PAIR/P.947/97

RADIOLYSIS OF REACTIVE AZO DYES IN AQUEOUS SOLUTION.

Agustin N.M. Bagyo, Winarti Andayani, H. Winarno
Ermin Katrin, Endrawanto Widayat dan Yanti
S. Soebianto

RADIOLYSIS OF REACTIVE AZO DYES IN AQUEOUS SOLUTION

Agustin N.M.Bagyo, Winarti Andayani, Hendig Winarno, Ermin Katrin,
Endrawanto Widayat, and Yanti S. Soebianto *

ABSTRACT

RADIOLYSIS OF REACTIVE AZO DYES IN AQUEOUS SOLUTION. The effects of irradiation on aerated reactive dye solutions have been studied. The uv-vis absorption of solutions were observed before and after irradiation. HPLC with uv-detector was used to analyze the products of degradation. Oxalic acid was the main degradation product and a small amount of succinic acid was also detected. Less effective degradation at higher pH might be caused by any structural changes of the azo compound.

ABSTRAK

RADIOLISIS ZAT WARNA REAKTIF AZO DALAM LARUTAN AIR. Telah dipelajari pengaruh iradiasi pada larutan zat warna reaktif azo yang diiradiasi dengan aliran udara. Pengukuran absorbansi larutan sebelum dan sesudah iradiasi dilakukan dengan spektrofotometer uv-vis. Hasil penguraian dianalisis dengan menggunakan HPLC yang dilengkapi dengan detektor uv. Asam oksalat merupakan hasil utama dari penguraian tersebut dan asam suksinat yang terdapat dalam jumlah sedikit. Penurunan penguraian pada pH tinggi mungkin disebabkan oleh perubahan struktur dari senyawa azo.

INTRODUCTION

The increase of textile industry in Indonesia gives impact on the environment. The waste that contain some non-biodegradable materials such as reactive azo dyes cannot be degraded by conventional treatment. Radiation-induced degradation and decoloration of disperse and acid dyes have been reported by some researchers (1-2). The results were promising, so that radiation technology should be an alternative for the treatment of the waste.

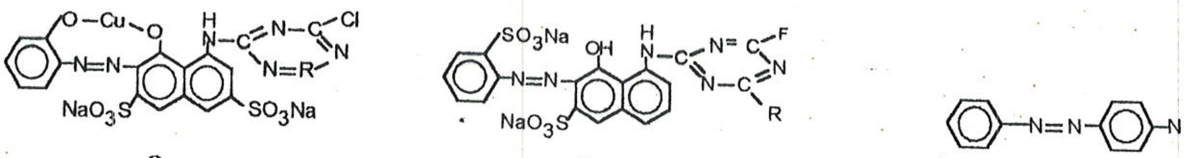
This paper summarizes studies on radiation degradation and decoloration of reactive azo dyes in water as a model system of textile industrial waste.

---

* Centre for Applications of Isotopes and Radiation, The Indonesian National Atomic Energy Agency, PO Box 7002 JKSKL, Jakarta 12070, Indonesia

MATERIALS

Reactive azo dyes used in this study were cibacron violet (CV), cibacron orange (CO) and cibacron golden yellow (CGY) (Fig 1). Cibacron golden yellow has the chemical index-reactive orange 45 but the structure is not known due to the industrial patent (Fig 1c). The dyes samples were used without purification. A 50 ppm of each dye solution was prepared by dissolving the dye in pure water. Gamma-rays irradiation was carried out while the solution was aerated. The dose rate was determined by Fricke dosimeter, total absorbed dose were varied from 0 to 10 kGy (5 kGy/h). Irradiation was also carried out in various pH. Shimadzu UV 1600 spectrophotometer was used to measure the uv-vis absorption of the solutions, and pH-meter was used to measure the pH. The degradation products were determined using HPLC with a biograd column, and uv detector. The standards of organic acids used were oxalic, succinic, formic, acetic and propionic acids.



a b c

Fig. 1. Structure molecules of Cibacron Violet (a), Cibacron Orange (b) and Cibacron Golden Yellow (c)

RESULTS AND DISCUSSION

Degradation products. Figure 2 showed that the initial solutions had different pH due to their chemical structures. The decline of pH upon irradiation indicated the formation of acidic product, and the identified products were compared with acids standards (oxalic, succinic, formic, acetic and propionic acid). Figure 3 showed the chromatogram of CGY radiolysis products (a) and the acids standards (b). Oxalic acids was the main radiolysis product, and small amount of succinic acid was also formed.

Degradation of the dye molecules is induced by the reaction with oxidative species from water radiolysis. The oxalic acid might be formed by the oxidation of benzene which is generated by the attack of oxidative species such as hydroxyl radicals on the dye molecules (4-5) (scheme 1-2).

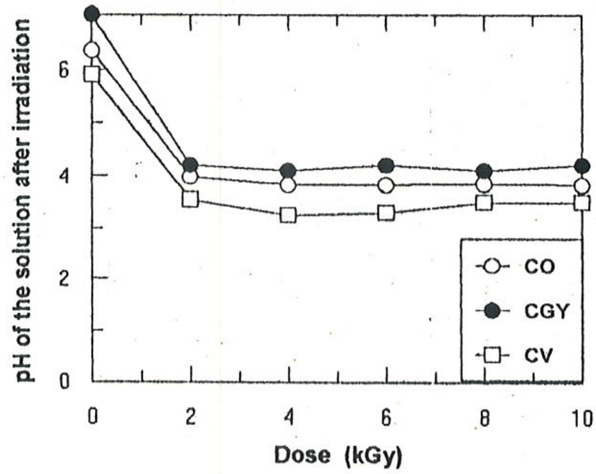


Fig. 2 The change of pH after irradiation

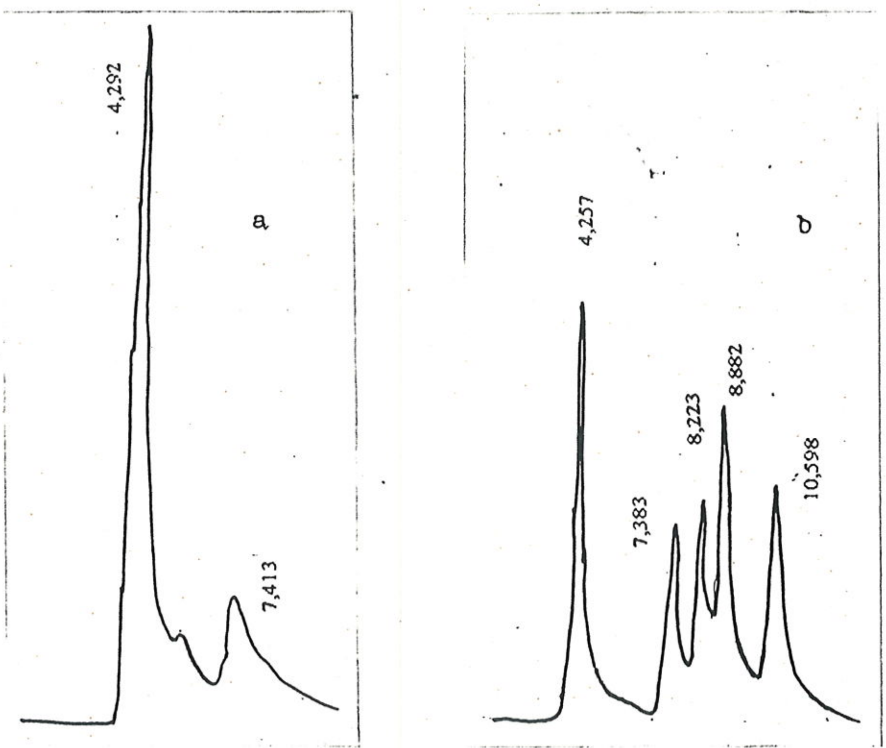


Fig. 3 (a). HPLC chromatogram of irradiated CGY at the dose of 10 kGy.
Fig. 3 (b). Chromatogram of organic acid standard : oxalic acid (4,257 min), succinic acid (7,383 min), formic acid (8,223 min), acetic acid (8,862 min) and propionic acid (10,598 min)

Effect of pH on the radiolysis of reactive azo dyes. Irradiation was carried out in aerated system, therefore oxidative species ($HO^{\cdot}$, $HO_2^{\cdot}$, H_2O_2) were dominant. Figure 4 showed that degradation increased with dose, and pH of the solution hardly affected the degradation of CV. The results showed that CGY was the most degradable compound, because it has less aromatic rings than CV and CO (Fig 1.).

We supposed that the effect of pH on the degradation of CGYand CO was more on the chemical structure of the compounds rather than the reactive species from the water. Structural changes of CGY and CO might occur at higher pH and induce less degradable compounds. Therefore degradation should be carried out at neutral pH because no more treatment to neutralize the waste.

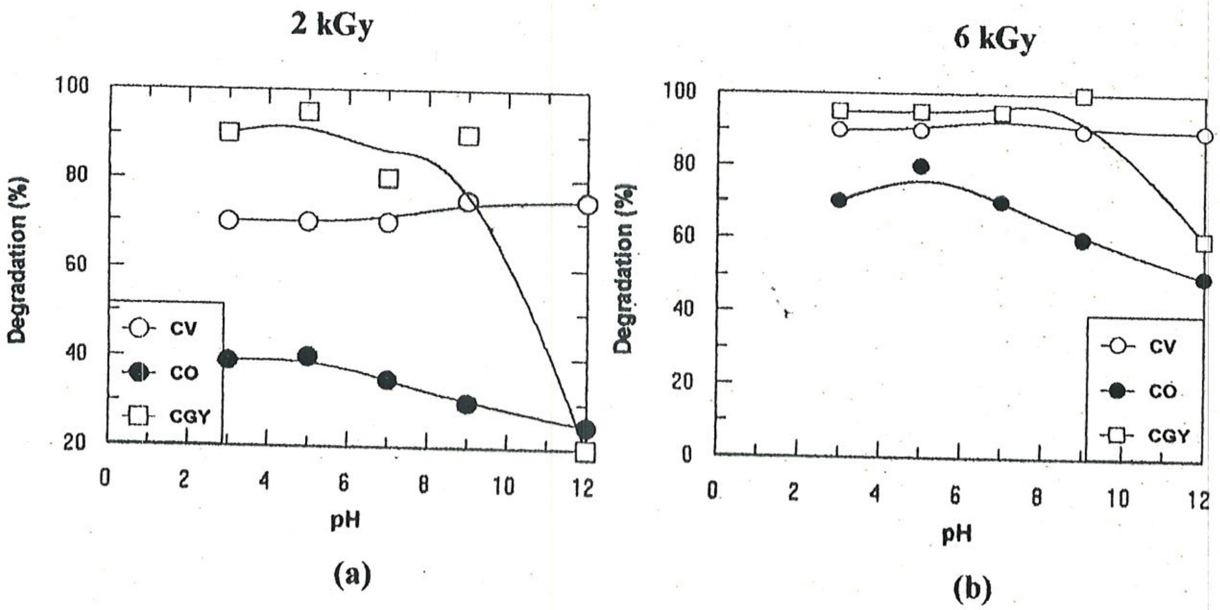
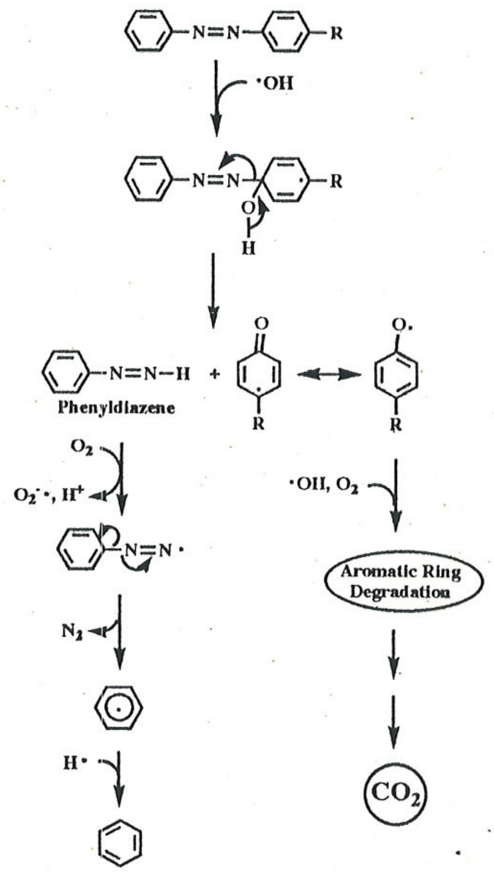
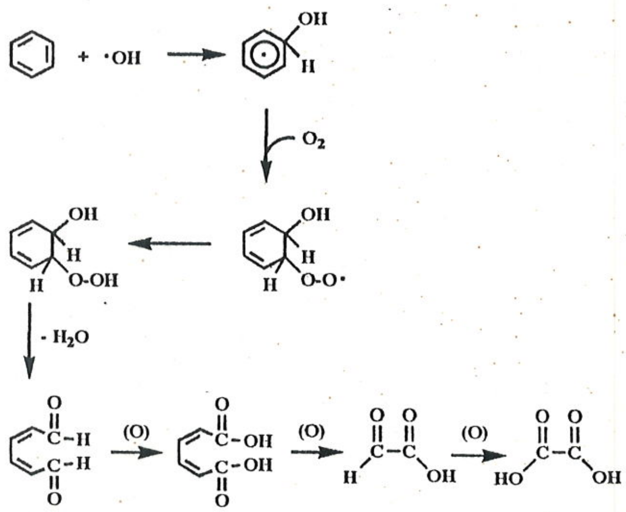


Fig 4. Effect of pH on the degradation of azo dyes (a) 2 kGy and (b) 6 kGy



Scheme 1.



Scheme 2.

CONCLUSION

Radiation degradation of reactive dye solutions in the aerated system can be carried out at neutral pH, and the main product is oxalic acid.

ACKNOWLEDGEMENT

The authors are grateful to Ms. Christina T.S, Mr. Syurhubel, and Mr. Armanu for their technical assistance. Thanks are also due to the member of Irradiation Facility Div. of CAIR.

REFERENCES

1. Bagyo, A.N..M., H. Arai, and T. .Miyata., Radiation-Induced Decoloration and Sedimentation of Colloidal Disperse Dyes in Water. Appl. Radiat.Isot., Vol. 48, No.2 (1997), pp. 175-181.

3. Vinodgopal, K and P.V. Kamat., Enhanced Rates of Photocatalytic Degradation of an Azo Dye Using SnO_2/TiO_2 Coupled Semiconductor Thin Films. Env.Sci & Tech., Vol. 29, No.3 (1995), pp. 841-845.

4. Spadaro, J.T., L. Isabelle., and V. Renganathan., Hydroxil Radical Mediated Degradation of Azo Dyes : Evidence for Benzene Generation. Env.Sci.Tech., Vol. 28, No. 7 (1994), pp. 1389-1393.

5. Nickelsen, M.G. and W.J Cooper., Removal of Benzene and Selected Alkyl-Substituted Benzene from Aqueous Solution Utilizing Continous High Energy Irradiation., Env.Sci & Tech., Vol. 26, No 1. (1992), pp. 144-152.