Effects of light sources and visible light-activated titanium dioxide photocatalyst on bleaching

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The objective of this study was to evaluate, using methylene blue (MB), the effects of various light sources on the bleaching action of hydrogen peroxide (H2O2) with two titanium dioxide (TiO2) photocatalysts — an ultraviolet light-activated TiO2 photocatalyst (UV-TiO2) versus a visible light-activated TiO2 photocatalyst (VL-TiO2). Five experimental solutions (VL-TiO2+H2O2, UV-TiO2+H2O2, H2O2, VL-TiO2, UV-TiO2) were prepared by mixing varying concentrations of H2O2 and/or TiO2 photocatalyst with MB solution. For H2O2-containing solutions (VL-TiO2+H2O2, UV-TiO2+H2O2, and H2O2), the concentration of H2O2 was adjusted to 3.5%. For the four different light sources, low- and high-intensity halogen lamps and blue LED LCUs were used. All the experimental solutions were irradiated by each of the light sources for 7 minutes, and the absorbance at 660 nm was measured every 30 seconds to determine the concentration of MB as an indicator of the bleaching effect. On the interaction between the effects of light source and bleaching treatment, the high-intensity halogen with VL-TiO2+H2O2 caused the most significant reduction in MB concentration. On the effect of light sources, the halogen lamps resulted in a greater bleaching effect than the blue LED LCUs.

Keywords: Bleaching, Titanium dioxide photocatalyst, Light source

INTRODUCTION

In recent years, tooth bleaching has become one of the most rapidly growing oral care sectors, fuelled by the patients’ demand for both healthy and esthetically appealing appearance. This is because for the majority of people, tooth appearance is one of the most important aspects of facial attractiveness, but which could be compromised by any discoloration or staining.

Presently, three kinds of tooth bleaching techniques are available: walking bleach, in-office bleach, and at-home bleach. Amongst which, in-office bleach and at-home bleach can be used to improve the color of discolored vital teeth. Thus, they inevitably became the popular choices for removing intrinsic enamel stains to the end of improving the esthetic appearance of teeth. For at-home tooth bleaching products, the active ingredient is an adduct of urea and hydrogen peroxide (H2O2), which on contact with water breaks down to urea and H2O2. As for in-office bleaching products, most of which contain 30–35% H2O2 and require light exposure and/or warming.

With H2O2-containing in-office bleaching products, two key factors determine the overall tooth whitening efficacy: hydrogen peroxide concentration and application duration. In a study by Sulieman2, in vitro tooth bleaching efficacy was examined and compared using gels containing 5–35% of H2O2. On the effect of hydrogen peroxide concentration, it was found that a higher concentration required a lower number of gel applications to produce uniform bleaching. On the effect of application duration, it was found that the efficacy rendered by the 5% solution approached that of the higher concentrations when the treatment time was extended.

On the effect of light energy on peroxide tooth bleaching, the chemical reaction rate can be increased by raising the temperature; for example, a 10°C increase can double the chemical reaction rate3. Accordingly then, high-intensity light sources have been used to raise the temperatures of H2O2-containing bleaching gels and accelerate the chemical reaction rates of the tooth bleaching process4. To date, a variety of light sources with varying wavelengths and spectral power characteristics have been used, such as halogen curing lights, plasma arc lamps, lasers, and light-emitting diodes5,6. However, according to some studies that used in vitro tooth models, some light sources induced significant increases in pulpal temperature during the tooth bleaching process, which may adversely impact patient sensitivity and pulpal health6,7.

Apart from using warming effects on tooth whitening gels to accelerate the tooth bleaching procedure, light sources can also be used to activate the peroxide in photosensitive or light-activated bleaching agents to accelerate the chemical redox reactions of the bleaching process8. Such light-activated bleaching agents purportedly contain ingredients that aid energy transfer from the light to...
the peroxide gel and which are often colored materials, such as carotene and manganese sulfate.\textsuperscript{8,9,10}

Leveraging on the use of light sources to expedite the tooth bleaching process, a bleaching agent which contained a visible light-activated titanium dioxide (VL-TiO\textsubscript{2}) photocatalyst was recently reported\textsuperscript{11}. In that study\textsuperscript{11}, the blended solution of VL-TiO\textsubscript{2} and H\textsubscript{2}O\textsubscript{2} reacted not only with ultraviolet light (<380 nm), but also with visible light (380–520 nm) — which is of the same wavelength of light used in some dental light curing units. Consequently, this innovative bleaching technique was employed for an in-office bleaching product which is currently marketed as Pyrenees (Mitsubishi Gas Chemical, Tokyo, Japan). However, the H\textsubscript{2}O\textsubscript{2} concentration in Pyrenees was lowered from 35\% to 3.5\%, thereby rendering it safe to be used as a commercial dental bleaching agent\textsuperscript{12}. Nonetheless, the effects of different light sources and their intensities on the bleaching action of this product are not well investigated and hence not well understood.

Therefore, the objective of this study was to evaluate, using methylene blue (MB), the effects of different light sources and their intensities on a visible light-activated TiO\textsubscript{2} photocatalyst (VL-TiO\textsubscript{2}) which was employed in Pyrenees.

**MATERIALS AND METHODS**

**Preparation of experimental solutions**

Five kinds of experimental solutions were prepared as follows and their formulations are shown in Table 1:

- Solution 1 (VL-TiO\textsubscript{2} + H\textsubscript{2}O\textsubscript{2}): Prepared by mixing 1.0 g of 0.1\% VL-TiO\textsubscript{2} solution (Mitsubishi Gas Chemical, Tokyo, Japan), 1.0 g of 35\% H\textsubscript{2}O\textsubscript{2} (Mitsubishi Gas Chemical), 1.0 g of 100-ppm MB solution (Methylenblau med. Puriss, Chroma-Gesellschaft Gmbh, Muenster, Germany), and 7.0 g of pure water. VL-TiO\textsubscript{2} was the same catalyst used for Pyrenees, and concentration of Solution 1 was 10\% that of Pyrenees as determined from a pilot study. Therefore, the concentration of H\textsubscript{2}O\textsubscript{2} in this solution was 3.5\%, the same as that in Pyrenees.
- Solution 2 (UV-TiO\textsubscript{2} + H\textsubscript{2}O\textsubscript{2}): Ultraviolet light-activated TiO\textsubscript{2} photocatalyst (UV-TiO\textsubscript{2}; ST-21, Ishihara Sangyo Co., Tokyo, Japan) was used instead of VL-TiO\textsubscript{2}. The other ingredients were the same as Solution 1.
- Solution 3 (H\textsubscript{2}O\textsubscript{2}): TiO\textsubscript{2} solution from Solution 1 or 2 was replaced with 1.0 g of pure water. In other words, no TiO\textsubscript{2} photocatalyst was added.
- Solution 4 (VL-TiO\textsubscript{2}): 1.0 g of 35\% H\textsubscript{2}O\textsubscript{2} from Solution 1 was replaced with 1.0 g of pure water. In other words, this solution did not contain any H\textsubscript{2}O\textsubscript{2}.
- Solution 5 (UV-TiO\textsubscript{2}): 1.0 g of 35\% H\textsubscript{2}O\textsubscript{2} from Solution 2 was replaced with 1.0 g of pure water. In other words, this solution did not contain any H\textsubscript{2}O\textsubscript{2}.

**Light irradiation**

Four visible light curing units were employed in this study (Table 2): two halogen lamps with different intensities (Hyper Lightel, 1,300 mW/cm\textsuperscript{2}, Ushio Electric, Tokyo, Japan; Optilux 501, 700 mW/cm\textsuperscript{2}, Demetron-Kerr, Danbury, CT, USA) and two blue LED LCU\textsuperscript{s} with different intensities (LEDemetron 1, 1,500 mW/cm\textsuperscript{2}, Demetron-Kerr, Danbury, CT, USA; Pencure, 650 mW/cm\textsuperscript{2}, J. Morita, Tokyo, Japan).

A volume of 3.0 mL of each experimental solution was poured into a quartz cell (1.0×1.0×4.5 cm) with a full capacity of 4.5 mL. One side of the cell was masked by a black paper sheet with a hole of 8 mm diameter, and each solution in the cell was irradiated through this hole for 30 seconds. During light irradiation, the solution was stirred using a magnetic stirrer (Mini Stealer, GL Sciences, Tokyo, Japan) and the absorbance at 660 nm was measured using a spectrophotometer.

**Table 1** Formulations of the experimental solutions

<table>
<thead>
<tr>
<th>Experimental solution</th>
<th>VL-TiO\textsubscript{2}</th>
<th>Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>VL-TiO\textsubscript{2} + H\textsubscript{2}O\textsubscript{2}</td>
<td>○</td>
<td></td>
</tr>
<tr>
<td>UV-TiO\textsubscript{2} + H\textsubscript{2}O\textsubscript{2}</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>H\textsubscript{2}O\textsubscript{2}</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>VL-TiO\textsubscript{2}</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>UV-TiO\textsubscript{2}</td>
<td>○</td>
<td>○</td>
</tr>
</tbody>
</table>

**Table 2** Visible light curing units employed in this study

<table>
<thead>
<tr>
<th>Light unit</th>
<th>Light source</th>
<th>Intensity (mW/cm\textsuperscript{2})</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hyper Lightel</td>
<td>Halogen</td>
<td>1,300</td>
<td>Ushio Electric, Tokyo, Japan</td>
</tr>
<tr>
<td>Optilux 501</td>
<td>Halogen</td>
<td>700</td>
<td>Demetron-Kerr, CT, USA</td>
</tr>
<tr>
<td>LEDemetron 1</td>
<td>Blue LED</td>
<td>1,500</td>
<td>Demetron-Kerr, CT, USA</td>
</tr>
<tr>
<td>Pencure</td>
<td>Blue LED</td>
<td>650</td>
<td>J. Morita, Tokyo, Japan</td>
</tr>
</tbody>
</table>
(Mini Photo 5, Sanshin, Tokyo, Japan). For the entire light irradiation duration of 7 minutes, the whole procedure of irradiating, stirring, and measuring the solution was repeated 14 times since absorbance was measured every 30 seconds. This experiment was repeated three times for each solution.

After every 30 seconds of light irradiation, the concentration of the remaining MB in the experimental solution was determined using a standard curve. The curve was previously drawn in the pilot study by plotting the known concentrations (Fig. 1) and the determined absorbance of a sample solution of MB at various concentrations. The concentration of MB was calculated according to the following equation:

\[
\text{Concentration of MB after irradiation (ppm)} = \frac{(A_x - A_0)}{(A_{10} - A_0)} \times 10.0
\]

\(A_{10}\) = absorbance of experimental solution before irradiation (MB: 10 ppm);
\(A_0\) = absorbance of blank solution (MB: 0 ppm), blank solution = 9.0 g of pure water and 1.0 g of TiO\(_2\);
\(A_x\) = absorbance of experimental solution after irradiation.

**Statistical analysis**

For each experimental solution, the mean and standard deviation from the three experiments were calculated. Statistical analysis of the concentrations of MB for each solution at intervals of 1, 4, and 7 minutes was performed using three-way analysis of variance (3-way ANOVA), two-way analysis of variance (2-way ANOVA), and Bonferroni test at 95% level of confidence. The factors analyzed were experimental solution, light curing unit, and light irradiation time. Statistical tests were performed using a computerized statistical program (SPSS for Windows release Ver.11, SPSS Inc., USA).

**RESULTS**

Three-way ANOVA and two-way ANOVA results are summarized in Table 3. The concentration of MB was significantly influenced by the experimental solution (\(F=15958.120, p<0.0001\)), light curing unit (\(F=7470.839, p<0.0001\)), and light irradiation time (\(F=1541.391, p<0.0001\)).

The changes in MB concentration in VL-TiO\(_2\)+H\(_2\)O\(_2\) and UV-TiO\(_2\)+H\(_2\)O\(_2\) groups at each irradiation time are shown in Figs. 2a and 2b and in Table 4. As the irradiation time increased, the MB concentration decreased in both groups. However, the rate of decrease in VL-TiO\(_2\)+H\(_2\)O\(_2\) group was greater than that in UV-TiO\(_2\)+H\(_2\)O\(_2\) group regardless of the light curing unit. Among the four kinds of light units, Hyper Lightel resulted in the most significant reduction in MB concentration and at an extent much more than the other three curing units. In VL-TiO\(_2\)+H\(_2\)O\(_2\) group, MB concentrations were statistically different among the light sources and light irradiation times at 1, 4, and 7 minutes, except Optilux 501 and LEDemetron 1 at 7 minutes (Table 4).

For H\(_2\)O\(_2\), VL-TiO\(_2\), and UV-TiO\(_2\) groups, the changes in MB concentration at each irradiation time are shown in Figs. 2c, 2d, and 2e respectively. In H\(_2\)O\(_2\),

![Fig. 1 Relationship between MB concentration and light absorbance calculated in the pilot study.](image-url)
Fig. 2 Comparison of changes in MB concentration as a function of irradiation time in: (a) VL-TiO$_2$+H$_2$O$_2$ solution; (b) UV-TiO$_2$+H$_2$O$_2$ solution; (c) H$_2$O$_2$-only solution; (d) VL-TiO$_2$-only solution; and (e) UV-TiO$_2$-only solution. Changes are shown for four kinds of light curing units and intensities between baseline and post-irradiation time intervals.

Table 4 Means and standard deviations of MB concentrations in VL-TiO$_2$+H$_2$O$_2$ group using four kinds of light units after 1, 4, and 7 min of light irradiation

<table>
<thead>
<tr>
<th></th>
<th>1 min</th>
<th>4 min</th>
<th>7 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hyper Lightel</td>
<td>5.02 (0.28)</td>
<td>0.79 (0.18)</td>
<td>0.54 (0.19)</td>
</tr>
<tr>
<td>Optilux 501</td>
<td>8.10 (0.43)</td>
<td>2.38 (0.23)</td>
<td>1.32 (0.15)*</td>
</tr>
<tr>
<td>LEDemetron 1</td>
<td>8.70 (0.13)</td>
<td>3.53 (0.10)</td>
<td>1.82 (0.11)*</td>
</tr>
<tr>
<td>Pencure</td>
<td>9.36 (0.40)</td>
<td>6.26 (0.48)</td>
<td>4.40 (0.30)</td>
</tr>
</tbody>
</table>

Mean (±SD); n=3.

*: Not statistically significant difference (p>0.05).
Table 5  Means and standard deviations of MB concentrations with Hyper Lightel after 1, 4, and 7 min of light irradiation

<table>
<thead>
<tr>
<th>Experimental solution</th>
<th>1 min</th>
<th>4 min</th>
<th>7 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>VL-TiO₂ + H₂O₂</td>
<td>5.02 (0.28)</td>
<td>0.79 (0.18)</td>
<td>0.54 (0.19)</td>
</tr>
<tr>
<td>UV-TiO₂ + H₂O₂</td>
<td>8.66 (0.16)</td>
<td>2.88 (0.24)</td>
<td>0.87 (0.26)</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>9.15 (0.08)</td>
<td>4.74 (0.11)</td>
<td>2.05 (0.16)</td>
</tr>
<tr>
<td>VL-TiO₂</td>
<td>9.00 (0.06)</td>
<td>7.25 (0.02)</td>
<td>6.61 (0.07)</td>
</tr>
<tr>
<td>UV-TiO₂</td>
<td>9.89 (0.10)</td>
<td>8.92 (0.31)</td>
<td>7.99 (0.39)</td>
</tr>
</tbody>
</table>

Mean (±SD); n=3.
Differences among all the mean values are statistically significant (p<0.05).

Fig. 3  Comparison of changes in MB concentration by Hyper Lightel as a function of irradiation time between baseline and post-irradiation time intervals for each experimental solution.

DISCUSSION

In this study, the effects of four kinds of light curing units with different light sources and/or intensities on the bleaching action of H₂O₂ with VL-TiO₂ photocatalyst were evaluated and then compared against the UV-TiO₂ photocatalyst. To quantify the bleaching effects, MB dye — an organic material — was used. Bleaching of MB can occur by destroying one or more of the double bonds in the conjugated chain or by cleaving the conjugated chain

To date, numerous in vitro models have been used to evaluate the efficacy of tooth bleaching products. The majority of these models used whole or cut human or bovine tooth specimens at their pre-existing colors. However, some in vitro models increased the levels of intrinsic tooth color by pre-staining with black tea or blood components. Nonetheless, with all in vitro models which used human or bovine teeth, the characteristics of teeth such as thickness of enamel or dentin, extent of penetration of bleaching agent, and initial tooth color inevitably varied from one to the other. To eliminate these variances, hematoporphyrin or β-carotene, in place of in vitro tooth models, was used in one study to investigate the effect of light irradiation on the bleaching effect of a titanium dioxide-containing bleaching agent. Similarly in this study, no teeth were used so that appropriate evaluations could be performed with minimal variation and better reproducibility. Although the experimental design in this study differed from the exact clinical situation, the method employed in this study seemed to be suitable and useful as a screening test for bleaching materials to determine their application methods before clinical application.

Bleaching is a decolorization or whitening process that can occur in a solution or on a surface. Chromophores, the color-producing components in a solution or surface, are typically organic compounds that possess extended conjugated chains of alternating single and double bonds that often contain heteroatoms, carbonyl groups, and aromatic rings in the conjugated system. Bleaching and decolorization of the chromophores can occur by destroying one or more of the double bonds in the conjugated chain, by cleaving the conjugated chain, or by oxidation of other chemical moieties in the conjugated chain.

As for the role of H₂O₂ — which is an active ingredient in all bleaching agents to date, it oxidizes a wide variety of organic and inorganic compounds. The mechanisms of these reactions are varied and dependent on the substrate, the reaction environment,
and the catalysts\textsuperscript{18\textdegree}. In general, the bleaching mechanism by H\textsubscript{2}O\textsubscript{2} is not well understood as it can form a number of different active oxygen species depending on the reaction conditions, including temperature, pH, light, and the presence of transition metals\textsuperscript{19\textdegree}. Under alkaline conditions, hydrogen peroxide bleaching generally proceeds via the perhydroxyl anion (HO\textsuperscript{2−}). Other conditions can give rise to free radical formation, for example, by homolytic cleavage of either an O-H bond or O-O bond in hydrogen peroxide to give H\textsuperscript{+}OOH and 2-OH (hydroxyl radicals) respectively\textsuperscript{18\textdegree}.

To accelerate the bleaching process, heat activation of the bleaching agent applied on the tooth surface by light, heat, or laser has been described in published literature. For example, Baik et al.\textsuperscript{\textdegree} reported on the use of a high-intensity light to increase the temperature of H\textsubscript{2}O\textsubscript{2}. The release of hydroxyl radicals from hydrogen peroxide is accelerated by a rise in temperature according to the following equation: H\textsubscript{2}O\textsubscript{2} + 211 kJ/mol → 2HO. This is in accordance with an increase in the speed of decomposition by a factor of 2.2 for each temperature rise of 10°C. Due to an increased release of hydroxyl radicals (thermocatalysis), an increase in efficacy is conceivable\textsuperscript{19\textdegree}. In the present study, the temperature rise that occurred during light irradiation by blue LED LCUs was lower than with the conventional halogen and high-intensity halogen light sources. Further, the conventional halogen lamp registered a lower temperature rise than the high-intensity halogen lamp\textsuperscript{19\textdegree}. This result agreed with a previous study which investigated the temperature rise during the polymerization of a resin cement\textsuperscript{20\textdegree}. Based on these results, it could be said that the H\textsubscript{2}O\textsubscript{2}-only experimental solution exhibited bleaching effect upon irradiation by the different light sources without any photocatalyst.

The bleaching effect of H\textsubscript{2}O\textsubscript{2} generally depends on the extent to which hydroxyl radicals are generated, which can be increased by ultraviolet light (UV) irradiation. This is because H\textsubscript{2}O\textsubscript{2} has a tendency to absorb UV, which then induces the molecular vibration and degradation of H\textsubscript{2}O\textsubscript{2}, subsequently leading to an increase in temperature\textsuperscript{21\textdegree}. For this reason, it might seem to be preferable to use a H\textsubscript{2}O\textsubscript{2} bleaching agent in conjunction with a strong UV light at a wavelength absorbed by H\textsubscript{2}O\textsubscript{2}. However, prolonged exposure to UV irradiation is a major exogenous cause of toxic irritation that leads to cellular damage and immune suppression, skin cancer, and photoaging\textsuperscript{22\textdegree}. Having mentioned these undesirable health effects arising from exposure to UV light, it is clear that the UV light is undesirable for tooth bleaching or whitening. Besides, the UV-TiO\textsubscript{2} photocatalyst investigated in this study was a semiconductor with a band-gap of 3.2 and absorbed only light with wavelength below 380 nm to generate electron-hole pairs, which could initiate photodecomposition. In complete consideration of the health concerns and photoirradiation constraint posed by the UV-TiO\textsubscript{2} photocatalyst, the VL-TiO\textsubscript{2} photocatalyst emerged as a favorable candidate to accelerate the in-office bleaching process.

It has been reported that a H\textsubscript{2}O\textsubscript{2}-based bleaching agent containing a VL-TiO\textsubscript{2} photocatalyst exhibited the highest absorbance in the UV region\textsuperscript{18\textdegree}. The H\textsubscript{2}O\textsubscript{2}-based bleaching agent absorbed more UV light than visible light, but it also showed strong absorbance of visible light due to the addition of the VL-TiO\textsubscript{2} photocatalyst. Absorbance was higher in the visible region closest to the UV region and was optimal in enhancing the bleaching effect of H\textsubscript{2}O\textsubscript{2} with the VL-TiO\textsubscript{2} photocatalyst. The spectrum of blue LED LCUs has a sharp peak at 470 nm and is distributed across a bandwidth of 20–80 nm or more\textsuperscript{19\textdegree}. In contrast, a halogen lamp emits a wide wavelength range, across the entire visible spectrum of light (VIS, \(\lambda=380–580\) nm) and deep into the infrared region (IR, \(\lambda>750\) nm)\textsuperscript{9\textdegree}. In this study, the high-intensity halogen light caused the MB concentration to decrease more significantly than the other three light curing units. Besides, the low-intensity halogen light also caused a steeper decrease in MB concentration than the high-intensity blue LED LCU. Based on the results obtained, it could be seen that a difference in the light spectrum of the halogen lamp was likely to affect the activity of the TiO\textsubscript{2} catalyst.

In experimental solutions containing only H\textsubscript{2}O\textsubscript{2} or the TiO\textsubscript{2} photocatalyst, there were little changes in the bleaching outcome. On the contrary, when these components were combined, the results improved dramatically. Therefore, it was likely that either TiO\textsubscript{2} or H\textsubscript{2}O\textsubscript{2} produced less free radicals than a combination of both the components. Between the two photocatalysts, it could be seen that the VL-TiO\textsubscript{2} photocatalyst was more effective toward bleaching than the UV-TiO\textsubscript{2} photocatalyst. For the commercial bleaching agent Pyrenees, it contained a low concentration of H\textsubscript{2}O\textsubscript{2} and the VL-TiO\textsubscript{2} photocatalyst, hence significantly and assuredly improving the safety for both the teeth and soft oral tissues. Moreover, despite the lower H\textsubscript{2}O\textsubscript{2} concentration, the bleaching performance of Pyrenees was comparable with the conventional bleaching agents that contained a higher concentration of H\textsubscript{2}O\textsubscript{2}\textsuperscript{16\textdegree}.

**CONCLUSIONS**

It was concluded that the high-intensity halogen lamp was more effective than the low-intensity halogen lamp and blue LED light curing units for tooth bleaching. This was shown using a bleaching solution which contained a low concentration of H\textsubscript{2}O\textsubscript{2} and VL-TiO\textsubscript{2} photocatalyst. Moreover, formulations that comprised both H\textsubscript{2}O\textsubscript{2} and a TiO\textsubscript{2} photocatalyst were markedly more efficacious for tooth whitening than either H\textsubscript{2}O\textsubscript{2} or TiO\textsubscript{2} photocatalyst alone.

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