The Degradations of Ethyl Violet Dye Solution by Gamma Radiation

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ABSTRACT. The effect of radiation on the color intensity of aerated, oxygen and nitrogen-saturated aqueous solution of ethyl violet (EV) has been investigated. The radiation degradation yield (Gd values) were found to be (0.087, 0.072 and 0.061) and (0.0006; 0.0043 and 0.0034) (mol/J, for aerated aqueous and dimethyl sulfoxide solutions, respectively. The relatively low degradation yield indicates the absence of chain reactions, and probably the poor efficiency and economics, in terms of the practical application of the radiation process. For applications in the radiation treatment of waste water, it was noted that in the presence of oxygen and at higher concentration of EV, the value of Gd increased markedly, so that it may be practical to monitor the extent of sterilization of water. In addition, the radiation processing of EV waste water may also become economically feasible. The effect of pH, light and temperature on pre- and post-irradiation stability have been studied. Suggestions are made for the possible use of EV aqueous and DMSO solutions as a chemical dosimeter in the range of absorbed dose 0.25 and 20 kGy respectively.
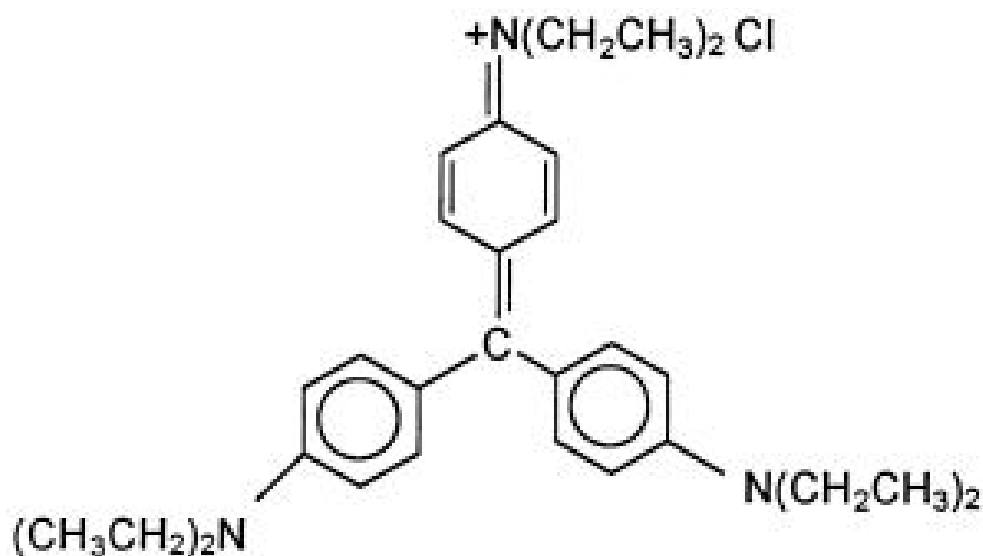
Introduction

Ordinary treatment processes do not easily degrade the majority of dye waste solutions originating from textile industry. The use of ionizing radiation for the treatment of textile dye waste effluents seems to be promising. This is because the effect of γ-rays can be intensified in aqueous solution by the primary products formed from the radiolysis of water[1,2]. From this point of view, the radiation-induced degradation of several dyes and acid-base indicator dyes in aqueous solution have been studied[3-7]. This characteristic has been the bases of

several studies on radiation-induced degradation of Chlorontine Fast Green (CFGBLL) in aqueous solutions. The compound is widely used as dye in the textile industry and therefore its effective degradation in wastewater can make this water suitable for re-use in textile manufacture or for other industrial or municipal purposes[8]. In addition to the above objectives, the radiation-induced decoloration of many indicator dyes has been used in chemical dosimeter[9,10].

In the present work, the effect of γ-radiation on the spectral absorption characteristics of aerated, de-aerated and oxygenated aqueous solutions of ethyl violet dye was investigated. The potential use of the system as a chemical dosimeter was also studied.

Experimental

Commercial ethyl violet, molecular weight 432.15 g/mole ($C_{31}H_{42}ClN_3$) obtained from CAC Co., Ltd, was used without further purification. Other reagents used are of analytical grade. Schematic diagram of ethyl violet is as follows:

Procedure

Irradiation of the dye solutions were held in 5 ml amber glass ampoules, placed in polystyrene cylindrical capsules of 5 mm wall thickness. The irradiations were carried out in central position of a Gamma-Cell ^{60}Co gamma-ray irradiator with annular geometry (approximately isotropic uniform photos incidence). The absorbed dose rate at the time of irradiation was 80 Gy min^{-1}. The solutions were irradiated to different doses (20-50 Gy) and 3-50 Kgy for ethyl violet and dimethylsulfoxide ethyl violet solution respectively. The temperature during irradiation was 25ºC. The optical absorption spectra and values of absorbance at specified wavelengths were measured with a double-beam

Cary Model 219 spectrophotometer, using a band-pass setting of 1.0 mm. The solutions were held in the object beam in quartz-glass, 10 mm pathlenght cuvettes, with the reference beam cuvette containing purified water.

Results and Discussion

Radiation-induced Changes of Absorption Spectra

The electronic absorption spectral data of ethyl violet in different solvents are summarized in Table 1. The absorption spectra of aerated aqueous and DMSO solutions following irradiation to different doses were measured. The results are shown in (Figs. 1 and 2) respectively. The unirradiated ethyl violet solution at pH4.5 has very strong absorption bands in visible region at 593 and 603 nm for aerated aqueous and DMSO solutions respectively. It can be seen that the amplitude of all absorption bands decreases gradually with the increase of the γ-ray photos dose and that the decrease at u.v. region is less pronounced than that at visible region.

TABLE 1. Summary of electronic absorption special date for ethyl violet different solvents (Beer's law valid is for concentrations up to 25 μM).

Solvent	λmax (nm)	Linear molar extinction coeff. $\in$m (M^{-1} cm^{-1})
Dimethyl sulfoxide	603	9.5×10^4
2-methoxy ethanol	594	5.0×10^4
Ethanol	594	11×10^4
Isopropanol	590	10×10^4
Water	593	8.0×10^4

Degree of Decoloration

Since EV solutions have two strong absorption bands at 593 and 603 nm for aerated aqueous and DMSO solutions, the degrees of decoloration were estimated from the reduction in absorbance, A, at each absorption band by using the relationship

$$\text{percentage decoloration} = \frac{A_o - Ai}{A_o} \times 100 \tag{1}$$

Where A_o is the absorbance of the unirradiated solution and A_i is the absorbance of the irradiated solution. Figs. 3 and 4 show the percentage decoloration of aerated aqueous and DMSO solution at different doses in the range of
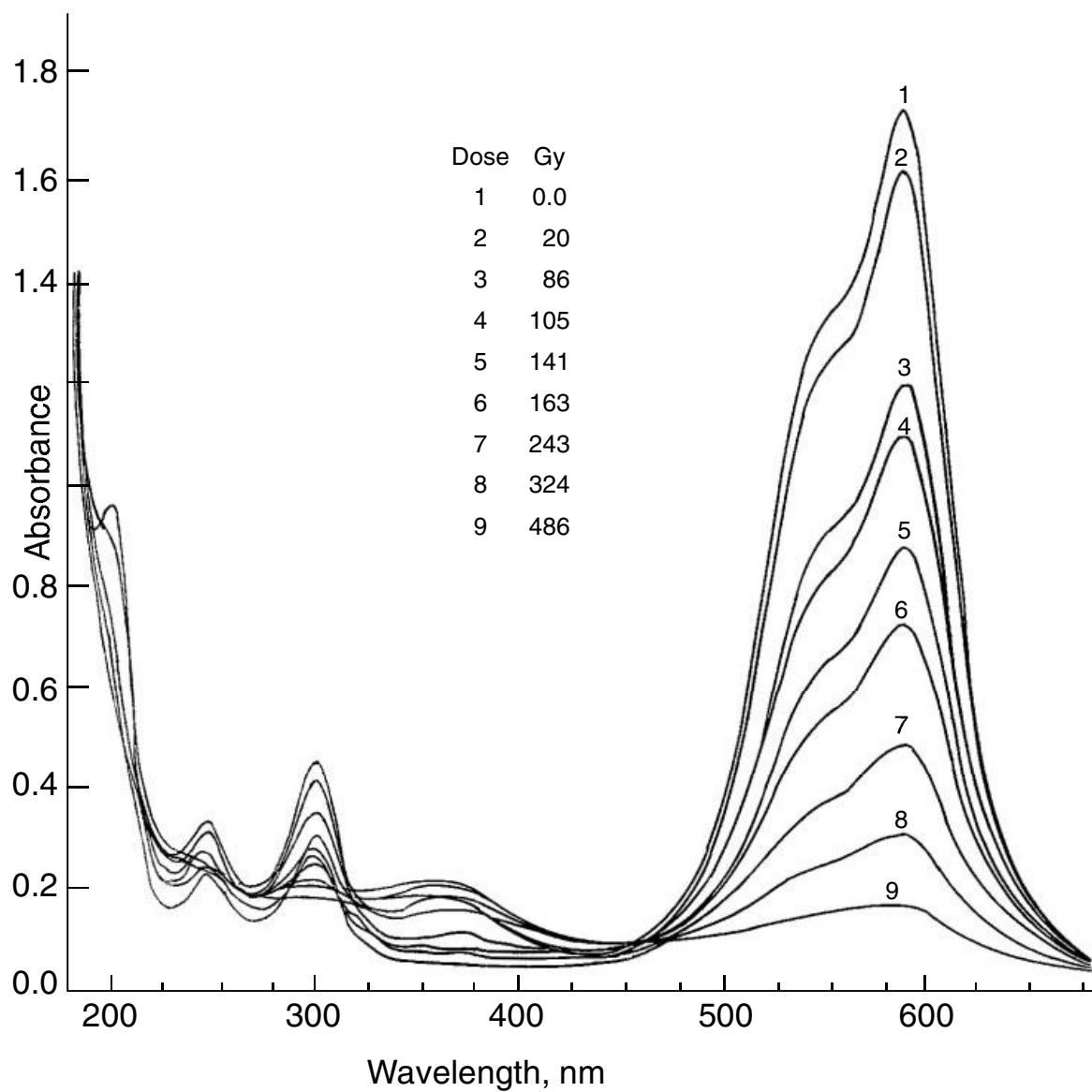
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FIG. 1. Absorption spectra of aerated aqueous ethyl violet solution unirradiated and irradiated to different doses at pH 4.5 [EV] = 20 (ML-1.
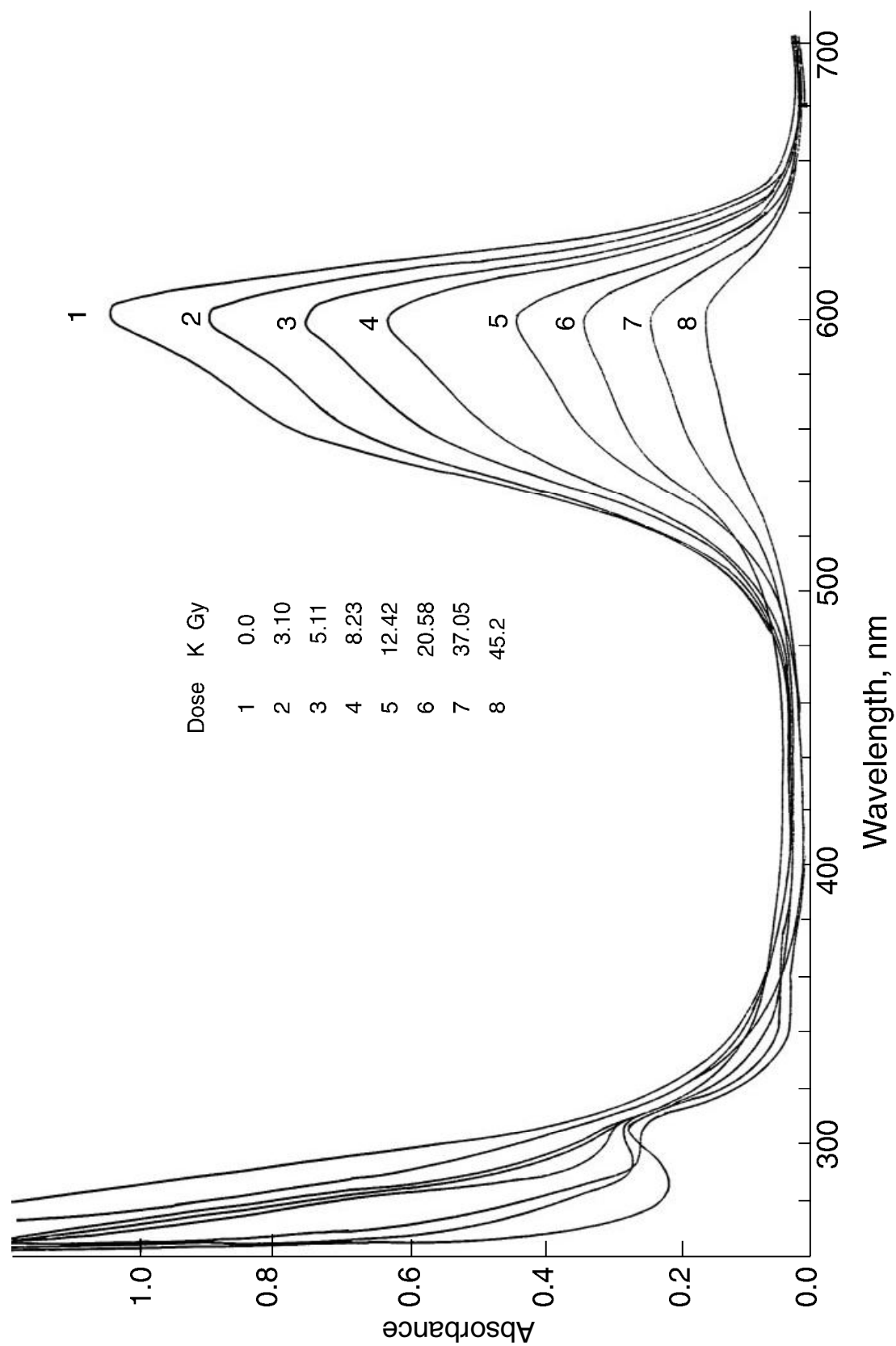
Dose	K Gy
1	0.0
2	3.10
3	5.11
4	8.23
5	12.42
6	20.58
7	37.05
8	45.2

Fɪɢ. 2. Absorption spectra of aerated dimethyl sulfoxide ethyl violet solution unirradiated and irradiated to different doses [EV] = 10 (ML-1.

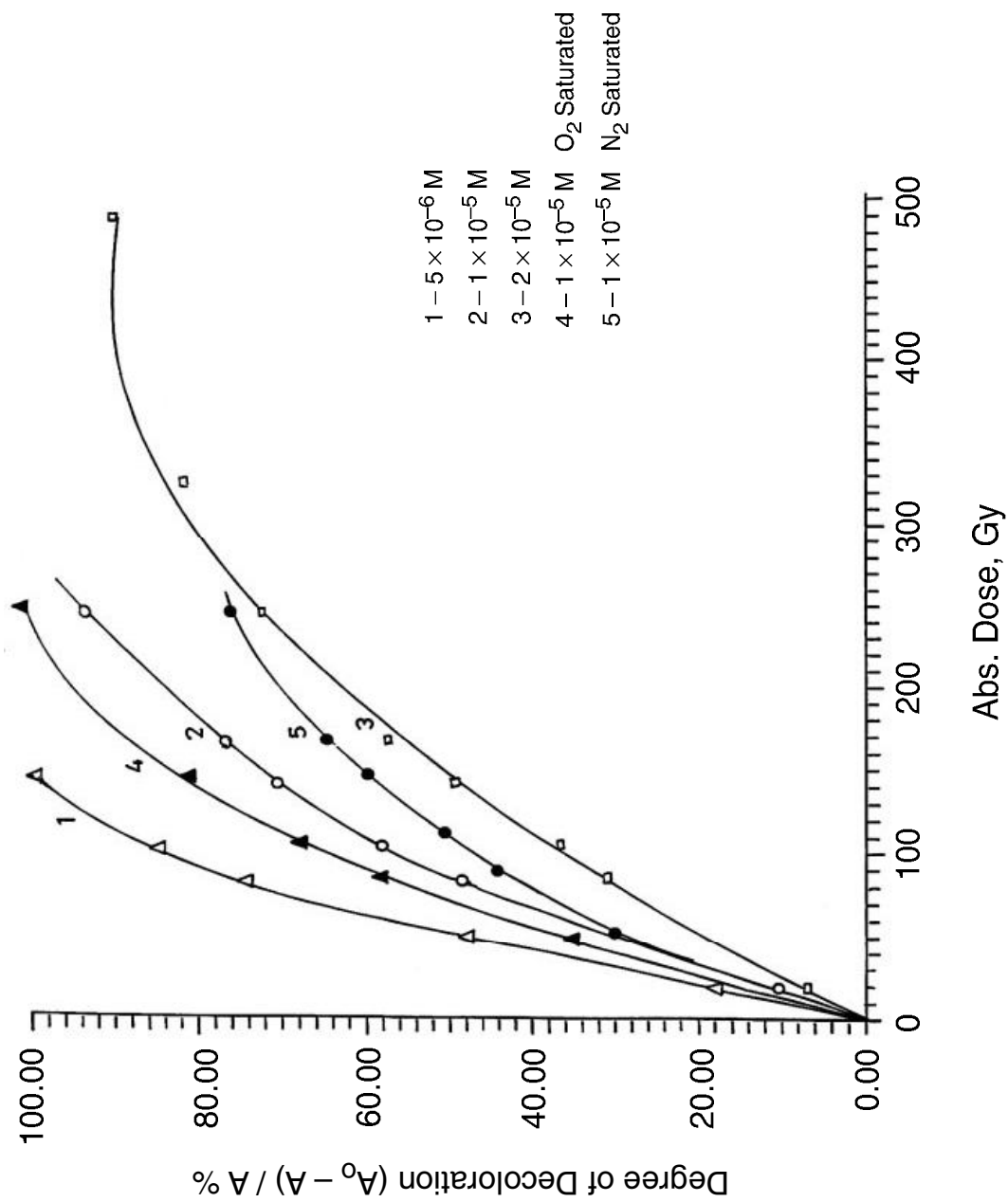*Ayed S. Al-Shihri and N.B. El-Assy*

Fig. 3. The degree of decolorization as a function of dose at various aerated aqueous dye concentration at pH 4.5 (1) 5 (ML-1 (2) 10 (ML-1 (3) 20 (ML-1 (4) 02 saturated (5) N2-saturated.
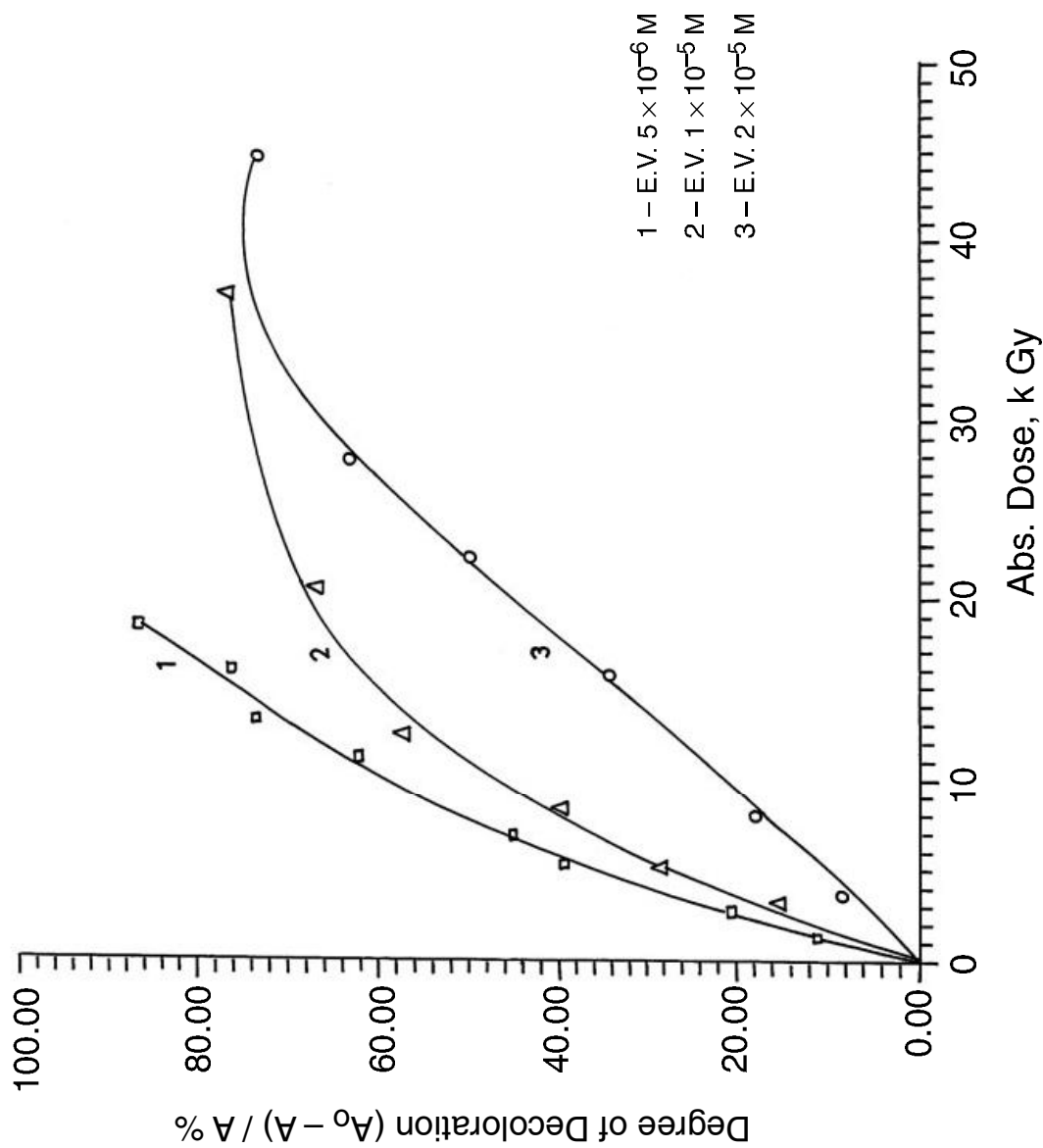
FIG. 4. A degree of decolorization as a function of dose at various aerated DMSO dye concentration. (1) 5 (ML-1 (2) 10 (ML-1 (3) 20 (ML-1.

the dye concentration from 5-20 (M L-1 at (593 and 603 nm, respectively. It can be seen that, for the same initial dye concentration, the degree of decoloration increases by increasing the dose and the degree of decoloration at the same dose decreases by decreasing the initial dye concentration.

The results obtained for O_2-saturated and N_2-saturated aqueous solutions of EV are also shown in Fig. 3. It is seen that, at the same dose, the percentage decoloration for the O_2-saturated solution is slightly higher than that of aerated solution which is also higher than that of the nitrogen-saturated solution. These results show that the decoloration reaction is promoted by oxygen. The increase in the degree of decoloration for the O_2-saturated solution over that of the N_2-saturated solution can be explained by considering the expected contribution of the HO_2 (and O_2-radicals, which are formed in the presence of oxygen according to the following reactions[10].

$$H^\bullet_{(aq)} + O_{2(g)} \rightarrow HO^\bullet_{(aq)} \qquad (2)$$

$$\text{and} \quad e^-_{(aq)} + O_{2(g)} \rightarrow {}^\bullet O^-_{2(aq)} \qquad (3)$$

In addition to the primary OH radicals and hydrated electrons liberated from the radiolysis of water, these species contribute to the decoloration reaction. The low bleaching yields of the dye in aerated solutions indicated that the OH radical is the principal oxidant which reacts with dyes via successive and/or competing pathways, some of which do not lead to decoloration[11]. The oxidizing radicals OH and HO_2-can react with the dye by ring addition and attack on functional groups[12]. The degradation reaction of the dye in the presence of oxygen leads to the formation of peroxides, which may also contributes to the decoloration reaction. After decoloration, the skeleton of the dye is degraded to lower molecular weight, mainly organic acids, which in turned are degraded to carbon dioxide and hydrocarbon[1].

Degradation Kinetics

The study of the degradation kinetics of aqueous solutions of EV was carried out for the concentration range from 5-20 (ML-1. It was found that the degration reactions is first order for all dye concentrations. The relationship between the residual concentration (determined spectrophotometrically at (max 593 and 603 nm) versus the absorbed dose for aqueous and DMSO solutions were shown in Figs. 5 and 6 respectively. It is seen that the variation of concentration has been plotted versus on semilogarithmic scale, thus obtaining straight lines in accordance with a first order radialytic effect
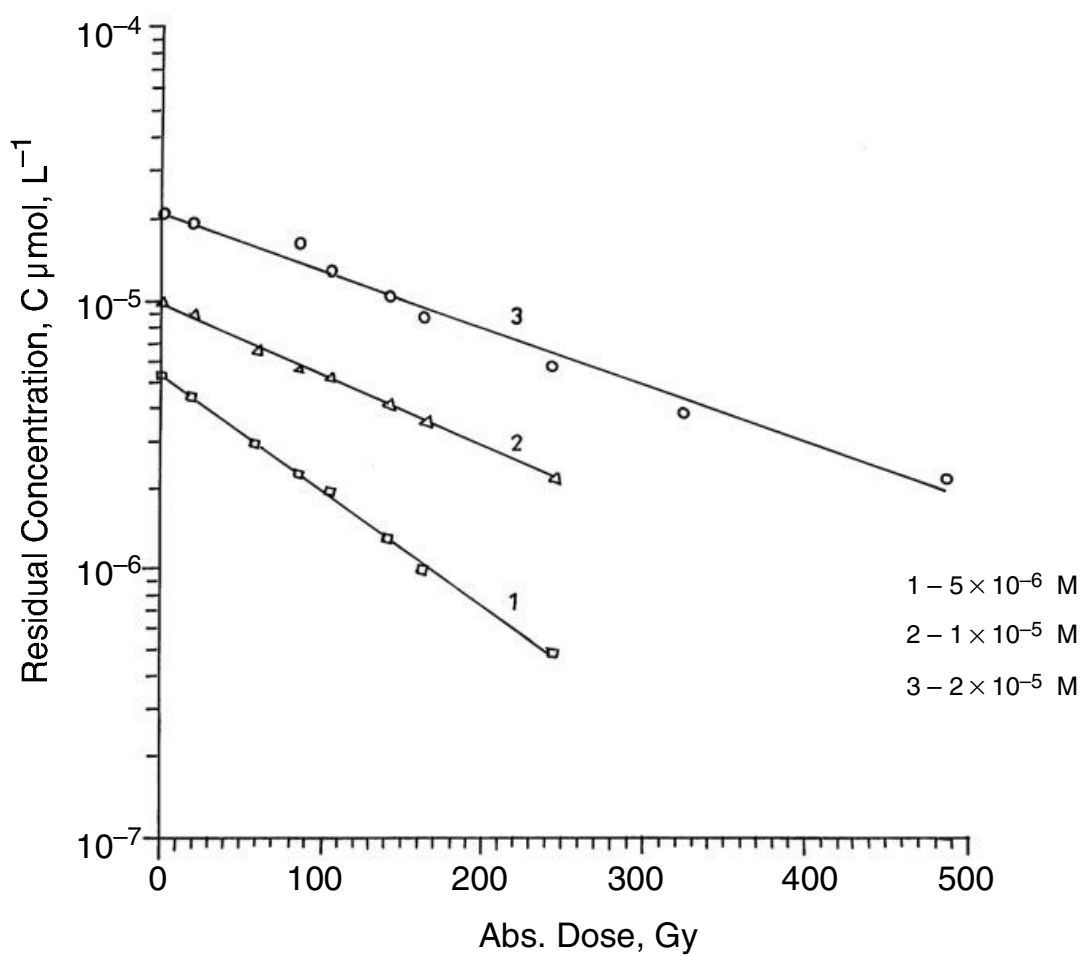
FIG. 5. Residual concentration (C) vs the absorbed dose, when the absorbance of the solutions is measured at (max 593 nm for aerated aqueous dye solution at pH 4.5. Initial concentrations Co: (1) = 5 (ML-1 (2) 10 (ML-1 (3) 20 (ML-1.
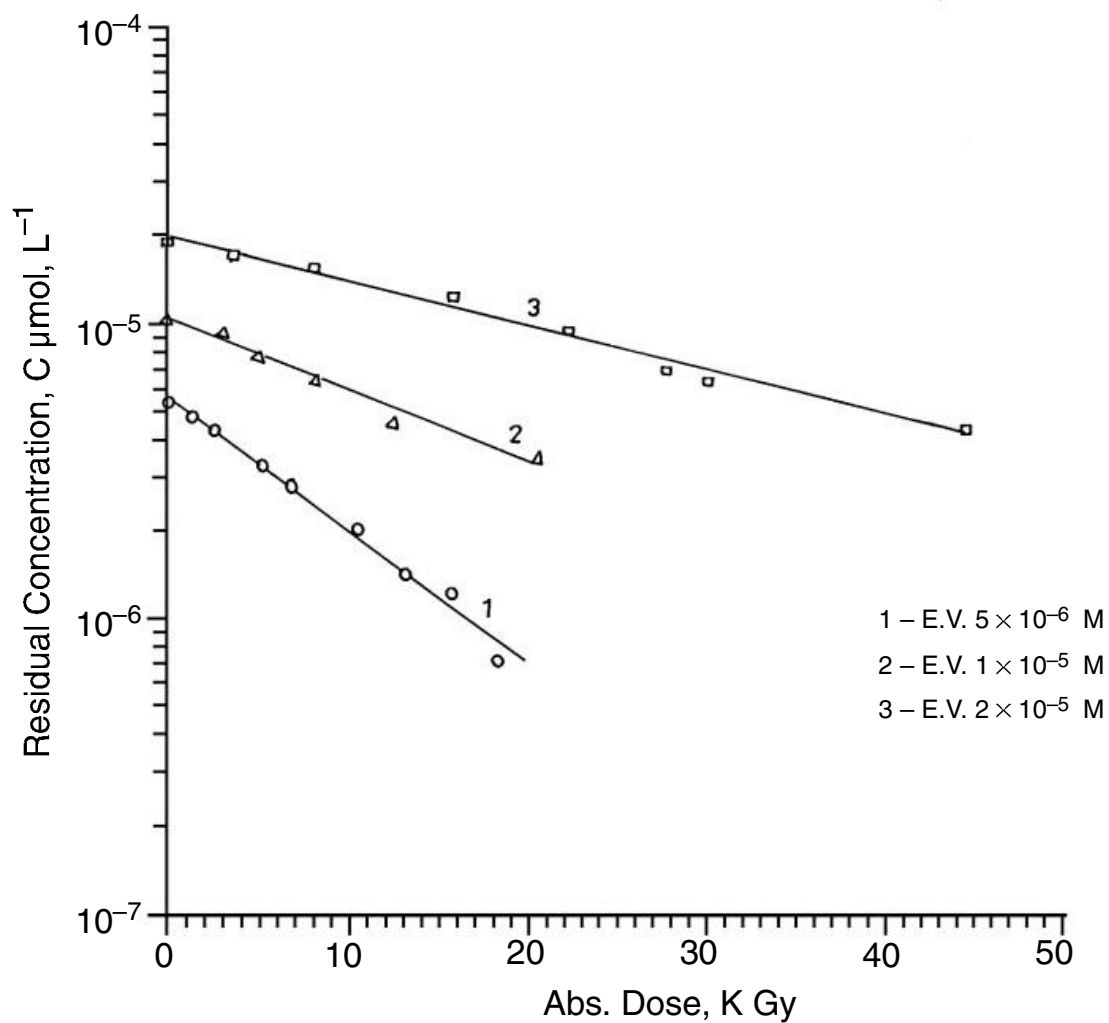
FIG. 6. Residual concentration (C) vs the absorbed dose, when the absorbance of dye in DMSO measured at (max 603 nm initial concentration Co: (1) = 5 (ML-1 (2) = 10 (ML-1 (3) = 20 (ML-1.

$$-dC = k1 \ CdD, \tag{4}$$

$$\ln C = \ln C_0 - k1 \ D, \tag{5}$$

where:

    C   = dye concentration (mL-1)

    C_0 = initial dye concentration (mL-1)

    D   = total absorbed dose (Gy)

    k1 = reaction rates constant

Degradation Yields

The yields of degradation (Gd) is defined as the number of moles degraded by absorption of 1J of energy (unit:mol/J). The Gd is calculated from the general relation[13].

    ΔA = the change in the absorbance at (max

$$Gd \ = \ \frac{\Delta A}{D.\varepsilon.p.b} \ , \ \text{mole/J} \tag{6}$$

    b   = the optical path length (1 cm)

    ρ = the density of solution (g /cm^3)

    e   = the linear molar extinction coefficient at (max (m$_2$/mol)

    D   = the absorbed dose (Gy)

Table 2 shows the Gd values for different concentration at 593 and 603 nm for aerated aqueous and DMSO dye solutions.

TABLE 2.

CoμML^{-1}	Gd, μmolJ^{-1}	
	Aqueous λmax 593nm	DMSO λmax 603nm
5	0.061	0.0034
10	0.072	0.0043
20	0.087	0.0060

Dye Stability and Dosimetry Recommendation

In a study of the dye solutions before and after irradiation, for storage over one month period in the presence or absence of ambient light at different tem-
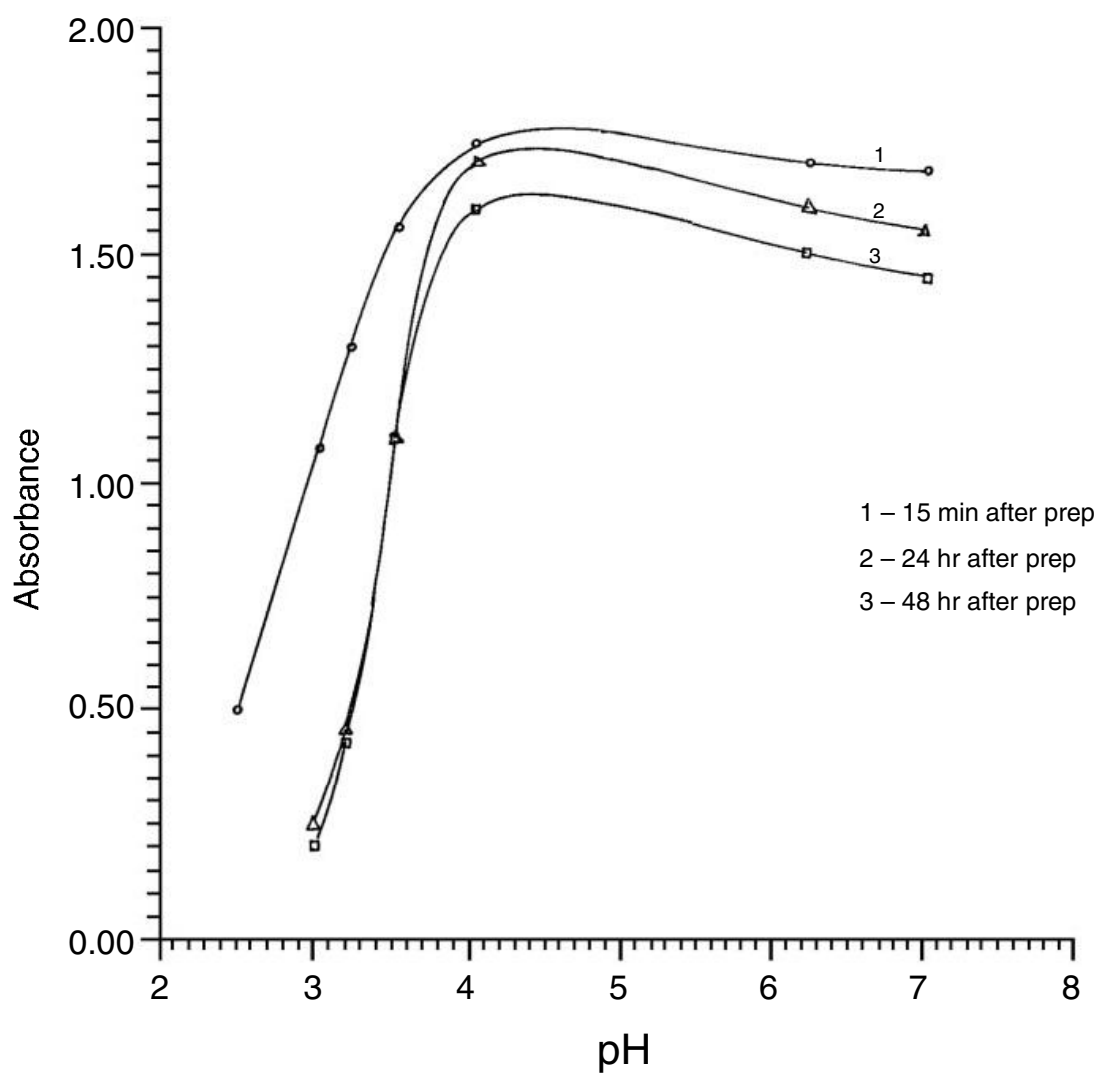
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FIG. 7. The variation of absorbance as a function of pH for aerated aqueous dye solution 20 (ML-1 at (max 593 nm (1) 15 min after prep. (2) 24 hr. after prep. (30 48 hr. after prep.
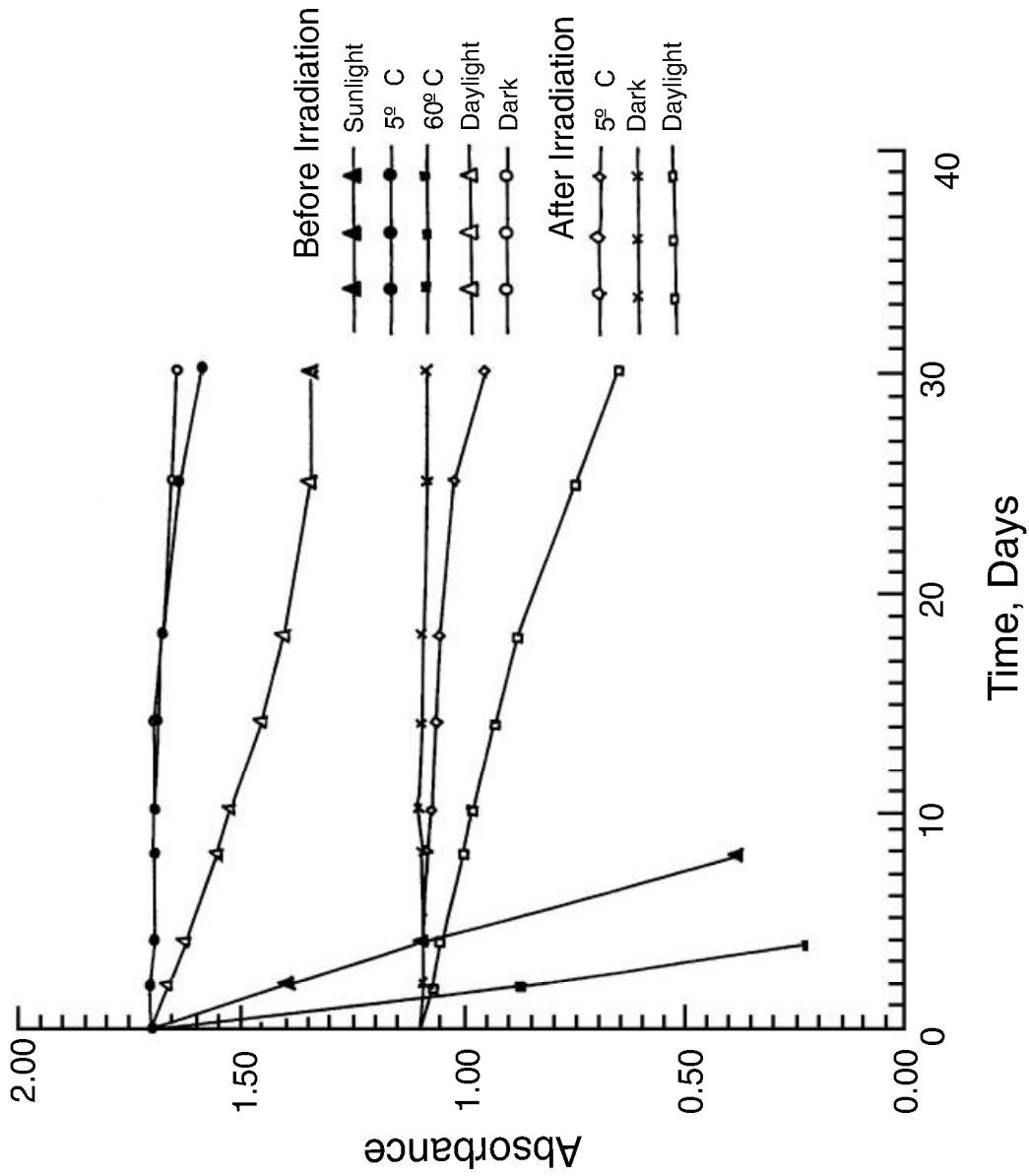
FIG. 8. Effect of different storage conditions on the absorbance (max = 593 nm) of unirradiated and irradiated 20 (ML-1 aqueous EV solutions at pH 4.5 and irradiated to 100 Gy.
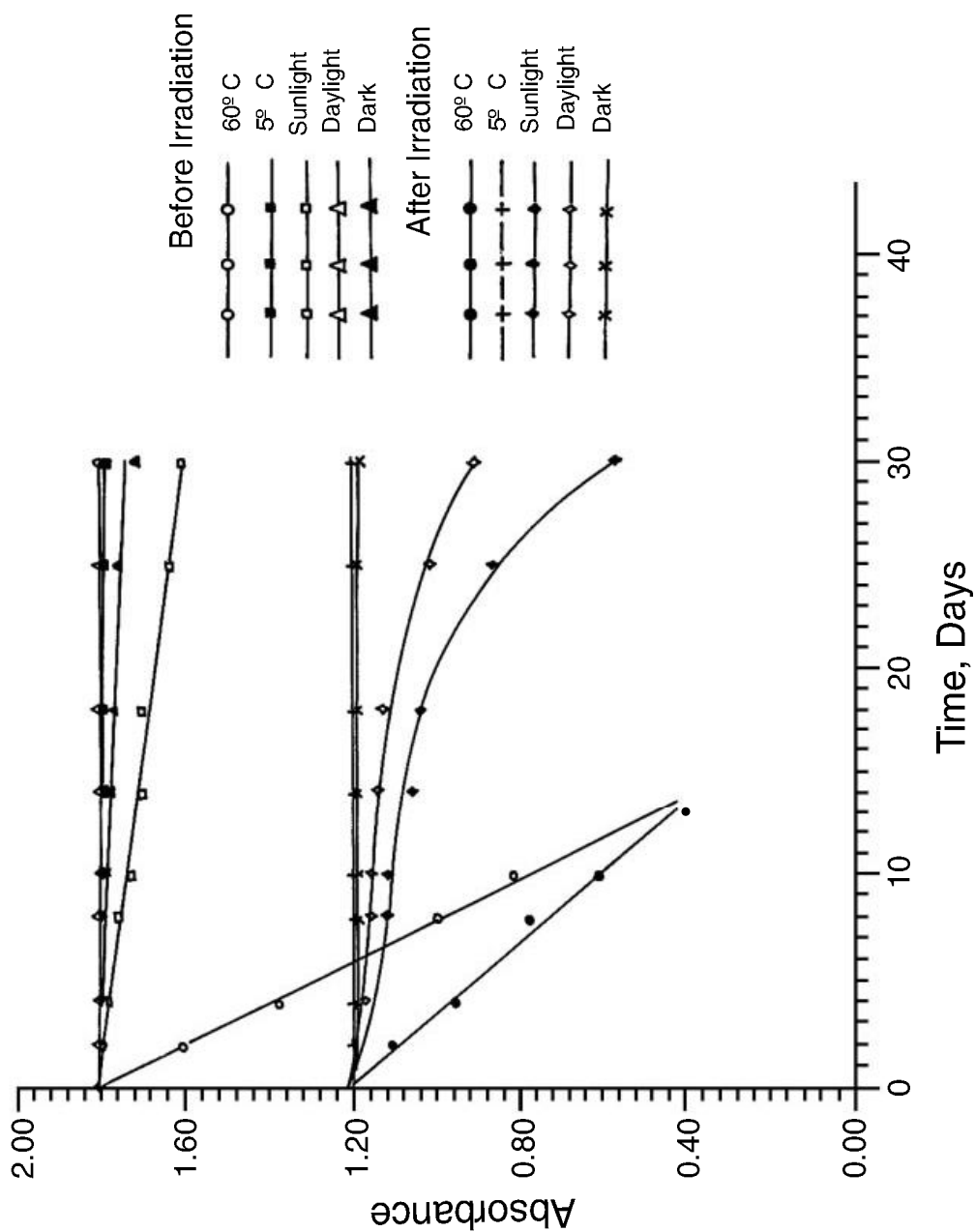
FIG. 9. Effect of different storage conditions on the absorbance ((max = 603 nm) of unirradiated and irradiated 20 (ML-1 DMSO EV solutions irradiated to 15.72 KGY.

peratures, the results indeed showed that the DMSO solutions of EV is more stable than aqueous dye solutions, nevertheless, Figs. 8 and 9 show that, in case of both, excessive temperature (60ºC) in the presence of indirect or direct sunlight causes pronounced fading. As indicated in Figs. 7-9, the greatest degree of stability is achieved in the case EV dye at pH 4-7 and stored in the refrigerator (5ºC). Based on the above results, EV solutions show promising dosimetric characteristics that have a number of useful applications in the field of chemical dosimetry particularly for food irradiation on the range of absorbed dose from about 0.25 to 20 KGY. Further developmental studies will be carried out.

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تأثير أشعة جاما على محلول صبغة الإثيل البنفسجية

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المستخلص.   تم في هذا البحث دراسة تأثير الأشعة على شدة واختفاء اللون لمحلول صبغة إثيل بنفسجي في غياب ووجود الأكسجين ، وقد عينت كفاءة الناتج الإشعاعي (Gd) في المحلول المائي للصبغة في وجود (DMSO) ، وفسر انخفاض قيمة (Gd) إلى غياب استمرارية التفاعلات المتسلسلة . ولكن في وجود تراكيز مرتفعة من (EV) وفي وجود الأكسجين تزداد كفاءة الفاعل (Gd) مما يمكن الاستفادة منها في مجالات التطبيق في حالة إعادة استخدام مياه الصرف بعد معالجتها بالإشعاع .

وقد تم دراسة تأثير تركيز الهيدروجين والضوء ودرجة الحرارة على صبغة (EV) قبل وبعد التشعيع في المحلول المائي وفي وجود (DMSO) لاحتمال استخدامها كمقياس للجرعات الإشعاعية في المدى ٢٥, ٠ – ٢٠ ك جراي على التوالي .