Photocatalytic Purification of Wastewater by Potocatalytic Degradation Reactions

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Abstract:

Photocatalytic degradation reactions have been done on dyes thats present in the industrial wastewater from Hilla textile factory. Titanium dioxide , and zinc oxide are used as a photocatalysts.Irradiation of reaction mixture was performed by the solar energy. The photcatalytic fragmentation of dyes in the solution has been followed spectrophotometrically by measuring the absorbance at λ max = 380 nm by using UV.visible spectrophotometer. The reactions were done at three different temperatures .It has been found that the efficiency of the photocatalytic degradation is increased with reaction time and increasing in temperature of the reaction. The effect of temperature on the reaction is used in the calculation of the activation energy by using Arrehnus plot ,it was about 21 $kJ\ mol^{-1}$. The results showed that titanium dioxide was more active in the photocatalytic degradation of dyes than zinc oxide under the same reaction conditions.

الخلاصة :

تم دراسة التفكك الضوئي للأصباغ الموجودة في المياه الصناعية المأخوذة من معمل نسيج الحلة باستخدام ثنائي اوكسيد التيتانيوم وأو كسيد الخارصين كعوامل مساعدة ضوئية مع التشعيع باستخدام ضوء الشمس الاعتيادي . تم متابعة التفكك الضوئي للأصباغ وذلك بوساطة قياس الامتصاصية للنموذج المعالج عند طول موجي مقداره (380) نانومتر باستخدام مطياف الأشعة المرئية - فوق البنفسجية .تم أجراء التفاعل بثلاث درجات حرارة مختلفة . وجد ان المعالجة تزداد مع تقدم زمن التفاعل وزيادة درجة حرارة التفاعل . تم الاستفادة من تأثير درجة الحرارة على سرعة التفاعل في حساب طاقة التنشيط للتفاعل بالاعتماد على علاقة ارينوس التي كانت مساوية إلى(21) $kJmol^{-1}$.أظهرت النتائج أن ثنائي اوكسيد التيتانيوم اكثر كفاءة في المعالجة مقارنة باوكسبد الخارصين وتحت نفس ظروف التفاعل .

Introduction:

Photochemistry on TiO_2 – water interfaces has become active research area since discovery of photocatalysis of water on TiO_2 electrodes (1), and photocatalytic mineralization of water pollutants in the presence of TiO_2 colloids(2). These discoveries had important implications for solar energy conversion and environmental clean up. Many efforts has been devoted to improvement of performance of titanium dioxide photocatalyst to make it suitable for widespread for industrial applications(3).

Titanium dioxide (TiO_2) photocatalysis system is a possible alternative complementary technology to current drinking water treatment processes(4) .TiO_2 photocatalysis does not require addition of consumable chemicals and does not produce hazardous waste products (5).When TiO_2 particles are illuminated with near UV irradiation ($\lambda < 400$ nm) ,electron hole pairs are generated within the metal oxide semiconductor . Valence band hole has a very positive reduction potential and is capable of oxidizing water, or hydroxide ions ,to form hydroxyl radicals in water(6).Hydroxyl radicals are known to be powerful , oxidizing agents(7). Porous and nano crystalline semiconducting films of wide band gap oxides such as anatase TiO_2 ,and ZnO form an important new class of electronic materials(8).

Heterogeneous dispersed semiconductor surface provides both fixed environment to influenced chemical reactivity of a wide range of adsorbates and a mean to initiate light induced redox reactivity in the weakly associated molecules . Among semiconductor materials, n-type TiO_2 and ZnO has been extensively used as a stable photocatalysts suspended in an aqueous solution .Initial interest in these photocatalytic reactions was promoted when Fujishima and Honda(9) discovered that water could be split to hydrogen and oxygen simultaneously upon illumination of TiO_2 with UV – light .Since then this observation promoted extension work focused on the production of hydrogen fuel from splitting of water by means of solar energy conversion and storage.(10). The activity of TiO_2 depends on generally intrinsic bulk and surface properties of the samples as well as on the nature of the photocatalytic reaction(11).

Recently stable photocatalysts such as TiO_2,ZnO and SnO have been used in the photodegradation of different organic pollutants in the air ,water and soil (12-14) .Using of this system can lead to complete mineralization of pollutants in to the different inorganic products such as H_2O and CO_2(15) .

Photocatalytic degradations reactions can be used in the decolarization and detoxification of industrial wastewater of textile factories (16). About 5% of the synthetic dyes are lost with the wastewater in the colorization processes(17).

The present work involves photocatalytic degradation of industrial wastewater over titanium dioxide and zinc oxide under irradiation with solar energy.

Experimental :

Titanium dioxide , and Zinc oxide powder have been used as photocatalyst in this work . These are supplied by (BDH) with purity of 99.99%.The study was done at October and November 2005.

The given wastewater is centrifuged to remove suspended and determine the maximum wavelength of absorption which was 380 nm .In all experiments irradiation was carried out in an open atmosphere with a solar energy. The reaction mixture consist of 500 ml of colored waste water with 0. 4g of solid catalyst . Sun light was collected by using concave lens with a focal length of 250mm.

The solution was kept homogeneous by using a magnetic stirrer in the suspended colored wastewater .Elevation in temperature of reaction was controlled using a suitable thermostat. In order to get same light intensity of sun light, all experiments are carried out at 75 minute before and after prayers noon.

Periodically , 2ml samples of reaction mixture were withdrawn by microsyringe,these samples are centrifuged to separate a solid catalyst .The absorbance of supernatant liquid is measured at 380 nm using UV-visible spectrophotometer (Cintra 5-GBC-Austrural) . The photocatalytic degradation of the dye was followed spectrophotometrically by comparing the absorbance at a desired intervals of times of treated samples with the absorbance of the stock solution.

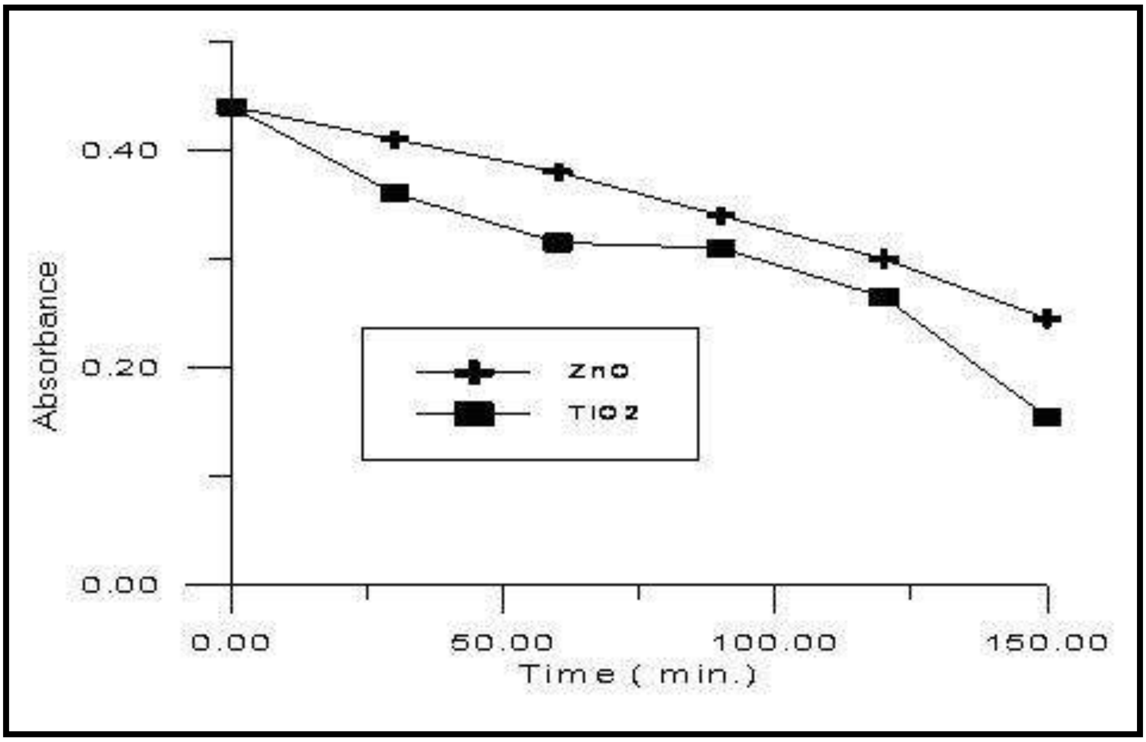
Results and Discussion :

The photocatalytic degradation of dyes in the colored water was followed by measuring the absorbance of treated samples . It has been found that , the presence of sun light and photocatalyst is very essential in the photodegradation of dyes . Figure(1) shows the relation between photocatalytic degradation and irradiation time. From this figure TiO_2 is appeared to be more active than ZnO , this result is probably due to the high surface area of TiO_2 with respect to ZnO(18).Also TiO_2 absorbs light with high efficiency. The effect of temperature on the reaction was monitored by raising reaction temperature, the reaction was done at 298K , 303K, and 308K.These results are shown in figures (2,3). The results showed that the efficiency of degradation is increased with the temperature increasing .In each case TiO_2 was more active than ZnO.

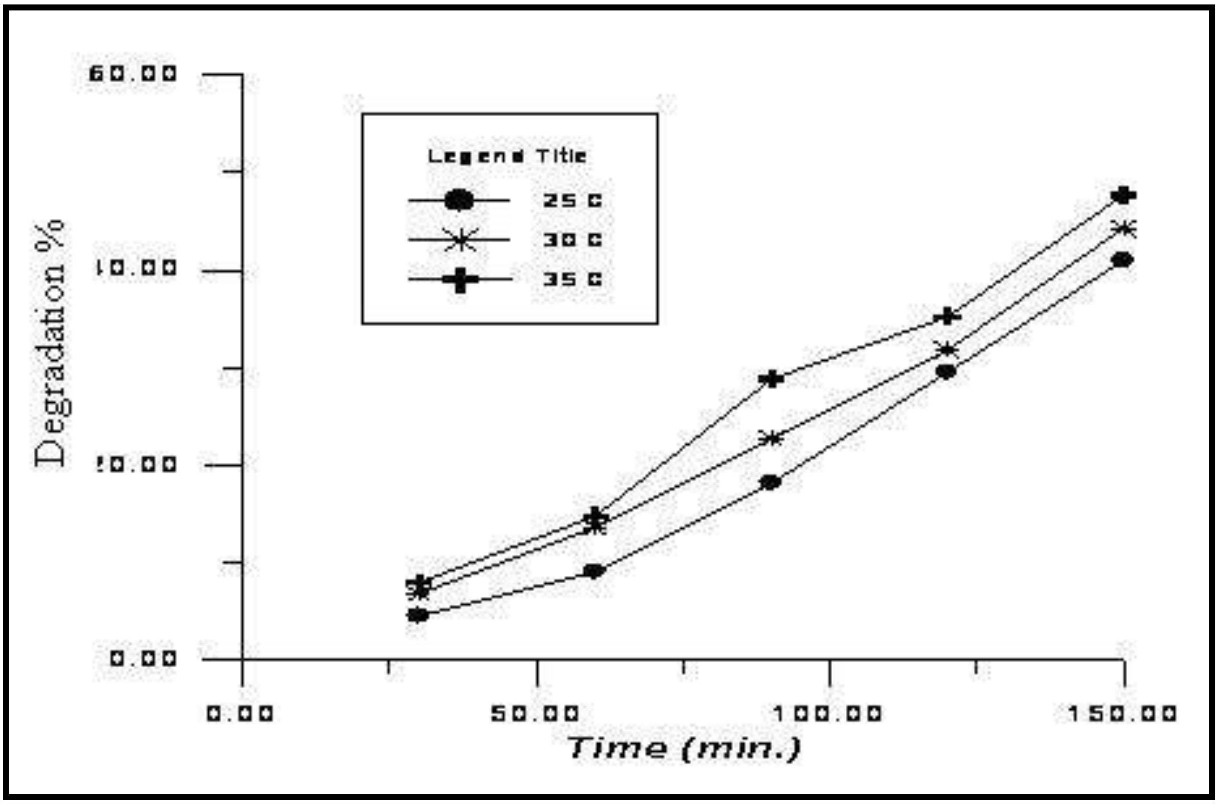
Variation in temperatures is not rate determining step in the photocatalyzed reactions(19). The rate determining step in this type of reactions is the electron transfer from valence band to the conduction band of photocatalyst(20).The variation in temperature of reaction may effect on the processes which are occurred in the photocatalyzed reactions. These processes are adsorption of reaction molecules in the active sites on the surface, formation of intermediates , and desorption of reaction products(21).

These processes are adsorption of reaction molecules in the active sites on the surface, formation of intermediates , and desorption of reaction products(21). These processes are strongly influenced by change in the temperature of reaction.

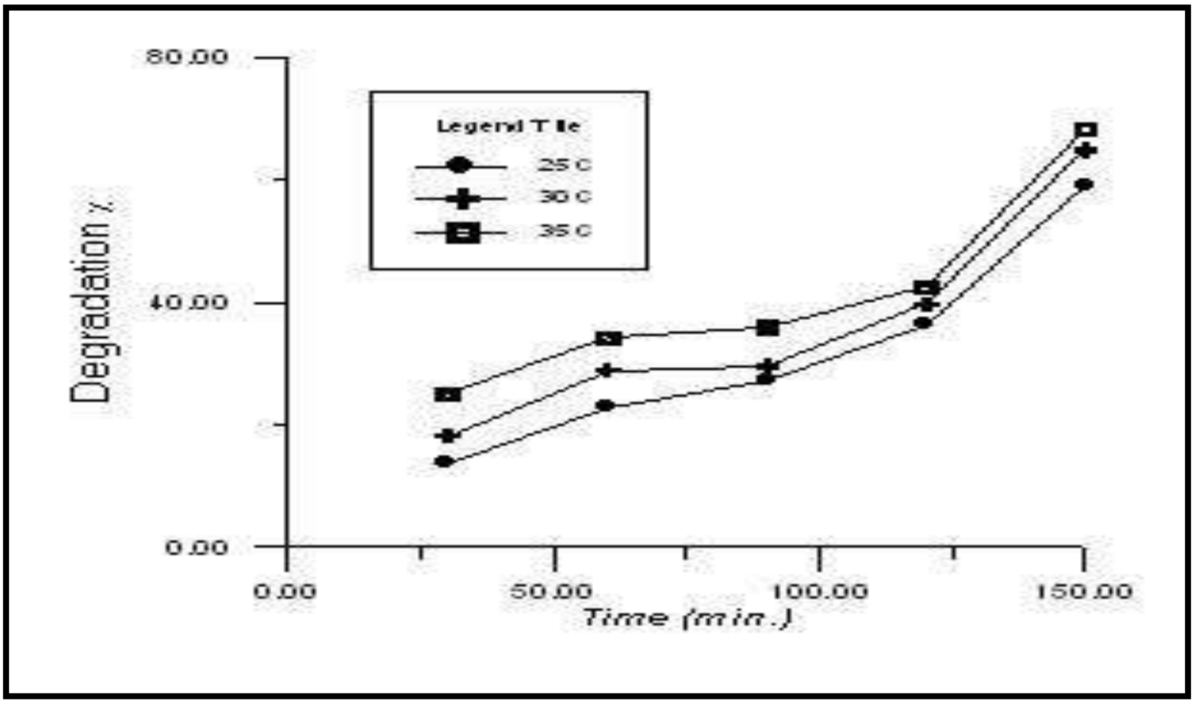
Complete decolarization of wastewater was achieved after 210 minute for TiO_2 and 250 minute for ZnO under the same reaction conditions .The resulted treated water can be recycles to the factory again to be used for industrial purposes ,or it can be disposed in to the soil with limited harmless.



Figure(1) Photacatalytic degradation of colored wastewater over ZnO and TiO_2 at 298K



Figure(2) Photocatalytic degradation of wastewater over ZnO at 298 , 303 , and 308K.



Figure(3) Photocatalytic degradation of wastewater over TiO_2 at 298, 303,and 308K

Activation Energy :

The effect of temperature on the reaction rate has been used in the calculation of activation energy for the reaction depending on Arrhenius equation**,** as the reaction is first order in its kinetics(22) .

$$\text{Logk} = \text{Log A} - \frac{E_a}{2.303\ RT} \qquad \text{--------------------}\ 1$$

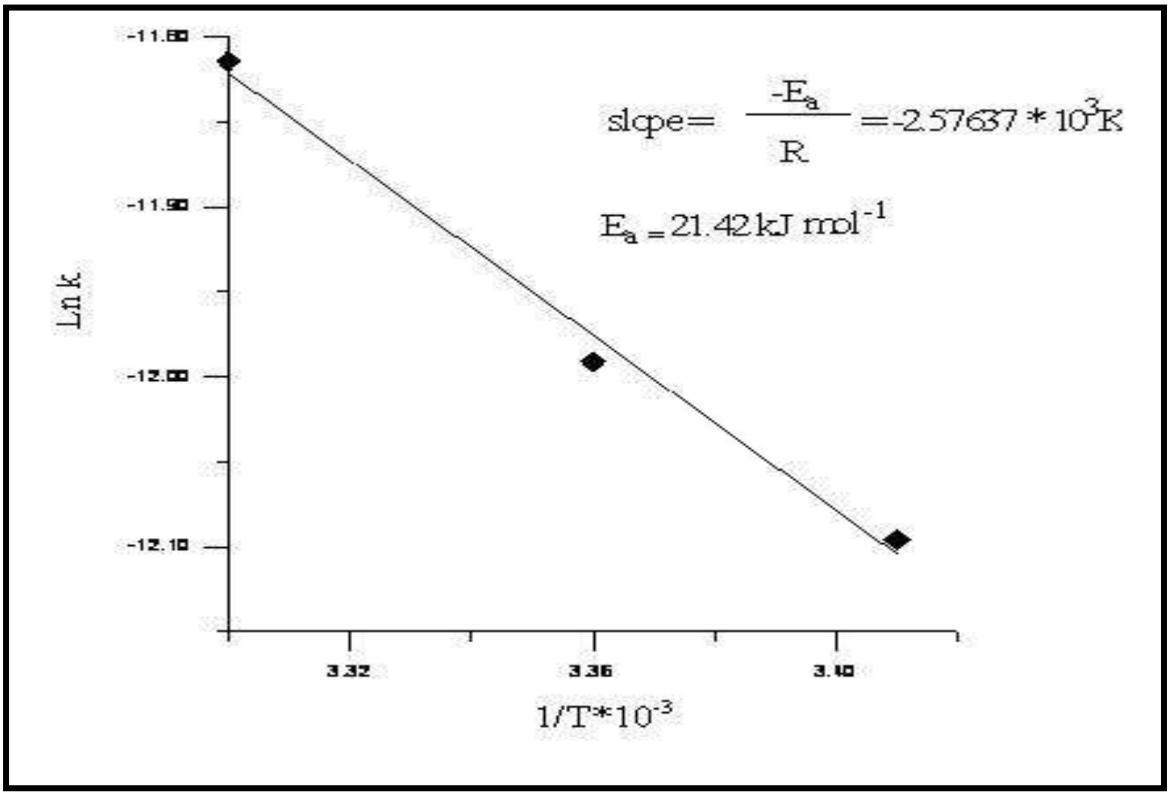
Rate constant for the photocatalytic decolarization of wastewater (k) was obtained by the equation

$$\text{Ln}(a - x) = \text{Ln}\,a - k\,t \qquad \text{----------------------}\ 2$$

$a = A_0 - A_\infty$
$x = A_0 - A_t$
$a - x = A_t - A_\infty$

Where A_0 , A_t and A_∞ is the absorbance of dye before irradiation , at agiven time , and the final time respectively. The resulted constant can be used in Arrehnius plot by plotting (Ln k) versus 1/T as shown in figure (4).The activation energy has been calculated and it was equal to 21.24 $kJmol^{-1}$.The activation energy in this case deals with electron transfer from valence band to the conduction band of the catalyst and it does not depend on the reaction type (23).

Proposed



Figure(2) Photocatalytic degradation of wastewater over ZnO at 298 , 303 , and 308K.

Mechanism :

The first step in the photocatalytic reactions is the absorption of light with energy that is equal to or greater than the band gap of semiconductor. This process produces conduction band electron and valence band hole as follow(24) :

$$Sc + hv \longrightarrow e^-_{cb} + h^+_{vb} \qquad \text{--------------------} \; 3$$

Conduction band electrons are captured by adsorbed oxygen , while valence band holes are captured by surface hydroxyl groups(25) as in

$$e^- + O_{2(ads)} \longrightarrow O^*_{2\,(ads)} \qquad \text{--------------------------------} \; 4$$

$$h^+ + OH^-_{(surf)} \longrightarrow {}^*OH_{(surf)} \qquad \text{--------------} \; 5$$

Reaction of super oxide radical with proton can produce peroxyl radical as follow(26):

$$H^+ + O^*_2 \longrightarrow HOO^* \qquad \text{-------------} \; 6$$

Photocatalytic degradation of dyes are occurred by reaction with $OH^\cdot_{(surf)}$ (27) as in

$$Dye + {}^*OH_{(surf)} \longrightarrow Degradation \qquad \text{-----------} \; 7$$

Reaction of H_2O molecules with O_2^- produces peroxyl radicals again as follow(28):

$$H_2O + O^-_{2\,(ads)} \longrightarrow OH^-_{(surf)} + HO^*_2 \qquad \text{----------} \; 8$$

$$HO^{*}_{2} + \text{dye} \longrightarrow \text{photodegradation} \qquad \text{----------}\ 9$$

Conclusions:

Using of TiO_2 in the decolarization of wastewater is more active than ZnO . Efficiency of the treatment is increased with increasing of reaction temperature ,for the two catalysts. Complete decolarization of wastewater is occurred after 210 min. when TiO_2 is used and 250 min when ZnO is used .The used photocatalysts can be recovered from the reaction mixture and then they dried to be used in other reactions. The treated water can be recycles into the factory for industrial purposes or it can be disposed into the soil with limited harmless..

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