Decolorization Kinetics of Ponceau S Dye
by Chemical Chlorination:
A Comparison with Sunlight/ Chlorine and UV/Chlorine Processes

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ABSTRACT: *Aqueous chlorination of Ponceau S dye (PS) was kinetically investigated through a classical method and under solar or UV radiations. For the classical method, the kinetics of PS chlorination was established by varying concentration ratios R = [Free chlorine (Cl(+I))]/[PS], pH, temperature, and bromide ions concentration. The decolorization reactions exhibited pseudo first-order kinetics with respect to Ponceau S dye and their apparent rate constants (k_{app}) increased when R increased, in fact, k_{app} reaches 0.205 min^{-1} when R=10. Important removal levels were obtained when pH= 10, 100% of decolorization obtained at only 5 minutes which means that the hypochlorite ion (ClO$^-$) was more reactive than hypochlorous acid (HClO) for decolorizing PS dye. Otherwise, the apparent rate constant of PS disappearance increased with increasing medium temperature and led to the activation energy of 39.64 Kj/mol. When bromide ions were present in the medium, the decolorization of the PS solutions was more important than the simple chlorination when R=2.5 and at pH 7.20 following an oxidation result of bromide ions by sodium hypochlorite to hypobromite and/or hypobromous acid, the addition to the N=N double bond of dye is easier in the case of Br(+I) than Cl(+I). Under UV or solar radiations, and when R=1 and at pH 4.5, the decolorization rates of PS solutions were clearly increased in comparison with dark chlorination. Thus, the comparative order obtained in terms of apparent rate constant was k_{app}(Cl(+I)/UV)> k_{app}(Cl(+I)/Sunlight)> k_{app}(Cl(+I)). The disappearance efficiencies were 47.6%, 52.4% and 99.2% respectively when using dark chlorination, Cl(+I)/Sunlight and Cl(+I)/UV processes. Thus, it was clear that the advanced oxidation processes have proven to be more effective in terms of water treatment by chlorination. Thus, compared with dark chlorination, the enhanced decolorization of PS could be attributed to the formation of reactive radicals that adopt essentially radical mechanisms that are faster compared to molecular attack.*

KEYWORDS: *Ponceau S dye; UV/Free chlorine; Sunlight/Free chlorine; Bromide ions; Kinetics.*

INTRODUCTION

Dyes are widely used in printing, food, cosmetics and clinical needs, especially in the textile industries for their chemical stability, ease of synthesis and variety of colors [1]. Among the many families of synthetic dyes, azo dyes are the most widely used (60 to 70%). However, these dyes, recognized as compounds with the highest bio-recalcitrance and toxicity due to their double bond N=N [2] are at the origin of the pollution once they are disposed of in the environment [3, 4]. The rejection of these compounds into the environment is undesirable not only for aesthetic reasons but also because their byproducts are toxic to aquatic life and mutagenic to humans [5-7].

There are several physical, chemical and physico-chemical methods of water depollution, including membrane filtration, coagulation-flocculation, adsorption, ion exchange, reverse osmosis, advanced oxidation processes and chlorination [8-15].

Various researches about the removal of Ponceau S azo dye have been conducted and reported in the literature by using different methods such as Advanced Oxidation Processes (AOPs) which are defined as the oxidation processes involving the generation of hydroxyl radicals (OH·) in enough quantity to effect water purification [16-18].

However, there is a lack of recent research using chemical chlorination especially for the Ponceau S dye. In fact, chemical chlorination is considered one of the most widely-used drinking water disinfection approaches in the world, owing to its low cost and high effectiveness against many pathogens as well as its stability in protecting microbiological quality.

The decolorization process using sodium hypochlorite (NaOCl) or chlorine gas, relies on electrophilic attack of the azo group and subsequent cleavage of the chromophore group (responsible for dye color) [19]. Elsewhere, in the presence of bromide ions and according to the operating conditions, chlorination can easily generate bromine oxidants such as bromine and Br(+I) which are more reactive than chlorine with organic micopollutants [20,21].

A combination of sunlight, UV irradiations and free chlorine has proven to be a promising wastewater treatment technique among other photoreactive systems. Recent studies have proposed the UV/chlorine process as a good alternative to UV/H_2O_2 due to its higher removal efficiency for organic pollutants [22-24].

During UV/chlorine process, chlorine is activated by UV photolysis to produce various reactive species such as hydroxyl radical (HO·), Chlorine Radical (Cl·) and ozone (O_3) [25]. The radical species react with the free chlorine present in the system to form other secondary radicals such as ClO·, ClOH·- and Cl_2·- [26].

This study aims to evaluate the decolorization kinetics of the Ponceau S (PS) dye, by chemical oxidation using free chlorine (HClO and/or ClO-) as oxidant and also in combination with sunlight and UV irradiations. At the first step, the evolutions of chlorination reactions were followed at different pH values and mass concentration ratio R = [Cl(+I)]/[PS]. The effect of temperature was also evaluated.

Elsewhere, we were interested in the study of the influence of bromide ions (Br-) on the chlorination of PS aqueous solution by BrO- and HOBr species, produced through the reaction of bromine with free chlorine. In fact, the evolution of chlorination reaction in presence of bromide ions was followed at different mass concentration ratios.

Finally, preliminary steps were designed to evaluate the effects of solar or UV irradiations on PS chlorination. The disappearance kinetics of PS was investigated at pH of 4.5 and a concentration ratio R of 1.

EXPERIMENTAL SECTION
Reagents

Sodium salt of Ponceau S (analytical grade) was from REACTIFS RAL. Its molecular formula is $C_{22}H_{12}N_4O_{13}S_4Na_4$ (FW =760.6 g/mol) with color index Number 27195. The structure of the Ponceau S is shown in Scheme 1.

The chemicals used for this study were sulphuric acid (98%) from scharlau chemie S.A, sodium hydroxide (98%) and potassium chloride (99.5%) were from Scharlab S.L. To obtain free chlorine for experiments, we used commercial concentrated bleach (12 degrees). The sodium metabisulfite (95%) was from Panreac while boric acid (99%), potassium dihydrogen phosphate (98%) and potassium bromide (99.5%) were from Riedel de Haën.

All reagents were used without further purification. Fresh solutions of free chlorine were prepared from the stock solution. Concentrations of free chlorine in stock solutions were measured out by iodometry titration.
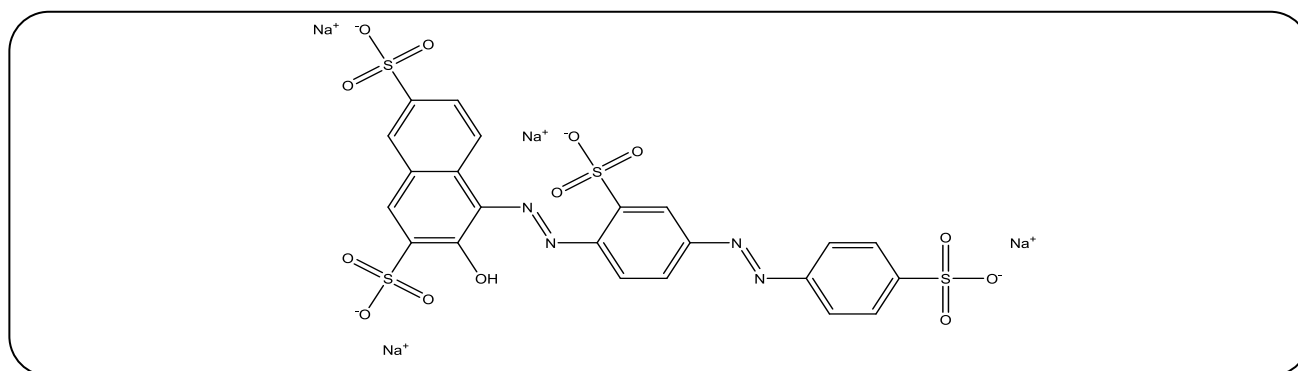
Scheme 1: Molecular structure of sodium salt of Ponceau S.

All experiments were carried out in volumetric flasks which were quenched in chlorinated aqueous solutions.

All aqueous solutions were prepared with ultrapure water (VWR Puranity TU 3 UV/UF Ultrapure Water System).

Procedure

Chlorination under various conditions as indicated, was carried out in volumetric flasks covered by aluminum foil and the PS removal efficiency was evaluated by using UV-vis spectrophotometer at $\lambda_{max}= 520$ nm.

For appreciating the effect of the free chlorine concentration, experiments were conducted by mixing constant volumes of PS solution (50 mg/L) prepared using buffer solution pH 7 to progressive volumes of diluted free chlorine solution (0.3 g/L).

To establish the effect of pH on the decolorization of PS aqueous solutions, three pH values (4.5, 7.8 and 10) were selected. The buffer solutions of 4.5 and 7.8 were prepared by sodium hydroxide and potassium dihydrogen phosphate whereas pH 10 was prepared by sodium hydroxide, boric acid and potassium chloride. The initial mass concentration ratio [Free chlorine]/ [PS] of 3 was kept for each test.

In order to examine the effect of temperature on Ponceau S aqueous chlorination, experiments were carried out in 50 mL volumetric flasks. Each experimental run was performed by taking an appropriate amount of stock dye solution followed by the addition of hypochlorite ion solution. Samples were taken out from reaction medium periodically using a pipette and were immediately analyzed and then returned to the graduated flask.

In this step, sodium metabisulfite is added to stop the reaction until the mixture returns to ambient temperature.

To observe the effect of bromide ions on the chlorination of azo dye (PS) aqueous solutions, experiments were conducted by mixing constant volumes of PS solution (50 mg/L) to progressive volumes of Br (+I) solution (0.43 g/L). The pH of the two solutions was adjusted with sodium hydroxide for basic and by sulphuric acid for acidic media.

The effect of natural sunlight on chlorination kinetic was carried out in a Pyrex beaker which was completely opened to the air. However, chlorination experimental tests with UV-irradiated have led us to use a double quartz wall-jacket containing a high-pressure mercury lamp (Ingelec). The jacket, in which a continuous flow of water was maintained, has been immersed in the reaction medium at an adequate depth.

The Sunlight/Free chlorine and UV/Free chlorine photolysis were initiated by adding the free chlorine ([Free chlorine] = 0.6 g/L, pH 4.5) to a reaction flask containing the solution of PS ([PS] = 100 mg/L, pH= 4.5), pH of the PS and free chlorine solutions was adjusted with sulphuric acid.

For all experiments, analytic samples of 5 mL were withdrawn at known intervals and analyzed using the UV–Visible spectrophotometer. Decolorization of PS dye was monitored by measuring the absorbance at a maximum absorption wavelength of 520 nm.

Analytical methods

Concentrations of Ponceau S aqueous solution were followed by measuring the absorbance at 520 nm using a UV–Visible spectrophotometer (RAYLEIGH UV-1800) and cells were quartz model and have 1cm as optical length.

The disappearance efficiency of Ponceau S was calculated as followed:

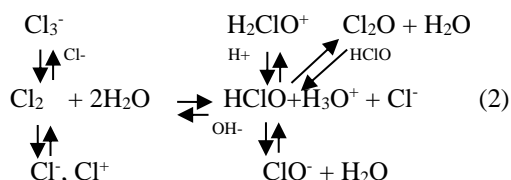$$\text{Disappearance efficiency}\,(\%\,) = \left(1 - [PS]_t \,/\, [PS]_0\right) \times 100 \quad (1)$$

Where $[PS]_0$ is the initial concentration of Ponceau S, and $[PS]_t$ is the mass concentration of Ponceau S at reaction time. It should be noted that the ratio $[PS]_t / [PS]_0$ can be easily confused with A_t / A_0 since that Beer-Lambert law was properly respected in the studied range of the PS concentration.

RESULTS AND DISCUSSION

Distribution of free chlorine species at various pH in aqueous medium

The UV spectra observed at various pH media (Fig. 1) show two absorption maxima at 236 and 292 nm with two isobestic points at 217 and 254 nm. The bands above mentioned were attributed to hypochlorous acid (λ_{max}= 236 nm) and its conjugate base (λ_{max}= 292 nm). The observed variations in spectra, by varying pH, are due to the evolution of acid-base equilibrium. When the pH falls below 4, the molecular chlorine (Cl_2) is formed [27, 28].

Under various conditions, there are other existing forms of chlorine such as hypochloronium acidium ion (H_2OCl^+), chloronium ion (Cl^+) and chlorine radical ($Cl^{\cdot}$) (eq.2) [29, 30].

$$
\begin{array}{ccc}
Cl_3^- & H_2ClO^+ & Cl_2O + H_2O \\
\Big\updownarrow {\scriptstyle Cl^-} & {\scriptstyle H^+}\Big\updownarrow\Big\uparrow {\scriptstyle HClO} & \nearrow \\
Cl_2 \;\; + 2H_2O & \rightleftharpoons \;\; HClO + H_3O^+ + Cl^- & (2) \\
\Big\updownarrow & {\scriptstyle OH^-}\Big\updownarrow & \\
Cl^-, Cl^+ & ClO^- + H_2O &
\end{array}
$$

UV-Visible absorption spectra of aqueous solutions of PS at various pH

The UV-visible spectrum of PS exhibits four distinguishable absorption bands, three in the UV region (238, 311 and 351nm) and one in the visible region (520 nm) with a shoulder about 490 nm. While the bands at 311 and 351 nm ascribed to the $\pi\rightarrow\pi^*$ transitions representing two adjacent rings (naphthalene ring). The band at 238 nm is attributed to the $\pi\rightarrow\pi^*$ transition within the benzenoid system. The band in the visible region (λ= 520 nm), responsible for the color, is attributed to the absorption of the $n\rightarrow\pi^*$ transitions of N=N chromophore group [31, 32].

The UV-vis spectra of PS at different pH values are presented in Fig. 2.
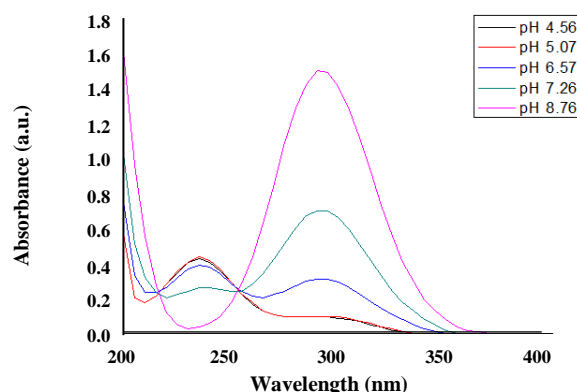

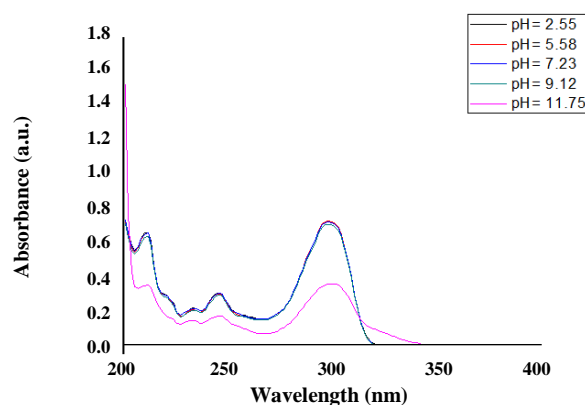*Fig. 1: UV spectra of free chlorine aqueous solution at various pH values.*

Fig. 2: UV-Visible absorption spectra of PS aqueous solution at different pH values, $[PS]_0$= 6.57.10^{-5}M.

Fig. 2 shows a batochromic and hypochromic shifts at higher pH values, especially for azo group band. This change is attributed to structural modification yielding an increased conjugation in the PS molecule.

Effect of concentration ratio [free chlorine]/ [PS] on PS chlorination reaction

To appreciate the effect of free chlorine on color of azo dye (PS) aqueous solutions, Preliminary test was performed to learn about the efficiency of the chlorination on PS decolorization. Fig. 3 shows the UV-vis spectra obtained before and after 20 hours of PS aqueous solution chlorination.

The spectra show a complete disappearance of the band around 520 nm indicating complete degradation of the azo group chromophore, while the ultraviolet bands (at 351 nm, 311 nm and 238 nm) attributed to naphthalene ring
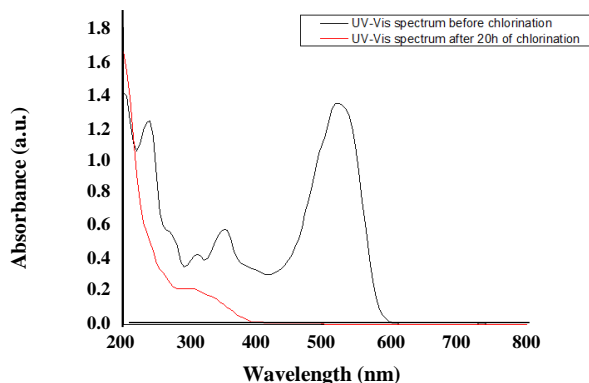
Fig. 3: UV-Visible spectra of Ponceau S aqueous solution before and after 20 hours of chemical chlorination using sodium hypochlorite (R=2.5; Initial pH = 7.11).

and benzenoid system were observed to gradually diminish but still persisted, this can be due to the fact that naphthalene ring and benzenoid system remained intact and resistant to the attack by polarized $Cl^{\delta+}-O^{\delta-}$ bond of free chlorine species. Finally, free chlorine especially oxidizing species (HOCl and ClO^-) can be added to the azo group (–N=N–) destructing the long conjugated π systems and consequently causing discoloration.

To appreciate the effect of concentration ratio on color of azo dye (PS) aqueous solutions, experiments were conducted by mixing constant mass concentration of PS to progressive mass concentrations of diluted free chlorine. Fig. 4(a) shows that the kinetics of color disappearance of PS increased with increasing ratio in relation to contact time.

The kinetics analysis ln ($[PS]_0/[PS]_t$) = f (time) reported in Fig. 4(b) shows a pseudo first-order against dye for each mass concentration ratio of chlorination reaction.

The Table 1 summarizes the apparent constant rate of each mass concentration ratio (k_{app}) with their correlation coefficient (r^2).

As shown in Fig. 4(c) that the plot of k_{app} against the concentration ratio R gives a linear trend line for the concentration ratios R=0.5, 1, 1.5, 2 and 2.5. However, a high increase of the apparent rate constant is observed when R=10, this can be due to the condensation of hypochlorous acid HClO, major species when pH is equal to 7, to Cl_2O which may contribute to the decolorization of the PS aqueous solution.
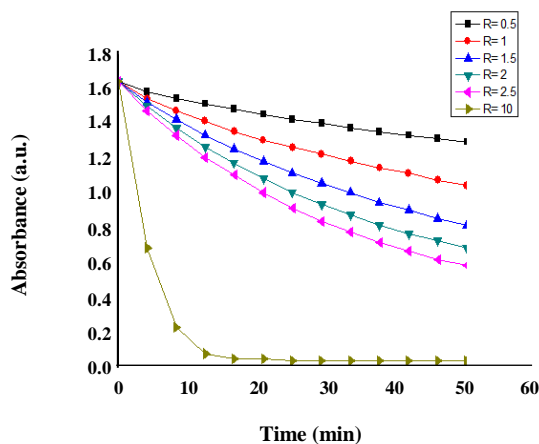
(a)
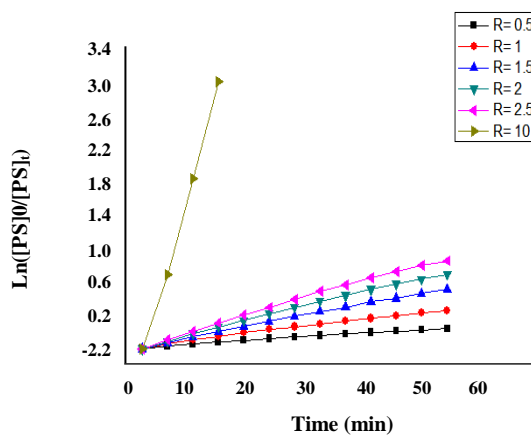
(b)
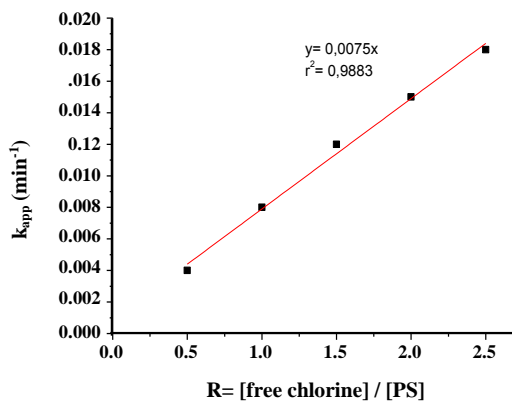
(c)

Fig. 4: (a) Evolution of color disappearance of PS in relation to chlorination time at different mass concentration ratio R = [free chlorine]/[PS]. (b) Evolution of ln ([PS]₀/ [PS]ₜ) at different concentration ratio in relation to time. (c) Evolution of the chlorination apparent rate constant k_{app} in relation to the concentration ratio R.

Table 1: Evolution of apparent constant rate with concentration ratio [free chlorine]/ [PS].

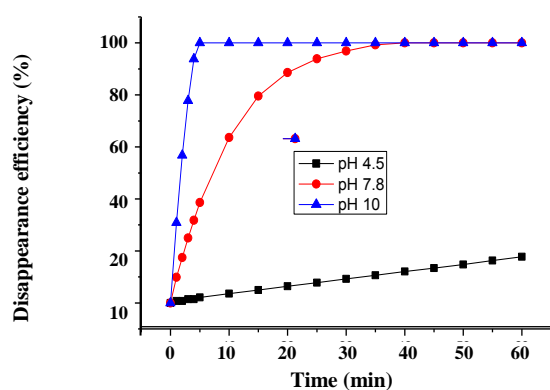| R= [free chlorine]/[PS]	0.5	1	1.5	2	2.5	10
k_{app} (min^{-1})	0.004	0.008	0.012	0.015	0.018	0.205
r^2	0.965	0.974	0.992	0.991	0.991	0.994

Fig. 5: Evolution of the decolorization of PS solution by chlorine according to the pH of the medium. Reaction conditions: [PS]$_0$ = 0.065 mM, [free chlorine]$_0$ = 0.195 mM, temperature = 25°C

Influence of pH media on aqueous Ponceau S chemical chlorination

To establish the effect of pH on the decolorization of PS aqueous solutions, three pH values (4.5; 7.8; 10) were analyzed. The initial mass concentration ratio [Free chlorine] / [PS] of 3 was kept for each test.

Decolorization kinetics of PS in solution was greatly affected by pH of the medium. At the end of these treatments, decolorization was reduced by 100% at only 5 minutes for pH 10 and 40 minutes for pH 7.8. In contrast, at acidic pH of 4.5, the dye was much more recalcitrant and persisted to the chlorination reaction for 60 minutes and about only 17% of decolorization was obtained. Otherwise, the profiles of chlorination kinetic curves show that the reaction was pseudo zero order for pH 10 and pH 4.5, whereas the same reaction exhibits a pseudo first order for pH 7.8

The chemical structure is affected at basic pH for the dye while the hypochlorous/ hypochlorite ratios differ according to the pH of medium. Provided the azo bond in dye structure was responsible for the color, the bond attack by hypochlorous acid (preponderance of HClO at acidic pH) was more difficult in comparison with hypochlorite species. The fast decolorization speed obtained at pH 10

can be attributed to the vulnerability of the more conjugated species existing in higher basic medium [28].

The effect of medium temperature on PS chemical chlorination

The kinetics of decolorization of the PS was followed at four different temperatures of the medium 30, 40, 50 and 60 °C, and at pH 7 when the mass concentration ratio

R= [Free chlorine]/ [PS] was equal to 3.

Fig. 6(a) shows that the initial dye decomposition rates increase with increasing reaction temperature. This can be explained by the Arrhenius equation: $k = A\ e^{-Ea/RT}$ (8)

Where k_{app} (Eq. (8)) is the apparent rate coefficient, A is the pre-exponential constant, E_a is the activation energy, R is the gas constant, and T is the temperature measured in Kelvin.

Linear curves were obtained by plotting $\ln\left([PS]_0/[PS]_t\right)$ = f (reaction time) for the studied reaction temperatures. Thus, in each case, it indicates that the kinetic reaction exhibits a pseudo first order with respect to dye.

The plot of -ln k_{app} against 1/T gives a linear trend line and its slope can be used to determine activation energy which is close to 39.64 kJ/mol (see Fig. 6(b)), however its y-intercept is significantly different from zero; this can be due to the occurrence of consecutive and parallel reactions.

The chlorination of Ponceau S with sodium hypochlorite in the presence of bromide ions

The concentrations of bromide ions at most surface waters can vary from a few μg/L to as much as several mg/L, which are impacted by various circumstances.

Thus, the chlorination of bromide ion containing water produces reactive brominated species, which subsequently react with natural organic matter [33].

The presence of bromide in hypochlorite solutions when pH (7 < pH < 10) lead to the formation of hypobromous acid HOBr and hypobromite ion OBr$^-$ [34]. It was reported that at pH values below 6, hypobromous acid will convert to Br_2, Br_3^-, bromine chloride, and other halide complexes [35].
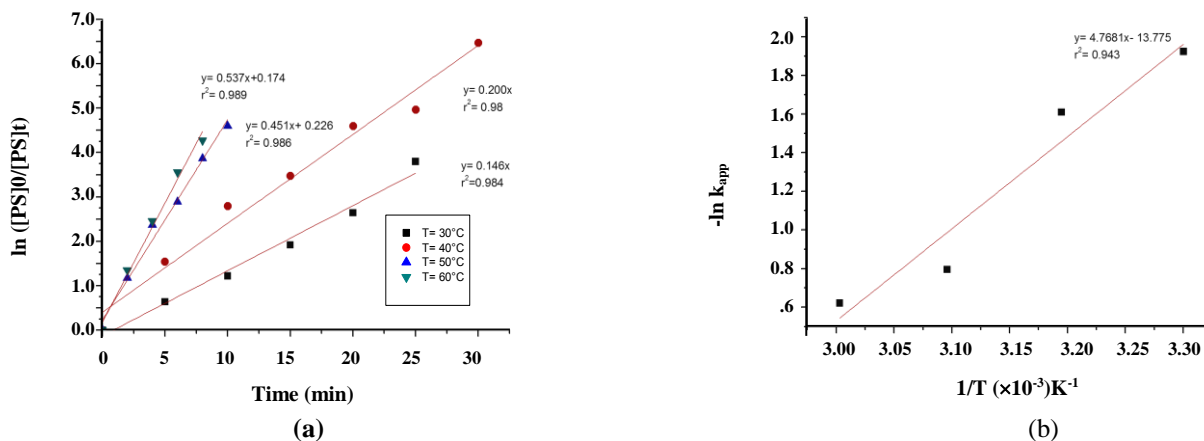
Fig. 6: (a) Influence of temperature on the decolorization of PS aqueous solution by free chlorine.
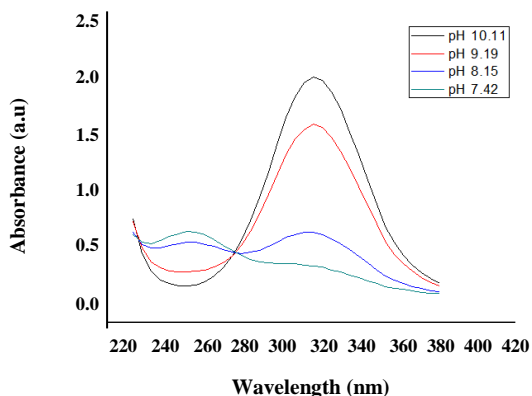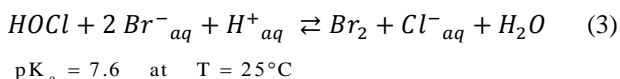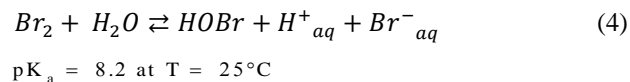*(b) Representation of Arrhenius law for the Ponceau S chlorination in aqueous medium.*

Fig. 7: Distribution of HOBr and OBr⁻ in aqueous solution in relationship to pH.

$$HOCl + 2\,Br^-{}_{aq} + H^+{}_{aq} \rightleftarrows Br_2 + Cl^-{}_{aq} + H_2O \qquad (3)$$

$$pK_a = 7.6 \quad at \quad T = 25°C$$

This oxidation step is followed by rapid hydrolysis of the molecular bromine to form hypobromous acid.

$$Br_2 + H_2O \rightleftarrows HOBr + H^+{}_{aq} + Br^-{}_{aq} \qquad (4)$$

$$pK_a = 8.2 \quad at \quad T = 25°C$$

The distribution of HOBr and OBr⁻ in aqueous solution in relationship to pH

The UV spectra at various pH values was recorded using a UV-Vis spectrophotometer with a spectrometric cell (2 cm path length) observed in Fig. 7 shows two absorption maxima at 265 nm and 330 nm with one isobestic point at 285 nm. The bands above mentioned were attributed to hypobromous acid (λ_{max}=265 nm) and its conjugate base (λ_{max}=330 nm) [36].

Chlorination of Ponceau S with sodium hypochlorite in the presence of bromide ions

Fig. 8(a) shows prelliminary study conducted by recording the UV-vis spectra obtained before and after 48 hours of chlorination in presence of bromide ions of PS aqueous solution. The spectra show the discoloration of the solution and complete disappearance of the band around 520 nm indicating complete degradation of the azo chromophore group. As indicated for typical addition of free chlorine, the same mechanistic process is adopted in this case; in fact free bromine especially oxidizing species (HOBr and BrO⁻) first attacks azo group and opens –N=N-bonds leading to the discoloration of the dye.

For appreciating the effect of bromide ions on the chlorination of azo dye (PS) aqueous solutions, experiments were conducted by mixing constant volumes of PS solution (50 mg/L) to progressive volumes of Br (+I) solution (0.43 g/L). The pH of the two solutions was adjusted with sodium hydroxide (0.1 M) for basic and by sulphuric acid for acidic medium.

The kinetics analysis ln ([PS]$_0$/[PS]$_t$) = f (time) reported in Fig. 8(b) shows a pseudo first-order against dye for each mass concentration ratio of the reaction.

The following table (Table 2) summarizes the apparent constant rate of each mass concentration ratio (k$_{app}$) with their correlation coefficient (r^2).
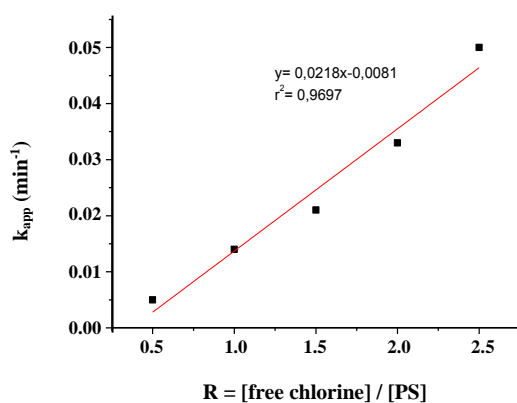
Table 2 shows that the specific rate constant is increased with increasing concentration ratio. In fact,
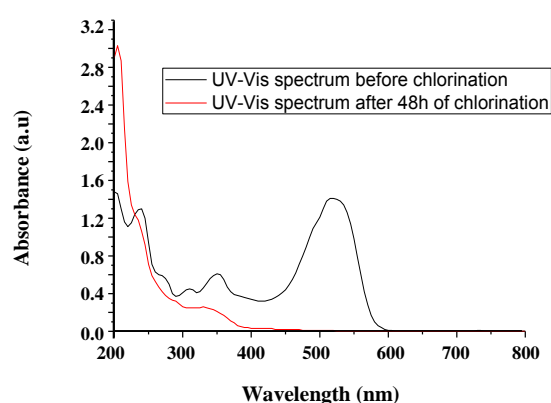
(a)
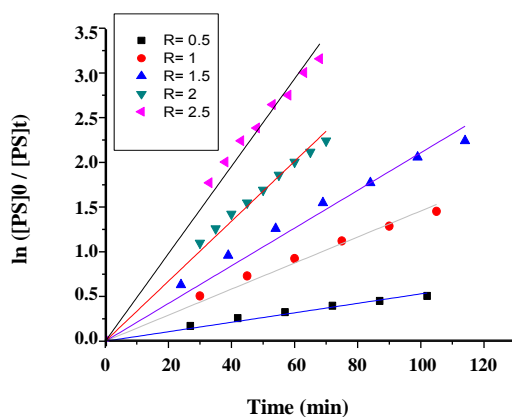
(b)

(c)

Fig. 8: (a) UV-visible spectrum obtained for Ponceau S aqueous solution before and after 48 hours of chemical chlorination in presence of bromide ions (R=2.5 ; pH(t=0)= 7.20). (b) Evolution of ln ([PS]0/[PS]t) at different concentration ratio in function of time. (c) Evolution of the constant rate k in relation to the concentration ratio R.

the constant rate in the case of chemical chlorination in presence of bromide ions is superior for each concentration ratio than the case of the chemical chlorination using sodium hypochlorite (Table 1). This can be due to the easy addition of $Br^{\delta+}–O^{\delta-}$ on azo double bond in comparison with $Cl^{\delta+}– O^{\delta-}$, which depends on the difference between the polarization of Halogen–O bonds; this character must be accented by the polarity of solvent molecules (H_2O).

It can be seen from Fig. 8(c) that the plot of the apparent constant rate k_{app} against the concentration ratio R gives a linear trend line within the studied concentration ratios range.

### The comparison of PS decolorization via chlorination, sunlight/chlorine and UV/chlorine processes

The time dependent decolorizations of PS aqueous solution under chlorination, UV/Chlorine and Sunlight/Chlorine processes were compared. The experiments were conducted at pH 4.5 and R= 1.

As shown in the Fig. 9, the sunlight/chlorine photolysis enhanced the PS decolorization rate compared with that of Dark chlorination. The observed pseudo zero order of this decolorization has led to an apparent rate constant which was 7.8 times higher than that of chlorination. Moreover, UV/chlorine process evidently enhanced the decolorization rate of PS compared to chlorination and sunlight/chlorine process. In fact, about 98% of decolorization was reached in 60 minutes of exposition to UV irradiations.

This indicates that the combination of sunlight/UV irradiations and free chlorine results in much stronger oxidation than Dark chlorination. Direct photolysis of HOCl/OCl⁻ produces HO• and Cl•, which can oxidize organic compounds into smaller molecules [37]. The oxidation capacities of HO• and Cl• are much higher than that of free chlorine, with standard electrode potentials of HO• and Cl• at + 2.7 and + 2.4 V, respectively, compared with a free chlorine electrode potential of only + 1.395 V.

$$HOCl + h\upsilon \rightarrow HO^{•} + Cl^{•} \tag{5}$$

$$OCl^{-} + h\upsilon \rightarrow O^{•-} + Cl^{•} \tag{6}$$

On the other hand, chlorine can react with HO• and Cl• (eq (7–8)), acting as scavenger of these reactive radicals [38].

$$HO^{•} + HOCl \rightarrow ClO^{•} + H_2O \tag{7}$$
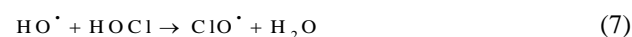
$$k = 2.0 \times 10^{9} M^{-1} s^{-1}$$

Table 2: Kinetic constant in relation to mass concentration ratio.

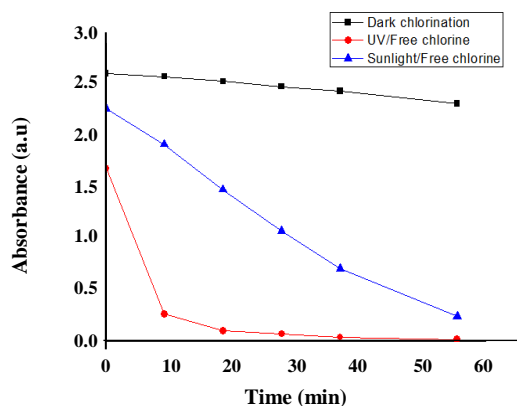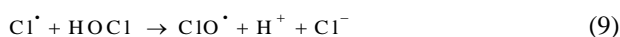| R	0.5	1	1.5	2	2.5
k_{app} (min^{-1})	0.005	0.014	0.021	0.033	0.050
r^2	0.971	0.986	0.984	0.992	0.989

Fig. 9: Comparison of the Ponceau S disappearance kinetics with different systems: Dark chlorination, sunlight/Free chlorine and UV/ Free chlorine.

$$HO^\bullet + OCl^- \rightarrow ClO^\bullet + OH^- \tag{8}$$
$$k = 8.8 \times 10^9 \, M^{-1} s^{-1}$$

$$Cl^\bullet + HOCl \rightarrow ClO^\bullet + H^+ + Cl^- \tag{9}$$
$$k = 3.0 \times 10^9 \, M^{-1} s^{-1}$$

$$Cl^\bullet + OCl^- \rightarrow ClO^\bullet + Cl^- \tag{10}$$
$$k = 8.2 \times 10^9 \, M^{-1} s^{-1}$$

Some studies have also reported that when free chlorine is exposed to solar or UV irradiations at 254 nm, the production ratio of OH$^\bullet$ generated by OCl$^-$ (pH>8) is only around 0.1 when HOCl (pH 5) given 0.7 OH$^\bullet$ under sunlight and 0.9 OH$^\bullet$ with 254 nm under UV irradiations [39].

It's important to note that OH$^\bullet$ is a non selective oxidant that can react with organic parts with rate constants related to rates of controlled diffusion [40], while Cl$^\bullet$ is a selective oxidant which reacts with rich moieties in electron toward oxidation, H-abstraction, and addition to unsaturated C-C bonds [41].

The radical reactivity and competitiveness of Cl$^\bullet$ and OH$^\bullet$ radicals enhance the destruction of the molecule conjugation responsible for the dye color. Otherwise, these radicals may contribute to the opening of benzenoid system and naphtalenic rings that remained resistant against free chlorine species attack.

CONCLUSIONS

The chlorination of a 50 mg/L Ponceau S aqueous solution kinetic disappearance increases with increasing concentration of chlorine. The chlorination was also investigated at different pH values which showed that free chlorine has actions on PS disappearance with different efficiency. Important and fast removal levels were obtained at basic pH which means that the hypochlorite species (ClO$^-$) was more efficient than hypochlorous acid (HClO) for decolorizing PS aqueous solutions. Elsewhere, apparent kinetic constant of PS disappearance pseudo first order kinetic increases with increasing medium temperature and lead to activation energy of 39.64 kJ/mol.

In this work, the effect of Br$^-$ on the chlorination kinetics of PS was also investigated when pH (7< pH <10). The experimental results show that important removal levels were obtained in the case of chlorination in presence of bromide. In fact, BrO$^-$ and HOBr species are more reactive than ClO$^-$ and HOCl species. The apparent constant rate in the case of chemical chlorination in presence of bromide ions when the concentration ratio was equal to 1.5 was determined to be 0.021 min^{-1} which was 1.75 folds of that of the case of chemical chlorination using sodium hypochlorite.

When sunlight/free chlorine and UV/free chlorine processes were applied to the mixture (R=1; pH=4.5), an appreciable improvement in disappearance rate of dye in comparison to the simple chlorination. This showed clearly that radicals (especially Cl$^\bullet$ and OH$^\bullet$), generated photolytically by sunlight and UV radiations were responsible for this phenomenon. An enhanced knowledge on the intermediate and/or ultimate fate of the molecule, is however necessary.

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