

The Investigation of color removal by Photocatalytic and Chemical Oxidation of Red Reactive Textile Dye

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**Abstract**

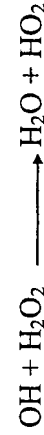
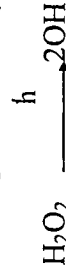
The photocatalysis and other advanced oxidation processes (AOPs) have been used to investigate the degradation of red reactive textile dye in aqueous solutions via exposing to direct sun-light for ٢٤ hours in direct sun light.

Results showed that photocatalysis (TiO<sub>2</sub> and ZnO suspensions) processes were more effective than photochemical (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) and H<sub>2</sub>O<sub>2</sub> and chemical (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>) oxidation. The best value of degradation reached ٧٥% mineralization, which was achieved with ZnO / dye suspension (١ gm/l). The concentration of dye was measured in the  $\lambda_{max}$  of UV-visible spectrum of dye (٧١٥ nm). The work involves the studying of kinetics of photodegradation of dye by using UV light emitting from medium pressure mercury lamp at ٢٦٥ nm and ٢٥°C<sup>0</sup> in the stable light intensity and presence of TiO<sub>2</sub> and ZnO catalysts, it has been found that the photodegradation constant of aqueous solution of dye (١٠٠ mg/l) was  $٢,١١ \times ١٠^{-٤} \text{ sec}^{-١}$  and  $١,٨٢ \times ١٠^{-٤} \text{ sec}^{-١}$  respectively. It was also found the initial rate of photodegradation of dye increases as its initial concentration increases which was higher in the presence of TiO<sub>2</sub>. The adsorption constant and reaction rate constant of dye over TiO<sub>2</sub> and ZnO in same conditions was (٢٥,٧ mg/l and  $٢,٦٢ \times ١٠^{-٢} \text{ mg/l.s}$ ) for TiO<sub>2</sub> and (١٨,٢ mg/l and  $٢,٢٢ \times ١٠^{-٢} \text{ mg/l.s}$ ) for ZnO respectively.

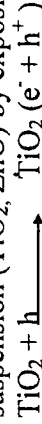
### Introduction

Various degradation processes were used for the removal of hazardous contamination of organic compounds in water and wastewater. The existence of textile dyes in surface water or effluents of wastewater may lead to the pollution of sources of drinking water and cause environmental problems as a result of large quantity of aqueous waste generated by textile industry. Utilizing of sunlight, which has a good intensity in UV region, can perform the degradation of water pollutants. There are two spectra for UV range of the solar spectrum, the smaller refers to direct UV (radiation without scattering) and its value reaches  $22 \text{ Wm}^{-2}$  between 300 and 400 nm, the bigger correspond to the global UV (direct diffuse) and its value is  $46 \text{ Wm}^{-2}$  in the same range (1).

Advanced oxidation processes (AOPs) were developed for degradation of pollutants in water via generating the hydroxyl radical.  $\text{UV}/\text{H}_2\text{O}_2$  is one of common advanced oxidation processes, which generate the hydroxyl radical as in the following mechanism (2,3):

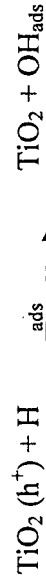


The highly degradation hydroxyl radical can be produced by semiconductor (SC) suspension ( $\text{TiO}_2$ ,  $\text{ZnO}$ ) by exposing to UV radiation (4,5,6) as in following steps:

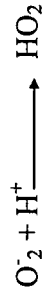


$e^-$  : electron

$h^+$  : hole



Oxygen can trap the electron and generate the hydroxyl radical as following (7,8,9):



The hydroxyl radicals attack the organic molecules and abstract a hydrogen atom as following mechanism:





Advanced oxidation processes were used for the removal of reactive textile dyes<sup>(11)</sup>, azo dyes<sup>(1)</sup>, benzene<sup>(11)</sup>, and acetone<sup>(11)</sup>, also the use of photocatalysis processes were used for the degradation of herbicides<sup>(12)</sup>, ammonium salts<sup>(13)</sup>, chlorophenol<sup>(13)</sup> and methylene blue dye<sup>(11)</sup>.

## The Experimental part

### Materials :

Photocatalyst titanium dioxide (Degussa P25 mainly anatase 70%) with surface area of 50m<sup>2</sup>/g and 27-30nm mean size<sup>(14)</sup>. Riedel - De Haen, supplied zinc oxide 99,99%, 50 percent hydrogen peroxide (Aldrich). Ferrous chloride (BDH) was used to preparation of Fenton's reagent. Red reactive dye is commercial one and supplied by cotton textile factory at Diwaniya City.

### Instruments

Shimadzu UV-visible 160 spectrophotometer was used to determine the concentration of undegraded dye molecules. Medium pressure mercury lamp 150 W (MPML) supplied by PHYWE was used in all kinetics experiment, which fitted with a focusing lens to make a parallel beam of radiation. MPML emits UV light in range 202-274 nm with maximum intensity at 250nm.

### Photocatalytic Degradation

The photocatalytic experiments were performed using 50 ml Pyrex flasks placed under direct sun light for 2 hrs contains the aqueous suspensions of TiO<sub>2</sub>/dye ZnO/dye. The dye concentration was 100 mg/L in all experiments and photocatalyst concentration was 1-1 g/l. The suspensions were magnetically stirred through the irradiation in air. The rate of degradation of dye was measured by spectrophotometer at  $\lambda_{max}$  (210nm) of dye after filtration with Millipore filters (0.45µm) to remove the catalyst. The primary experiments were performed in the dark in the same conditions. Also same experiment were carry out in the presence of direct sun light without photocatalyst.

### Fenton and Photo-Fenton system

Fenton and photo-Fenton homogenous solutions were prepared by mixing of H<sub>2</sub>O<sub>2</sub>/iron molar ratio between 10 and 20<sup>(15)</sup> and (100mg/l) of dye at pH 2,8 because to Fenton's system has a maximum catalytic activity at this pH<sup>(11)</sup>. The solution exposed to direct sun light for 2 hrs with open to air. The disappearance of dye was measured at its  $\lambda_{max}$  of dye using spectrophotometer.

### Effect of hydrogen peroxide

Hydrogen peroxide in the range 0-20 mg/L was added to aqueous dye solution (100 mg/L), then the solution exposed to direct sun light for 2 hrs. The concentration of dye was measured at its  $\lambda_{max}$  using spectrophotometer. some experiments were carry out in the dark but no positive results were obtained.

### Kinetics experiment

The kinetics of photodegradation experiments of dye were performed by using UV light from medium pressure mercury lamp (HPML) with two lens at 365nm by using Chance OVI glass filter which was calibrated with the Cintra 5 double beam spectrophotometer, the calibration showed that the transmitted light was concentrated at 365nm. The light intensity was measured by actinometry technique described by Hatchard and Parker<sup>(19)</sup> which was  $1.5 \times 10^{-6}$  einstein/l.s. The kinetic experiments were performed in the presence of TiO<sub>2</sub> and ZnO at 25 with continuous agitation by magnetic stirrer and air bubbling (10cm<sup>3</sup>/min). The temperature of suspensions was maintained by using regulator thermostat.

The UV -visible spectrophotometer was used to measure the concentration of undegraded dye at its  $\lambda_{max}$  after removing the catalyst by centrifuge. Several experiments were carried out in presence of TiO<sub>2</sub> and ZnO in the dark or irradiation without photocatalyst.

### Results and Discussion

Textile dyes are common compounds present in industrial effluents that are resisting the natural degradation. The possible purification systems for textile wastewater are oxidation processes, which remove the color of dyes.

Advanced oxidation processes (AOPs) which generate a highly chemical oxidation witnessed a huge expansion through the recent years hence the to degradation of a wide number of organic and inorganic contaminants in polluted waters. The disadvantages of advanced oxidation processes are that the final products of degradation process may have toxicity. The color removal of the dye obtained in the presence work was measured by recording the absorption spectra of solution by using auto-scan spectrophotometer (Shimadzu UV-160) with wavelength range 400-800 nm, 3 ml of irradiated solution was taken from the flasks and the undergraded dye was measured at  $\lambda_{max}$  (715 nm). Figure (1) shows the absorption spectrum of aqueous solution of red reactive textile dye.

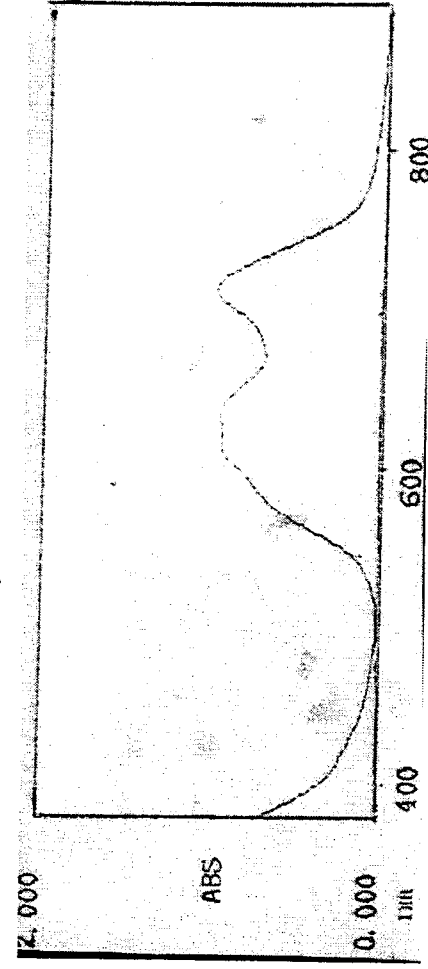


Figure (1) visible spectrum of aqueous solution of dye

### Effect of photocatalytic processes

Heterogeneous Photocatalytic with semiconductors such as TiO<sub>2</sub>, ZnO... have some specific applications, which show high activity of water contaminants degradation. The TiO<sub>2</sub> and

ZnO are effective in the presence of  $H_2O_2$ . The photodegradation processes need the presence of oxygen and water which react with  $h_+$  and  $e^-$  to form hydroxyl radicals and  $H_2O_2$ . Table (1) shows the energetic properties of photocatalysts used in present study. Figure (2) shows the relation between the color decrease (%) with photocatalyst concentration, it is clear that the efficiency of decolorization is directly proportional to slurry concentration, which meaning the increasing of surface area of photocatalyst and hence the activity is increased. Figure (3) shows the concentration gradient of dye with increase of photocatalyst concentration. The dark experiments show that no degradation was detected, also the illumination experiments carried out without photocatalyst show no positive effect. so the presence of photocatalyst, light intensity, pH of medium, concentration of substrate, time of irradiation, radius of catalyst particles, and air are essential parameters in photodegradation process (4).

The best value in the present work was obtained with ZnO (1,0 gm/l) which reached 94,9% of color removal, The ZnO and  $TiO_2$  semiconductors have the same energetic properties (table 1), but ZnO have more efficiency in visible region.

Table (1) common energetic properties of  $TiO_2$  and ZnO (13)

| SC      | $VB(V_{\text{L}}NHS)$ | $CB(V_{\text{L}}NHS)$ | $BG, ev$ | $BG, nm$ |
|---------|-----------------------|-----------------------|----------|----------|
| $TiO_2$ | +3,1                  | -0,1                  | 3,2      | 387      |
| ZnO     | +3,0                  | -0,2                  | 3,2      | 387      |

### Effect of Fenton and Photo-Fenton systems

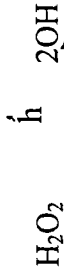
Figure (4) shows the relation between color decrease of dye and the ratio of  $H_2O_2/Fe^{+2}$  system. In the Fenton and Photo-Fenton processes the pH must be adjusted to 3,8. The degradation efficiency of dye is enhanced by effect of hydroxyl radicals, which is generated by Fenton's reagent ( $H_2O_2/Fe^{+2}$ ),  $Fe^{+2}$  ions are rapidly oxidized to  $Fe^{+3}$ . In present work the Fenton and Photo-Fenton processes have showed lower degradation efficiencies in comparison with heterogeneous  $TiO_2$  and ZnO photocatalysis.

Figure (5) shows the decreasing of dye concentration as the  $H_2O_2/Fe^{+2}$  increases. The literatures (1,2,3) indicate that the Fenton and photo-Fenton systems have a good efficiency when the solution of contaminants irradiated with UV-light.

The use of high ferrous ion produces a large quantity of  $\cdot OH$  through a short time causing fast consumption of hydrogen peroxide, but the use of low ferrous ion quantity causes the redox cycles of iron to be in an effective manner.

### Effect of hydrogen peroxide

Figure (1) shows the decolorization efficiency (%) of dye in the presence of  $H_2O_2$ /sun light, the results indicated that the  $H_2O_2$  has a higher effect on water pollutants when UV-light is used as source of radiation to photolytic hydrogen peroxide activation:



Factors that affect the decolorization efficiency by  $\text{H}_2\text{O}_2$  involve light intensity, color intensity,  $\text{H}_2\text{O}_2$  concentration, time of irradiation and pH. The values obtained from present shows that the use of  $\text{H}_2\text{O}_2$  with sunlight is extremely slow. Sometimes the color removal was negligible. The dark experiments do not give any degradation. Which indicate that the light (UV especially) is a main factor in the generate of free radical from  $\text{H}_2\text{O}_2$ .

### Kinetics of Photodegradation process

The photodegradation of dye in presence of  $\text{TiO}_2$  and  $\text{ZnO}$  under UV illumination show high activity comparison with sunlight, which correlate with energetic properties of  $\text{TiO}_2$  and  $\text{ZnO}$  (table 1). It is known that photocatalyst loading and initial substrate concentration have clear effect on the efficiency of rate of photodegradation reaction process.

The photodegradation rate follows the first order kinetics as figure (7) shows, from the slope of this figure, the photodegradation constants at surface of  $\text{TiO}_2$  and  $\text{ZnO}$  were  $2.01 \times 10^{-4} \text{ sec}^{-1}$  and  $1.82 \times 10^{-4} \text{ sec}^{-1}$  respectively. Figure (8) shows the concentration gradient of dye over surface of  $\text{TiO}_2$  and  $\text{ZnO}$ , it is clear that the degradation efficiency over  $\text{TiO}_2$  is more than  $\text{ZnO}$ .

The degradation kinetics of dye follows Langmuir-Hinshelwood (L-H model) mechanism with reaction rate  $r$  varying proportionally to the fraction of photocatalyst surface covered by the dye  $\theta$  (21,22).

$$r = K r_0 = (K C K_r / 1 + K C)$$

Where  $K_r$  is the reaction rate constant,  $K$  is adsorption constant,  $C$  is the dye constant at any time. In dilution solutions  $K C \ll 1$  and the reaction rate is of apparent first order, while in higher concentration  $K C \gg 1$  and the reaction rate is zero order, so:  $\ln C_0 / C = K_r K t$

The relation between the reciprocal ( $1/r_0$ ) and reciprocal of the initial concentration ( $1/C_0$ ) is linear as figure (9) shows, from the slope and intercept, adsorption constant  $K$  and reaction rate constant  $K_r$  can be calculated respectively, which were ( $25.2 \text{ mg/l}$  and  $2.63 \times 10^{-2} \text{ mg/l.s}$ ) for  $\text{TiO}_2$  and ( $18.2 \text{ mg/l}$  and  $2.22 \times 10^{-2} \text{ mg/l.s}$ ) for  $\text{ZnO}$ . The plot of initial rate Photodegradation ( $r_0$ ) versus initial dye concentration ( $C_0$ ) is showed in figure (10). Table 2 shows that the apparent first order rate constant of dye photodecomposition in presence of  $\text{TiO}_2$  and  $\text{ZnO}$  decrease as the initial concentration is increased and the rate of photodecomposition is increased. This was also obtained previously (20,23).

Table (2) The initial rate ( $r_0$ ) of dye photodegradation at different initial concentration ( $C_0$ ) over photocatalysts  $\text{TiO}_2$  and  $\text{ZnO}$  [ $1 \text{ gm/l}$ ] at  $25^\circ\text{C}$  under UV illumination.

| Conc.m<br>g/l | $K_d \text{ sec}^{-1}$ |              | Calculated rate, mg/l.s |              | Observed rate mg/l.s |              |
|---------------|------------------------|--------------|-------------------------|--------------|----------------------|--------------|
|               | $\text{TiO}_2$         | $\text{ZnO}$ | $\text{TiO}_2$          | $\text{ZnO}$ | $\text{TiO}_2$       | $\text{ZnO}$ |
| 25            | 5.52                   | 5.21         | 0.0138                  | 0.0134       | 0.0143               | 0.0141       |
| 35            | 4.28                   | 4.07         | 0.0151                  | 0.0142       | 0.0156               | 0.0139       |
| 50            | 3.60                   | 3.22         | 0.0183                  | 0.0163       | 0.0179               | 0.0174       |
| 75            | 2.56                   | 2.45         | 0.0192                  | 0.0184       | 0.0193               | 0.0189       |
| 100           | 2.11                   | 1.82         | 0.0212                  | 0.0182       | 0.0243               | 0.0181       |
| 125           | 1.76                   | 1.64         | 0.0227                  | 0.0205       | 0.0231               | 0.0229       |

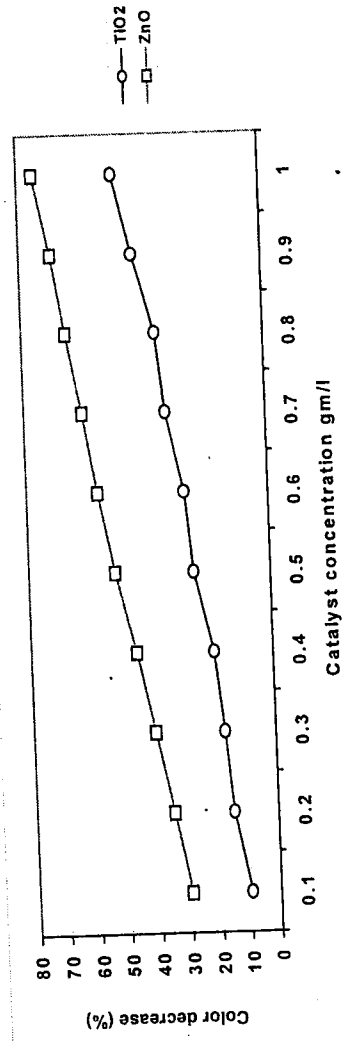


Figure (2) Effect of TiO<sub>2</sub> and ZnO concentration on color decrease of dye.

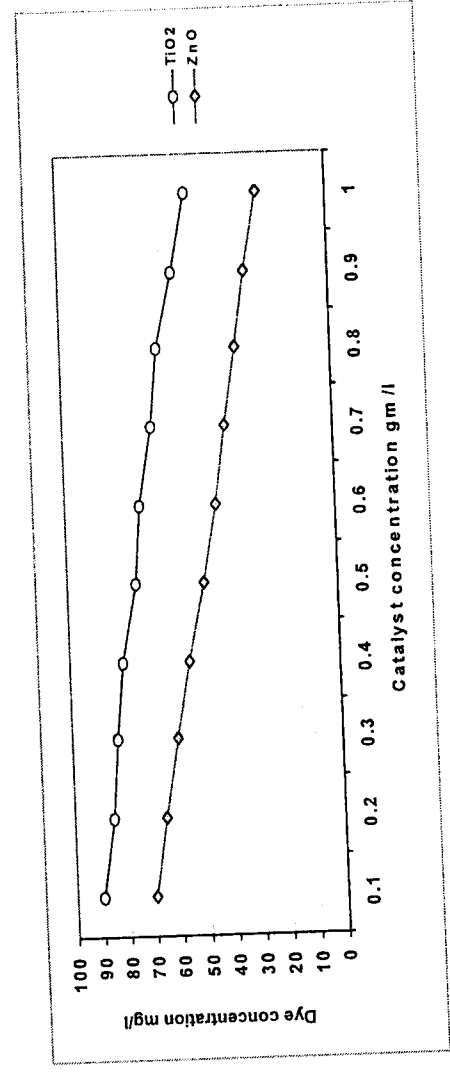


Figure (3) Degradation of dye by TiO<sub>2</sub> and ZnO treatment.

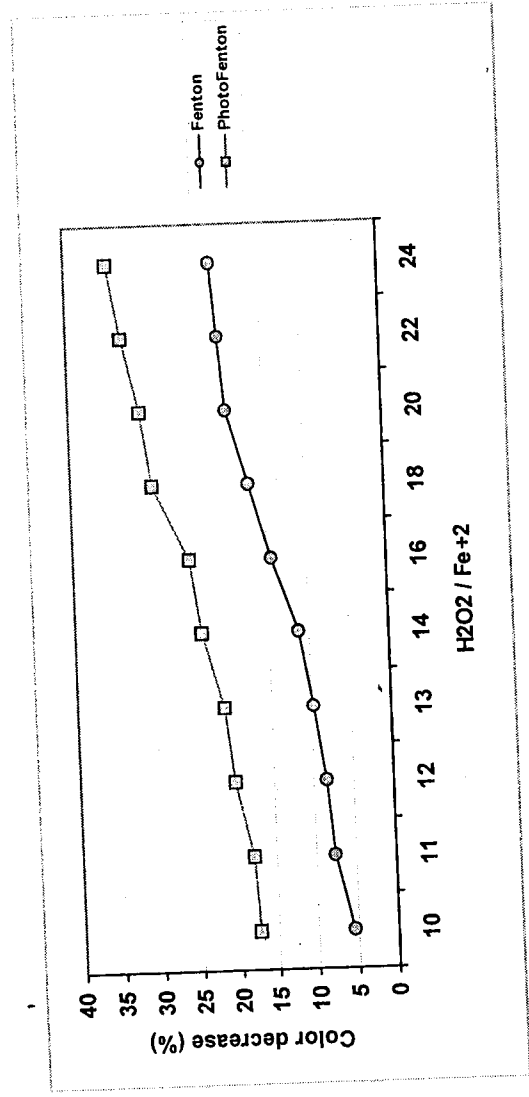


Figure (4) Effect of Fenton and Photo-Fenton reagent on color decrease of dye.

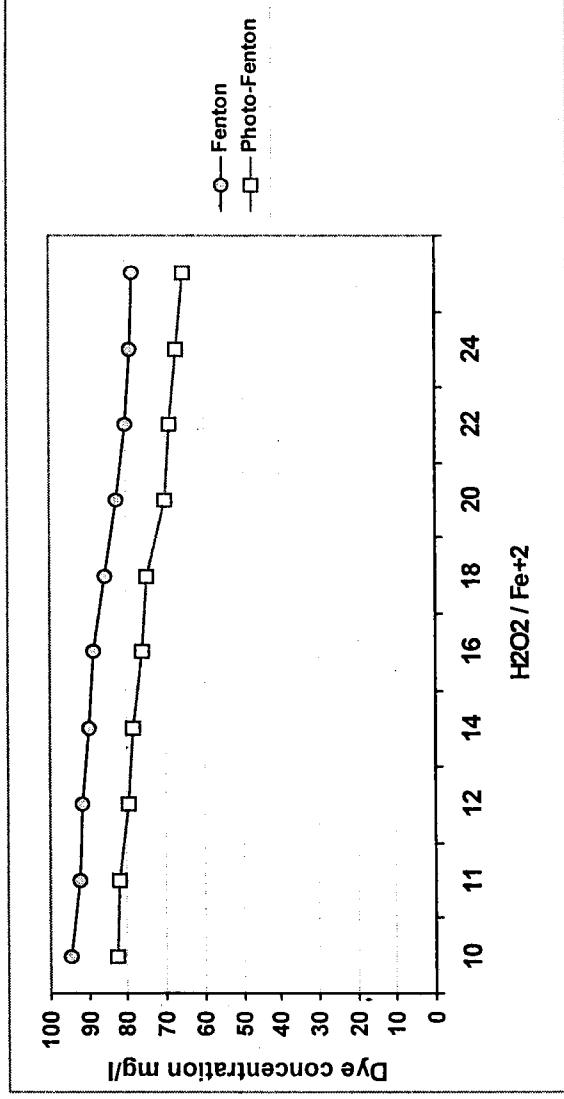


Figure (5) Degradeation of dye by Fenton and Photo-Fenton treatment.

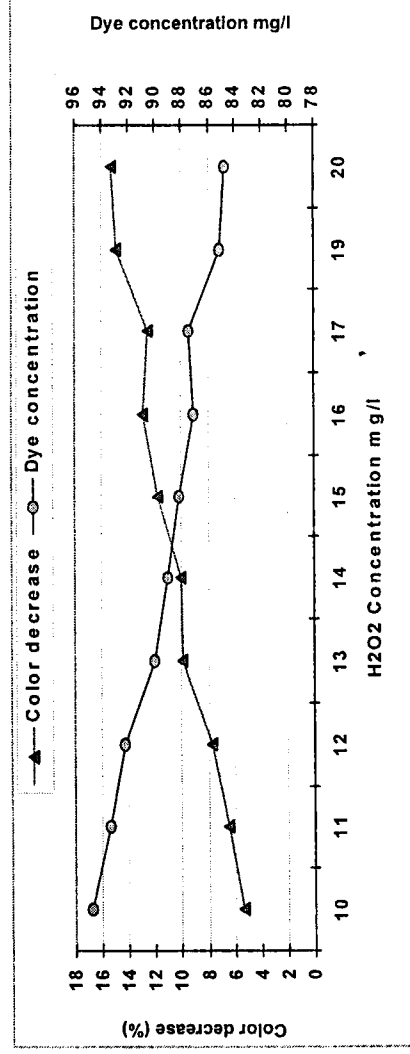
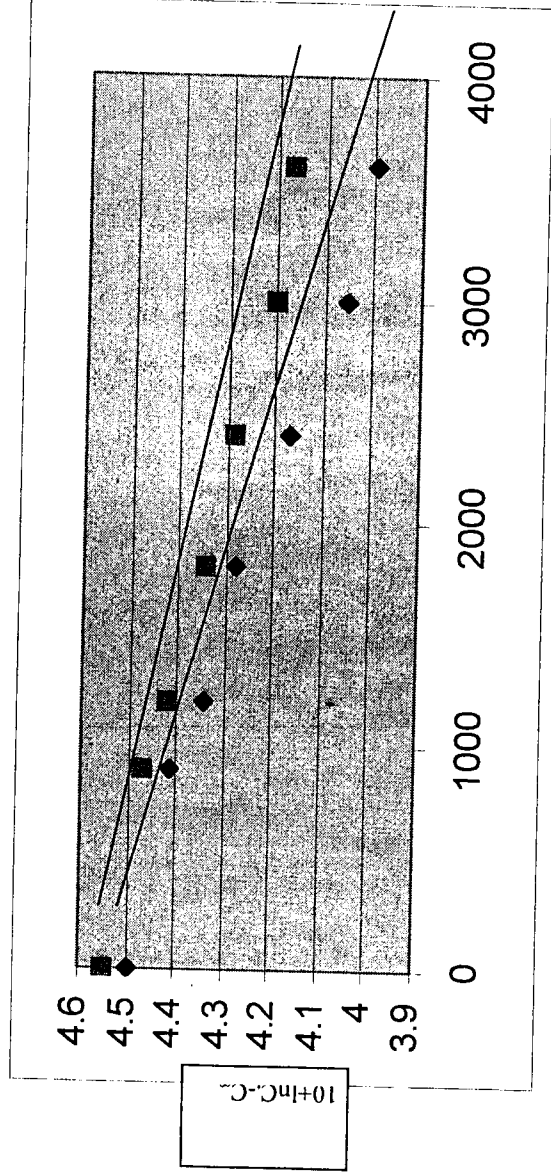


Figure (6) Effect of hydrogen peroxide concentration of color decrease and dye degradation.





Fig(7)plot of  $\ln C_t/C_\infty$  versus irradiation time for the photodegradation of dye (100mg/l) in aqueous suspension of  $TiO_2$  ( $\diamond$ ) and  $ZnO$  ( $\blacksquare$ ) [1mg/l] at  $25C^\circ$  under UV illumination.

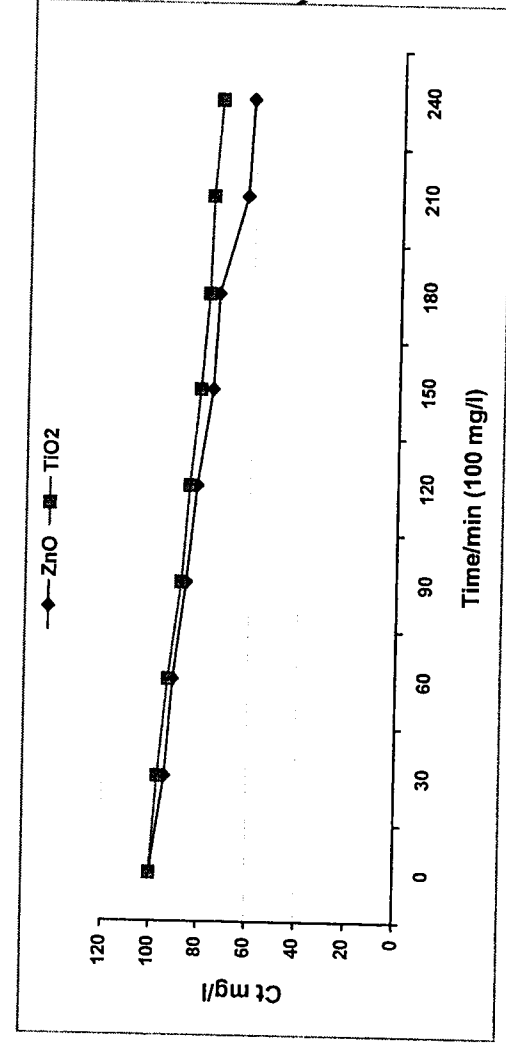


Fig (8)Effect of irradiation time on photocatalytic degradation of dye (100 mg/l) in aqueous suspension of  $TiO_2$  and  $ZnO$  (1 gm/l) in direct sun light.

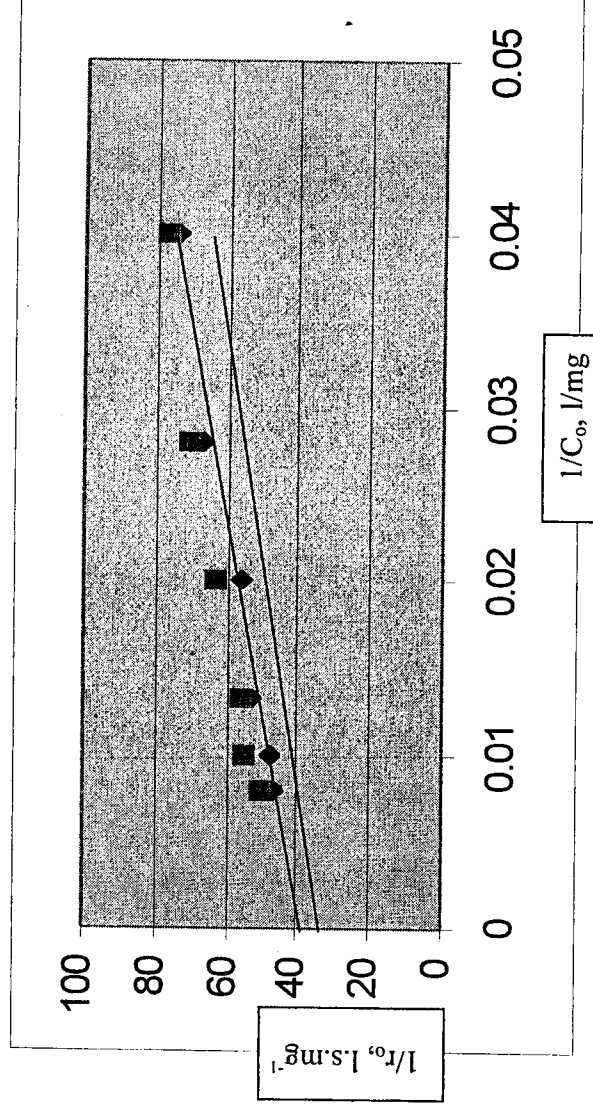


Fig (9) plot of the reverse of initial rate photodegradation against the reverse of initial dye concentration in aqueous suspension of ZnO (◇) and TiO<sub>2</sub> (■) [1mg/l] at 25°C under UV illumination.

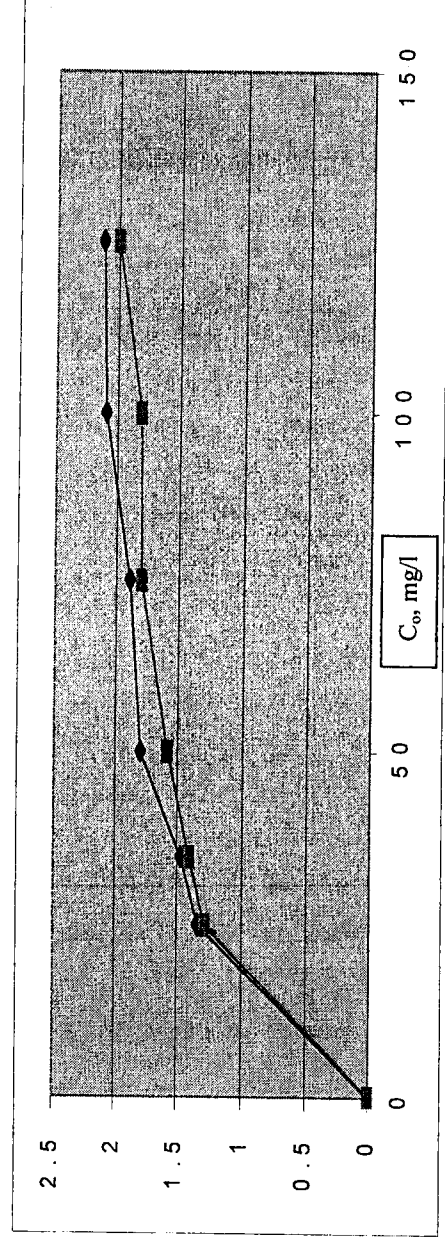


Fig (10) Plot of initial rate photodegradation versus initial dye concentration in the presence of TiO<sub>2</sub> (◇) and ZnO(■) [1gm/l] at 25°C under UV illumination.

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إزالة لون صبغة الأنسجة الحمراء الفعالة باستخدام طرائق الأكسدة الضوئية المحفزة والطرائق الكيميائية

حسن عباس حبيب

جامعة القادسية

كلية التربية

قسم الكيمياء

## الخلاصة

تم استخدام طرائق الأكسدة الضوئية المحفزة وطرائق الأكسدة المتقدمة الأخرى (AOPs) (Advanced Oxidation Processes) لغرض فحص التحطم لصبغة الأنسجة الفعالة الحمراء في المحلول المائي المتعامل عن طريق تشييع الصبغة لفترة 24 ساعة في ضوء الشمس المباشر. تضمنت الدراسة متابعة تحطم الصبغة بتركيز 100 ملغم/لتر. أوضحت النتائج بأن تجارب الأكسدة الضوئية المحفزة باستخدام عالق ثاني أكسيد التيتانيوم  $\text{TiO}_2$  وعلق أو كسيد الزنك  $\text{ZnO}$  أعطت نتائج أفضل من طرائق الأكسدة الضوئية الكيميائية باستخدام  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$  و Fenton's reagent. كذلك نتائج أفضل من طريقة الأكسدة الكيميائية باستخدام  $\text{Fe}^{+2}/\text{H}_2\text{O}_2$ . تم الحصول على أفضل نتائج لتحطم الصبغة عند استخدام عالق  $\text{ZnO}$  (1.0 غم/لتر) حيث بلغت نسبة الإزالة بحدود 75%. تم قياس تركيز الصبغة باستخدام تقنية امتصاص الأشعة المرئية وفوق البنفسجية عند  $\lambda_{\text{max}}$  للصبغة (715 ن.م) تضمن البحث دراسة حركية تحطم الصبغة باستخدام الأشعة فوق البنفسجية الصادرة من مصباح زئبقي متوسط الضغط عند الطول الموجي 365 نانومتر وفي درجة حرارة 25 درجة مئوية وبوجود  $\text{ZnO}$  و  $\text{TiO}_2$  حيث وجد أن ثابت تفكك الصبغة لمطولها المائي ذي التركيز 100 ملغم/لتر كان  $2.1 \times 10^{-4} \text{ s}^{-1}$  و  $1.82 \times 10^{-4} \text{ s}^{-1}$  على التوالي. ووجد كذلك بان السرعة الابتدائية لتحطم الصبغة تزداد بزيادة التركيز الابتدائي لها والتي تكون بوجود  $\text{TiO}_2$  أعلى من  $\text{ZnO}$ . وتم حساب ثابت سرعة التفاعل وثابت الأمتزاز للصبغة على سطح  $\text{TiO}_2$  و  $\text{ZnO}$  ووجد بأنهما كانا  $2.63 \times 10^{-2} \text{ mg/l.s}$  و  $2.22 \times 10^{-2} \text{ mg/l.s}$  و  $18.2 \text{ mg/l}$  و  $25.2 \text{ mg/l}$ .