

Evaluation of a frugal process for water treatment: application of an advanced UV-Chlorine oxidation process in Côte d'Ivoire

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Abstract:

This study concerns the implementation of a frugal process for water treatment in Côte d'Ivoire. Decolorization and decontamination reactions were carried out using a combination of ultraviolet radiation and chlorine. Humic acid and phenol were used as model compounds to monitor process efficiency. These compounds were placed in the presence of a commercial bleach solution in a photo reactor. The photoreactor used was the rayonet with UV-C lamps at 254 nm. Various analyses were carried out, including UV/Vis spectrophotometry at specific wavelengths taken from the literature, 3D spectrofluorimetry (EEM emission-excitation matrices), and UV-coupled high-performance liquid. The experimental results showed an effective decomposition of humic acid and therefore a decolorization, but also consequent degradation of phenol under specific conditions. These effects are most pronounced when UV/chlorine is coupled, from $t = 5$ min (UV/chlorine) $\gg t = 60$ min under UV $\gg t = 120$ min under chlorine. Also, the production of secondary chlorination compounds due to the presence of chlorine was observed, and remains relatively very low during bleach photolysis reactions compared to other cases. The UV/chlorine combination has therefore proved highly effective as a water treatment application, and can be combined with existing treatment processes.

Keywords: Decolorization; Decontamination; Frugal; Humic acid; Phenol; UV/Chlorine.

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1 Introduction

Access to drinking water is still a major issue. In fact, according to a report by the World Health Organization (WHO), there are still around 2 billion people in the world who do not have access to drinking water, causing illness and death every year [1]. Many countries suffer from inadequate or unsuitable drinking water infrastructures for a variety of reasons, including geographical, economic and political realities. This research focuses exclusively on sub-Saharan Africa. In these regions, the situation is worrying. In fact, only 24% of supply services are securely managed with appropriate infrastructure. And for the remaining 76%, water is supplied directly from surface water without prior treatment, or with inappropriate treatment [2]. The main problem in these regions is the often uncontrolled and unregulated pollution of water resources. In the case of Côte d'Ivoire, there are, on the one hand, legal provisions introduced by the government that struggle to be respected, as in the case of the national environmental policy (PNE); and, on the other hand, insufficient awareness, education and information of the population [3, 4]. This is in contrast to Western countries, where measures and programs are better applied and monitored, and where water resources are of better quality and fairly stable [1].

Thus, wastewater, industrial effluents, pesticides and gold mining are the main factors in the pollution of water resources in Côte d'Ivoire and generally in these regions of sub-Saharan Africa [5, 6]. The consequences of this pollution can be seen in the physical and chemical characteristics of the raw water to be treated: color, taste,

odor, toxic compounds and bacteriology [7]. It should also be noted that the effects of climate do not contribute to improving the quality of these waters, due to the reduction and continuous irregularity of precipitation [8].

Until 2018, access to drinking water in Côte d'Ivoire was mainly based on groundwater, which is generally of better quality and less likely to be polluted. However, following a study carried out by SAFEGE, which highlighted the rapid and uneven urbanization of the country's biggest cities, water supply services are having to evolve and are increasingly being provided from surface water, due to water stress. And since surface waters are very much affected by pollution problems, and they require much more effective and adapted means [4, 5, 7].

Scientific research has brought to light various types of treatment processes: chemical coagulation processes, membrane processes such as nanofiltration and ultrafiltration, biological processes using bacteria and advanced oxidation processes such as photolysis, photocatalysis or ozone. [9-11]. However, these processes do not take sufficient account of the financial issues and realities specific to the geographical areas in need. In fact, access to drinking water and sanitation for all in these Sub-Saharan African countries is hampered by a lack of qualified human resources, and often does not receive the financial attention or priority it needs to overcome existing difficulties.

The problem of access to drinking water in Côte d'Ivoire can therefore be summed up in three points. Firstly, the lack

of awareness, education and information; secondly, the poor quality of the water to be treated (which is one of the consequences of the first); and finally, the local and financial inadequacy of the applicable treatment processes. The challenge will therefore be to define and study treatment processes that take into account the realities of these geographical areas, as outlined above.

That said, we cannot deny that efforts are being made to improve Côte d'Ivoire's drinking water supply services. Various projects are underway to meet the UN's 2030 target.

This is how we introduced the concept of "*jugaad innovation*" to address the issues raised above. *Jugaad* is a Hindi term referring to a solution born of intelligence and ingenuity: *making do with what you've got*. This concept was first introduced by Indian researchers to encourage the world to think frugally and flexibly, simply, efficiently with less cost or fewer resources and according to realities. The authors showed that we need to innovate and constantly adapt to the reality of our system. Armed with this notion, we decided to apply this model: *thinking simply while taking existing realities into account to the development of a water treatment process applicable in sub-Saharan Africa, specifically in Côte d'Ivoire* [12].

Similarly, according to a WHO/UNICEF study on drinking water systems in sub-Saharan Africa, only 24% are adapted to needs, 34% are elementary or basic, and the remaining 42% are limited, outdated or non-existent [1]. This perfectly illustrates the inadequacy and insufficiency of existing supply systems. Moreover, water treatment processes in

Côte d'Ivoire are generally a succession of several processes: pre-oxidation or pre-chlorination, coagulation-flocculation, decantation, filtration and a disinfection stage. These sub-processes are fairly efficient, but become ineffective depending on the quality of the resource to be treated, and require significant additional resources. This is because the treatment processes to be applied depend closely on the water resource to be treated [13].

Chlorine has always been widely used as a disinfectant and oxidant for water treatment. Its use has many advantages, including effectiveness against a wide range of pathogens (micro-organisms), lower cost and, above all, continuous protection in distribution networks. Similarly, advanced oxidation processes (AOP) are effective in treating a wide variety of chemical, physical and biological species/components. And, these processes encompass different parameters essentially resulting in oxidation. Among the different types of AOP, are oxidations (H_2O_2 , O_3 and their coupling), photo-oxidations (UV/ H_2O_2 , UV/ O_3), fenton, electrochemical oxidations, heterogeneous photocatalysis and others [9, 14]. In this case, we are interested in the coupling of UV and chlorine in order to increase the efficiency of the oxidizing effect of this process. Indeed, this coupling leads to the formation of reactive oxidizing species ($OH\cdot$; $Cl\cdot$; $O\cdot^-$; $ClO\cdot$, etc.) thanks to the activation of chlorine under the effect of UV radiation, which gives these species a strong oxidizing power; and the most powerful is $OH\cdot$ [15]. In fact, this system has been applied many times in the context of organic pollutants degradation in order to study their efficiency and reaction kinetics [16-20].

The aim of this study is to apply an advanced oxidation process to the existing water treatment process in Côte d'Ivoire, taking into account local constraints and realities. The aim is to define a framework conducive to the application of this not-yet-optimized technology, and thus enable the treatment processes used in Côte d'Ivoire to be improved and adapted. The process consists of combining UV-C radiation with a wavelength of 254 nm and bleach (sodium or calcium hypochlorite). Essentially, this work presents water decolorization, a very important feature for treatment cases in Côte d'Ivoire. Indeed, surface waters show very high levels of color, up to 6000 mg/L Pt/Co (platinum cobalt color scale) according to the Hazen scale. Secondly, water decontamination is to be achieved using UV/Chlorine coupling. The model compounds chosen were humic acid, which occurs naturally in surface waters, for the case of water decolorization. Phenol, found in cosmetics and the plastics and petroleum industries, was chosen as an intermediate for water decontamination [21]. Several experiments were carried out under the effect of chlorine alone, then under UV-C light 254 nm alone and then under their combination. These experiments were monitored qualitatively and quantitatively using 3D fluorescence (Excitation-Emission Matrix), UV/Vis spectrophotometry and high-performance liquid chromatography (HPLC/UV).

2 Materials and methods

2.1 Reagents

Humic acid (HA) and phenol were obtained from Sigma-Aldrich. The commercial solution of sodium hypochlorite

(NaOCl) was purchased from ONYX (France) and kept refrigerated at 4°C. Sodium thiosulfate ($Na_2S_2O_3$), potassium iodide (KI) and acetic acid (CH_3COOH) were of analytical quality. Mineral water from VOLVIC (France) was used as the solvent for the experiments, in order to approximate as closely as possible, the conditions of natural surface waters, and also due to their known compositions. We also opted for the use and preparation of phosphate buffer solutions at different pH values (4, 6, 7, 9 and 11), because of their isotonic and non-toxic properties, enabling us to best describe the actual conditions of the waters to be treated in Côte d'Ivoire.

2.2 Solution preparation

- **Dosage of sodium hypochlorite**

The colorimetric determination of the commercial bleach solution was carried out using solutions of sodium thiosulfate ($Na_2S_2O_3$), potassium iodide (KI) and acetic acid (CH_3COOH). The commercial solution was measured at: $C(ClO^-) = C(Cl_2) = 1.32 \text{ mol/L}$ corresponding to $D^\circ Chl = 29.5$. The required volumes are then added according to the experimental protocols, using a propette. The chlorine concentration chosen for the various experiments is relatively low, in order to be as close as possible to that defined by drinking water standards, but also to minimize the formation of secondary compounds.

To quench the oxidizing effect of chlorine, small volumes of prepared sodium thiosulfate solution was added.

- **Preparation of humic acid (HA) solution**

The HA solution ($C = 20 \text{ mg/L}$) was prepared by dissolving 0.2 g of the compound in 1 liter of mineral water using a volumetric flask. The solution was then stirred overnight and immersed in an ultrasonic bath for 30 s, all at a temperature of 25°C . Finally, the solution was filtered through a $0.22 \mu\text{m}$ membrane filter cartridge to remove undissolved particles. The HA solution was diluted to the desired concentration according to the experimental protocols. In the absence of a TOC meter, the HA solution is quantified each time on the basis of absorbance values obtained from UV/Vis spectrophotometric analyses. Concentrations of HA and Cl_2 used are gathered in table 1.

Table 1

Concentrations used.

Reagent	Humic acid (HA)	Chlorine (Cl_2)
Concentration (mg/L)	20	5

- **Preparation of the phenol solution**

The phenol solution ($C = 0.1 \text{ M}$) is prepared by dissolving 0.9411 g of the compound in 100 mL of buffer solution prepared according to the defined

experimental protocol. Then, a dilution is carried out using a micropipette to obtain $C = 0.1 \text{ mM}$. This solution is placed under stirring for complete dissolution. Concentrations are summarized in table 2.

Table 2

Concentrations used.

Reagent	Phenol	Chlorine (Cl_2)
Concentration (mM)	0.1	0.1

- **Preparation of phosphate buffer solutions**

Buffer solutions at various pH values are used to understand their influence on the reactions produced. These are preparations of Na_2HPO_4 ; $\text{Na}_2\text{H}_2\text{PO}_4$ and NaOH solutions at concentrations of 0.1 or 0.05 M. The method for preparing solutions is showed in table 3.

2.3 Photo UV reactor

The reactor used is the rayonet RPR-200. It is cubic in shape and has a cylindrical plate with several cavities into which quartz tubes can be inserted. UV lamps of selected wavelengths are arranged around the plate. It operates with a cooling fan to stabilize the temperature at around 40°C .

Table 3

Buffer solutions.

pH	Preparation methods
4	For 100 mL of $\text{Na}_2\text{H}_2\text{PO}_4$ add 8.2 mL of NaOH
6	For 100 mL of Na_2HPO_4 add 11.2 mL of NaOH
7	For 100 mL of Na_2HPO_4 add 58.2 mL of NaOH
9	For 100 mL of Na_2HPO_4 add 97.4 mL of NaOH
11	For 100 mL of Na_2HPO_4 (0.05 M) add 6.6 mL of NaOH

2.4 UV/Vis spectrophotometer analysis

The UV/Vis absorbance of the samples was measured using MELTER TOLEDO's UV5BIO spectrophotometer. The measurement range is between $\lambda = 200$ and 800 nm. The instrument is equipped with a quartz cell with a path length of 1 cm. The prepared solutions were analyzed and irradiance intensities by position [22] are shown in the table 4. As a decolorization index for the experimental solution of HA, we used the absorbance at the specific wavelength of 436 nm, specific to chromophore groups [23, 24]. The specific wavelength at 254 nm also reflects the proportion of aromatic compounds with different degrees of activation. It therefore allows us to observe the effective decomposition of humic acid [25].

2.5 MEE fluorescence analysis

JASCO's FP-8500 high-performance spectrofluorometer was used to obtain the excitation emission matrices with high sensitivity. The instrument comprises a xenon arc lamp as radiation source and a sample chamber for quartz cells (10 x 10 mm). Analyses at excitation wavelengths are between 200 and 500 nm, and at emission wavelengths between 250 and 750 nm, with a step width of 5 nm for each wavelength.

2.6 High-performance liquid chromatography HPLC/UV analysis

The high-performance liquid chromatography used is reverse-phase, with an apolar stationary phase. The technical nature of this analysis is based on the existing affinities between the constituents to be analyzed and the mobile stationary phase. After separation on a column, they are then detected by UV radiation according to their characteristic absorption wavelength. In our case, the column used is the Kinetex C18 with a mobile phase of 60% distilled water, 40% acetonitrile and 0.01% sulfuric acid. The liquid flow rate is 0.7 mL/min.

3 Results and discussion

3.1 Decolorization of humic acid solution

3.1.1 Light-free decolorization of HA with chlorine using UV/Vis spectrophotometry

Before bringing the chlorine and humic acid into contact, observation tests were carried out on the humic acid alone under normal temperature conditions to ensure that no changes occurred.

Table 4
Irradiance intensities by position [22].

Wavelength (nm)	Distance from lamp			Units
	Center	2 inches	1.5 inch	
254	12,8	16	21	(mW/cm ²)

Figure 1 displays the UV-Vis spectrum of humic acid along with the area where its decolorization can be observed. Next, the humic acid solution was brought into contact with chlorine under stirring at a known concentration in a closed reactor. The HA absorbance values show a slight, continuous decrease over time. This decrease becomes very slow after 1 h. A similar result was obtained with [26]. Various experiments were carried out over a longer period of 24 hours (Figure 2) to confirm the continuity of the reaction.

The effect of chlorine has been stopped by adding sodium thiosulfate solution to each sample prior to UV/Vis analysis. Absorbance values are very high at wavelengths between 250 and 280 nm as a

result of this neutralization, and this is visible as early as the sample at t=30 min. Even after 24 hours of reaction, there is still a quantity of chlorine found after colorimetric dosage that has not reacted with humic acid. And the A_{436} color abatement rate (absorbance at 436 nm) after 24 hours under these conditions is around 63% ($A_{436}^{24h}/A_{436}^0 = 0.37$).

The same reaction is carried out without the inhibiting sodium thiosulfate solution, in order to better observe absorbance at 254 nm and 292 nm (Figure 3). Note that when the bleach solution is added, an outgrowth occurs at wavelengths around 270-300 nm. This corresponds to the appearance of the UV-vis spectrum of bleach at the particular pH level of 7 (Figure 4).

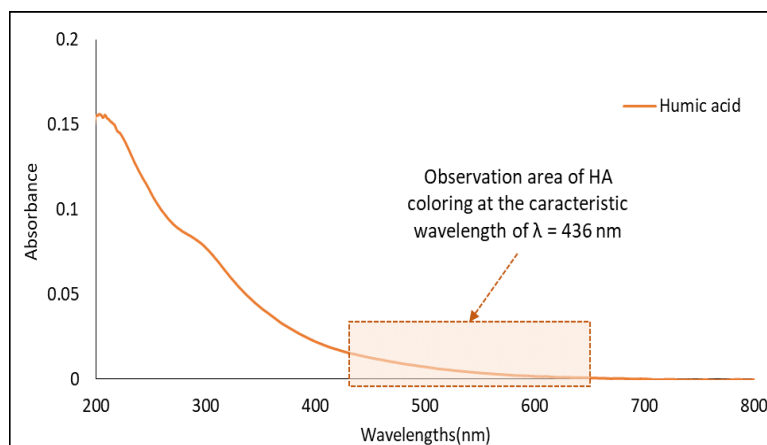


Fig. 1. UV/Vis spectrum of humic acid prepared at 20 mg/L.

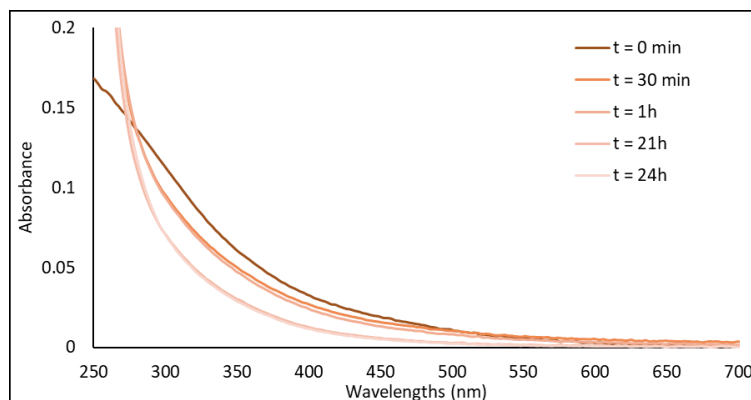


Fig. 2. UV-Vis spectrum of the decomposition of HA versus time without buffer solution (24 h) ($C_{HA}^0 = 20$ mg/L ; $C_{chlorine}^0 = 5$ mg/L ; $pH_{initial} = 7.21$).

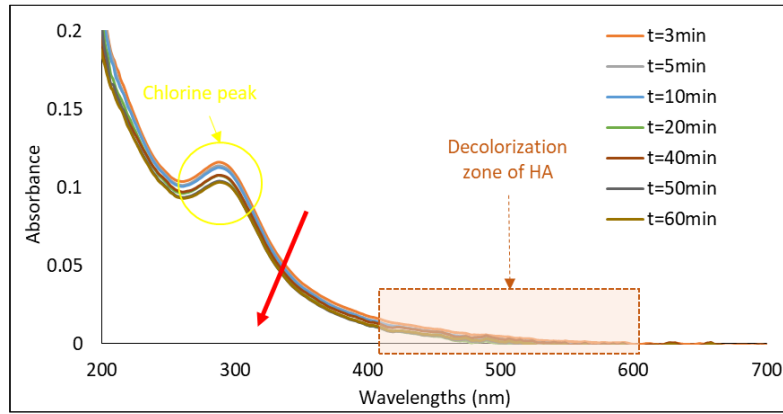


Fig. 3. UV-Vis spectrum of the decomposition of HA versus time without buffer solution ($C_{HA}^0 = 20$ mg/L ; $C_{chlorine}^0 = 5$ mg/L ; $pH_{initial} = 7.21$).

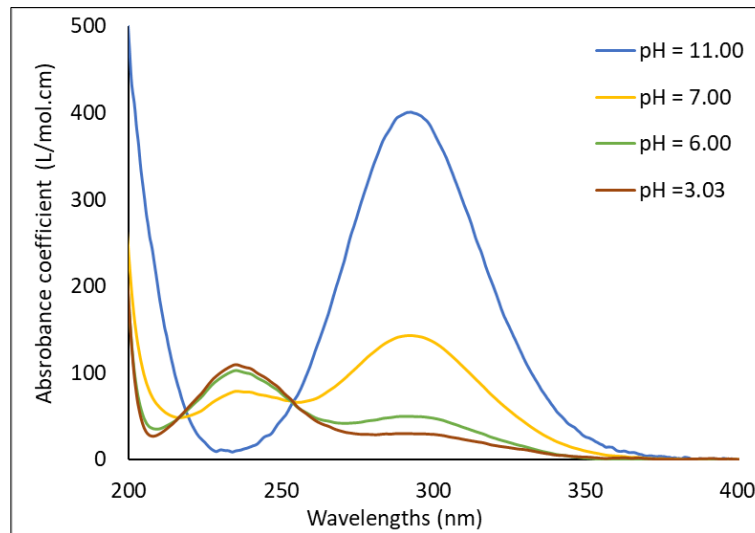


Fig. 4. UV/Vis spectra of bleach at different pH levels.

After 10 min of reaction, the color abatement rate reaches around 37% ($A_{436}^{10min}/A_{436}^0 = 0.63$). After 1 h of reaction, this rate approaches 58% ($A_{436}^{1h}/A_{436}^0 = 0.42$), and reaches 63% after 24 h of reaction ($A_{436}^{24h}/A_{436}^0 = 0.37$). Thus, humic acid decolorization occurs fairly rapidly during the first hour and becomes practically slow thereafter. It should be noted that the decolorization reaction is most significant during the first 10 minutes of the reaction, and its speed decreases

drastically after 30 min of contact with the bleach.

At wavelength $\lambda = 254$ nm, the experimental results of the UV-Vis spectrum of HA are somewhat confused with that of bleach. It is therefore difficult to give clear information on the evolution of aromatic compounds. As for the outgrowth at $\lambda = 292$ nm corresponding to the presence of chlorine, it is still present after 1 hour and decreases slowly after the first 10 minutes (Figure 5).

3.1.2 Decolorization of HA under UV light using UV/Vis spectrophotometry

An identical humic acid solution as above was exposed to UV light using the Rayonet RPR-200 photoreactor, without bleach. Figure 6 shows the evolution of these UV-Vis spectra during this reaction. Absorbance values gradually decrease, and after 1 h of reaction, the color abatement rate reaches around 90% ($A_{436}^{1h}/A_{436}^0 = 0.1$). Thus, the solution is practically discolored after 1 h.

Simple photolysis of humic acid also shows the appearance of two clearly observable peaks for 30 min of reaction (Figure 6). These peaks appear at 235 nm and 300 nm, respectively, and can be explained by the decomposition of chromophore and fluorophore fractions (double bonds, phenolic and aromatic compounds) [24]. It is also reflected in the progressive decrease in absorbance at 254 nm. The evolution curve of the abatement rate at $\lambda = 436$ nm decreases with the same trend as that at 254 nm (Figure 7).

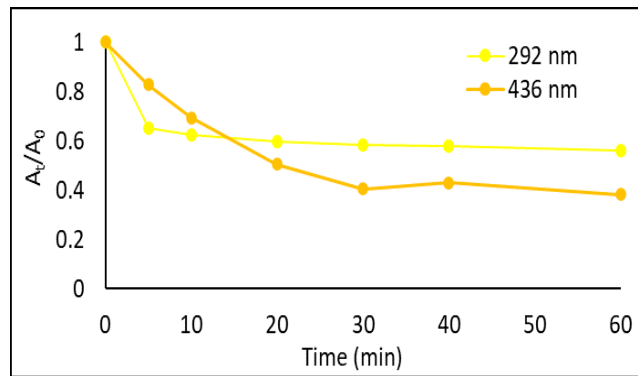


Fig. 5. Evolution of absorbance at 292 nm (chlorine) and 436 nm (HA color) during reaction of HA with chlorine.

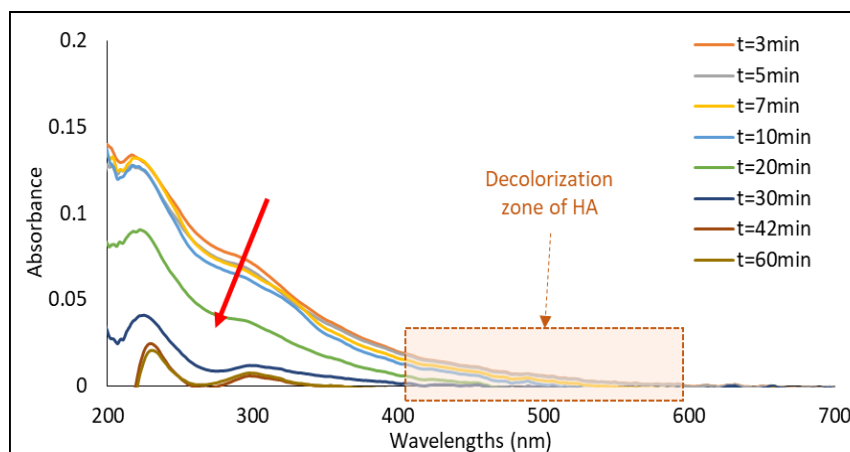


Fig. 6. UV-Vis spectrum of the decomposition of HA versus time under UV254 radiation ($C_{HA}^0 = 20$ mg/L ; $pH_{initial} = 7.23$).

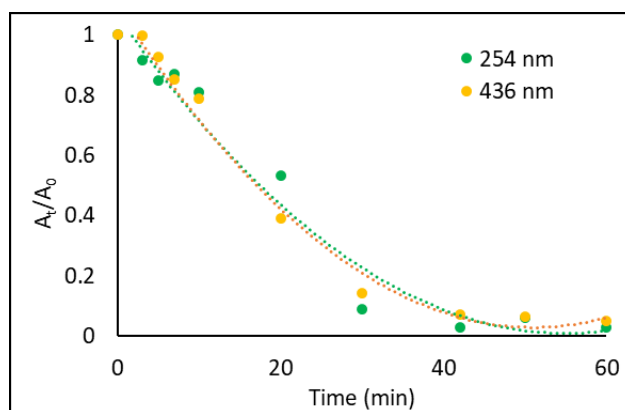


Fig. 7. Evolution of absorbance at 254 nm (aromatic compounds) and 436 nm (HA color) during reaction of HA under UV254.

3.1.3 Decolorization of HA with light in the presence of bleach via UV/Vis spectrophotometry

The reaction of HA solution in the presence of chlorine and under UV254 irradiation was carried out in the Rayonet photo reactor under the same initial conditions (concentrations and ratios). This reaction is much faster than the previous ones, so much so that it is impossible to observe the formation of intermediate peaks (Figure 8).

Figure 8 shows a rapid disappearance of chlorine as early as 5 min into the reaction, as the outgrowth at $\lambda = 292$ nm disappears while decomposition continues. This decomposition continues without the presence of chlorine and becomes slower. As a result, almost 90% of the HA is decolorized, as the absorbance at $\lambda=436$ nm is very low or even non-existent after 10 min. Chlorine photolysis is therefore a very rapid photo-oxidation reaction.

3.1.4 Evolution of bleaching kinetics

Figure 9 shows the decrease in the characteristic color wavelength $\lambda = 436$ nm under the different experimental conditions performed. This clearly demonstrates that photolysis of bleach \gg simple UV photolysis \gg simple oxidation to bleach. Also, it should be noted that the reaction evolves with the duration of UV exposure. And, having the necessary data for the determination of the bleach rate constant, the HA+UV reaction was stopped at 40 min. We also placed an HA solution under UV irradiation after 1 hour of reaction in the presence of bleach, in order to confirm the rapid photolysis effect of bleach; and subsequently, a similar HA solution after 1 hour of reaction in the presence of bleach, to which we added sodium thiosulfate in order to neutralize the bleach before exposing this solution to UV irradiation. In the first case, HA decreases more rapidly than in the second (Figure 9). Consequently, the presence of bleach (chlorine) in this system is important.

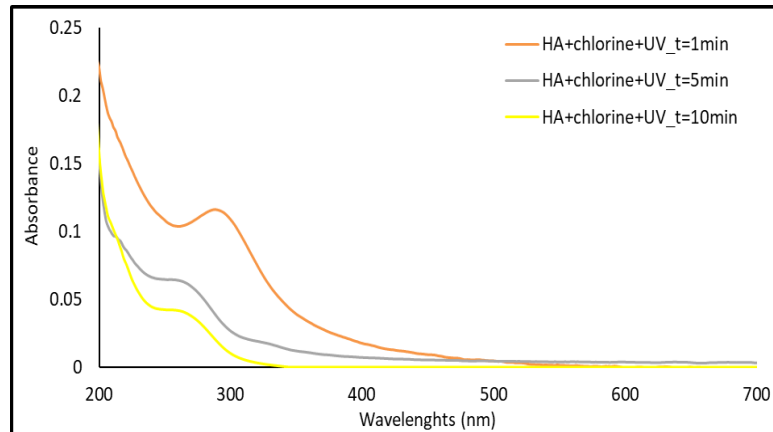


Fig. 8. UV-Vis spectrum of the decomposition of HA in presence of chlorine versus time under UV254 radiation ($C_{HA}^0 = 20$ mg/L ; $C_{chlorine}^0 = 5$ mg/L ; $pH_{initial} = 7.21$).

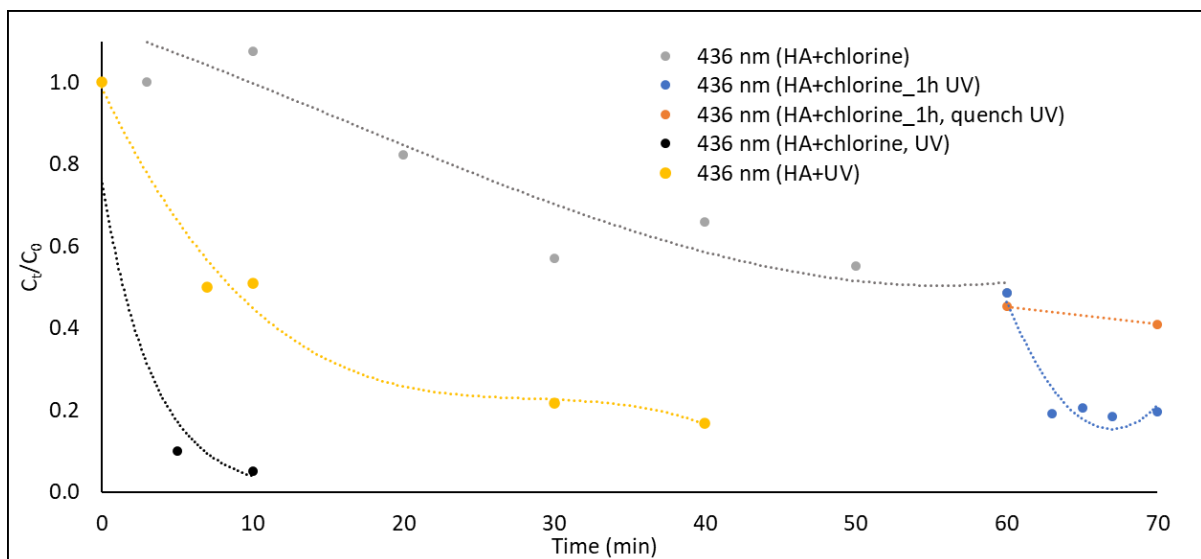


Fig. 9. Synthesis and comparison of reactions (chlorine vs UV vs UV/chlorine).

It can be noted that, exposure to UV radiation causes greater decolorization than exposure to chlorine alone. This is probably due to the fact that UV light causes chemical bonds to break, releasing chemical groups or compounds responsible for this rapid fading. Chlorine, on the other hand, also acts by oxidizing these chemical groups and causing some breaks, resulting in a slower decolorization of the solution. The combination of these two systems results in even greater decolorization: they have a synergistic effect [15]. The kinetics of these

reactions were determined from experimental results obtained by UV/Vis spectrometry, and can be seen in figure 10. The determination coefficient expressed for each plot is close to 1, enabling us to deduce a first-order kinetic reaction. Thus, all these decolorization reactions under these different conditions follow pseudo-first-order kinetics [27]. A number of experiments were carried out to reduce the uncertainty of these results. The velocity constants deduced are shown in table 5.

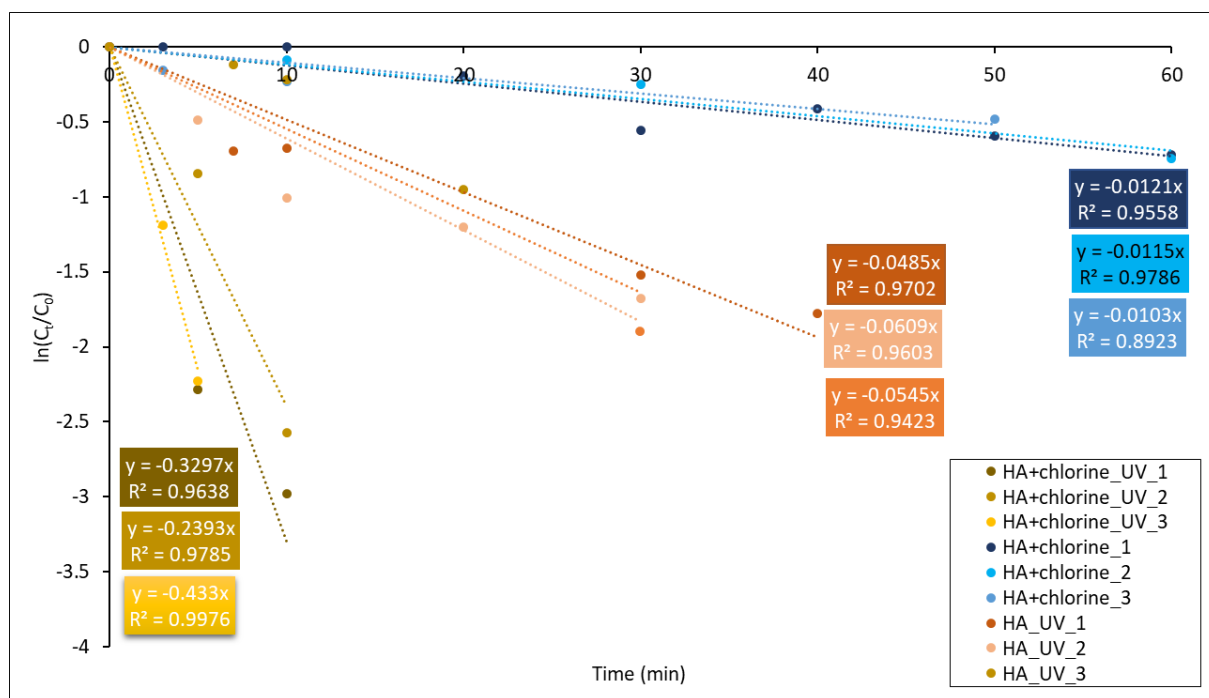


Fig.10. Kinetics reaction of decolorization of HA under different conditions (chlorine; UV; UV/chlorine).

Table 5

Deduced rate constants.

Conditions	Rate constant k (min ⁻¹)
Bleach (chlorine only)	0.012
UV	0.048
UV/Chlorine	0.433

3.1.5 Decolorization of HA analyzed under MEE fluorescence

The analytical sophistication of fluorescence provides better information on decolorization, in particular on fluorophore and chromophore groups, depending on the wavelength applied. This spectrochemical method offers greater sensitivity and selectivity than the UV/Vis method [25, 28-31]. And, over the last few decades, fluorescence has been used extensively in

the application of water treatment processes. Figure 11 shows the application to our study.

The initial sample of HA shows a broad peak of fluorescence intensity at the excitation wavelength of 254 nm and the emission wavelength of 450 nm. This peak reflects the presence of aromatic and aliphatic functional groups in humic acid.

Figure 12 shows the intensities of emission spectra obtained at the 254 nm excitation wavelength.

In the case of UV/chlorine coupling, the intensities of emission spectra decrease progressively but are still present at very low levels. As a result, even though decolorization is complete, there are still compounds or species resulting from these oxidation reactions that need to be

identified and quantified. However, the supramolecular structure of humic acid makes this difficult. It is therefore ideal to turn to a simpler organic molecule (phenol), enabling us to observe and identify the species produced and their reaction mechanisms.

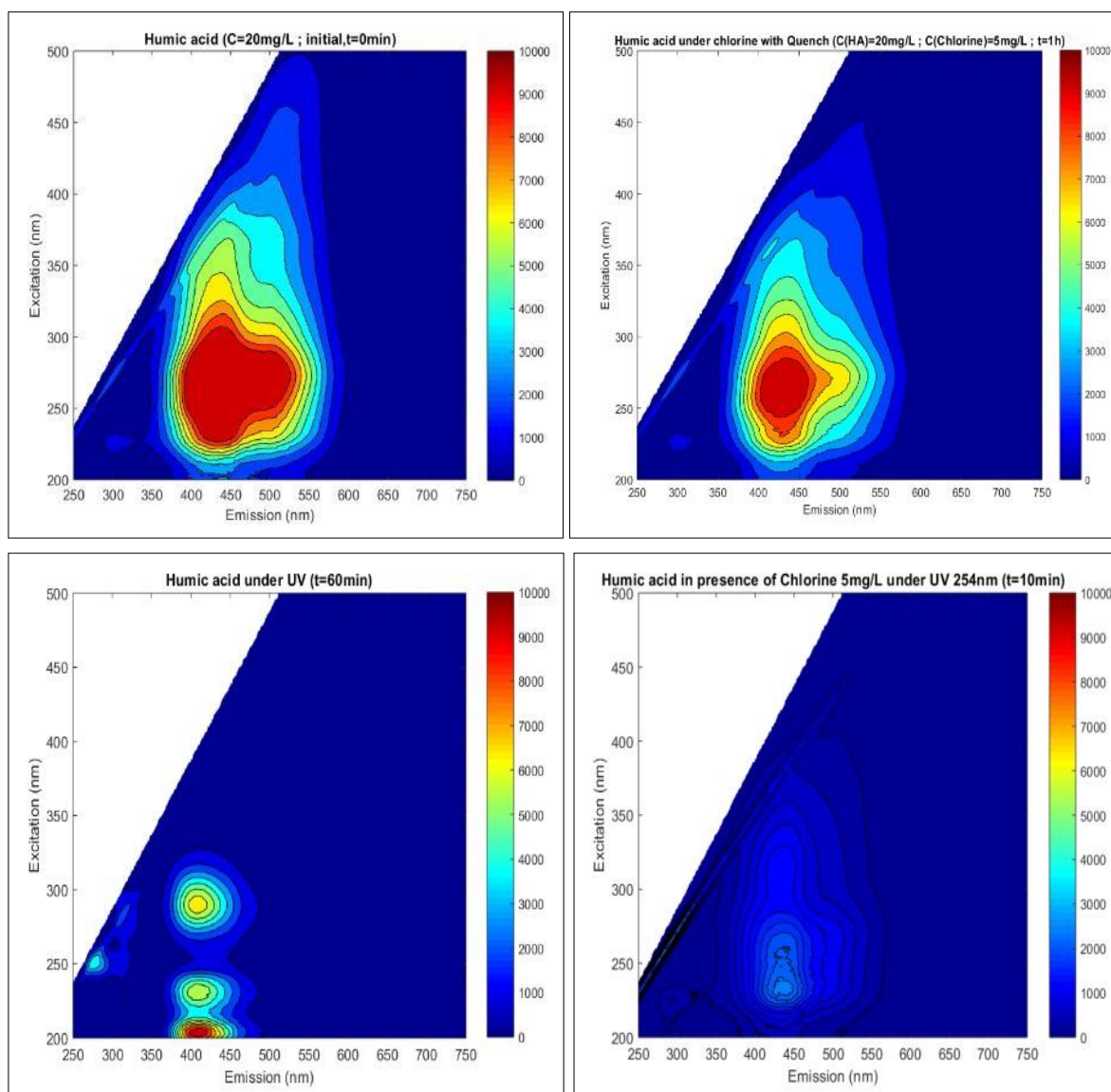


Fig. 11. EEM fluorescence diagrams of HA solution under different conditions: chlorine 1 h with quench; UV 1 h; UV/Chlorine 10 min.

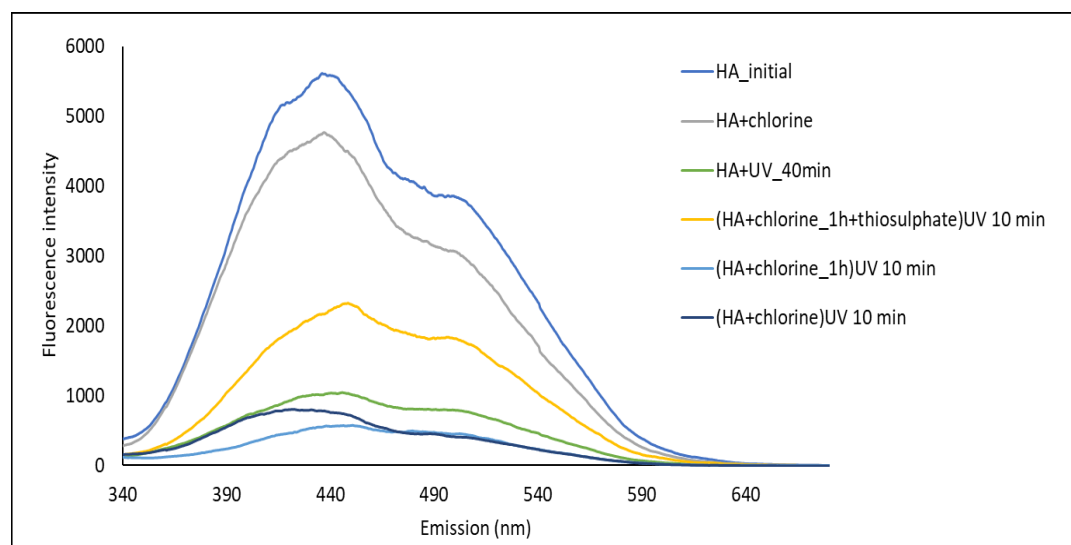


Fig. 12. Intensities of the obtained emission spectra.

3.2. Water decontamination: phenol application

3.2.1 Effect of pH

It should be noted that we will dwell specifically only on neutral and basic media due to the research context, but also to many existing results on acid medium [32]. Figure 13 shows the evolution of the phenol spectrum at different pH levels. Also, the reaction of phenol in the presence of bleach at different pH is shown in figure 14. The reaction at pH=11 is the fastest: 80% of the phenol is degraded after 30 min. The reaction at pH=7 is fast from the start, then becomes constant after 5 min. Under the effect of UV light in the Rayonet photo reactor, phenol degradation is much more rapid and complete: after 5 min at pH=11 and 10 min at pH=7, due to the pH-dependent UV/Vis absorption coefficient of this model molecule (Figure 15). In the presence of the UV/chlorine system, the reaction is even 2 times faster in less than 5 min (Figure 16). The synergistic effect of this coupling is again verified. This can be explained by

the fact that under UV light, phenol and bleach have specific absorption coefficients at the 254 nm wavelength.

3.2.2 Secondary chlorination compounds formed

Although the phenol disappears rapidly, the compounds formed have been observed and identified. These are chlorinated compounds, notably chloro-phenols: 2-methylchlorophenol (2-MCP), 4-methylchlorophenol (4-MCP) and 2,6-dichlorophenols (2,6-DCP) [33]. These compounds were quantified by HPLC/UV and their evolution over time as a function of pH are shown in figures 17 to 19. At pH = 7, a small quantity of 2-MCP and its isomer 4-MCP was found at the beginning, disappearing very rapidly over time. Concentrations of chlorinated compounds are higher during reactions in contact with bleach, which has been widely reported in the literature (the formation of secondary chlorination compounds) [34-37]. However, the chlorinated compounds formed are very weak during the photolysis of bleach and are sometimes present in the reaction

process as intermediates and then degraded. As a result, UV/chlorine coupling reduces the production of chlorinated

compounds [38]. Figure 20 shows the evolution of chlorination rates according to the pH and experimental conditions applied.

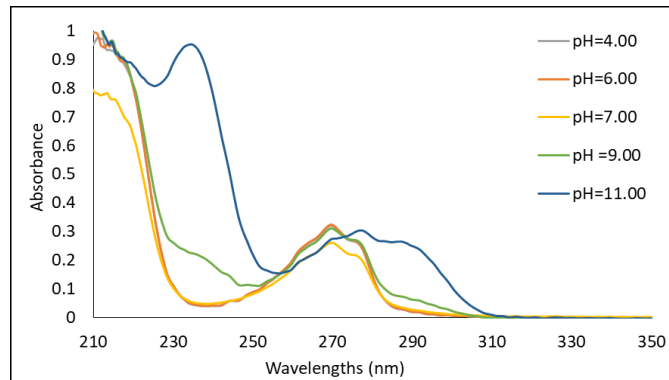


Fig. 13. UV/Vis spectrum of phenol prepared at 0.1 mM at different pH values.

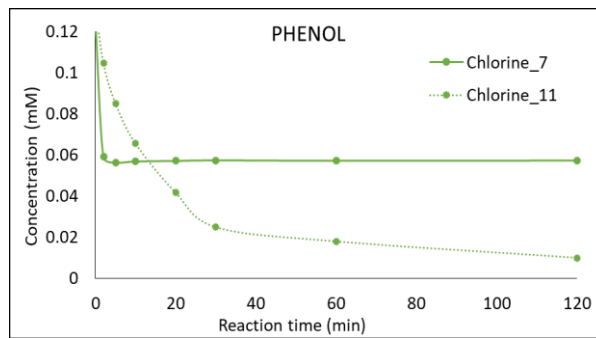


Fig. 14. Phenol degradation in the presence of bleach and without UV.

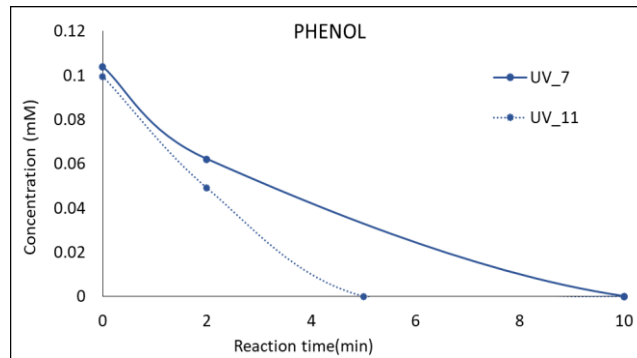


Fig. 15. UV degradation of phenol (pH = 7 and 11).

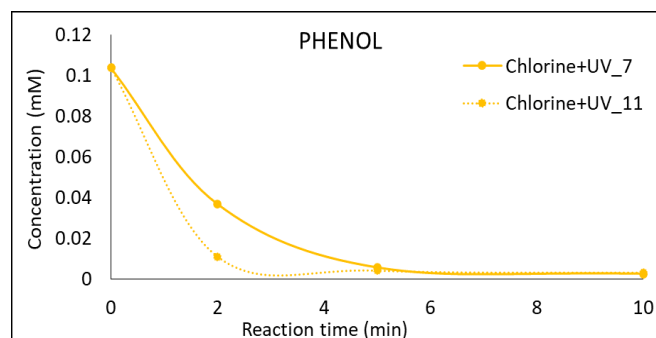


Fig. 16. Phenol degradation under UV/Chlorine (pH = 7 and 11).

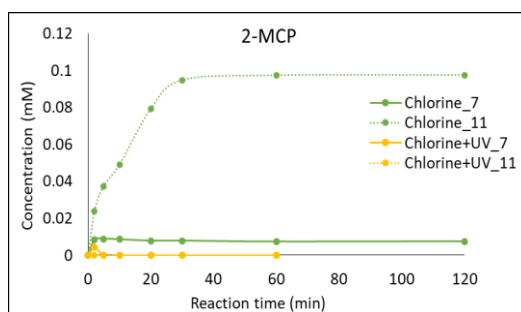


Fig.17. Evolution of 2-MCP.

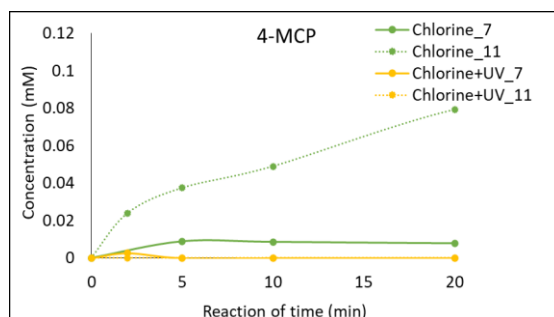


Fig. 18. Evolution of 4-MCP.

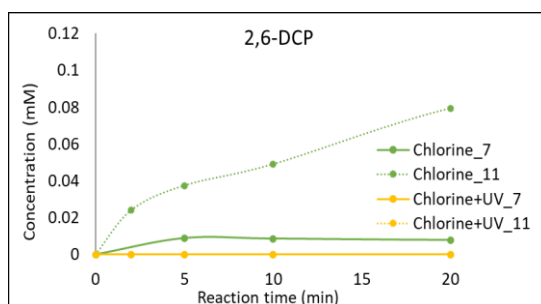


Fig. 19. Evolution of 2,6-DCP.

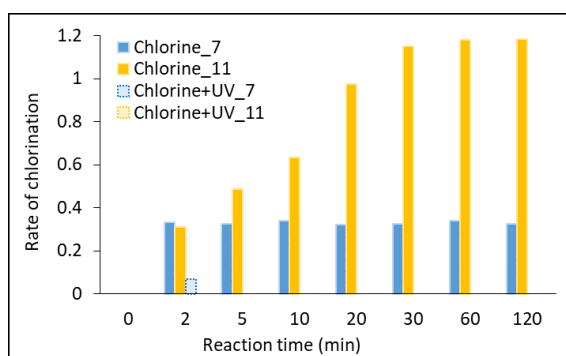


Fig. 20. Chlorination rate of phenol.

3.2.3 Molar balances and proposed reaction equation model

Molar balances were calculated for all species identified by UV HPLC. Figure 21 shows a comparison of these balances over

time and according to experimental conditions. The molar balance is virtually zero for reactions under bleach photolysis. Phenol degradation is therefore complete under these conditions, producing carbon dioxide and water ($\text{CO}_2 + \text{H}_2\text{O}$). For reactions in the presence of bleach alone,

the molar balance of species is virtually constant throughout, resulting in the presence of secondary chlorination compounds. The degradation of phenol under photolysis of bleach involves the formation of a number of intermediate compounds, which we were unable to observe due to the rapidity of the bleach photolysis reaction [15]. These quinone-type compounds open

the aromatic ring to give aliphatic chains, which are then progressively reduced to CO₂ and H₂O. Under the influence of UV radiation, monomolecular and bimolecular reaction mechanisms are possible, depending strongly on pH and radiation wavelength [15, 39]. The proposed model reaction equations are gathered in figure 22.

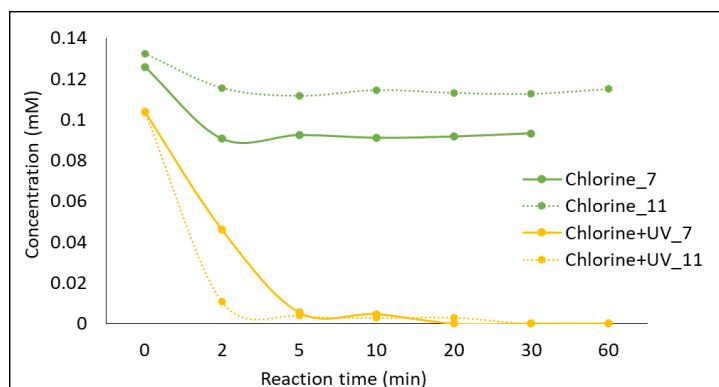


Fig. 21. Molar balance of reactions in the presence of phenol (chlorine, UV).

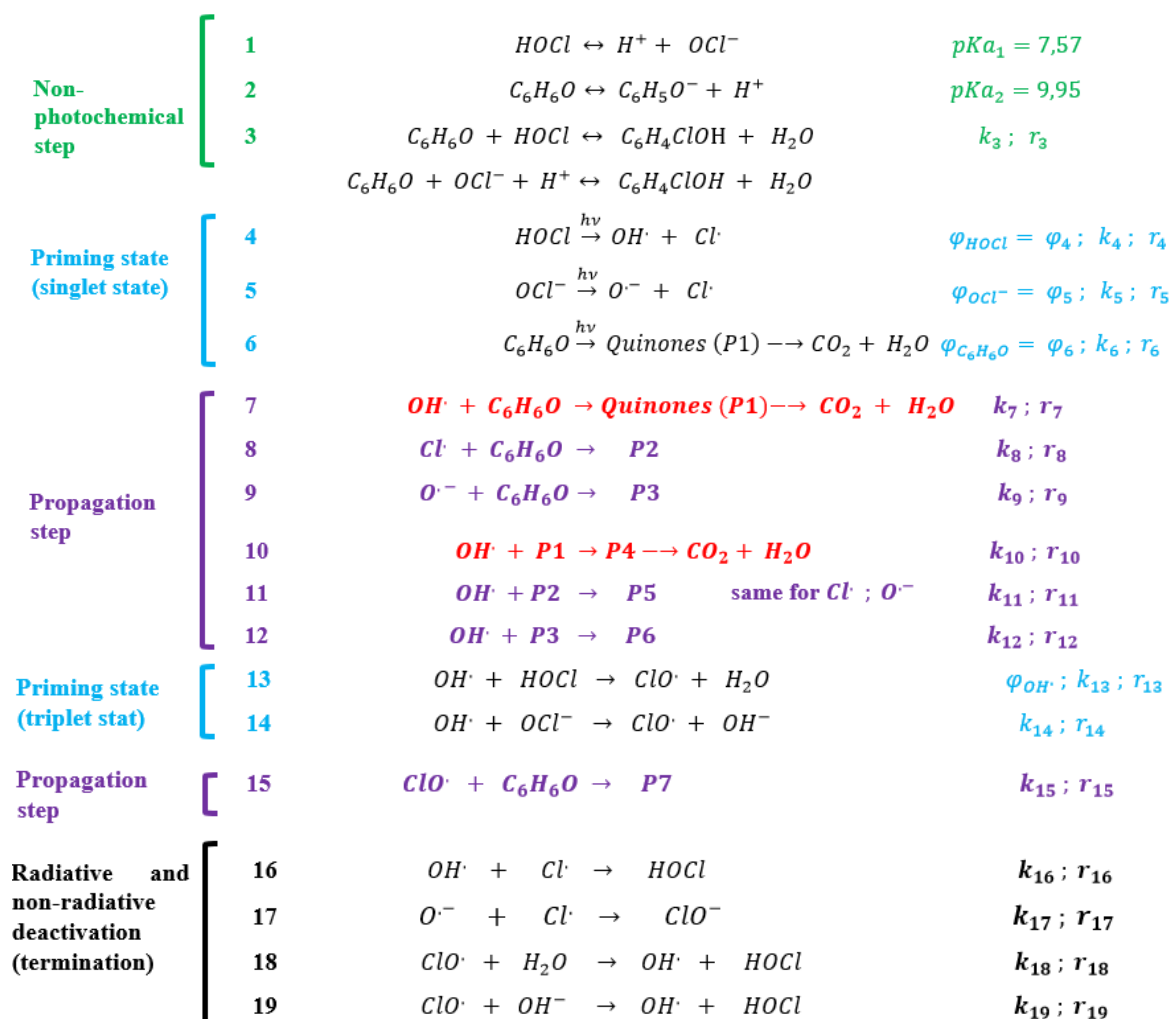


Fig. 22. Set of possible reaction equations.

4 Conclusion

Experimental results show that both humic acid and phenol degradation are significantly influenced by ultraviolet (UV) radiation and the presence of bleach (sodium or calcium hypochlorite). The data suggest that combined exposure to UV radiation and chlorine results in greater degradation of humic acid than exposure to either alone. This leads to a synergistic effect between the oxidative properties of UV radiation and the reactive nature of the free radicals produced when chlorine is irradiated. UV-Vis spectra show that during HA decolorization, some aromatic and aliphatic functional groups are more resistant to degradation than others, and the decolorization process is time-dependent and non-uniform. The pseudo-first-order reaction was also confirmed. Excitation-emission matrix (EEM) fluorescence showed that decolorization of humic acid under combined UV and chlorine irradiation is efficient and rapid, with 90% of humic acid decolorized in just 5 minutes. This almost complete decolorization was achieved by degradation of the chromophore and fluorophore chemical groups under UV254.

Thanks to HPLC/UV, some intermediate compounds were identified. Secondary chlorination compounds were identified under reactions in the presence of bleach alone, but become very weak under the UV/chlorine system. Moreover, molar balances enabled us to affirm that phenol degradation under UV/chlorine is total and not that under simple oxidation of bleach.

From the above, two possible types of photolysis are introduced: direct photolysis and indirect photolysis. Direct photolysis

refers to the direct effect of ultraviolet light on the model compound, i.e. photochemical degradation; and indirect photolysis refers to the action of photons on the intermediate molecule, preferably bleach, which then induces a reaction with the chosen model compound. More specific research is required, and the application of UV-B LEDs is planned in order to correctly model possible reaction mechanisms according to pH and determine all the main possible reactions, as this system presents a wide range of radicals.

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