

PHOTOCATALYTIC DEGRADATION OF EOSIN Yellowish DYE IN AQUEOUS SOLUTION USING TITANIUM DIOXIDE AS CATALYST: IMPACT OF VARIOUS PARAMETERS AND KINETIC STUDY

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ABSTRACT

Eosin Yellow, a type of heterocyclic dye consisting of bromine atoms, finds its applications in various industries, such as dyeing, printing, leather industry, and fluorescent pigment production. This study investigated the process of photocatalytic degradation of eosin yellowish dye in water solutions using titanium dioxide as a catalyst, as well as its degradation in the absence of semiconductors. The effect of specific factors including initial concentration of eosin yellowish dye and photo catalyst (TiO₂), pH levels, and temperature on this degradation process was also tested. The results showed that increasing the concentration of TiO₂ improved the above dye degradation. Moreover, it is found that shifting the pH from acidic to alkaline conditions enhanced dye degradation. This study also determined the order of eosin yellowish dye using integral rate laws and established that the degradation of the dye follows a first-order reaction at 517 nm.

KEYWORDS: Dyeing, Semiconductors, PH, Temperature, First order.

INTRODUCTION

The environmental impact of eosin yellowish dye arises from its widespread use in various industries, and the potential of its release into the environment through manufacturing processes and waste disposal. One of the main concerns is water pollution, as the dye can be discharged as wastewater, causing contamination of water bodies (Ihab *et al.*, 2018; Seema & Babulal, 2009). This can affect ecosystems and harm aquatic life due to its synthetic and potentially toxic components. Additionally, some components of the dye may have the ability to bioaccumulate in food chain, posing risks to organisms higher up in the food web. Improper disposal practices of materials containing eosin yellowish dye particles can also cause environmental contamination, whether through direct dumping or incineration, releasing harmful substances into air, soil, or water. To mitigate these impacts, it is essential for industries to implement proper wastewater treatment procedures, adopt sustainable

practices, and explore greener alternatives with lower toxicity and reduced environmental persistence (Ahmed *et al.*, 2011; Fabian *et al.*, 2022). Furthermore, regulatory measures and responsible handling and disposal practices are crucial in minimizing the environmental footprint of eosin yellowish and ensuring its safe use in a manner that preserves environmental integrity.

In recent days, there has been significant research about the photo-degradation of dyes and organic pollutants. Many studies have been done on photocatalysts and their effect on dyes in aqueous solutions (Raad & Salah-Aldin, 2019; Rabindranathan *et al.*, 2003). However, the photodegradation of dyes was done using different techniques, such as photochemical, chemical, or thermal processes (Shinwar *et al.*, 2015). Moreover, different dyes are sold in markets as coloring materials. The classification of dyes depends on their structure, application, and color. In general, their classification is according to the chromophoric group in molecules, such as fast green, toluidine, Congo

red dyes, azo dyes, etc. (Rauf *et al.*, 2011). Degradation of dyes has been successfully done in the last few decades using the catalysis process that is motivated by TiO₂ (Zaied & Bellakhal, 2009). The holes are examined by the hydroxyl group in solution to produce the hydroxyl radical OH, which tends to be a strong oxidizing agent and can produce the-oxidation of organic pollutants (Parsa *et al.*, 2011; Daneshvar *et al.*, 2003). Eosin Yellowish dye is a heterocyclic compound dye which contains bromine atoms. It has various applications in different fields; because of its vivid color, it is practically used in printing ink, dyeing, leather industry, printing, etc. (Gouvêa *et al.*, 2000). In addition, Eosin Yellowish is effective for depolarization in biological methods because of its complex aromatic structure and stability (Daneshvar *et al.*, 2003). In this paper, the photo-degradation of this dye in aqueous solutions has been studied accompanied with investigating the effect of some parameters such as different temperatures and pH on the degradation process. Different concentrations were used in the presence of ultraviolet light and titanium dioxide as a catalyst. Finally, the

comparison of degradation of dye has been done as shown in table

2. EXPERIMENTAL PART

In general, experiments have been carried out at different concentrations of eosin yellowish dye and photo catalyst (TiO₂) under different temperatures and PH. Moreover, ultraviolet light with and without semiconductor TiO₂ rutile has been used in this study. The solvent is composed of an aqueous solution. A spectrophotometer was used to measure the optical density (absorbance) of eosin yellowish during its photo-degradation, at 517 nm.

Chemical:

-The eosin yellowish dye was supplied by (BDH) Gurr Certistain, VWR International Ltd, Poole, BH15 1TD, England, Microscopy (C.I. 45380). Table 1 Shows the Characteristics of eosin yellowish dye.

- Titanium dioxide was supplied -by- Alpha chemika™ Mumbai 200002, India.

- Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Fisher-Scientific, UK.

Table (1):-Properties-of-eosin-yellowish-dye.

Chemical-Name	--2-((2,4,5,7-tetrabromo-6-oxido-3-oxo-3H-xanthen-9-yl)) .benzoate
Chemical- ----formula	C ₂ OH ₈ Br ₄ NaO ₅
Molecular mass	692
Color	red crystalline powder
λ_{max}	517 nm

Molecular Structure

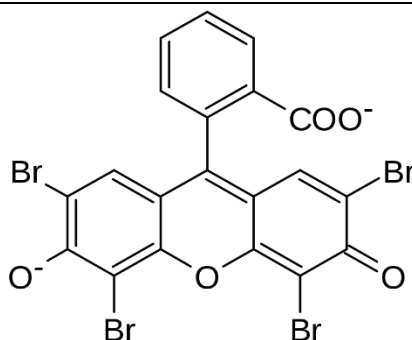


Table (2): Shows the effect of various-photo catalysts on the degradation of photo catalytic eosin yellow.

No.	photo catalyst	Light source	Illuminati on time	Degradation % or/ and rate	References
1	Poly (pyrrole-co-aniline)-coated TiO ₂ /nanocellulose composite(P(Py-co-An)-TiO ₂ /NCC	Solar Light Irradiation	90 min	92.3% of dye was degraded	Anirudhan & Rejeena 2015)
2	La-ZnO-GO	Solar Light Irradiation	210 min	89% of dyes was degraded	Samuel, <i>et al.</i> , 2018).
3	ZnO	UV light with eight UV tubes (Philips) of 18 W each using a wavelength of 365 nm.	120 min	Concentration data semilogarithmic plots draw a straight line. For commercial ZnO, fitted line correlation constant was found to be R ² = 0.9731	(Ihab <i>et al.</i> , 2018).
4	NaCl 0.05M	Electrocoagulation Fe-Fe electrode pair	30 min	100% color changed at pH of 5.6, current density of 20mA/cm ² ,	(Jayanthi <i>et al</i>)
5	1000 ppm of EY , 0.1 g portion of the pineapple peels	Removal of EY by the PP is that of a combined chemisorption and physisorption mechanism.		The removal of EY by PP is an endothermic and a spontaneous process. The maximum adsorption capacity was found to be 11.76 mg/g without any modification of the adsorbent.	Fabian <i>et al.</i> , 2022).

Apparatuses used:

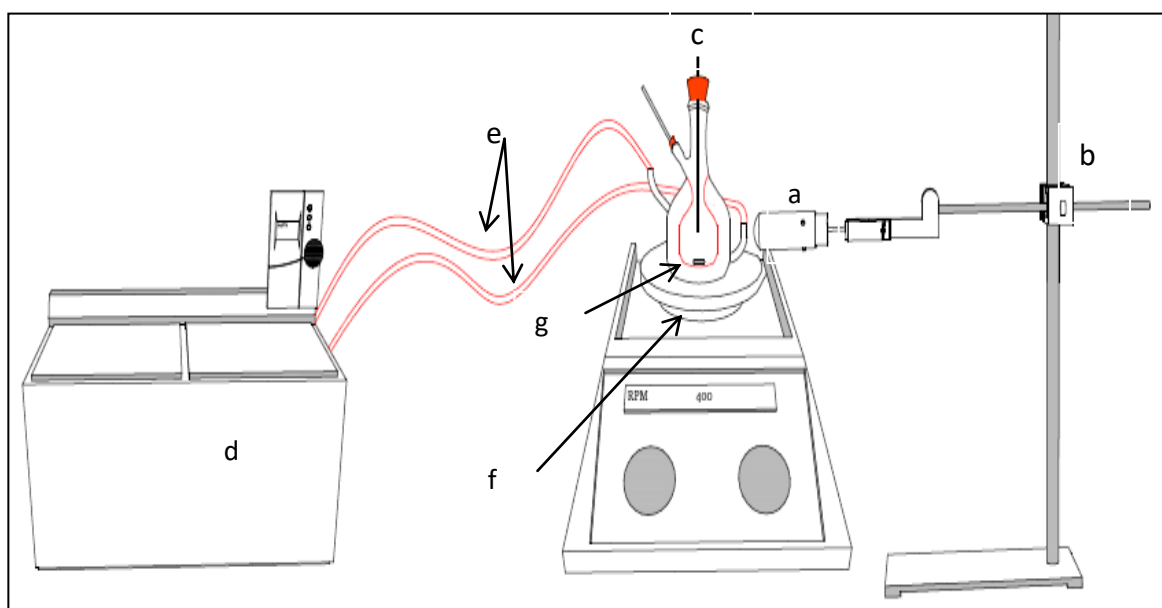
- 1- Centrifuge type KUBOTA 2010.
- 2- Ultraviolet Visible Spectrophotometer type perkin Elmer lambda 25.
- 3- Visible spectrophotometer (Jenway, 6700)
- 4- Ultraviolet (UV) GERMICIDAL lamp wavelength 254 nm power 8 watt.
- 5- pH meter mettle Toledo of accuracy level ± 0.01 .

- 6- Magnetic stirrer and magnetic bar .type lab teach.

Photo catalytic diagram:

All section of photolytic process is-illustrate in-the-figure 1.

- a) UV. (Ultra violet) light as light source.
- b) Clamp & Stand.

**Fig. (1):** Diagram of photo-degradation system

- c) Photolytic-cell-is-made-from borosilicate.
- d) Thermostat.
- e) Inlet and Outlet tube.
- f) Magnetic stirrer.
- g) Magnetic-bar.

Experimental procedures

The stock solution of eosin yellowish dye was prepared and diluted to different concentrations, and from each concentration, 500 ml was added into a reactor with a volume of 600 ml inside a box in a dark place using UV lamp as a light source, as shown in Figure 1. In this study, different weights of TiO₂ (0.01, 0.05 g/dm³) were added to eosin yellowish dye as a

photocatalyst. A syringe with a volume of 5 ml was used to collect samples at each specific time and transfer them to the ultraviolet-visible spectrophotometer type Perkin-Elmer Lambda 25, which was used to analyze the collected samples.

RESULT AND DISCUSSION

Various experiments involving ultraviolet light were conducted to investigate its effects. Figure 2 illustrates the spectral exchange in the ultraviolet-visible range during the degradation process of 20 ppm eosin yellowish dye at 20°C over different time intervals.

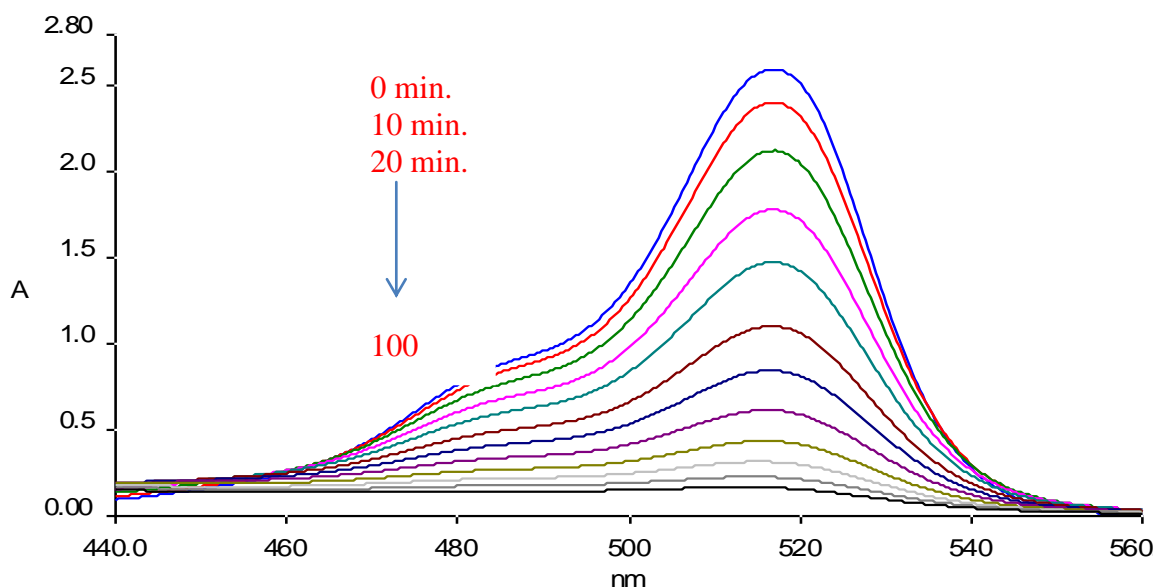


Fig. (2): Ultraviolet Visible Spectral-for 20 ppm-of eosin-yellowish degradation in different times.

Effect of initial concentration

The experiments were carried out using ultraviolet light to analyze the behavior of eosin yellowish at various concentrations (5, 10, 15, and 20 ppm). **Eosin yellowish degradation at the above concentrations** in aqueous solutions was performed using Ultraviolet (UV) water sterilization lamps with a power output of 8 watt as a light source. Figure 3 shows a visual illustration of the experimental setup and the results obtained from these investigations.

At wavelength 517 nm, the optical density (absorbance) of eosin yellowish was measured among the degradations by spectrophotometer. **The lowest concentration of eosin yellowish (5 ppm) showed high transparency to light compared to the highest concentration of dye (20 ppm) which showed less transparency to light, indicating a better dye degradation at lower concentrations.** (Shinwar *et al.*, 2021; Shinwar *et al.*, 2022; Shinwar *et al.*, 2023; Mohammed & Shinwar, 2020).

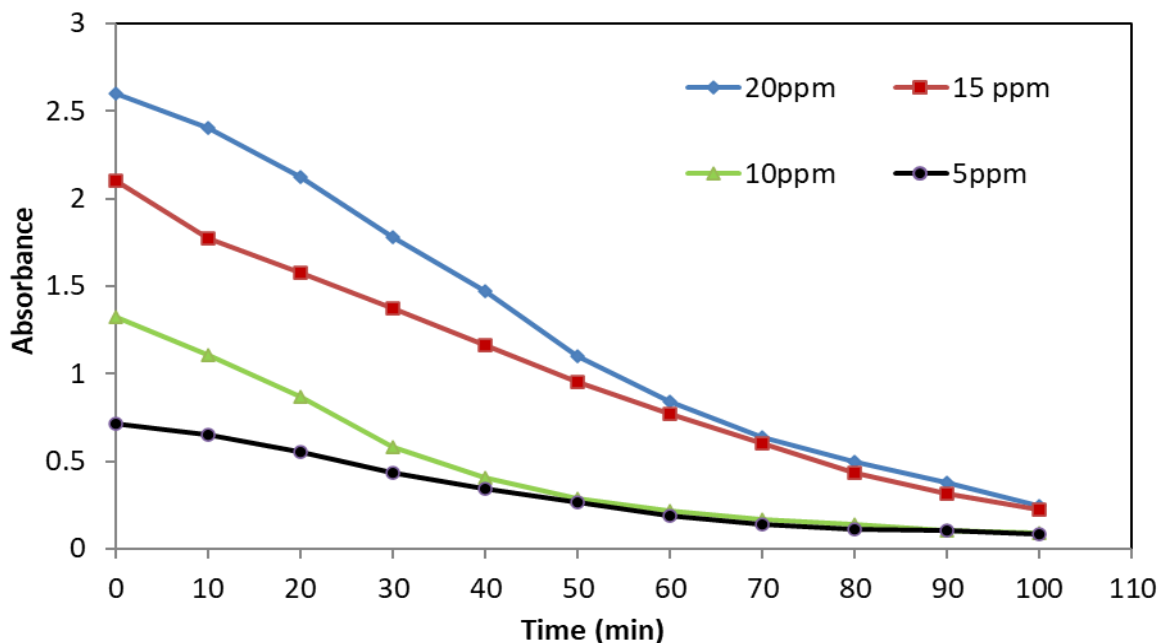


Fig. (3): Shows the optical density of eosin yellowish dye using ultraviolet light at wavelength of 517, and 20 C°.

Tables (3): Shows the rate constant of degradation of 5 ppm of eosin yellow dye at different temperatures, using UV radiation at 517 nm.

Peak (nm)	k at 20 C° (min ⁻¹)	k at 25 C° (min ⁻¹)	k at 30 C° (min ⁻¹)	k at 35 C° (min ⁻¹)
517	0.0515	0.0529	0.066	0.072

Tables (4): Shows the optical density of degradation of 5 ppm of eosin yellowish dye at different temperatures using UV radiation at 517 nm.

Time (min.)	20 C°		25 C°		30 C°		35 C°	
	O.D	Ln (O.Do/ O.Dt)	O.D	Ln (O.Do/ O.Dt)	O.D	Ln (O.Do/ O.Dt)	O.D	Ln (O.Do/ O.Dt)
0	0.694	0	0.666	0	0.648	0	0.635	0
5	0.578	0.182898	0.516	0.255183	0.447	0.371332	0.394	0.477274
10	0.419	0.504601	0.35	0.643357	0.225	1.05779	0.092	1.931836
15	0.25	1.021011	0.214	1.135314	0.156	1.424035	0.076	2.122892
20	0.174	1.383417	0.155	1.457865	0.125	1.645577	0.062	2.326491
25	0.146	1.558865	0.132	1.618488	0.085	2.031239	0.06	2.35928
30	0.129	1.68266	0.107	1.828461	0.064	2.315008	0.041	2.740053
35	0.117	1.780298	0.097	1.926579	0.054	2.484907	0.031	3.019638
40	0.1	1.937302	0.09	2.00148	0.049	2.58207	0.03	3.052428

Determination-of-order-of degradation-

Determination order by using the integral equation: The integral rate laws have been used to determine the order of eosin yellowish. The correlation coefficient is measured with the most fitted linear curve, as shown in figure 4 (Atkin &

Julio, 2006). Equation (1) illustrates the first-order equation. (Shinwar *et al.*, 2021; Shinwar *et al.*, 2022; Shinwar *et al.*, 2023; Mohammed & Shinwar, 2020; Haydar *et al.*, 2018).

$$\text{Rate} = k[A] \tag{1}$$

Tables (5): shows the optical density of degradation of 5 ppm eosin yellowish dye using UV radiation at 517 nm.

Time (min.)	Absorbance at 517nm	Ln (O.Do/ O.Dt)
0	0.694	0
5	0.578	0.182898
10	0.419	0.504601
15	0.25	1.021011
20	0.174	1.383417
25	0.146	1.558865
30	0.129	1.68266
35	0.117	1.780298
40	0.1	1.937302

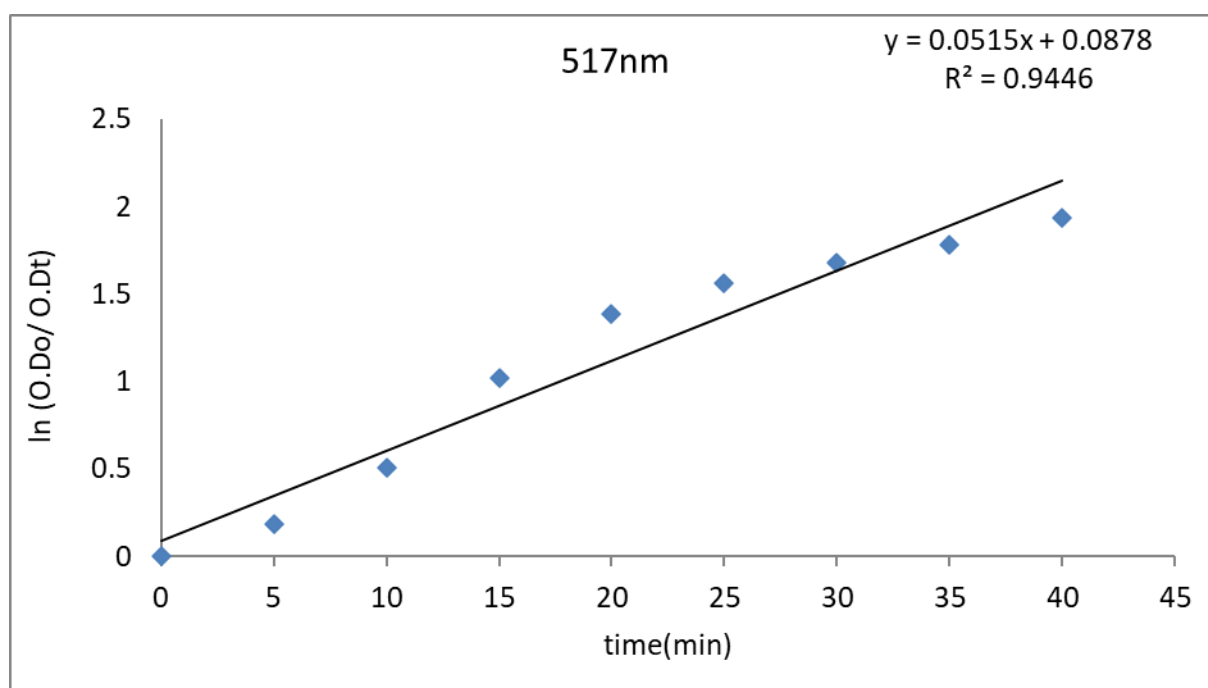


Fig. (4): Degradation-of 5-ppm-of eosin yellowish-dye for first-order plot using UV light at 517 nm, and- 20 C°.

Determination of order of eosin yellowish dye degradation by using a differential equation: The rate of eosin yellowish dye degradation is determined by the studied peak at 517 nm. The plotting log-log graphical method, showed in Figure 5, The

first order of peak at 517 nm degradation was found for this dye (Shinwar *et al.*, 2021; Shinwar *et al.*, 2022; Shinwar *et al.*, 2023; Mohammed & Shinwar, 2020; Haydar *et al.*, 2018).

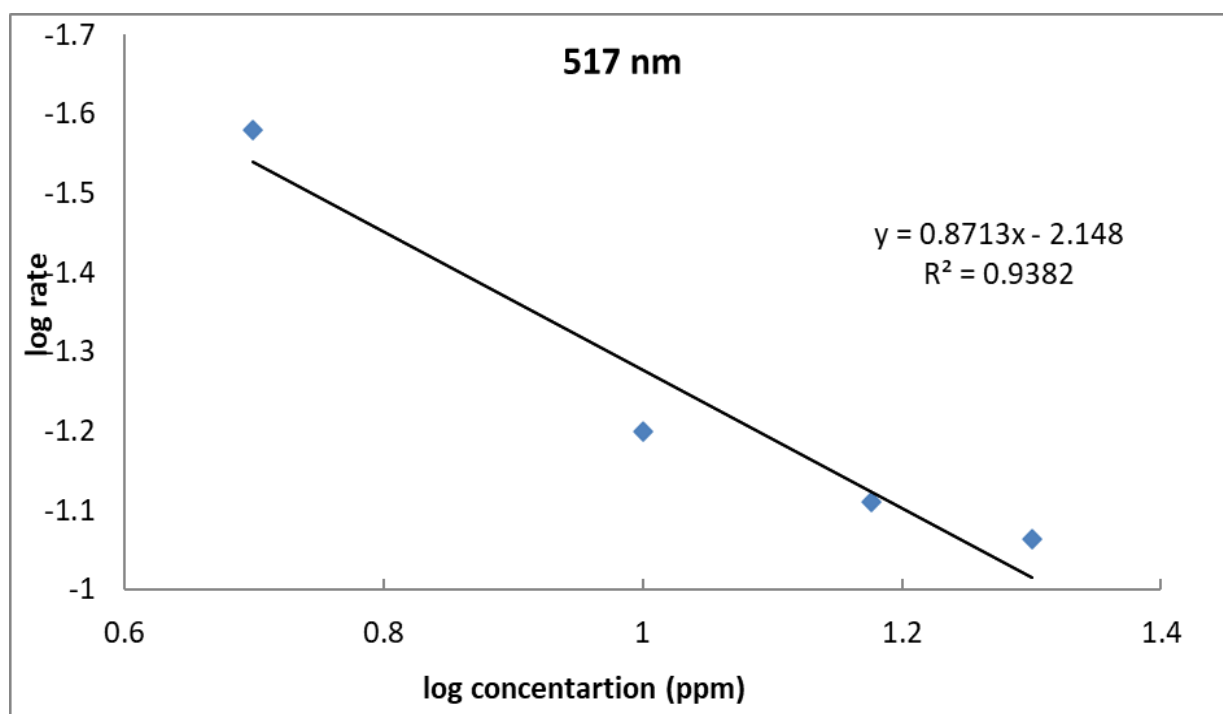


Fig. (5):-Log-rate-with log-(conc.)-graphical-plot-for-eosin yellowish dye degradation (517 nm) by ultraviolet light at 20 C°.

Effect of catalyst dose

Photo-degradation of eosin yellowish dye have-been-measured-using UV light with catalyst (TiO₂)-0.01 and 0.05 gm/dm³. In this process the semiconductor (catalyst) has important parameters, and by increasing the concentration of catalyst, will activate more sites on the photo catalyst, which generates more OH[•] radicals. Moreover, the degradation of eosin yellowish dye was performed inside a box with an Ultraviolet (UV) GERMICIDAL lamp at wavelength of 254 nm at power 8 w. (Ahmed *et al.*, 2011). Also, 5 ml of sample was centrifuged at 300 rpm before measuring the optical density using spectrophotometer. Respectively, the

absorbance of eosin yellowish dye was measured by spectrophotometer at 517 nm. As shown in Figure 6, more degradation occurs by increase the amount of TiO₂ catalyst also increase the removal efficiency. (Salam *et al.*, 2018). The reason is due to the production of more OH[•] radicals as a result of increasing the catalyst concentration. The maximum level of degradation of eosin yellowish dye was catalyst by using 0.05 g/dm³. Using higher concentrations of catalyst did not enhance degradation of eosin yellowish dye as it will prevent penetration of UV light through the dye aqueous solution (Bandara & Ranasinghe, 2007).

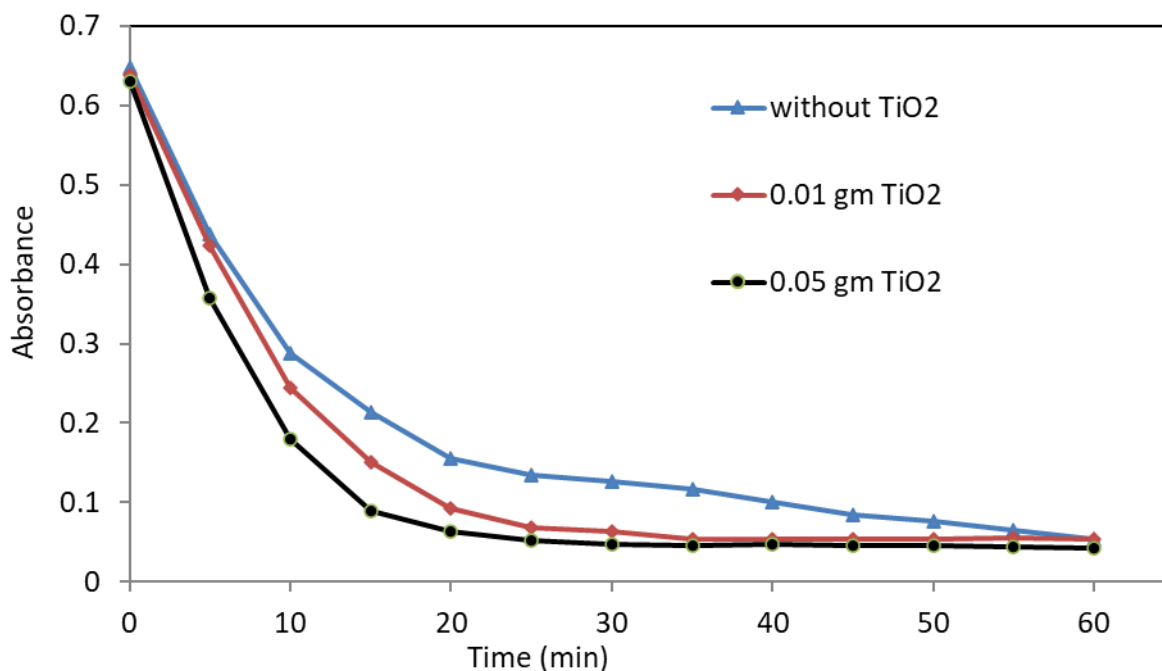


Fig. (6): Shows the effect of using 0.01 and 0.05 g/dm³ of TiO₂ on degradation of 5ppm of eosin yellowish dye, using Ultraviolet light at a Wavelength of 517nm.

Tables (6): Shows rate constant of degradation of 5 ppm of eosin yellowish dye using different concentrations of catalyst at 517 nm of UV radiation.

Peak nm	k at 20 C° (min ⁻¹) without catalyst	k at 20 C° (min ⁻¹) with 0.01g TiO ₂	k at 20 C° (min ⁻¹) with 0.05g TiO ₂
517	0.0515	0.0653	0.071

By increasing temperature and catalyst, the rate constant of degradation of this dye was changed and not remain constant, the rate constant increased when we added catalyst as shown in Table (5). Because the rate constant effected by temperature and catalyst. (Shinwar *et al.*, 2021).

Effect of Ph

A series of experiments have been performed by using ultraviolet light with different values of pH to determine the effect of pH on photo-degradation of eosin yellowish dye. The pH range 3-12 was tested in this research to show the effect of pH. The-effect-of-pH-on degradation was illustrated in Figure-(7)-which by increasing pH, the degradation becomes faster. The degradation rate increases in high alkaline medium at pH 12 (Elaziouti *et al.*,

2011).-The pH of solution is-the-key-factor-for the photo catalytic reaction and can have an effect-on- the- adsorption- of -dyes -on -the photo catalyst surface. The- adsorption ability-of eosin yellowish dye on- the- TiO₂ catalyst-surface- was- very- high- at- acidic solution (pH = 3),-but-dropped-when-the solution pH rise from-3, 6, 9 and 12 and no adsorption occurred at pH = 12 (Shinwar *et al.*, 2021; Shinwar *et al.*, 2022; Shinwar *et al.*, 2023; Mohammed & Shinwar, 2020; Haydar *et al.*, 2018).

The pH of the medium determines which type of dye is adsorbed on the surface and how it is degraded. The variation of pH has to be visualised in terms of the surface characteristics of the semiconductor as a function of pH (Mohammed & Shinwar, 2020).

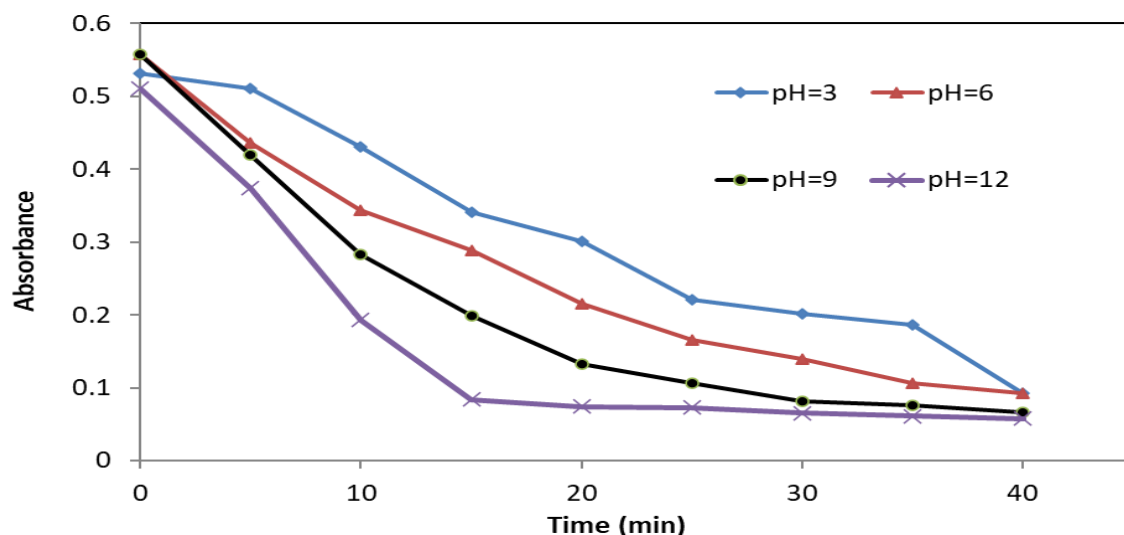


Fig. (7): Shows the effect of using pH values of 3, 6, 9 and 12 on degradation of 5ppm of eosin yellowish dye, using by Ultraviolet light at a wavelength of 517.

Effect of different temperatures

Sequence of experiments were performed to investigate the effect of-using different temperatures (20, 25, 30 and 35) on the degradation of eosin yellowish dye under UV-light at 517 nm. As shown in figure 8 the degradation enhanced by increasing the

temperature because the kinetic energy of the molecules increase collide with photon of the ultraviolet light become faster and more degradation occurs (Shinwar *et al.*, 2021; Shinwar *et al.*, 2022; Shinwar *et al.*, 2023; Mohammed & Shinwar, 2020).

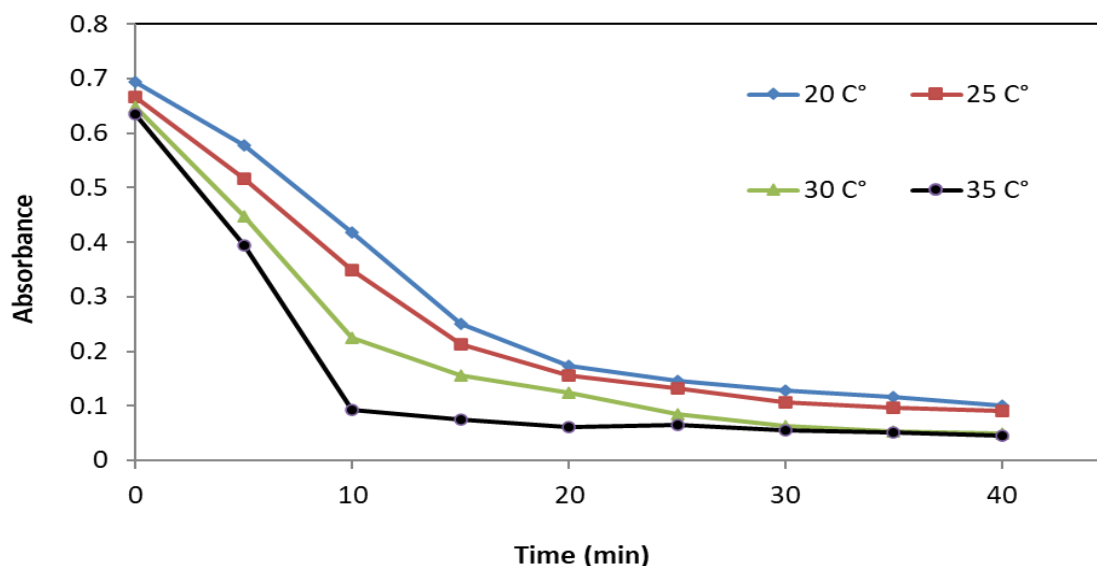


Fig. (8):-Degradation-of 5-ppm of eosin yellowish-dye-using 517 nm of UV-light-at-different temperatures.

CONCLUSION

TiO₂ UV-light irradiated catalysts have been used to examine the eosin yellowish dye aqueous solutions photo catalytic degradation. All in all, eosin yellowish was- degraded in aqueous solution using ultraviolet-light-in-the presences of TiO₂-as-a photo catalyst. However, -the-degradation-of eosin yellowish dye was **affected**-by various- parameter such as initial

concentration of eosin yellowish dye, TiO₂ dose, different temperature and pH of solution. Moreover, state of being made better for eosin yellowish dye degradation was 5 ppm concentration which is the major- effective on the degradation. Furthermore, the removal of eosin yellowish dye was found enhanced by increasing the TiO₂ quantity at 0.05 gm/dm³. In addition, it was also found that increasing of temperature improve the degradation of dye used

in this study. As well as the color during degradation was disappeared to be colorless at the end of degradation. By the same token, the order has been measured and found first order kinetic at 517 nm.-The-rate constant-gradually rises when temperatures increase, as well by adding-TiO₂ the-rate-constant-heighten-as-appears-in-table 3 and 6. Finally, the-eliminated-efficiency-of eosin yellowish dye-was encouraging-in-the-high-basic-medium-at pH 12-and-arrive the most possible value. In basic medium, hydroxyl-radical-•OH-an-oxidant be able to be formed, therefore intensify- the- rate-of- photo degradation-of-the-dye.

ACKNOWLEDGMENT AND DEDICATION

This paper is dedicated to the soul of my sister “**Ronak**”, unfortunately, she passed away on September 2022 due to lung cancer.

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پوخته

Eosin Yellow پیک دهیت ژ بویاغه کا ئاویتی ئەندامی کو گەردا برۆمی تیدا ههیه و بکاردهیت دبواری بویاگرن و نسخرن و کۆتال هتد.... . شکاندنا ئەقئ بویاغئ دناف ئاقیدا دگهل هاندەرەکن وهکی دوانه ئۆکسیدی تیتانیۆم و بی هاندەر هاتیه خاندن. کاریگه ریا هوکارین جیاواز ژ خهستیا ئەقئ بویاغئ و برا جیاواز ژ هاندەری و pH ین جودا و ههروهها کاریگه ریا زیده کرنا پلا گهرمی هاتیه خاندن و پیقان ب ریکا ئامپیرئ UV-Visible spectrophotometer ل درپژیا شه پۆلی 517 nm . ب زیده کرنا برا TiO_2 پتر ئەف بویاغه دهیته شکاندن. گهورینا pH ژ ناهه نده کا ترش بو ناهه نده کا تفت شکاندنا ئەقئ بویاغئ دی باشتر لیکهت. پلا کارلیکی بو ئەقئ بویاغئ هاتیه ده رئیخستن ب ریکا integral rate laws . جوولا ئەقئ بویاغئ هاتیه ده رئیخستن و شکاندنا ئەقئ بویاغئ دکارلیدا پله ئیکه first order د 517 nm.

الخلاصة

Eosin Yellow صبغة حلقيه غير متجانسة تحتوي على ذرات بروم تستخدم في المجالات منها الصباغة ، والطباعة ، والجلود ، والأصباغ الفلورية ، وما إلى ذلك. تمت دراسة التحلل التحفيزي الضوئي لصبغة Eosin Yellow في محلول مائي مع محفز ثاني أكسيد التيتانيوم وكذلك بدون هذه المحفزات. ثم تم فحص تأثير العوامل المختلفة مثل تراكيز عده لصبغة Eosin Yellow ، واستخدام جرعات مختلفة لهذه المحفزات، حيث درجة الحموضة ودرجة الحرارة المختلفة وقياس هذه النتائج تم بواسطة جهاز UV-Visible spectrophotometer عند 517 نانومتر. وجد ان عند زيادة جرعة TiO_2 راينا ان ازالة هذه الصبغة يتحسن. بالإضافة إلى ذلك ، تغيير وسط المحلول من الوسط الحامضي إلى الوسط القاعدي يؤدي إلى تحسين ازالة صبغة Eosin Yellow. ومن ثم تم فحص درجة التفاعل لهذه الصبغة Eosin Yellow بواسطة قوانين المعدل المتكامل (integral rate laws) . تم فحص درجة التفاعل لهذه صبغة وجد أن التحلل كان من الدرجة الأولى (first order) عند 517 نانومتر.