

Effect of pH on Homogeneous Photodegradation of Eosin Y Dye

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Abstract

Eosin Y (EY), an anionic dye, also known as Eosin Yellow or Bromoeosin, or Acid red 27 is an industrial dye. The residual dye, discharged as one of the components of the untreated effluent, into the adjacent surface and causes water pollution. Photodegradation of EY was investigated at 29 °C in homogeneous aqueous media using UV_A light (≈400 – 320 nm) in acetate buffer solution as a function of pH (3.08-7.08). At higher pH, there was no effect of this light on the dye in the solution. Results show that the initial rate of photocolorization increased with decreasing the pH of the dye solution.

Keywords: photocolorization, pH effect, Acid red 27, UV light, homogeneous media.

Introduction

In the recent past, Asia contributed 42% of the total dye user market [1]. The global dyestuff market was estimated to be about 6.6 billion US dollars in 1999 and EY has been one of the widely used dye. pH causes changes in its structural configuration in water (Figure 1). Due to its vivid red fluorescence, EY is used in the textile, printing, leather, and cosmetic industries. It is reported that in industries about 15% of total dye used, is lost during processing with water and the effluent pollutes the natural water system [2]. Several physical methods such as membrane filtration, adsorption on activated charcoal, reverse osmosis, flocculation, chemical method, and bio-treatment are applied to remove dye from wastewater. Scientists are still trying to degrade dyes from wastewater by heterogeneous oxidation using semiconducting photocatalyst [3-10]. Recently, Hossain *et al.* [11]

tried to degrade EY by homogeneous oxidation using the Fenton process (i.e. in presence of H₂O₂ and Fe²⁺). However, homogeneous photo-degradation of EY dye has not been studied yet. This study reports the influence of only H⁺/OH⁻ ion concentrations on the degradation of EY dye in aq. solution, in the presence of UV_A light alone.

Materials and Methods

Microcrystalline yellowish Eosin Y (reagent grade) was collected from the local market and used without any further treatment. Other analytical grade (AR) chemicals, such as glacial acetic acid, and sodium acetate, etc., were purchased from E. Merck, Germany. Deionized water was used to prepare all solutions. The spectra were recorded with Shimadzu UV-vis 160 (Japan) spectrophotometer.

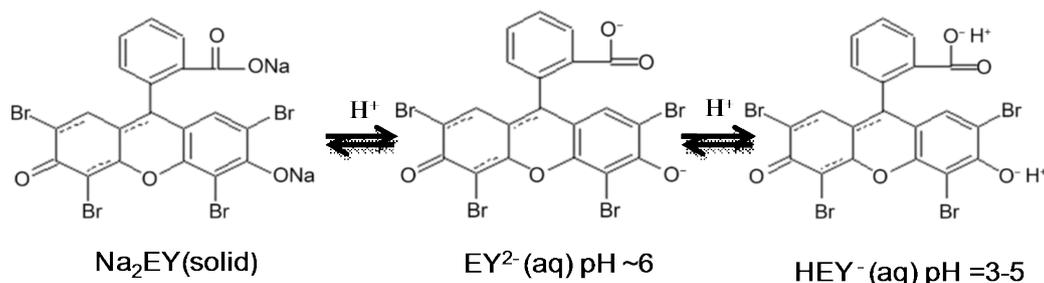


Figure 1: Structure of Eosin Y (EY) at different pH

Preparation of stock solution of Eosin Y (EY) dye

A stock solution of 1.00×10^{-2} M of EY was prepared by dissolving 0.692g solid dye in water in a 100 mL volumetric flask. This stock solution was wrapped with aluminum foil and kept in the dark. EY solutions with five different concentrations 1×10^{-5} , 2×10^{-5} , 3×10^{-5} , 4×10^{-5} , and 5×10^{-5} M were prepared from the stock solution and their absorbance was measured at 515 nm (λ_{max} of EY). The plot of absorbance vs. the respective concentration showed the compliance of the system with the Beer-Lambert law. 4.96×10^4 L \cdot mol $^{-1}$ \cdot cm $^{-1}$ is the molar absorption coefficient of EY (at pH = 6.2).

Determination of photodegradation

Photodegradation of EY was performed in the UV lamp house which was a rectangular wooden box (25 \times 20 \times 25 cm) with its internal surface wrapped with aluminum foil (Figure 2). The circular shape of UV_A lamp (20 cm length, 20W), was attached at the inner top of the chamber, as the light source. 50 mL beaker (dia. 4.0 cm) made of borosilicate glass was used as the reactor. A small bar magnet agitated the solution.

In a typical photolysis experiment after every five minutes, the beaker was taken out from the lamphouse and the absorbance was recorded. The removal of the solution for spectroscopic analysis does not affect the photolytic process very much. Because before and after the UV irradiation step the weight of the beaker with EY solution was maintained constant by the addition of deionized water to minimize the error due to vaporization of water from the beaker during photolysis reaction. Furthermore, the photolysis process is carried out in the darkroom.

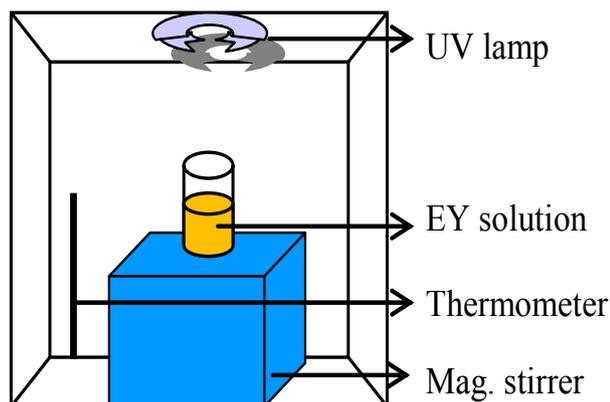


Figure 2: Schematic diagram of UV lamp house for the photodegradation of EY dye

Determination of initial rates

Habib *et al.* reported in 2004, and 2013 [12,6] that pseudo-first-order kinetics give rather perfect rate data than normally accepted second-order kinetics. The concentration of EY solution was measured at different time intervals e.g. 5,10,15,20 min. etc. and the pseudo-first-order rate constant (k' , min $^{-1}$) was obtained from the slope of LnA vs. time (min.) plot. The initial rates were calculated from the observed pseudo-first-order rate constants, according to the following Eq. (1)

$$R_i = \frac{d[EY]}{dt} = k[EY] = k' \frac{A_0}{\epsilon l} \quad \text{eq. 1}$$

Where, ϵ = molar absorption coefficient of EY (L \cdot mol $^{-1}$ \cdot cm $^{-1}$), k' = pseudo-first-order rate constant (min $^{-1}$) obtained from the plot of slope of LnA vs. time (min), R_i = initial rate (mol \cdot L $^{-1}$ \cdot min $^{-1}$), l = cell path length (1 cm), A_0 = absorbance at $t = 0$ (min).

Determination of % of decolorization

The percentage of decolorization was calculated as

$$[(X_0 - X_t) / X_0] \times 100$$

where, X_t is the absorbance at the time 't' and X_0 is the absorbance at the time 't' = 0 (min).

Results and Discussion

The spectrum of EY in aqueous solution (Figure 3) shows four absorption peaks at 515, 340, 301, and 253 nm corresponding to the chromospheres containing a polycyclic aromatic ring, carboxylic group, carbonyl group, and benzene ring, respectively.

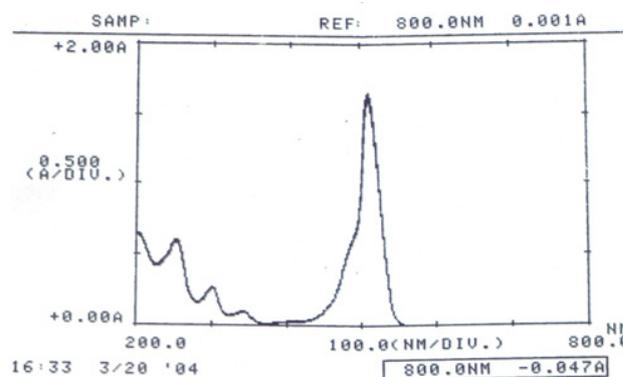


Figure 3: The spectrum of Eosin Y (aq.), pH = 6.2
[EY] = 3.0×10^{-5} M

EY solutions of 3.00×10^{-5} M with six different pH (from 2 to 9) were made by taking 15 mL of (1.00×10^{-4} M) solution in a 50 mL volumetric flask. The pH of the solutions was controlled by using the acetate

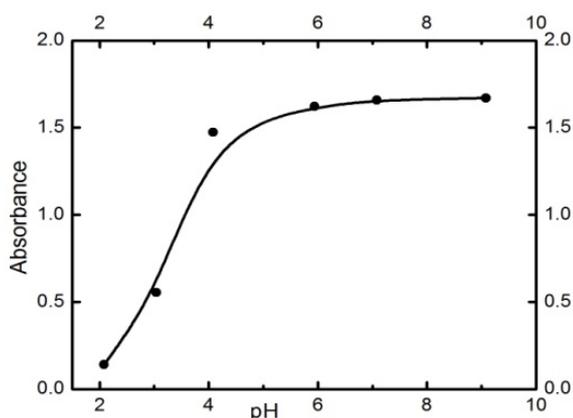


Figure 4: Effect of pH on the absorbance of EY solution (3.00×10^{-5} M)

buffer. The plot of absorbance vs. pH of the 3.00×10^{-5} M solution shows (Figure 4) that the absorbance of EY solution at neutral pH is 1.66. With increasing the pH (up to 9) the absorbance remains almost constant however, the absorbance decreases with lowering the pH of the solution.

pH Effect on the absorbance of Eosin Y solution

At low pH, the EY solution gets protonated and

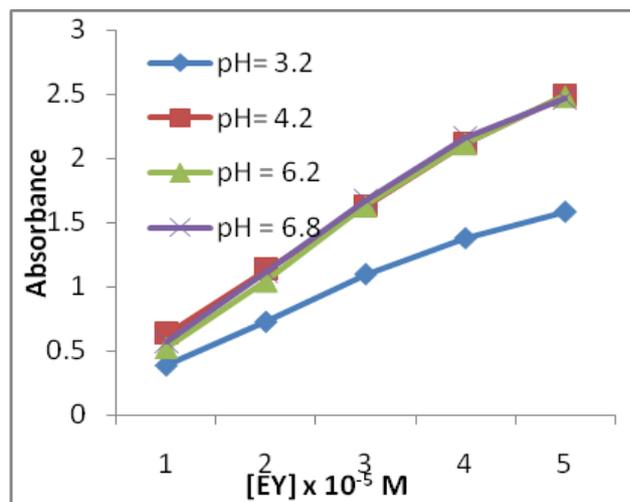


Figure 5: Variation of absorbance of EY solution at different pH

decreases the conjugation (Figure 1) and vice-versa. At neutral to basic pH range, the dye solution remains unprotonated ionic form i.e EY^{2-} . Therefore, the absorbance remains constant at this pH range.

Determination of ϵ at different pH

Since the absorbance of EY solution at a particular

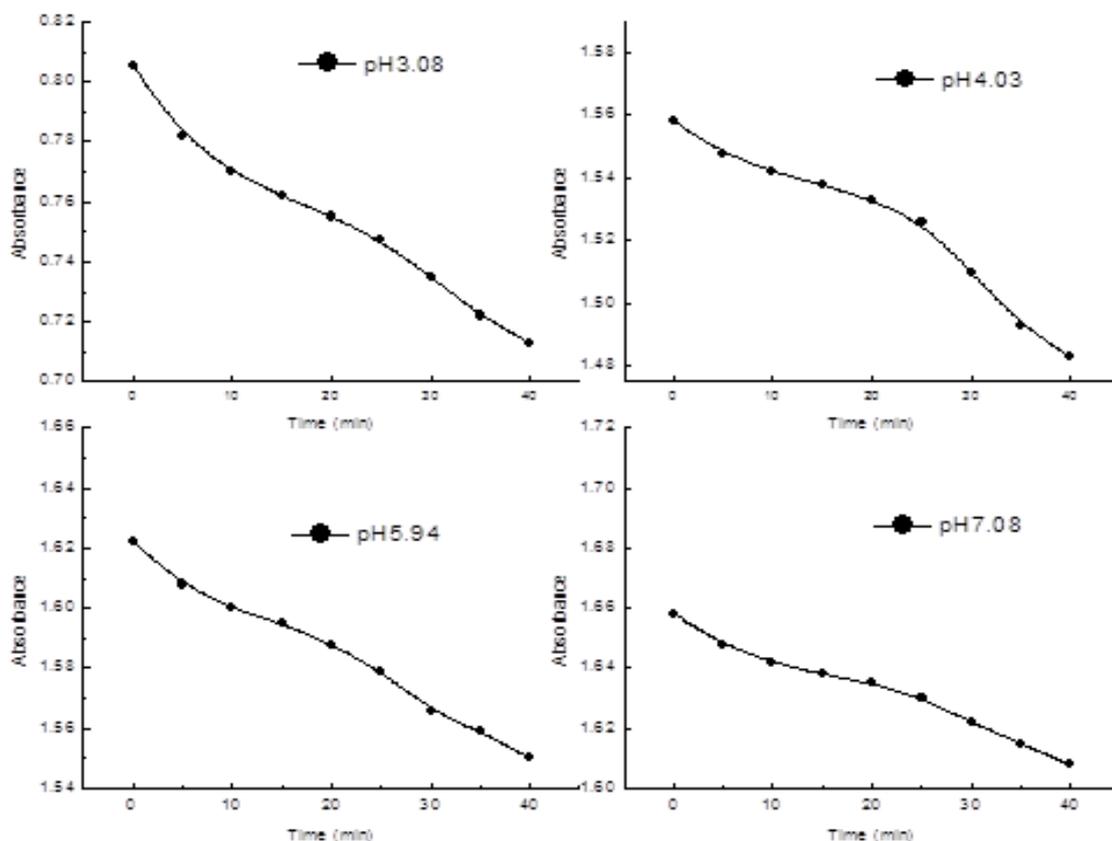


Figure 6: The disappearance of the color of EY solution with illumination time of UV_A light at different pH

concentration varies with pH therefore it is necessary to check the validity of the Beer-Lambert law and find out the molar absorption coefficient at different pH. For that reason at a particular concentration of EY, the absorbance was measured at four different pH. Similarly, the molar absorption coefficient of four different EY solutions was calculated from the corresponding absorbance vs. concentration plots. As the absorbance decreases with decreasing the pH of EY solution in the same way the molar absorption coefficient decreases with decreasing the pH of EY solution (Figure 5).

Although the photodecolorization and photodegradation of organic dyes are not the same things they are related. It is considered that the photodecolorization of EY solution is proportional to its photodegradation. [11]. With UV light irradiation, at a particular concentration of EY the initial rate of photo-degradation increases with decreasing the pH (see Fig. 6 and Table 1). After 40 minutes of irradiation of UV_A light, the photodegradation of EY solution at pH ≈ 3 was only 11% (Figure 6 and Table 1). The illumination of dye solution by UV_A light initiates the generation of kinetically important oxidizing radicals in the low pH range. These radicals ultimately lead to the degradation of EY to CO₂, H₂O, Br⁻(aq.), and Na⁺(aq.). In the pH range of the dye solution above 7, UV_A light causes hardly any degradation (Table 1). The initial rate of decolorization of EY increases with lowering the pH. This was also observed in Fenton's process [13]. The decrease of the initial rate of decolorization or the decrease of the percentage of decolorization of Eosin Y under UV light irradiation with pH suggests that the electron transfer process, which causes the degradation, becomes increasingly difficult as the initial pH of the solution increases.

Table 1: Influences of pH on initial rate and percentage of decolorization of EY solution with UV_A light

The pH of EY solution	Initial rate of decolorization (molL ⁻¹ min ⁻¹)	Percent of decolorization (%)
3.08	1.76×10 ⁻⁷	11.43
4.03	1.00×10 ⁻⁷	5.29
5.94	0.60×10 ⁻⁷	4.32
7.08	0.50×10 ⁻⁷	3.01

Conclusions

Photodegradation of EY dye in homogeneous media certainly depends on the pH of the solution. At low pH (3.08) without the presence of any photocatalyst, the

percentage of degradation of EY is about 12. Though this quantity is small but not negligible. It decreases with increasing the pH of the solution. At neutral media (pH = 7.08) the photodegradation is almost negligible. There is no effect on the absorbance of EY solution at the basic pH range. The initial rate of decolorization also increases with increasing the pH of the solution. This is because the electron transfers process, causing the degradation, becomes increasingly difficult as the initial pH of the solution is decreased.

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