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Dosimetric investigations on radiation-induced Ag nanoparticles in a gel dosimeter

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Abstract

Radiation-induced Ag° nanoparticles (NPs) in silver nitrate gel dosimeter incorporating various components was investigated in the dose range of 0–100 Gy. The gel responses were analyzed at 450 nm, a Surface Plasmon Resonance band of AgNPs. The radiation sensitivity of the gel increases with increasing Ag^+ concentrations and isopropanol, % and decreases with boosting gelatin content and H^+ ions. This gel features good water equivalency in energies from 0.3 to 20 MeV and has potential applications in the dose range of 5–100 Gy based on the selected compositions. Thus, it can cover blood irradiation and radiotherapy dosimetry applications.

Keywords Radiochromic gel · Ag nanoparticles · Surface plasmon resonance band · Absorption spectroscopy · Dosimetry · Radiotherapy

Introduction

The preparation and application of nanomaterials are currently hot topics in research and development due to their exceptional optical properties. Among metal nanoparticles, silver nanoparticles (AgNPs) represent one of the most commercially interesting nanomaterials because of their novel properties and their potential application [1, 2]. The AgNPs have characteristics optical absorption spectrum in the UV–Visible region between 390 and 450 nm [3]. In addition, the position of the Surface Plasmon Resonance (SPR) band is mainly dependent on the AgNps size [4] and on the surrounding medium [5]. Synthesis of nanoparticle clusters by γ-radiation induced method has proved to be effective [6].In this method, The species of hydrated electrons (e^-_{aq}) and hydrogen atoms ($H^·$) formed from radiolysis of water, are very reactive and effective as reducing agents with standard reduction potentials, E° (H_2O/e_{aq}^-) = – 2.87 V and E° ($H^+/H^·$) = – 2.3 V respectively. Therefore, both of them can reduce Ag^+ ions in gel dosimeter to a state of zero [4, 6–9].

AgNPs could be successfully applied for radiation detection and dosimetry [10, 11] and for dose enhancement in radiotherapy applications [12–15]. The silver nitrate dosimeter features a linear response and good measurements reproducibility [10]. The influence of γ-rays on silver nitrate was examined [6, 16–20]. It is actually suggested as a liquid detector based on precursors of Ag nanoparticles and 1% sodium citrate, where the ionizing radiation induces the formation of spherical AgNPs, recognized by the appearance of a sharp peak around 410 nm in the absorbance spectrum of the colloidal solution [21]. However, most of dosimetric characteristics were not addressed completely in this study [21]. Funaro et al. [10] studied an aqueous colloidal solution of Ag^+ and 0.1 sodium citrate as a detector covering the dose range of 2–120 Gy [10]. However, from these results [10], it seems that this detector/dosimeter has a reasonable change after 10 or 20 Gy dose level. In addition, the authors [10, 21] did not use a capping agent to stabilize the AgNPS formed by radiation and prevent the coagulation of AgNPs in the aqueous detector solutions. Radiation-induced reduction of Au^+ ions into maroon-colored dispersions of plasmonic gold (Au°) nanoparticles in the presence of a lipid surfactant was studied as a liquid dosimeter without using any capping

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agent for radiotherapy dose levels [22]. Ascorbic acid, an antioxidant agent, was added to the Au^{+} ion solution to remove the oxidizing OH radicals that can inhibit AuNPs formation [22]. However, their results indicate a great standard uncertainty (~20% in some cases) of the repeated dosimeteric analyses and a low radiation sensitivity at doses less than 10 Gy [22]. Soliman [11] introduced a new radiochromic gel dosimeter based on silver nitrate in gelatin (8%) for ^{137}Cs irradiation that cover the dose range of 5–100 Gy. The author found that the dose response of the dosimeter is linear up to 100 Gy and the overall uncertainty of dose estimation by $AgNO_3$ was around 4.56% [11]. This dosimeter has a temperature coefficient of ~0.339% per °C. The response of this gel increases gradually when kept at room temperature and can stand stable in the fridge conditions (~6 °C) [11]. In addition, silver nitrate with 250 mM was added to a normoxic PAGAT gel dosimeter and studied for radiotherapy use [23]. However, the influence of gelatin content, pH and alcohol on the $AgNO_3$ gel responses were no addressed in these literatures [11, 23].

One of the goals of the present investigation is to prepare Ag^{+} gel dosimeter, improve its radiation sensitivity by adding isopropanol as a hydroxyl radical scavenger and optimize the gelatin content, isopropanol addition and pH in the gel matrix. Thus, we studied the influences of gelatin content, isopropanol and pH on the gel response irradiated by using ^{60}Co gamma rays up to a dose level of 100 Gy. In additions, the theoretical energy dependency and water equivalency were discussed in this study. The aforementioned factors and theoretical calculations were not addressed in the previous literature [11]. We aimed also to study the effects of Ag^{+} concentrations on the gel response. The stability of the gel dosimeter as well as the uncertainty parameters were also discussed.

Experimental

Materials

We used silver nitrate (99.8%), skin porcine gelatin (G2500) and isopropanol (99.5%) from Sigma-Aldrich. Glacial acetic acid and doubly distilled water to prepare Ag^{+} gel dosimeters. We used these chemicals without any extra purification.

Preparation of the gel dosimeters

An aqueous gelatin solution (4% w/v) was prepared at 40 °C under continuous magnetic stirring for 2 h in order to obtain a clear gelatin solution. Various amounts of aqueous $AgNO_3$ solution was added to the gelatin solution after cooling the gelatin solution down to 31–34 °C in order to prepare the required concentration of $AgNO_3$ (50, 100 and 150 mM). Then, these solutions were continued stirring for further 1 h in order to get highly homogenous mixtures. After that, the gelatin solutions (pH ≈ 5.2) were introduced into plastic cuvettes ($1 \times 1 \times 3$ cm^3) then allowed to form gels in a refrigerator at 6 °C in the dark. The effect of gelatin contents on the dosimeter response was investigated by preparing dosimeter solutions with different gelatin amounts (4%, 6% and 8% wt/v) and100 mM of $AgNO_3$ and without the use of buffer. To study the effect of isopropanol on the gel response, aqueous gelatin solutions (4% w/v) with 100 mM of $AgNO_3$ containing different isopropanol 0, 10, 20 and 30% v/v were prepared by aforementioned method.

To study the effect of pH on the gel dosimeter response, different gel dosimeters of 100 mM of $AgNO_3$ in 4% wt/v gelatin solutions were prepared by the same mentioned method and adjusted to different pH values (6, 5.2 and 3) by using buffer solutions containing sodium acetate with acetic acid. The normal composition without using the buffer has a pH = 5.2.

Irradiation and characterization of the gel dosimeters

The gel dosimeters were subjected to gamma radiation in the range 5–100 Gy using a ^{60}Co Gamma Cell GC-220 Excel (MDS Nordion, Canada) using a specially designed polystyrene holder to ensure electronic equilibrium and adequate depth-dose build up during irradiation. The dose rate at time of the experiments was 1.0 kGy h^{-1}. The dose rate to water of the gamma cell was measured using alanine dosimeters by the National Physical Laboratory (NPL) in England; thus this calibration and absorbed doses are traceable to NPL, a primary laboratory.

We analyzed the Ag^{+} gel dosimeters before and after subjected to different absorbed doses using a UV–Vis spectrophotometer (Evolution 500, Thermo Electron Corporation, England) which collects spectra from 350 to 750 nm using a band width of 2 nm.

To perform the dose response functions of Ag^{+} gel dosimeters, the unirradiated gel samples are analyzed using spectrophotometer at 450 nm, introduced into the gamma cell phantom and exposed to γ-radiation at different absorbed doses (three samples were utilized at each dose point). After irradiation, the gel samples are read out then the responses are analyzed. The response functions are established in terms of change in net absorbance, ΔA ($=A_i–A_o$), where A_i and A_o are the absorbance at 450 nm of the irradiated and unirradiated gel dosimeter, respectively as a function of absorbed doses.

The batch variability of the gel dosimeter irradiated at different doses in the gamma cell for all concentrations and the overall uncertainty and uncertainty parameters that affect absorbed dose monitoring were estimated.

Results and discussion

All gel dosimeters prepared have very faint yellow color (background) before irradiation indicating the formation of AgNPs by the action of heat during the preparation [24]. Upon irradiation, the color of gel dosimeter changes to a visual yellow color and finally to yellowish brown as the dose increases indicating the formation of γ-induced Ag-NPs.

The effect of gelatin content; absorption spectra and response curves

Gelatin, which is composed of peptides and proteins, has been used as a very effective stabilizing agent and capping agent for preparation of colloidal silver because of its high molecular weight [2]. Ag^+ ions could be bound to gelatin via electrostatic interaction (ion–dipole) interaction due to its oxygen and nitrogen-rich structures in the carboxyl and the amine groups, respectively. This led to a very tight bond with silver ions [20, 25] and so the AgNPs could be kept from agglomerating [5].

The particle size of AgNPs usually depends on both precursor ion and stabilizer concentrations. When AgNPs aggregate and the conduction electrons near the surface of AgNPs are delocalized the SPR band shifts to lower energy. This will lead to shift of the absorption and scattering peaks to longer wavelengths (i.e. red-shift). As the nanoparticles destabilize, the intensity of original extinction peak will decrease (due to the weakening of the stablility of NPs), and frequently the SPR peak will become broad [26]. Figures 1 and 2 show the absorption spectra at 4% and 8% gelatin, respectively. There is no considerable change is observed in FWHM corresponding to no obvious changes in particles size distribution of AgNPs formed during irradiation. The absorption spectrum of γ-irradiated gel dosimeter exhibits an SPR band at wavelength 450 nm. Based on the observed wavelength of the SPR band, it is likely that the diameter of the obtained AgNPs might be around 65–72 nm as calculated from Mie theory [27]. This is in agreement with the data previously obtained [11]. This band is caused by the SPR of conducting electrons from the surface of AgNPs formed during the irradiation process [4]. The intensity of this band increases with the increase of the absorbed doses. Meanwhile, the peak broadening decreases gradually with increasing absorbed dose due to uniformity of AgNPs size distribution [28]. The competition between nucleation and growth process in the formation of nanoparticles can determine the size of nanoparticles which is influenced by certain parameters such as the choice of

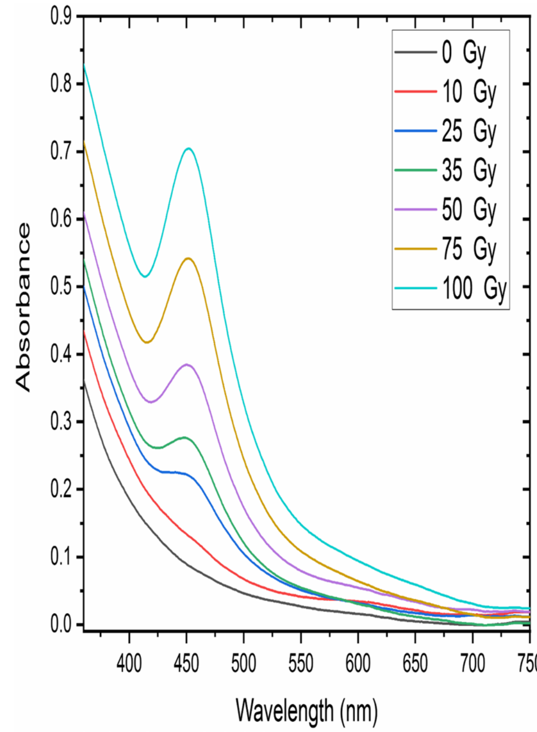

Fig. 1 Absorption spectra of the gel dosimeter containing 100 mM $AgNO_3$ and 4% gelatin irradiated at different absorbed doses (0–100 Gy)

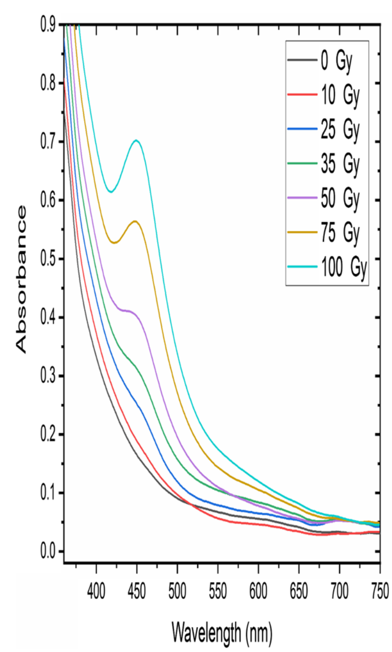

Fig. 2 Absorption spectra of the gel dosimeter containing 100 mM $AgNO_3$ and 8% gelatin irradiated at different absorbed doses (0–100 Gy)

solvents and stabilizer, the precursor to stabilizer ratio, pH during synthesis, and absorbed dose [18] and all of these parameters will be determined in this study. It was shown (Figs. 1, 2) that the change of absorbance is higher in the case of gelatin 4% as compared to gelatin 8%, indicating that the increase of gelatin could minimize the reduction of Ag^+ ions to AgNPs with radiation. Thus, selection of composition should be based on the application of use (i.e. for blood irradiation dosimetry the gelatin content of 8% can be a good candidate while for radiation therapy it is better to use the composition of gelatin of 4%). For modern radiation therapy such as microbeam radiation therapy of synchrotron radiation, the dose of 10 Gy or more are applicable in this field especially for peak dose measurements [29, 30]. One of co-authors (Y.S. Soliman) and a group of ID-17 beamline at the European Synchrotron Radiation Facility, France are writing an article on the use of Ag^+ ions in gelatin for synchrotron radiation therapy in kV energy range (≈100 kV).

Figure 3 shows the change of response (λ_{max} = 450 nm) of the gel dosimeter of 100 mM $AgNO_3$ at 4, 6 and 8% gelatin as a function of absorbed doses and the radiation sensitivity at different gelatin %. The gel response increases linearly with the increase of absorbed dose up to 100 Gy. The relation between the response of dosimeter and absorbed has a good linearity over the range of 10 to 100 Gy. The obtained r^2 at this range was 0.9994, 0.9995 and 0.9981 for 50, 100, and 150 mM $AgNO_3$ respectively. The intensity of the SPR peak at 450 nm increases as the $AgNO_3$ concentration increases for irradiated gel dosimeter, indicating more reduction of Ag^+ to Ag-NPs with increasing radiation exposure. The response of composition containing 4%

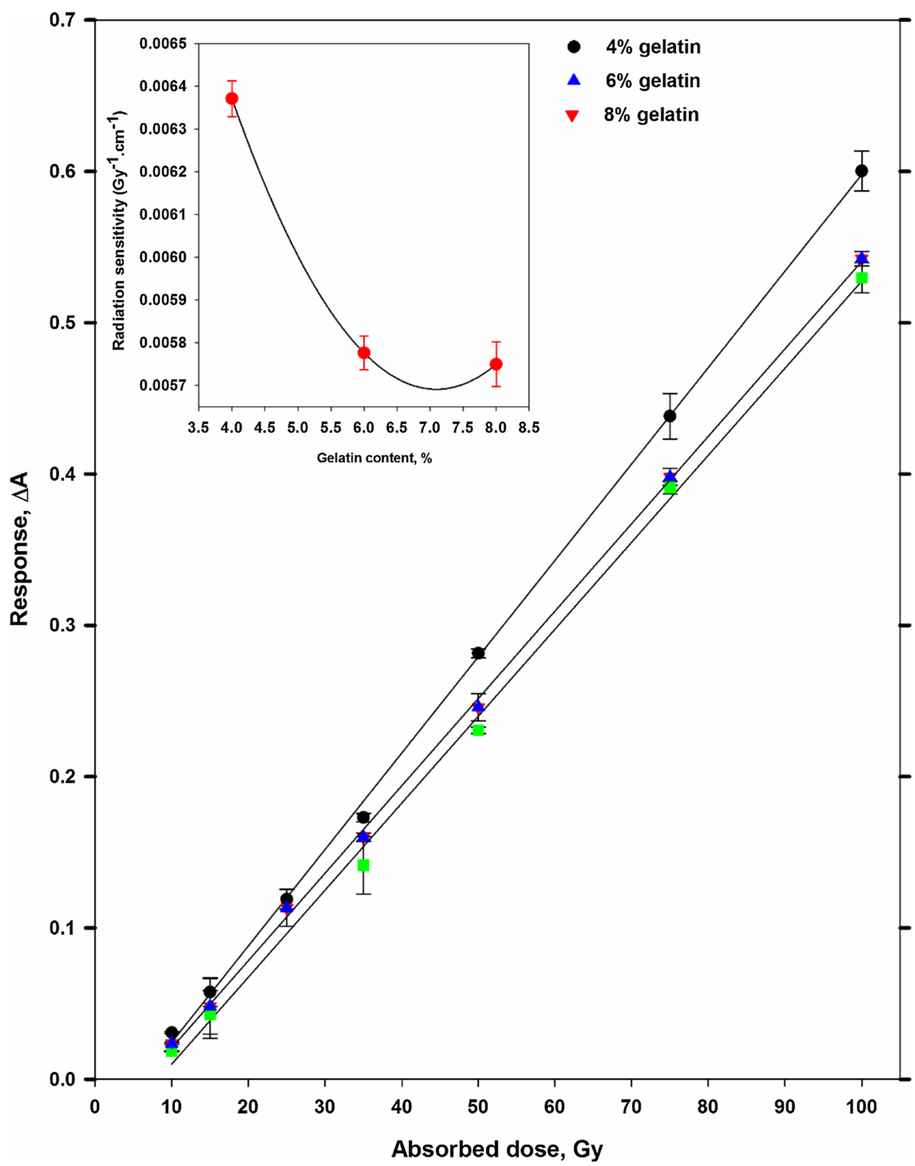

Fig. 3 Dose response curve of Ag^+ gel dosimeter (100 mM $AgNO_3$) at different gelatin%; net absorbance change at 450 nm as a function of absorbed dose (10–100 Gy). The inserted figure represent the radiation dose sensitivity of Ag^+ gel dosimeter as a function of gelatin content, % for the dose range of 10–100 Gy. The radiation sensitivities are the slope of the response curves. Error bars denote the standard deviation of the mean values

gelatin with radiation is higher than the response of other compositions. This is indicated by the radiation sensitivity, slope of the dose response curves, as a function of gelatin content, % (see the inserted curve in Fig. 3). It was found that, the increase of gelatin content from 4 to 8% minimize the radiation sensitivity of Ag^+ gel dosimeter with ~ 10.8%. Thus, we speculated that there would be an optimal stabilizer concentration precursor for Ag^+ concentration to obtain good radiation-induced Ag^+ reduction to AgNPs. Based on these results, we used gelatin 4% for further investigation to obtain better sensitivity.

The effect of Ag^+ concentrations on the dosimeter performance

Figures 1 and 4 display the absorption spectra for the gel dosimeter (4% gelatin) containing silver nitrate of 100 and 50 mM, respectively. The absorbance at 450 nm is higher in the case of 100 mM $AgNO_3$ than 50 mM $AgNO_3$ composition. Table 1 displays the color change of the gel dosimeter with the increase of absorbed doses. Upon irradiation, yellow color develops in the gel and its intensity increases significantly with increasing absorbed doses that can be visually checked. The obtained color is distinctive for metallic Ag°. Figure 5 shows the change of response of the gel dosimeter 4% gelatin at different $AgNO_3$ concentrations (50, 100 and 150 mM $AgNO_3$) as a function of absorbed dose and radiation sensitivity against silver nitrate concentrations. The gel response increases linearly with the increase of absorbed dose up to 100 Gy. The obtained r^2 at this range was 0.9992, 0.9994 and 0.9992 for 50, 100, and 150 mM $AgNO_3$ respectively. The intensity of the SPR peak at 450 nm increases as the $AgNO_3$ concentration increases for irradiated gel dosimeter, indicating more reduction of Ag^+ ions to AgNPs. The gel dosimeter containing 150 mM Ag^+ can be applicable from 5 to 100 Gy which covers blood irradiation and radiotherapy dose verification. As shown from the inserted curve in Fig. 6, the increase of $AgNO_3$ concentration improves the radiation sensitivity of the gel dosimeter. The radiation sensitivity increases by ~ 17.3% with increasing Ag^+ concentrations from 50 to 150 mM. Thus, an appropriate composition should be selected based on the required dose range of application.

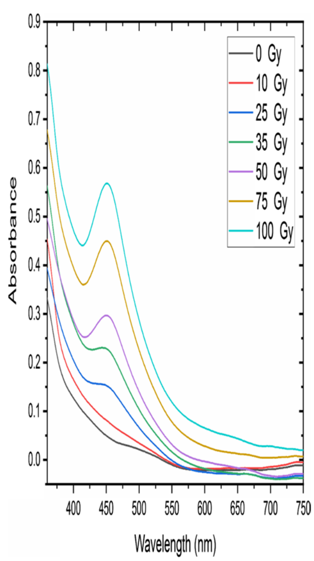

Fig. 4 Absorption spectra of the gel dosimeter containing 50 mM $AgNO_3$ and 4% gelatin that unirradiated and irradiated at different absorbed doses (0–100 Gy)

Table 1 Scanned images of silver nitrate gel dosimeter (4% gelatin and 150 mM Ag^+) at different doses using an Epson Perfection V850 Pro scanner, made by Seiko Epson Corporation

Absorbed dose (Gy)	Unit
0.0	
5.0	
15.0	
25.0	
35.0	
50.0	
75.0	
100.0	

The influence of isopropanol on the gel response and Ag^+ ion reduction

Figure 6 display the dose response curves of silver nitrate gel dosimeter (4% gelatin and 100 $AgNO_3$) at different isopropanol content and the radiation sensitivity against isopropanol content, %. All responses increase linearly with increasing absorbed dose up to 100 Gy. In addition, the gel response increases with increasing isopropanol content, indicating that isopropanol promote the reduction of Ag^+ into AgNPs. The radiation sensitivity increases significantly with the increase of isopropanol content on the gel from 0 to 20% then tends to saturate with increasing isopropanol from 20 to 30%. The increase of isopropanol in the gel from

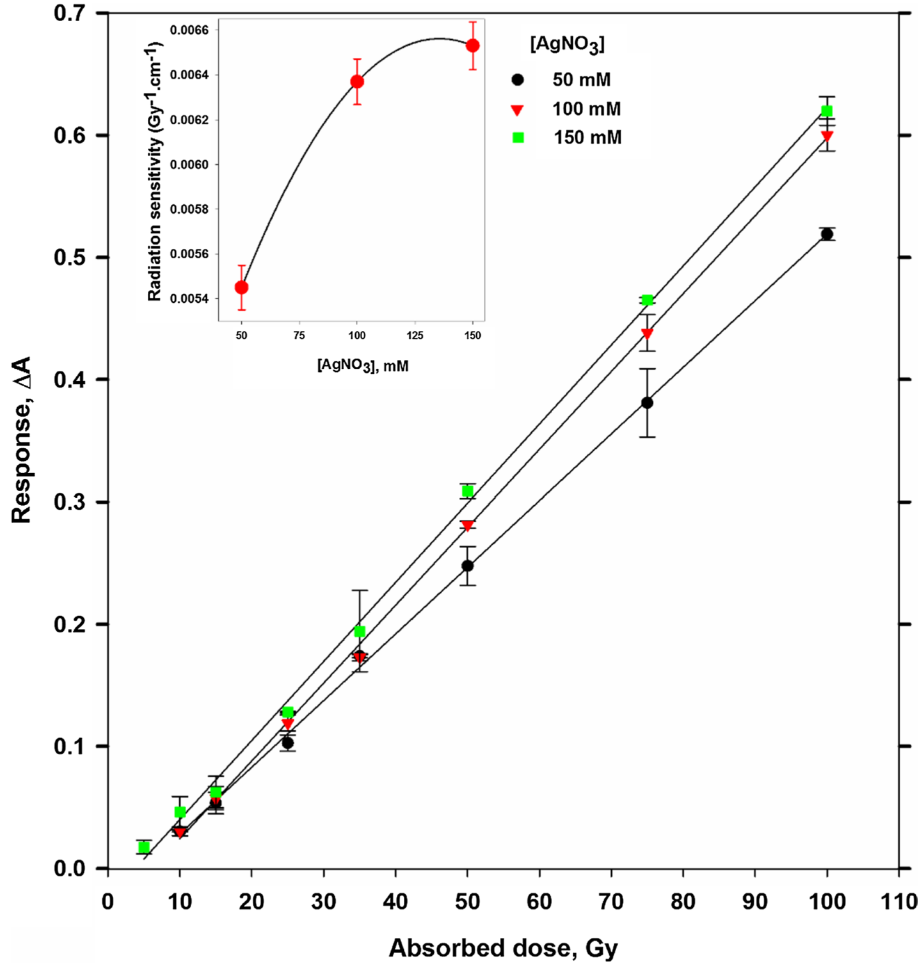

Fig. 5 Dose response curve of Ag^+ gel dosimeter (4% gelatin) at different $AgNO_3$ concentrations; net absorbance change at 450 nm as a function of absorbed dose (10–100 Gy for 50 and 100 mM of $AgNO_3$ and 5–100 Gy for 150 mM of $AgNO_3$). The inserted figure represents the radiation dose sensitivity of Ag^+ gel dosimeter as a function of $AgNO_3$ concentrations. Error bars denote the standard deviation of the mean values

0 to 20% or to 30% enhances the radiation sensitivity by 16.75 or 19.11%, respectively. Thus, it is better to use 20% isopropanol on the gel composition to get better radiation sensitivities at lower doses.

During water radiolysis, strong oxidizing agents of $OH^\cdot$ radicals are produced [Eq. (1)], enabling the metal atoms or the Ag^+ ions to oxidize into a higher oxidation state [31, 32]. In addition, hydrate electrons (e^-_{aq}) are formed which act as a strong reducing agent, enhancing the reduction of Ag^+ ions into Ag° atoms as Eq. (2) [6]. Thus, the two processes contradict each other, decreasing the efficiency of radiation on the reduction of Ag^+ ions.

$$H_2O \xrightarrow{\gamma\text{-rays}} e^-_{aq}, H_3O, H^\cdot, OH^\cdot, H_2, H_2O_2, H_3O^+ \tag{1}$$

$$Ag^+ + e^-_{aq} \xrightarrow{\gamma\text{-rays}} Ag^\circ \tag{2}$$

Isopropyl alcohol plays an important role in scavenging the formed $OH^\cdot$ radicals by forming $(CH_3)_2C^\cdot(OH)$ radicals as Eq. (3) which hinder the oxidation process of Ag° or Ag^+ ions to higher oxidation state and promote the reduction of Ag^+ ions into Ag° metals [6, 33, 34] as shown in Eqs. (5 and 6). This process will increase the sensitivity of the gel dosimeter towards gamma radiation. Furthermore, the secondary radicals $(CH_3)_2C^\cdot OH$ are formed upon reaction of $(CH_3)_2CH(OH)$ with $H^\cdot$ radicals leading also to a reduction of Ag^+ ions as Eq. (6).

$$(CH_3)_2CH(OH) + OH^\cdot \rightarrow (CH_3)_2C^\cdot(OH) + H_2O \tag{3}$$

$$(CH_3)_2CH(OH) + H^\cdot \rightarrow (CH_3)_2C^\cdot(OH) + H_2 \tag{4}$$

$$(CH_3)_2C^\cdot(OH) + Ag_2^+ \rightarrow Ag_2 + CH_3COCH_3 + H^+ \tag{5}$$

$$(CH_3)_2C^\cdot(OH) + Ag_n^+ \rightarrow Ag_n + CH_3COCH_3 + H^+ \tag{6}$$

The effect of pH on the gel response

The formation and stability of γ-radiation induced Ag nanoparticles depend on the pH of the medium. The radiolysis species of hydrated electron and hydrogen atoms

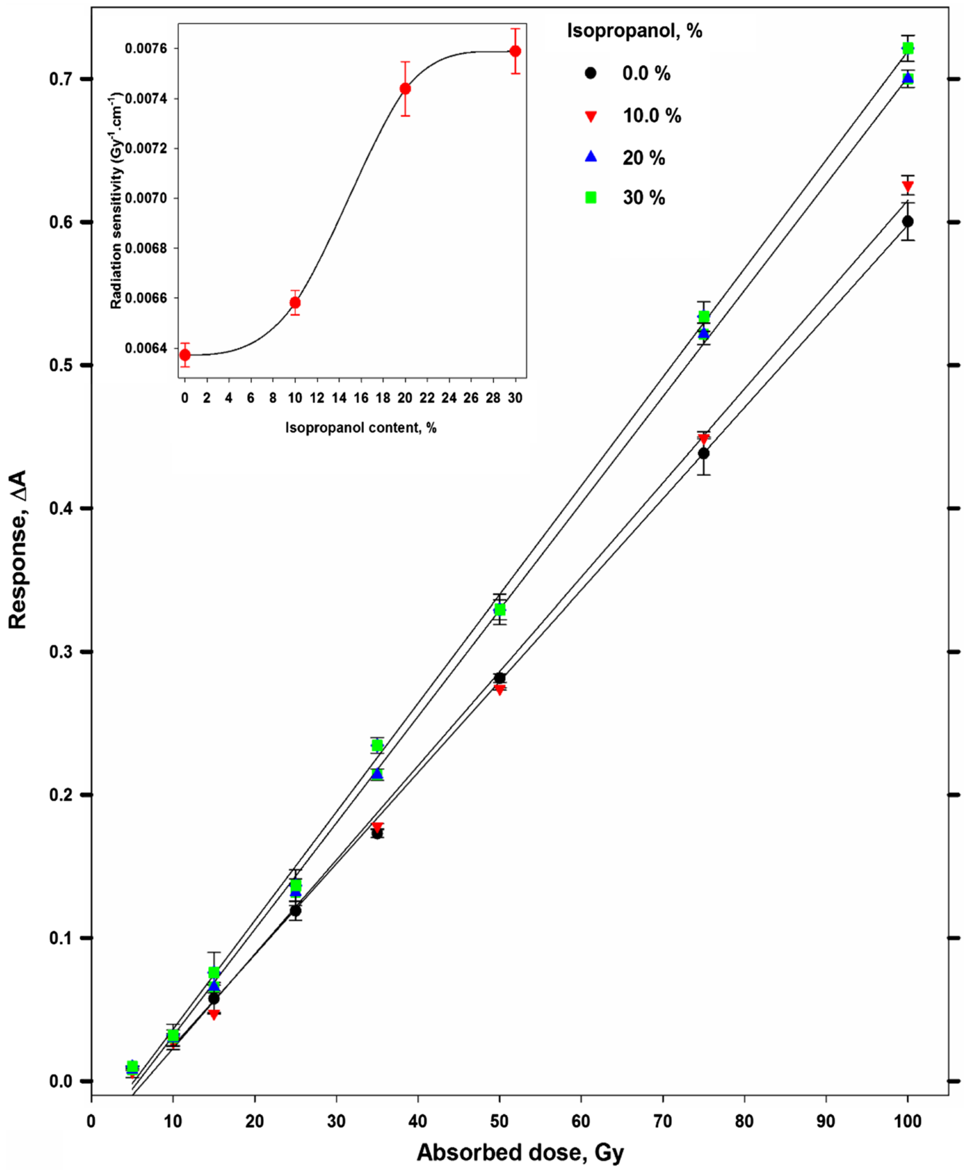

Fig. 6 Dose response curve of Ag^+ gel dosimeter containing 100 mM $AgNO_3$ at different isopropanol content %; net absorbance change at 450 nm as a function of absorbed dose (5–100 Gy). The inserted figure represents the radiation dose sensitivity of Ag^+ gel dosimeter as a function of silver nitrate concentrations. Error bars denote the standard deviation of the mean values

are consequently interacted with the solute ions dependent on their reactivates [Eqs. (7 and 8)]. At lower pH, almost all hydrated electrons are rapidly scavenged by H^+ ions producing H atoms. Hence at lower pH values, the possibility of reducing Ag^+ ions becomes low [35]. This is observed also in our presented results in Fig. 7 that the response decrease significantly with the decrease of pH. At pH (5–6), γ-radiation induced AgNPs are nearly stable. This indicates that our results are in the agreement with the previously published studies [36, 37], which indicating that the reduction of Ag^+ to AgNPs is unfavorable in the case of acidic medium. In strongly basic medium (> pH 9) hydrated electrons react with water to create $OH^·$ ions and a brown precipitate is appeared due to formation of Ag(OH). Thus, we avoided to use the high pH value in this study.

$$e^-_{aq} + H_3O^+ \rightarrow H + H_2O \quad (7)$$

$$e^-_{aq} + H_2O \rightarrow H + OH^· \quad (8)$$

Stability of the gel dosimeter

The variation of response of irradiated gel dosimeter at 50 Gy stored in a dark place at 6 °C as a function of storage time relative to that measured immediately after irradiation (zero time) is shown in Fig. 8. It is shown that the irradiated gel dosimeter stored in the dark at 6 °C show that silver nanoparticles synthesized by gamma radiation are stable over a period of 15 days. The increase in response is around

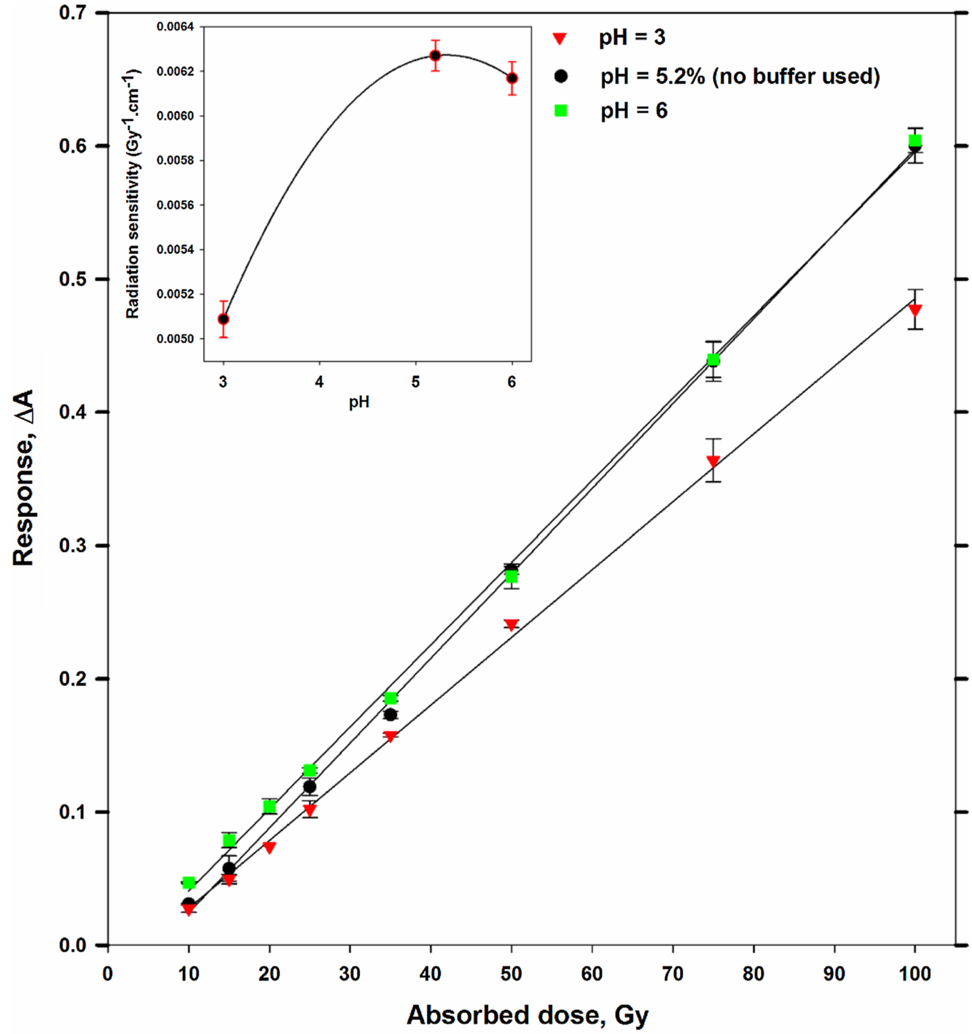

Fig. 7 Dose response curve of Ag^+ gel dosimeter containing 100 mM AgNO3 and 4% gelatin at different pH; net absorbance change at 450 nm as a function of absorbed dose (10–100 Gy). The inserted figure represent the radiation dose sensitivity of Ag^+ gel dosimeter as a function of pH variations for the dose range of 10–100 Gy. Error bars denote the standard deviation of the mean values

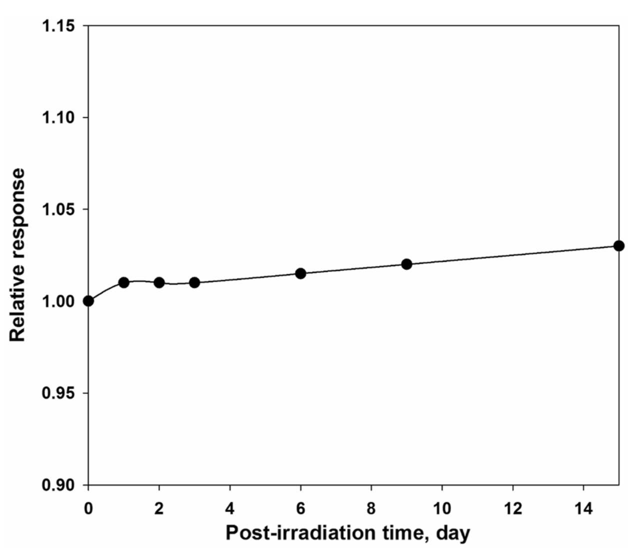

Fig. 8 Post-irradiation stability of 100 mM Ag^+/gel dosimeter irradiated at 50 Gy and stored in the dark at 6 °C at different intervals of time

3%. Under light, the response of Ag^+ gel dosimeter is highly varied with time [11]. Thus, it is recommended to store the gel dosimeter in the dark at low temperature to retard the growth of response and to inhibit the reduction of Ag^+ ions into metallic AgNPs.

Water equivalency of Ag^+ gel dosimeter

Figure 9 shows the mass energy-absorption coefficient, $(\mu_{en}/\rho)_{Gel}$, of Ag^+ gel dosimeter (50 and 100 mM) relative to the $(\mu_{en}/\rho)_W$ of water as a function the photon energy ranging from 1 keV to 20 MeV. This figure presents also the energy dependence of soft tissue and alanine dosimeter to compare with Ag^+ gel dosimeter. The data of μ_{en}/ρ were deriven from the online NIST mass energy-absorption coefficient tables and physical reference data presented on the website [38]. It is obvious that the Ag^+ gel dosimeter is considered as a water equivalent dosimeter in the photon energy range of 300 keV–20 MeV, showing its ability for use in

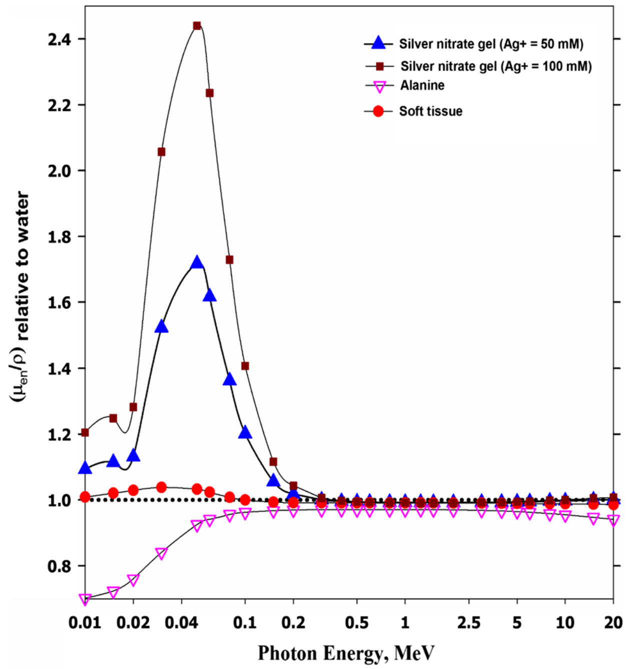

Fig. 9 The mass energy-absorption coefficient, $(\mu_{en}/\rho)_{Gel}$, of Ag^+ gel dosimeter (50 and 150 mM Ag^+) relative to $(\mu_{en}/\rho)_W$ of water against photon energy in the range of 0.1–20 MeV and compared with alanine dosimeter and soft tissue

radiation dosimetry without any need to correct the response for energy dependency.

Uncertainty budget

There are various parameters that can contribute to uncertainty of absorbed dose measurements such as calibration of the gamma cell, uniformity of Ag^+ gel dosimeter (batch homogeneity), stability of response, absorbance measurement and calibration curve fit. Table 2 summarizes the uncertainty parameters of Ag^+ gel dosimeter. The uncertainties components were determined as previously described in details [39–42]. The overall uncertainty (2σ) of response was found to be 5.16.

Table 2 Uncertainty budget of Ag^+ gel dosimeter in the dose range up to 100 Gy

Source of uncertainty	Type of uncertainty	Standard uncertainty (%)
Calibration irradiation dose rate	B	1.145[a]
Irradiation facility	B	0.44
Instrumental variation	A	0.04
Reproducibility of measurements	A	0.40
Batch variability	A	1.5
Calibration curve fit	A	1.6
Post-irradiation stability	A	0.40
Combined standard uncertainty (u_c), 1 σ		2.58
overall uncertainty (2σ)		5.16

[a]As quoted from calibration certificate

Summary and conclusion

Radiochromic gel dosimeters based on silver nitrate were formulated at different gelatin content, isopropanol content, Ag^+ concentrations and pH. The dosimetric characterizations of these compositions were investigated using a spectrophotometric technique. The absorption spectrum of γ-irradiated gel dosimeter exhibits a SPR peak at 450 nm of AgNPs formed upon irradiation. The peak intensity grows linearly with increasing the dose up to 100 Gy. The formation of AgNPs is enhanced by the increase of Ag^+ ions and the decrease of gelatin content as summarized in a three-dimensional (3D) diagram (Fig. 10). For 100 mM composition with gelatin content of 4 and 8%, the sensitivity is 6.37×10^{-3} and 5.92×10^{-3} Gy^{-1} cm^{-1}, respectively. While, for 200 mM composition with gelatin content of 8%, the sensitivity is 6.64×10^{-3} Gy^{-1} cm^{-1} [11] that is nearly comparable to the value (6.53×10^{-3} Gy^{-1} cm^{-1}) of the gel composition of 150 mM with 4% gelatin of the present study. Thus, with optimization of the gelatin content, the radiation sensitivity at low Ag^+ concentration can be adjusted similarly as the gel dosimeter of high Ag^+ and high gelatin content,

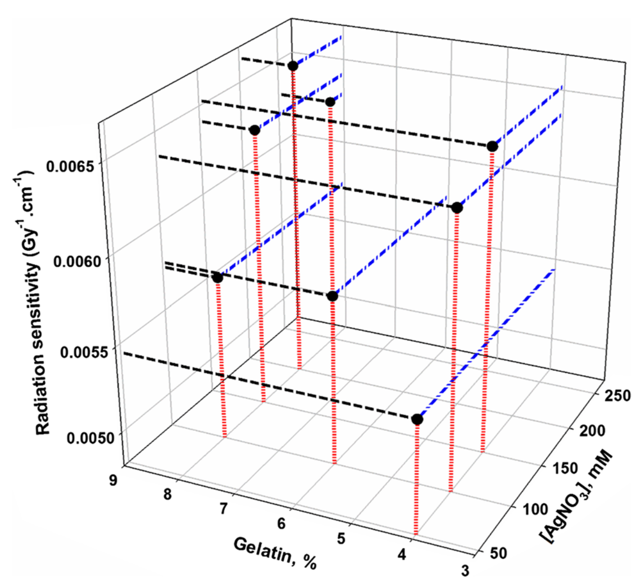

Fig. 10 3D diagram representing the radiation sensitivity of the gel dosimeter without isopropanol as a function of silver nitrate concentrations and gelatin, %. The radiation sensitivity values of the gel dosimeter containing 100, 150, 200 and 250 mM of Ag^+ ions at 8% gelatin are taken from Soliman, 2014 [11]. While, the other values are derived from the present study

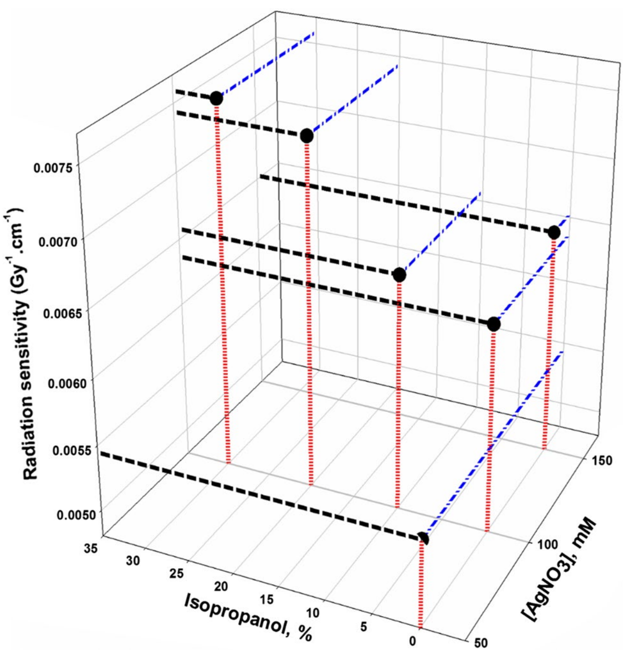

Fig. 11 3D diagram representing the radiation sensitivity of the gel dosimeter with 4% gelatin as a function of silver nitrate concentrations and isopropanol, %

which presented in the previous study [11]. Furthermore, the addition of isopropanol to this dosimeter enhances the production of AgNPs in the gel matrix and hence increases the gel response with an absorbed dose. Isopropanol scavenges the strong oxidizing agent of $OH^{\cdot}$ radicals formed by H_2O radiolysis and forms isopropanol radicals $(CH_3)_2C^{\cdot}(OH)$ that can reduce the Ag^+ ions into Ag° metals. A 3D diagram (Fig. 11) summarize the combined effects of isopropanol and Ag^+ ions on the radiation sensitivity of the radiochromic gel dosimeter (4% gelatin). The increase of isopropanol in the gel (100 mM Ag^+) from 0 to 20% enhances the radiation sensitivity by 16.75%. For the gel composition of 100 mM Ag^+, gelatin content of 4% and isopropanol 20%, the sensitivity is 7.44×10^{-3} Gy^{-1} cm^{-1} that is higher than the sensitivity of 150 mM Ag^+ without isopropanol by ~ 14% (the sensitivity is 6.53×10^{-3} Gy^{-1} cm^{-1} for the last compositions) as shown in Fig. 11. Thus, for lower dose applications less than 10 Gy it is preferable to select a composition of high isopropanol % and high Ag^+ ion concentration, and low gelatin %. The detection limit of all studied responses is varied from 5 to 10 Gy based on the composition used.

The response of the gel dosimeter is influenced by pH. The reduction of Ag^+ ions decreases with the increase of H^+ ions in the gel matrix. This is due to that H^+ acts as a radical scavenger for solvated electrons (e^-_{aq}), strong reducing agents, formed by H_2O radiolysis, decreasing the probability of reducing Ag^+ ions by e^-_{aq}. Thus, it is recommended to use this gel dosimeter without the addition of buffer solution. The Ag^+ gel dosimeter should be stored in the dark at fridge to retard the reduction of Ag^+ ions to AgNPs, which are spontaneously occurred with storage time at room temperature [11]. The overall uncertainty (2σ) of the dosimeter is 5.16%. The possible dose application of these gel dosimeters are from 5 to 100 Gy based on the selected compositions and parameters. This indicating the usefulness of this gel for blood irradiation and for radiotherapy upon adjusting the parameters. This study will guide the researchers to select their optimum conditions based on required applications. Finally, a new study was initiated to improve the radiation sensitivity of this gel dosimeter by using some other solvents and formate salts. In addition, based on this study, we planned to select a composition of high radiation sensitivity to apply in radiotherapy dose verifications.

Declarations

Conflict of interest The authors declare that there is no conflict of interest in this manuscript.

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