The basic chemistry and photochemistry behind hydrogen peroxide tooth whitening.

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ABSTRACT

Tooth whitening using hydrogen peroxide gel formulations is a complex process which involves both chemistry and physics, and there is still some controversy about the efficiency of whitening processes, particularly with respect to the roles of pH, temperature and irradiation with light. In this work we avoid the complications of the physics by studying the basic interactions between whitening agents and stain molecules in simple solutions. Firstly, we demonstrate that whitening is most effective at pH 8-9. Then we demonstrate that blue light irradiation has a clear and large impact on the whitening process, and that IR irradiation serves only to increase the temperature. While raising the temperature can give a slight improvement to stain removal, it can easily lead to inefficiency through the acceleration of exothermic decomposition reactions which produce only water and oxygen.

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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 temperature, and the role of illumination with visible or IR light, (Tavares et al, 2003; Luk et al, 2004; Ziemba et al, 2005; Joiner, 2006; Buchella and Attin, 2007; Dominguez et al, 2011). 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 internalised stains in the tooth enamel. It also needs to reach the dentine which can become yellowed with ageing, due to intrinsic 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 amelogen 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 the enamel into the dentine in a time of the order of 10-30min at room temperature (Bowles and Zeph, 1987; Adibfar et al, 1992; Benetti et al, 2004; Gokay et al, 2005; Carmargo et al, 2007). Active radicals produced by hydrogen peroxide degradation are believed to be extremely short lived (Lurie et al, 1991; Louit et al, 2005; Maezono et al, 2011). 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. 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 paper is to investigate these chemical processes using a simple methodology for which the results are entirely unambiguous. In this way, we can remove the complexities of the physics of diffusion, and thus demonstrate the importance of pH, chemical activators, light, and heat on the basic whitening process. Such experiments can also be used to fully optimise the whitening gel chemistry and composition.

MATERIALS AND METHODS

For the purpose of this study we have formulated a whitening compound based upon the commercially available Zoom treatment (Discus Dental, USA) and have tested this in relation
with the BriteSmile (Discus Dental, USA) blue light illumination system, and Zoom (Discus Dental, USA) white light system, used in the dental office.

The whitening agent used in this work consists of two components which are mixed at the point-of-use. The first component, ‘peroxide’ consists only of 37.2% hydrogen peroxide (Sigma, UK) at its intrinsic pH~4, and the second component, ‘activator’, comprises of up to 5.88%wt/wt potassium hydroxide (Sigma, UK) and 0.004%wt/wt ferrous gluconate monohydrate (Sigma, UK) in water. In this way the hydrogen peroxide is kept at low pH during storage (to prevent peroxide decomposition) and then raised to pH=8 at the point-of-use, and at the same time ferrous gluconate is added to enhance the production of radicals through Fenton-like catalytic reactions.

In order to demonstrate the effect of the whitening agent on stain molecules, a solution of tea was prepared to which the whitening agent is added. The tea solution was prepared by boiling 0.2g of loose leaf black tea (Tesco, UK) in 10ml of water. Four volumes of ‘peroxide’ were added to one volume of ‘activator’ and then to one volume of stain solution at the point-of-test. The resulting hydrogen peroxide concentration is 25%. The absorbance of the solution at 450nm was measured as a function of time, thus providing a direct and unambiguous measure of the chemical activity of the peroxide on the complex blend in the stain solution. Multiple experiments of this kind were carried out using a standard plate reader (BioTek ELx800, USA) within a 96 well plate. Additional experiments were carried out using stain solutions formed from coffee, tobacco and red wine, and qualitatively similar results were achieved in all cases (data not presented). The addition of other chemicals such as co-solvents and humectants (eg glycerine and polypropylene glycol) was also tested in this work, and these were not found to affect the results described herein.

**EXPERIMENTAL RESULTS.**

The effect of pH and visible illumination

Most chemical reactions are highly dependent on pH. It is therefore essential to study the basic whitening process while using pH as a parameter. In a first experiment, the pH of the final solution (i.e. the ‘peroxide’ + ‘activator’ + stain solution) was varied by adjusting the KOH concentration in the ‘activator’ precursor. This allowed the study of the absorbance of solution in the dark to be undertaken. The results are shown here (Figure 1) and a clear dependence of the reaction rate on pH is evident. The fastest reaction rates were achieved at pH 8 to 9.

Similarly, we show results (Figure 2) of stain degradation by hydrogen peroxide under illumination with the BriteSmile lamp (465nm blue LED) at the standard working distance (giving a measured power density of ~60mW/cm²). The reaction rate was found to increase with irradiation at this wavelength, notably by a factor of approximately 3 at pH 7 or above. The
increase in reaction rate was found to depend upon the distance of the lamp from the test plate, that is to say, demonstrating a dependence on the intensity of the light. At pH values of 8-9 significant bubbling occurs in the solution due the formation of oxygen, and at pH >9 the solution rapidly overheats due to thermal-run-away.

Qualitatively the same results were obtained using a Zoom light source (white light source at a power density of 150mW/cm²) at its correct working distance. However, we noted that the solutions were more prone to heating and run-away at pH 8-9 with this higher power density source.

The effect of heat and IR radiation

The effects of both heat and IR irradiation on the reaction rate were investigated in a second experiment. For the later we used an LED array at a wavelength of 850nm (Osram Opto Semiconductors OSTAR, GmbH). We present the absorbance results in the dark at 24°C, and when heated externally to 37°C, and also under the IR illumination at 50mW/cm² (Figure 3). The solution heated to 37°C actually reached 45°C by the end of the experiment due to self-heating. It was not possible to do similar experiments above 45°C because the solutions would run-away and spill over. The sample under 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 results for the blue light irradiation (for comparison) and for control samples which contain water in place of hydrogen peroxide.

It is evident that heating shows some in enhancement to the reaction rate, and that irradiation with IR has a similar effect. This enhancement is not as marked as that found for blue light (where no heating was detected) and so we can clearly identify the separate effects arising from heat and photo-activation.

It can also be seen that there is some stain removal effect under the action of light in the controls, that is to say, in the absence of any hydrogen peroxide. This is caused by the direct photo-bleaching of the stain molecules which can occur when the photonic energy is greater than the bond strength of specific bonds within the stain molecule.

DISCUSSION

The results presented here clearly show the whitening effect without knowledge of the detailed, complex chemical reactions which are occurring. However, 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.
Basic peroxide chemistry

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

$$\text{H}_2\text{O}_2 \leftrightarrow \text{H}^+ + \text{HOO}^-$$

giving rise to an acidic pH of typically ~4 (the pKa 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 figure 1 can in part be attributed to the generation of this species.

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. Based upon the results we have shown here we therefore conclude that the optimum pH for the whitening process is around 8-9.

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.

$$\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^\cdot + \text{OH}^-$$

The OH radicals are strongly oxidizing ($E=2.73\text{eV}$) and no doubt lead to the break-down of stain molecules. This reaction depends upon pH (Kremer, 2003) is most efficient at pH 3-6, above this the efficiency drops as the Fe$^{3+}$ ions precipitate (Abbot and Brown, 1990) though this can be inhibited to some extend by the addition of chelators such as gallic acid and EDTA. In the absence of stain molecules with which to react (or insufficient time to diffuse to the stain molecules) other reactions will be initiated which ultimately lead to the production of oxygen and water, as well as the reversion of the ferric ion to the ferrous state:

$$\text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{OOH}^\cdot + \text{H}^+$$

$$\text{Fe}^{3+} + \text{OOH}^\cdot \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2$$
The effect of light

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

The mechanisms by which light can enhance whitening are varied and complex. In the first case, we can expect direct bleaching by bond-breaking in the stain molecule (chromogen). This occurs when photons have sufficient energy to break the chemical bonds directly. However, in the control in figure 3 the contribution from this process to the net bleaching effect is seen to be small. The only bonds which can be broken optically are the weaker bonds (such as O-O bonds) since the energy of the photon needs to be greater than the bond dissociation energy, For visible light that equates to energies of around 1.8 to 3.0eV. Typical energies associated with common bonds are well known (Table I). In particular, we see that the energy required to dissociate HO-OH is low, and corresponds to wavelengths in the visible spectrum. Additionally, the light can destabilise the chromogens by raising the energy states of the C=O, C=C and C=C-C=C conjugated bonds making them more reactive with the radicals introduced by the hydrogen peroxide. We therefore assert that the increased reaction rate under blue light seen in figure 2 may in part due to direct bond-breaking within the stain molecule, but is mainly due to radical generation from the peroxide and subsequent chemical reactions.

Another group of processes through which the light can interact with the hydrogen peroxide are known as the photo-Fenton reactions, a good review of which can be found in the literature (Pignatello et al, 2004). 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 some contribution from photo-Fenton reactions (by comparing solutions with differing amounts of ferrous gluconate (data not presented). However, the main contribution is from the blue light irradiation itself (seen with no ferrous gluconate present) at least at pH 8-9.

Interaction with stain molecules

The way in which the radicals react with stain molecules 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 tooth 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 cleaving 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 (Takeuchi et al, 2007).

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 unambiguously determine the effects of pH, chemical activators, heat, and light illumination in the basic chemistry. Most previous literature on this topic deals with the clinical testing of agents on human teeth, and consequently this has led to conflicting opinions as to what the roles of temperature, illumination with visible light, and irradiation with IR are in the whitening process. From our own work it has become clear that illumination with high intensity blue light plays a large and important role in the generation of radicals and the subsequent break down of stains. Conversely, Irradiation with IR light at 850nm merely serves to heat the solution, which can then lead to a lesser enhancement in the stain removal. 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.

ACKNOWLEDGEMENTS

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REFERENCES


FIGURES AND TABLES

**Figure 1.** The relative absorbance of tea stain solution subjected to whitening agents at various pH's in the dark. The pH values are those in the final solution comprising of ‘peroxide’ + ‘activator’ + stain.

**Figure 2.** The relative absorbance of tea stain solution subjected to whitening agents at various pH's under illumination with blue light (465nm) at an intensity of 60mW/cm², via the BriteSmile in-office system. The pH values are those in the final solution comprising of ‘peroxide’ + ‘activator’ + stain.
Figure 3. The relative absorbance of tea stain solution subjected to whitening agent under illumination with IR light (850nm) at an intensity of 50mW/cm², and in the dark at temperatures of 24°C and 37°C. Also shown for comparison is the blue light data from figure 2, and data for controls which contain water in place of the peroxide.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond energy (eV)</th>
<th>Corresponding wavelength (nm)</th>
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<tr>
<td>C=O</td>
<td>8.0</td>
<td>155</td>
</tr>
<tr>
<td>C=C</td>
<td>6.3</td>
<td>197</td>
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<tr>
<td>O-H</td>
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</tr>
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<td>C-H</td>
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<td>C-C</td>
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<tr>
<td>C-O</td>
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</tr>
<tr>
<td>O-O</td>
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<td>770</td>
</tr>
<tr>
<td>HO-OH (Bach et al 1996)</td>
<td>2.12</td>
<td>585</td>
</tr>
</tbody>
</table>

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