Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2018, 7 (1): 144-150

(International Peer Reviewed Journal)

Sonolytic Degradation of Eosin Yellow

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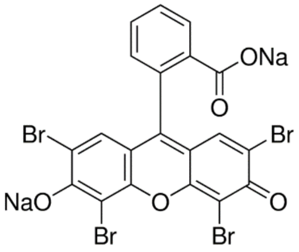
Accepted on 19th December 2017, Published online on 27th January 2018

ABSTRACT

Ultrasound response method is used to study degradation of eosin yellow in aqueous media in ultrasound fast cleaner. It was observed that the colour removal efficiency was influenced by pH, hydrogen peroxide, concentration, frequency of ultrasound. It was found that the dye degradation followed apparent first order kinetics. The rate constant increased by decreasing dye concentration and was affected by the pH of the solution with the highest degradation obtained at 7.5 pH and period of exposure was 90 min. The best and optimum condition for degradation of eosin yellow are developed. Process of degradation was followed spectrophotometrically at maximum wavelength of 517nm. A tentative mechanism is porposed for Sonochemical degradation method has been discussed.

Graphical Abstract:



Structure of eosin yellow

Keywords: Eosin yellow, Hydrogen peroxide, Sonolytic degradation.

INTRODUCTION

Eosin Y, a heterocyclic dye containing bromine atoms, is used in the fields of dyeing, printing, leather, printing ink and fluorescent pigment, etc. The direct release of wastewater containing Eosin Yellow will cause serious environmental problem due to its dark color and toxicity [1]. Synthetic dyes are extensively used in several industries including textile, paper, printing, cosmetics and pharmaceuticals [2-4]. The chemical effects of sonication arise from acoustic cavitation, namely the formation, growth and explosive collapse of bubbles in a liquid, which produces unusual chemical and physical environments. The collapse of bubbles generates localized ‘‘hot spots’’ with transient temperature of about 5000 K and pressures of about1000 atm [5]. Under such extreme conditions, water molecules dissociate into $^{\cdot}OH$ radical and H

radical. The radical species can either recombine or react with other molecules to induce sonochemical degradations. In the literature, several studies about the degradation of dye in aqueous media have been reported [6-10]. The photocatalytic degradation of organic pollutant is having a direct relevance in water remediation treatments. Many physical and chemical method treatment of textile waste waters, such as biological treatment, adsorption, coagulation, electro-coagulation, sonication, ozonation, the Fenton process, photo-chemical oxidation and chemical oxidation are studied well. The commonly used waste water treatment process includes absorption, oxidation, biological methods [11-19]. A simple mechanism for radical formation and depletion, during sonication of water is given below [20,21].

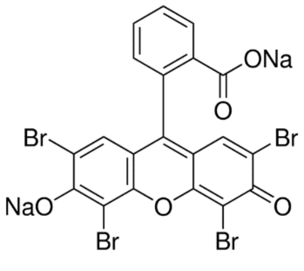
$$H_2O \rightarrow {}^{\cdot}OH + {}^{\cdot}H \text{ (Pyrolysis)}$$
$${}^{\cdot}OH + {}^{\cdot}H \rightarrow H_2O$$
$$2{}^{\cdot}OH \rightarrow H_2O + {}^{\cdot}O$$
$$2{}^{\cdot}OH \rightarrow H_2O_2$$

Eosin Y is used in cosmetics, pharmaceuticals, textiles as tissue stain, vital stain, and counter stain with hematoxylin. It is also used in special culture media [22,23]. Among most of dyes 10–15% of the dyes are lost in the effluent during dyeing process [24,25]. From the literature survey it is revealed that degradation of eosin yellow in ultrasound waves is not explored yet. On the basis of dyeing process, textile dyes are classified as reactive dyes, direct dyes, disperse dyes, acid dyes, basic dyes and vat dyes.

MATERIALS AND METHODS

Chemicals and Materials: Eosin yellow was obtained from S.D Fine India Ltd. The molecular structure is shown in table -1. Hydrogen peroxide were bought was from FINAR India Ltd., and were used as received. The concentration of the dye solution was monitored using absorbance recorded on UV-visible double beam spectrophotometer (Thermo scientific-evolution 201). Ultrasound fast cleaner 30kHz and 60 kHz provided by Life Care equipments Pvt. Ltd. and pH meter (Systronics model no. EQ -361) are used. The stock solution of dye was prepared in double distilled water conductance 1.5 $\times 10^{-6}$ and pH 6.8. The deionized water was used to prepare the solution throughout this study. Absorbance was measured at different time intervals by UV-visible spectrophotometer and decrease in colour of the dye was monitored spectrophotometrically at wavelength of 517nm.

Table 1. Characteristics and chemical structure of eosin yellow

Name	EOSIN YELLOW
λ (nm)	517
Molecular weight (g/mol)	691.88
Chemical structure	

Procedure: 60mgL^{-1} Eosin yellow dye solution was used as sample for analysis –

(i) In the first beaker 60 mgL^{-1}dye solution was taken and was kept in visible light only.

(ii) In the second beaker 60mgL^{-1}dye solution was taken was exposed to ultrasound.

(iii) In the third beaker 60 mgL^{-1}dye solution and 1500 mgL^{-1}$H_2O_2$was takenand was kept in ultrasound fast cleaner.

After keeping these beakers for 2.5 h, the absorbance of solution in each beaker was measured with the help of UV visible spectrophotometer. No change was observed in first and second beakers while in third beaker absorbance has decreased.

Typical Run: It was observed that optical density decreases with increase in time of irradiation and a plot of absorbance v/s time was a straight line. It is indicated that the sonolytic degradation of eosine yellow followed pseudo-first order kinetics. The results of sonolytic degradation of eosine yellow are graphically represented in Fig. 1.

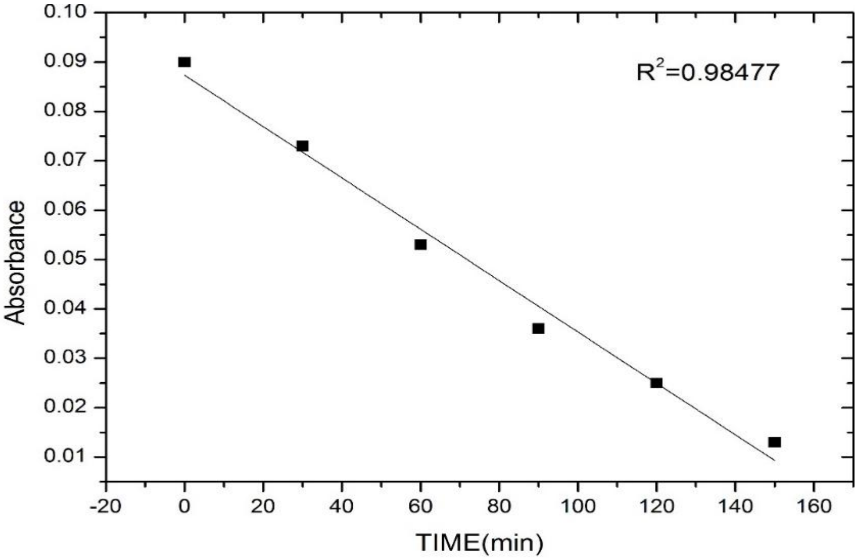


Fig 1. Typical run Standard curve of Eosin Y at wave length of 517nm.

Analysis: The discoloration yield is calculated as:

$$Y = 100\left(\frac{1 - A_{517}(t)}{A_{517}(0)}\right)$$

Where, Y= discoloration yield, $A_{517}(t)$ = absorbance of (t) time, $A_{517}(0)$ = absorbance of (0) time.

RESULTS AND DISCUSSION

Effect of different light source: The purpose of this experiment was to investigate the effect of light source on eosine yellow degradation. Degradation was observed in the dark, in solar light, artificial light in mercury lamp but in all these experiments lower or no degradation were observed.

Effect of dye concentration: Fig 2 showed that maximum discoloration of 60 mgL^{-1} Eosin yellow was observed at 90 min and colour removal rate was up to 61.49%. However when dye concentration was 20, 40, 80,100mg/L only 50.72%, 27.62%, 20.29%, 26.97% was obtained respectively. This can be explained that when dye concentration increases OH does not increase accordingly which causes the decrease in removal rate. High dye concentration reduces the permissibility of photon into high concentrated dye solution. The effect of concentration of dye 20 -100 mg L^{-1} have been also tested. The results indicated that the degradation of dye is much dependent on concentration of solution.

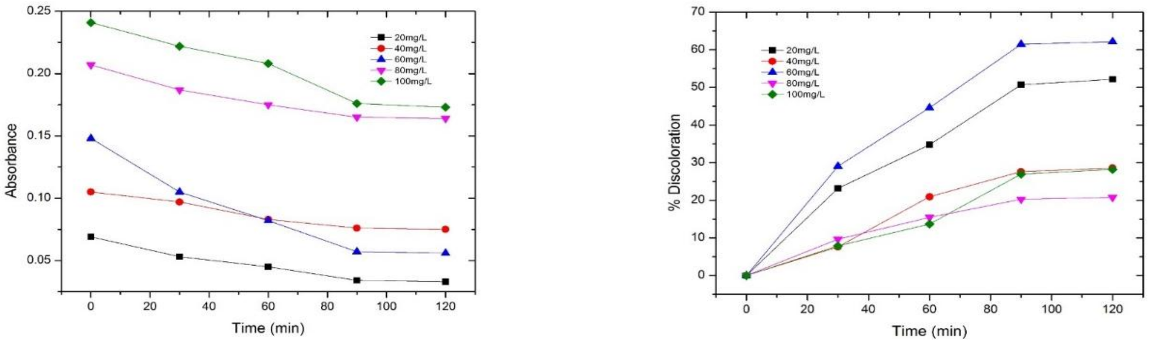


Fig 2. Effect of concentration on the degradation of Eosine yellow
[20-100mgL^{-1} of Eosin yellow, 1500mgL^{-1} of $H_2 O_2$, 7.5 pH, frequency of 30 kHz]

Effect of pH: Fig.3 showed that maximum discoloration of dye was seen with 7.5 pH at 90 min and colour removal rate was up to 43.94%. However when dye concentration was at 2.5 pH, 5.0 pH, 10.0 pH, 12.5 pH only 15.29 %, 37.50%, 30.19%, 30.95% of colour removal was observed. Hence pH 7.5 was found to be optimum pH for this study. In wastewater treatment, the pH value is very crucial parameter and always be taken into consideration. In this case, sonication depend on the pH of the aqueous media to be treated; experiments were conducted in the pH range 2-10. It was noted that degradation of eosin yellow is quite fast in the solution at 7.5 pH.

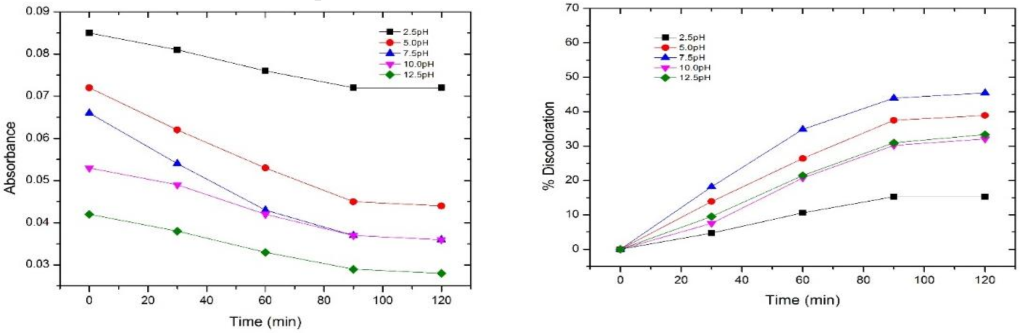


Fig 3. Effect of pH on the degradation of Eosin yellow
[60mg/L of Eosin yellow, 1500mg/L of $H_2 O_2$, 2-10 pH, frequency of 30 kHz].

Effect of $H_2 O_2$ addition: Hydrogen peroxide decomposition in water leads to the generation of hydroxyl radicals. The effect of hydrogen peroxide was studied to illustrate the implications of hydroxyl radicals on decomposition rate. Fig.4 shows the degradation curve for eosin yellow at different $H_2 O_2$concentration. Significant enhancement was observed in degradation rate for ultrasound system at 1500 mgL^{-1}.

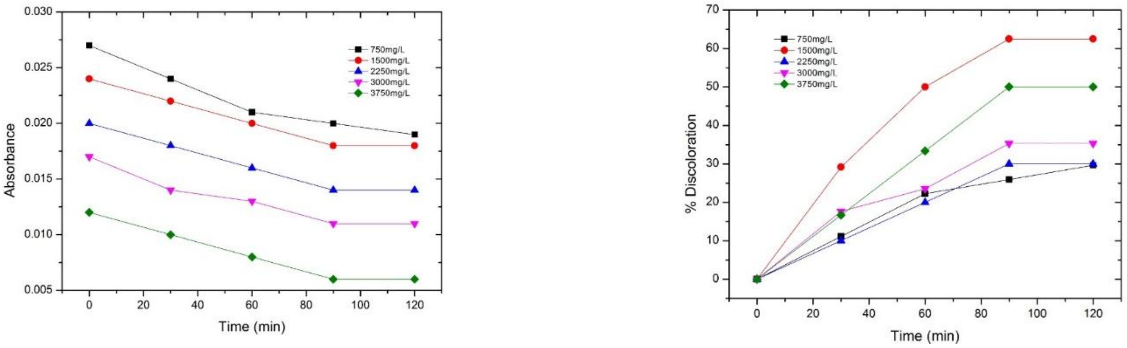


Fig 4. Effect of hydrogen peroxide on degradation of Eosin yellow
[60mgL^{-1} of Eosin yellow,750-3750mg/L of$H_2 O_2$, 7.5 pH, frequency of 30 kHz]

Discoloration of 1500mgL^{-1}$H_2\,O_2$ was almost complete at 90 min and colour removal rate was up to 62.50%. However, when dye with 750, 2250, 3000, 3750 mgL^{-1}H_2O_2 was used only 25.93%, 30.0%, 35.29%, 50.0% of colour removal was obtained respectively. Sonolytic degradation of eosin yellow was studied in the range of 750mgL^{-1} to 3750mgL^{-1} of $H_2\,O_2$. Results indicate that the rate of the degradation increases in the oxidant concentration because more peroxide ions are available for the oxidation. But by further increasing $H_2\,O_2$ the rate of discoloration decreases because of recombination.
Recombination effect is given by following equation
So due to scavangerging effect, the rate of discoloration does not increase significantly after 1500mgL^{-1} of $H_2\,O_2$.$OH + H_2O_2 \rightarrow H_2O + HO_2$

$$HO_2 + {}^{\cdot}OH \rightarrow H_2\dot{O} + O_2$$

$${}^{\cdot}OH + {}^{\cdot}OH \rightarrow H_2O_2$$

Effect of ultrasound frequency: The whole data was repeated at 60 kHz frequency. But maximum discoloration was observed at 30 kHz. At higher frequency more${}^{\cdot}OH$ radicals are formed but are removed due to recombination effect.

Kinetics study: Results showed that degradation of eosin yellow by $H_2\,O_2$assisted sonochemical process fitted approximately to pseudo-first order kinetics. The related regression coefficients are given in graph.
The related kinetic equation is given as

$$\ln C/C_{0\,=}\ -Kt$$

where C$_0$ intial concentration of dye & and C is dye concentration of time t. t is sonolysis time and k is rate constants (min^{-1}). The linear plot between ln A/A$_0$& sonolysis time is given Fig 5.

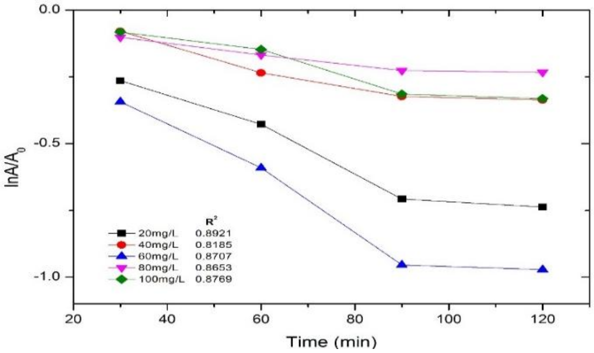


Fig 5. Change of absorbance of eosine yellow under ultrasound
20-100 mg L^{-1} of eosine yellow, 1500 mg L^{-1}$H_2\,O_2$, 7.5 pH, frequency 30 kHz

Mechanism: Unusual physical and chemical environments are produced due to sonication. Chemical effects produced due to sonication lead to acoustic cavitation which further lead to formation of bubbles, growth of bubbles and collapse of bubbles. The collapse of bubbles generate localized hot spots which has transient temperature of about 5000K and pressure of 1000 atm [5]. Under such extreme condition water molecules dissociated in to${}^{\cdot}OH$ radicals and${}^{\cdot}H$ radical. This radical species can recombine or rate was other molecules. Some of the reaction is given as under.

Sonicated Water and Generation of Radicals:

$$H_2O \ \rightarrow H^{\cdot} + OH$$
$$Dye + {}^{\cdot}OH \rightarrow Oxidized\ product$$
$$H_2O^{)))} \rightarrow {}^{\cdot}OH + \ H_2\ O_2$$
$$H^{\cdot} + {}^{\cdot}OH \rightarrow H_2O$$
$$H^{\cdot} + O_2 \ \rightarrow HO_2$$
$$2\,{}^{\cdot}OH \rightarrow H_2\ O_2$$
$$2H\dot{O}_2 \rightarrow O_2 + O_2$$

$$H\dot{O}_2 +^{\cdot}O_2^- + H^+ \rightarrow H_2\ O_2 + O_2$$
$$H\dot{O}_2 +^{\cdot}OH + H^+ \rightarrow H_2O + O_2$$
$$O_2^- +^{\cdot}OH \rightarrow OH^- + O_2$$
$$H_2\ O_2 + H^- \rightarrow^{\cdot}OH + H_2O$$
$$O_2 \rightarrow 2\dot{O}$$
$$0 + H_2O \rightarrow 2^{\cdot}OH$$

Again OH radical is active radical for sonochemical degradation.

APPLICATIONS

Eosin yellow dye widely uses in textiles, cosmetics, pharmaceuticals industries etc. The effluents of dye are harmful not only to humans but also to aquatic life. By using this method, this dye can be degraded easily in effluents and in less time as well as at low cost.

CONCLUSIONS

This study demonstrated that the Eosin yellow industrial textile dye in effluents can be removed sonolytically and degradation reaction showed apparent first-order kinetics. The whole process was dependent of pH, concentration of H_2O_2 and dye concentration. Higher removal of dye content is observed at lower initial dye concentration. H_2O_2 played an important role that is well defined by changing concentration of H_2O_2. Sonodegradation of Eosin yellow increased at 60mgL^{-1} concentration of dye solution, 1500mgL^{-1}H_2O_2, 7.5 pH, under ultrasonic frequency of 30 kHz at 90 minutes conditions.

ACKNOWLEDGEMENTS

Author is thankful to UGC for giving Maulana azad national fellowship. Award letter no. and date - F1-17.1/2015-16/MANF-2015-17-GUJ-55548/ (SA-III/Website)

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