

ZnO-Assisted Photodegradation of Some Dyes in Aqueous Solutions Under Direct Solar light

Batol S. Hussein

Chemistry Department / College of Education
University of Al-Qadisiya

ABSTRACT

Zinc oxide (ZnO) has been investigated in the photocatalytic degradation of 13 dyes in aqueous solution with different structure. This catalyst was shown to be more effective for photodegradation of many structural classes of organic dyes in aqueous solution, using solar light. We study the rate of degradation at different temperature between (27-36)°C for two hours in mid March 2012 , Also, study the effect of ZnO catalyst on the efficiency of photocatalytic degradation for all dyes .However, the results indicate that photodegradation rates differ significantly of families of dyes with different functionalities, This dyes improve high effect in the photodegradation rate. Kinetic analysis indicates that the photodegradation rates of dyes be approximated as first-order kinetics. Natural sunlight was effectively used to photo bleach some of the dyes. These observations indicate that all the dyes could be degraded completely at different time intervals and also revealed well photocatalytic activity under visible light. It is concluded that solar light induced degradation of dyes in wastewater is a viable technique for wastewater treatment.

1- Introduction

Textile dyes are designed to be resistant to microbial, chemical, thermal and photolytic degradation. After the dyeing process, a lot of non-bonded dyes are released into the wastewater, which can also be treated by Advanced Oxidation Processes (AOP s) in order to destroy the dye molecule and to decolorize the wastewater and reduce organic pollution[1].

It is well-known that under the experimental conditions of such methods, which can be very useful because of the short-time of treatment, hazardous compounds can be formed due to formed radicals such as hydroxyl radicals ($\cdot\text{OH}$). The hydroxyl radicals is high and the oxidation is unselective they are able to oxidize and finally mineralize nearly all organic compounds yielding CO_2 and inorganic ions in the end which again means a remedy of the pollution problem [2-3]. Different physical, chemical, and biological treatment processes have been employed to treat

various municipal and industrial wastewaters such as chemical biological[4-5].

Photocatalytic decolorization process is one of the emerging advanced technology which are considered as a suitable alternative for the degradation of dyes in waste water , many catalysts like TiO_2 , ZnO , ZrO_2 , WO_3 , SrO_2 , Fe_2O_3 , CeO_2 , CdS and ZnS have been attempted for the photocatalytic degradation , TiO_2 and ZnO have been especially investigated in the degradation of several environmental pollutants [6-9]. Different of the commonly methods were used in the degradation of colored chemicals the heterogeneous photocatalysis is the most efficient technique, in some of the processes ZnO has been reported to be more economical for the treatment of industrial effluents and more efficient than TiO_2 [10-11].

The emitted radiation by the sun is the incentive for many fundamental processes on earth like atmospheric circulation, photosynthesis and ocean currents [12-14].

The purpose of this study was to investigate the degradation of the 13 dyes with ZnO as photocatalytic in aqueous solution in direct sunlight and under various experimental conditions. The temperature effect on rate of 13 dyes degradation was studied under sunlight in the range(27-36) °C.

2- Experimental

2-1- Materials

In this study, all chemicals were used without further purification. The photocatalyst ZnO was purchased from Merck (99% purity). All dyes were purchased from Aldrich and the properties of dyes is shown in Table (1) , Figure (1) shows the molecular structure of all dyes .

2-2- Spectroscopic Measurements

UV-Visible spectra of aqueous solutions of all dyes were recorded by Shimadzu UV-Visible 1650 spectrophotometer , UV-Visible 7804C spectrophotometer (SUNNY) was used to measure absorbance of dyes solutions at λ_{max} . ZnO suspensions were centrifuged of by using Centrifuge CORP Triup International, Italy instruments.

2-3- Experimental Procedure

All photocatalytic reaction experiments were carried out in presence of direct sunlight. We attended a concentration of 13 dyes listed in the following table the concentration of all dyes 1×10^{-5} M, all dye solutions were prepared using double distilled water, 0.5 gm of ZnO which added for 1L of dyes solutions. Samples of 200 mL of dye which taken and placed in petridishes dish of each dye then covered with aluminum foil and placed for 150 minutes under direct sunlight in March 2012 .The temperature was measured at different time periods within the photodegradation of dyes

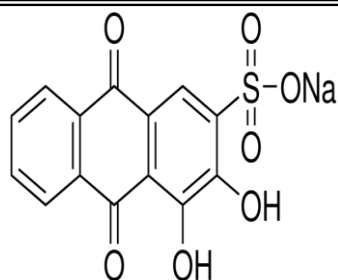
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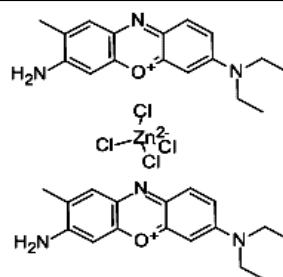
under sunlight. Samples were taken and ZnO was separated from by centrifugation to measured absorbance by using spectrophotometer to record the results.

Table(1): Properties of dyes used in this study .

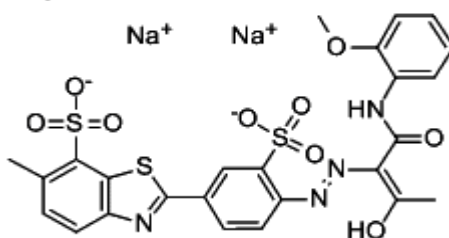
No	Name of dye	Class of dye	Properties
1	Toluidine Blue	thiazine	$C_{15}H_{16}ClN_3S$ F.W. = 305.83 $\lambda_{max} = 626 \text{ nm}$
2	Rose Bengle	Xanthene	$C_{20}H_2Na_2O_5I_4Cl_4$ F.W. = 1017.65 $\lambda_{max} = 549 \text{ nm}$
3	Brilliant Cresly Blue	Xanthene	$C_{34}H_{40}Cl_4N_6O_2Zn$ F.W. = 771.92 $\lambda_{max} = 622 \text{ nm}$
4	Alizarin Red S	thiazine	$C_{14}H_7NaO_7S$ F.W. = 342.26 $\lambda_{max} = 512 \text{ nm}$
5	Direct Yellow 27	monoazo	$C_{24}H_{20}N_4Na_2O_9S_3$ F.W. = 650.62 $\lambda_{max} = 393 \text{ nm}$
6	Direct Violet 51	diazo	$C_{32}H_{27}N_5Na_2O_8S_2$ F.W. = 719.70 $\lambda_{max} = 549 \text{ nm}$
7	Trypan Blue	diazo	$C_{34}H_{24}N_6Na_4O_{14}S_4$ F.W. = 960.81 $\lambda_{max} = 607 \text{ nm}$
8	Azor A	thiazine	$C_{14}H_{14}ClN_3S$ F.W. = 291.8 $\lambda_{max} = 632 \text{ nm}$
9	Azor B	thiazine	$C_{15}H_{16}ClN_3S$ F.W. = 305.83 $\lambda_{max} = 646 \text{ nm}$
10	Azor C	thiazine	$C_{13}H_{12}ClN_3S$ F.W. = 227.8 $\lambda_{max} = 611.5 \text{ nm}$
11	Rhodamine 6G	Xanthene	$C_{28}H_{31}ClN_2O_3$ F.W. = 479.03 $\lambda_{max} = 526.5 \text{ nm}$
12	Rhodamine B	Xanthene	$C_{28}H_{31}ClN_2O_3$ F.W. = 479.02 $\lambda_{max} = 554 \text{ nm}$
13	Eosin B	Xanthene	$C_{20}H_6N_2Na_2O_9Br$ F.W. = 624.08 $\lambda_{max} = 514 \text{ nm}$



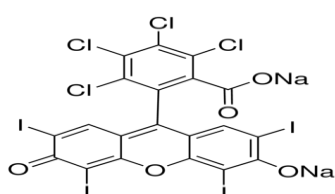
Toluidine Blue



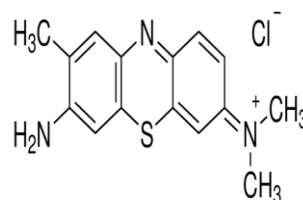
Brilliant Cresyl Blue



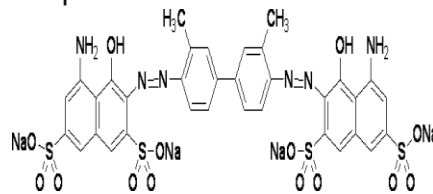
Direct Yellow 27



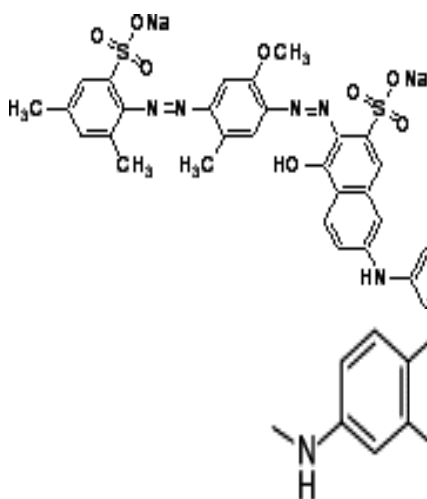
Rose Beng



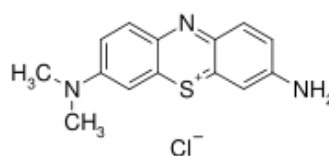
Alizarin Red S



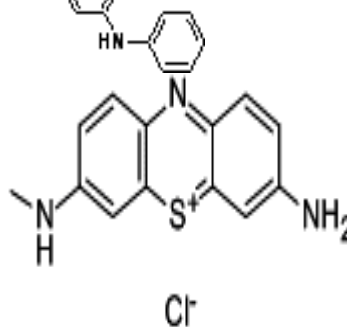
Trypan Blue



Direct Violet



Azor A



Azor C

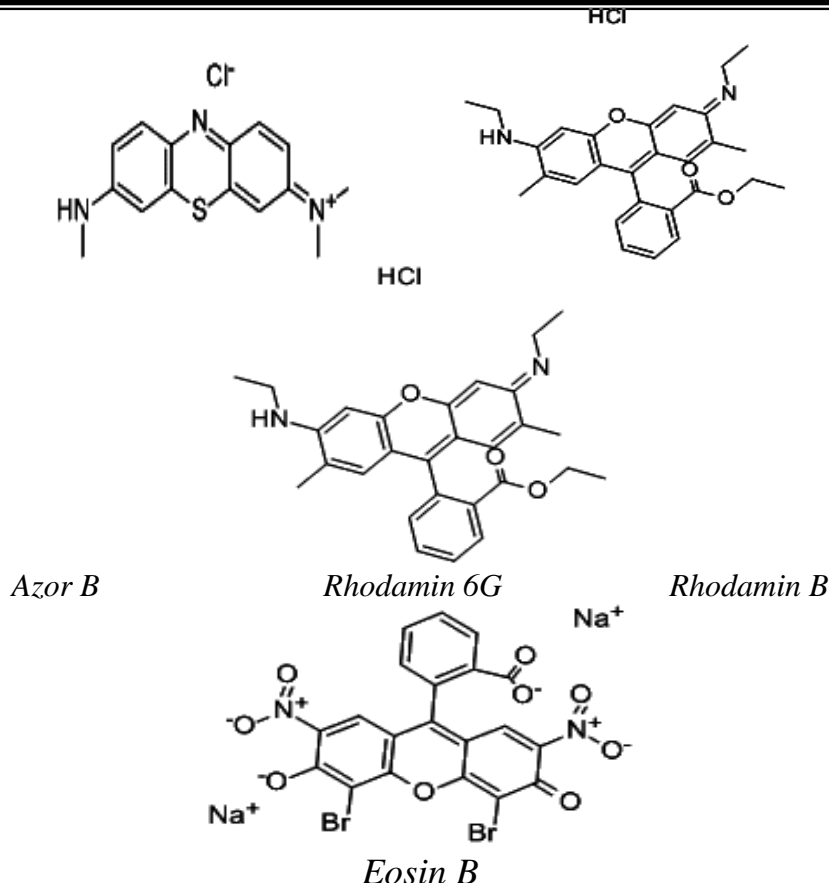


Fig (1): Molecular structures of dyes.

3- Results and Discussion

Today it is possible to know all the geometric and physical fundamentals which are effect on the solar irradiation for various locations on earth and different times of the year. The degradation of 13 dyes was performed in the presence of ZnO as a photocatalyst under direct sunlight. In this work we investigated photocatalysis degradation bleaching in aqueous solutions after exposing to direct sunlight for 150 min in sunny day in March 2012 where the temperature between (27-36°C). Efficiency of photocatalytic degradation processes was determined from the equation (1) [15]:

$$\text{Efficiency (\%)} = (C_0 - C_t) / C_0 \times 100 \quad \dots\dots\dots(1)$$

Where C_0 is the initial value of dye solution at $t=0$ min and C_t is the final value of dye solution during different periods of time such as $t=10, 25, 40, 60, 120$ and 150 min of photocatalysis processes in presence of ZnO .

3-1- Effect of Initial ZnO

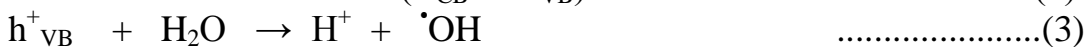
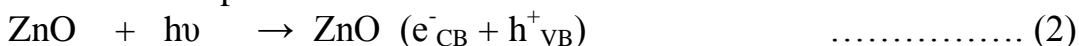
The ZnO/Dye system in present work shows a good efficiency, the photodegradation of dyes in presence of ZnO and the ratio of C_t / C_0 at 150

min of the irradiation time were showed in Figures (2-5). In Figure (2) observe that Azor B was the fastest photobleaching dye among other dyes studied than Azor A, Azor C and Alizarin Red S. It also observes in Figure(3) the Eosin B was the faster photobleaching than Rhodamin B and Rhodamin 6G. In Figure (4) this indicates that the Trypan Blue was the faster photobleaching than Direct Violet 51 and Direct Yellow 27. In Figure (5) observe Rose Bengal was faster photobleaching than Toluidine Blue and Brilliant Cresly Blue dyes. ZnO is an extensively studied semiconductor employed in the photocatalytic removal of contaminants in water, pure ZnO nanomaterials have limited efficiency because of the low light utilization rates resulting from the wide-band gap (3.2 eV). Different factors affect on photocatalytic degradation such as nature and concentration of the organic substrate, concentration and type of the semiconductor, light source and intensity, pH, temperature [16]. ZnO nanomaterials absorb only a small portion of light and exhibit rapid recombination of electrons and holes reducing their photocatalytic activity [17-18]. The principle of semiconductor assisted photocatalysis includes:

- 1- Direct band gap excitation of the semiconductor results in electron-hole separation.
- 2- Photo generated the holes scavenged in aqueous solutions by surface hydroxyl groups to generate the strong oxidizing hydroxyl radicals which can promote the oxidation of the organic contaminant at the ZnO surface .
- 3- The electron in the conduction band reduces the oxygen that is adsorbed on the photocatalyst.

3-2- Photocatalytic degradation mechanisms

In the photocatalytic oxidation process, the photo excited ZnO and an electron-hole pair is formed as follows:



Where, e_{CB}^- is the electron in the conduction band and h_{VB}^+ is the hole in the valence band. Zinc oxide (e_{CB}^- and h_{VB}^+) is photo excited ZnO with the formation of electron in the conduction band and hole in the valence band then dyes was believed to be destroyed through direct oxidation by the $\cdot\text{OH}$ radicals and $\text{O}_2^{\cdot-}$ radicals as shown in equation (5)[19]. In Figures (6-9) is shown that for 150 min under sun light , respectively, the highest percentage degradation 99.5 % for Azor A , 97.5 % for Eosin B , 98% for Trypan Blue and 99 % for Rose Bengal of the dyes have been degraded from aqueous solutions. Therefore, the number of active sides on the

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photocatalyst surface increases, which in turn increase the number of hydroxyl and superoxide radicals then the rate of hydroxyl radical ($\cdot\text{OH}$) production increases which would allow the degradation to be faster [20]. Several earlier studies reported that the photocatalytic degradation of dyes using ZnO [21-22].

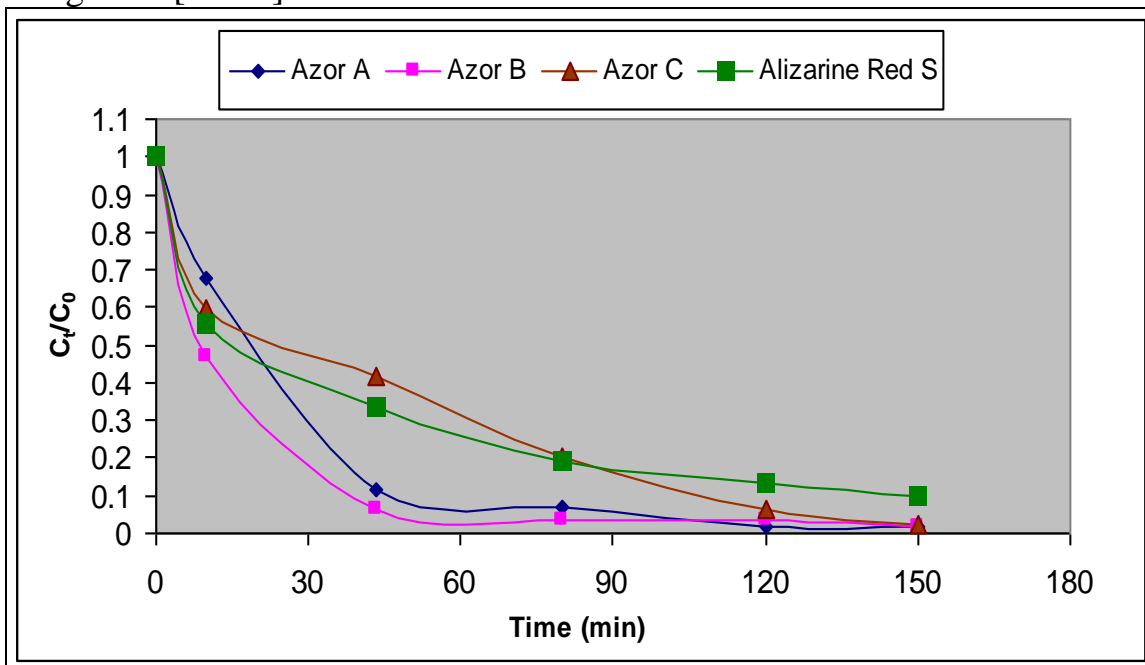
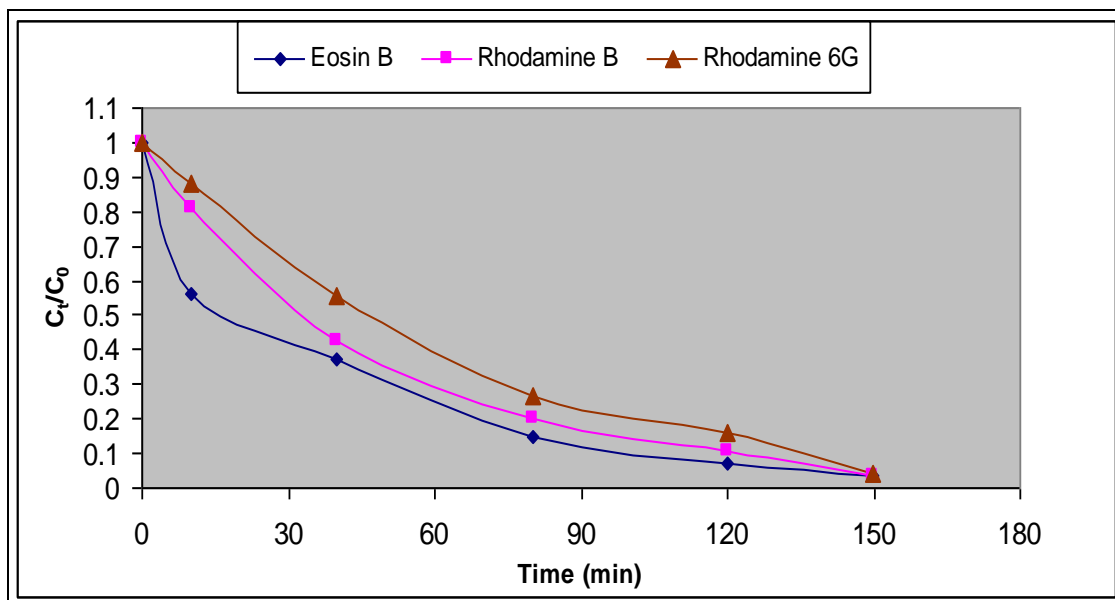
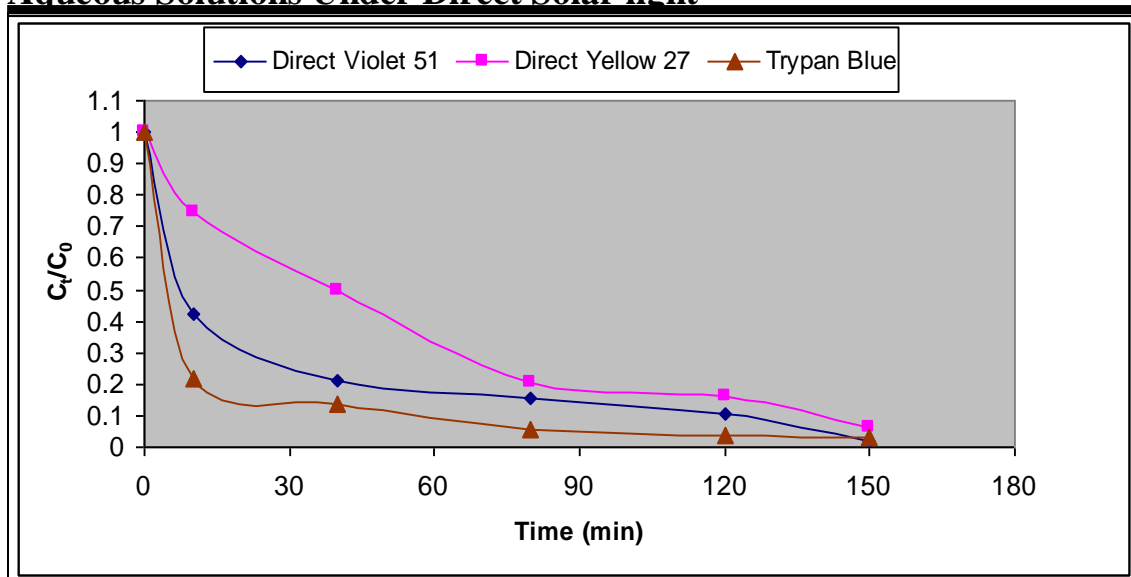


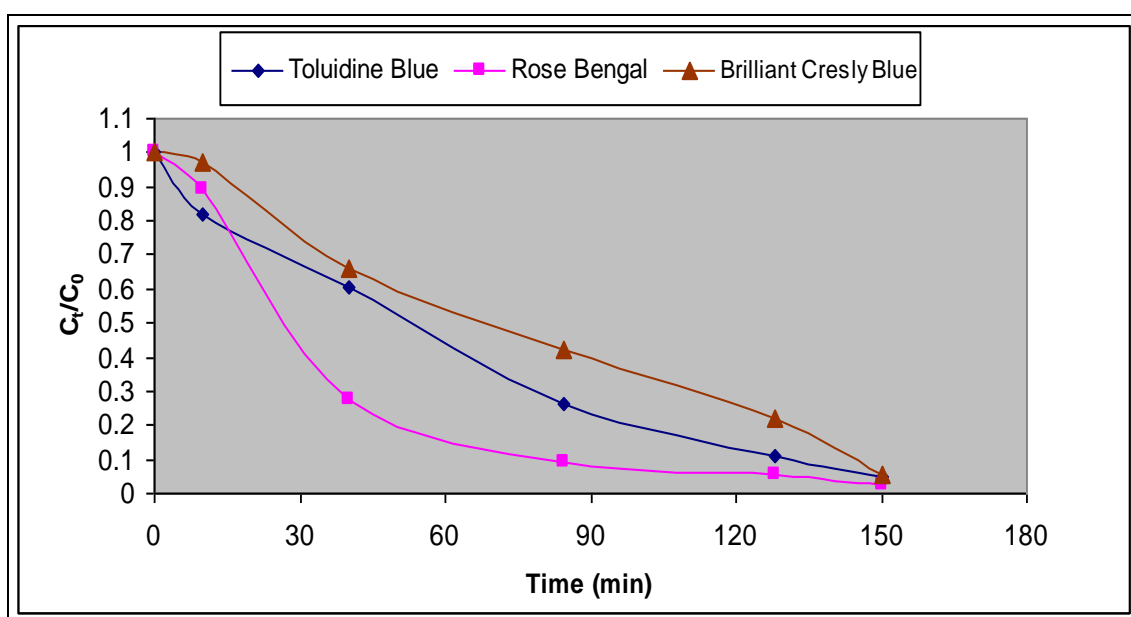
Fig (2): Photobleaching rates of dyes under natural sunlight indicate: Azor B > Azor A > Azor C > Alizarine Red S .



Fig(3): Photobleaching rates of dyes under natural sunlight indicate : Eosin B > Rhodamin B > Rhodamin 6G .



Fig(4): Photobleaching rates of dyes under natural sunlight indicate :
Trypan Blue > Direct Violet 51 > Direct Yellow 27.



Fig(5): Photobleaching rates of dyes under natural sunlight indicate :
Rose Bengal > Toluidine Blue > Brilliant Cresly Blue.

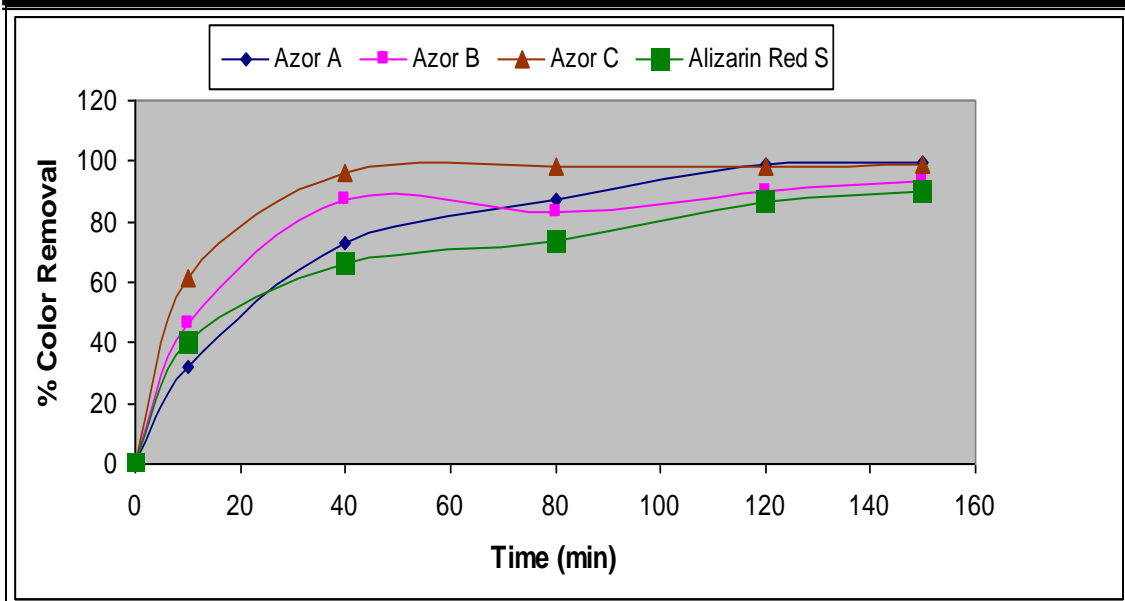


Fig (6): The percentage color removal of photocatalytic degradation of dye under sun light irradiation at different periods of times.

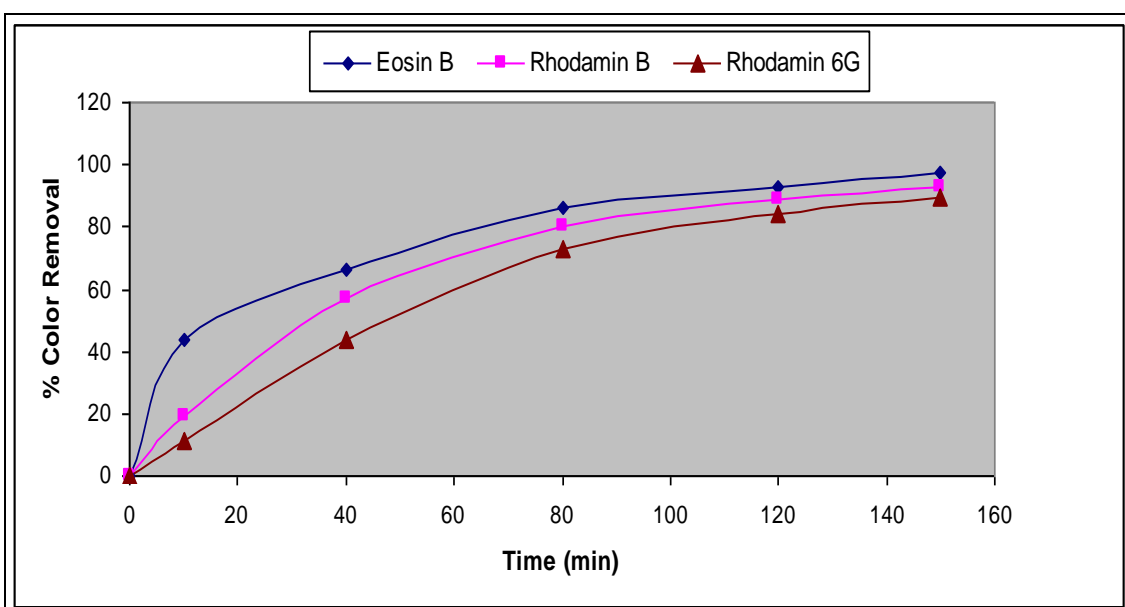


Fig (7): The percentage color removal of photocatalytic degradation of dye under sun light irradiation at different periods of times.

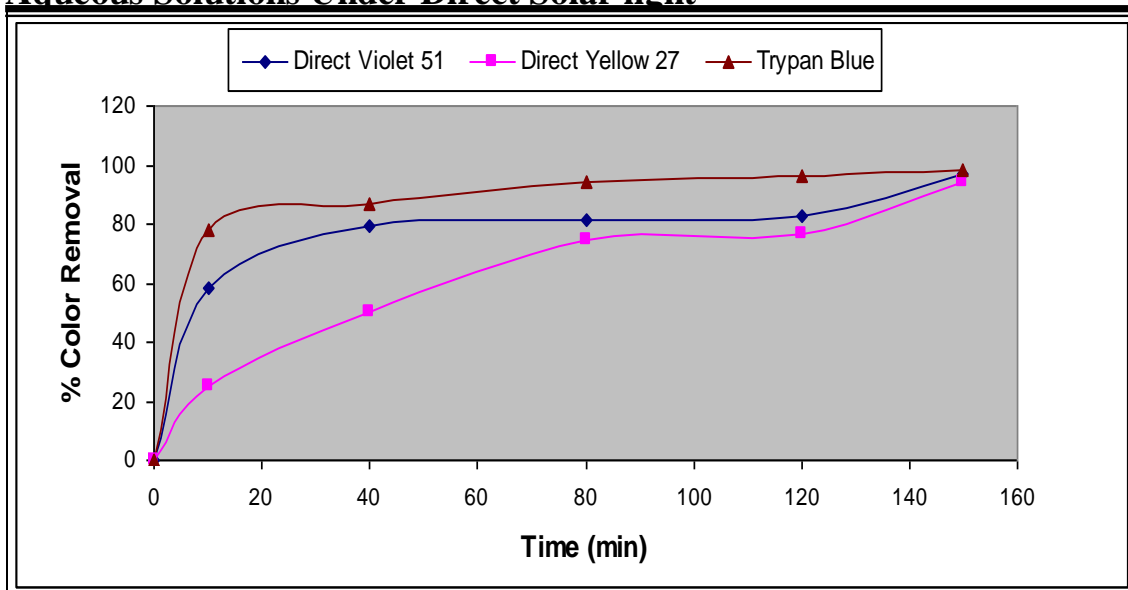


Fig (8): The percentage color removal of photocatalytic degradation of dye under sun light irradiation at different periods of times.

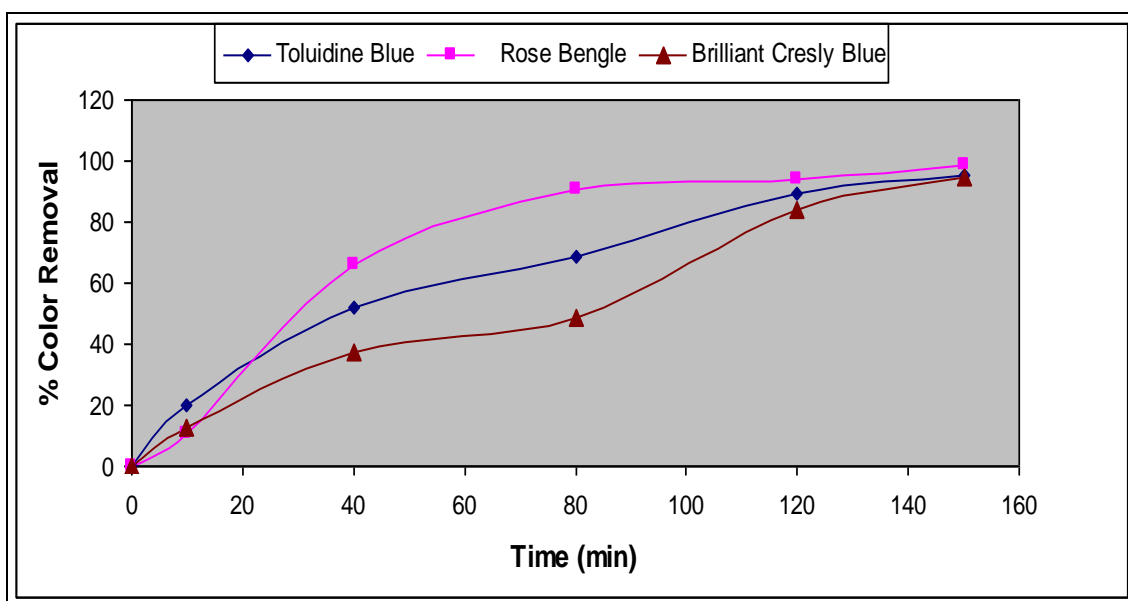


Fig (9): The percentage color removal of photocatalytic degradation of dye under sun light irradiation at different periods of times.

3-3- Effect of Temperature on photodegradation reaction

Figures (10-13) shown the higher color removal of dyes was achieved at higher temperature 36°C for all dyes as complete degradation even after 150 min. The effect of increasing temperature was observed on the photodegradation of dyes by varying the temperature at range 27°C to 36°C and rate constant k was determined from the first order plots. Variation in temperatures is not rate determining step in the photocatalyzed reactions. The rate determining step in this type of reactions is the

electron transfer from valence band to the conduction band of photocatalyst.

Among the effects studied, only two can be considered significant: temperature and the interaction between dyes and catalyst concentration. Mathematically, this implies that the means of the groups that make up the two levels of these effects can be considered significantly different [23].

When working at a low temperature, the desorption of the products formed limits the reaction because it is slower than the degradation on the surface and the adsorption of the reactants. On the other hand, at a higher temperature, the limiting stage becomes the adsorption of the dye on the ZnO catalyst which helps the reaction to compete more efficiently with (e^-/h^+) recombination. The increased rate of reaction with increasing in the temperature may be attributed to the effect of temperature on the adsorption and desorption processes on the surface of ZnO [24].

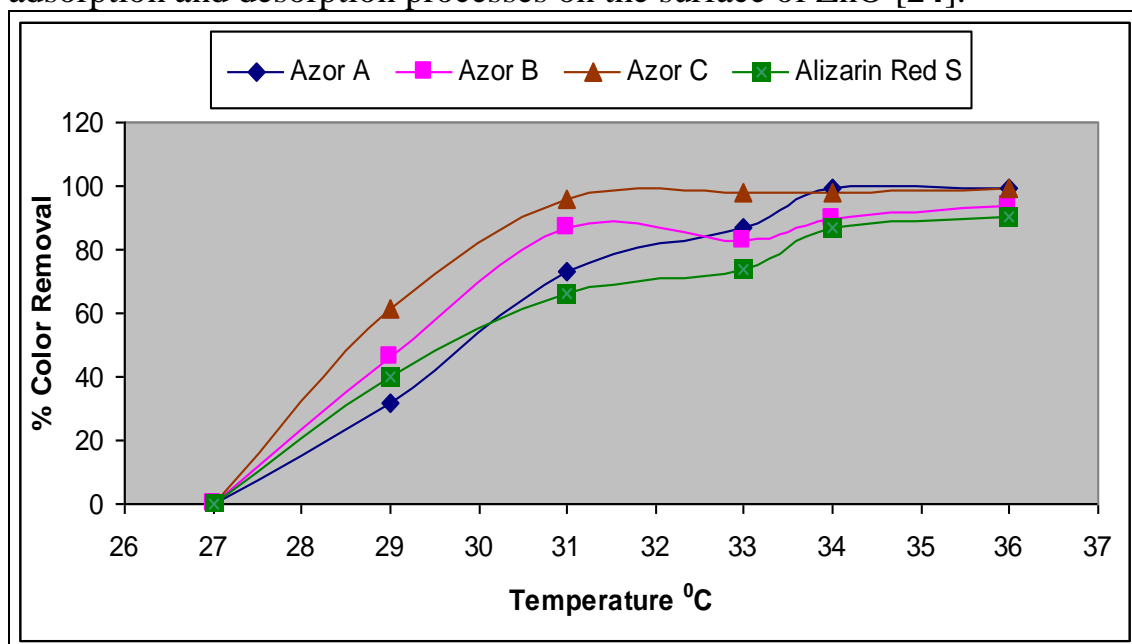


Fig (10): Effect of temperature on the photocatalytic degradation of dyes conc.= 1×10^{-5} M in presence of 0.5 g/L ZnO.

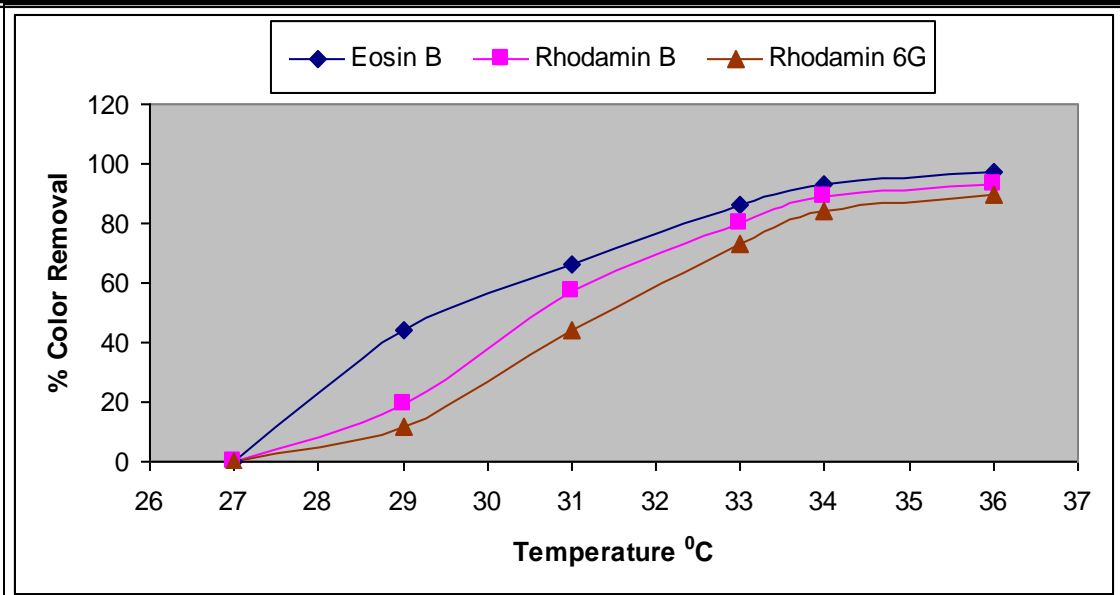


Fig (11): Effect of temperature on the photocatalytic degradation of dyes conc.= 1×10^{-5} M in presence of 0.5 g/L ZnO.

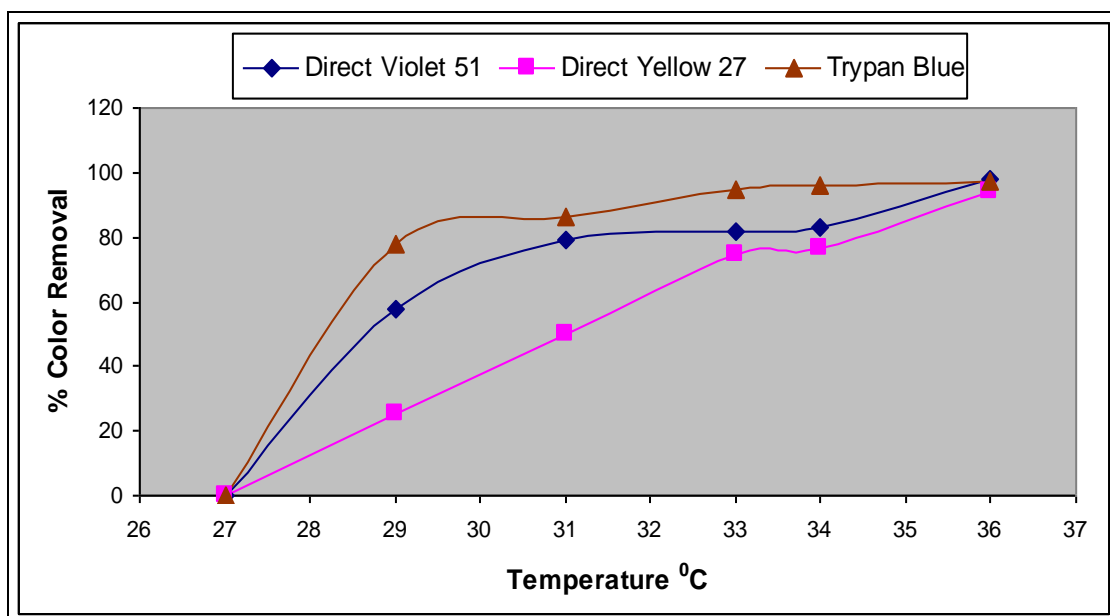


Fig (12): Effect of temperature on the photocatalytic degradation of dyes conc.= 1×10^{-5} M in presence of 0.5 g/L ZnO.

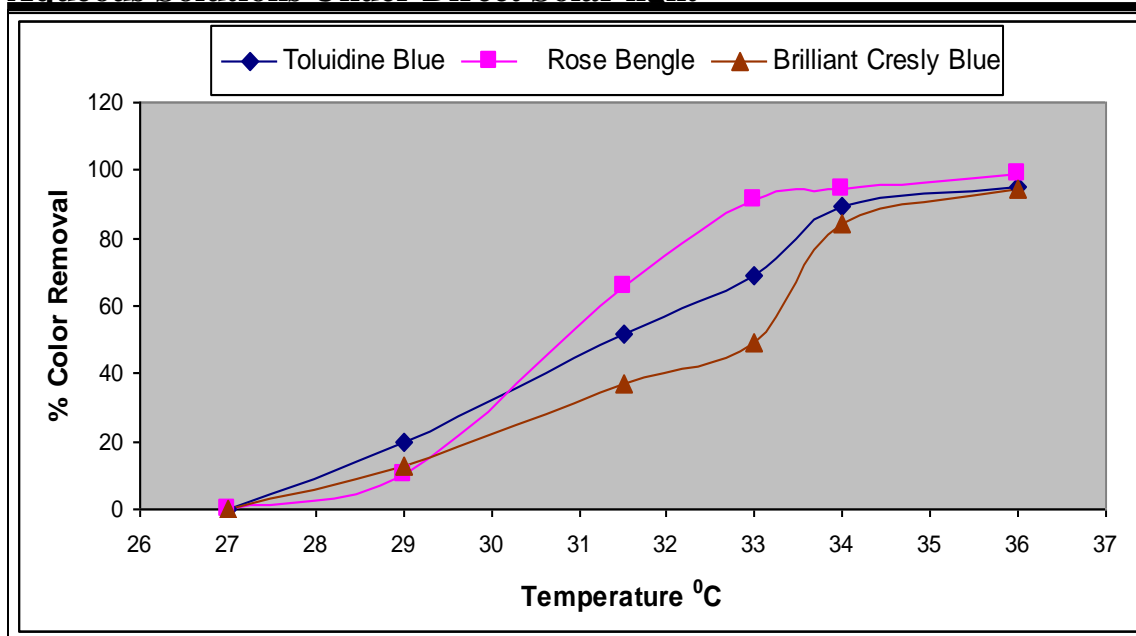


Fig (13): Effect of temperature on the photocatalytic degradation of dyes conc.= 1×10^{-5} M in presence of 0.5 g/L ZnO.

3-4- Effect of sunlight

Degradation of all dyes was performed under sunlight which could be effective for photocatalysis degradation, the best results was reached 99.5% color removal for Azor A at high temperature 36 °C under sunlight at various time intervals as shown in Figure (6-9), all experimental were carried out in sunny day in March month , It was attempted to determine the ZnO assisted of such photodegradation by varying the chemical structures of dyes, The effect of photocatalysis degradation of wave length as shown in table (1) for each dye under sunlight at various time interval between (0-150)min.

The oxidation reactions induced by sunlight. Common processes are: 1, the loss of one or more electrons from a chemical species as a result of photo excitation of that species. 2, the reaction of a substance with oxygen under the influence of light. When oxygen remains in the product this latter process is also called photo oxygenation. Reactions in which neither the substrate nor the oxygen are electronically excited are sometimes called photo initiated oxidations. The waste water of dyes contains a wide range of compounds with different concentrations. Based on the concentrations and the type of contaminants exist in the wastewater, and they can be branched out based on chemical structure, solubility and the nature of daughter compounds[25].

In this present it was observed that the increase in the intensity of solar light resulted in the increase in the efficiency of color removal of dyes. The enhancement of the rate of the degradation also observed with

other studies [26-27]. The photocatalytic degradation of the dye occurs on the surface of the catalyst where $\cdot\text{OH}$ and O_2 radicals are available. Hydroxyl radicals are formed from the holes in valence band reacting with either H_2O or $\cdot\text{OH}$ adsorbed on the catalyst surface. The $\cdot\text{OH}$ radicals are strong enough to break the different bonds in the dye molecules ($\text{N}=\text{N}$, $\text{C}-\text{C}$, $\text{C}=\text{C}$, $\text{C}-\text{N}$, $\text{C}-\text{S}$ and $\text{C}=\text{N}$) adsorbed on the surface of the catalyst which lead to the formation of CO and in organic ions such as NH_4^+ , NO_3^- , Cl^- and SO_4^{2-} [28-29]. Photocatalysis is a process by which a semiconducting material absorbs light of energy more than or equal to its band gap, there by generating holes and electrons.

4. Conclusions

In the present work, It is evident that ZnO catalyzed photodegradation using solar light is a suitable technique for removal of dyes in wastewater from textile industries. The intermediates formed during the course of degradation give strong evidence for the destruction of the dye into smaller fragments. Photocatalytic degradation of all dyes depends on the amount of catalyst, concentration of dye at different conditions. This ZnO photocatalyst is economically cheap, simple and this involves natural sunlight when compared to other oxidative processes.

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التجزئة الضوئية بمساعدة اوكسيد الخارصين لبعض الأصباغ

تحت ضوء الشمس المباشر

بتول صالح حسين

جامعة القادسية/ كلية التربية / قسم الكيمياء

الخلاصة :

تحققت التجزئة الضوئية المحفزة باستعمال 13 صبغة من محاليلها المائية كانت تراكيبها مختلفة باستعمال اوكسيد الخارصين ZnO . أوضح تأثير العامل المحفز الذي أصبح أكثر تأثيراً للتجزئة الضوئية لبعض الأصناف التركيبية من الأصباغ العضوية من محاليلها المائية باستعمال أشعة الشمس . تم دراسة حركية سرعة التجزئة بدرجات حرارة مختلفة تتراوح ما بين (27-36) درجة مئوية خلال زمن مقداره ساعتين ونصف في منتصف شهر مارس (2012) . درست أيضاً تأثير المحفز اوكسيد الخارصين على كفاءة التجزئة الضوئية المحفزة لجميع الأصباغ . أشارت النتائج إن سرعة التجزئة الضوئية تختلف بشكل ملحوظ لكل صبغة باختلاف المجموعة الفعالة , أثرت الأصباغ بصورة كبيرة على سرعة التجزئة . أشارت حركية التجزئة ان سرعة التجزئة الضوئية للأصباغ حركات من الدرجة الاولى . أثبت استعمال ضوء الشمس فعالية في تجزئة معظم الأصباغ . وأشارت الدراسة ان جميع الأصباغ نستطيع تجزئتها بصورة تامة بمعدلات زمنية مختلفة وبوجود الضوء المرئي . ونستنتج ان ضوء الشمس يساعد على تجزئة الأصباغ في مياه الصرف وهي تقنية قابلة للتطبيق في معالجة المياه الصرف .