

PAIR/P, 822/95

RADIATION-INDUCED DEGRADATION AND  
DECOLORATION OF DISPERSE DYES IN  
WATHER

Agustin N.M. Wibagyo, Winarti A.  
Surtipanti S.\*

## RADIATION-INDUCED DEGRADATION AND DECOLORATION OF DISPERSE DYES IN WATER

Agustin N.M.Bagyo, Winarti Andayani and Surtipanti, S \*

### ABSTRACT

RADIATION-INDUCED DEGRADATION AND DECOLORATION OF DISPERSE DYES IN WATER. The aim of the study was to find out the possibility of using gamma rays to degrade or decolorize disperse dyes in water. Disperse dyes in aqueous solutions, i.e. Terasil Black CMS (TB CMS), Terasil Red 4G (TR 4G), Terasil Golden Yellow (TGY), Terasil Navy (TN) and Terasil Blue BGE (TB BGE) were irradiated with doses of 0-10 kGy at dose rates of 2 and 5 kGy/h. During irradiation, oxygen or air was bubbled through a porous plate at the bottom of the reaction vessel. The parameters examined were the change of absorption spectra, pH, total organic carbon (TOC), chemical oxygen demand (COD), and the percentage of disperse dyes precipitated after adding coagulants. By adding nitric acid to acidify the TB CMS, TR 4G, TGY and TB BGE solutions after irradiation, precipitation occurred at doses of 6, 12, 8 and 4 kGy, respectively. The precipitation was also induced by addition of coagulants i.e. iron (II) sulfate, aluminum sulfate, ammonium iron (III) sulfate and calcium hypochlorite.

In oxygen bubbling solutions, the degradation and decoloration occurred faster than in air bubbling condition.

### ABSTRAK

PENGARUH IRADIASI PADA PENGURAIAN DAN PENGHILANGAN WARNA LARUTAN ZAT WARNA DISPERSI. Penelitian ini bertujuan untuk melihat kemungkinan penggunaan sinar gamma untuk menguraikan dan menghilangkan warna larutan zat warna dispersi dalam air. Larutan-larutan zat warna Terasil Black CMS (TB CMS), Terasil Red 4G (TR 4G), Terasil Blue (TB) dan Terasil Golden Yellow (TGY) diiradiasi dengan dosis 0-10 kGy, dengan laju dosis 2 dan 5 kGy/jam, sambil dialiri gas oksigen atau udara. Parameter, yang diamati ialah perubahan spektrum, pH, jumlah karbon organik, kebutuhan oksigen kimia, dan persentase zat warna dispersi yang mengendap setelah penambahan koagulan. Penambahan asam nitrat ke dalam larutan TB CMS, TR 4G, TB dan TGY sesudah diiradiasi menyebabkan terjadinya pengendapan masing-masing pada dosis 6, 12, 4 dan 8 kGy.

---

\* Centre for Application of Isotopes and Radiation,  
National Atomic Energy Agency, Jakarta, Indonesia

Pengendapan juga terjadi setelah penambahan koagulan antara lain, fero sulfat, aluminum sulfat, feri amonium sulfat, dan kalsium hipoklorit. Penguraian dan pengurangan warna lebih cepat terjadi dalam aliran oksigen dibandingkan dalam aliran udara.

## 1. INTRODUCTION

Application of radiation processing in industry is based on the use of high energy radiation, i.e gamma rays or electrons to initiate processes which are important for achieving a desired qualities of products. Radiation processing can be applied in various sectors, such as medicine, electronics, computers, communications, printing and packaging. This technique which is environmentally safe, is now being applied also in waste treatment as a solution to certain environmental problems (1).

One of the serious cause of environmental problems is waste water containing dyes from textile industry. The dyes can not be degraded easily by ordinary treatments. On the other hand the effect of radiation can be intensified in aqueous solution in which the dye molecules will be degraded effectively by the primary products formed from the radiolysis of water (2). Thus, ionizing radiation maybe can be used for the treatment of textile dyes waste effluents.

Radiation-induced decoloration and degradation of water soluble azo and anthraquinone dyes had been studied earlier and the results were promising, especially in the presence of oxygen during irradiation (3-6).

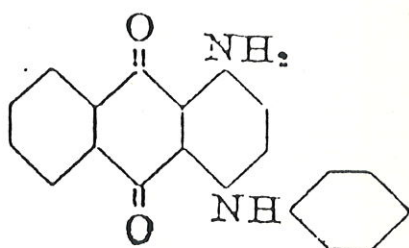
This paper summarizes studies on degradation and decoloration of disperse dyes in water using irradiation in combination with precipitation by adding nitric acid or coagulants.

## 2. MATERIALS AND METHODS

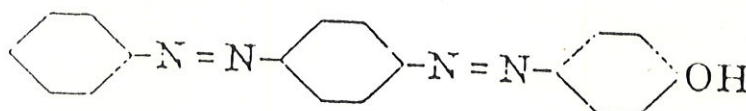
### 2.1. Materials

Disperse dyes used in this study were Terasil Black CMS 200% (TB CMS), Terasil Red 4G (TR 4G), Terasil Golden Yellow (TGY), Terasil Navy (TN) and Terasil Blue BGE 200% (TB BGE). The dyes were obtained from Ciba Geigy Co. Jakarta, Indonesia and were used without purification.

The TB CMS, TR 4G, TGY and TN are commercial azo dyes and TB BGE is a commercial anthraquinone dye.



Anthraquinone dye



Azo dye

## 2.2. Sample Preparations and Treatments

### A. Commercial Azo Dyes

#### 2.2.1 Terasil Black CMS (TB CMS)

TB CMS solution (50 ppm) was prepared by dissolving the dye in distilled water. Irradiation was done at doses of 0, 2, 4, 6, 8 and 10 kGy with a dose rate of 2 kGy/h. During irradiation, oxygen was bubbled through a porous plate at the bottom of the reaction vessel. The same experiment was also done by bubbling nitrogen instead of oxygen in the reaction vessel. After irradiation, 100 ul of nitric acid was added into about 10 ml of sample and the solution was kept for two days, the upper layer was taken for analysis. The parameters examined were absorption spectra, pH and total organic carbon (TOC).

#### 2.2.2 Terasil Red 4G (TR 4G)

TR 4G solution (50 ppm) was prepared by dissolving the dye in distilled water. Irradiation was done at doses of 0, 2, 4, 6, 8 and 10 kGy with a dose rate of 2 kGy/h. During irradiation, oxygen was bubbled through a porous plate at the bottom of the reaction vessel. After irradiation, 100 ul of nitric acid was added into about 10 ml of sample and the solution was kept for two days, the upper layer was taken for analysis. The parameters examined were absorption spectra, pH and total organic carbon (TOC).

TR 4G solution (100 ppm) was irradiated at 5 kGy with a dose rate of 5 kGy/h. During irradiation, air was bubbled through the solution. After irradiation, iron (II)

sulfate (200 ppm) was added into 100 ml of the solution. The parameters examined were, the percentage of TR 4G precipitated by iron (II) sulfate, and chemical oxygen demand (COD) of the solution.

#### 2.2.3 Terasil Golden Yellow (TGY)

TGY solution (50 ppm) was prepared by dissolving the dye in distilled water. Irradiation was done at doses of 0, 2, 4, 6, 8 and 10 kGy with a dose rate of 2 kGy/h. During irradiation, oxygen was bubbled through a porous plate at the bottom of the reaction vessel. After irradiation, 100 ul of nitric acid was added into about 10 ml of sample and the solution was kept for two days, the upper layer was taken for analysis. The parameters examined were absorption spectra, pH and total organic carbon (TOC).

TGY solutions (50 and 100 ppm) were irradiated at 5 kGy with a dose rate of 5 kGy/h, at various pH, i.e 3, 5, 7, 9 and 12, with and without the addition of iron (II) sulfate. The concentration of iron (II) sulfate added was 200 ppm. The parameter examined was the percentage of TGY precipitated by iron (II) sulfate.

#### 2.2.4 Terasil Navy (TN)

Terasil Navy solution was irradiated with doses of 1, 2, 3, 4 and 5 kGy with a dose rate of 5 kGy/h, pH 9 and the concentration varies between 50 and 200 ppm. During irradiation, air was bubbled through the solution. After irradiation, calcium hypochlorite, aluminum sulfate and ammonium iron (III) sulfate were added as coagulants. The

percentage of TN precipitated by each coagulant was measured.

## B. Commercial Anthraquinone Dye

### 2.2.5 Terasil Blue BGE (TB BGE)

TB solution (50 ppm) was prepared by dissolving the dye in distilled water. Irradiation was done at doses of 0, 2, 4, 6, 8 and 10 kGy with a dose rate of 2 kGy/h. During irradiation, oxygen was bubbled through a porous plate at the bottom of the reaction vessel. After irradiation, 100 ul of nitric acid was added into about 10 ml of sample and the solution was kept for two days, the upper layer was taken for analysis. The parameters examined were absorption spectra, pH and total organic carbon (TOC).

### 2.3. Methods of Analyses

The absorption spectrum was measured using a UV-VIS spectrophotometer. The pH of the solution was measured using a pH meter. Total organic carbon (TOC) in the solution was determined using a TOC meter. Chemical oxygen demand was measured using chromic method.

## . RESULTS AND DISCUSSION

### A. Commercial Azo Dyes

The TB CMS solution shows a clear absorption at 535 nm and a weak absorption at 295 nm in the UV-VIS spectra as shown in Fig. 1 (a). Fig. 2 (a) shows the UV-Visible spectra of irradiated Terasil Red 4 G (TR 4G) solutions. The unirradiated solution has a clear absorption band at

490 nm and a slight shoulder around 350 nm. Fig 3 (a) shows the spectra change of irradiated Terasil Golden Yellow (TGY) solutions. The unirradiated solution has a clear absorption at 360 nm. The former absorptions band are considered to be the main absorption assigned to conjugated system of the dye molecules, and the latter band of TB CMS and TR 4G are substituted aromatic rings.

Fig. 1 (a), 2 (a) and 3 (a) also show the changes of the spectra after irradiation in oxygen saturated condition. After irradiation, the intensity of the main absorptions decreased gradually as the dose increased. These decreases are obviously due to the destruction of conjugated system of the dye molecules by the attack of OH radicals as just in the case of water-soluble azo dyes (3). At low dose irradiation, the intensity decrease was relatively small. This finding is in contrast to water-soluble azo dyes (3), where a great decrease of absorption intensity has occurred after irradiation with low doses.

After irradiation, when concentrated nitric acid was added to reduce the pH to around 1 and the solution was kept for two days, the upper layer of the irradiated solution became clear and precipitation occurred. Degree of precipitation was determined by measuring the spectra of the upper layer as shown in Fig. 1 (b), 2 (b) and 3 (b). The main absorption band decreased markedly especially at doses above 6 kGy for TB CMS, 12 kGy for TR 4G, and 8 kGy for TGY while, another peak appeared at 295 nm



sharply, for all doses. It appeared that precipitation occurred effectively at such doses, and no precipitation occurred in the non-irradiated solution.

On the contrary, in the nitrogen saturated solution, the band intensity at 535 nm and 490 nm decreased only a little after irradiation as shown in Fig. 1 (c) and 2 (c). The spectral change of TR 4G in nitrogen saturated solution were the same as in oxygen solution. These data suggest that dye molecules in the solution are strongly protected by surfactants.

In dye solution, OH radicals may attack the surfactant as well as the dye molecules to produce surfactant radicals. In the absence of oxygen, these surfactant radicals can migrate to the dye molecules contained in the same particle and add to them leading to destruction of conjugated system of the dye molecules. In the presence of oxygen, only direct attack of OH radicals to the dye molecules can contribute to the destruction of the conjugated system. However, in the absence of oxygen, the destructed conjugated system sometimes recover as in the case of acid red solution (6) by abstraction of hydrogen atom from the other molecules, therefore the band intensity became almost constant beyond 4 kGy for TB CMS.

The changes of total organic carbon (TOC) of TB CMS, TR 4G and TGY solutions irradiated in oxygen-saturated conditions are shown in Fig. 5. In oxygen saturated solution, the TOC content decreased slowly at doses below

6 kGy for TB CMS, then decreased rapidly at doses above 6 kGy. But for TR 4G, the TOC contents decreased steadily with dose, especially in nitric acid-added solutions. These results correspond to the change of absorption spectra of TR 4G as illustrated in Fig. 2 (b). The TOC content of TGY did not change much either after irradiation or after the addition of nitric acid. This fact does not corresponds to the results of its absorption spectra measurements (Fig. 3 b), which may be caused by the increasing of soluble components from colloidal particles of the disperse dye due to irradiation. In nitrogen-saturated solution (Fig. 6), the TOC content increased with dose. This increase may be caused by the increase of soluble components from colloidal particles of the disperse dye due to irradiation. In the present study, the TOC values were measured using a Dohrman DC-80 TOC meter. The principle of this instrument is based on the oxydation of organic components in water by an oxydizing agent ( $K_2S_2O_7$ ) and UV light. Some insoluble organic components in colloidal disperse dye particles may not be oxydized in the above TOC meter reactor. However, after irradiation, these components became soluble, and can be measured as TOC. The percentage of Terasil Red 4G precipitated by iron (II) sulfate after irradiation at 5 kGy in air-bubbled solution was 93%, and the COD value was 90%. Tabel 1 shows that the amounts of terasil navy precipitated by calcium hypochlorite (30 ppm) in 50 and 100 ppm

samples after being settled for 3 days were 62% and 95%, respectively. When 200 ppm of terasil navy was irradiated at 3 kGy, the percentage of the dye precipitated after adding calcium hypochlorite (30 ppm) and settled for 1 day was 97%. At the same concentration (200 ppm), the percentage of terasil navy precipitated by aluminum sulfate and ammonium iron (III) sulfate and settled for 3 hours were 95% and 89%, respectively (8). However, if the dye solution contain glucose, precipitation does not occur although the condition is the same as above (8).

The percentage of terasil golden yellow precipitated by iron (II) sulfate (200 ppm) in 50 and 100 ppm solutions, irradiated at 5 kGy and pH 9 were 95.9% and 97.9%, while in unirradiated solutions were 93% and 93.7%, respectively. The percentage of irradiated terasil golden yellow precipitated without adding iron (II) sulfate at concentrations 50 and 100 ppm were 97.3% and 96.3%, respectively (11).

The pHs of both azo and anthraquinone dyes (TB CMS, TR 4G, TGY and TB BGE) in the oxygen-saturated solution after irradiation are shown in Fig. 8. The pHs decreased after irradiation due to the formation of organic acid just as in degradation of water-soluble azo dye solution by irradiation (4).

## B. Commercial Anthraquinone Dye

Fig. 4 (a) shows the spectra change of irradiated terasil blue BGE (TB BGE) in oxygen bubbling solutions. The unirradiated solution has a clear band at 760 nm and a slight shoulder at around 560 nm. After irradiation, the intensity of the 760 nm band decreased slightly with dose. However, after irradiation when nitric acid was added and settled for two days, precipitation occurred even at low dose as shown in Fig. 4 (b). These results suggest that chemical state of the surfaces of dye particles was changed by irradiation. The surfaces were oxidized by irradiation, especially in the presence of oxygen, and many carboxyl groups (-COOH), or organic acids of large molecular weight were formed at the surfaces. These organic acids dissociate into  $\text{COO}^-$  and  $\text{H}^+$  in neutral pH, so that they will be soluble in neutral water. When nitric acid was added, these groups may change into free acids which are usually insoluble in acidic water, and then they are readily precipitated (7).

Fig. 7 shows the change of TOC content in oxygen-saturated TB BGE solutions due to irradiation and the addition of nitric acid after irradiation. The TOC content did not change much either after irradiation or after the addition of nitric acid. This fact does not correspond to the results of its absorption spectra measurements (Fig. 4 b). This is probably due to the increase of soluble components from colloidal particles of the disperse dye after

irradiation.

The structures of the two disperse dyes are different, as terasil blue is anthraquinone with an aromatic ring which is difficult to degrade using gamma radiation. On the other hand, Terasil Black CMS has N=N bond which is weak and easy to degrade. The same results has also been reported by SUZUKI et al. (2, 3) where the degree of decoloration of soluble azo dye at 1 kGy was almost 100%, while that of soluble anthraquinone dye at 1 kGy was only 50%. After the addition of nitric acid, the phenomena of both disperse dyes solutions were slightly different. For azo type (TB CMS, TR 4G, and TGY) sedimentation occurred at 6, 12 and 8 kGy, respectively, while for anthraquinone type (TB BGE) sedimentation occurred at lower dose (2 kGy). The sedimentation occurred because the disperse dyes were carrying negative charge, and after the addition of nitric acid neutralization occurred. This phenomena is also influenced by the shape and the length of molecules. Anthraquinone dye has thin shape, so that neutralization and aggregation occurred very easily at low dose, while the shape of azo dye is rather thick, so that its degradation need higher dose (9).

#### 4. CONCLUSIONS

1. Decoloration and sedimentation of disperse dyes can be done by irradiation followed by the addition of acid up to pH 1, the necessary dose varies with the type of the dye.
2. In general, irradiation with high dose is needed for degradation of disperse azo dyes, while disperse anthraquinone dyes need only a relatively low dose.
3. Almost all of the disperse dyes can be precipitated by adding nitric acid after being irradiated, especially anthraquinone dyes which need only a small dose.
4. The addition of coagulants, i.e. calcium hypochlorite, ammonium iron (III) sulfate, aluminum sulfate, or iron (II) sulfate induced decoloration and sedimentation.

#### ACKNOWLEDGEMENTS

Apart of this study was supported by the Science and Technology Agency of Japan (STA) under the Scientist Exchange Program. The authors are grateful to Dr. H. Arai and Dr. T. Miyata of JAERI for their valuable discussions. Thanks are also due to Mr. Armanu and Ms. Christina T.S for their technical assistance.

#### REFERENCES

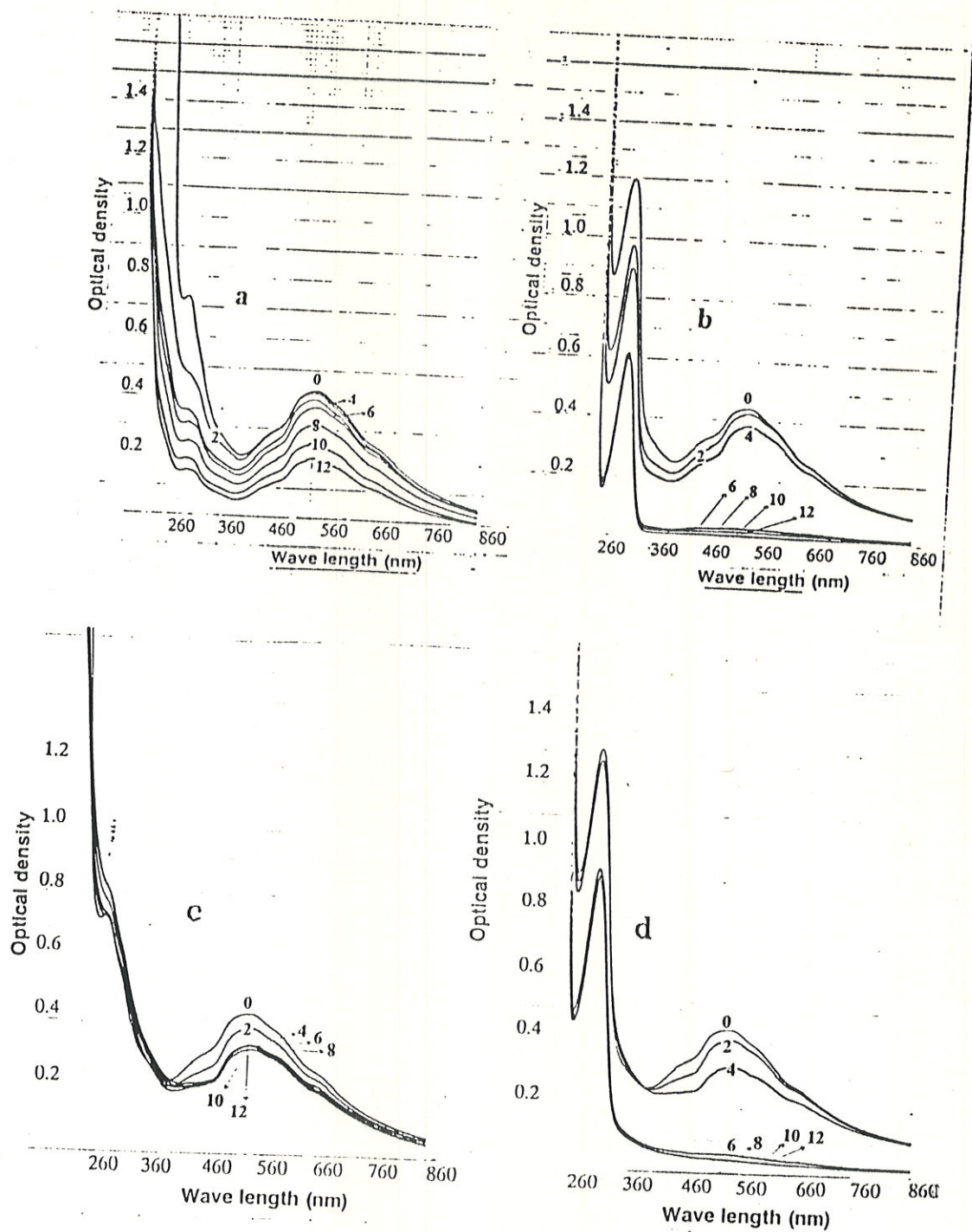
1. MARKOVIC, V., Radiation processing in industry : Improving product quality with a versatile technique, IAEA Yearbook 1991, Part B : Application of Nuclear Techniques and Research 1991, IAEA, Vienna (1991) B 53.

2. SUZUKI, N., MIYATA, T., SAKUMOTO, A., HASHIMOTO, S., and KAWAKAMI, W., The degradation of an azo dye in aqueous solution by high intensity electron beam irradiation, Int.J.of Appl.Radiat and Isot, 29, (1978)103.
3. SUZUKI, N., NAGAI, T., HOTTA, H., and WASHINO, M., The radiation-induced degradation of azo dyes in aqueous solution, Int.J.of Appl.Radiat and Isot, 26 (1975)726.
4. NAGAI, T., and SUZUKI, N., The radiation-induced degradation of anthraquinone dyes in aqueous solutions, Int. J. of Appl.Radiat.Isot, 27 (1976)699.
5. KAWAKAMI, W., HASHIMOTO, S., MIYATA, T., SAKUMOTO, A., TOKUNAGA, T., CHIGIRA, M., and WASHINO, M., Radiation treatment of waste water XI. Treatment of dye wastewaters and its cost, JAERI-M7994, (1978)
6. HOSONO, M., ARAI, H., AIZAWA, M., YAMAMOTO, I., SHIMIZU, K., and SUGIYAMA, M, Decoloration and degradation of azo dye in aqueous solution, Appl.Radiat.Isot, 44 (1993)1199.
7. BAGYO, N.M.A., ARAI, H., and MIYATA, T., Radiation-induced decoloration and sedimentation of colloidal disperse dyes in water, (1993) (to be published).
8. WINARTI, A., SUMARTONO, A., ARMANU., and SURTIPANTI, S, The effect of gamma irradiation on azo dyes (Terasil Navy) in aqueous solution, Proceeding Apisora CAIR-Batan, (1993)447.
9. ARAI., H., (Personal communication) 1995.

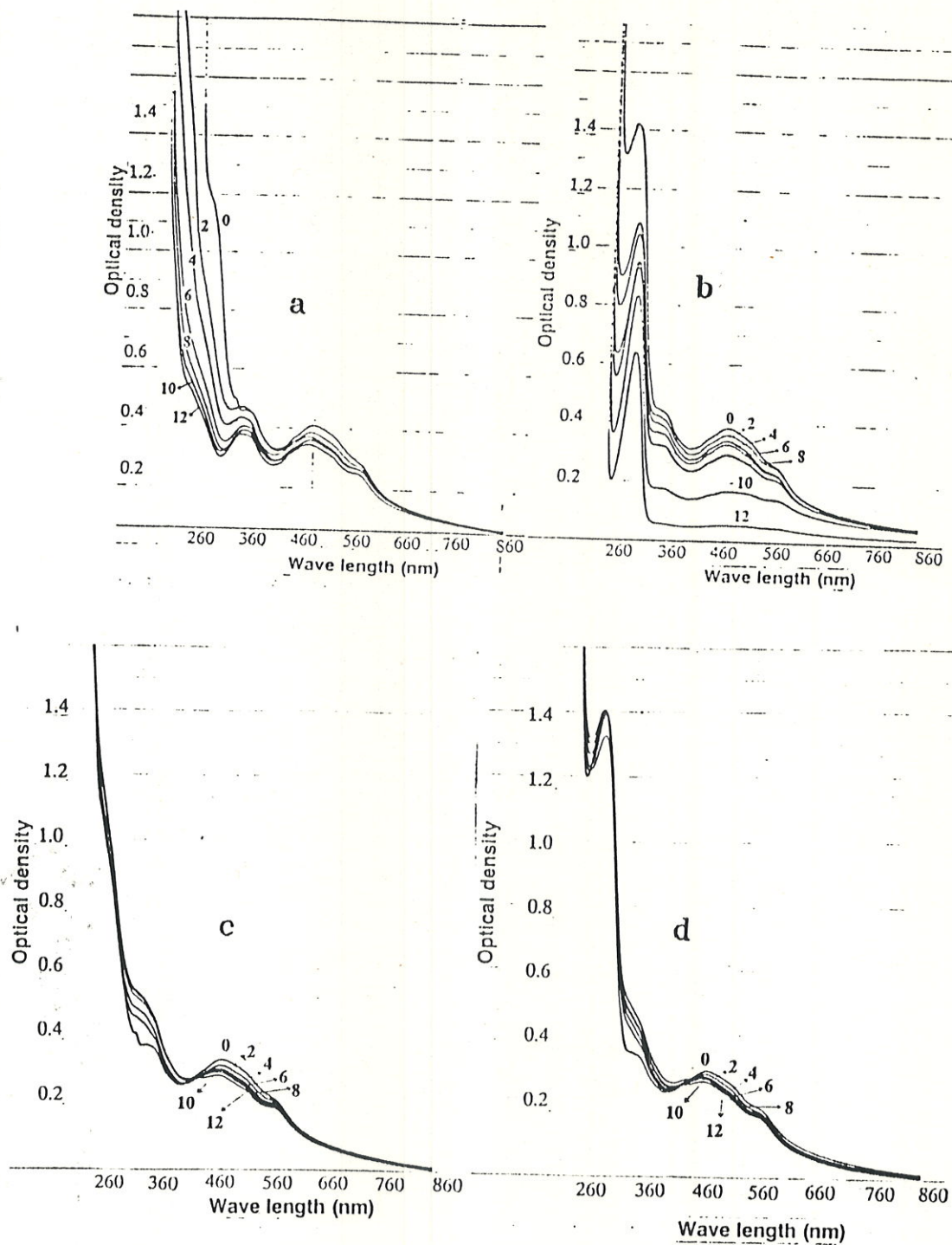
Table 1. Effect of calcium hypochlorite (30 ppm), aluminum sulfate (100 ppm) and ammonium iron (III) sulfate (100 ppm) on disperse dye Terasil Navy precipitation in irradiated aqueous solution at pH 9.

Dose (kGy)	Sample conc. (ppm)	Coagulants	Precipitation (%)							
			0 h	1 h	3 h	5 h	0 d	1 d	2 d	3d
0	200	Ca(OCl) <sub>2</sub>	0	2	4	5	-	-	-	-
		Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0	45	87	95	-	-	-	-
		FeNH <sub>4</sub> (SO <sub>4</sub> ) <sub>3</sub>	0	38	75	90	-	-	-	-
3	200	Ca(OCl) <sub>2</sub>	0	15	30	42	-	-	-	-
		Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	0	60	95	99	-	-	-	-
		FeNH <sub>4</sub> (SO <sub>4</sub> ) <sub>3</sub>	0	53	89	95	-	-	-	-
5	50	Ca(OCl) <sub>2</sub>	-	-	-	-	7	20	30	62
	100	Ca(OCl) <sub>2</sub>	-	-	-	-	19	82	91	95
3	200	Ca(OCl) <sub>2</sub>	-	-	-	-	22	97	99	99

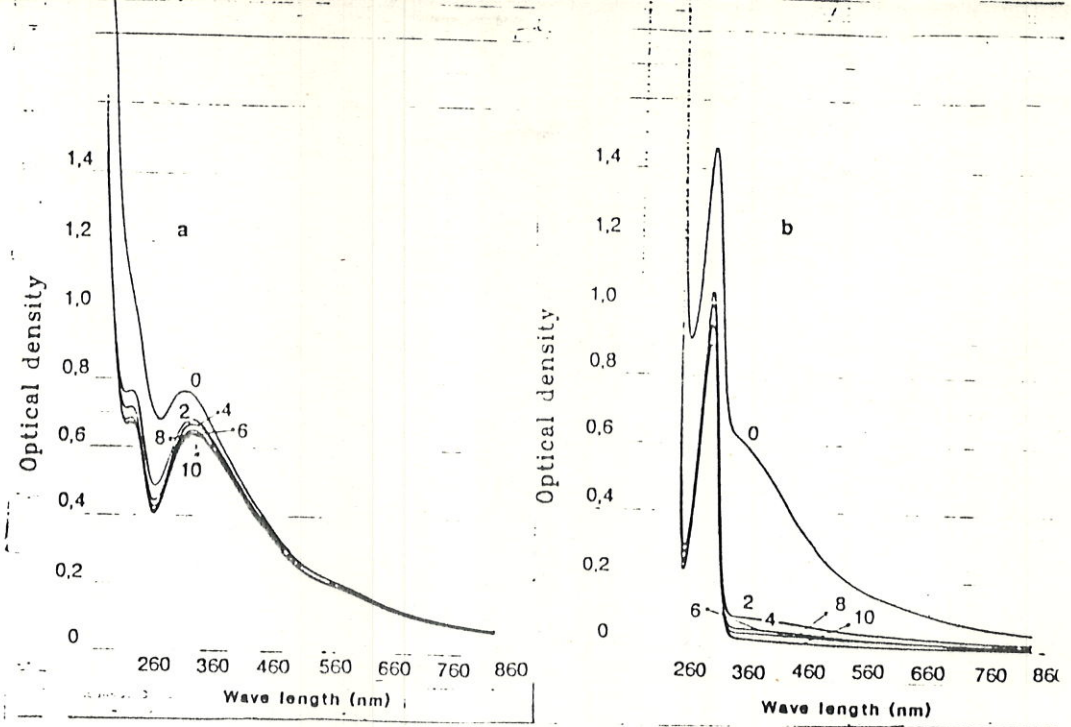




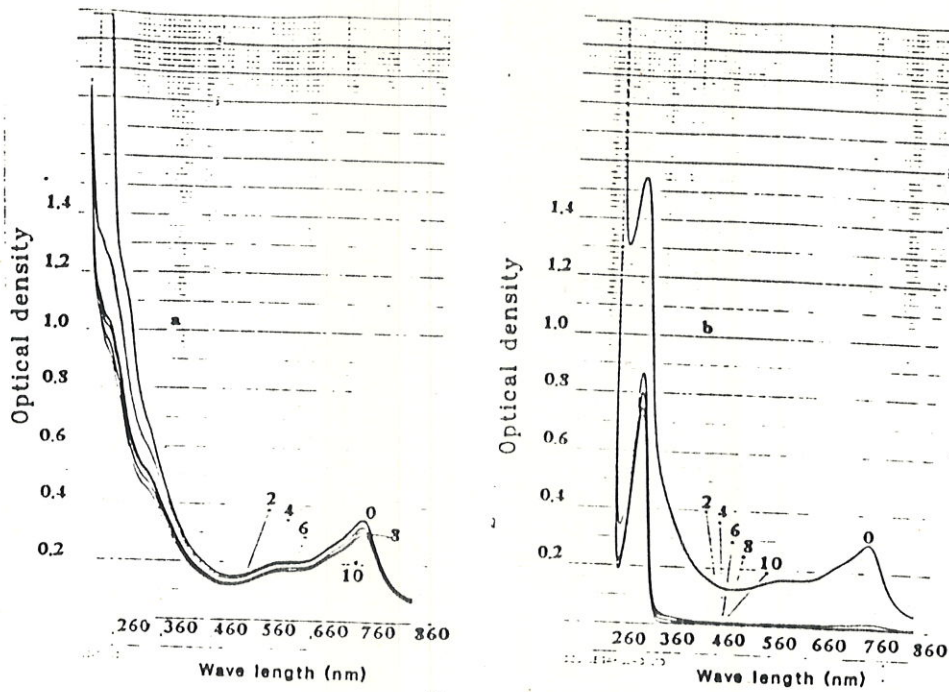
**Fig. 1 Absorption Spectra of Irradiated TB CMS Solutions**  
 (0, 2, 4, 6, 8 and 10 represent the dose in kGy)  
 a : in O<sub>2</sub> bubbling solution  
 b : in O<sub>2</sub> bubbling solution + HNO<sub>3</sub>  
 c : in N<sub>2</sub> bubbling solution  
 d : in N<sub>2</sub> bubbling solution + HNO<sub>3</sub>



**Fig. 2 Absorption Spectra of Irradiated TR 4G Solutions**  
 (0, 2, 4, 6, 8 and 10 represent the dose in kGy)  
 a : in O<sub>2</sub> bubbling solution  
 b : in O<sub>2</sub> bubbling solution + HNO<sub>3</sub>  
 c : in N<sub>2</sub> bubbling solution  
 d : in N<sub>2</sub> bubbling solution + HNO<sub>3</sub>



**Fig. 3 Absorption Spectra of Irradiated TGY Solutions**  
 (0, 2, 4, 6, 8 and 10 represent the dose in kGy)  
 a : in O<sub>2</sub> bubbling solution  
 b : in O<sub>2</sub> bubbling solution + HNO<sub>3</sub>



**Fig. 4 Absorption Spectra of Irradiated TB BGE Solutions**  
 (0, 2, 4, 6, 8 and 10 represent the dose in kGy)  
 a : in O<sub>2</sub> bubbling solution  
 b : in O<sub>2</sub> bubbling solution + HNO<sub>3</sub>

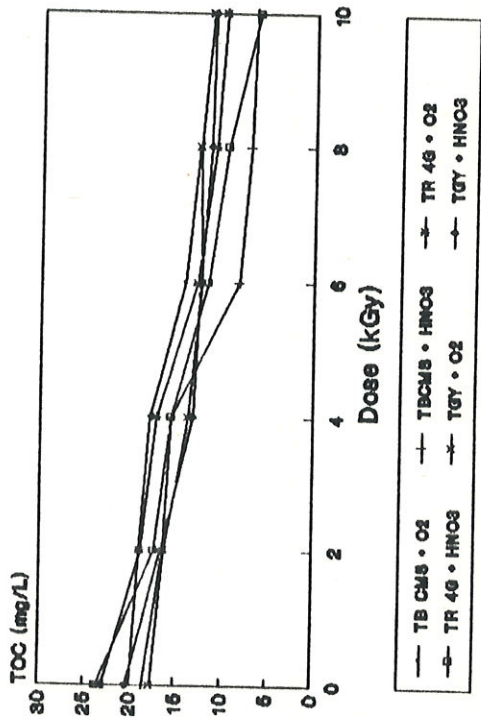


Fig. 5 Effect of irradiation on TOC

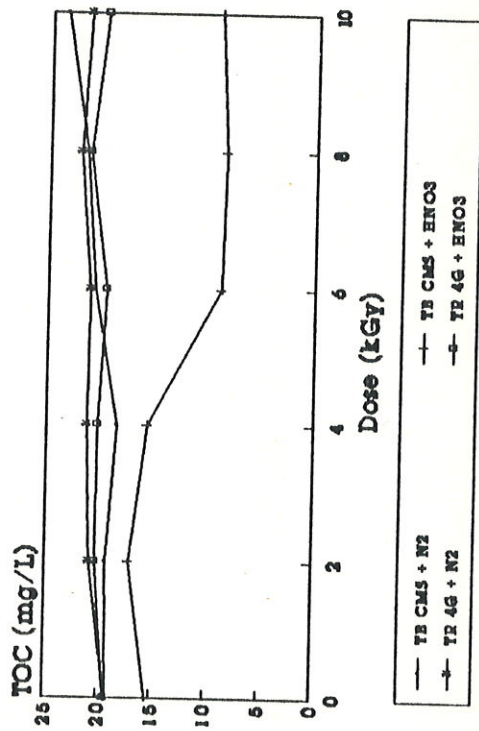


Fig. 6 Effect of irradiation on TOC

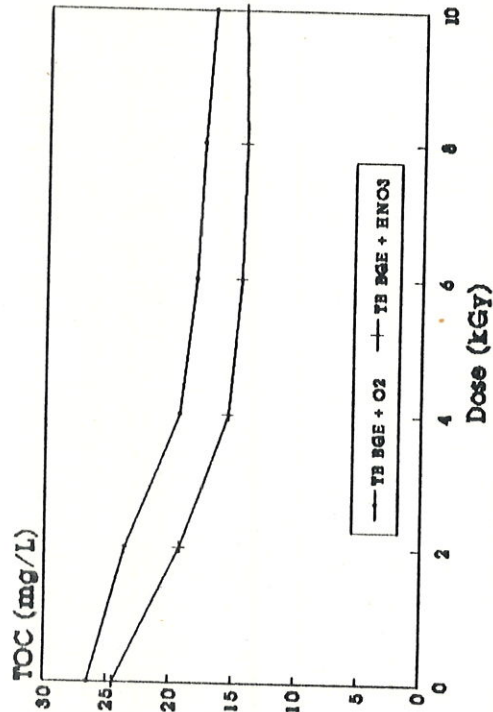


Fig. 7 Effect of irradiation on TOC

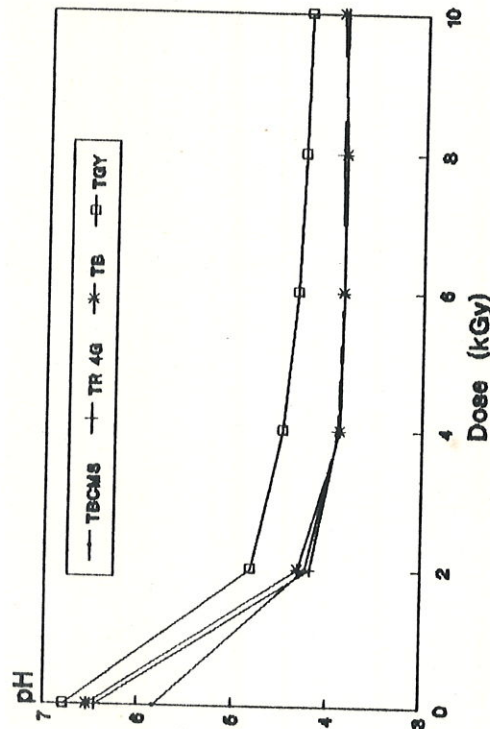


Fig. 8 Change of pH after irradiation