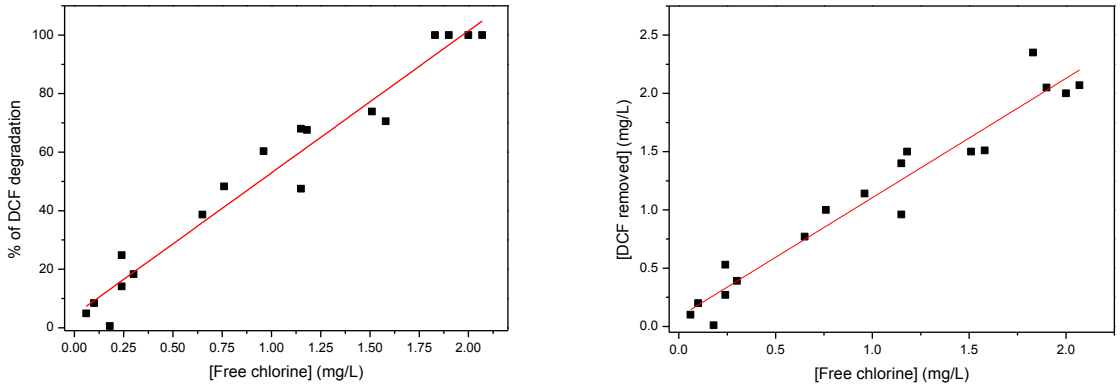

Figure 2: DCF degradation percentage (left) and DCF removed concentration (right) as a function of free chlorine concentration after irradiation in LaVie system, [DCF] = 2.5 mg/L

One can see that the percentage of DCF degradation increases with the higher free chlorine concentration values. It appears that a linear relationship exists with a good correlation coefficient (R^2) of 0.9565 and the following equation 2 : Y = 48.52(± 2.51) X + 4.41 (± 3.03). This result means that DCF disappearance is greatly improved in the presence of free chlorine and it is totally reach for a free chlorine concentration upper than 1.75 mg/L in our experimental conditions. This implies the involvement of free chlorine in the degradation process.

Moreover, from the second graph on figure 2, it also appears that a linear relationship exists with a good correlation coefficient (R2) of 0.9399 and the following equation 3: Y = 1.0236(± 0.00626) X + 0.0815 (± 0.07558). This equation relationship allows us to determine the concentration of DCF removed whatever the free chlorine concentration is and the opposite. For example, if we considered an initial concentration of DCF equal to 0.5 mg/L, the expected percentages of elimination of DCF could be calculated as a function of free chlorine concentration and are presented in Table 1:

[Free chlorine] (mg/L)	**% of DCF elimination**
0.05	27
0.1	37
0.2	57
0.3	78
0.5	100

Table 1: Calculated DCF degradation percentage as a function of free chlorine concentration using equation 3 after irradiation in LaVie system, [DCF] = 0.5 mg/L

In the same time, free chlorine concentration concentrations were almost systematically measured in the mixture before and after irradiation and in dark conditions. The values gathered in figure 3 show that after irradiation free chlorine concentrations decrease strongly (more than 80%) while in dark conditions the decrease is less marked (less than 20%) considering experimental errors. This also confirms the free chlorine involvement in DCF degradation mechanism.

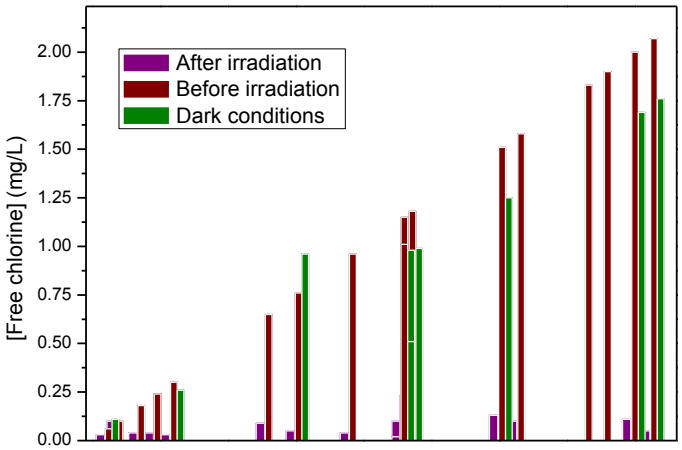

Figure 3: Free chlorine concentration after and before irradiation in LaVie system and in dark conditions at room temperature

In order to evaluate the repeatability and reproducibility of the process, DCF degradation was considered as a function of free chlorine concentration in triplicate and a box plot representation was selected. The figure 4 shows that DCF degradation intermediate percentages are of the same order of uncertainty.

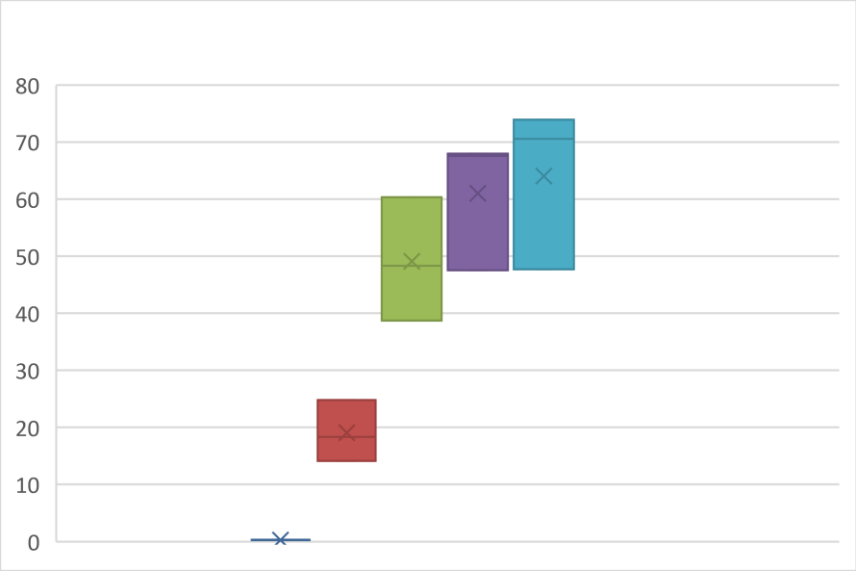

Figure 4: Box plot presentation of DCF degradation percentage as a function of free chlorine concentration

In the same way, a box plot presentation of free chlorine concentration was established as presented in figure 5. One can see that except for the lowest concentration, the free chlorine concentration was obtained with good repeatability and reproducibility.

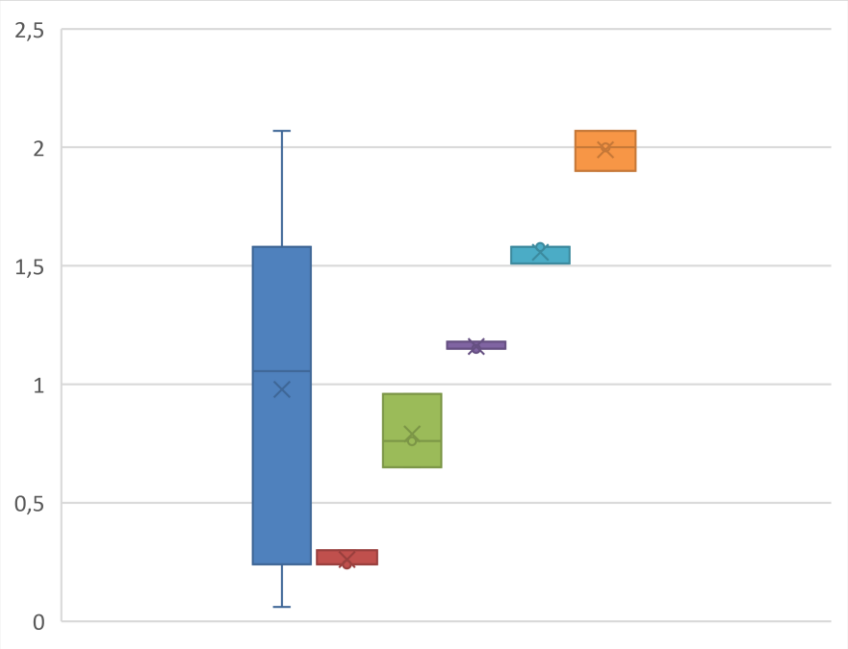

Figure 5: Box plot presentation of free chlorine concentration as a function DCF degradation percentage

The high variability of free chlorine concentration at very low concentration is attributed to the very small volume (few µL) of Javel water added in 1L of tap water, to the real uncertainty of the measured free chlorine concentration by spectrophotometric method and the fast evolution of free chlorine in the solution (evaporation and so on).

4-2-1- Effect of free chlorine concentration on DCF degradation at "low" concentrations

To corroborate the expected results on DCF degradation in the presence of free chlorine using previous established equation 1, a supplementary set of experiments were realised with low concentrations ([DCF] around 0.6-0.8 mg/L and around 0.1 mg/L < [free chlorine] < around 0.3 mg/L. The data are presented in appendix (Table 4S).

DCF degradation percentage was plotted as a function of Javel water volume added in 1L of tap water. The results presented on figure 6 show that the increase of Javel water leads to DCF elimination improvement even if DCF is weakly degraded in the absence of Javel water.

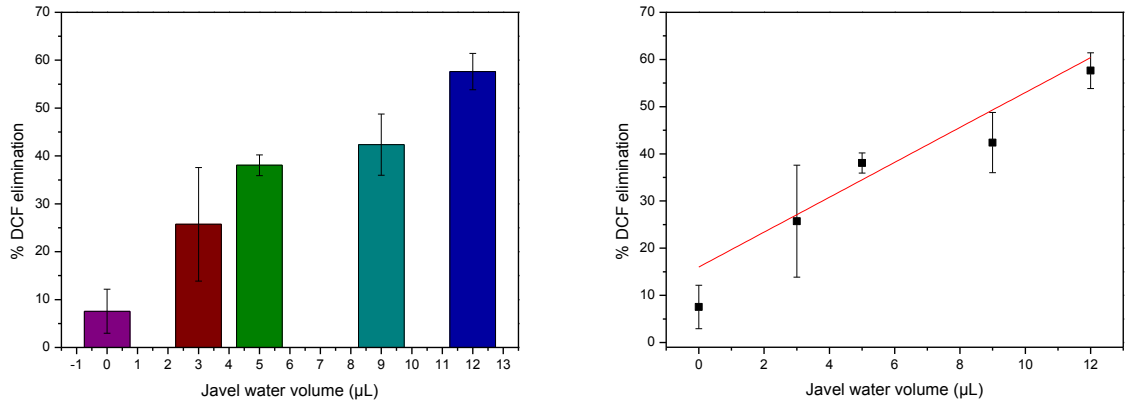

Figure 6: DCF degradation percentage as a function of Javel water volume (left) and linear adjustment (left) after irradiation in LaVie system, [DCF] around 0.6-0.7 mg/L

One can see that a linear relationship exists with a quite good correlation coefficient (R^2) of 0.8548 and the following equation 4 : Y = 16.004 (± 5.159) X + 3.699 (± 0.7466). According to this equation, DCF total disappearance could be obtained with a volume of Javel water around 23 µL.

The effect of free chlorine was estimated using the data and the equation 1 to calculate free chlorine concentration as presented in appendix. As for Javel water volume, the same trend was observed for DCF degradation with the increase of free chlorine concentration (cf. Figure 7).

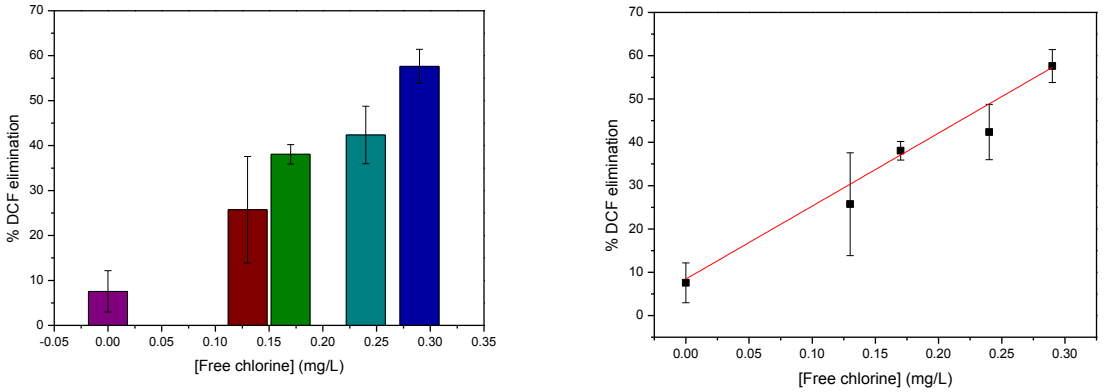

Figure 7: DCF degradation percentage as a function of free chlorine degradation (left) and linear adjustment (left) after irradiation in LaVie system, [DCF] around 0.6-0.7 mg/L

However, a relationship with a better correlation (R^2 = 0.9733) was obtained with a linear equation as followed: Y = 168.494 (± 12.901) X + 8.436 (± 2.684). According to this equation, DCF total

disappearance could be obtained with a free chlorine concentration of 0.54 mg/L. This agrees with the expected results calculated in the first set of experiments (Table 1).

4-3- Effect of oxygen concentration on DCF degradation

Many reactive species could be photogenerated from tap water in the presence of free chlorine. Among them, hydroxyl radicals, other reactive oxygen species (ozone, singlet oxygen) could be formed under irradiation depending of irradiation wavelength range.

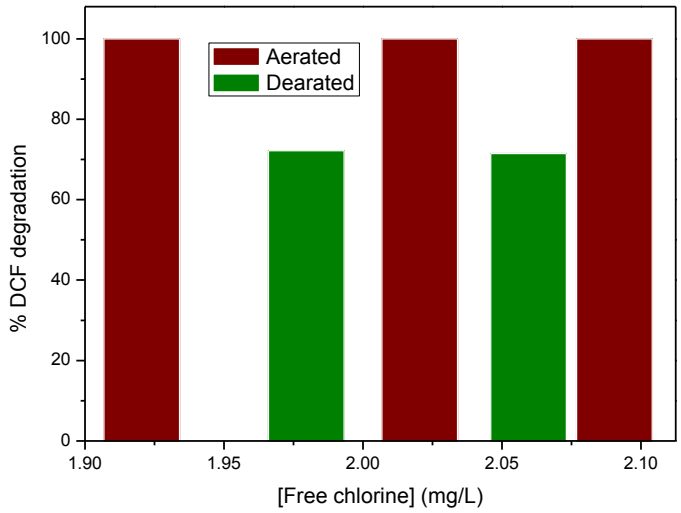

Figure 8: DCF degradation as a function of free chlorine concentration in tap water spiked with Javel water after irradiation in LaVie system in aerated and deaerated conditions, [DCF] = 2.5 mg/L and [Free chlorine] around 2 mg/L.

To demonstrate the involvement of oxygen species, a set of experiments was undertaken in deaerated solutions with a concentration of free chlorine equal to around 2 mg/L. In our conditions, the concentration of oxygen was equal to 4.8 and 0.31 mg/L in aerated and deaerated solution, respectively.

In figure 8, it can be clearly noticed that the removal of oxygen (around 95%) from the solution decreases the DCF elimination with 34% of DCF remaining. This result supports the hypothesis of the involvement of oxygen species in the degradation of DCF according to the following equations as described by Remucal et al. (2016) with irradiation wavelength higher than 320 nm:

$$ClO^- + h\nu \rightarrow Cl^- + O(^3P) \qquad \Phi(O(^3P))_{UV\text{-}A} = 0.28$$

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

5- Conclusion

This study on LaVie system allows to demonstrate the effect of free chlorine on DCF elimination. Thus, it has been clearly proved that DCF degradation is improved with the presence of free chlorine and a relationship has been established to precisely determine the percentage of elimination of DCF as a function of free chlorine. In our experimental conditions ([DCF] around 0.5 mg/L), DCF could be totally degraded in the presence of around 0.54 mg/L that is to say around 25 µL of Javel water addition.

Moreover, the involvement of oxygen in the degradation process was showed with the significant decrease of DCF elimination in deaerated conditions and in the presence of free chlorine suggesting that ozone is partly responsible of DCF degradation making LaVie system an innovative process of oxidation involving hydroxyl radicals and reactive oxygen species.

6-References

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

7-Appendices

Table 1S: DCF elimination percentage in the presence of free chlorine in tap water after irradiation in LaVie system, [DCF] = 2.5 mg/L and [free chlorine] = 0.1 to 2 mg/L.

Sample	Chlore libre (mg Cl_2/L)	[DCF] (mg/L)	% Abattement
2 T0	0.10	2.37	8.44
2 T15	0.10	2.17	
2 T15 blank		2.41	
3 T0	0.30	2.13	18.31
3 T15	0.03	1.74	
3 T15 blank	0.26	2.13	
4 T0	0.76	2.07	48.31
4 T15	0.05	1.07	
4 T15 blank	0.96	2.06	
5 T0	1.15	2.06	67.96
5 T15	0.10	0.66	
5 T15 blank	0.98	2.12	
6 T0	1.83	2.35	100.00
6 T15		0,00	
6 T15 blank		2,34	
7 T0	2.07	2.00	100.00
7 T15	0.05	0.00	
7 T15 blank	1.76	2.00	

Table 2S: DCF elimination percentage in the presence of free chlorine in tap water after irradiation in LaVie system, [DCF] = 2.5 mg/L and [free chlorine] = 0.1 to 2 mg/L.

Sample	Chlore libre (mg Cl_2/L)	[DCF] (mg/L)	% Abattement
2 B T0	0.06	2.05	4.88
2 B T15	0.03	1.95	
2 B T15 blank	0.11	2.05	
3 B T0	0.24	2.14	24.77
3 B T15	0.03	1.61	
3 B T15 blank	/	2.12	
4 B T0	1.01	2.02	41.40
4 B T15	0.02	1.06	
4 B T15 blank	0.51	2.02	
5 B T0	1.18	2.22	67.57
5 B T15	0.23	0.72	
5 B T15 blank	0.99	2.30	
6 B T0	1.51	2.03	73.89
6 B T15	0.13	0.53	
6 B T15 blank	1.25	1.97	
7 B T0	2.00	2.07	100.00
7 B T15	0.11	0.00	
7 B T15 blank	1.69	2.04	

Table 3S: DCF elimination percentage in the presence of free chlorine in tap water after irradiation in LaVie system, [DCF] = 2.5 mg/L and [free chlorine] = 0.1 to 2 mg/L.

Sample	Chlore libre (mg Cl_2/L)	[DCF] (mg/L)	% Abattement
2 C T0	0.18	1.85	0.54
2 C T15	0.04	1.84	
2 C T 15 blank	/	1.85	
3 C T0	0.24	1.91	14.14
3 C T15	0.04	1.64	
3 C T15 blank	/	1.93	
4 C T0	0.65	1.99	38.69
4 C T15	0.09	1.22	
4 C T15 blank	/	1.99	
5 C T0	0.96	1.89	60.32
5 C T15	0.04	0.75	
5 C T15 blank	/	1.89	
6 C T0	1.58	2.14	70.56
6 C T15	0.10	0.63	
6 C T15 blank	/	2.15	
7 C T0	1.90	2.05	100.00
7 C T15	/	0.00	
7 C T15 blank	/	2.04	

Table 4S: DCF elimination percentage in the presence of free chlorine in tap water after irradiation in LaVie system, [DCF] around 0.6 to 0.7 mg/L and [free chlorine] = 0 to 0.3 mg/L

	Javel water Volume (mL)	[Free chlorine] mg/L calculated	DCF (mg/L)	% DCF elimination	% DCF average	% DCF standard deviation
faible 0A T0	0	below detection limit	0.81	8.64%	7.55%	4.60%
faible 0A T15 blanc			0.81			
faible 0A T15			0.74			
faible 0B T0			0.87	11.49%		
faible 0B T15 blanc			0.86			
faible 0B T15			0.77			
faible 0C T0			0.80	2.50%		
faible 0C T15 blanc			0.79			
faible 0C T15			0.78			
faible 1A T0	3	0.13	0.64	18.89%	25.72%	11.87%
faible 1A T15 blanc			0.64			
faible 1A T15			0.52			
faible 1B T0			0.69	18.85%		
Faible 1B T15 blanc			0.68			
faible 1B T15			0.56			
faible 1C T0			0.78	39.42%		
faible 1 C T15 blanc			0.73			
faible 1C T15			0.47			
faible 2A T0	5	0.17	0.68	38.06%	38.05%	2.15%
faible 2A T15 blanc			0.67			
faible 2A T15			0.42			
faible 2B T0			0.66	35.90%		
faible 2B T15 blanc			0.65			
faible 2B T15			0.43			
faible 2C T0			0.65	40.20%		
faible 2C T15 blanc			0.66			
Faible 2C T15			0.39			
faible 3A T0	9	0.24	0.75	42.55%	42.37%	6.38%
faible 3A T15 blanc			0.77			
faible 3A T15			0.43			
faible 3B T0			0.74	35.90%		
faible 3B T15 blanc			0.72			
faible 3B T15			0.48			
faible 3C T0			0.86	48.66%		
faible 3C T 15 blanc			0.84			
faible 3C T15			0.44			
faible 4A T0			0.86	53.43%		

faible 4A T15 blanc	12	0.29	0,85		57.63%	3.81%
faible 4A T15			0,40			
faible 4B T0			1,03	58,59%		
faible 4B T15 blanc			1,03			
faible 4B T15			0,43			
faible 4C T0			0,96	60,86%		
faible 4C T15 blanc			0,93			
faible 4C T15			0,37			