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Ponceau S Dye Removal Using UV/Chlorine Process: Affecting Factors, COD Removal and Comparison with UV/H_2O_2 and UV/Persulfate Systems

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Abstract: *The purpose of this work was to examine the degradation of Ponceau S (PS) using the UV/chlorine process under various operating parameters. The temporal evolution of the conductivity and the chemical oxygen demand (COD) of the reaction medium were also investigated. The degradation efficiency of PS by UV/chlorine process was compared to other advanced oxidation processes, such as UV/$S_2O_8^{2-}$ and UV/H_2O_2 processes. All reaction kinetics exhibited pseudo-first-order kinetics with respect to PS dye and their apparent rate constants were: $k_{app}(UV/H_2O_2) = 0.0519\ min^{-1} < k_{app}(UV/S_2O_8^{2-}) = 0.0746\ min^{-1} < k_{app}(UV/chlorine) = 0.283\ min^{-1}$. The action of solar irradiation on the PS degradation was appreciably effective. At pH = 4.22 and when [chlorine] = 0.2 mM, PS degradation using UV/chlorine process yielded more than 70% in only 10 min of dye degradation. The presence of inorganic anions showed an inhibition effect on decolorization kinetics for carbonate species compared to that observed for sulfates. The high COD removal efficiency was obtained for UV/persulfate process (73%) in comparison with that obtained for other AOPs.*

Keywords: *Ponceau S dye; UV/chlorine; UV/$S_2O_8^{2-}$; UV/H_2O_2; advanced oxidation processes*

■ INTRODUCTION

Due to their widespread use in textile and printing, dyes are contributing to a growing problem of colorful and toxic water pollution. These effluents are considered a major source of environmental pollution [1]. The dye industry's massive scale presents a toxic challenge. With over 100,000 synthetic dyes in commercial use, global production reaches 700,000 tons annually. Wastewater pollution stems from 1–15% dye loss during manufacturing processes [2]. These effluents cloud water and introduce complex toxins, necessitating treatment. Many dyes contain carcinogenic azo-bonded aromatics, compounding health risks. Tackling this issue requires effective wastewater management to safeguard water transparency and mitigate potential harm to ecosystems and human well-being [3]. Thus, the removal of color and detoxification of textile wastewater containing dispersed dyes is considered an increased necessity. In this perspective, it has been reported that conventional chlorination has been ineffective in removing dispersed dyes and their metabolites. Accordingly, effective technologies should be applied to remove these contaminants from water [4].

Based on a synergy of oxidizing agents HClO ($E° = 1.611$ V), ClO^- ($E° = 0.81$ V, pKa = 7.5), H_2O_2 ($E° = 1.77$ V, pKa = 11.6), $S_2O_8^{2-}$ ($E° = 2.01$ V, pKa = −3.5) and an activator such as UV irradiations, metals or solar irradiations; advanced oxidation processes (AOPs) have demonstrated high performance for treatment of contaminated water without any secondary pollutants [5]. AOPs are known as the processes that generate reactive oxygen species (ROS) such as hydroxyl radical ($HO^•$), chlorine radical ($Cl^•$) and sulfate radical anion ($SO_4^{•-}$), which are strong oxidizing agents that able to destroy organic pollutants [6]. In recent years, researchers have focused on other reactive species. Reactive chlorine species (RCS), have been used for the degradation of organic pollutants in which chlorine is activated by ferrous ions and UV irradiation. UV/$S_2O_8^{2-}$, UV/O_3, UV/H_2O_2, and UV/chlorine have been widely used for water and wastewater treatment [7-8].

In fact, the UV/chlorine process involves a synergy between UV and free chlorine (Cl_2, HClO/ClO^-) and has drawn great attention to the abatement of chemical pollutants and the inactivation of microorganisms in aqueous environments (*Cryptosporidium parvum* and *Giardia lamblia*) [9-10]. However, the degradative efficiency of the UV/chlorine process towards organic micropollutants remains sensitive to the influence of various parameters, such as pH and the presence of inorganic anions (SO_4^{2-}, HCO_3^-, and Cl^-).

Direct photolysis of HOCl/OCl^- produces $HO^•$ and $Cl^•$ (Eq. (1)), which can oxidize organic compounds. 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 [11].

$$HOCl \xrightarrow{hv} HO^• + Cl^• \quad (1)$$

On the other hand, chlorine can react with $HO^•$ and $Cl^•$ (Eq. (2–11)), acting as a scavenger of these reactive radicals [12].

$$HO^• + HOCl \rightarrow ClO^• + H_2O \quad (2)$$

$$HO^• + OCl^- \rightarrow ClO^• + OH^- \quad (3)$$

$$Cl^• + HOCl \rightarrow ClO^• + H^+ + Cl^- \quad (4)$$

$$Cl^• + OCl^- \rightarrow ClO^• + Cl^- \quad (5)$$

$$Cl_2^{•-} + ClO^- \rightarrow ClO^• + 2Cl^- \quad (6)$$

$$Cl^• + Cl^- \leftrightarrow Cl_2^{•-} \quad (7)$$

$$ClOH^{•-} + H^+ \leftrightarrow Cl^• + H_2O \quad (8)$$

$$HO^• + Cl^- \leftrightarrow ClOH^{•-} \quad (9)$$

$$2ClO^• + HO^• \rightarrow Cl_2^- + H^+ \quad (10)$$

$$ClO_2^- + HO^• \rightarrow ClO_2^• + HO^- \quad (11)$$

UV/H_2O_2 and UV/$S_2O_8^{2-}$ systems allow the generation of highly reactive primary radicals such as $SO_4^{•-}$ and $HO^•$ radicals. The sulfate radical ($SO_4^{•-}$) is a very strong oxidant (E_0 ($SO_4^{•-}$/SO_4^{2-}) = 2.60–3.10 V). This radical is generated by the scission of the peroxide bond of persulfate (Eq. (12)) [13].

$$S_2O_8^{2-} \xrightarrow{hv} 2SO_4^{•-} \quad (12)$$

These radicals can be scavenged by persulphates (Eq. (13) and (14)) at considerable concentrations [14]:

$$SO_4^{•-} + SO_4^{•-} \rightarrow S_2O_8^{2-} \quad (13)$$

$$SO_4^{•-} + S_2O_8^{2-} \rightarrow SO_4^{2-} + S_2O_8^{•-} \quad (14)$$

Researchers and practitioners have turned their attention to the UV/chlorine process. This surge of interest has led to an increase in published papers. These studies focus on the method's effectiveness in degrading harmful pollutants, highlighting its growing importance [15-16]. It has been reported that the UV/chlorine process is effective in degrading different pollutants, such as Brilliant Red X-3B [17], ^{1}H-benzotriazole [18], and diclofenac [19]. However, many aspects of UV/chlorine are still unknown. There is a lack of recent application on the use of UV/chlorine for dye degradation. According to this description, this is the first study to investigate the degradation of Ponceau S (PS) dye aqueous solution using the UV/chlorine process, highlight its kinetic behavior, and compare its effectiveness with other advanced oxidation processes.

This paper first investigated the degradation kinetics of PS in the UV/chlorine process at different pH values and free chlorine concentrations. The effects of inorganic anions such as bicarbonates (HCO_3^-), sulfates (SO_4^{2-}), and chloride (Cl^-) on PS degradation in the UV/chlorine process were also evaluated. Furthermore, PS degradation kinetics were compared using solar/chlorine, UV/chlorine and LED/chlorine processes. The UV/chlorine system has been compared, in terms of degradation, to the UV/H_2O_2 and UV/$S_2O_8^{2-}$ systems. Finally, the mineralization of PS dye was investigated by determining chemical oxygen demand (COD) for the processes studied.

■ EXPERIMENTAL SECTION

Materials

PS dye (analytical grade) was from REACTIFS RAL. Its molecular formula is $C_{22}H_{12}N_4O_{13}S_4$ (MW = 672.63 g/mol) with color index number 27195. The structure of the PS is shown in Fig. 1.

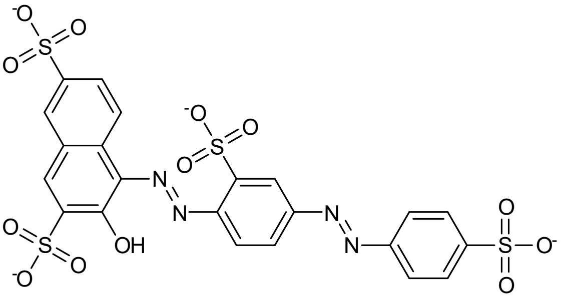

Fig 1. Molecular structure of Ponceau S dye

Analytical grade chemicals and reagents used for this study were sulfuric acid (98.0%) from Scharlau Chemie S.A, sodium hydroxide (98.0%) and potassium chloride (99.5%) from Scharlab S.L. To obtain free chlorine for experiments, we used commercial concentrated bleach (12 degrees). The sodium metabisulfite (95.0%) was from Panreac, while boric acid (99.0%), potassium dihydrogen phosphate (98.0%) and potassium bromide (99.5%) were from Riedel de Haën. Hydrogen peroxide (H_2O_2, 50.0%) was purchased from PROCHILABO. Otherwise, $HgSO_4$ and $K_2Cr_2O_7$ were purchased from Panreac. 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 by iodometric titration. All experiments were carried out in volumetric flasks quenched in chlorinated aqueous solutions.

Instrumentation

All aqueous solutions were prepared with distilled water (GFL water stills model 2004). The pH measurements were carried out using a HACH sensION+ pH meter, and the pH was adjusted to the desired value by the addition of a few drops of H_2SO_4 (0.1 M). The spectrophotometer used in this work is a Rayleigh UV-1800 type controlled by "UV-Software". Measurements were carried out in quartz cuvettes with an optical path length of 1 cm. The measurements of the COD concentrations were achieved using the Bloc Digest 12 equipped by Regulating Unit "Selecta".

Procedure

Free chlorine solutions were prepared by diluting commercial bleach (NaOCl) in ultrapure water. The free chlorine concentration was determined using an iodometric method. Chlorination under various conditions was carried out in volumetric flasks covered by aluminum foil. The PS removal efficiency was evaluated by using a UV-vis spectrophotometer at λ_{max} = 520 nm. The effect of natural sunlight on chlorination kinetics was carried out in a Pyrex beaker. The experience took place under a clear sky, with the sun at its peak, from 12:00 pm to 02:00 pm in December.

Degradation studies of PS dye by UV/chlorine, UV/H_2O_2, and $UV/S_2O_8^{2-}$ processes were handled in a 1 L cylindrical beaker using a high-pressure mercury lamp (250 W, Ingelec) as a source of UV irradiation. A stir bar was placed inside the reactor to ensure homogeneous UV exposure and homogeneous solution (Fig. 2). Free chlorine, H_2O_2, and persulfate were added before UV irradiation. Selected anion species were added to the reactor to evaluate their effects on the efficiency of PS dye degradation.

COD was determined by a closed reflux colorimetric method according to standard methods for the Examination of Water and Wastewater [20]. The COD concentrations were calculated for each PS dye sample treated by the UV/chlorine, UV/H_2O_2, and $UV/S_2O_8^{2-}$ processes. The COD concentrations were established by the spectrophotometric method at λ_{max} = 605 nm, and the oxygen amount needed for the oxidation

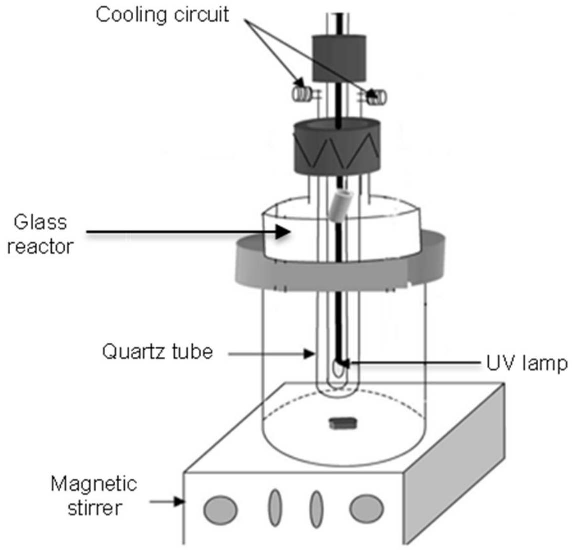

Fig 2. Experimental setup for the irradiation experiments

of organic matter was determined in incubated samples with potassium dichromate $K_2Cr_2O_7$ and mercuric sulfate $HgSO_4$ at an acidic pH for 2 h at 120 °C. For all experiments, analytic samples of 5 mL were withdrawn at known intervals and analyzed using the UV-visible spectrophotometer. The decolorization of PS dye was monitored by measuring the absorbance at 520 nm.

Analytical methods

PS dye concentrations were followed by measuring the absorbance at 520 nm using a UV–vis spectrophotometer. The disappearance efficiency of PS dye was calculated in Eq. (15):

$$\text{Disappearance efficiency}(\%) = \left(1 - [\text{PS}]_t / [\text{PS}]_0\right) \times 100\% \quad (15)$$

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

■ RESULTS AND DISCUSSION

Comparison of UV/Chlorine, UV/$S_2O_8^{2-}$ and UV/H_2O_2 Processes

UV-based advanced oxidation processes, including UV/H_2O_2, UV/$S_2O_8^{2-}$, and UV/chlorine, have been recognized as promising technologies that provide opportunities to degrade many pollutants. In fact, highly reactive species such as ($OH^•$, $SO_4^{•-}$, and RCS) could be produced in these processes in order to degrade target micro-pollutants. Generally, $OH^•$ reacts non-selectively with organic compounds through a series of reactions, including H-abstraction, electron transfer, and addition [21]. In comparison, $SO_4^{•-}$ (E° = 2.60–3.10 V) is preferable for electron transfer reactions and less for H-abstraction or addition reactions (Eqs. (16–20)), which explains that $SO_4^{•-}$ is more selective to electron-rich moieties.

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{•-} \quad (16)$$

$$S_2O_8^{2-} + M^{n+} \rightarrow SO_4^{•-} + SO_4^{2-} + M^{(n+1)+} \quad (17)$$

$$SO_4^{•-} + M^{n+} \rightarrow M^{(n+1)+} + SO_4^{2-} \quad (18)$$

$$2S_2O_8^{2-} + 2H_2O \rightarrow 3SO_4^{2-} + SO_4^{•-} + O_2^{•-} + 4H^+ \quad (19)$$

$$SO_4^{•-} + OH^- + SO_4^{2-} + OH^• \quad (20)$$

UV/chlorine process involves reactive species such as $Cl^•$ (E° = 2.410 V), $OH^•$ (E° = 2.81 V) and $Cl_2^{-•}$ (E° = 2.09 V) that may contribute to PS degradation. Thus, the degradation of PS dye in UV/chlorine process can be described as follows (Eq. (21)):

$$-\frac{d[PS]}{dt} = k_{OH^•}[PS] + k_{RCs}[PS] + k_{chlorine}[PS] + k_{UV}[PS] \quad (21)$$

where $k_{OH^•}$, k_{RCs}, $k_{chlorine}$ and k_{UV} represent the first-order rate constants of PS degradation by $OH^•$ oxidation, RCS oxidation, dark chlorination, and direct photolysis, respectively. However, the literature reports that $Cl^•$ and $Cl_2^{-•}$ are more selective and kinetically faster than $OH^•$. The $Cl^•$ could attack electron-rich compounds readily via one-electron oxidation, H-abstraction, and addition to unsaturated C–C bonds.

The comparison of UV/chlorine and UV/H_2O_2 processes has shown that the photodecomposition of chlorine is faster than that of H_2O_2 and leads to the formation of chlorate. Researchers have reported that the oxidation of some pollutants by the UV/chlorine process leads to more degradation by-products than the UV/H_2O_2 process, and in particular to the formation of chlorinated by-products [22].

This study aims to compare PS removal kinetics in aqueous media by using UV/chlorine, UV/$S_2O_8^{2-}$ and UV/H_2O_2 processes. The kinetic results obtained under the experimental conditions ([PS] = 0.044 mM; [H_2O_2] = [Cl (+I)] = [$S_2O_8^{2-}$] = 0.2 mM; pH = 7.75 and T = 25 °C) are given in Fig. 3. The PS degradation during UV/chlorine, UV/persulfate and, UV/H_2O_2 treatment satisfied pseudo-first-order kinetics, and the pseudo-first-order rate constants of PS (k_{obs}) were 0.283, 0.0746, and 0.0519 min^{-1} respectively (Fig. 2). This comparative study revealed that the UV/chlorine process was the most useful for improving the PS degradation rate.

Evolution of PS Spectrum After Chlorination Treatment

The evolution of the PS absorption spectrum after the UV/chlorine oxidation is presented in Fig. 4. The UV-visible spectrum of PS exhibits four distinguishable absorption bands, three in the UV region (238, 311, and 351 nm) and one in the visible region (520 nm). While the

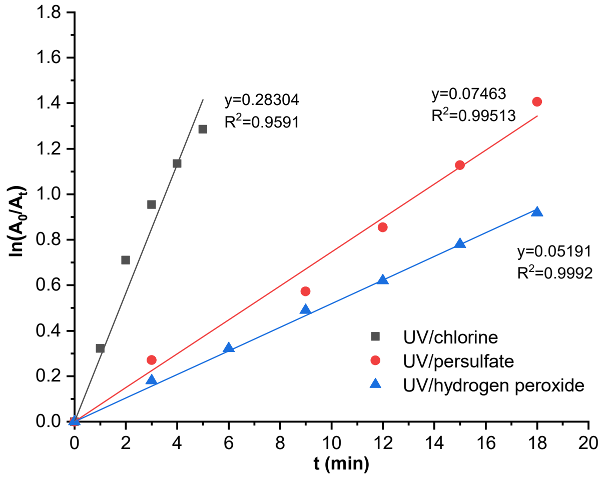

Fig 3. First-order plots for the PS degradation of PS at UV/chlorine, UV/$S_2O_8^{2-}$ and UV/H_2O_2 systems. Experimental conditions: [PS] = 0.044 mM; [H_2O_2] = [Cl(+I)] = [$S_2O_8^{2-}$]= 0.2 mM; pH = 7.75; T = 25 °C

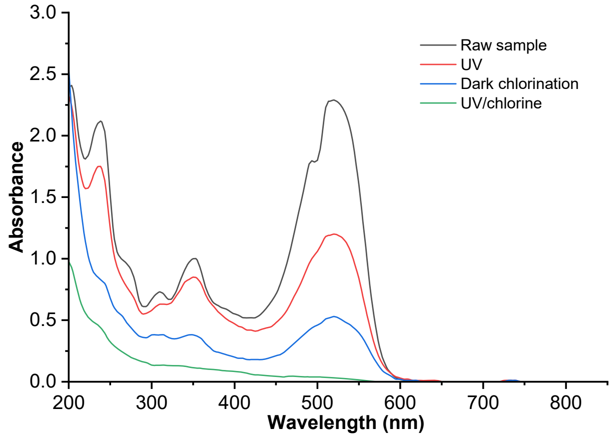

Fig 4. Changes in the UV-vis absorbance spectrum in PS dye solution during UV/chlorine process. Experimental conditions: [PS] = 0.044 mM; [chlorine] = 0.200 mM; pH = 7; T = 25 °C

bands at 311 and 351 nm ascribed to the π→π* transitions representing two adjacent rings (naphthalene ring). The band at 238 nm is attributed to the π→π* transition within the benzenoid system. The band in the visible region (λ = 520 nm) is attributed to the absorption of the n→π* transitions of the N=N chromophore group [23]. After the UV/chlorine oxidation, the intensity of the bands in the UV-vis spectrum of PS solution declined. This can be attributed to the azo band cleavage and degradation of the aromatic and naphthalene groups. The dark chlorination and UV photolysis cannot successfully cleavage all the bands, especially in the visible region, which indicates that full degradation has not occurred under the employed experimental conditions.

Effect of Initial pH

The solution pH can affect the domination of the ClO^- and HOCl species. Fig. 5 depicts PS degradation at 0.2 mM chlorine at different pH values. The experiments were conducted at initial pH values of 4.22, 6.81, 7.66, and 10.38. Within this pH range, a pseudo-first-order kinetic model can describe the PS decolorization kinetics with:

$$r=-\frac{d[PS]}{dt}=k[PS] \tag{22}$$

where k is the observed rate constant, t is the irradiation time and [PS] is the dye concentration at time. Integrating (Eq. (22)) and considering the verified linearity of the curve yield Eq. (23).

$$\ln\frac{[PS]_0}{[PS]_t}=-kt \text{ or } \ln\left(\frac{A_0}{A_t}\right)=-kt \tag{23}$$

The slope of the plot of ln (A_0/A_t) against time yields the k values, where A_0 is the initial dye absorbance. The k values are represented in Fig. 4. The optimal rate of PS decolorization is obtained when the initial pH is around 4, with a rate constant of 0.3426 min^{-1}.

As can be seen, the highest and the lowest efficacy were observed at pH = 4.22 and pH = 10.38 respectively.

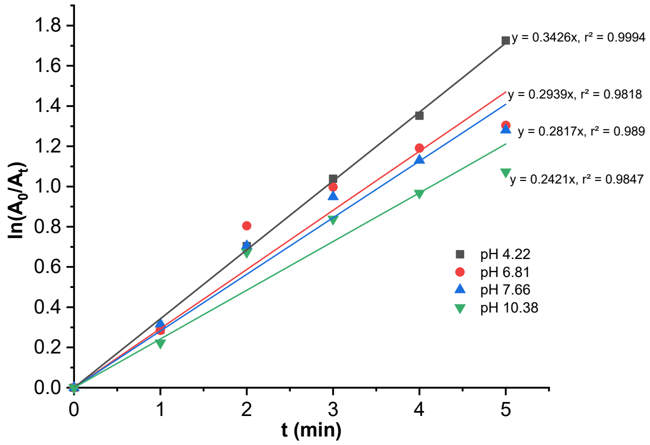

Fig 5. First-order plots for the decolorization of PS by UV/Chlorine process at different values of pH. Experimental conditions: [PS] = 0.044 mM; [Cl (+I)] = 0.2 mM, pH= 4.22–10.38; T = 25 °C

Besides, PS removal efficiencies were very close together for pH = 6.81 and 7.66. Indeed, at acidic conditions (3 < pH < 6.5), HOCl is dominated in the solution in which pKa of HOCl/OCl⁻ is 7.5 at 25 °C while OCl⁻ is dominated at pH > 8.5. Therefore, it was shown that HOCl photolysis resulted in higher efficiency than OCl⁻. It has been reported that the quantum yield for HOCl (0.62) was more than OCl⁻ (0.55) under UV irradiation of 254 nm. In fact, more $OH^•$ and $Cl^•$ were generated at acidic conditions in which higher HOCl decomposition occurred compared to OCl⁻ [24].

Effect of Chlorine Dosage

Fig. 6 shows PS degradation with various chlorine dosages at pH = 4.2 during a 10 min reaction time. In chemical oxidation, the dose of oxidant plays a crucial role in the production of free radicals. Accordingly, an increase in chlorine dosage enhanced the generation of $Cl^•$ and $OH^•$. The results show that the degradation rate increased when chlorine concentration increased from 0.10 to 0.20 mM, in which 90% of the dye was eliminated during the 10 min reaction time at 0.16 mM. An Increase in dosage to 0.20 mM did not change dye removal efficiency. This phenomenon can be related to the scavenging effect of HOCl and OCl⁻ in excess dosage, according to Eqs. (2–6) [25]. The radical $ClO^•$ is the main product of the scavenging effect in excess dosage of chlorine.

Elsewhere, the degradation rate of PS dye adopted pseudo-first order kinetics for all chlorine concentrations studied. Kinetic results of PS dye degradation with different free chlorine concentrations used during the UV/chlorine process are shown in Fig. 6. The overall rate law for the PS dye degradation can be expressed as Eq. (30).

$$\ln\left(\frac{[PS]_t}{[PS]_0}\right)=\ln\left(\frac{A_t}{A_0}\right) \tag{24}$$

Table 1 shows the apparent rate constant values for studied chlorine concentrations.

Effect of Inorganic Anions

The most common inorganic ions existing in water bodies are nitrate (NO_3^-), chloride (Cl^-), sulfate (SO_4^{2-}), and carbonate (CO_3^{2-}). The presence of these anions can affect the reaction mechanism of the UV/chlorine process and subsequently influence the degradation efficiency of PS dye. In fact, these ions inevitably influence the reaction mechanism and the formation of free radicals generated from the UV/chlorine system. These inorganic ions have strongly reactive radicals ($OH^•$, $Cl^•$, and $ClO^•$) scavenging capacities, creating less reactive radicals, such as $SO_4^{•-}$ and $CO_3^{•-}$. Generally, the presence of Cl^-, SO_4^{2-} and HCO_3^-. They may induce or reduce the oxidation rate of different dyes (Eq. (7,9,25–30)).

$$Cl_2^{•-}+OH^- \rightarrow ClOH^{•-}+Cl^- \tag{25}$$

$$ClOH^{•-}+Cl^- \rightarrow Cl_2^{•-}+OH^- \tag{26}$$

$$OH^•+HCO_3^- \rightarrow HCO_3^•+OH^- \tag{27}$$

$$OH^•+CO_3^{2-} \rightarrow CO_3^{•-}+OH^- \tag{28}$$

$$Cl^•+HCO_3^- \rightarrow CO_3^{•-}+HCl \tag{29}$$

$$Cl_2^{•-}+HCO_3^- \rightarrow 2Cl^-+H^++CO_3^{•-} \tag{30}$$

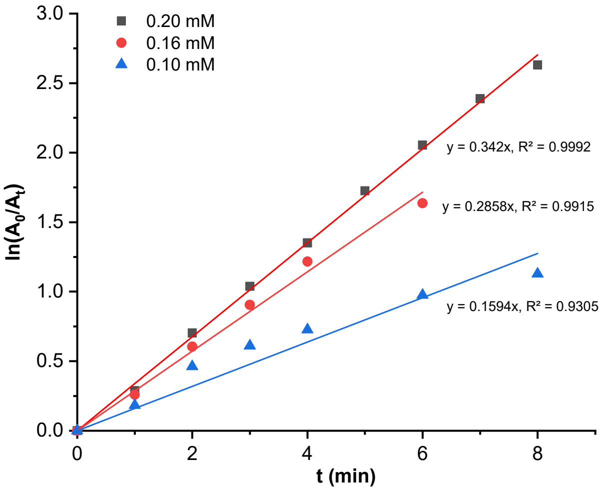

Fig 6. First-order plots for the decolorization of PS by UV/chlorine process at different chlorine concentrations. Experimental conditions: [PS] = 0.044 mM; pH = 4.22; T = 25 °C

Table 1. Apparent rate constant values for studied concentrations. Experimental conditions: [PS] = 0.044 mM; pH = 4.22; T = 23 °C

[Cl(+I)] (mM)	k_{app} (min⁻¹)
0.10	0.1594
0.16	0.2858
0.20	0.3420

The experiments were performed to investigate the influence of these inorganic ions with a concentration of 0.2 g/L added to the treated solution of PS by the UV/chlorine process. The results are represented in Fig. 7.

The effects of inorganic ions on the UV/chlorine process indicated the following order: no salt > sulfate > bicarbonate. Among the selective anions, bicarbonate had the most negative impact on PS disappearance efficiency, while sulfate ions had a negligible effect on PS decolorization. However, the presence of chloride ions remarkably increases the degradation of PS. Indeed, the percentage of degradation increases from 74% to 90% when Cl^- ions are present. The positive influence of chloride ion addition on PS degradation can probably be ascribed to the presence of $Cl_2^{-\bullet}$, which act as important reactive species for the degradation of several pollutants (carbamazepine, phenols) [26].

Cl^- can play a dual role in the efficiency of photochemical degradation processes. This can be attributed to the transformation of $Cl^\bullet$ and $OH^\bullet$ into reactive but highly selective radicals, e.g., $Cl_2^{-\bullet}$ and $ClOH^{-\bullet}$ inducing a promoting or inhibiting effect on the removal of organic substances. HCO_3^- quickly reacts with both $OH^\bullet$ and RCS (particularly $Cl^\bullet$) with a rate constant of 2.2×10^8 $M^{-1}s^{-1}$ and reacts with Cl_2 with a rate constant of 8.0×10^7 $M^{-1}s^{-1}$ to produce. The radical $CO_3^{\bullet-}$, is a selective oxidant that preferentially reacts with sulfur ring-containing and aromatic amine compounds [27].

The disappearance efficiency of PS in the UV/chlorine system decreased from 74.74% to 55.76% as the HCO_3^- concentration increased from 0.0 to 0.2 g/L, as shown in Fig. 7. This is probably due to the scavenging of $OH^\bullet$ by HCO_3^- to produce $CO_3^{\bullet-}$. The carbonate radical (E° = 1.78 V) is less reactive than $OH^\bullet$ radicals, which decreases the PS decolorization rate (Eq. (29)). SO_4^{2-} scavenged both $OH^\bullet$ (k = 1.0×10^6 $M^{-1}s^{-1}$) and $Cl^\bullet$ (k = 2.5×10^8 $M^{-1}s^{-1}$) to produce $SO_4^{\bullet-}$, which is a more selective oxidation species than $OH^\bullet$. In addition, $SO_4^{\bullet-}$ usually prefers to react with contaminants containing amino groups and naphthalene rings.

Effect of UV Light Source

The degradation of PS dye was compared in systems involving chlorine alone, LED/chlorine, UV/chlorine, and solar/chlorine processes (Fig. 8). In the first 10 min of treatment, the UV/chlorine process decolorized 84.05% of the aqueous PS solution, followed by the solar/chlorine process, which decolorized only 15.35%. While the LED/Chlorine process as well as the simple chlorination process, reached only 4.63% during 20 min of treatment. This comparative study showed that light sources have a very important effect on the degradation of pollutants through the UV/chlorine process. In fact, the oxidation capacities of $OH^\bullet$ and $Cl^\bullet$

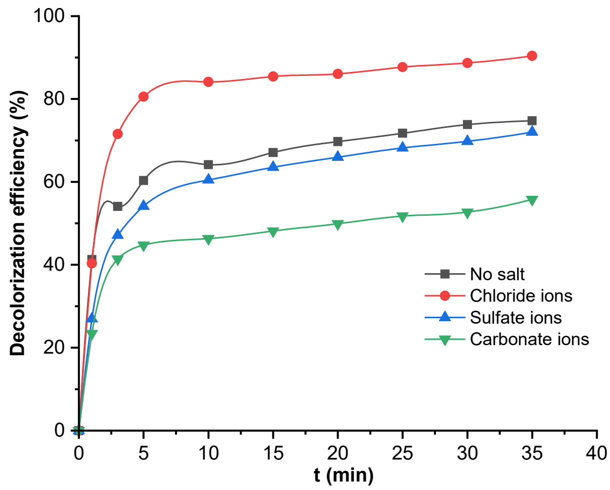

Fig 7. Effect of inorganic anions on PS decolorization. Experimental conditions: [PS] = 30 mg/L; [free chlorine] = 0.015 g/L; [inorganic anions] = 0.2 g/L; pH = 7

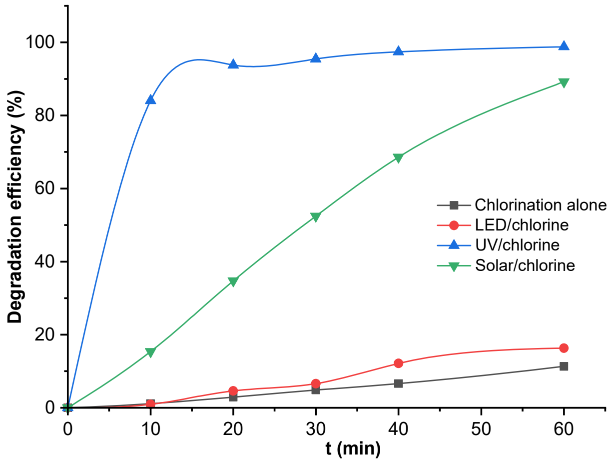

Fig 8. PS degradation by chlorination alone, UV/chlorine and sunlight/chlorine processes. Experimental conditions: [PS] = 60 mg/L; [chlorine] = 0.06 g/L; pH = 5.03.

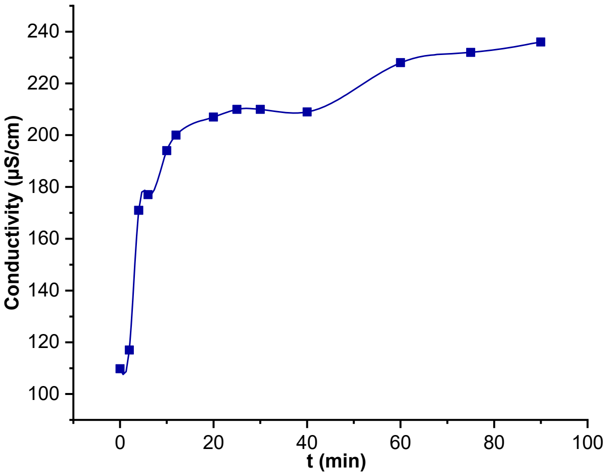

Fig 9. Evolution of conductivity during PS degradation using UV/chlorine process

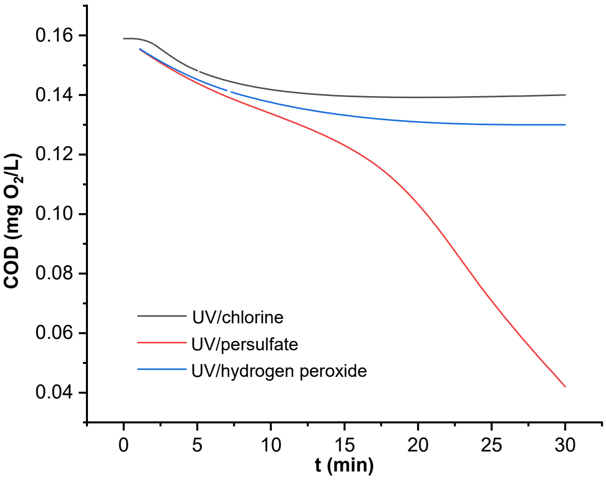

Fig 10. COD removal from the PS dye in AOP studied. Experimental conditions: [PS] = 0.044 mM; [H_2O_2] = [chlorine] = [$S_2O_8^{2-}$] = 0.2 mM, pH = 4.22; T = 25 °C

are much higher than that of free chlorine, with standard electrode potentials of $OH^•$ and $Cl^•$ at +2.7 and +2.4 V, respectively, compared with a free chlorine electrode potential of only +1.395 V.

Evolution of Conductivity During Ponceau S Degradation by UV/Chlorine System

In order to evaluate the mineralization of the dye by the UV/chlorine process, the conductivity of the medium was monitored. Fig. 9 shows an increase in conductivity during PS degradation by the UV/chlorine process. Conductivity increases after 2 min of irradiation by the process, reaching a maximum of 236 µS/cm after 90 min of treatment. The evolution of conductivity during treatment is dependent on the presence of ions (carbonates, sulfates, nitrates, etc.). Taking into account the molecular structure of PS, the liberated ions are probably nitrates and/or nitrites, sulfates, carbonates, and hydrogen carbonates.

COD Removal

Fig. 10 shows COD removal from the PS dye by UV/chlorine, UV/persulfate and UV/H_2O_2 processes. COD removal was relatively poor for UV/chlorine and UV/H_2O_2 processes, while UV/persulfate system shows a higher mineralization degree. COD removal efficiencies obtained during 30 min, were 28.90 and 18.23% for UV/chlorine and UV/H_2O_2 processes, respectively. In contrast, high COD removal efficiency was obtained (73%) for UV/persulfate process. According to the comparison of these three AOPs (Fig. 2), the UV/chlorine process shows the highest efficiency in PS degradation. However, COD removal efficiency was lower in the case of UV/chlorine process; this could be explained by the fact that the oxidation of organic compounds may produce resistant compounds, which are hardly decomposed to smaller compounds. This situation can intensify when chlorine radicals contribute to degradation of organic compounds. Moreover, it should be noted that even high COD removal could not be a guarantee for the evaluation of UV/chlorine process.

■ CONCLUSION

This study investigated the kinetics of PS dye degradation by UV/chlorine, with UV/$S_2O_8^{2-}$ and UV/H_2O_2 systems. PS degradation was greatly enhanced in the UV/chlorine process. In fact, PS degradation depends on various parameters such as pH, UV light source, concentration and also the presence of inorganic ions. Higher removal rates were obtained in the UV/chlorine process compared with solar/chlorine and LED/chlorine processes. PS degradation was inhibited by the presence of inorganic anions (HCO_3^- and SO_4^{2-}), with the highest effect in the case of carbonate ions. However, the presence of chloride ions promoted the PS degradation rate. High COD removal efficiency from the

PS dye was obtained (73%) for UV/persulfate in comparison with UV/chlorine and UV/H_2O_2 processes.

■ CONFLICT OF INTEREST

The authors have no financial or proprietary interests in any material discussed in this article.

■ AUTHOR CONTRIBUTIONS

Baylassane Chatib: Conceptualization, Investigation, Methodology, Writing – original draft, Resources, Writing – review and editing, Visualization. Yasmine Laftani: Conceptualization, Investigation, Resources. Abdelghani Boussaoud: Conceptualization, Resources, Supervision. Mohsine Hachkar: Resources.

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