RADIOLYSIS OF REACTIVE AZO DYES IN AQUEOUS SOLUTION

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ABSTRACT

RADIOLYSIS OF REACTIVE AZO DYES IN AQUEOUS SOLUTION. The effects of radiation on aerated reactive dye solutions i.e Cibacron Violet, Cibacron Orange and Cibacron Yellow solutions have been studied. Parameters analysis were the change of pH after radiation, the change of absorption, degradation products and effects of pH on the radiolysis. The uv-vis absorption of solutions were observed before and after irradiation. pH variation was done from pHs 3, 5, 7, 9 and 12. Irradiation was done at doses of 0, 2, 4, 6, 8 and 10 kGy with dose rate of 5 kGy/h and was determined by a Fricke dosimeter. HPLC with UV detector was used to analyze the degradation products. Oxalic acid was the main degradation product and small amount of succinic acid was also detected.

Key words : radiolysis, radiation, dyes, reactive azo dyes

INTRODUCTION

The increase of textile industry in Indonesia gives an impact on the environment. Dye wastes from textile industry are not easily degraded by ordinary treatment processes. Radiation-induced degradation and decoloration of insoluble and soluble azo and anthraquinone dyes were studied and they were found to decolorize easily, especially in the presence of oxygen during irradiation. The results were promising, so that radiation technology should be an alternative for the treatment of the waste [1-3].

Azo dyes were easily decolored by the attack of OH radicals formed from the radiolysis of water and the dye molecules are degraded to the lower molecular weight compounds, finally to carbon dioxide, in the presence of oxygen.

In the presence of oxygen, the hydrogen atom reacts rapidly with oxygen, leading to the formation of the oxidizing HO_2 radical.

$$H^{\bullet} + O_2 \longrightarrow HO^{\bullet}_2$$

Chemical oxidation of organic species in the presence of oxygen is due to the interaction of oxidizing radicals (such as OH and HO_2 radicals) with them in the aqueous solution.

This paper summarizes studies on radiation degradation and decoloration of reactive azo dyes in water as a model systems of textile industrial waste. The use of reactive azo dyes as a model of pollutant because the dye was commonly used as a coloring material in textile industry and difficult to remove the color from the waste.

EXPERIMENTAL AND METHODS

Reagents

Reactive azo dyes Cibacron Violet (CV), Cibacron Orange (CO) and Cibacron Golden Yellow (CGY), NaOH, H_2SO_4, H_3PO_4 0,005%, Oxalic acid, Succinic acid, Formic acid, Acetic acid, and Propionic acid.

Preparation of solutions

Dye solutions were prepared by dissolving CV, CO and CGY in pure water with a dye concentration of 50 ppm. The 500 ml solutions were placed in a Pyrex reaction vessel (5 cm dia. and 16 cm height). The solution in various pH of 3, 5, 7, 9 and 12 were prepared by adjusted the solution by the addition of NaOH or H_2SO_4.

Irradiation procedures

Irradiation was done using cobalt-60 gamma-rays at room temperature with various dose of 0, 2, 4, 6, 8 and 10 kGy. During irradiation air was bubbled through a porous plate at the bottom of the reaction vessel. The dose rate of 5 kGy/h was determined by a Fricke dosimeter. Irradiation was also carried out in the various pHs i.e 3, 5, 7, 9 and 12 and adjusted by the addition of NaOH or H_2SO_4.

Analysis

The change of the spectrum was measured with a Shimadzu UV 1600 spectrophotometer. The pH of the solution was measured with Methrom 620 pH-meter. The degradation products were determined by using HPLC with a Biograd column and uv detector. The standard organic acids were oxalic, succinic, formic, acetic and propionic acid.

The degree of degradation of the dye was calculated from the decrease of maximum absorbance by using the following equation :

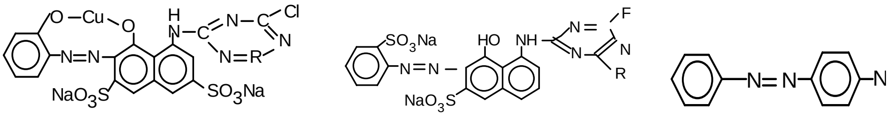
$$\text{Degradation \%} = \frac{Ao - Ai}{Ao} \times 100\%$$

where Ao and Ai are the absorbances before and after irradiation, respectively.

RESULTS AND DISCUSSION

Degradation products

The structure of Cibacron Violet (CV), Cibacron Orange (CO) and Cibacron Golden Yellow (CGY) are shown in 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). Figure 2 showed that the initial solutions had different pH due to the their chemical structures. The decline of pH upon irradiation indicated that formation of acidic product, and the identified products were compared with standard acids (oxalic, succinic, formic, acetic and propionic acid). The formation of oxalic acid that could be detected as degradation products of the reactive dyes are shown from Tabel 1. Figure 3 showed an example chromatogram of reactive dyes i.e CGY radiolysis products (a) and the standard acids (b). Based on that figure, it is suggested that oxalic acids was the main radiolysis products, and small amount of succinic acid was also formed.



a **b** **c**

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

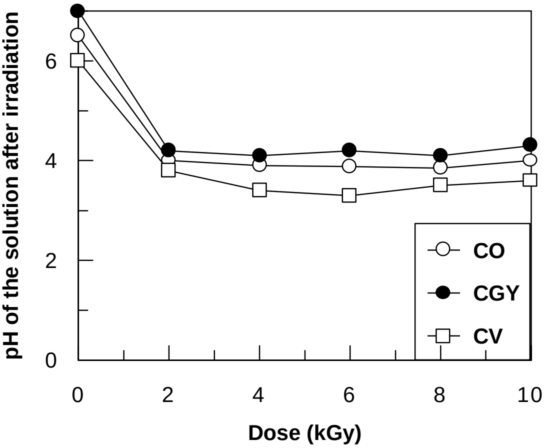


Figure 2. The change of pH after irradiation.

Degradation of the dye molecules is induced by the reaction with oxidative species from the water radiolysis. The oxalic acid might be formed by the oxidation of benzene which is generated by the attack oxidative species such as hydroxyl radicals on the dye molecules (scheme 1-2 in Figure 4) [4-5]. At further oxidation oxalic acid could be change into carbondioxide and water molecules.

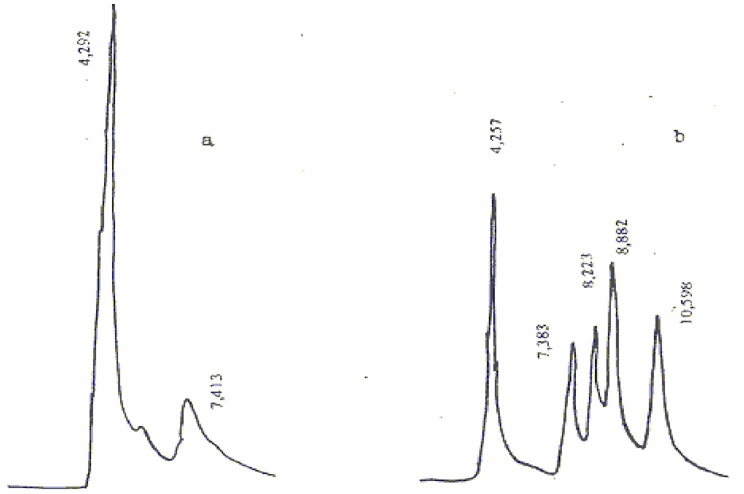
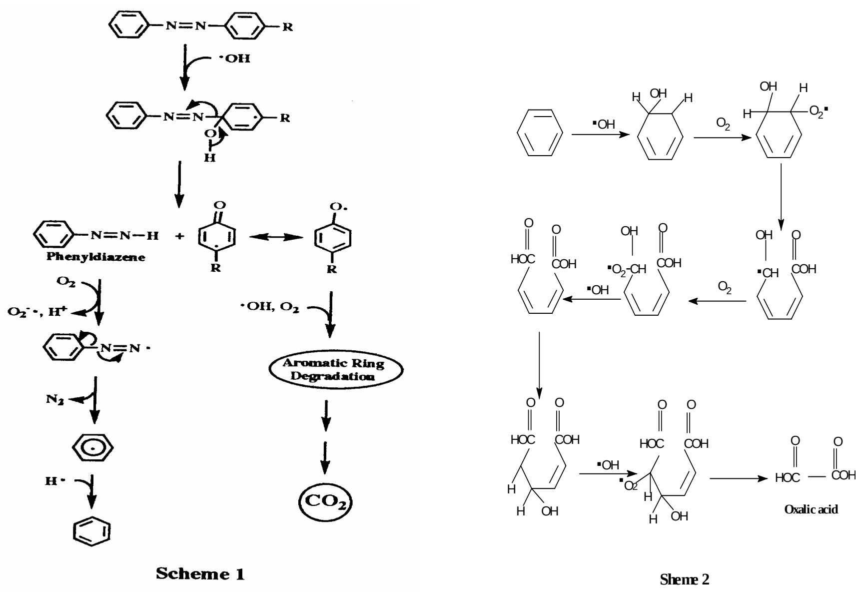


Figure 3 (a). HPLC chromatogram of irradiated CGY at dose of 10 kGy.
Figure 3 (b). Chromatogram of organic acid : oxalic acid (4,257 min), succinic acid (7,383 min), formic acid (8,223 min), acetic acid (8,882 min) and propionic acid (10,598 min).

Tabel 1. The formation of Oxalic acid from Reactive Dyes

Dose (kGy)	Oxalic Acid (ppm)		
	Cibacron Violet	Cibacron Orange	Cibacron Golden Yellow
0	-	-	-
2	0.03	42.8	-
4	0.04	40.6	2.6
6	0.02	36.8	9.3
8	0.01	36.2	6.4
10	0.01	25.6	0.2



Scheme 1

Sheme 2

Figure 4. Mechanism degradation of azo dye.

Effect of pH on the radiolysis of reactive azo dyes

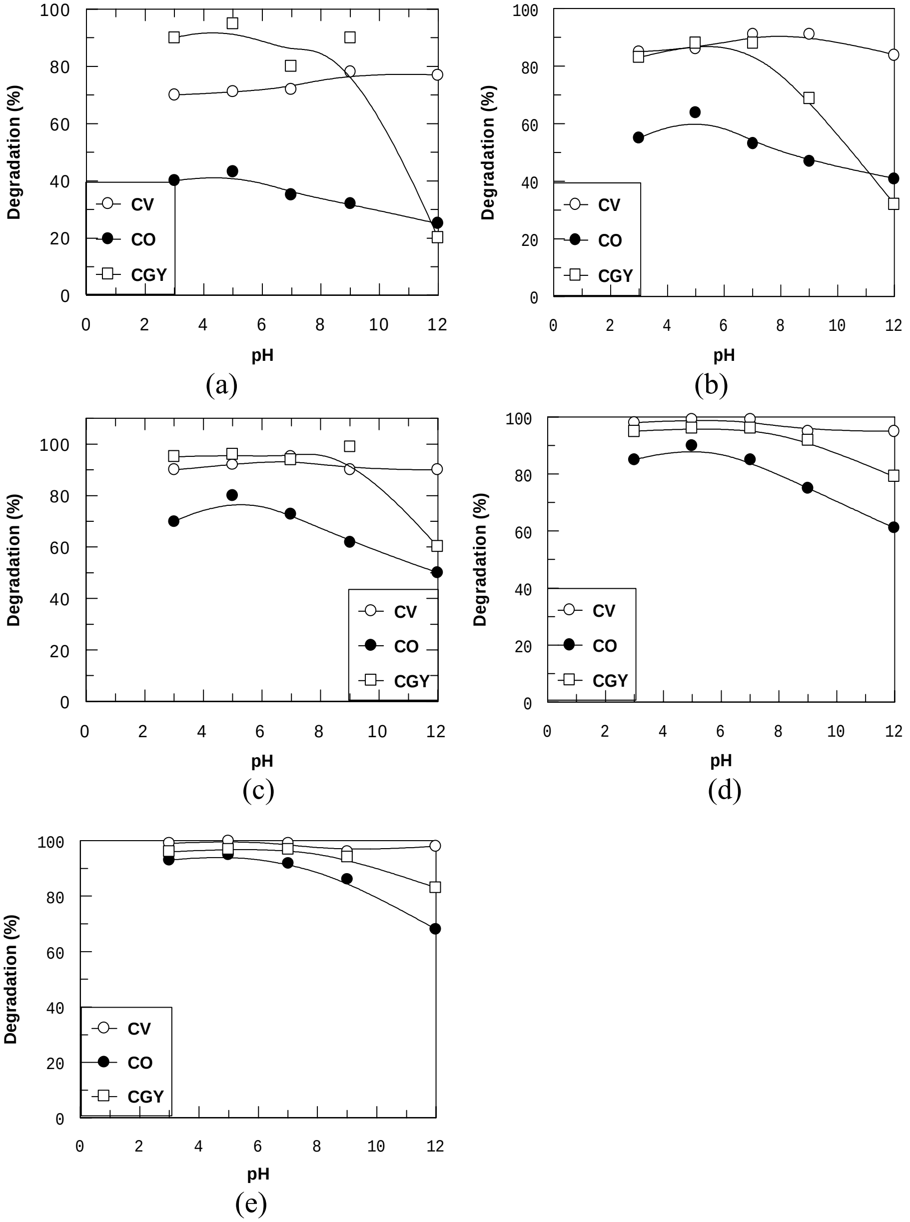
The degradation at different pH values for some reactive dyes (CGY, CV and CO) was studied by irradiating different aqueous dye solution to a dose of 0, 2, 4, 6, 8, 10 kGy. The dependence of the degradation process on pH is shown in Fig. 5a, b, c, d, e, respectively. It can be seen that CGY and CV dyes are degraded in the pH range from 3- 9 with a reduced sensitivity at high pH. CO molecules hardly degraded at low dose but degraded completely at high dose (10 kGy). Observation behaviour of the effect of the pH on the degree of degradation is not quite clear. A possible explanation might be based on the acid-base properties of the OH radicals. In strong basic solution, the OH radicals dissociate to the less reactive $O^{\bullet -}$ radicals :

$$^{\bullet}OH \rightleftarrows H^{+} + {}^{\bullet}O^{-} \quad (pH=11.9)$$

In fact the degradation scheme depends on the relative reactivity of the various species, availability of oxygen, dose , pH of the solution and temperature (6).

In acidic solution : $e^{-}_{aq} + H^{+} \longrightarrow H^{\bullet}$, k=$2.3\times10^{10}$ L mol^{-1} s^{-1} the reducing H atoms are scavenged by oxygen leading to a formation of $HO_2^{\bullet}$

which can be involved in the degradation process. The $O_2^{\bullet -}$ species are not very reactive but at pH>7 the $^{\bullet}OH$ radicals are the major primary attacking transients. The sharp decrease in the degradation at pH>9 may be a result of the low reactivity of $O^{\bullet -}$ and $O_2^{\bullet -}$ species to the attack of the dyes.



(a) (b) (c) (d) (e)

Figure 5. Effect of pH on the degradation of azo dyes (a) 2 kGy, (b) 4 kGy, (c) 6 kGy, (d) 8 kGy and (e) 10 kGy.

CONCLUSIONS

Radiation degradation of reactive dye solutions in aerated system can be carried out but the necessary dose varies with the type of the dye. Irradiation at neutral pH is preferred to obtain maximum degradation. Degradation products that could be dectected mainly is oxalic acid.

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