PHOTOCATALYTIC DEGRADATION OF SUMIFIX SUPRA BLUE BRF

Moh Pak Yan[1], Razak Ali[2] and Wan Azelee Wan Abu Bakar[2]

[1]School of Science and Technology
Universiti Malaysia Sabah, 88999 Kota Kinabalu, Sabah, Malaysia
[2]Faculty of Science,
Universiti Teknologi Malaysia, 81310, Skudai, Johor Bahru, Johor, Malaysia

ABSTRACT. *Oxidative degradation of textile azo dye, Sumifix Supra Blue BRF (SSBBRF) in aqueous solution of suspended TiO_2 with the present of UV irradiation and H_2O_2 has been studied. The addition of H_2O_2 in the photocatalytic system has enhanced the degradation degree of SSBBRF solution. However, H_2O_2 concentration that more than 5×10^{-4} mol/L would detriment the degradation process. Study on the kinetics of oxidative degradation of SSBBRF solution in the TiO_2/UV or $TiO_2/H_2O_2/UV$ systems show that the systems are following the pseudo-first order reaction with the rate constant, k, of the optimal system is equal to 0.0434 min^{-1}.*

KEYWORDS. Advanced oxidation processes, photocatalytic degradation, TiO_2, H_2O_2

INTRODUCTION

Dyes have been identified as the most problematic compounds due to their strong colour property and highly molecular structure constitution (Balciolu and Arslan, 1997; Spadaro *et al.* 1994). The dye molecules cannot be treated efficiently by an activated sludge processes or any combination of biological, chemical and physical methods (Tanaka *et al.*, 2000; Lin and Lin, 1993.) in which these methods only transfer dyes molecule from liquid to solid form (Moh, 2002). Among chemically synthesized dyestuff, azo dyes that are less sensitive to temperature, liquor ratio, addition of common salt and the pH of solution are produced in the largest quantities (Tanaka *et al.*, 1999; Zollinger, 1991). Furthermore, recent study indicated that approximately 12% of synthetic dye is lost annually during manufacturing and processing operations and that 20% of the resultant colour enter the environment through effluents from industrial wastewater treatment plants (Arslan *et al.*, 2000).

Many researchers have reported that azo dyes can be decolourised by advanced oxidation processes (AOPs). AOPs are ambient temperature processes involving the formation of hydroxyl radical (•OH) that aggressively and almost indiscriminately oxidised and mineralized the organic pollutants to water and carbon dioxide (Arslan, 2000; Ghaly, 2001). Among the AOPs, titanium dioxide-mediated heterogeneous photocatalytic ($TiO_2/$ UV–A) treatment process are capable of absorbing near-UV spectral region (300 nm < » < 400 nm) to initiate radical reactions. Their application would practically eliminate major operating costs when solar radiation is employed instead of artificial UV light (Arslan, 2000).
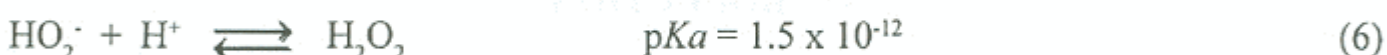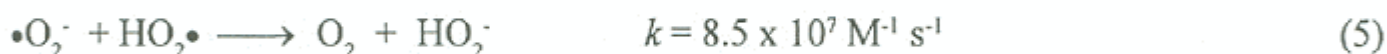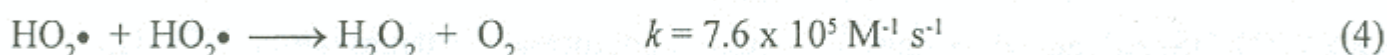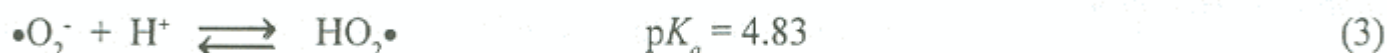
The initiating event of this photocatalytic degradation is the absorption of light by titanium dioxide particles in the region of wavelength below 400 nm (Zhang et al., 1998). The adsorbed photon must be greater than band-gap of the titanium dioxide particles (ΔE_{BG} = 3.2 eV) to form the electron-hole pairs (Zhang et al., 1998; Okamoto et al., 1985; Hoffmann et al., 1995).

$$TiO_2 + h\nu \longrightarrow TiO_2(e^-_{CB} + h^+_{VB})_{surf} \tag{1}$$

The oxygen molecule, which adsorb on the surface of titanium dioxide (TiO_2) molecule, prevents the recombination of electron-hole pairs by trapping the electrons. Subsequently, superoxide radical anions ($\bullet O_2^-$) are formed (Okamoto, 1985; Hoffmann, 1995; Dionysiou, 2000).

$$O_2 + e^-_{CB} \longrightarrow \bullet O_2^- \tag{2}$$

It is likely that H_2O_2 is formed from $\bullet O_2^-$ according to the following reactions (Okamoto, 1985; Pelizzetti, 1993).

$$\bullet O_2^- + H^+ \rightleftharpoons HO_2\bullet \qquad\qquad pK_a = 4.83 \tag{3}$$

$$HO_2\bullet + HO_2\bullet \longrightarrow H_2O_2 + O_2 \qquad\qquad k = 7.6 \times 10^5 \; M^{-1} \, s^{-1} \tag{4}$$

$$\bullet O_2^- + HO_2\bullet \longrightarrow O_2 + HO_2^- \qquad\qquad k = 8.5 \times 10^7 \; M^{-1} \, s^{-1} \tag{5}$$

$$HO_2^- + H^+ \rightleftharpoons H_2O_2 \qquad\qquad pKa = 1.5 \times 10^{-12} \tag{6}$$

The $\bullet OH$ radicals can be formed from H_2O_2 by anyone of the following reactions, but most probably via Equation 9 with respect to photocatalysis process Okamoto, 1985; Hoffmann, 1995; Dionysiou, 2000).

$$H_2O_2 + h\nu \; (\gg < 310 \, nm) \longrightarrow 2 \bullet OH \tag{7}$$

$$H_2O_2 + \bullet O_2^- \longrightarrow \bullet OH + OH^- + O_2 \tag{8}$$

$$H_2O_2 + e^- \longrightarrow \bullet OH + OH^- \tag{9}$$

On the other hand, holes may also react with either H_2O or OH^-, which adsorb on titanium dioxide surface to generate $\bullet OH$ radicals (Dionysiou, 2000; Hisanaga, 1990)

$$H_2O + h^+_{VB} \longrightarrow \bullet OH + H^+ \tag{10}$$

$$OH^- + h^+_{VB} \longrightarrow \bullet OH + OH^- \tag{11}$$

Equation 7 to 11 implies that the addition of H_2O_2 into TiO_2-mediated system may accelerate the photocatalytic process.

The purpose of this work was to investigate the effect hydrogen peroxide (H_2O_2) in titanium dioxide-mediated heterogeneous photocatalytic (TiO_2/UV–A) system towards the degradation simulated textile waste effluent, Sumifix Supra Blue BRF (SSBBRF).

EXPERIMENTAL

Chemical Reagents

All the chemical reagents in this research are being used without further purifications. Titanium (IV) oxide ($TiO_2 > 99.0\%$ of anatase form), which manufactured by Sigma Chemical Co. Ltd., was used as photocatalyst. Hydrogen peroxide (H_2O_2 35% w/w, 1L = 1.13 kg), manufactured by Riedel de-Haën was added in order to accelerate the photo-oxidation process. Sumifix Supra Blue BRF, which manufactured by Sumitomo Chemical Co. Ltd. was chosen as a representative compound found in textile-dyeing effluent. Elgastat UHQ deionised system, manufacture by Elga Ltd., England, was used to produce deionised water for preparing the chemical reagents.

Experimental Set-up

In this research, a cylindrical Pyrex photo-reactor of 400-mL capacity was used for the preliminary treatment SSBBRF solution using TiO_2-mediated photocatalytic processes. The photoreactor set-up of this study is shown in Figure 1.
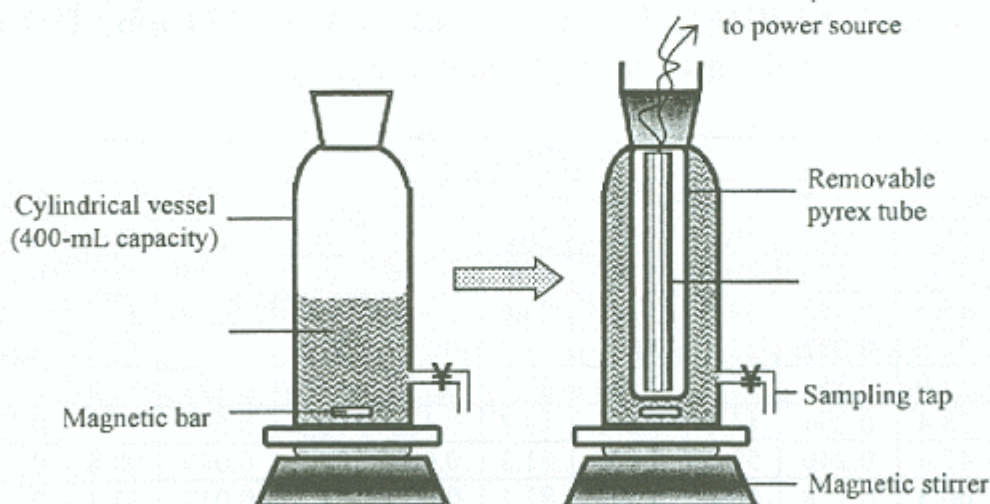

Figure 1. Photo-reactor set-up for TiO_2/UV and TiO_2/H_2O_2/UV system

Methods

For each experiment, 500-mL reaction solution of 5×10^{-5} mol/L SSBBRF was prepared using the deionised water. TiO_2 powder (ca. 0.1250 g) was added into the solution and the magnetic stirrer was switched on to keep TiO_2 suspended in the solution. Finally, the vessel was capped with a removable pyrex tube and the UV lamp was placed through the

tube as shown in Figure 1. Samples were withdrawn at 0, 10, 20, 30, 45, 60, 90 and 120-minute time intervals and analysed by Shimadzu UV-Visible spectrophotometer of UV-1601PC model to obtain the UV-visible lights absorption of the samples (at λ_{mas}: 613 nm). The experiment was repeated with the present of H_2O_2 ($1 \times 10^{-5}, 5 \times 10^{-5}, 1 \times 10^{-4}, 5 \times 10^{-4}$ and 1×10^{-3}-mol/L H_2O_2).

RESULTS AND DISCUSSION

Table 1 shows the absorbance (λ_{max} = 613 nm) and degree of degradation, D_{Abs}, of the collected SSBBRF solution at different time interval. Obviously, in the presence of 354-nm UV radiation and TiO_2 powder, the addition of H_2O_2 will increase the degradation of the SSBBRF solution. During the first-hour contact time, only 47.4% of 5×10^{-5}-mol/L SSBBRF solution was degraded in the absence of H_2O_2, whilst 53.2%, 61.3%, 84.9%, 90.8% and 84.2% of the degradations were observed with $1 \times 10^{-5}, 5 \times 10^{-5}, 1 \times 10^{-4}, 5 \times 10^{-4}$ and 1×10^{-3}-mol/L H_2O_2 concentration respectively. Further, after 2-hour contact time, only 73.8% of the SSBBRF solution was degraded in the absence of H_2O_2, whilst 80.0%, 91.9%, 96.6%, 99.4% and 98.7% of the SSBBRF solutions were degraded with $1 \times 10^{-5}, 5\ 10^{-5}, 1 \times 10^{-4}, 5 \times 10^{-4}$ and 1×10^{-3}-mol/L H_2O_2 concentration respectively.

Table 1. Absorbance, Abs (λ_{max} = 613 nm), and degradation degree, D_{Abs} (%), of SSBBRF solution treated in TiO_2 suspended photocatalytic system with different initial H_2O_2 concentration. ([SSBBRF]$_i$: 5×10^{-5} mol/L, UV λ: 354 nm, TiO_2:solution = 0.5 g/L, contact time: 2 hours)

Contact time (min)	[H₂O₂], (mol/L)											
	Absence		1×10^{-5}		5×10^{-5}		1×10^{-4}		5×10^{-4}		1×10^{-3}	
	Abs	D_{Abs}	Abs	D_{Abs}	Abs	D_{Abs}	Abs	D_{Abs}	Abs	D_{Abs}	Abs	D_{Abs}
0	0.534	0.0	0.526	0.0	0.509	0.0	0.524	0.0	0.531	0.0	0.476	0.0
10	0.451	15.5	0.440	16.4	0.389	23.6	0.342	34.7	0.364	31.5	0.362	24.0
20	0.403	24.5	0.392	25.5	0.350	31.2	0.251	52.1	0.260	51.0	0.281	41.0
30	0.363	32.0	0.351	33.3	0.320	37.1	0.183	65.1	0.173	67.4	0.219	54.0
45	0.329	38.4	0.294	44.1	0.256	49.7	0.123	76.5	0.099	81.4	0.128	73.1
60	0.218	47.4	0.246	53.2	0.197	61.3	0.079	84.9	0.049	90.8	0.075	84.2
90	0.212	60.3	0.178	66.2	0.096	81.1	0.037	92.9	0.012	97.7	0.021	95.6
120	0.140	73.8	0.105	80.0	0.041	91.9	0.018	96.6	0.003	99.4	0.006	98.7

Figure 1 clearly shows that the degradation rate of SSBBRF solution was enhanced by the addition of H_2O_2 concentration. Furthermore, as shown in Figure 2, the rate constant of the degradation process was increased with the increasing H_2O_2 concentration. However, H_2O_2 concentration that more than 5×10^{-4} mol/L shows detrimental effect on the degradation process. Therefore, the optimum H_2O_2 concentration for the photocatalytic degradation of 5×10^{-5}-mol/L SSBBRF solution is 5×10^{-4} mol/L.
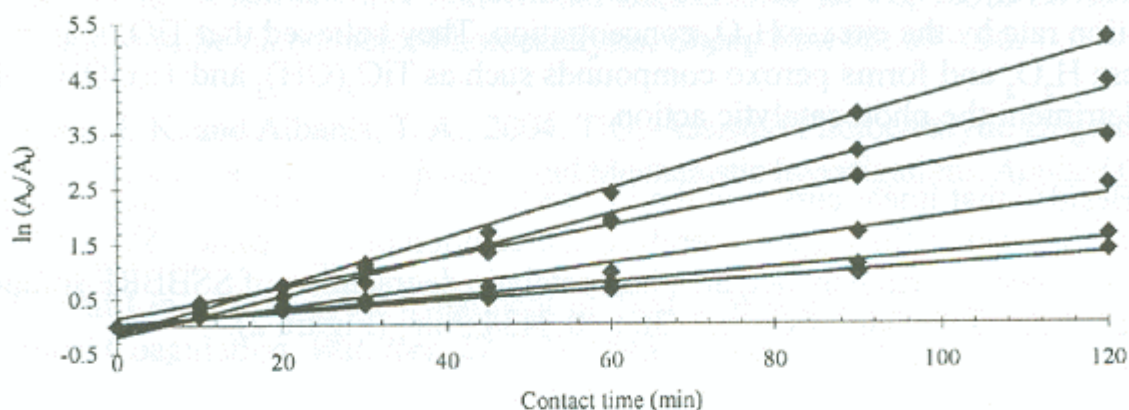
Figure 2. Effects of H_2O_2 on the photocatalytic degradation of the SSBBRF solution. (a) absence, (b) 1×10^{-5}, (c) 5×10^{-5}, (d) 1×10^{-4}, (e) 5×10^{-4}, and (f) 1×10^{-3}-mol/L H_2O_2. ([SSBBRF]$_i$: 5×10^{-5} mol/L, UV λ: 354 nm, TiO_2:solution = 0.5 g/L, contact time: 2 hours)

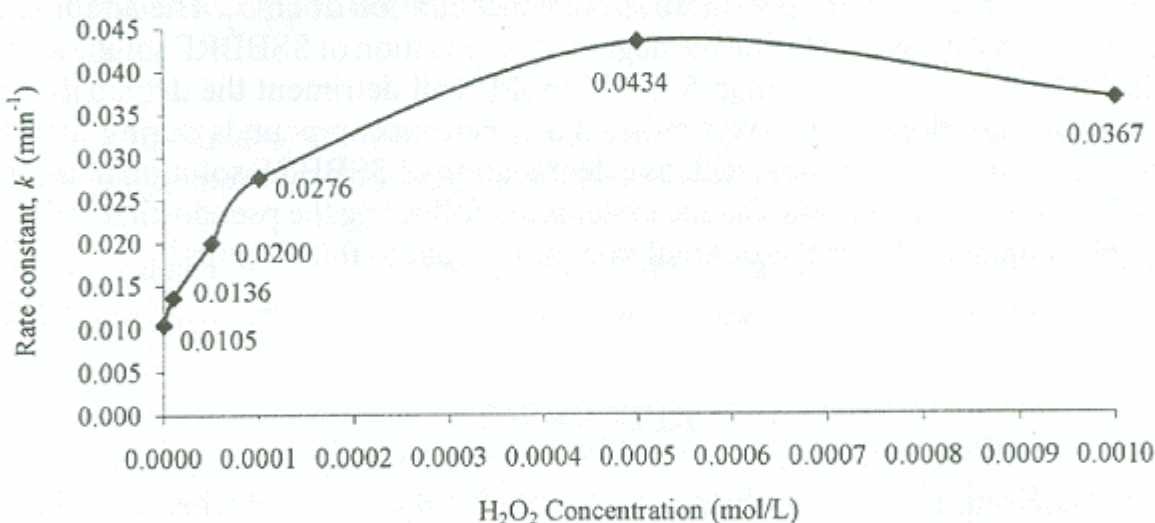**Figure 3. Rate constant, k, of the degradation of SSBBRF solution in TiO_2/H_2O_2/UV system with different initial H_2O_2 concentration. (a) absence, (b) 1×10^{-5}, (c) 5×10^{-5}, (d) 1×10^{-4}, (e) 5×10^{-4}, and (f) 1×10^{-3}-mol/L H_2O_2. ([SSBBRF]$_i$: 5×10^{-5} mol/L, UV λ: 354 nm, TiO_2:solution = 0.5 g/L, contact time: 2 hours)**

The result agree with Konstantinou *et. al* (2004) where they reported that H_2O_2 can become scavenger of valence band holes and hydroxyl radicals ($\bullet$OH), when present at high concentration:

$$H_2O_2 + 2\,h^+_{VB} \longrightarrow O_2 + 2H^+ \tag{12}$$

$$H_2O_2 + \bullet OH \longrightarrow H_2O + HO_2\bullet \tag{13}$$

$$HO_2\bullet + \bullet OH \longrightarrow H_2O + O_2 \tag{14}$$

However, Rivera *et. al* (1993) have different explanation about the decrease of degradation rate by the excess H_2O_2 concentration. They believed that TiO_2 may react with the excess H_2O_2 and forms peroxo compounds such as $TiO_2(OH)_2$ and $Ti(OOH)(OH)_3$ that would detriment the photocatalytic action.

Besides that linear curves in the Figure 1 also show that the kinetics of reactions is following the pseudo-first order. Therefore, the addition of H_2O_2 (that $< 5 \times 10^{-4}$ mol/L) in the TiO_2/UV system will enhance the photocatalytic degradation of SSBBRF solution with the rate constant, k, ranging from 0.0136 to 0.0434 min^{-1} (Figure 2).

CONCLUSION

The photo-oxidative degradation of simulated textile wastewater, Sumifix Supra Blue BRF (SSBBRF) solution, in TiO_2-mediated system demonstrates that the oxidation reactivity of the systems varied with different concentration of H_2O_2. The addition of H_2O_2 in the TiO_2/UV system will enhance the degree of degradation of SSBBRF solution. However, the addition of H_2O_2 that more than 5×10^{-5} mol/L will detriment the degradation process due to the consumption of hydroxyl radicals and peroxo compounds during the oxidation process. Study on the kinetics of oxidative degradation of SSBBRF solution in the TiO_2/UV or TiO_2/H_2O_2/UV system shows that the systems are following the pseudo-first order reaction with the rate constant, k, for the optimal system is equal to 0.0434 min^{-1}.

REFERENCES

Arslan, I., Balciolu, I. A., and Bahnemann, D. W., 2000. Advanced Chemical Oxidative of Reaktive dyes in simulated dyehouse effluents by ferrioxalate – Fenton/UV-A and TiO_2/UV-A processes. *Dyes and Pigment* **47**, 207 – 218.

Balciolu, I. A. and Arslan, I., 1997. Treatment of Textile wastewater by Heterogeneous Photocatalytic Oxidation Processes. *Environmental Technology* **18**, 1053 – 1059.

Dionysiou, D. D., Suidan, M. T., Bekou, E., Baudin, I. and Laine, J., 2000. Effect of Ionic Strength and Hydrogen Peroxide on the Photocatalytic Degradation of 4-Chlorobenzoic Acid in Water. *Applied Catalysis B: Environmental* **26** (3), 153 – 171.

Ghaly, M. Y., Härtel, G., Mayer, R. and Haseneder, R., 2001. Photochemical Oxidation of *p*-Chlorophenol by UV/H_2O_2 and Photo-Fenton Process. A Comparative Study. *Waste Management* **21**, 41 – 47.

Hisanaga, T., Hirada, K. and Tanaka, T., 1990. Photocatalytic Degradation of Pollutant Over TiO_2 in Different Crystal Structures. *Applied Catalysis B: Environmental* **30**, 37 – 44.

Hoffmann, M. R., Martin,, S. T., Choi, W. and Bahnemann, D. W., 1995. Environmental Applications of Semiconductor Photocatalysis. *Chem. Rev.* **95**, 69 – 96.

Konstantinou, I. K. and Albanis, T. A., 2004. TiO_2-Assisted Photocatalytic Degradation of Azo Dyes In Aqueous Solution: Kinetic and Mechanistic Investigations. *Applied Catalysis B: Environmental* **49**, 1 – 14.

Lin, S. H. and Lin, C. M., 1993. Treatment of Textile Waste Effluents by Ozonation and Chemical Coagulation. *Wat. Res.* **27** (12), 1743 – 1748.

Moh, P. Y., 2001. *Photo-Oxidative Degradation of Sumifix Supra Blue BRF in Titania-Assisted and Ozone-Assisted Systems.* Thesis of Master of Science, Universiti Teknologi Malaysia (not published).

Okamoto, K., Yamamoto, Y., Tanaka, H., Tanaka, M. and Itaya, A., 1985. Heterogeneous Photocatalytic Decomposition of Phenol Over TiO_2 Powder. *Bull. Chem. Soc. Jpn.* **59**, 2015-2022.

Pelizzetti, E. and Minero, C., 1993. Mechanism of the Photo-Oxidative Degradation of Organic Pollutants Over TiO_2 Particles. *Electrochimica Acta* **38** (1), 47 – 55.

Rivera, A. P., Tanaka, K. and Hisanaga, T.,1993. Photocatalytic Degradation of Pollutant over TiO_2 in Different Crystal Structures. *Applied Catalysis B: Environmental*, **3**, 37 – 44.

Spadaro, J. T., Isabelle, L. and Renganathan, V., 1994. Hyroxyl Radical Mediated Degradation of Azo Dyes: Evidence for Benzene Generation. *Enviro. Sci. Technol.* **28**, 1389 – 1393.

Tanaka, K., Padermpole, K. and Hisagana, T., 2000. Photocatalytic Degradation of Commercial Azo Dyes. *Wat. Res.* **34**, 327 – 333.

Zhang, F., Zhao, J., Shen, T., Hikada, H., Pelizzetti, E. and Serpone, N., 1998. TiO_2-Assisted Photodegradation of Dye Pollutants II: Adsorption and degradation Kinetic of Eosin in TiO_2 Dispersions Under Visible Light Irradiation. *Applied Catalysis B: Environmental* **15** (1-2), 147 – 156.

Zollinger, H., 1999. *Colour Chemistry: Syntheses, Properties and Application of Organic Dyes and Pigments.* 2nd and revised ed. London: Edward Arnold.