PHOTOCATALYTIC DEGRADATION OF SUMIFIX SUPRA BLUE BRF

Moh Pak Yan\textsuperscript{1}, Razak Ali\textsuperscript{2} and Wan Azelee Wan Abu Bakar\textsuperscript{2}

\textsuperscript{1}School of Science and Technology
Universiti Malaysia Sabah, 88999 Kota Kinabalu, Sabah, Malaysia
\textsuperscript{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\textsubscript{2} with the present of UV irradiation and H\textsubscript{2}O\textsubscript{2} has been studied. The addition of H\textsubscript{2}O\textsubscript{2} in the photocatalytic system has enhanced the degradation degree of SSBBRF solution. However, H\textsubscript{2}O\textsubscript{2} concentration that more than 5 \times 10^{-4} mol/L would detriment the degradation process. Study on the kinetics of oxidative degradation of SSBBRF solution in the TiO\textsubscript{2}/UV or TiO\textsubscript{2}/H\textsubscript{2}O\textsubscript{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\textsuperscript{-1}.

KEYWORDS. Advanced oxidation processes, photocatalytic degradation, TiO\textsubscript{2}, H\textsubscript{2}O\textsubscript{2}

INTRODUCTION

Dyes have been identified as the most problematic compounds due to their strong colour property and highly molecular structure constitution (Balcıolu and Arslan, 1997; Spadaro \textit{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 \textit{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 \textit{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 \textit{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\textsubscript{2}/ UV–A) treatment process are capable of absorbing near-UV spectral region (300 nm < λ < 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 ($\Delta E_{BG} = 3.2$ eV) to form the electron-hole pairs (Zhang et al., 1998; Okamoto et al., 1985; Hoffmann et al., 1995).

\[
\text{TiO}_2 + h\nu \longrightarrow \text{TiO}_2(e^\text{CB}_\text{surf} + h^+\text{VB}_\text{surf}) \quad (1)
\]

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 (•O$_2^-$) are formed (Okamoto, 1985; Hoffmann, 1995; Dionysiou, 2000).

\[
\text{O}_2 + e^\text{CB}_\text{surf} \longrightarrow \text{•O}_2^- \quad (2)
\]

It is likely that H$_2$O$_2$ is formed from •O$_2^-$ according to the following reactions (Okamoto, 1985; Pelizzetti, 1993).

\[
\text{•O}_2^- + \text{H}^+ \rightleftharpoons \text{HO}_2^- \quad \text{pK}_a = 4.83 \quad (3)
\]

\[
\text{HO}_2^- + \text{HO}_2^- \longrightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad k = 7.6 \times 10^5 \text{ M}^{-1} \text{s}^{-1} \quad (4)
\]

\[
\text{•O}_2^- + \text{HO}_2^- \longrightarrow \text{O}_2 + \text{HO}_2^- \quad k = 8.5 \times 10^7 \text{ M}^{-1} \text{s}^{-1} \quad (5)
\]

\[
\text{HO}_2^- + \text{H}^+ \rightleftharpoons \text{H}_2\text{O}_2 \quad \text{pK}_a = 1.5 \times 10^{-12} \quad (6)
\]

The •OH radicals can be formed from H$_2$O$_2$ by anyone of the following reactions, but most probably via Equation 9 with respect to photocatalysis process Okamoto, 1985; Hoffmann, 1995; Dionysiou, 2000).

\[
\text{H}_2\text{O}_2 + h\nu \ (\nu < 310 \text{ nm}) \longrightarrow 2 \text{•OH} \quad (7)
\]

\[
\text{H}_2\text{O}_2 + \text{•O}_2^- \longrightarrow \text{•OH} + \text{OH} + \text{O}_2 \quad (8)
\]

\[
\text{H}_2\text{O}_2 + e^- \longrightarrow \text{•OH} + \text{OH}^- \quad (9)
\]

On the other hand, holes may also react with either H$_2$O or OH$^-$, which adsorb on titanium dioxide surface to generate •OH radicals (Dionysiou, 2000; Hisanaga, 1990)

\[
\text{H}_2\text{O} + h^+_{\text{VB}} \longrightarrow \text{•OH} + \text{H}^+ \quad (10)
\]

\[
\text{OH}^- + h^+_{\text{VB}} \longrightarrow \text{•OH} + \text{OH}^- \quad (11)
\]

Equation 7 to 11 implies that the addition of H$_2$O$_2$ 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$_2$O$_2$/UV system](image)

Methods

For each experiment, 500-mL reaction solution of $5 \times 10^{-5}$ 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 $\lambda_{\text{max}}$: 613 nm). The experiment was repeated with the present of $\text{H}_2\text{O}_2 (1 \times 10^{-3}, 5 \times 10^{-5}, 1 \times 10^{-4}, 5 \times 10^{-4}$ and $1 \times 10^{-3}\text{-mol/L H}_2\text{O}_2$).

RESULTS AND DISCUSSION

Table 1 shows the absorbance ($\lambda_{\text{max}} = 613$ nm) and degree of degradation, $D_{\text{Abs}}^3$, 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 $\text{H}_2\text{O}_2$ will increase the degradation of the SSBBRF solution. During the first-hour contact time, only 47.4% of $5 \times 10^{-5}\text{-mol/L SSBBRF}$ solution was degraded in the absence of $\text{H}_2\text{O}_2$, 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 $1 \times 10^{-3}\text{-mol/L H}_2\text{O}_2$ concentration respectively. Further, after 2-hour contact time, only 73.8% of the SSBBRF solution was degraded in the absence of $\text{H}_2\text{O}_2$, whilst 80.0%, 91.9%, 96.6%, 99.4% and 98.7% of the SSBBRF solutions were degraded with $1 \times 10^{-4}, 5 \times 10^{-5}, 1 \times 10^{-4}, 5 \times 10^{-4}$ and $1 \times 10^{-3}\text{-mol/L H}_2\text{O}_2$ concentration respectively.

Table 1. Absorbance, Abs ($\lambda_{\text{max}} = 613$ nm), and degradation degree, $D_{\text{Abs}}^3 (\%)$, of SSBBRF solution treated in TiO$_2$ suspended photocatalytic system with different initial $\text{H}_2\text{O}_2$ concentration. ([SSBBRF]$_i$: $5 \times 10^{-5}\text{ mol/L, UV }\lambda$: 354 nm, TiO$_2$:solution = 0.5 g/L, contact time: 2 hours)

<table>
<thead>
<tr>
<th>Contact time (min)</th>
<th>$[\text{H}_2\text{O}_2]$ (mol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Abs $D_{\text{Abs}}^3$</td>
</tr>
<tr>
<td>0</td>
<td>0.534 0.0</td>
</tr>
<tr>
<td>10</td>
<td>0.451 15.5</td>
</tr>
<tr>
<td>20</td>
<td>0.403 24.5</td>
</tr>
<tr>
<td>30</td>
<td>0.363 32.0</td>
</tr>
<tr>
<td>45</td>
<td>0.329 38.4</td>
</tr>
<tr>
<td>60</td>
<td>0.218 47.4</td>
</tr>
<tr>
<td>90</td>
<td>0.212 60.3</td>
</tr>
<tr>
<td>120</td>
<td>0.140 73.8</td>
</tr>
</tbody>
</table>

Figure 1 clearly shows that the degradation rate of SSBBRF solution was enhanced by the addition of $\text{H}_2\text{O}_2$ concentration. Furthermore, as shown in Figure 2, the rate constant of the degradation process was increased with the increasing $\text{H}_2\text{O}_2$ concentration. However, $\text{H}_2\text{O}_2$ concentration that more than $5 \times 10^{-4}\text{ mol/L}$ shows detrimental effect on the degradation process. Therefore, the optimum $\text{H}_2\text{O}_2$ concentration for the photocatalytic degradation of $5 \times 10^{-5}\text{-mol/L SSBBRF}$ solution is $5 \times 10^{-4}\text{ mol/L}$.
Figure 2. Effects of $\text{H}_2\text{O}_2$ on the photocatalytic degradation of the SSBBRF solution. (a) absence, (b) $1 \times 10^{-5}$, (c) $5 \times 10^{-5}$, (d) $1 \times 10^{-4}$, (e) $5 \times 10^{-4}$, and (f) $1 \times 10^{-3}$-mol/L $\text{H}_2\text{O}_2$. ([SSBBRF]: $5 \times 10^{-5}$ mol/L, UV $\lambda$: 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$_2$O$_2$/UV system with different initial $\text{H}_2\text{O}_2$ concentration. (a) absence, (b) $1 \times 10^{-5}$, (c) $5 \times 10^{-5}$, (d) $1 \times 10^{-4}$, (e) $5 \times 10^{-4}$, and (f) $1 \times 10^{-3}$-mol/L $\text{H}_2\text{O}_2$. ([SSBBRF]: $5 \times 10^{-5}$ mol/L, UV $\lambda$: 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 $\text{H}_2\text{O}_2$ can become scavenger of valence band holes and hydroxyl radicals (•OH), when present at high concentration:

$$\text{H}_2\text{O}_2 + 2 h^+_{\text{VB}} \rightarrow \text{O}_2 + 2\text{H}^+$$  \hspace{1cm} (12)

$$\text{H}_2\text{O}_2 + \text{•OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2\text{•}$$ \hspace{1cm} (13)

$$\text{HO}_2\text{•} + \text{•OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$$ \hspace{1cm} (14)
However, Rivera et al. (1993) have different explanation about the decrease of degradation rate by the excess H$_2$O$_2$ concentration. They believed that TiO$_2$ may react with the excess H$_2$O$_2$ and forms peroxy 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$_2$O$_2$ (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$_2$O$_2$. The addition of H$_2$O$_2$ in the TiO$_2$/UV system will enhance the degree of degradation of SSBBRF solution. However, the addition of H$_2$O$_2$ that more than $5 \times 10^{-4}$ 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$_2$O$_2$/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


