

Study of Photobleaching Mechanism in Methylene Blue Sensitized Gelatin Using a Single Beam UV-Vis. Fibre Optics Spectrophotometer

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ABSTRAK

Dalam penyelidikan ini, kami telah mengkaji kesan fotopelunturan metilin biru (MB) didopkan dalam gelatin matrik menggunakan spektrofotometer gantian optik uv-sinar nampak. Pemancaran sampel dengan cahaya uv-sinar nampak menyebabkan pengurangan puncak penyerapan dengan bertambahnya masa pemancaran. Ini menunjukkan dengan adanya pemancaran, pewarna molekul MB difotolunturkan kepada molekul MB tanpa warna. Keputusan hasil kajian ini menunjukkan proses fotopelunturan yang lambat berlaku pada kepekatan pewarna yang tinggi dalam matrik gelatin. Kajian ini menunjukkan metilin biru (MB) didopkan dalam matrik gelatin membuka kemungkinan yang baru dalam penggunaan bidang holografi.

ABSTRACT

In the present study, we have investigated the photobleaching of the methylene blue (MB) doped in Gelatin matrix using uv-visible fibre optic spectrophotometer. Illumination of the sample by uv-visible radiation resulted in a decrease of the absorption peak with the increasing of irradiation time. This indicates that upon irradiation MB dye molecule is photoreduced to its leuco form (colorless) of MB. The present experimental results indicate a slower photobleaching process occurring at higher concentration of dye doped in gelatin matrix. This study shows that the MB doped in gelatin solid matrix opens a new possibility in real-time holography applications.

Keywords: Photobleaching, methylene Blue gelatin, absorbance spectra photochemical reaction

INTRODUCTION

In recent years, holography finds very wide applications in the field of technology particularly in the usage of holograms memory elements. Holography memories could conceivably store huge amounts of digitized information conveniently and inexpensively. Holographic recording materials based on the dye-polymer system have contributed significantly to the recent growth of holographic applications (Pradeep *et al.* 2000).

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It has been reported by Cristina *et al.* (1987) that certain dyes in the presence of electron donor became colorless when irradiated. This bleached dye is known to be the product of the light excited dye and an electron taken from the surrounding medium. The new molecule is known in chemistry as the leuco form of the dye (leuco dye). This leuco dye has been reported to be a strong reducing agent that is capable of reducing a variety of substances such as the dichromate ion into trivalent chromium.

Methylene Blue (MB) is the most used dye for formation of high spatial frequency amplitude and phase holograms with a conventional He-Ne laser as a light source. Photobleaching of MB is the principal mechanism of grating formation. It is known that MB cannot be bleached in a pure form. In order to bleach the MB molecules, they must be put into a suitable optical quality matrix. The matrices widely used for this purposes are: polyvinyl alcohol (PVA), poly(methylmethacrylate) (PMMA), dichromated gelatin and acrylamide base (Toshihiro *et al.* 1979; Sergio 1987; Cristina *et al.* 1987). In this study, the photobleaching mechanism of MB doped in gelatin matrix was investigated in details.

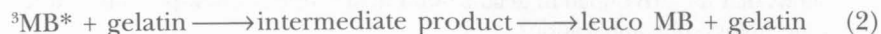
PHOTBLEACHING MECHANISM

The photochemical reactions that are believed to occur during the photobleaching of MB sensitized gelatin can be explained as follows (Cristina *et al.* 1987; Nadia 1991):

- (i) During illumination, the MB dye molecule absorbs a photon and is brought into the excited state (i.e. $^1\text{MB}^*$ is the first excited state and $^3\text{MB}^*$ is the transition of dye molecule to another state with a longer lifetime).



- (ii) The gelatin acts as an electron donor to bring MB to its leuco form (colorless):



- (iii) The excited MB dye molecules can return to the electronic ground state by a radiationless transition (Cristina *et al.* 1987), then:



or the dye-dye interactions produce the non-bleached molecules.



EXPERIMENTAL DETAIL

MB and gelatin supplied by BDH Chemicals Ltd. England were used as received. The molecular structure of the MB dye is shown in Fig.1. The

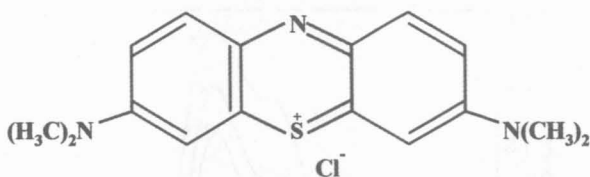


Fig. 1: The molecular structure of the methylene blue dye

preparation of MB doped Gelatin samples is similar to the one reported by Pradeep *et al.* (2000). The solution of gelatin was prepared by dissolving the required amount of gelatin in distilled water. A homogeneous solution with 8% (w/v) of gelatin was obtained after the solutions were heated at 80°C. The MB was then added to the gelatin solution and the mixture was heated for 5 min. Three solutions with different dye concentrations, namely 6.3×10^{-4} mol/l, 1.9×10^{-3} mol/l and 3.1×10^{-3} mol/l were prepared in the present study. The MB doped gelatin solid samples were obtained by keeping the solutions at room temperature in the dark for 48 hours. The solid gelatin sample was then kept in a dessicator under vacuum for another 24 hours. Finally, the samples were cut into were cut into circular shape with diameter 10 mm for the following investigation.

The optical absorbance and transmission spectra of the MB sensitized gelatin samples were recorded at room temperature using uv-visible fibre optics spectrophotometer (OCEAN Optics S2000, Inc), incorporated with a personal computer. The photochemical reaction in the samples were monitored by recording the absorbance and transmission curves for the exposure time 600 s with the intervals of 60 s.

RESULTS AND DISCUSSION

It is known that absorption is defined as the transfer of energy from an electromagnetic field to a molecular entity (Barakat *et al.* 2001). The optical absorption spectra of a pure gelatin sample and MB doped gelatin samples at three different dye concentrations are shown in Fig. 2. The pure gelatin matrix was transparent throughout the spectrum region 450 nm-800 nm with a very low absorbance level (i.e. ~ 0.06). For MB doped gelatin samples, we observed that a well-resolved characteristic absorption peak centered at 668 nm with a shoulder at 620 nm. The observed absorption peak at 668 nm is corresponding to the transitions between the ground state (S_0) and first excited singlet state (S_1) of the dye molecules when the sample irradiated with photon energy (Sergey *et al.* 1998). Nadia and Roger (1991) reported that the MB sensitized gelatin had an absorption band in the red part of the spectrum with the maximum absorption located around 670 nm. The main absorption peaks increases at higher concentration due to the increase in the number of dye molecules (Pradeep *et al.* 2000)

Fig. 3 shows that the absorption spectra for MB doped gelatin samples obtained for two dye concentrations (i.e 6.3×10^{-4} mol/l and 3.1×10^{-3} mol/l) at

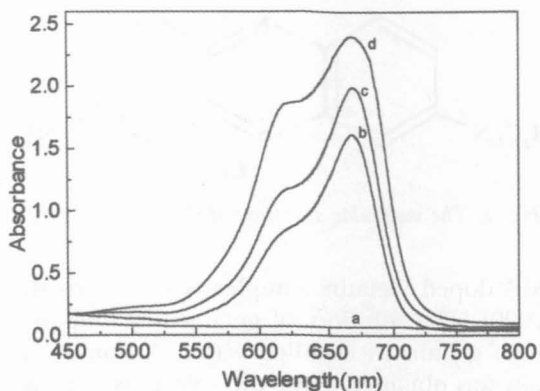


Fig. 2: The absorption spectra of (a) a typical pure gelatin sample and three different dye concentration of methylene blue with (b) 6.3×10^{-4} mol/l; (c) 1.9×10^{-3} mol/l and; (d) 3.1×10^{-3} mol/l

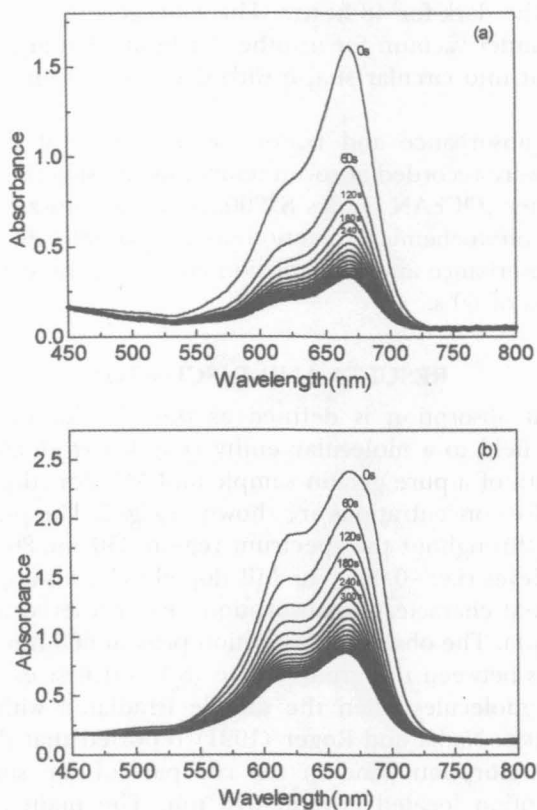


Fig. 3: Variation in the optical absorption spectra during uv-visible irradiation for 600 seconds at dye concentrations of : (a) 6.3×10^{-4} mol/l; (b) 3.1×10^{-3} mol/l

the interval of 60s. We observed that the main absorption peak located at 668 nm decreases gradually and becomes broadened and weaker with the increasing of irradiation time. The decrease in absorbance indicates that the uv-visible irradiation causes photobleaching of MB molecules doped in gelatin matrix. It has been reported by Carretero *et al.* (2001), as a consequence of light absorption, the MB dye molecule is photoreduced in a photochemical reaction resulting in a production of leuco form of dye molecules.

Kubota *et al.* (1976) had suggested that to favor the photoreduction of MB it is necessary to have an electron donor such as ethylene diamine tetraacetic acid (EDTA) in dichromated gelatin sensitized with MB. However, in the present study of MB sensitized gelatin, it is noticeable that the addition of EDTA is not necessary and that the reduction of the excited molecule is probably performed by the gelatin itself. This study shows that photobleaching of MB embedded in solid matrix is an appropriate medium for holographic elements, particularly for reflection grating (Nadia *et al.* 1988).

Effect of Dye Concentration on Photobleaching

Fig. 4 shows the decrease of absorbance peak (668 nm) with irradiation time for three different MB dye concentrations in gelatin matrix (i.e. 6.3×10^{-4} mol/l, 1.9×10^{-3} mol/l and 3.1×10^{-3} mol/l). Obviously, it could be observed from this figure that at lower concentration of MB (6.3×10^{-4} mol/l) the absorbance of the sample decreased much faster than that at a higher concentration of MB (3.1×10^{-3} mol/l). This indicates that the photoreduction of MB dye molecules to leuco MB appears much slower at higher concentration. These results were in a good agreement with those reported by Cristina *et al.* (1987) and Pradeep *et al.* (2000). They had reported that the sample with lower MB concentration shows faster rate of bleaching and for achieving faster bleaching at higher concentrations, higher exposure energy is needed. According to Cristina *et al.* (1987), the faster photobleaching process at lower concentration is due to the deexcitation process which is shown in Eqns. 4 and 5, where by increasing the concentration of the dye, one increases the possibility of an interaction between the two neighbored excited dye molecules ($^1\text{MB}^*$ and $^3\text{MB}^*$) and the nonexcited dye molecules (MB) resulting in the return of the excited molecule to the ground state.

Optical Transmission Spectra

The photobleaching phenomenon during uv-visible irradiation can also be observed by monitoring the changes in optical transmission spectra. *Fig. 5* shows the recorded transmission spectra of the MB doped gelatin sample at a dye concentration of 3.1×10^{-3} mol/l. Before uv-visible irradiation, the colored transparent sample has a high optical transmission in the wavelength range of 450 nm-510 nm and 720 nm-800 nm with ~71% and ~80% of transmission, respectively. Obviously, the irradiation of the MB doped gelatin sample leads to an increase in overall transmission throughout the spectrum region with the increase of irradiation time. During irradiation, the lower optical transmission

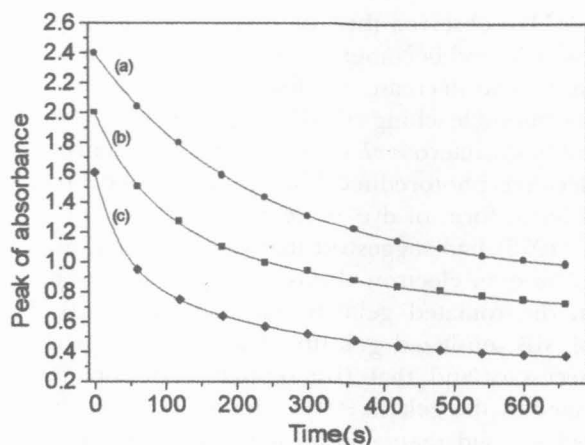


Fig. 4: Plot of absorption peak versus irradiation time at three different dye concentration with (a) 3.1×10^3 mol/l; (b) 1.9×10^3 mol/l and; (c) 6.3×10^4 mol/l

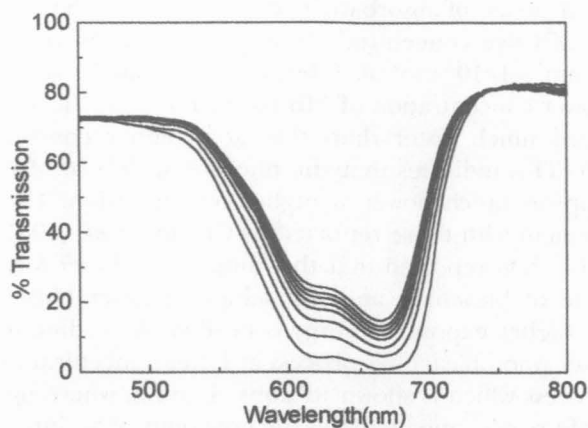


Fig. 5: Transmission spectra changes during uv-visible irradiation for methylene blue doped in gelatin sample at dye concentration of 3.1×10^3 mol/l

in the region of 600 nm-680 nm increases gradually which is purely due to the gradual photodegradation of MB dye molecule to leuco MB. After 600 s of irradiation, the bleached sample shows a higher transmission value of ~73% and ~83% in the wavelength range of 450 nm-510 nm and 720 nm-800 nm, respectively. This indicates that most of the MB is transformed into leuco MB upon uv-visible irradiation.

The Aging Effect

Another phenomenon showed that, after uv-visible irradiation, the absorbance peak of the sample (dye concentration 6.3×10^4 mol/l) was recovered after

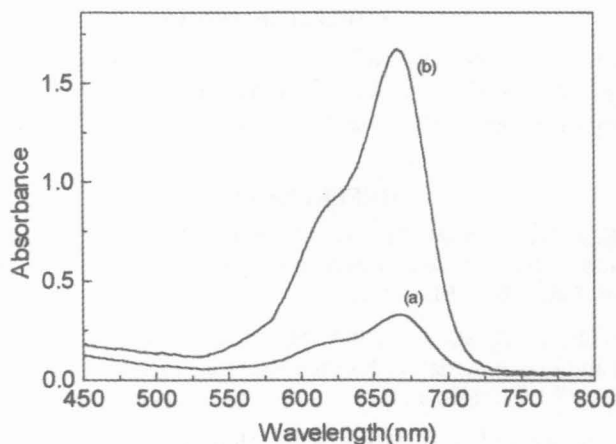


Fig. 6: Absorbance spectra for: (a) after uv-visible radiation and (b) after being exposed to atmospheric air for 12 hr

storage in the dark at room temperature for 12 hours (Fig. 6). It can be seen that the blue color of the MB doped gelatin matrix was restored after being exposed to atmospheric air. According to Nadia *et al.* (1988), this effect is due to the reoxidation of the leuco form of the dye molecules:



This means that the dye can return to its unexcited state when it is in contact with the molecular oxygen, which will remove the extra oxygen.

CONCLUSION

In this paper, the photochemical reactions of the MB doped in gelatin solid matrices have been studied by using uv-visible fibre optics spectrophotometer. The photobleaching of MB upon uv-visible irradiation was confirmed by a decrease of the absorption peak with the increasing of the exposure time. The colored MB dye molecule is photoreduced to its leuco form (colorless) of MB upon irradiation. The present experimental observation shows that a slower photobleaching process occurs at higher concentration of dye doped in gelatin matrix. This is mainly due to the dye-dye interaction between two neighbours excited dye molecule and nonexcited dye molecule resulting in the return to the ground state of the excited molecule. It is also observed that the bleached gelatin sample was recovered to its original color within 12 hours after uv-visible irradiation, because the leuco form of the dye can return to the nonexcited state when it is in contact with the molecular oxygen as reported by other researchers.

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