COMPARISON OF ADVANCED OXIDATION PROCESSES FOR DEGRADING PONCEAU S DYE: APPLICATION OF THE PHOTO-FENTON PROCESS

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The majority of this work is devoted to the examination of the degradation of Ponceau S (PS) in an aqueous medium using the photo-Fenton process. The influence of the pH of the medium, H_2O_2 dose, ferrous ion dose and the presence of inorganic ions on degradation kinetics was analyzed. Before that, the efficiency of this process was compared to three other advanced oxidation processes (AOPs), such as H_2O_2/UV, Fenton (Fe^{2+}/H_2O_2), and solar photo-Fenton. All dye degradation kinetics obeyed a pseudo-first order, and their apparent rate constants were represented by the following ratios: k_{app} ($H_2O_2/UV/Fe^{2+}$) = 0.295 min^{-1} k_{app}(sunlight/Fe^{2+}/H_2O_2) = 0.141 min^{-1} k_{app}(Fe^{2+}/H_2O_2) = 0.111 min^{-1} k_{app}(H_2O_2/UV) = 0.031 min^{-1}.

Under optimum conditions, the photo-Fenton oxidation yielded more than 94.3 % in only 10 min of dye degradation. Elsewhere, the addition of the salts in an aqueous medium has, in general, an inhibition effect on the decolorization kinetics.

Keywords: Ponceau S; H_2O_2/UV; Fenton; photo-Fenton; solar photo-Fenton

СПОРЕДБА НА СОВРЕМЕНИ ОКСИДАЦИОНИ ПРОЦЕСИ ЗА ДЕГРАДАЦИЈА НА БОЈАТА PONCEAU S: ПРИМЕНА НА ПРОЦЕСОТ НА ФОТО-FENTON

Овој труд е посветен на испитувањето на деградацијата на бојата Ponceau S (PS) во водна средина со примена на процесот на фото-Fenton. Беше извршена анализа на влијанието врз кинетиката на деградација на pH на средината, количината на H_2O_2, количината на јоните на Fe како и присуството на неоргански јони. Претходно беше извршена споредба на ефикасноста на овој процес во однос на три други современи оксидациони процеси (AOP): H_2O_2/UV, Fenton (Fe^{2+}/H_2O_2) и соларен фото-Fenton. Сите кинетики на деградацијата на бојата следеа кинетика од псевдопрв ред, каде нивните константи на брзината се претставени со следниве односи: k_{app} ($H_2O_2/UV/Fe^{2+}$) = 0,295 min^{-1} k_{app}(сончева светлина/Fe^{2+}/H_2O_2) = 0,141 min^{-1} k_{app}(Fe^{2+}/H_2O_2) = 0,111 min^{-1} k_{app}(H_2O_2/UV) = 0,031 min^{-1}.

При оптимални услови оксидацијата со фото-Fenton дава принос од над 94,3 % во само 10 min. Познато е дека додавањето на соли во водната средина, општо земено, ја инхибира кинетиката на обезбојување.

Клучни зборови: Ponceau S; H_2O_2/UV; Fenton; фото-Fenton; соларен фото-Fenton

1. INTRODUCTION

The advancements in the industrialization of dye production have dealt colossal damage to the aquatic environment in the form of toxic dye efflu-ent. Textile industries present the maximum percentage of the synthetic dyes (around 56 %) of world's total annual production [1]. Due to continuous discharge of textile dyes into the water sources, different toxic and carcinogenic chemical

compounds have been introduced into the aquatic life, as well as into humans and animals. It has been estimated that among the various classes of dyes, azo and diazo dyes, with their complicated aromatic structures, are extensively used in industrial dyeing and printing processes [1].

Azo/diazo dyes are difficult to degrade by the current conventional treatment processes. They are characterized by the presence of the nitrogen-nitrogen bond (–N=N–), in addition to aromatic and naphtalenic systems with substituted auxochromes (such as OH, NH_2, CO_2H, $-SO_3$ and Cl) [2, 3]. It is known that biocide or non-biodegradable components pose a major threat to health and the environment. Industries such as textile dyeing face a real challenge of removing the residual dyes from their effluents to a satisfactory level before discharging them into the environment [4].

Treatments of effluents containing dyes and chemicals by conventional processes like flocculation, trickling filters and electrodialysis are not effective toward all dyes and chemicals removal and are not economically viable [4, 5].

Recently, wastewater treatments have been marked by the application of Advanced Oxidation Processes (AOPs), which offer promising opportunities to degrade or even mineralize pollutants using mild temperature and pressure conditions. Among these AOPs, those involving hydrogen peroxide such as H_2O_2/UV, the Fenton process and the photo-Fenton process can generate highly reactive and no selective radical species, like hydroxyl radical (HO•) [6,7]. H_2O_2/UV is the most frequently applied UV-AOP at full scale and has been investigated at both the laboratory and the pilot scales [8]. Many studies have reported applications of UV-AOPs to attenuate pharmaceuticals, remove taste and odor compounds, eliminate pollutants and improve the quality of treated water [9].

Fenton's reagent, a mixture of ferrous (Fe^{2+}) ion as a catalyst and hydrogen peroxide, which generates hydroxyl radicals, has been used extensively for the oxidation of organic matter in water. It has been reported that the Fenton process could be rapidly adopted in textile wastewater treatment [5]. It was demonstrated that the performance of the Fenton process is carried out in an acidic medium [10].

The classical Fenton process could be photo-assisted by using UV radiations that involve an additional pathway for the catalyst regeneration, which increases the oxidation rate. A drawback of this process is the important economic cost arising from the utilization of artificial light [11, 12].

An economic alternative for the photo-Fenton process suggests the use of the sun as a source of light [13]. The solar photo-Fenton process has been shown to be capable of degrading different organic contaminants in a low-cost application [6].

Fenton processes have appreciable advantages, such as a short reaction time and the fact that reagents are inexpensive and their reaction is easy to operate. However, they present some restrictions that can be summarized as follows: the pH must be very acidic for Fenton and photo-Fenton processes; the temperature of the medium should not exceed 40–50 °C to avoid hydrogen peroxide degradation; and lastly, sludge formation in the case of using the Fenton process [5].

Within this context, the overall objectives of this study are: (a) to compare the decolorization rates of Ponceau S (PS) dye by photo-Fenton processes with other AOPs, like H_2O_2/UV, Fe^{2+}/H_2O_2 and solar photo-Fenton; (b) to examine the effect of major system parameters (initial pH, initial concentrations of H_2O_2 and Fe^{2+}) on the decolorization of PS by the photo-Fenton process. The effect of the anions HCO_3^-, SO_4^{2-}, and NO_3^- on the decolorization rates was also examined.

2. EXPERIMENTAL

2.1. *Reagents*

The diazo dye, Ponceau S (Abbreviation: PS; Acid Red 112; color index number: 27195; molecular formula: $C_{22}H_{12}N_4Na_4O_{13}S_4$; molecular weight: 760.6 g/mol; λ_{max}: 520 nm) was purchased from REACTIFS RAL and was used as received without further purification. The chemical structure of PS is given in Figure 1. Hydrogen peroxide (H_2O_2, 50 %) was purchased from PROCHILABO.

$Fe(SO_4)\cdot7H_2O$ was supplied by SIGMA-ALDRICH. Na_2SO_4 was obtained by Carlo Erba Reactifs-sds.

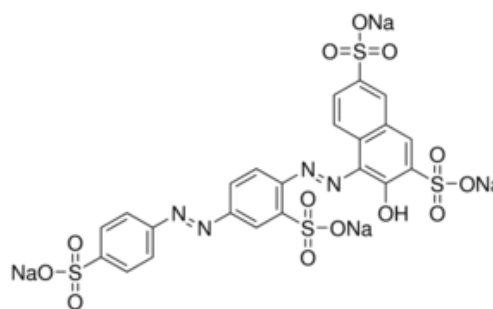Otherwise, $NaNO_3$ and $NaHCO_3$ were purchased from Riedel-de-Haën.

Fig. 1. Chemical structure of Ponceau S.

The pH of the solutions was adjusted using H_2SO_4 obtained from SD-Fine Chemical Limited (SDFCL).

All stock and working solutions were prepared in ultrapure water with a resistivity of 0.055 µS/cm, which was obtained using a VWR PURANITY TU unit.

All chemicals were used as received. The hydrogen peroxide concentration was measured by iodometry.

The UV-visible (UV-vis) spectra of PS diazo dye was recorded from 200 to 800 nm using a UV-vis spectrophotometer (Rayleigh UV-1800) with a spectrometric quartz cell (1 cm path length). The maximum absorbance wavelength (λmax) of PS was found at 520 nm.

2.2. *Methodology*

A stock solution of 0.06 mM of PS dye was prepared by dissolving the required amount in ultrapure water and kept in the dark. All volumetric flasks were covered with aluminum foil to prevent the passage of light. All working solutions of H_2O_2 were prepared from the commercial solution (H_2O_2, 50 %) by dilution in ultrapure water to the required concentration. The pH measurements were carried out using a HACH sensION+ pH-meter calibrated with standard buffers of pH 4.01, 7.00 and 10.00 (25 °C), and the pH was then adjusted to the desired value by the addition of a few drops of H_2SO_4 (0.1 M).

All experiments were performed in an aerated 1-L cylindrical reactor, in which we immersed a double-walled quartz sleeve containing a high-pressure mercury lamp (250 W, Ingelec). Continuous circulation of water in the sleeve was used to maintain an adequate temperature in the treated solution. Constant agitation was assured by means of a magnetic stirrer placed at the reactor base.

The pH of the dye solution, the catalyst solution and the H_2O_2 solution was adjusted to the desired values. In the Fenton experiments, the Fe^{2+} ions were first added to the dye solution and homogenized for 15 min. Then, the H_2O_2 solution was added, and the reaction proceeded for 30 min. It may be noted that the Fe^{2+} ions were provided from the solution of $FeSO_4 \cdot 7H_2O$ (5 mM). Natural solar photo-Fenton experiments were performed under a clear sky when the sun was around its zenith. This was achieved at pH 3 by adding the Fe^{2+} ions to the dye solution. The reaction mixture was homogenized for 15 min. After this time, the H_2O_2 was quickly added, and the oxidation proceeded for 30 min.

By applying the photo-Fenton process, the pH of all reagents was adjusted to 3, the catalyst was first added to the dye solution, the mixture was homogenized for 15 min, and the H_2O_2 was then quickly added. The lamp was turned on, and the decolorization process proceeded for 30 min. For the H_2O_2/UV process, a desired molar ration of dye/H_2O_2 at pH 3 was irradiated for 30 min. AOP experiments with UV irradiation were carried out in dark conditions to avoid externallight interference.

For all AOPs, analytic samples of 5 ml were withdrawn at known intervals and analyzed using the UV–vis spectrophotometer. Decolorization of PS dye was monitored by measuring absorbance at a maximum absorption wavelength of 520 nm. The decolorization efficiency was determined by Eq.1:

$$\% \text{ Decolorization } = \left(\frac{A_0 - A_t}{A_0}\right) * 100 \qquad (1)$$

where A_0 is the initial absorption of PS, and A_t is the absorption of PS at reaction time.

3. RESULTS AND DISCUSSION

3.1. *Comparison of H_2O_2/UV, Fe^{2+}/H_2O_2, Fe^{2+}/H_2O_2/UV, solar photo-Fenton processes*

It is well known that all AOP processes, especially those involving hydrogen peroxide, like H_2O_2/ UV, Fe^{2+}/H_2O_2, Fe^{2+}/H_2O_2/UV systems, can produce highly oxidative species, like hydroxyl radical $HO^{\bullet}$ ($E = 2.8$ eV) and hydroperoxyl radical $HO_2^{\bullet}$, among others. However, many researchers have reported that the $HO^{\bullet}$ attacks the majority of organic molecules in wastewater [11]. This radical is known to be slightly selective and has an electrophilic character to react on organics [14–16], organometallics [17–19], inorganic ions [16], proteins [20], agrichemicals [21, 22] and dyes [4, 5].

This first step of this study attempted to compare Ponceau S removal kinetics in aqueous media by using H_2O_2/UV, Fe^{2+}/H_2O_2, Fe^{2+}/H_2O_2/UV and solar photo-Fenton systems. The kinetic results obtained under the experimental conditions ([PS] = 0.06 mM; [H_2O_2] = 1 mM; [Fe^{2+}] = 0.06 mM; pH = 3 and T = 23 °C) are given in Figure 2.
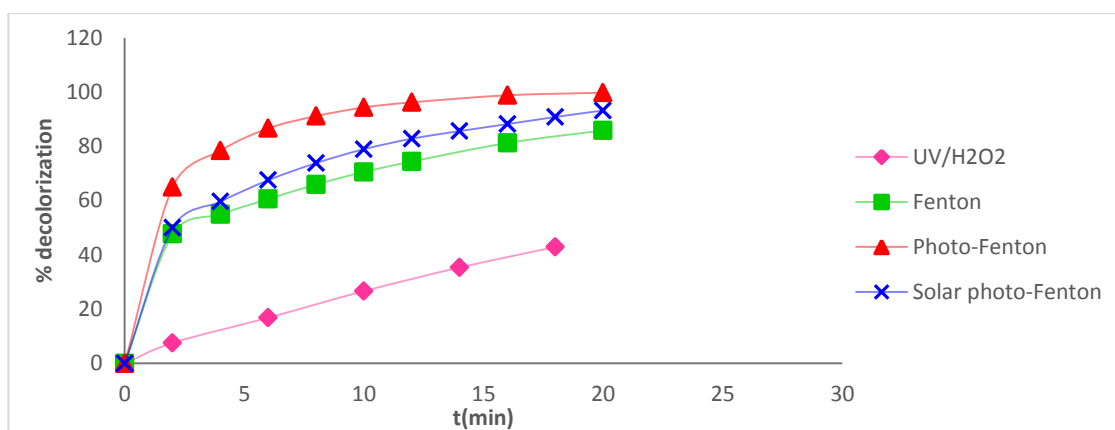
Fig. 2. Effect of different AOPs on the PS decolorization.
Experimental conditions: [PS] = 0.06 mM; [H$_2$O$_2$] = 1 mM; [Fe^{2+}] = 0.06 mM; pH = 3 and T = 23 °C.

To compare the efficiency of the oxidizing systems cited above against the dye disappearance, it has been noted, within 10 min of treatment, that the photo-Fenton process decolorized 94.3 % of the dye solution, followed by the solar photo-Fenton system, which destroyed 78.9 %, while the Fenton process degraded 70.5 %. The H$_2$O$_2$/UV process was slower than the three other methods, with a 26.6 % decolorization at 10 min.

Comparative studies revealed that the photo-Fenton process was the most useful for improving the PS decolorization rate. Therefore, it would be the most suitable to decolorize PS aqueous solutions.

Elsewhere, the decolorization of the dye with each of the systems adopted a pseudo-first-order kinetic, and the apparent rate constant values that emerged are provided in Table 1.
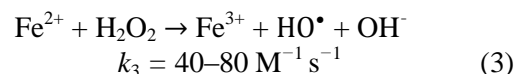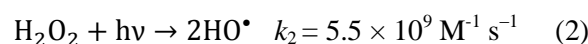
T a b l e 1

Apparent rate constant values for studying systems. Experimental conditions: [PS] = 0.06 mM; [H$_2$O$_2$] =1 mM; [Fe^{2+}] = 0.06 mM; pH = 3 and T = 23°C.

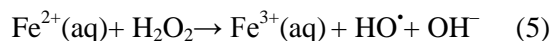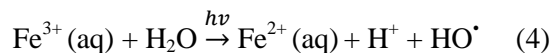| Oxidizing system	Apparent rate constant (min^{-1})
H$_2$O$_2$/ UV	0.031
Fe^{2+}/H$_2$O$_2$	0.111
solar photo-Fenton	0.141
Fe^{2+}/H$_2$O$_2$/UV	0.295

It is important to point out that all the examined oxidizing systems can generate several highly reactive radicals, among which is the hydroxyl radical HO$^{\bullet}$. The main reactions leading to the production of HO$^{\bullet}$ radicals are the photolysis of H$_2$O$_2$ by homolytic scission of the O-O bond in the case of the UV/H$_2$O$_2$ system (Eq. 2) and the catalyzed decomposition of H$_2$O$_2$ by Fe^{2+} in the Fenton process (Eq. 3). In photo-Fenton system, supplementary reactions that increase the hydroxyl radical dose and therefore the efficiency of degradation are discussed in the photo-Fenton process section, presented below [11].

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet} \quad k_2 = 5.5 \times 10^9 \text{ M}^{-1}\text{ s}^{-1} \quad (2)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-}$$
$$k_3 = 40\text{–}80 \text{ M}^{-1}\text{ s}^{-1} \quad (3)$$

3.2. *The photo-Fenton process*

The photo-Fenton process is one AOP that is increasingly studied. In fact, researchers reported that irradiation of the Fenton reaction system with UV-vis light strongly accelerated the rate of degradation of a variety of pollutants, due to the photochemical reduction of Fe^{3+} back to Fe^{2+}. As a result, the photo-Fenton process (Eq. 4 and 5) is faster than the conventional Fenton process [10, 23].

$$Fe^{3+} (aq) + H_2O \overset{h\nu}{\rightarrow} Fe^{2+} (aq) + H^{+} + HO^{\bullet} \quad (4)$$

$$Fe^{2+}(aq) + H_2O_2 \rightarrow Fe^{3+}(aq) + HO^{\bullet} + OH^{-} \quad (5)$$

It is worthwhile to stress that the rate of production of free radicals mainly depends on different experimental parameters, including pH solution and reagents' initial concentrations.

3.3. *Effect of initial pH*

It has been reported that pH is a crucial parameter that affects the evolution of the photo-Fenton process. In this section, we examine the effect of pH on the kinetics of PS decolorization.

The experiments were conducted with initial pH values of 3, 4, 5 and 6. Within this pH range, the PS decolorization kinetics can be described by a pseudo-first-order kinetic model, with:

$$r = -\frac{d[PS]}{dt} = k[PS] \qquad (6)$$

where k is the observed rate constant, t is the irradiation time and $[PS]$ is the dye concentration at time t.

Integrating (Eq. 6) and taking into account the verified linearity of the calibration curve, Eq. 7 can be considered:

$$\ln\left(\frac{[PS]}{[PS]_0}\right) = -kt \quad \text{or} \quad \ln\left(\frac{A}{A_0}\right) = -kt \qquad (7)$$

The slope of the plot of $\ln(A_0/A)$ against time yields the k values, where A_0 is the initial dye absorbance. The k values are represented in Figure 3.

The optimal rate of PS decolorization is obtained when the initial pH is around 3, with a rate constant of 0.8459 min^{-1}; beyond this pH value, and until pH 6, the dye removal kinetics have been delayed.

To ensure that Fe^{2+} and Fe^{3+} species exert their catalytic role, avoiding any precipitation of inactive iron oxyhydroxides and maximizing the concentration of photoactive species, the application of the photo-Fenton process implies operating in a narrow pH range (2.8–3.5) [23].
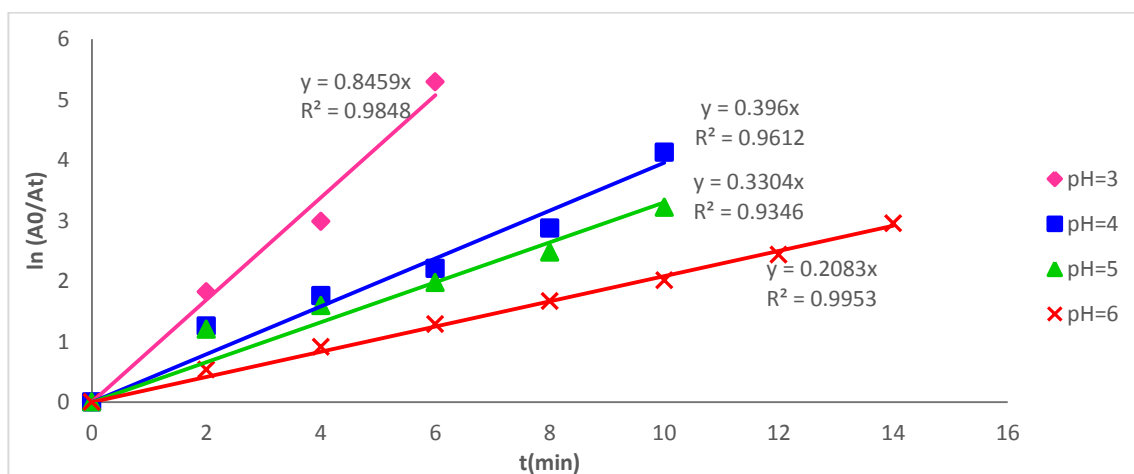

Fig. 3. First-order plots for the decolorization of PS by the photo-Fenton process at different values of pH. Experimental conditions: $[PS] = 0.06$ mM; $[Fe^{2+}] = 0.06$ mM; $[H_2O_2] = 1$ mM and $T = 23$ °C.

At pH 3, the predominant species in an aqueous Fe^{3+} salt solution is [Fe (II) (H$_2$O)$_5$ (OH)]$^+$ or simply Fe(OH)$^{2+}$, which undergoes a photoreaction to produce Fe^{2+} and supplementary HO$^•$ radicals as follows:

$$Fe\,(OH)^{2+} \xrightarrow{h\nu} Fe^{2+} + HO^• \qquad (8)$$
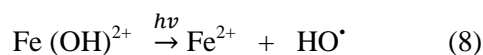
At very low pH values, an iron complex [Fe (II) (H$_2$O)$_6$]$^{2+}$ is formed and reacts more slowly with H$_2$O$_2$, therefore producing fewer HO$^•$ radicals [24].

In addition, hydrogen peroxide is solvated in the presence of the H$^+$ ions to form [H$_3$O$_2$]$^+$. Thus, oxonium ions make H$_2$O$_2$ more stable and reduce its reactivity toward ferrous ions [25]. In contrast, at increasing pH, ferric ions were subsequently transformed to the mono and the hydroxo complexes as [Fe(H$_2$O)$_5$(OH)]$^{2+}$ and [Fe(H$_2$O)$_4$(OH)$_2$]$^+$ [26].

3.4. *Effect of H$_2$O$_2$ concentration*

Depending on its concentration, H$_2$O$_2$ may enhance or inhibit the photo-Fenton process. Figure 4 shows the relationship between the PS decolorization and the initial concentration of H$_2$O$_2$ at pH 3 in the photo-Fenton process.

The PS decolorization using the photo-Fenton process at different oxidant dosages can be described by a pseudo-first-order kinetic model. The results verify that increasing the amount of H$_2$O$_2$ added from 0.1 mM to 1.5 mM increases the decolorization from 44.5 % to 98.8 % after about 8 min of irradiation (Fig. 4). It is clear that H$_2$O$_2$ promoted the generation of hydroxyl radicals HO$^•$, including those photogenerated by competitive hydrogen peroxide photolysis.
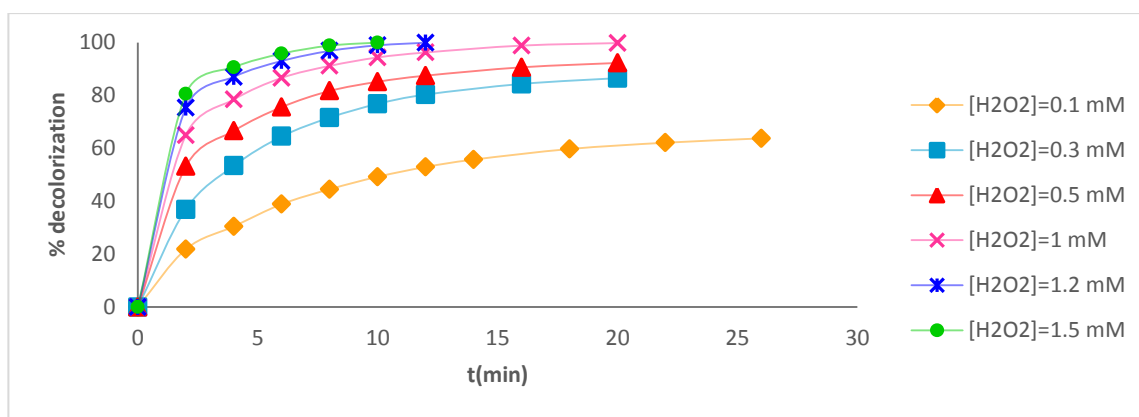
Fig. 4. Effect of H$_2$O$_2$ concentration on PS decolorization.
Experimental conditions: [PS] = 0.06 mM; [Fe^{2+}] = 0.06 mM; pH = 3 and T = 23 °C.

Moreover, the increase of the H$_2$O$_2$ initial concentration from 1 mM to 1.5 mM causes no significant change in decolorization, since at high concentrations, H$_2$O$_2$ acts as a hydroxyl radical quencher. Consequently, the HO$^\bullet$ concentration is lowered by various degradation reactions [27].

Thus, 1 mM of H$_2$O$_2$ appears as an optimal concentration for PS decolorization by the photo-Fenton process.

3.5. *Effect of Fe^{2+} concentration*

The amount of ferrous ion is one of the main parameters influencing the photo-Fenton process. The effect of the addition of Fe^{2+} on the PS decolorization while maintaining the initial H$_2$O$_2$ concentration at 1 mM has been studied in this experiment. The obtained results are represented in Figures 5 and 6.
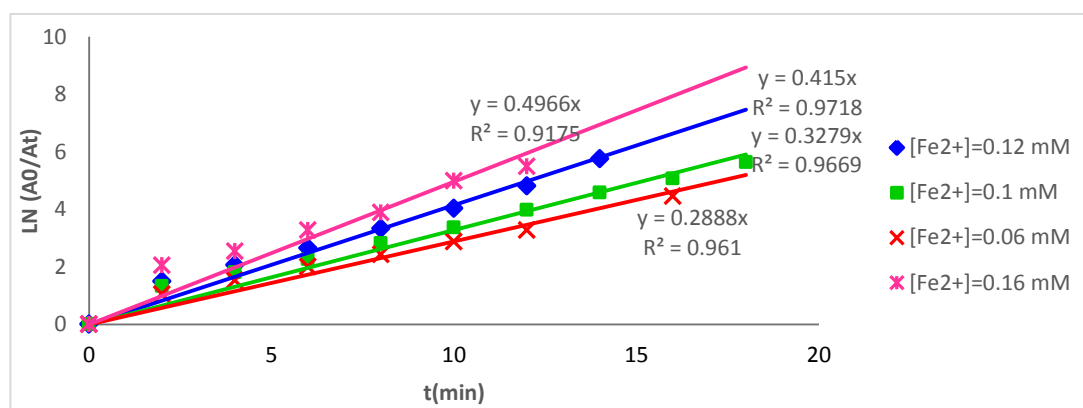

Fig. 5. First-order plots for the decolorization of PS by the photo-Fenton process at different Fe^{2+} concentrations.
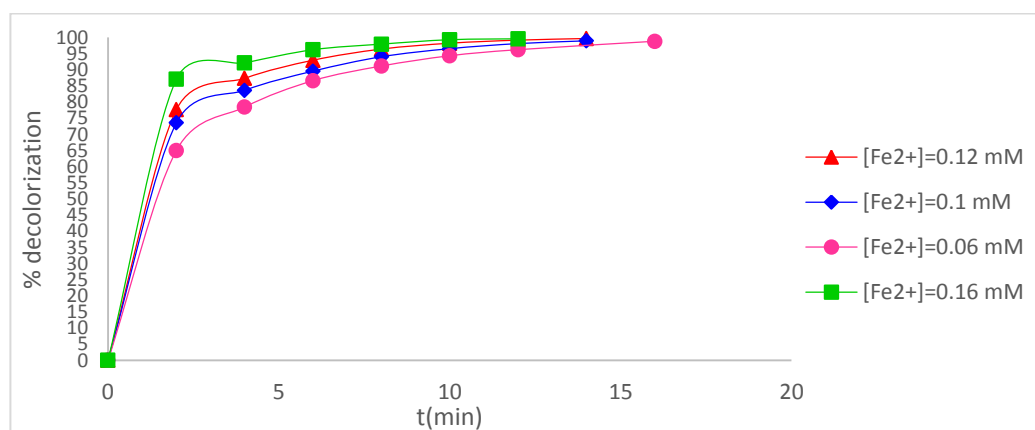Experimental conditions: [PS] = 0.06 mM; [H$_2$O$_2$] =1 mM; pH = 3 and T = 23 °C.

Fig. 6. Effect of Fe^{2+} concentration on PS decolorization.
Experimental conditions: [PS] = 0.06 mM; [H$_2$O$_2$] = 1 mM; pH = 3 and T = 23 °C.

It can be observed that the addition of Fe^{2+} above 0.06 mM did not affect the decolorization rate. It is known that when Fe^{2+} concentration is increased, its catalytic decomposition effect on H_2O_2 increases. Hence, a great amount of Fe^{3+} was produced, which underwent a reaction with hydroxyl ions to form $Fe(OH)^{2+}$, that strongly absorbed UV radiations. Thus, the strength of UV light would decrease, as can be seen in Eq. 9 – Eq. 11 [2].

$$Fe^{2+}(aq) + H_2O_2 \rightarrow Fe^{3+}(aq) + HO^{\bullet} + OH^- \quad (9)$$

$$Fe^{3+}(aq) + OH^- \rightarrow Fe(OH)^{2+} \quad (10)$$

$$Fe(OH)^{2+} \xrightarrow{hv} Fe^{2+} + HO^{\bullet} \quad (11)$$
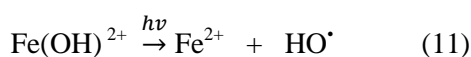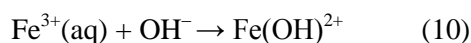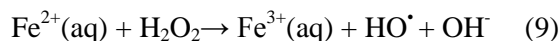
3.6. *Effect of inorganic anions*

Inorganic anions may be added to facilitate the dyeing process (e.g. Cl^-, CO_3^-) or may be present naturally in wastewater (e.g. NO_3^-). They may induce or reduce the oxidation rate of different dyes [28]. The main goal of this evaluation was to examine the effect of inorganic ions like bicarbonate, sulphate and nitrate on the kinetics of PS decolorization by the photo-Fenton process.

Three experiments were performed to investigate the influence of these inorganic ions, with a concentration of 0.5 mM added to the treated solution of PS by the photo-Fenton process. The results are presented in Figure 7.
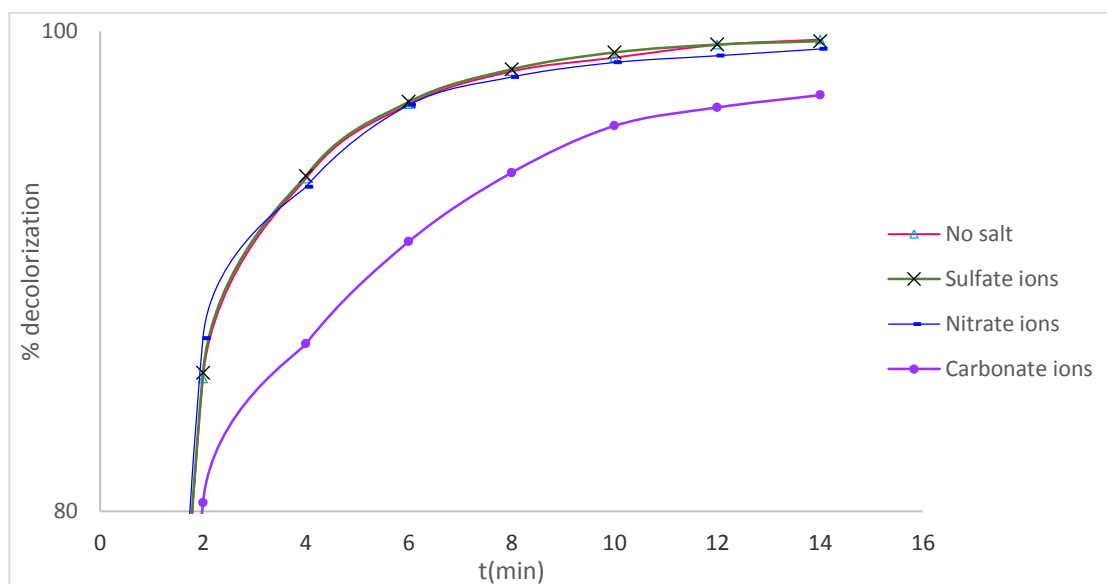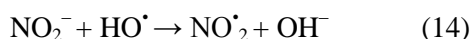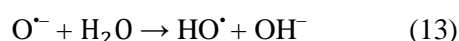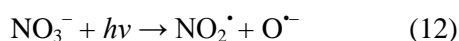

Fig. 7. Effect of inorganic anions on PS decolorization.
Experimental conditions: [PS] = 0.06 mM; [H_2O_2] = 1 mM; [Fe^{2+}] = 0.06 mM; [Inorganic anions] = 0.5 mM; pH = 3 and *T*= 23 °C.

The results show that the presence of $NaNO_3$ had a negligible effect on PS decolorization. This may be attributed to the scavenging of $HO^{\bullet}$ radicals by NO_3^-. Many studies show that photolysis of aqueous nitrate solutions can occur to form nitrite radicals (Eq. 12 – to Eq. 14), decreasing the availability of $HO^{\bullet}$ radicals for the photodegradation process [28; 29].

$$NO_3^- + hv \rightarrow NO_2^{\bullet} + O^{\bullet-} \quad (12)$$

$$O^{\bullet-} + H_2O \rightarrow HO^{\bullet} + OH^- \quad (13)$$

$$NO_2^- + HO^{\bullet} \rightarrow NO_2^{\bullet} + OH^- \quad (14)$$

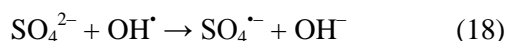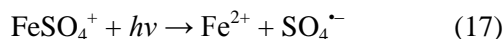The influence of carbonate ions on PS decolorization has been studied in this experiment. The results obtained demonstrate that the presence of carbonate ions decreases the decolorization rate of PS due to the scavenging of $HO^{\bullet}$ by HCO_3^- to produce $CO_3^{\bullet-}$ (Eq.15). The carbonate radical ($E° = 1.78$ V/ENH at pH = 0) is less reactive than $HO^{\bullet}$ radicals, which decreases the PS decolorization rate.

$$HCO_3^- + OH^{\bullet} \rightarrow CO_3^{\bullet-} + H_2O \quad (15)$$
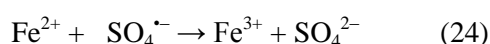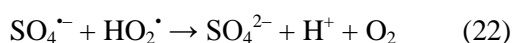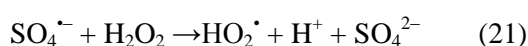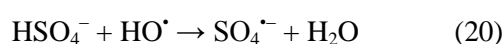
In addition, it is reported that in presence of carbonate ions, ferrous carbonate complexes [$Fe(CO_3)$, $Fe(CO_3)_2^{2-}$ and $Fe(CO_3)(OH)^-$] dominate the speciation of Fe^{2+} in natural waters containing greater than 1 mM carbonate alkalinity [29].

Moreover, it appears from Figure 7 that sulfate ions have no effect on PS decolorization, which can be assigned to forming complexes with

Fe^{2+} that are not easily oxidized [30]. Sulphate ions can form iron complexes (Eq.16), absorbing photons (Eq. 17) and generating sulphate radicals that can act as hydroxyl radical scavengers (Eq.18) [31].

$$Fe^{3+} + SO_4^{2-} \leftrightarrows FeSO_4^{+} \qquad (16)$$

$$FeSO_4^{+} + hv \rightarrow Fe^{2+} + SO_4^{\bullet-} \qquad (17)$$

$$SO_4^{2-} + OH^{\bullet} \rightarrow SO_4^{\bullet-} + OH^{-} \qquad (18)$$

These sulphate ions and their radicals in acidic medium can react as follows (Eq. 19) to (Eq. 24):

$$H^{+} + SO_4^{2-} \leftrightarrows HSO_4^{-} \qquad (19)$$

$$HSO_4^{-} + HO^{\bullet} \rightarrow SO_4^{\bullet-} + H_2O \qquad (20)$$

$$SO_4^{\bullet-} + H_2O_2 \rightarrow HO_2^{\bullet} + H^{+} + SO_4^{2-} \qquad (21)$$

$$SO_4^{\bullet-} + HO_2^{\bullet} \rightarrow SO_4^{2-} + H^{+} + O_2 \qquad (22)$$

$$SO_4^{\bullet-} + SO_4^{\bullet-} \rightarrow S_2O_8^{2-} \qquad (23)$$

$$Fe^{2+} + SO_4^{\bullet-} \rightarrow Fe^{3+} + SO_4^{2-} \qquad (24)$$

Overall, it can be said that the presence of sulphate ions in the treated mixture can inhibit the photo-Fenton process.

4. CONCLUSION

Advanced oxidation processes are found to be effective for the degradation of refractory compounds. Different AOPs have been reported to select the most appropriate technique for Ponceau S decolorization.

We can conclude from our results that the decolorization rate of the photo-Fenton process strongly differs from the three other AOPs under study.

The dye decolorization is fast for the Fenton process and becomes even faster for the photo-Fenton process. The photo-Fenton process proved more effective than the solar photo-Fenton process, while the UV/H_2O_2 process decreases the decolorization rate. The decolorization of PS in an aqueous solution by the photo-Fenton process strongly depends on the studied system parameters (initial pH, H_2O_2 and Fe^{2+} concentrations). At optimum conditions, the photo-Fenton process degrades 99.77 % in only 20 min. It is described by a pseudo-first-order kinetic model with a rate constant of 0.2951 min^{-1}.

Removal of the dye from the solution was inhibited by the presence of inorganic anions (NO_3^{-}, HCO_3^{-} and SO_4^{2-}), with the highest effect in the case of carbonate ions. The addition of inorganic anions in the dye solutions examined has, in general, an adverse effect on the decolorization rates.

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