

# Investigating hydrogel dosimeter decomposition by chemical methods

**Kevin Jordan**

London Regional Cancer Program, London Health Sciences Centre, Department  
Medical Biophysics, Western University, London, Ontario, Canada

E-mail: kevin.jordan@lhsc.on.ca

**Abstract.** The chemical oxidative decomposition of leucocrystal violet micelle hydrogel dosimeters was investigated using the reaction of ferrous ions with hydrogen peroxide or sodium bicarbonate with hydrogen peroxide. The second reaction is more effective at dye decomposition in gelatin hydrogels. Additional chemical analysis is required to determine the decomposition products.

## 1. Introduction

The issue of hydrogel dosimeters disposal becomes important as larger volumes and more frequent usage becomes widespread. Materials with toxic reactants and products will require extra procedures for safe disposal. Preferably, non-toxic chemistries will be selected for gel preparation and safe and convenient disposal procedures will be available for clinical users. One aspect of *Green chemistry* is to replace toxic materials with non-toxic alternatives. An example, is the trend to replace halogenated chemistries in industrial and domestic environments. Genipin hydrogels were specifically developed because of this chemistry was used in medicine and the food industry. Most of the current, 3-D, radiochromic, hydrogel dosimeters are relatively safe to produce and handle. One disposal method involves breaking ferrous-xylenol orange or leuco-dye-micelle gels into small pieces and air drying. The solid film can then be disposed in a land-fill. This process is possible for a few litre volumes but as larger quantities are consumed this process becomes impractical. Also, molds may grow on the drying gels, contaminating the laboratory.

Globally dye contamination of water and soils is a common problem associated with textile industries. Many researchers are examining inexpensive methods to clean up dye contaminated water and soils. They tend to examine low cost approaches such as: solar photochemistry, locally available catalytic materials such as clays, sands and mining tailings. This literature is a resource for hydrogel dosimeter remediation ideas since low cost and low toxicity are starting criteria for the research. The radiochromic dosimeters often contain a dye or dye precursor such as a leucodye. Generally these specific compounds are chosen for their low toxicity. However, introduction of dyes into the environment should be minimized as a matter of principle. If these molecules can be degraded prior to leaving the laboratory it is preferred. Typically, these compounds are less than one thousandth of the total mass of a hydrogel dosimeter and gelatin represents 5% or more of the mass. For this reason, promising reactions in contaminated water based on generation of OH radicals may not work due to the scavenging effect of the gelatin [1]. Also, the radiochromic hydrogel dosimeters are acidic, with pH ~ 2 being typical. This allows acidic reactions to be examined and still follow the *atom economy*



*principle of Green chemistry*. In this investigation, several methods of hydrogel degradation are examined and may stimulate ideas for practical gel decomposition methods.

This study is limited to the leuco-crystal violet micelle hydrogel dosimeters (LVC) and it is expected that results are applicable to similar triphenylmethane dyes, such as malachite green. The Fenton reaction involves generation of OH radicals by the breakdown of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) by ferrous ions. This common reaction is used globally for treatment of waste water and sewage. The Fenton reaction for oxidative degradation of water contaminated with malachite green from textile industries was investigated [1]. Further studies examined the use of the Fenton reaction to decompose crystal violet in water [2] and the enhanced reaction with granular activated carbon [3]. Reaction rates can be increased using near UV (sunlight) to drive the corresponding photo-Fenton reaction, degrading chlorinated phenol [4].

Direct photochemical degradation of dyes in hydrogels may be possible for certain chemistries. However, the dyes crystal violet and malachite green have adequate photochemical stability to be useful when designing stable radiation dosimeter materials. In water, crystal violet is stable to exposure to simulated sunlight but decomposes with the addition of  $\text{H}_2\text{O}_2$  [5]. However, the addition of mannitol quenched the decomposition reaction, indicating OH radical is involved. It is anticipated similar quenching results would be observed with hydrogels. Also, only a small fraction of the leucodye is converted to dye for doses below 100 Gy. The colourless leucodyes are not sensitive to visible wavelengths. UV exposure is an option, but it is anticipated that gelatin will preferentially absorb the UV light, limiting the effectiveness of this approach.

Another chemical degradation approach of organic pollutants involves the reaction of sodium bicarbonate and hydrogen peroxide to produce peroxydicarbonate ( $\text{HCO}_4^-$ ), superoxide ion ( $\text{O}_2^{\cdot-}$ ) and singlet oxygen ( $^1\text{O}_2$ ) [6]. The formation of  $\text{HCO}_4^-$ , within metabolic conditions, is currently under investigation and it is interesting that cells would also use this mechanism for the disposal of metabolic waste [7].

In this study, several approaches to the decomposition of leuco-crystal violet and crystal violet in gelatin hydrogel micelle dosimeters were examined for extent of reaction. Direct, thermal decomposition at temperatures near the boiling point were not investigated because it is anticipated that few dosimeter users would have access to fume hoods for control of air quality.

## 2. Methods

Previously irradiated samples of leuco-crystal violet (LCV) micelle gelatin hydrogel were melted in a 50 C water bath. The gel composition was: 5 % by mass, gelatin, 25 mM trichloroacetic acid, 4 mM Triton X100 surfactant and 1 mM LCV. In the first sample, 1 mM ferrous ammonium sulphate was added with stirring. After 10 minutes, 100 mM  $\text{H}_2\text{O}_2$  was added to the solution. The solution was divided for subsequent experiments. In one case the upper surface was illuminated with 365 nm UV light to a fluence of ~100 J while examining for photobleaching. The experiment was repeated with ~250 J of 630 nm red light. To another sample sodium bicarbonate ( $\text{NaHCO}_4$ ) and additional  $\text{H}_2\text{O}_2$  was added.

The second experiment involved the addition of 300 mM  $\text{H}_2\text{O}_2$  to the melted gel followed by the slow addition of 50 mM  $\text{NaHCO}_4$  to minimize foaming. The sample was maintained at 50 C and observed for two hours.

## 3. Results

The introduction of ferrous ammonium sulphate to the warm gelatin solutions resulted in a darkening of the material due to the formation of crystal violet and the addition of  $\text{H}_2\text{O}_2$  accelerated the conversion to dye. However, even with excess  $\text{H}_2\text{O}_2$  the samples did not fade to colourless solutions. UV light exposure also failed to visibly bleach the dark solutions. Red light exposure had minimal effects on colour change of the gel dosimeter at room temperature. However, the combination of  $\text{NaHCO}_4$  and  $\text{H}_2\text{O}_2$  in warm melted gels resulted in colour fading in less than one hour. Figure 1 shows a four month old sample of LCV micelle gel before and after the reactions with  $\text{NaHCO}_4$  and  $\text{H}_2\text{O}_2$ .

Subsequent lowering of the pH to less than 7 resulted in the sample changing from an opalescent to a clear colourless solution.



**Figure 1.** Oxidative decomposition of leuco-crystal violet hydrogel dosimeter: left panel, before treatment, right panel, sample after two hour reaction with bicarbonate and hydrogen peroxide.

#### 4. Discussion

Iron chemistry deserves further investigation because of its biological importance and because many hydrogel dosimeters employ similar reactions. It is a catalyst in the production of several oxidative species with the OH radical being the most reactive. In the case of gelatin hydrogels, the OH radical is scavenged primarily by the gelatin polymer, making it an inefficient species for oxidizing the low concentrations of dye and leuco-dye. In principle by adding larger amounts both the gelatin and dyes would be decomposed. But more efficient reactions may exist. Singlet oxygen chemistry also is expected to be helpful since it has a lower redox potential, leading to fewer possible reactions and fewer products to consider. In this study the addition of photosensitizer dyes was not examined in an attempt to minimize the number of additional chemicals added. Solar photochemistry should also be a very cost effective method of disposal under optimal conditions. Electrochemical methods may also be practical in a laboratory setting.

It would be very helpful if the gelatin could be recovered from the hydrogel for reuse or separate disposal but this may not be feasible. In the case of LCV-micelle-gelatin hydrogels, a combination of sodium bicarbonate and hydrogen peroxide appears to be an effective method of decomposition requiring further validation by examining the oxidation products.

#### 5. References

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