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Characterization of ferrous-methylthymol blue-polyvinyl alcohol gel dosimeters using nuclear magnetic resonance and optical techniques

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ABSTRACT

A new composition of Ferrous sulphate-Metheylthymol blue (MTB)-Polyvinyl alcohol (PVA) dosimeter is introduced in this work and evaluated using nuclear magnetic resonance (NMR) and absorbance spectrophotometry techniques. The Fricke-MTB-PVA dosimeters were irradiated using a medical linear accelerator in a cubic water phantom. The dose response of the dosimeters was investigated using NMR in terms of spin-spin relaxation rate (R_2), and ultraviolet and visible regions (UV–Vis) spectrophotometry in terms of absorbance. The dosimeter presents a linear dose response for doses up to 20 Gy with UV–Vis and 40 Gy with NMR method. The sample with 0.1 mM MTB, 5% PVA by weight showed highest dose sensitivity for both techniques. The Fricke-MTB-PVA dosimeter developed in this work has a significant advance over the Fricke-MTB-gelatin system: the NMR sensitivity was remarkably improved; the auto-oxidation rate was seven times lower, and no significant dose rate or photon energy effects were observed.

1. Introduction

The developments of techniques and treatments in radiation therapy are aimed to deliver three dimensional (3D) dose distributions to conform high doses to tumours with sparing the surrounding normal tissues (Schreiner, 2015). The validation and verification dose distributions for the treatment planning system (TPS), leads to introduce different dosimeters such as: thermoluminescent materials (Khanal et al., 2015), diodes (Chan et al., 2006), radiosensitive film (Nakano et al., 2012; Morales et al., 2014), and 3D gel dosimeters (Johansson et al., 1997; Baldock et al., 2010; Rabaeh et al., 2017).

Gel dosimeters are able of recording the dose distributions in 3D with formed into a different shapes by choosing a suitable mould (Ibbott, 2006; Schreiner, 2015). In addition, these gels can evaluate dose distributions under actual treatment conditions, as planned in TPS with a full coverage. So far, two main gel dosimeters are available for TPS, polymer gels and radiochromic ones (Vandecasteele and De Deene, 2013).

The radiochromic Fricke gel dosimeters are water equivalent 3D dosimeter. In this gel system, the ionizing radiation makes oxidation of ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}) during irradiation when dissolved in an acidic medium, which have different light absorption and paramagnetic properties (Fricke and Morse, 1927; Fricke and Hart, 1955; Gore et al., 1984; Davies and Baldock, 2008). It can be read using optical spectroscopy (Appleby and Leghrouz, 1991), optical computed tomography (OCT) (Kelly et al., 1998), or MR longitudinal (spin-lattic) and transverse (spin-spin) relaxation rates ($1/T_1$ and $1/T_2$, respectively) (Gore et al., 1984; Olsson et al., 1990; Audet and Schreiner, 1997; Galante et al., 2008; Marrale et al., 2014).

The Fricke gel dosimeters are easy for preparation and have good sensitivity, but there is diffusion for Fe^{3+} after irradiation which may lead to damage the dose image (Schreiner, 2015). Different approaches have been performed on Fricke-like dosimeters to limit the rate of auto-oxidation and the diffusion of Fe^{3+} ions: use of different ligands and nanoparticles (Penev and Mequanint, 2013; Maeyama et al., 2014), substitution of gelatin or agarose with Polyvinyl alcohol (PVA) (Chu et al., 2000; Smith et al., 2015; Marini et al., 2017), and using metal indicator such as Xylenol orange (XO) (Gupta and Narayan, 1985; Davies and Baldock, 2008; Eyadeh et al., 2014). XO can lower the diffusion coefficient of Fe^{3+} in Fricke systems (Rae et al., 1996; Kron

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et al., 1997), it produces a visible optical color change during the irradiation (Gupta and Narayan, 1985; Kelly et al., 1998., Davies and Baldock, 2008).

More recently, the metal indicator Methylthymol blue (MTB) was replaced instead of XO in Fricke gel systems. The maximum absorbance of Fe^{3+}-MTB occurred at a higher wavelength compared to Fe^{3+}-XO (620 vs. 585 nm), which can be scanned using OCT with a red-light source (Penev and Mequanint, 2015; Colnot et al., 2017; Eyadeh et al., 2018).

The new Fricke gelatin dosimeter with MTB-containing gels has been found with high sensitivity, and unaffected diffusion comparing with these XO-containing gels (Penev and Mequanint, 2015; Colnot et al., 2017; Penev and Mequanint, 2017). Previous studies reported that by using PVA matrix, a synthetic common water-soluble polymer, as a gelling agent in the Fricke-XO dosimeter, the rate of auto-oxidation and diffusion coefficient was significantly lower than similar preparation reported for porcine gelatin or agarose (Chu et al., 2000; Hill et al., 2002; Smith et al., 2015; Marini et al., 2017), so using the gelling agent PVA with Fricke-MTB gel dosimeter may reduce the ferric ions spread and the rate of auto-oxidation.

The purpose of this work is to prepare and evaluate the new Fricke-MTB-PVA gel dosimeter using UV/Vis spectrophotometry and NMR technique. The dose response of the dosimeter was evaluated at different concentrations of PVA and MTB dye. Formulations of Fricke-MTB-gelatin, Fricke-XO-PVA, and Fricke-XO-gelatin dosimeters were prepared to compare with the sensitivity of Fricke-MTB-PVA dosimeter.

2. Materials and methods

2.1. Gel dosimeters preparation

The dosimeters were fabricated and categorized into main four types: Fricke-MTB-PVA (4 formulations), Fricke-MTB-gelatin (1 formulation), Fricke-XO-PVA (1 formulation), and Fricke-gelatin-XO (1 formulation). All components used in the preparation of gel dosimeters were obtained from Sigma Aldrich (St. Louis, USA) with analytical grade reagents. The components were 300 Bloom porcine skin gelatin, PVA (MW 89–98 kDa), ferrous ammonium sulphate (FAS) (ammonium iron (II) sulphate hexahydrate), sulphuric acid (SA), Methylthymol blue sodium salts (MTB), Xylenol orange (XO) disodium salt, and double distilled water.

Table 1 shows the concentrations of the components that used for various Fricke-gel dosimeters prepared in this study.

As shown from Tables 1 and 7 stock solutions of SA, FAS, XO, and MTB were prepared separately in 1 L volumetric flasks. The gel preparation began with the addition of 2.5% or 5% (w/v) PVA powder in 1 L double distilled water at room temperature and stirred at 90 °C for 2 h using a hot stirrer. After cooling the PVA-water solutions to 37 °C, 100 mL stock solutions of MTB and XO were added separately to the 100 mL PVA hydrogels and stirred slowly for another 0.5 h to get homogenous Fricke-MTB-PVA dosimeters (Gel 4 to Gel 7) and Fricke-XO-PVA dosimeter (Gel 3). In addition, 4% (w/v) gelatin was dissolved in 1 L double distilled water and heated to 50 °C for 2 h, then 100 mL stock solutions of MTB and XO were added separately to the 100 mL gelatin-water solutions after cooling to approximately 37 °C to get the Fricke-MTB-gelatin and Fricke-XO-gelatin dosimeters (Gel 1 and Gel 2). Then all the dosimeters were filled into NMR tubes (1 cm diameter and 20 cm height) and cuvettes ($1 \times 1 \times 1\ cm^3$), sealed, and stored in a refrigerator (10 °C) before irradiation. The absorbance and relaxation time T_2 were measured approximately 2 h of irradiation.

Table 1
Compositions of various Fricke-gel dosimeters prepared in this study.

Gel	Water (mL)	PVA % (w/v)	Gelatin % (w/v)	SA (mM)	FAS (mM)	MTB (mM)	XO (mM)
Gel 1	96	-	4	25	0.1	0.1	-
Gel 2	96	-	4	25	0.1	-	0.1
Gel 3	95	5	-	25	0.1	-	0.1
Gel 4	97.5	2.5	-	25	0.1	0.1	-
Gel 5	95	5	-	25	0.1	0.05	-
Gel 6	95	5	-	25	0.1	0.1	-
Gel 7	95	5	-	25	0.1	0.2	-

2.2. Irradiation of dosimeters

All irradiations of dosimeters were performed using a medical linear accelerator (Varian Medical Systems, USA) with a $30 \times 30\ cm^2$ field size and normal incidence calibrated using ionization chamber (Vandecasteele et al., 2011). Each sample was placed in a $30 \times 30 \times 30\ cm^3$ cubic water acrylic phantom at depth of 5 cm with 100 cm SSD. For dose response, the gel cuvettes and tubes were irradiated of up to 40 Gy with a 6 MV photon beam and 600 cGy/min dose rate. The effects of photon energy and dose rate were examined using 6, 10, and 15 MV photon beams and 134, 268, and 600 cGy/min dose rates at different doses. Three samples (cuvettes and tubes) were measured at each absorbed dose, but no significant differences were found.

2.3. UV–Vis spectrophotometry measurements of gel dosimeters

The different light absorption with the irradiated samples was measured using the UV–Vis spectrophotometer (Thermo Scientific, USA) in the wavelength range of 350–750 nm. The response of the gel cuvette samples was recorded as the absorbance at 620 nm MTB-containing dosimeters and 585 nm for XO-containing dosimeters. The impacts of the scanning temperature on the response of the gel dosimeters were analyzed by putting cuvette samples in an air cooled peltier cell (Thermo Scientific, USA).

2.4. NMR measurements of gel dosimeters

The relaxation rate ($R_2 = 1/T_2$) measurements of NMR tubes contain gel dosimeters were obtained using 0.5 T NMR (Bruker, Germany) at the temperature of 20 °C, except for the study of the impact the scanning temperature on the responses of gel samples. A standard multi –Spin-Echo CPMG sequence was used to measure relaxation time (T_2), with an echo time of 1 ms and a delay of 10 s between scans.

3. Results and discussion

3.1. Dose response of the dosimeter formulations

3.1.1. UV–Vis absorption spectra of MTB-PVA gel dosimeter system

Absorbance spectra of irradiated Fricke-MTB-PVA gel samples (Gel 6 formulation) is demonstrated in Fig. 1 which displays a broad absorption peak centered at 620 nm, where the optical density increases with dose. This wavelength is very closed to red-light source that used in charge-coupled device (CCD) camera or 3D OCT. In addition, the optical density decreases with dose at about 445 nm. This is the same center absorption peaks for MTB-gelatin-gel system (Penev and Mequanint, 2015; Colnot et al., 2017; Eyadeh et al., 2018). In case of the XO-contain gels the optical densities were increased with dose at around 585 nm and decreased at around 435 nm, which agrees with previous studies (Davies and Baldock 2008; Jin et al., 2012; Penev and Mequanint, 2013). All the dose response calibration curves were plotted using the maximum intensity of the absorption band (at 620 nm for MTB-contain gels and at 585 nm for XO-contain gels).

3.1.2. Dose response functions of MTB-PVA gel dosimeter system

The effect of PVA concentration (2.5% and 5%) by weight and MTB concentration (0.05, 0.1, and 0.2 mM) on the dose response were