

## Radiation Induced Degradation of an Azo Dye Solution for Use in Dosimetric Applications

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(Received on 17th December 2015, accepted in revised form 1<sup>st</sup> June 2016)

**Summary:** The radiation induced color degradation of 4-(p-nitrophenyl-azo)-1-naphthol dye solution was studied in N,N- dimethylfomamide. The solutions were readout using absorption spectrophotometry technique at  $\lambda_{max}$  625 nm and 472 nm, respectively. The dose range was affected by dye concentration, where the useful dose range was found to be 0.5- 3.5kGy, depending on dye concentration .Magnesium chloride was then added in different concentrations, and the dose range was found to decrease to be 900Gy.The decoloration percent was calculated and found to increase proportionally with the absorbed dose. The radiation chemical yield "G (-Dye)" was calculated for both azo dye alone and in combination with MgCl<sub>2</sub> solutions. In brief, Azo dye solutions in DMF exhibit good stability during the storage time period, while Azo dye with magnesium chloride solutions shows decoloration process over the storage time period of 21 days.

**Key words:** 4-(p-nitrophenyl-azo)-1-naphthol, Gamma radiation dosimetry, Magnesium chloride, G value, Dimethylfomamide

### Introduction

There is a wide range of available studies that have investigated the bleaching of color as a result of radiation (1-3). Recently, researchers have examined the effects of oxidation-reduction conditions on the degradation of methyl orange (4). Several attempts have been made for some dyes in non- aqueous solutions and dyes incorporating polymeric materials (5, 6). A considerable number of literatures have been published on many Azo dyes for radiation dosimetry (7). Recent developments in textiles, leather and food stuff were carried out using Azo dyes (8). Comparing between the color bleaching and the applied radiation for some Azo dyes was previously studied (9). Studies of Rhodamine B show a considerable momentum in measuring the dose range up to 15kGy (10). Non aqueous solutions of some dyes are used as chemical dosimeters (11). Radiation induced color bleaching of an azo dye; called methyl red in poly (vinyl butyral) has been examined as a high dose dosimeter (12). Considerable investigations on Sudan red and Sudan blue were carried out where the absorbance was influenced by the absorbed dose. One of the interesting diazo dyes is Sudan red in different solvents, such as chloroform, xylene and ethyl acetate. It was reported that it was suitable to measure doses below 10 kGy(13). Aqueous solution of Alizarin yellow GG (AY-GG) undergoes degradation under the effect of radiation (14).

In the present work, color degradation of 4-(p-nitrophenyl-azo)-1-naphthol in N,N-dimethylformamide was studied. MgCl<sub>2</sub> was added

in different concentrations ,and its effect on the dose range was investigated .G-value was calculated for Azo dye in DMF and Azo/MgCl<sub>2</sub>,respectively .Stability of the dye under different environmental conditions was studied from dosimetric point of view.

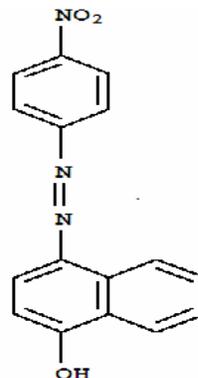


Fig. 1: Structure formula of 4-(p-nitrophenyl-azo)-1-naphthol.

### Experimental

#### Materials

4-(p-nitrophenyl-azo)-1-naphthol, mo.wt 293.28 product of BHD laboratory chemicals division [England]

N, N- Dimethylfomamide pure reagent for analysis, el-nasr pharmaceutical chemicals Co. Egypt.

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Magnesium chloride-6 hydrate,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  mo.wt 203.3 BDH laboratory England

### Method

Stock solution of [4-PNPAN] was prepared by dissolving 0.04gm of dye in 50ml of N,N-dimethylformamide then, 1.5ml, 2ml and 2.5ml from the stock solution were diluted to 100ml of DMF. so, the obtained concentration of dye were  $4.09 \times 10^{-5}\text{M}$ ,  $5.46 \times 10^{-5}\text{M}$  and  $6.82 \times 10^{-5}\text{M}$  of azo dye respectively. On the other hand stock solution of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  was prepared as 1gm of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  dissolved in 100ml DMF. Another three dye solutions containing  $\text{MgCl}_2$  incorporating azo dye were subsequently prepared. Taking 1, 2,3ml of stock  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  solution in 100ml volumetric flask containing 2ml from the stock azo dye solution, then completed to 100ml with DMF. In this case, we have another three solutions containing  $4.92 \times 10^{-4}\text{M}$ ,  $9.84 \times 10^{-4}\text{M}$  and  $14.76 \times 10^{-4}\text{M}$   $\text{MgCl}_2$  and  $5.46 \times 10^{-5}\text{M}$  of azo dye. The prepared solutions were irradiated with gamma radiation in the  $^{60}\text{Co}$  gamma chamber 4000A (product of India). Following this, the absorbed dose rate was measured to be 2.688 kGy/h using reference alanine dosimeter. Next, the azo dye solutions were prepared in tubes (1.5cm diameter, 8cm length). In order to get a good accuracy of the absorbed radiation doses in the gamma chamber, a specially designed wooden rack was used to hold the tubes at the central spatial position of the chamber. The rack was such designed in a manner that all tubes are exposed to the same radiation dose within the most homogeneous region of the irradiation chamber. In the subsequent stage, three tubes for each dose were put in the rack. The irradiation was carried out to different interval time according to the required dose. The irradiated solution of each dose was measured on Uvikon 860 spectrophotometer (product of KONTRON Co. Ltd, Switzerland) to determine the absorption spectra and also for the unirradiated solutions.

## Results and Discussion

### Absorption Spectra

Spectrophotometric measurements of 4-(p-nitrophenyl-azo)-1-naphthol solution containing  $5.46 \times 10^{-5}\text{M}$  azo dye solution in DMF were stated under the effect of irradiation dose. The results are clear in Fig. 2. The absorption spectra of the solution before irradiation show two absorption bands peaking at 472nm and 625 nm in the visible region significant for a green color. The amplitude of these peaks gradually decreases with increasing of absorbed dose of  $\gamma$ -ray photons. This radiation induced decrease in

absorption band can be said to be due to radiation induced degradation of the main skeleton of the dye molecule.

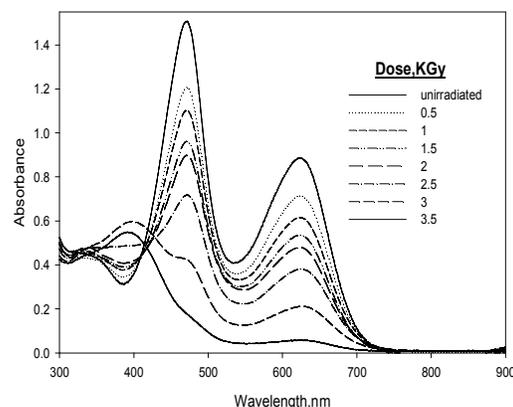
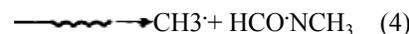
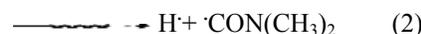
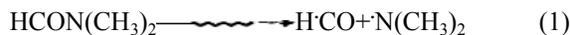


Fig. 2: Absorption spectra of azo dye solution in DMF [4-PNPAN] =  $5.46 \times 10^{-5}\text{M}$ .

A possible explanation for this might be that the structure of Azo dyes assigned with the presence of one-N=N- group or more binded to at least one aromatic group. The attached chromophores and auxochromes are considered to be the main source of Azo dye color. The explanation for this decoloration process is that the radiolysis product of N,N-dimethylformamide by  $^{60}\text{Co}$   $\gamma$ -irradiated is the following (15):



We can conclude that -N=N-breakdown is accomplished by a reduction process from hydrogen radical produced as a result of N,N-dimethylformamide's fragmentation (7). Accordingly H-N-N-H was produced, leading to the absence of the main source of color.

Fig. 3 shows the absorption spectra of dye solution containing  $5.46 \times 10^{-5}\text{M}$  of azo dye and  $4.92 \times 10^{-4}\text{M}$  of  $\text{MgCl}_2$  before and after irradiation. The absorption bands at 472 nm and 645 nm decrease rapidly with exposure to gamma radiation. The most interesting finding was that  $\text{MgCl}_2$  accelerates the degradation process. The dose range was reduced to 1 KGy.

From the above Fig. it was noticed that the presence of  $MgCl_2$  accelerates the bleaching reaction of azo dye. In addition, the degradation process is affected by  $MgCl_2$  concentration.

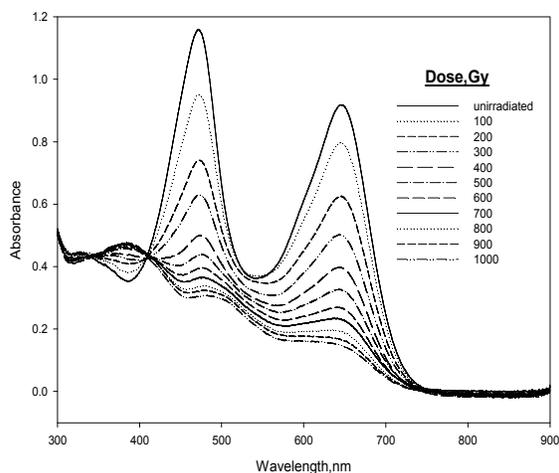


Fig. 3: Absorption spectra of Azo dye / $MgCl_2$  before and after irradiation [ $MgCl_2$ ]= $4.92 \times 10^{-4} M$ .

Response Curves

Fig. 4 and 5 show the response curves of 4 p nitro phenyl-azo- 1-naphthol solutions containing different dye concentrations as a change in the optical density ( $\Delta A$ ) at 625 nm and 472 nm respectively, against the absorbed dose [ $\Delta A = A_o - A_i$ ], Where  $A_o$  and  $A_i$  are optical densities before and after irradiation. It can be noticed that all curves have the same shape but differ in sensitivity.

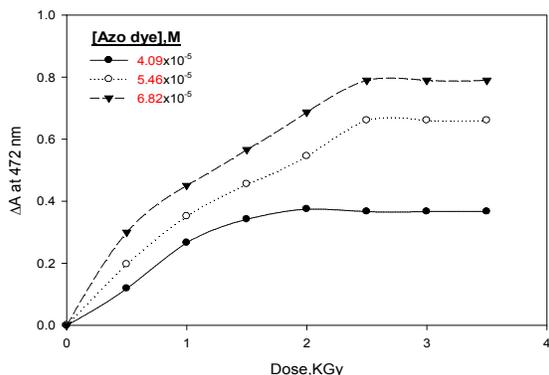


Fig. 4: Variation of ( $\Delta A$ ) against dose, at  $\lambda_{max} = 472 \text{ nm}$ .

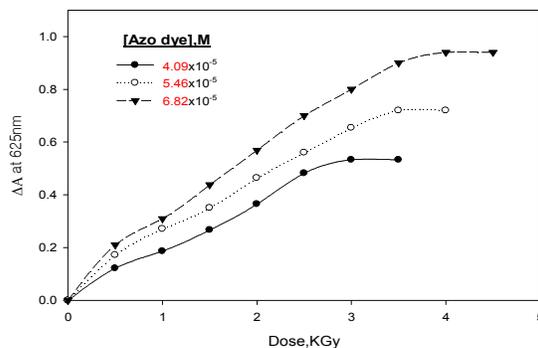


Fig. 5: Change of ( $\Delta A$ ) against absorbed dose, at  $\lambda_{max} = 625 \text{ nm}$ .

Fig. 6 and 7 represents the response curve of Azo dye containing  $5.46 \times 10^{-5} M$  of Azo dye and different  $MgCl_2$  concentrations mainly  $4.92 \times 10^{-4} M$ ,  $9.84 \times 10^{-4} M$  and  $14.76 \times 10^{-4} M$  respectively. The response for both absorption peaks is at 472 nm and 645 nm. It was found that the response increases in a gradual manner with increasing the dose, and the dose range in presence  $MgCl_2$  100-1000 Gy for both absorption peaks are at 472 nm and 645 nm.

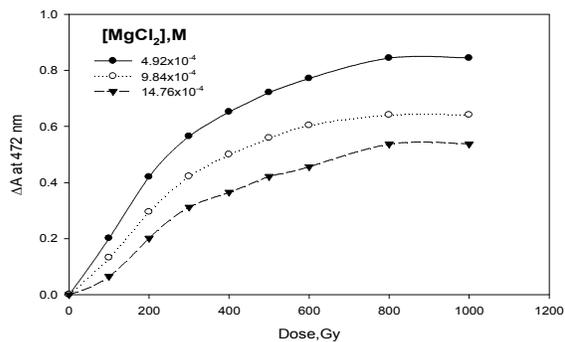


Fig. 6: Variation of ( $\Delta A$ ) against absorbed dose, at  $\lambda_{max} = 472 \text{ nm}$ .

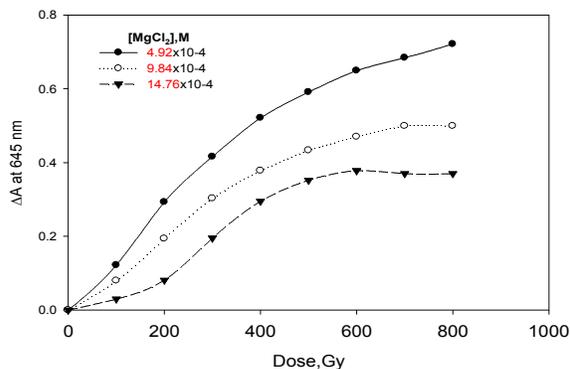


Fig. 7: Variation of ( $\Delta A$ ) against absorbed dose, at  $\lambda_{max} = 645 \text{ nm}$ .

### The Radiation Chemical yield(G-value)

The Radiation chemical yield 'G (-dye)' is defined by the number of molecules degraded by the absorption of dose equivalent to 100eV and was calculated from the general relation (16):

$$G (-dye) = 9.65 \times 10^6 \times \Delta A / D \cdot \epsilon \cdot \rho \cdot b \quad (100eV)^{-1} \quad (5)$$

Where  $\Delta A$  is the change in absorbance at  $\lambda_{max}$ ,  $\epsilon$  is the linear molar extinction coefficient at a given optical maximum wavelength in  $Lmol^{-1}cm^{-1}$ ,  $\rho$  is the density of dosimeter in  $g\ cm^{-3}$ ,  $D$  is the absorbed dose in (Gy). Applying Beer's law relation, the molar extinction coefficient is calculated as 21118  $Lmol^{-1}cm^{-1}$  at 472nm and 16828  $Lmol^{-1}cm^{-1}$  at 625nm. From the response curves, replace the slope in the above equation, the obtained G (-dye) are shown in Table-1. Also, regarding different  $MgCl_2$ /Azo dye solutions, the calculated G-value was represented in Table-2.

Table-1: G-values for different concentrations of azo dye in DMF at 472 nm and 645 nm.

Dye concentration, M	G-value ( $100eV^{-1}$ )	
	at 472 nm	At 625 nm
$4.09 \times 10^{-5}$	0.05367	0.17673
$5.46 \times 10^{-5}$	0.16159	0.2573
$6.82 \times 10^{-5}$	0.3103	0.29413

Table-2: G-values of azo dye with different  $MgCl_2$  concentrations at 472 nm and 645 nm.

$MgCl_2$ concentration, M	G-value ( $100eV^{-1}$ )	
	At 474 nm	At 646 nm
$4.92 \times 10^{-4}$	1.23	1.0275
$9.84 \times 10^{-4}$	0.89653	0.6479
$14.76 \times 10^{-4}$	0.5853	0.1713

### Decoloration Percent

The decoloration percent  $(A_0 - A_i / A_0) \times 100$ , where  $A_0$  is the absorbance of the unirradiated solution and  $A_i$  is that for the irradiated solution, was measured at 472 nm and 625 nm for azo dye in DMF of concentration,  $5.455 \times 10^{-5}$  as seen in Fig. 8, thus the degree of decoloration increases with increasing of the absorbed dose.

### Properties of Azo-Mg solution

Freshly prepared Azo dye in DMF exhibits two sharp peaks at 472 nm and 625 nm, the absorbance of these peaks undergoes good stability. However, the absorbances of Azo-Mg solution decrease. Fig 9 presents the spontaneous reduction in absorbance to an extent almost zero after about three weeks, indicating that the reduction process of the azo group. We can conclude that 4-(p-nitrophenyl-azo)-1-naphthol acts as magnesium absorber, so the dye

concentration deflated and the decoloration process becomes faster. When the solution of azo/Mg is irradiated with gamma-rays the azo group- N=N- may get reduced due to H-radical liberated from radiolysis products of N,N-dimethylformamide. As a result, the numbers of chromophores are dropped and the color fades from dark green to colorless. The results are shown in Fig 9.

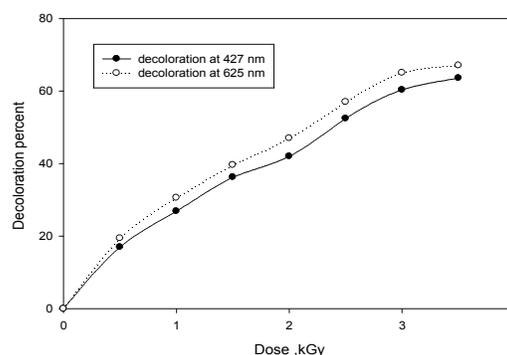


Fig. 8: Decoloration percent at 472 nm and 625 nm.

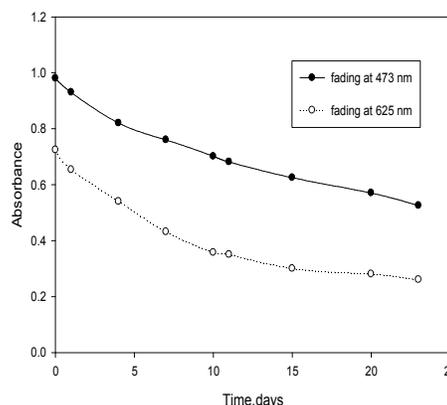


Fig. 9: Fading of Azo/  $MgCl_2$  at 643 nm and 473 nm.

### Conclusion

The radiation-induced color degradation of 4-(p-nitrophenyl-azo)-1-naphthol dye solution was studied in N,N-dimethylformamide. The dose range was affected by the dye concentration. It was found that the useful dose range varies from 0.5-3.5 kGy depending on dye concentration. Magnesium chloride was added in different concentrations, the dose range fell to 900Gy. G-value was calculated for both azo dye in DMF and with  $MgCl_2$ . It was found that G-value is directly proportional to Azo dye concentration and inversely with  $MgCl_2$  concentration. The decoloration percent shows direct proportionality with dye concentration. Azo dye

solution in DMF exhibits good stability, while azo dye with magnesium chloride shows decoloration process over the storage time period of 21 days. These solutions can be used as dosimeters for food and blood irradiation applications.

#### Acknowledgements

The author wishes gratefully to thank all members of radiation dosimetry department, NCRRT for their co-operation and helpful assistance.

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