Decolorization of Diazo Dye Ponceau S by Fenton Process

Muhammad Muslim[1], Md. Ahsan Habib[1*], Tajmeri Selima Akhter Islam[1],
Iqbal Mohmmad Ibrahim Ismail[2] and Abu Jafar Mahmood[1]

[1]Department of Chemistry, Faculty of Science, University of Dhaka, Dhaka 1000 Bangladesh
[2]The Center of Excellence in Environmental Studies, Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

----

Abstract

An attempt has been taken to decolorize and mineralize Ponceau S (PS), a diazo dye, in aqueous solution by Fenton process. Effects of solution pH, concentrations of H_2O_2, Fe(II) and PS on the decolorization of PS have also been studied through batch experiments. About 90% decolorization was found under the optimal conditions [PS]: [H_2O_2]: [Fe(II)] = 1:12:2 and [H_2O_2]/[Fe(II)] = 6 at pH 2.85 in 40 minutes. The overall results revealed that mineralization was rather slower as compared with the decolorization.

Keywords: Diazo dye; Fenton process; decolorization; mineralization.

Introduction

Azo-dyes are widely used in textile, printing, cosmetic, food colorants and pharmaceutical industries worldwide. Moreover such azo/diazo-dyes are also used in laboratories as either biological stains or pH indicators. Such a diazo-dye, Ponceau S (PS), is used in clinical laboratories as a protein-binding dye for staining blood serum proteins [1]. PS is also used in the textile dying industry, and in coloring leather and paper [2].

Azo/diazo dyes show persistent nature in the environment because of strong electron withdrawing character of the azo-group(s) which stabilizes the aromatic compounds against conversion by oxygenases. This durability nature makes azo-dyes as pollutants in the environment as the dyes discharged into the environment as effluent. Most of the synthetic azo-dyes including PS, and their biodegradation products, sulfonated and unsulfonated aromatic amines are toxic against aquatic organisms and suspicious of being carcinogenic and mutagenic to human [3-11].
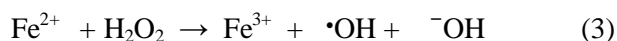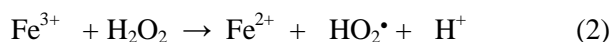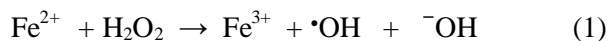
Therefore, the wastewater containing the above mentioned dyes require proper treatment before discharge into the nearby water body.

Various methods for removal of synthetic azo/diazo-dyes from wastewaters have been reported in the literature. These include adsorption on inorganic or organic matrices, biological activation, coagulation, chemical oxidation and electrochemical oxidation methods [3-5, 9-11]. Due to some drawbacks of the above mentioned methods, Advanced Oxidation Processes (AOPs) have been widely applied because of generation of highly reactive hydroxyl radical (·OH) which are responsible to degrade/mineralize the dye compounds [12]. As AOPs processes, Fenton's and photo-Fenton's type reactions are very promising since they achieve high reaction yields with a low treatment cost [13]. Electrochemical advanced Fenton process has been appied to decolorize/degrade Ponceau S in aqueous system [14].

----

*Corresponding Authors' Email: habibchemdu@yahoo.com
ajmahmood10@gmail.com

Fenton's reagent, a mixture of ferrous (Fe^{2+}) ion and hydrogen peroxide which produces hydroxyl radicals (Eq. (1)), has been used extensively for oxidation of organic matter in water, and to reduce the chemical oxygen demand (COD) and total organic carbon (TOC) content [15]. In Fenton's process, the generated Fe^{3+} ion reacts with H_2O_2 to re-generate Fe^{2+} ion which again reacts with H_2O_2 and form hydroxyl radicals (Equs. (2-3)). It has been reported that the Fenton process could be adopted rapidly in a textile wastewater treatment system [16]. The use of Fe^{2+}/H_2O_2 as an oxidant for wastewater treatment is attractive since iron is highly abundant and non-toxic, and a 30% hydrogen peroxide aqueous solution is easy to handle and environmentally not harmful.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + {}^{-}OH \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2{}^{\bullet} + H^+ \qquad (2)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + {}^{-}OH \qquad (3)$$

In the present work, we have investigated the decolorization/mineralization of Ponceau S by Fenton process in aqueous system. The influence of different operational parameters (pH, H_2O_2, Fe^{2+}, PS concentration, and optimal $[H_2O_2]_0/[Fe^{2+}]_0$ ratio) which affect the efficiency of Fenton reactions, in PS oxidation was also investigated.

Experimental
Materials

Ponceau S (PS), acid red 112 (C.I. 27195), was obtained from local dye suppliers and used as received without further purification. The structure of the dye is shown in (Fig. 1).
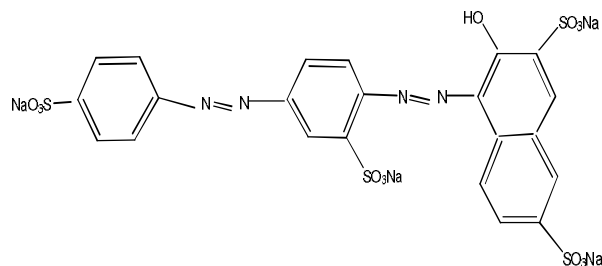

Figure 1. **Structure of Ponceau S (PS)**

Mohr's salt, hydrogen peroxide, hydrochloric acid, sodium hydroxide, sulfuric acid, nitric acid and potassium nitrate were purchased from BDH; all the chemicals were AnalaR grade and used without further purification. Double distilled and deionized water was used throughout the experiment.

Procedure

Decolorization of PS solution was carried out by Fenton process. Desired reaction mixtures were prepared from Mohr's salt, H_2O_2 and the dye stock solution. The desired pH of the solutions was adjusted with NaOH or HCl as required and measured using a pH meter (digital, Orion, Japan). The required amounts of Fe^{2+} and H_2O_2 were added simultaneously into the dye solution. A magnetic stirrer was used in order to achieve a homogeneous mixture, and the reaction time was recorded when the H_2O_2 solution was added. Samples of the dye solution were withdrawn during the course of the reaction, at periodic intervals, and analyzed using a UV-visible double-beam spectrophotometer (Shimadzu 160 A, Japan). The color of the dye solution in the reaction mixture at different times, was obtained by the measure of the absorbance at its maximum wavelength (λ_{max}= 520 nm) and by computing the concentration from calibration curve.

Percent and initial rate of decolorization

Decolorization or color removal of PS was calculated as, (X_t/X_o) x 100, where X_t is the absorbance at time 't' and X_o is that at $t = 0$. On the other hand, percent color remaining is $[(X_t - X_o)/X_o]$ x 100.

Initial rate (R_i) of decolorization. The equation $R_i = k[PS]_i$ was used to determine R_i, by multiplying the apparent first order rate constant k with the initial concentration of PS, $[PS]_i$. k was determined from the slope of the plot $\ln([PS]_i/[PS]_t)$ vs time.
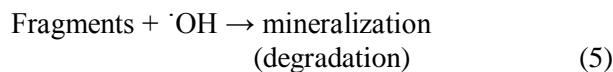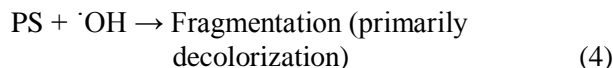
Results and Discussion

In the presence of Fe(II) and H_2O_2, PS solution starts loosing color in the absence of any light. The spectra were recorded as a function of time in the cell compartment, with water as

reference (data not shown). The spectra have considerable similarity with those that observed in the presence of ZnO and visible light [17], although decolorization is much faster. Previous investigation [18] using Fenton process show that the oxidizing power of the combination of Fe(II) + H_2O_2 is influenced by various factors, these factors have been controlled by using only Fe(II), keeping the temperature, initial pH, etc. constant.

In the present study, temperature has been kept constant and a Fe(II) salt has been used. The color changes have been recorded at 520 nm (λ_{max} of PS) under constant solution pH. The spectral changes have been associated with the decolorization of PS solution containing Fe(II) and H_2O_2. It has been found that decolorization precede the mineralization. It is caused by formation of $^{\cdot}OH$ radicals in the system (Equs. 1-3) which is highly reactive non-specific oxidant [19].

The - N = N - of PS is the most active site for oxidative attack by a ^{-}OH radical [20,21]. This attack causes the PS molecules to be fragmented into two intermediates, one containing naphthalene moiety and the other, a benzene ring. During the process the solution starts loosing color. The hydroxyl radicals also attack the fragments leading to their complete conversion to CO_2 and H_2O, SO_4^{2-} ions result from - SO_3^- groups. Such conversions may proceed by hydrogen abstraction from one of the intermediates and – C = C – addition [21].

The overall degradation of PS by Fe(II) + H_2O_2 can be represented by two ideal steps:

$$PS + {}^{\cdot}OH \rightarrow Fragmentation\ (primarily \qquad decolorization) \qquad\qquad (4)$$

$$Fragments + {}^{\cdot}OH \rightarrow mineralization \qquad\qquad (degradation) \qquad\qquad (5)$$

Fragments may also be reactive intermediates. The oxidation in equation (4) may also be done by other species, such as dissolved oxygen, other radicals, etc. Fragments may also be reactive intermediates. After initiation of fragmentation, radical intermediates and $HO_2^{\cdot}$ radicals may also be agents for subsequent fragmentation of remaining PS molecules. All

these cause much faster decolorization than that done by ZnO + visible light and H_2O_2 + UV processes [22].

Effect of pH

Fig. 2 shows that about 75 % decolorization of PS in solution takes place after 5 minutes at initial pH = 2.85 ([PS] = 5.00×10^{-5} M, [H_2O_2] = 6.00×10^{-4} M and [Fe(II)] = 4.00×10^{-5} M).
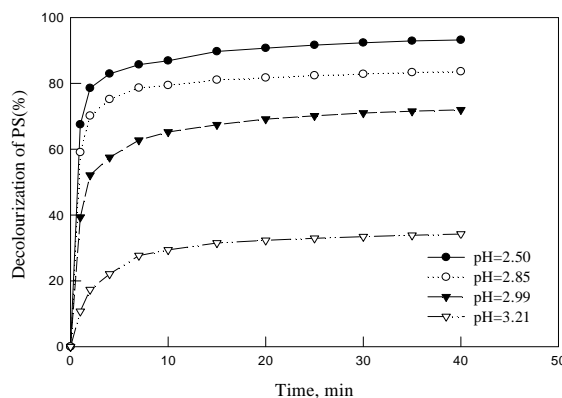
Figure 2. **Influence of pH on the decolorization of PS solution by Fe(II) + H_2O_2. [H_2O_2] = 6.00 x 10^{-4} M, [PS] = 5.00 x 10^{-5}M, [Fe(II)] = 4.00 x 10^{-5} M**

This decolorization reaches at about 82 % after 40 minutes. At the same concentrations of the reactants, the initial rate of decolorization starts decreasing abruptly above 2.9 (Fig. 3). At pH 3.21 only about 26 % decolorization takes place after 5 minutes. Although not to the same extent, the trend in the changes of decolorization pattern is similar to that of OG [22].
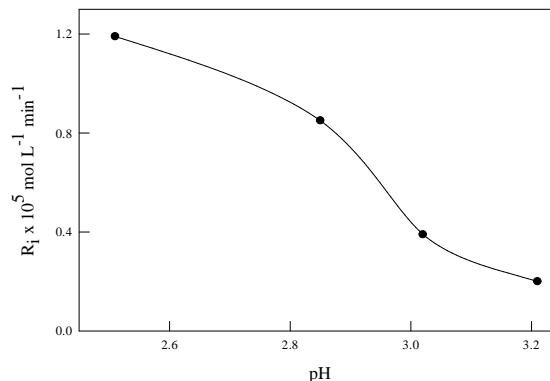
Figure 3. **Influence of pH on the initial rate of decolorization of PS in solution by Fe(II) + H_2O_2. [H_2O_2] = 6.00×10^{-4} M, [PS] = 5.00×10^{-5}M, [Fe] = 4.00×10^{-5} M**

The formation of Fe^{3+} initiates the Fe^{3+}/H_2O_2 stage (Equ. (2)) in the decolorization of PS in solution. Apparently this stage starts getting prominent with time, as indicated with slower change of decolorization at each initial pH (Fig. 3).

Effect of H_2O_2

The increase of H_2O_2 concentration increases decolorization but it is fairly rapid up to about first 5 minutes (Fig. 4). Afterwards decolorization increases slowly.
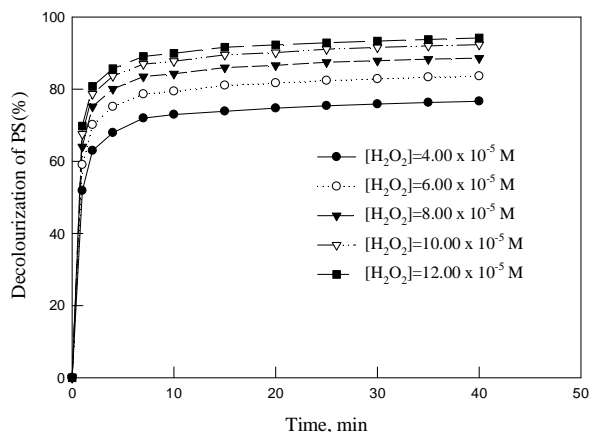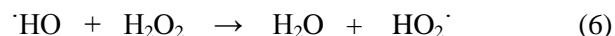

Figure 4. **Influence of $[H_2O_2]$ on decolorization of PS solution by Fe(II) + H_2O_2. pH = 2.85, [PS] = 5.00×10^{-5} M, [Fe] = 4.00×10^{-5} M**

The increase of H_2O_2 concentration from 4.00×10^{-4} M to 12.00×10^{-4} M, at pH 2.85, [PS] = 5.00×10^{-5} M and [Fe(II)] = 4.00×10^{-5} M, after 5 minutes reaction, decolorization increases from about 68 % to 88 %. After 40 minutes of reaction the increase in decolorization is from about 77 % to about 94 %. That is, with 12.00×10^{-4} M H_2O_2 after 35 minutes of reaction only about increase 6% decolorization has been achieved. In terms of the initial rate of decolorization (Fig. 5) the three folds increase in concentration (from 4.00×10^{-5} M to 12.00×10^{-5} M) there is less than three folds increase in the rate (Table 1). This is because during the first 5 minutes most of the PS molecules are attacked by $\cdot$OH radical.

This seems to be the predominant event so long $[H_2O_2]/[Fe(II)] > 20$, even though $[Fe(II)]/[PS] < 1$. Subsequently $\cdot$OH radicals find it convenient to attack H_2O_2 molecules which are in

large excess [23], according to the following equation (6):

$$\cdot HO + H_2O_2 \rightarrow H_2O + HO_2\cdot \qquad (6)$$

Further generation of $\cdot$OH radicals needs to be through the much slower reaction between Fe^{3+} and H_2O_2 (Equ. 2).
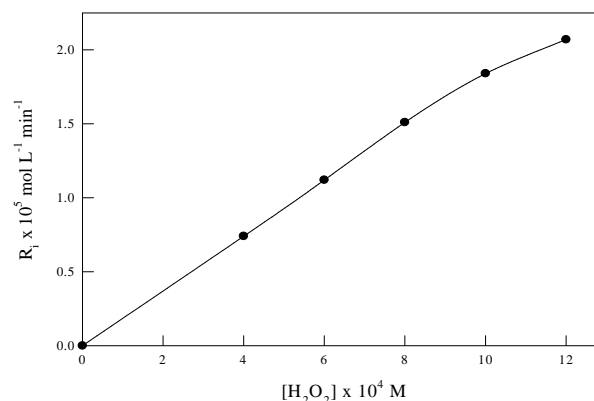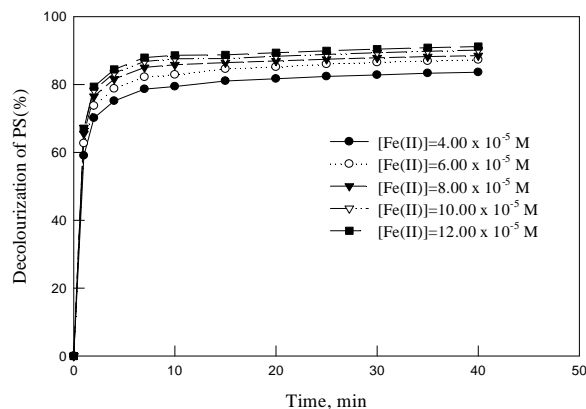

Figure 5. **Influence of $[H_2O_2]$ on the initial rate of decolorization of PS solution by Fe(II) + H_2O_2. pH=2.85, [PS]=5.00×10^{-5} M, [Fe(II)] = 4.00×10^{-5} M**

Effect of Fe(II)

Figs. 6 and 7 show the effect of increasing Fe(II) concentration on the decolorization and the initial rate of decolorization of PS in solution respectively. Doubling the Fe(II) concentration from 4.00×10^{-5} M to 8.00×10^{-5} M increases the decolorization by about 7 %, from 75% to about 82% after 5 minutes. After 40 minutes these increases are about 84% and 89% respectively. Thus higher concentrations of Fe(II) cause higher decolorization but the overall differences in decolorization after 5 minutes and 40 minutes are not that spectacular. The initial rates of decolorization of PS in solution (Fig. 7) are 1.11×10^{-5} molL^{-1} mim^{-1}, 1.48×10^{-5} mol L^{-1} min^{-1} and 1.68×10^{-5} mol L^{-1} min^{-1} at Fe(II) concentrations 4.00×10^{-5} M , 8.00×10^{-5} M and 12.00×10^{-5} M respectively (Table 1).

These correspond to only about 34% and 51% enhancement on the basis of the initial rate of decolorization of PS. These data suggest that there is a considerable deceleration of the initial rate of decolorization of PS in solution, probably, beyond certain concentration of Fe(II). If 4.00×10^{-5} M be

the limit of the linear increase of the initial rate of decolorization of PS in solution (Fig. 7) with Fe(II) concentration, it is found that at [PS] = 5.00 x 10^{-5} M and pH 2.85, 15 folds higher concentration of H_2O_2 ([H_2O_2] : [Fe(II)] = 15 : 1) is needed to maintain the linear increase of the initial rate of decolorization up to this concentration of Fe(II). Obviously this is the minimum H_2O_2 concentration which required under the present conditions.
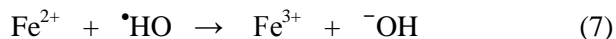

Figure 6. **Influence of [Fe(II)] on the decolorization of PS solution by Fe(II) + H_2O_2. pH=2.85, [PS]=5.00 $\times$ 10^{-5} M, [H_2O_2]=6.00 $\times$ 10^{-4} M**
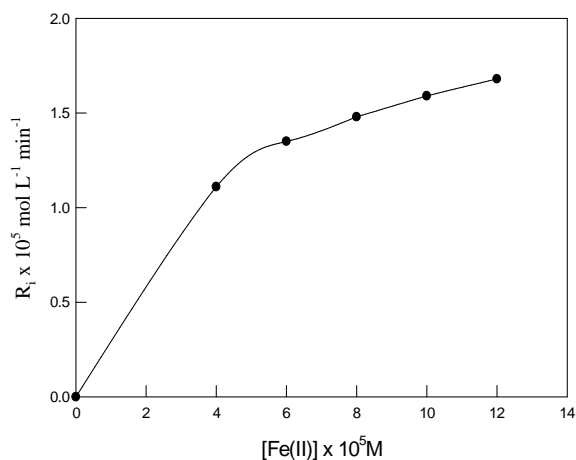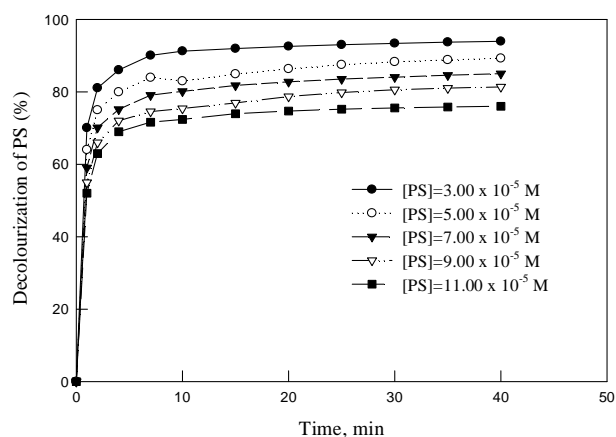

Figure 7. **Influence of [Fe(II)] on the initial rate of decolorization of PS solution by Fe(II) + H_2O_2. pH=2.85, [PS]=5.00 $\times$ 10^{-5} M, [H_2O_2]=6.00 $\times$ 10^{-4} M**

With higher concentrations of Fe(II) equations (2) and (7) become favorable. Ultimately considerable deceleration in the initial rate of decolorization becomes unavoidable.

$$Fe^{2+} \quad + \quad {}^{\bullet}HO \quad \rightarrow \quad Fe^{3+} \quad + \quad {}^{-}OH \qquad (7)$$

Effect of PS concentration

Fig. 8 shows that after 5 minutes decolorization of PS drops from about 85 % to about 65% when its concentration is raised from 3.00×10^{-5} M to 11.00×10^{-5} M (pH = 2.85) and [H_2O_2] = 6.00×10^{-4} M) and [Fe(II)] = 4.00×10^{-5} M).

Figure 8. **Influence of [PS] on the decolorization of PS solution by Fe(II) + H_2O_2. pH = 2.85, [H_2O_2] = 6.00 x 10^{-4} M) and [Fe(II)] = 4.00 x 10^{-5} M)**

After 40 minutes corresponding decolorization is about 94 % and 70 % respectively. The initial rate of decolorization increases with the increase of PS concentration (Fig. 9), but this increases is only about 71 % and about 140 % when PS concentrations are 5.00 $\times$ 10^{-5} M and 9.00 $\times$ 10^{-5} M respectively, on the basis of the initial rate 0.65 $\times$ 10^{-5} mol L^{-1} min^{-1} at [PS] = 3.00 $\times$ 10^{-5}. According to (Fig. 10) the initial rate of decolorization of PS should increase linearly, may be up to 5.00 x 10^{-5} M, when [H_2O_2] / [Fe(II)] = 15 and pH of the solution is 2.85. At this fixed ratio of H_2O_2 to Fe(II) and pH, further increase of PS concentration beyond this limit, initiates deceleration of the initial rate of decolorization of PS in solution. This limit is set by the ratio of [Fe(II)] to [PS]. The relative ratio of the concentration of the metal ion with respect to the organic substrate is critical in Fenton process [24-26].

Accordingly [Fe(II)]/[PS] should have an optimum value for the best utilization of $^\bullet OH$ radicals for decolorization/degradation of PS in solution [26]. (Fig. 9) shows that deceleration starts when [Fe(II)]/[PS] value becomes < 0.8, as this onsets other competitive process for $^\bullet OH$ radicals.

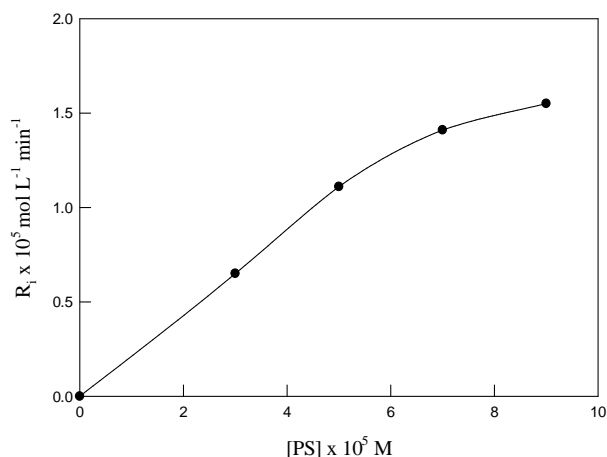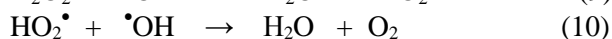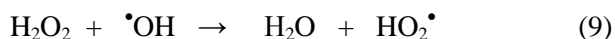*Figure 9.* **Influence of [PS] on its initial rate of decolorization in solution by Fe(II) + H_2O_2, pH=2.85, [H_2O_2]=6.00 × 10^{-4} M, [Fe(II)] = 4.00 × 10^{-5} M**

Table 1 presents a comparative view of the effects of pH, concentration of H_2O_2, Fe(II) and PS on the decolorization process of PS in solution. Although low pH seems to favor complete decolorization of PS in solution within 60 minutes, [PS] : [H_2O_2] : [Fe(II)] being 1.25 : 15 :1, the probability of scavenging of $^\bullet OH$ radicals by equation (8) remains high, Moreover, the ratio 1.25 : 15 :1 cannot be considered optimum for practical purposes [28].

$$^\bullet OH \ + \ H^+ + \ e \ \rightarrow \ H_2O \qquad (8)$$

Table 1 shows that [Fe(II)]/[PS] < 1 situation can be compensated by using higher H_2O_2 concentration. For example, when [Fe(II)]/[PS]<1 by maintaining [H_2O_2]/[Fe(II)] = 25, more than 90% decolorization is possible at pH 2.85 in 40 minutes. However, in this case, too much $^\bullet OH$ radicals may be generated and competitive process like equations (9) and (10) may be predominant. On the other hand, if the [Fe(II)]/[PS]) is kept slightly above 1, about 87 % decolorization can be

$$H_2O_2 \ + \ ^\bullet OH \ \rightarrow \ H_2O \ + \ HO_2^\bullet \qquad (9)$$
$$HO_2^\bullet \ + \ ^\bullet OH \ \rightarrow \ H_2O \ + \ O_2 \qquad (10)$$

achieved after 40 minutes reaction with [H_2O_2] = 6.00 × 10^{-4} M ([H_2O_2] / [Fe(II)] = 10). Considering all of the above, an optimum ratio of the concentration of reactants appears to be [PS] : [H_2O_2] : [Fe(II)] = 1:12:2 (Table 1) and about 90% decolorization can be achieved with ([H_2O_2]/[Fe(II)] = 6 at pH 2.85 in 40 minutes.

Table 1. **Influence of various parameters on decolorization of PS solutions by Fe(II) + H_2O_2 (Temp 30 ^{o}C).**

[PS] × 10^5M	pH	[H_2O_2] × 10^4M	[Fe(II)] × 10^5M	Initial rate, Ri × 10^5 mol L^{-1} min^{-1}	% decolorization after 40 min.
5.00	2.85	4.00	4.00	0.75	76.65
		6.00		1.11	83.61
		8.00		1.51	88.57
		10.00		1.84	92.34
		12.00		2.07	94.18
5.00	2.85	6.00	4.00	1.11	83.61
			6.00	1.35	87.30
			8.00	1.48	88.50
			10.00	1.59	90.13
			12.00	1.68	91.20
3.00	2.85	6.00	4.00	0.65	93.96
5.00				1.11	83.61
7.00				1.41	76.03
9.00				1.55	69.65
5.00	2.50	6.00	4.00	1.38	93.19
	2.85			1.11	83.61
	2.99			0.56	71.97
	3.21			0.24	34.21

Conclusion

The results showed that Fenton process is powerful method for decolorization of Ponceau S. The results indicate that the degree of decolorization of PS was obviously affected by the initial concentration of the dye, Fe(II), H_2O_2, and value of solution pH. The optimum conditions for the decolorization of PS were observed at pH = 2.85 with an optimum ratio of [H_2O_2]/[Fe(II)] = 6.

References

1. V. S. Bannur, V. S. Kulgod, S. S. Metkar, K. S. Mahajan and K. J. Sainis, *Anal. Biochem.*, 267 (1999) 382.

2.   R. C. Meena, R. B. Pachwarya, V. K. Meena and S. Arya, *Am. J. Environ. Sci*., 5 (2009) 444.

3.   W. Haug, A. Schmidt, B. Nortemann, D. C. Hempel, A. Stolz and H. J. Knackmuss, *Appl. Environ. Microbiol*., 57 (1991) 3144.

4.   M. Kudlich, P. L. Bishop, H. J. Knackmuss and A. Stolz, *Appl. Microbiol. Biotechnol*., 46 (1996) 597.

5.   K. T. Chung, S. E. J. Stevens and C. E. Cerniglia, *Crit. Rev. Microbiol*., 18 (1992) 175.

6.   B. N. Ames, J. McCann and E. Yamasaki, *Mutat. Res*., 31 (1975) 347.

7.   S. W. Oh, M. N. Kang, M. W. Cho and M. W. Lee, *Dyes Pigm*., 33 (1997) 119.

8.   W. G. Levine, *Drug Metab. Rev*., 23 (1991) 253.

9.   J. I. Garrote, M. Bao, P. Castro and M. J. Bao, *Water Res*., 29 (1995) 2605.

10. E. Forgacs, T. Cserhati and G. Oros, *Environ. Int*., 30 (2004) 953.

11. M. A. Oturan, N. Oturan, C. Lahitte and S. Trevin, *Electroanal. Chem*., 507 (2001) 96.

12. Y. M. Li, Y. Q. Lu and X. L. Zhu, *J. Hazard. Mater*,. 132 (2006) 196.

13. R. Bauer and H. Fallman, *Res. Chem. Intermed*., 23 (1997) 341.

14. H. S. El-Desoky, M. M. Ghoneim and N. M. Zidan, *Desalination* 264 (2010) 143.

15. F. A. Momani, C. Sans and S. A. Esplugas, *J. Hazard. Mater*., 107 (2004) 123.

16. S. F. Kang, C. H. Liao and S. T. Po, *Chemosphere*, 41 (2000) 1287.

17. M. Muslim, M. A. Habib, A. J. Mahmood, T. S. A. Islam and I. M. I. Ismail, *Inter. Nano Lett*., 2:30 (2012) doi:10.1186/2228-5326-2-30.

18. H. Kusic, N. Koprivance and L. Srsan, *Photochem. Photobiol., A : Chem.,* 181 (2006) 195.

19. G. M. Collona, T. Caronna and B. Marcandalli, *Dyes Pigm.*, 41 (1999) 221.

20. Z. Sun, Y. Chen, Q. Ke, Y. Yang and J. Yuan, *J. Photochem. Photobiol. A: Chem.*, 149 (2002) 169.

21. J. Li, C. Chen, J. Zho, H. Zhu and J. Orthman, *J. Appl. Catal.,* 37 (2002) 331.

22. M. Muslim, 2009. Photoelectrochemical studies of some dyes, PhD thesis, University of Dhaka, Bangladesh.

23. M. S. Lucas and J. A. Peres, *Dyes Pigm.*, 71 (2006) 236.

24. E. Neyens and J. Baeyens, *J. Hazard. Mater.*, 98 (2003) 33.

25. M. Muruganandham and M. Swaminathan, *Dyes Pigm.*, 63 (2004) 315.

26. S. Irmak, H. I. Yavuz and O. Erbatur, *Appl. Catal., B: Environ.*, 63 (2006) 243.