

**THE IMPACTS OF UV DIRECT PHOTOLYSIS AND (UV/H₂O₂, UV/NaOCl)
ADVANCED OXIDATION PROCESSES ON THE DEGRADATION OF
MONOCHLORAMINE USING LOW PRESSURE (LP) LAMP**

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ABSTRACT

The aim of this study was to investigate the use of photochemicals processes (photolysis, H₂O₂/UV_{LP} and NaOCl/UV_{LP}) to eliminate monochloramine compound using a Low Pressure Hg lamp as an irradiation source (254 nm). First, it was found that the direct photolysis treatment might be considered as a suitable way to degrade this product (≈ 98 % rate of depletion under UV dose at 8000 mj/m²). Besides, this degradation was greatly improved by H₂O₂/UV_{LP} thanks to the high production of •OH from photolysis of H₂O₂. However, no big advantages were observed when we have employed NaOCl/UV_{LP} comparatively to H₂O₂/UV_{LP}. This fact would be attributed to the weak production of radicals •OH which was showed by a test conducted with a probe molecule: the terephthalic acid (TA). In addition the system NaOCl/UV_{LP}

could generate also Cl• creating thus, a competition between these two species towards the target compound. In another site, kinetics data for the three systems were best represented by a pseudo-first-order and the photodecomposition of monochloramine has conducted to the formation of by-products like: nitrate and nitrite. No formation of ammonia was observed during this process.

INTRODUCTION

Chlorine has been used as an oxidant in water treatment over the last 100 years. Although many benefits have been gained from this treatment, there are also some disadvantages [1]. It is well known that chlorine could react with naturally occurring organic matter present in water to form halogenated disinfection by-products (DBPs) that might be dangerous for

human health [2]. In 1974, Rook discovered that hypochlorous acid and hypobromous acid also react with naturally occurring organic matter to create many water disinfection by products [3]. Among chlorinated DBPs, inorganic chloramines (mono-, di- and trichloramine) are common in water and contain reduced nitrogen in the form of ammonia [4]. Chloramines have been used by water utilities for almost 90 years, and their use is closely regulated. More than one in five Americans uses drinking water treated with chloramines. Therefore, in several industrial processes using in general chlorinated municipal water, residuals of combined chlorine have to be removed because chloramines could damage reverse osmosis membranes and deionization resins [5]. They could also affect the taste, flavor and smell of drinks and liquids. Chloramine could also change the chemical properties of water leading consequently to an increase of the corrosion and thus to the metals leaching from pipes [6].

Dechlorination was used to remove free and combined chlorine residuals from disinfected wastewater and cooling water prior to discharge into the environment [5]. Among methods used before, we could list: activated carbon filtration and addition of a reducing agent like sulfur dioxide or a sulfite salt [7]. More recently, in swimming pools the dechlorination was achieved using photochemical processes in presence of UV irradiation [8], [9].

Under UV irradiation of HOCl and ClO⁻, various primary reactive intermediates are formed and are rapidly converted into secondary photooxidants like •OH and Cl• [10-16]. In addition, recombination rate of these radicals was relatively slow [17]. Therefore, the primary quantum yields for the formation of these species and the photodecomposition rates of free chlorine might depend on wavelength of light and on pH [10, 14, 16].

Recently Urs von Gunten et al found that UV dose of 2.2×10^4 j.m⁻² gives 70% efficiency in the degradation of monochloramine [18]. Ormeci et al also showed that UV dose at (254 nm) at about 1.2×10^4 j.m⁻² and 1.5×10^4 j.m⁻² were needed to obtain a 50% decay of monochloramine in deionized and treated water, respectively [13]. Besides photodecomposition of monochloramine by direct photolysis in the same conditions has given essentially two by-products: nitrate (NO⁻³) and nitrite (NO⁻²) [19]. Photodecay mechanism of this compound was given first by Li and Blatchely and also by De Laat. These authors have demonstrated the role played by oxygen [5, 9].

The present study was undertaken in order to investigate and to compare the efficiency of three photochemical systems (at 254 nm) in the monochloramine depletion. These are mainly: photolysis, H₂O₂/UV_{LP} and NaOCl/UV_{LP} (with constant concentration during the experiment). The effect of sodium bicarbonate used as scavenger for hydroxyl radicals, was examined during the photodecomposition of NH₂Cl by NaOCl.

Additionally, experiments will be conducted with a probe molecule, terephthalic acid (TA) to compare the production of radicals •OH issued from H₂O₂/UV_{LP} and NaOCl/UV_{LP}. The kinetics of the degradation under different experimental conditions was also discussed.

MATERIALS AND METHODS

Chemicals and reactor

The basic chemicals used are 10-15% NaOCl (from Sigma Aldrich), 25% NH₄OH (from Sigma Aldrich) and 30% H₂O₂ (from Merck). Solutions of monochloramine ([NH₂Cl]₀ ≈ 6 or 12 mg/l) were freshly prepared before each experiment by using a total nitrogen-to-chlorine molar ratios (N/Cl) = 1 and by a dropwise addition of sodium hypochlorite (NaOCl) into a well-stirred solution containing ammonia (NH₄OH). The reaction time was about one hour at pH = 9.69. Under these conditions, the conversion of free chlorine into monochloramine was >98%. A stock solution of terephthalic acid (TA 98%) (5×10^{-2} M) (from Sigma Aldrich) was prepared in alkaline medium (pH = 9). All solutions were prepared with demineralized water using "ISO 5 Milipore" water system.

All experiments were conducted in a cylindrical photoreactor with an effective volume of 800 mL, a diameter of 90 mm, a height of 175 mm and a thickness of 6 mm. All the vessels coming from Heraeus Noblelight company, were made of glass. The total length and diameter of the cooling tube was 340 mm and 39 mm respectively, while the total length and diameter of immersion tube was 380 mm and 25 mm respectively. Both cooling and immersion tubes are made up of quartz which permit transfer of UV radiation through them. The free ozone lamp (GPH212T5L/4, 10 W) from Heraeus Noblelight was used as a UV light source. The temperature was kept constant at 20 ± 1 °C by water circulation using a (Julabo FL300 apparatus) thermostat. A continuous dosing pump from PHD 2000 Infusion (Harvard Apparatus) was used for continuous supply of H₂O₂ (1000 mg/L or 0.029 M stock solution) and NaOCl (640 mg/L or 0.008 M) to keep the concentration constant during the time of the experience. Aliquot samples of 10 ml were taken from the vessel with a syringe. A magnetic stirrer (from IKA-WERKE) was used to keep the solution well mixed.

Sample analysis

Monochloramine, free chlorine and hydrogen peroxide were analyzed by using spectrometer (SPI Handmeter type D141) and the appropriate reagents. The detection limits for the different compounds are: (H₂O₂: 0-17 ppm ± 0.1 ppm; free chlorine: 0-12 mg/L ± 0.03 mg/L; Monochloramine 0-12 mg/L ± 0.03 mg/L). For H₂O₂ determination, a molybdate reagent was used with a photometric detection wavelength at 350 nm. The hypochlorite (free chlorine) reacts immediately with DPD

(N, N-diethyl-pphenylendiamine) reagent to yield a pink color; the total chlorine was also quantified. The bounded chlorine oxidizes the iodide present in the reagent to form iodine, this latter reacts with the DPD and the difference between the results of total and free chlorine yields the bounded chlorine. The photometric detection wavelength was 530 nm. A digital pH-meter (Hanna HI 3222) was used to measure all pH solutions. Nitrites (NO²⁻), nitrates (NO³⁻) and ammonium (NH⁴⁺) were analyzed with special reagents from Hach-Lange on (DR 5000) UV-Visible spectrophotometer. Experiments were conducted separately in presence of terephthalic acid (TA) with H₂O₂ and NaOCl allowing the measure and the comparison of the amount of radicals •OH generated by both systems. However, it is clear that these species could react with (TA) to produce a highly fluorescence compound: 2-hydroxyterephthalic acid (2-OHTA) [20]. Therefore solution containing: 5×10⁻⁴ M of (TA) and (NaOCl 5 mg/L or 6.71 × 10⁻⁵ M) or (H₂O₂ 5 mg/L or 1.47 × 10⁻⁴ M) were prepared in distilled water at pH = 8.79. The irradiation time for both solutions was 10 min. The detection of these two species was made by photoluminescence PL (PIT Quanta Master Model QM-1) at 425 nm after an excitation at 315 nm.

Kinetics expressions

For a solution containing a single absorbing compound (C) that is characterized by $A = \epsilon_{\lambda} \cdot l \cdot [C]$ (where A absorbance, ϵ_{λ} molar absorptivity, [C] molar concentration of absorbing compound, l optical path length) it can be demonstrated that:

$$\frac{d[C]}{dt} = -I_{o,\lambda} \cdot \epsilon_{\lambda} \cdot [C] \cdot \phi_{\lambda} \quad (\text{Eq. 1})$$

Where,

$I_{o,\lambda}$: intensity of incident radiation at wavelength λ (E.cm⁻².s⁻¹),
 ϵ_{λ} : molar absorptivity of the compound at wavelength λ (M⁻¹.cm⁻¹), [C]: concentration of target compound (M), ϕ_{λ} : quantum yield (mole.E⁻¹).

Eq. (1) can be solved to indicate the time-dependent behavior of the target compound:

$$[C]_t = [C]_o \exp(-I_{o,\lambda} \cdot \epsilon_{\lambda} \cdot \phi_{\lambda} \cdot t) = [C]_o \exp(-k_{pc} \cdot t) \quad (\text{Eq. 2})$$

$$\ln \frac{[C]_t}{[C]_o} = -k_{pc} \cdot t \quad (\text{Eq.3})$$

The rate of decomposition of [C] follows pseudo-first kinetics, measured values of [C]₀, [C]_t and time t were used in

conjunction with linear regression to estimate rate constant (k_{pc}) for photodecay of NH₂Cl using only direct photolysis.

To model the oxidation of monochloramine in water using UV radiation the direct photolysis as well as the advanced oxidation process based on •OH and/or Cl• radicals have to be taken into account. The following rate law can be used to describe the decay of a compound C [21]:

$$-\frac{d[C]}{dt} = (k_{pc} + k_{OH^{\bullet},C} [OH^{\bullet}]) [C] \quad (\text{Eq. 4})$$

For the NaOCl/UV system in the presence of sodium bicarbonate (•OH) scavenger:

$$-\frac{d[C]}{dt} = (k_{pc} + k_{Cl^{\bullet},C} [Cl^{\bullet}]) [C] \quad (\text{Eq. 5})$$

Where k_{pc} is the first-order direct photolysis rate constant, k_{OH[•],C} is the rate constant for the oxidation by hydroxyl radicals, k_{Cl[•],C} is the rate constant for the oxidation by chlorine radicals, [C] is the concentration of the compound, [•OH] is the concentration of hydroxyl radicals, and [Cl•] is the concentration of chlorine radicals.

Under the condition that the •OH radical or Cl• concentration is constant (steady state) due to the continuous dosing of the H₂O₂ or NaOCl during the experiments time and the k_{pc} the direct photolysis constant previously determined, Eq. (4) and Eq. (5) reduces to

$$-\frac{d[C]}{dt} = (k_{app} \cdot [OH^{\bullet}]) [C] \quad (\text{Eq. 6})$$

$$-\frac{d[C]}{dt} = (k'_{app} \cdot [Cl^{\bullet}]) [C] \quad (\text{Eq. 7})$$

This pseudo first-order rate law can be used to determine experimentally the overall reaction rate constant k_{app} and k'_{app}.

RESULTS AND DISCUSSION

Actinometry using H₂O₂ for UV fluence calculation and lamp efficiency

Hydrogen peroxide actinometry experiments were performed to determine the fluence rate in the quartz tube for the Low Pressure (LP) lamp [22, 23]. For high values of optical density of the H₂O₂ solution (concentrated medium, D > 2), the photonic fluxes of the lamps calculated from the general equation:

$$[C]_o - [C] = \frac{\Phi \cdot P_0}{V \cdot t} \quad (\text{Eq.8})$$

With:

$[C]_0$: concentration of compound C at time $t = 0$ (mol/L)

$[C]$: concentration of compound C at time t (mol/L)

Φ : quantum yield of the actinometry compound ($\Phi_{H_2O_2} = 0.5$)

P_0 : incident photonic flux (Einslein s^{-1}) (1 Einslein = 1 mol photons)

V : volume of the solution (L)

t : time irradiation (min)

Hence, the incident photon flux of (LP) lamp at 254 nm was 4.87×10^{-6} Einslein s^{-1} . Consequently, the power of the lamp is 2.29 W (typical efficiency 22.9 %) which can be calculated using the following relation:

$$P = \frac{N \cdot h \cdot c \cdot P_0}{\lambda} \quad (\text{Eq.9})$$

Where P is the power of the lamp, N is the Avogadro's number (6.023×10^{23}), h is Planck's constant (6.63×10^{-34} J.s), c is the light velocity (2.99×10^8 m. s^{-1}), p_0 is the photonic flux in Einstein. s^{-1} , and λ is the maximum lamp wavelength (254×10^{-9} m).

As far as the average fluence rate (UV Dose) is concerned, "Bolton UVCalc1B software" is used to estimate it. Actually, in the software both reflection and refraction are taken into account as the beam of UV radiation passes through an air/quartz/water interface [24]. The fluence rate is estimated according to the followed dimensions: 2.5 cm width (the distance between the quartz cooling jacket and the reactor wall) and 16 cm height (the height of the reaction medium in which the lamp is immersed). In addition the software was run to estimate also the average fluence rate for different transmittance values at 254 nm as the penetration of light through the reactor is changed with the concentration.

UV-Visible spectra study

The UV-visible study was carried out on hydrogen peroxide, sodium hypochlorite, monochloramine, and ammonium hydroxide using DR 5000 Hach-Lange spectrometer. The purpose of this section is to determine the maximum wavelength and the extinction molar coefficient (ϵ) for the different products used in this study. The molar extinction coefficient, ϵ , is a measurement of how strongly a chemical species absorbs light at a given wavelength. It is an intrinsic property of the species. The recorded spectra are presented in figure. 1.

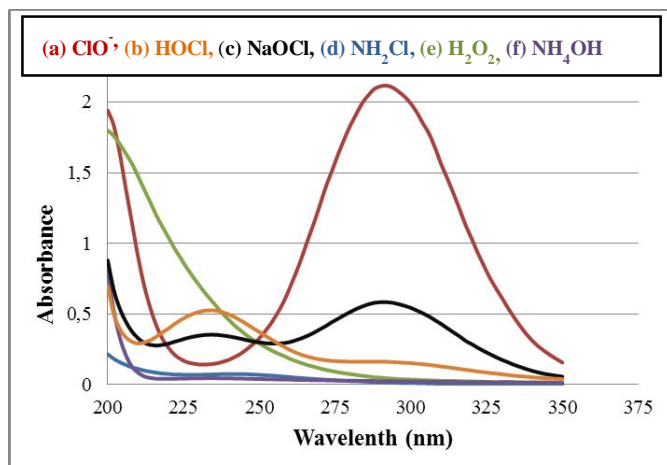


Fig. 1 UV-visible spectra of: (a) NaOCl (ClO^-) ($10^{-2}M$; pH=10.67); (b) NaOCl (HOCl) ($10^{-2}M$; pH=4.8); (c) NaOCl (50%HOCl, 50% ClO^-) ($10^{-2}M$; pH=7.2 \approx pKa=7.5); (d) NH_2Cl (6mg/L; pH=10.67); (e) H_2O_2 ($10^{-2}M$; pH=6.20); (f) NH_4OH ($10^{-2}M$; pH=10.70); $T^\circ = 20 \pm 1^\circ C$

Hypochlorous acid and hypochlorite ion (HOCl/ ClO^-), which are the two forms of free chlorine at neutral pH, absorb UV radiation in the field of wavelengths between 200 and 360 nm (figure. 1. (a), (b), (c)). Additionally, the spectrum of HOCl presents two bands: one centred on 234 nm ($\epsilon \approx 52.6 M^{-1}.cm^{-1}$) and a second band around 300 nm ($\epsilon \approx 15.3 M^{-1}.cm^{-1}$); ClO^- has a characteristic band centred at 292 nm ($\epsilon \approx 211.7 M^{-1}.cm^{-1}$). It should be noticed that monochloramine has an absorption band at 244 nm with a maximum extinction coefficient equal to $643.77 M^{-1}.cm^{-1}$ (fig.1. (d)). The UV-absorption spectrum of monochloramine obtained in this work is very consistent with the spectra reported in literature [25, 26]. Hydrogen peroxide (H_2O_2) and ammonium hydroxide (NH_4OH) do not show any maximum band. In general all these absorb in the UV region.

Hydroxyl radicals generation under H_2O_2/UV and NaOCl/UV

Fig. 2 shows the changes of PL spectra of TA solution at pH equal to 8.78, in the presence of H_2O_2 and NaOCl under dark and UV_{LP} light irradiation for 10 minutes. No PL signal was observed in the absence of UV light irradiation. However, the highest PL intensity at about 425 nm was observed with H_2O_2/UV_{LP} and the lowest one with NaOCl/ UV_{LP} . This can be explained by the dissociation of H_2O_2 or NaOCl and the generation of the Terephthalic acid radical (TA \bullet) which is easily formed by ($\bullet OH$) than by ($Cl\bullet$). From these results it can be said that the H_2O_2/UV_{LP} system generates a greater amount of ($\bullet OH$) comparatively to that of NaOCl/ UV_{LP} system. The concentrations used are: 5 mg/L or 1.47×10^{-4} M in H_2O_2 and 5 mg/L or 6.71×10^{-5} M in NaOCl.

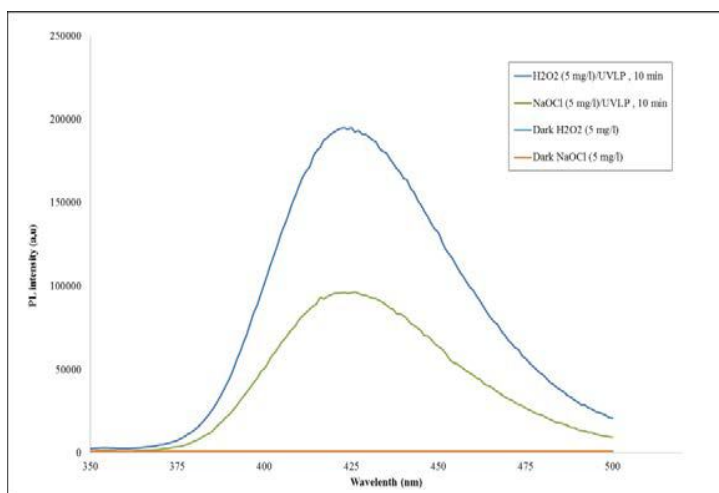
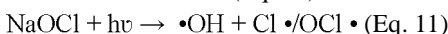
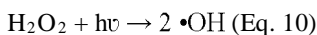


Fig. 2 Photoluminescence (PL) spectral of 5×10^{-4} M terephthalic acid (TA) solution at pH 8.78 (excitation at 315 nm) in dark and after 10 min UV_{LP} (254 nm) irradiation in the presence of (5 mg/L H_2O_2) and (5 mg/L NaOCl); $T^\circ = 20 \pm 1$ °C

Once the radicals (Cl^\bullet and $\bullet OH$) are liberated from these two species (H_2O_2 and NaOCl) and by taking in to account the competitions toward the probe molecule (TA), they react with this compound to give Terephthalic acid radical (TA^\bullet) and finally with ($\bullet OH$) to give a fluorescent product: 2-hydroxyterephthalic acid (2-OHTA). The reactions (Eq.10 and Eq.11) and mechanism describing the processes are represented below (figure 3):



The TA react either with $\bullet OH$ or Cl^\bullet to give in first step the radical TA which in turn react preferentially with $\bullet OH$ to give 2-OHTA:

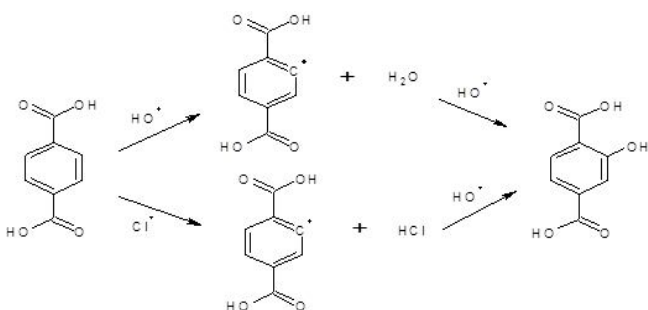


Fig. 3 Schematic Reaction Mechanism Of TA With ($\bullet OH$) And (Cl^\bullet) Free Radicals

Photolysis of monochloramine by UV_{LP} lamp

The photodecay monochloramine, taken at two different concentrations (6 mg/L or 1.16×10^{-4} M) and (12 mg/L or 2.33×10^{-4} M) was studied as a function of UV dose at pH 9.69 and with UV_{LP} (254 nm). After each exposure period, samples were collected and the concentration was measured by the DPD (N, N-diethyl-phenylendiamine) method. The result depicted in figure (04), showed that monochloramine was susceptible to degrade by this process. Indeed, the rate of degradation in these conditions was equal to 98% for a UV dose 16000 mj/cm^2 (figure 04). In another part we observed that only 2336.4 mj/cm^2 was needed to obtain a 50% decay of the compound. During the process of direct photolysis, we observed a change in the spectra of monochloramine within the exposure time. Moreover, we noticed a decrease of the band located at 244 nm followed by the formation of a strong one around 200 nm which could be attributed to formation of two main by-products: Nitrate (NO_3^-) and Nitrite (NO_2^-). It was important to indicate that NH_2Cl remained almost constant in dark conditions.

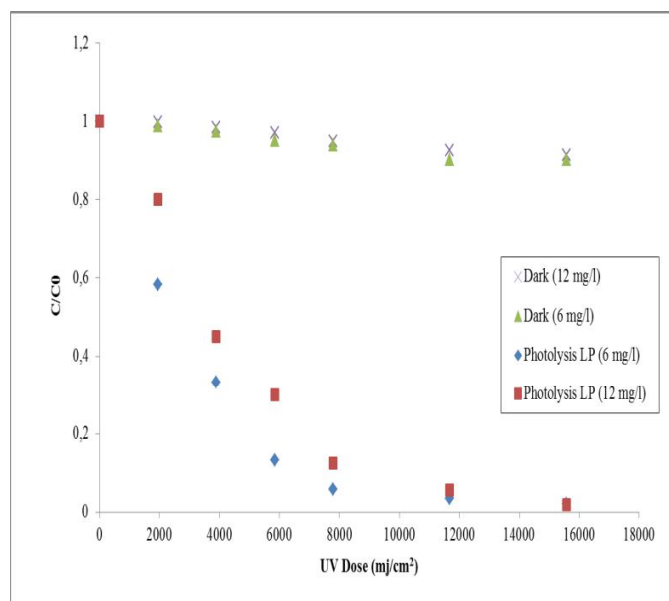


Fig. 4 UV Photodecay Of The Concentration Of Compound Chlorine As The Function Of UV Dose For 254 Nm Wavelength Of Exposure (Ph = 9.69 \pm 0.5); $T^\circ = 20 \pm 1$ °C

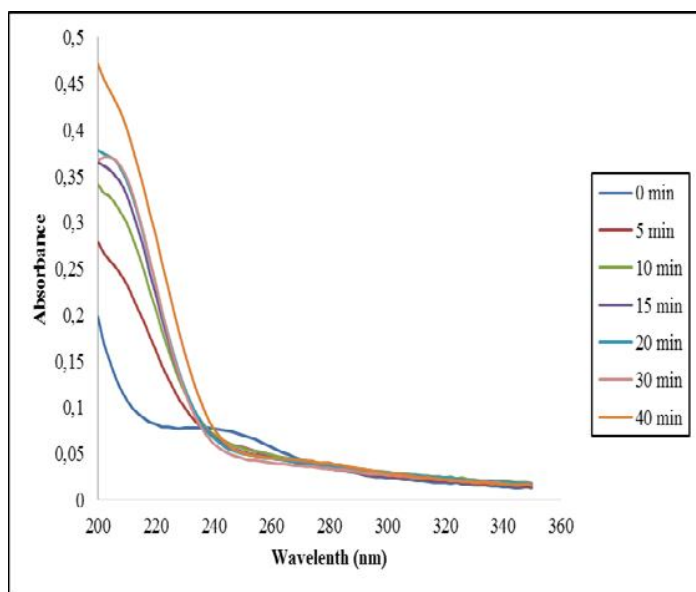


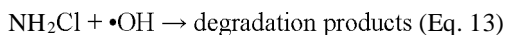
Fig. 5 Spectrum Evolution Of NH_2Cl (6 Mg/L) Photolysis With UV_{LP} , $\text{Ph} = 9.69 \pm 0.5$; $T^\circ = 20 \pm 1^\circ\text{C}$

Monochloramine degradation by $\text{H}_2\text{O}_2/\text{UV}_{\text{LP}}$

The results on degradation of NH_2Cl (6 mg/L or 1.16×10^{-4} M) and (12 mg/L or 2.33×10^{-4} M), under the UV_{LP} lamp with continuous dosing to insure a constant concentration of H_2O_2 (5 mg/L or 1.47×10^{-4} M) are plotted in figure (6). The results indicate that the degradation is faster and more effective in the presence of H_2O_2 compared to those obtained in direct photolysis. The results can be interpreted by taking into account the absorption of H_2O_2 at 254 nm where hydrogen peroxide is rapidly dissociated, producing thus radicals $\bullet\text{OH}$, a non-selective and powerful oxidant, which decomposes the monochloramine very quickly [27-29].



Where Φ is the quantum yield of the homolytic H_2O_2 photodissociation,



As with photolysis, NH_2Cl remained almost constant in dark conditions and in the presence of H_2O_2 .

The variation of the spectral absorbance of the monochloramine, show a sensitive decrease of the absorption band located at 244 nm, due to the action of $\bullet\text{OH}$ radicals (produced in situ from H_2O_2 photolysis at 254 nm) and the formation of an isobestic point at 237 nm (figure 7). At this point, all the chemical species have the same molar absorptivity (ϵ) or -more generally- are linearly related [30].

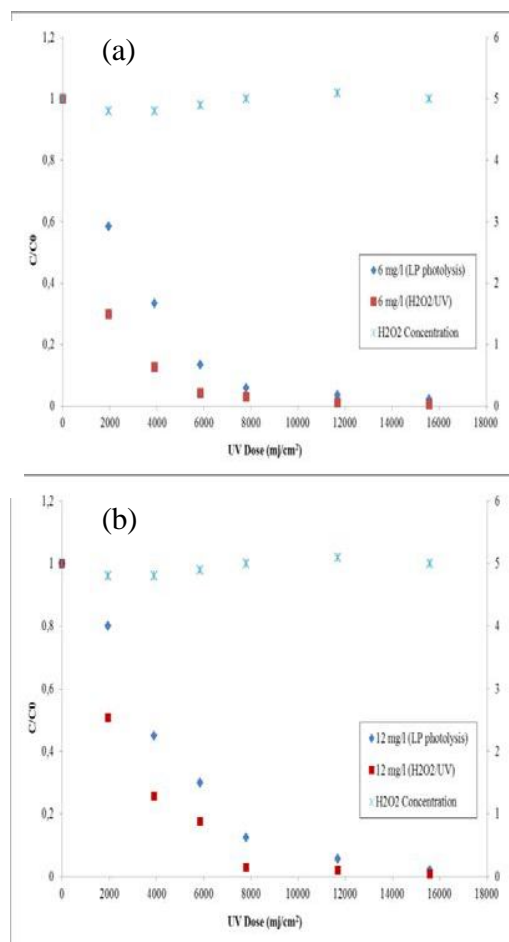


Fig. 6 Relative Concentration Of Compound Chlorine As The Function Of UV Dose With Photolysis And $\text{UV}_{\text{LP}}/\text{H}_2\text{O}_2$ (5 Mg/L) Continuous Dosing, (A) $[\text{NH}_2\text{Cl}]_0 = (6 \text{ Mg/L})$ And (B) $[\text{NH}_2\text{Cl}]_0 = (12 \text{ Mg/L})$; $\text{Ph} = 9.69 \pm 0.5$; $T^\circ = 20 \pm 1^\circ\text{C}$

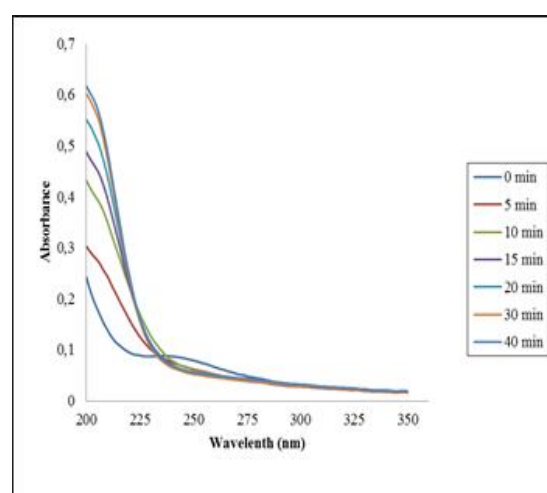


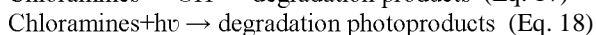
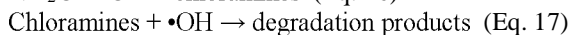
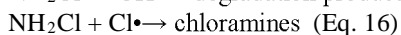
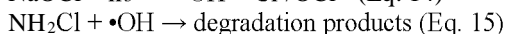
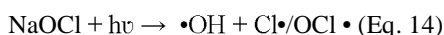
Fig. 7 Spectrum Evolution Of NH_2Cl (6 Mg/L) With $\text{UV}_{\text{LP}}/\text{H}_2\text{O}_2$ (5 mg/L) Continuous Dosing; $\text{Ph} = 9.69 \pm 0.5$; $T^\circ = 20 \pm 1^\circ\text{C}$

Monochloramine degradation by NaOCl/UV_{LP} in the presence and in absence of •OH radical scavenger

As with direct photolysis and with H₂O₂, solutions of NH₂Cl were stable in presence of NaOCl (5 mg/L or 6.71 × 10⁻⁵ M). Figure 08 depicted degradation process of NH₂Cl (6 mg/L or 1.16 × 10⁻⁴ M and 12 mg/L or 2.33 × 10⁻⁴ M) by UV_{LP}/NaOCl continuous dosing in absence and in the presence of the scavenger: NaHCO₃ (10⁻¹ M).

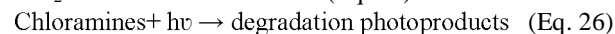
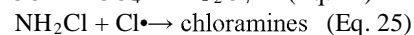
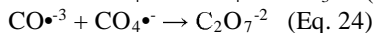
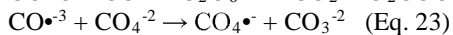
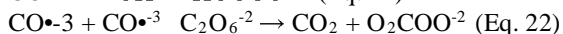
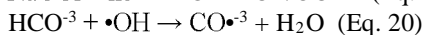
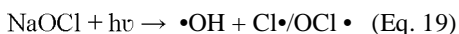
First, in its absence we have observed no significant difference in the efficiency rate for degradation by photolysis and NaOCl/UV_{LP} processes:

Without scavenger:



By contrast, the degradation has become increasingly slow. These results indicated that •OH radicals were scavenged due to the formation of carbonate anion radical [31] and also inactive species as, CO₄²⁻ and C₂O₇²⁻ [32, 33]:

In the presence of scavenger:



It is interesting to mention that Cl• radicals may play an important role in the formation of chloramines which in turn could be degraded by direct photolysis.

The spectral evolution of the monochloramine is similar for both systems: NaOCl/UV_{LP} and H₂O₂/UV_{LP}. This fact may presume that we have the same final products with them. (figure. 09).

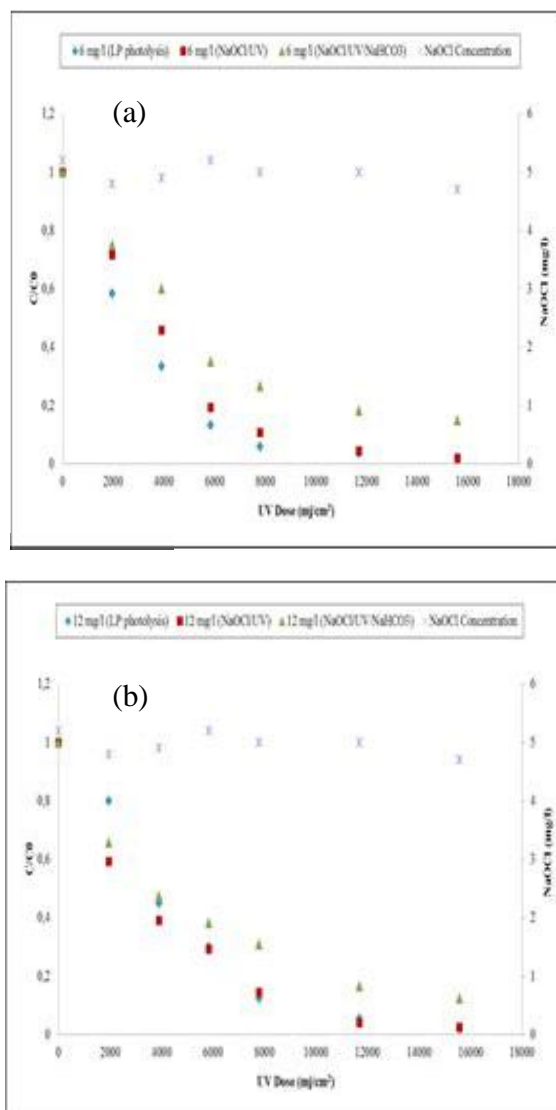


Fig. 8 Relative Concentration Of Compound Chlorine As The Function Of UV Dose With Photolysis, UV_{LP}/Naocl (5 Mg/L) Continuous Dosing And UV_{LP}/Naocl (5 Mg/L) Continuous Dosing / Nahco₃ (10⁻¹ M), (A) [NH₂Cl]₀ = (6 Mg/L) And (B) [NH₂Cl]₀ = (12 Mg/L); Ph = 9.69 ± 0.5; T° = 20 ± 1 °C

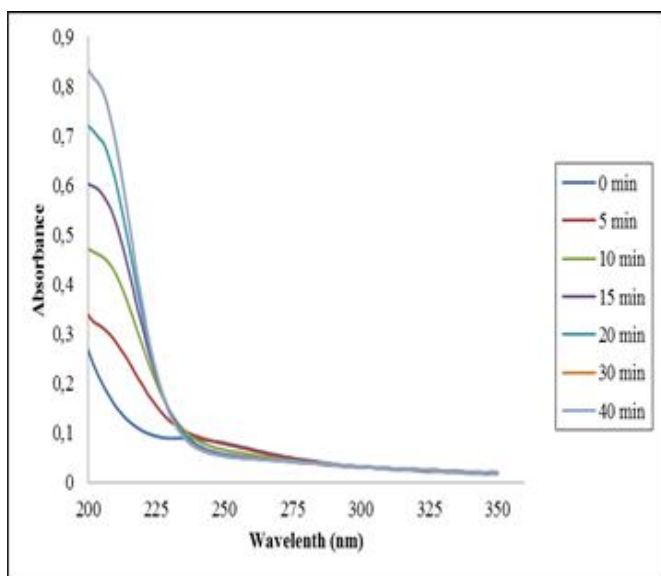
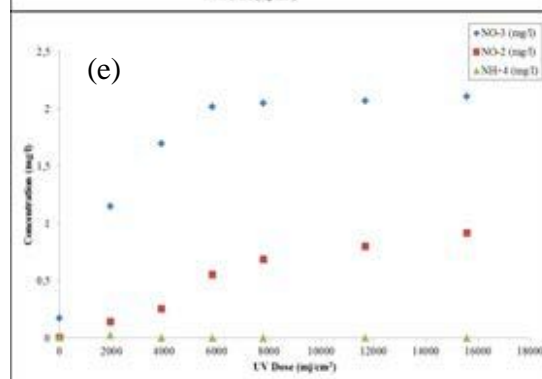
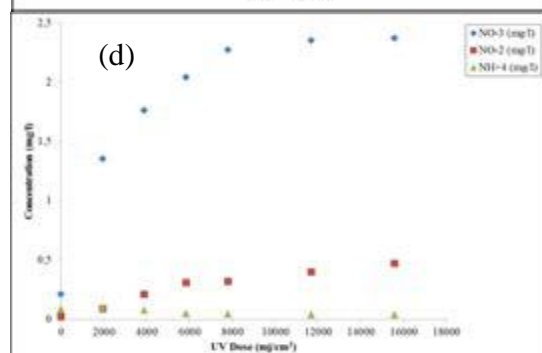
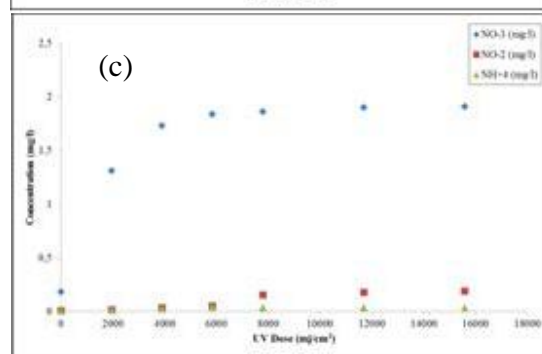
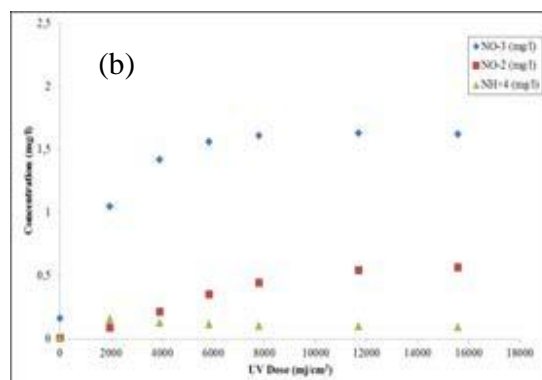
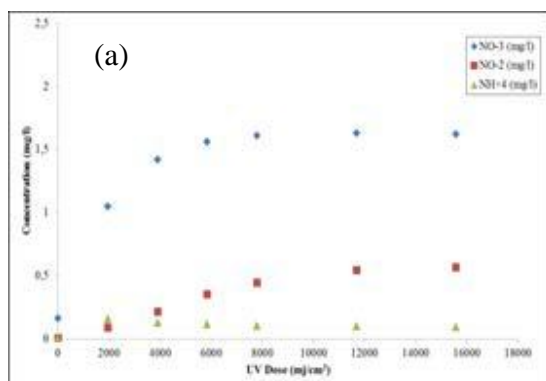


Fig. 9 Spectrum Evolution Of NH_2Cl (6 Mg/L) With $\text{UV}_{\text{LP}}/\text{Naocl}$ (5 Mg/L) Continuous Dosing; $\text{Ph} = 9.69 \pm 0.5$; $T^\circ = 20 \pm 1^\circ\text{C}$

Degradation photoproducts of NH_2Cl

The degradation of NH_2Cl (6 mg/L or 1.16×10^{-4} M) and (12 mg/L or 2.33×10^{-4} M) by the three processes, has led to the formation of photoproducts like: Nitrate (NO_3^-) and Nitrite (NO_2^-). Besides, no ammonia formation was observed during these processes (figure 10). These results were in agreement with those given by the literature [14]. Furthermore, some authors showed that Nitrite was the major product whereas Nitrate was the minor one during the photodecomposition of NH_2Cl in presence of dissolved oxygen [5]. In addition, it is interesting to emphasize that the highest amount of (NO_2^-) was formed with $\text{NaOCl}/\text{UV}_{\text{LP}}$ and the lowest one with $\text{H}_2\text{O}_2/\text{UV}_{\text{LP}}$. Other nitrogenous products like nitrogen gas (N_2) and/or nitrous oxide (N_2O) could also be formed. These results were also in agreement with those related by the literature [34].



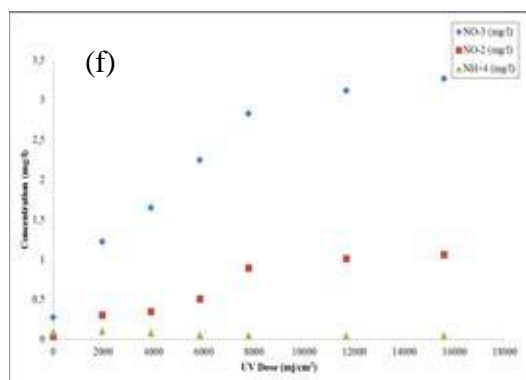


Fig. 10 Degradation Photoproducts Of NH_2Cl , Change In The Concentration Of NO^{-3} , NO^{-2} And NH^{+4} , (A) UV_{LP} Photolysis $[\text{NH}_2\text{Cl}]_0=(6 \text{ Mg/L})$, (B) UV_{LP} Photolysis $[\text{NH}_2\text{Cl}]_0=(12 \text{ Mg/L})$, (C), $\text{UV}_{\text{LP}}/\text{H}_2\text{O}_2$ $[\text{NH}_2\text{Cl}]_0=(6 \text{ Mg/L})$, (D) $\text{UV}_{\text{LP}}/\text{H}_2\text{O}_2$ $[\text{NH}_2\text{Cl}]_0=(12 \text{ Mg/L})$, (E) $\text{UV}_{\text{LP}}/\text{Naocl}$ $[\text{NH}_2\text{Cl}]_0=(6 \text{ Mg/L})$, (F) $\text{UV}_{\text{LP}}/\text{Naocl}$ $[\text{NH}_2\text{Cl}]_0=(12 \text{ Mg/L})$ $\text{Ph} = 9.69 \pm 0.5$; $\text{T}^\circ = 20 \pm 1 \text{ }^\circ\text{C}$

Study of the pseudo-first order kinetics

The logarithmic plot of (C/C_0) versus time has given straight lines for the tree systems. Therefore the experimental data could be best represented by a pseudo-first-order model (figure 11).

As results the k_{app} value for these processes might be deduced from the slopes of the curves (table 1). They showed also that the degradation at a constant concentration of H_2O_2 (5 mg/L or $1.47 \times 10^{-4} \text{ M}$) and under UV_{LP} light was faster than that observed with photolysis and NaOCl (5 mg/L or $6.71 \times 10^{-5} \text{ M}$) (continuous dosing) in presence and in absence of scavenger (NaHCO_3). This high efficiency could be attributed to radical $\bullet\text{OH}$ produced from photolysis of H_2O_2 at 254 nm [27-29]. Additionally, the rate constant calculated from NaOCl/ UV_{LP} and direct photolysis was found to be very close in spite of the participation of $\text{Cl}\bullet$ radical, produced from the first system. This results could be explained essentially by competition of $\bullet\text{OH}$ and $\text{Cl}\bullet$ towards monochloramine. However, we should precise that $\bullet\text{OH}$ could degrade NH_2Cl whereas $\text{Cl}\bullet$ could form chloramines in the same time making thus the degradation slow enough for both concentrations of our substrate. This fact was proved by addition of the scavenger (NaHCO_3). In this case we noticed a decrease in different values of the kapp (table 1).

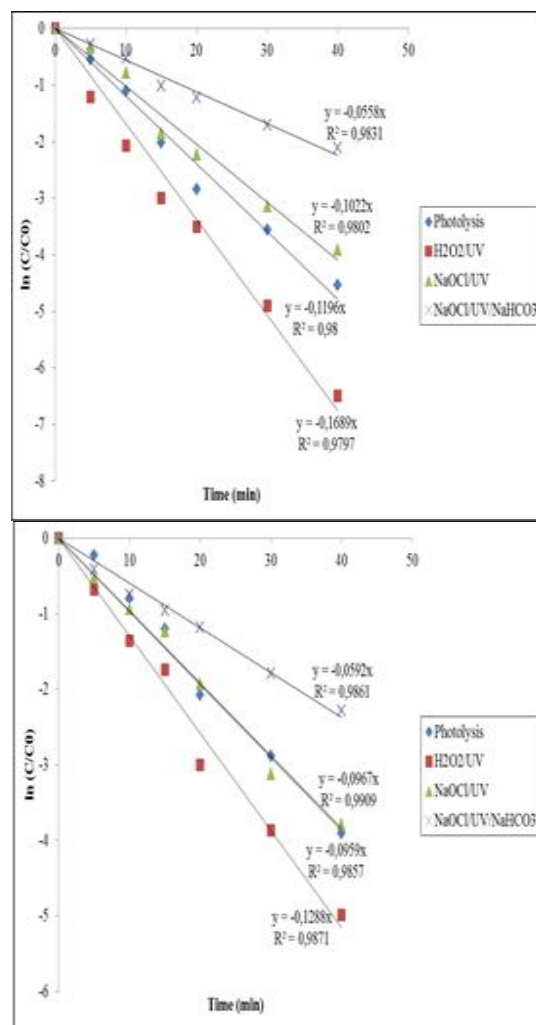


Fig. 11 Graphical Estimation Of The Pseudo-First Order Rate Constant Of UV_{LP} Direct Photolysis, $\text{UV}_{\text{LP}}/\text{H}_2\text{O}_2$ (5 Mg/L) Continuous Dosing, $\text{UV}_{\text{LP}}/\text{Naocl}$ (5 Mg/L) Continuous Dosing And $\text{UV}_{\text{LP}}/\text{Naocl}$ (5 Mg/L) Continuous Dosing / NaHCO_3 (10^{-1} M), (A) $[\text{NH}_2\text{Cl}]_0=(6 \text{ Mg/L})$, (B) $[\text{NH}_2\text{Cl}]_0=(12 \text{ Mg/L})$; $\text{Ph} = 9.69 \pm 0.5$; $\text{T}^\circ = 20 \pm 1 \text{ }^\circ\text{C}$

Table 1: Pseudo First Rate Constants Obtained Of NH_2Cl Degradation

Experiment conditions	6mg/L k_{app} (min^{-1})	R^2	12 mg/L k_{app} (min^{-1})	R^2
UV_{LP} direct photolysis	0.119	0.98	0.095	0.985
$\text{UV}_{\text{LP}}/\text{H}_2\text{O}_2$ (5 mg/L) continuous dosing	0.168	0.979	0.128	0.987
$\text{UV}_{\text{LP}}/\text{NaOCl}$ (5 mg/L) continuous dosing	0.102	0.98	0.096	0.99
$\text{UV}_{\text{LP}}/\text{NaOCl}$ (5 mg/L) continuous dosing / NaHCO_3 (10^{-1} M)	0.055	0.983	0.059	0.986

CONCLUSION

The results of this study indicate that:

1. Monochloramine absorbs photons at 254 nm and can be photolysed by UV light emitted by the lamp we used;
2. Monochloramine can be degraded more rapidly by $\text{H}_2\text{O}_2/\text{UV}_{\text{LP}}$ than by direct photolysis. This is due to the participation of radicals $\bullet\text{OH}$;
3. The $\text{NaOCl}/\text{UV}_{\text{LP}}$ process can form hydroxyl radicals simultaneously with chlorine radicals. The $\text{H}_2\text{O}_2/\text{UV}_{\text{LP}}$ system generates a greater amount of $\bullet\text{OH}$ radicals than the $\text{NaOCl}/\text{UV}_{\text{LP}}$ system. These results are obtained with basis of a probe molecule: TA and at $\text{pH} = 8.78$. The detection is made by PL;
4. $\text{NaOCl}/\text{UV}_{\text{LP}}$ which is also an advanced oxidation process is less effective than $\text{H}_2\text{O}_2/\text{UV}_{\text{LP}}$ in the degradation of monochloramine. This fact can be due to the formation $\text{Cl}\bullet$ that can form combined chlorine during the time exposure to the UV light;
5. The decomposition of monochloramine leads to the formation of nitrate and nitrite whatever the system used;
6. The variation of the spectral absorbance show decrease in the peak at 244 nm (monochloramine peak absorbance) with time and formation of an isosbestic point at 237 nm;
7. The degradation kinetics of monochloramine can be adjusted to a pseudo-first order kinetic model with direct photolysis, $\text{NaOCl}/\text{UV}_{\text{LP}}$ and $\text{H}_2\text{O}_2/\text{UV}_{\text{LP}}$.

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