A study of hydrogen peroxide chemistry and photochemistry in tea stain solution with relevance to clinical tooth whitening

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ABSTRACT

Objective: Tooth whitening using hydrogen peroxide is a complex process, and there is still some controversy about the roles of pH, temperature, chemical activators, and the use of light irradiation. In this work the basic interactions between whitening agents and stain molecules are studied in simple solutions, thus avoiding the physics of diffusion and light penetration in the tooth to give clarity on the basic chemistry which is occurring.

Method: The absorbance of tea stain solution at 450 nm was measured over a period of 40 min, with various compositions of whitening agent added (including hydrogen peroxide, ferrous gluconate and potassium hydroxide) and at the same time the samples were subjected to blue light (465 nm) or infra-red light (850 nm) irradiation, or alternatively they were heated to 37 °C.

Results: It is shown that the reaction rates between chromogens in the tea solution and hydrogen peroxide can be accelerated significantly using ferrous gluconate activator and blue light irradiation. Infra red irradiation does not increase the reaction rate through photochemistry, it serves only to increase the temperature. Raising the temperature leads to inefficiency through the acceleration of exothermic decomposition reactions which produce only water and oxygen.

Conclusion: By carrying out work in simple solution it was possible to show that ferrous activators and blue light irradiation significantly enhance the whitening process, whereas infra red irradiation has no significant effect over heating. The importance of controlling the pH within the tooth structure during whitening is also demonstrated.

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1. Introduction

For more than a decade now tooth whitening has been carried out in the dental office using products which are extensively based upon hydrogen peroxide chemistry, and a range of take home kits and over the counter solutions have also become available. However, there is still some controversy as to how the whitening process works, in particular with respect to the role of pH, activators, temperature, and illumination with visible or IR light.1–6 This is perhaps not surprising because whitening is after all a complex mix of physical and chemical processes – that is to say the complete understanding resides in the domains of both physics and chemistry. In the first instance, the whitening agent needs to diffuse deep into the structure of the tooth in order to reach the deep internalized stains in the tooth enamel. It also needs to reach the dentine which can become yellowed with ageing, due to intrinsic and
extrinsic staining mechanisms and also due to structural changes in proteins within the dentine itself. The route by which the agent diffuses into the tooth is not yet clear since the enamel is complex, consisting of rod-like grains of hydroxyapatite with amelogenin proteins between the boundaries. Additionally, enamel is faulted with defects and cracks at both the macroscopic and microscopic levels. However, there is clear evidence that the hydrogen peroxide molecules are able to penetrate through faults in the enamel to the dentine in a time of the order of 10–30 min at room temperature.7–11 Active radicals produced by hydrogen peroxide degradation are believed to be extremely short lived.12–14 Consequently, we believe that the agent must first penetrate the tooth, and then the radicals must be generated at depth by an appropriate mechanism. Therefore, photo-activation may be an ideal vehicle for the generation of radicals since visible light can penetrate deep into the tooth.15 We are then in the realms of chemistry, and we might expect that the whitening process to at least be initiated by well-known chemical reactions.

The purpose of this work is to investigate these chemical processes using a simple methodology which avoids the complexities of the tooth structure. This is achieved by studying the actions of the various whitening processes upon simple stain solutions by using optical absorbance. Black tea has been chosen as the representative stain solution in the work presented here, though we have found qualitatively similar results using coffee, tobacco and red wine solutions. Tea solution contains a complex mix of stain molecules (chromogens) principally comprising of the rubigins. In common with other chromogens, these absorb visible light (particularly in the blue) and appear yellow or red in colour.

In this way, the complexities resulting from both chemical diffusion and optical transmission within the tooth have been avoided, allowing us to test the hypotheses that blue light, metallic salts, and high pH all enhance the reaction rates between hydrogen peroxide and stain molecules. The null hypotheses would be that no statistically significant differences in reaction rate can be seen when each of these elements are systematically varied.

2. Materials and methods

For the purpose of this study we have formulated a whitening compound consisting of two components which are mixed at the point-of-use. The first component, ‘peroxide’ consists only of 37.2% hydrogen peroxide mixed from water and 60% hydrogen peroxide (Sigma Aldrich, Gillingham, Dorset, UK) at its intrinsic pH ~ 4, and the second component, ‘activator’, comprises of 0–5.91% (wt/wt) potassium hydroxide (Sigma Aldrich, Gillingham, Dorset, UK) depending upon the pH required in the particular experiment (e.g. 0%, wt/wt gives pH = 4 and 5.91%, wt/wt gives pH = 9), and 0.004% (wt/wt) ferrous gluconate monohydrate (Sigma Aldrich, Gillingham, Dorset, UK).

In order to demonstrate the effect of the whitening agent on stain molecules, a solution of tea was prepared by boiling 0.2 g of loose leaf black tea (Tesco, Cheshunt, Hertfordshire, UK) in 10 ml of water for 10 min and then passing the solution through a 0.2 μm filter.

At the point of testing, four volumes of ‘peroxide’ were added to one volume of ‘activator’ and then to one volume of stain solution. The resulting hydrogen peroxide concentration in the final mix is 25%. The pH values given in the results section are those measured in the final mix.

The absorbance of the solution at 450 nm was measured as a function of time, thus providing a direct measure of the chemical activity of the hydrogen peroxide on the complex blend in the stain solution. The experiments were carried out within a 96 well plate (model Nunclon TKT-180-090Y, Thermo Scientific, Waltham, MA, USA) using a model ELx800 plate reader (BioTek, Seattle, WA, USA). In each run there were four identical repeats of the experiment, and four identical controls for which the ‘peroxide’ solution is simply substituted by water.

In order to study the effect of visible light, we have used the BriteSmile blue light illumination system (Discus Dental, Culver City, CA, USA) as used in the dental office. This system blue light illumination at a wavelength of 465 nm and at a measured power density of 60 mW/cm² at the standard working distance (32 mm).

To study the effect of infra-red irradiation we used an LED array at a wavelength of 850 nm (model Ostar, Osram Opto Semiconductors, Regensburg, GmbH) at a measured power density of 50 mW/cm².

Light intensity in the visible and IR spectrum was measured with a Powermax PS10 detector and a Fieldmax II – TO metre (Coherent, Ely, Cambridgeshire, UK). The measured variation in light intensity across the utilized wells was <10% in all experiments.

2.1. Analytical statistics

The key parameter being measured is the absorbance of the tea solution as a function of time, and we assert that a significant result occurs when the absorbance measured in experiment A differs from that in experiment B at a given time point (τ = 10 min) by more than 3(σA + σB) where σA and σB are the standard deviations arising from the two absorbance measurements. In experiments A and B the same stock tea solution is used, and averages are taken over 4 repeats in neighbouring wells. For σA and σB we simply take the repeatability of the absorbance measurement as quoted for the ELx800 instrument in rapid read mode which is 2%. The spread in values across the 4 repeats is found to be within this margin in all cases. Thus, a significant result is one for which the difference in the absorbance measured after 10 min is 12% or higher.

3. Results

3.1. The effect of pH and visible illumination

Most chemical reactions are highly dependent on pH and it is therefore essential to study the basic whitening process while using this as a parameter. The absorbance results are shown here firstly in the dark and at 22°C (Fig. 1) and a clear dependence of the reaction rate on pH is evident. The fastest reaction rates were achieved at pH 8–9.

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The pH values are those measured in the final solution comprising of ‘peroxide’ + ‘activator’ + stain.

Secondly, results are shown for stain degradation by hydrogen peroxide under illumination with the BriteSmile lamp at the standard working distance (Fig. 2). The reaction rate was found to increase with irradiation at this wavelength, notably by a factor of approximately 3 at pH 7 or above. At pH values of 8–9 visible bubbling occurs in the solution due to exothermic decomposition into water and oxygen, and at pH >9 the solution rapidly overheats due to thermal runaway.

In Fig. 3 results are presented this time as a function of the measured blue light intensity, and a clear systematic dependence of the reaction rate on light intensity can be seen. Data are also presented for the control samples (no hydrogen peroxide) and a small direct photo-bleaching of the stain solution can be seen for blue light at this wavelength.

The effects of both heat and IR irradiation on the reaction rate were also investigated at pH 8 (Fig. 4). The solution heated to 37 °C actually reached 45 °C by the end of the experiment due to the exothermic nature of the reaction. It was not possible to do similar experiments above 37 °C because the solutions would run away (i.e. uncontrollably overheat). The sample under infra-red (IR) irradiation was found to have heated to 34 °C by the end of the experiment due to absorption of the IR energy. Also shown in the figure are the aforementioned results for the blue light irradiation (for comparison) and results for control samples which contain water in place of
Fig. 5 – The relative absorbance of tea stain solution subjected to whitening agent with and without ferrous gluconate (FeG) activator at pH 8, both in the dark and under illumination with blue light (465 nm) at an intensity of 50 mW/cm².

hydrogen peroxide. Only the controls exposed to blue light (and not heat or IR) showed the direct photo-bleaching effect.

3.3. The effect of the ferrous gluconate activator

In Fig. 5 the effect of the ferrous gluconate (FeG) activator is shown at pH 8 both in the dark and under blue light irradiation, and in both cases the reaction rate is increased.

4. Discussion

The results presented here clearly show the whitening effect without knowledge of the detailed, complex chemical reactions which are occurring with the chromogens. It is evident that blue light shows a significant enhancement to the reaction rate (at least up to pH 8). On the other hand, direct heating to 37 °C without light illumination shows a lesser (but still significant) enhancement. Irradiation with infra-red (which lead to heating of the solution to 34 °C) gave an insignificant difference to direct heating to 37 °C. Thus, the different effects caused by light and heat are quite apparent.

The underlying reactions leading to radical formation are in fact quite well known, and will be discussed in a little more detail in this section.

4.1. Basic hydrogen peroxide chemistry

In solution the peroxide molecules exist in equilibrium with protons and perhydroxyl ions through the reaction

\[
\text{H}_2\text{O}_2 \leftrightarrow \text{H}^+ + \text{HO}_2^-
\]

giving rise to an acidic pH of typically ~4 (the \(pK_a\) is 11.62). If the pH is adjusted upwards, then this reaction is driven towards completion and large concentrations of perhydroxyl ions are generated. These ions are moderately oxidizing, and therefore we conclude that the stain removal seen in the dark (Fig. 1) may in part be caused by direct chemical reaction between hydrogen peroxide and the chromogens, but is principally due to reactions with the perhydroxyl ions that are generated as the pH is increased.

When the solution is heated this reaction rate increases, but at the same time the peroxide decomposes according to

\[
2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2
\]

and this reaction too is accelerated at high pH. This exothermic reaction can lead to the bubbling of the solutions under certain conditions and even to thermal-run-away, which is undesirable since it produces no reaction with the stain molecules.

4.2. Metal ion catalysis

It has been well known for many years that metallic salts promote the degradation of hydrogen peroxide in to OH ions and radicals via the Fenton reaction 16

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^+ + \text{OH}^-
\]

The OH radicals are strongly oxidizing (\(E = 2.73 \text{ eV}\) and no doubt lead to the break-down of chromogens. This reaction depends upon pH 7 and is most efficient at pH 3-6. Above this the efficiency drops as the Fe\(^{3+}\) and Fe\(^{4+}\) ions co-precipitate 17 though this can be inhibited to some extend by the addition of chelators such as gallic acid and EDTA. In the absence of chromogens with which to react (or insufficient time to diffuse to the chromogen sites) other reactions will be initiated which ultimately lead to the production of oxygen, as well as the reversion of the ferric ion to the ferrous state:

\[
\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{OOH}^+ + \text{H}^+
\]

\[
\text{Fe}^{3+} + \text{OOH}^+ \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2
\]

4.3. The effect of light

Enhancement using light is of interest in tooth whitening not only because the reaction rate is increased, but also because visible light can penetrate into the depth of the tooth, and therefore promote the radical production close to the site of the stain.

The mechanisms by which light can enhance whitening are varied and complex. In the first case, we can expect direct bleaching by bond-breaking and loss of conjugation in the chromogen. This occurs when photons are absorbed directly by the chromogen (as is the case with blue light and yellow-red stains) and when the photons have sufficient energy to break the chemical bonds. In the control solutions in Figs. 4 and 5 (where hydrogen peroxide was substituted with water) we see the contribution from this process under blue light, and note also that there is no significant effect when infra-red irradiation is used. The photon energy for the blue light and infra-red used in this study is 2.67 eV and 1.46 eV respectively. Typical energies associated with common bonds are well
known (Table 1) and it can be seen that the only bonds which can be broken directly by blue light are the weaker bonds (such as O–O bonds and HO–OH bonds).

Over and above the direct bleaching of the chromogen, we may see a more significant effect when both hydrogen peroxide and blue light are present together. The simplest mechanism for this would be one in which the hydrogen peroxide is directly cleaved into two radicals which subsequently react with the chromogen. However, although the blue light has sufficient photon energy for this cleavage, hydrogen peroxide does not absorb blue light significantly. Therefore, we believe that the chromogen absorbs the photon, and then transfers the energy to the hydrogen peroxide (resulting in the cleavage). Alternatively, the absorption of the photon could raise the energy states of the C–O, C=C and C=C–C=C conjugated bonds in the chromogen making them more reactive with the hydrogen peroxide molecules and its subspecies.

Another group of processes through which the light can interact with the hydrogen peroxide are known as the photofenton reactions, a good review of which can be found in the literature. These are reactions which are again associated with the metal salt activator such as the ferrous gluconate which we have used here. The detailed sub-reactions which occur depend upon many parameters such as the pH, and the nature of the molecule with which the radicals are interacting. In our work we see a statistically significant contribution from photo-Fenton reactions as evidenced by comparing reaction rates in the light and the dark, with and without ferrous gluconate (Fig. 5).

4.4. Interaction with stain molecules

The way in which the radicals react with chromogen is again varied and complex. For this reason we have also used other complex stain solutions in our work (i.e. coffee, tobacco and red wine). Stains and proteins in the teeth are complex, long chain organic molecules, and it is the conjugation length of the molecule which gives rise to the colour. Thus, stain removal is often attributed to the shortening of these molecules by the direct cleavage of conjugated bonds by the OH and OOH radicals. While it is no doubt true that the molecules are broken into shorter fragments, the detailed mechanisms for the interaction with radicals are specific to the particular molecule in question. For example, in the case of tea catechin, it is shown that an OH radical first interacts with functional chemical OH group on a phenol ring, and the unpaired electron then moves along the molecular chain initiating sub-reactions.

5. Conclusions

We have investigated the chemistry and photo-chemistry behind tooth whitening by carrying out some simple experiments in which the absorbance of stain solution is monitored while subjected to various whitening agents. In this way we avoid the complications of diffusion in the tooth structure, and study the effects of pH, chemical activators, and light illumination on the basic chemistry. At 20°C we see a significant enhancement (approx ×3) to the reaction rate under blue light illumination at an intensity of 50 mW/cm² or more, consistent with the theory that blue light plays an important role in the generation of radicals and the subsequent break down of stains. Conversely, any enhancement arising from irradiation with IR light at 850 nm (which at the same time heats the solution to 34°C) cannot be distinguished from that arising from direct heating to 37°C. It is difficult to control the whitening process via heating since this is found to lead to thermal-run-away through exothermic decomposition into water and oxygen. These compounds do not have the ability to breakdown stain molecules.

Conflict of interest statement

In this work we used whitening lamps which are marketed by Discus Dental.

Discus Dental is a Philips owned company.

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References


Table 1 - Typical bonds, bond energies (approximate) and associated optical wavelengths found in organic molecules.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond energy (eV)</th>
<th>Corresponding wavelength</th>
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<tr>
<td>C–O</td>
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<td>155</td>
</tr>
<tr>
<td>C–C</td>
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<td>197</td>
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<tr>
<td>O–H</td>
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<tr>
<td>C–H</td>
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<tr>
<td>C–C</td>
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<td>344</td>
</tr>
<tr>
<td>C–O</td>
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<td>349</td>
</tr>
<tr>
<td>O–O</td>
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<td>770</td>
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<tr>
<td>HO–OH (Bach et al.)</td>
<td>2.12</td>
<td>585</td>
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