

Photocatalytic Degradation of Salicylic Acid over Naked and Riboflavin Sensitized Zinc Oxide

التجزيء الضوئي المحفز لحمض الساليسليك بواسطة اوكسيد الزنك المجرد و المحسس بصبغة الرايبوفلافين

Abbas A .Drea , Abbas J.Attia ,Salih H.Kahdum ,and Ahmed A.Saadoon
University of Babylon/ Collage of Science/ Chemistry Department

Abstract :

Photocatalytic degradation of salicylic acid over suspended zinc oxide ,and its sensitized with riboflavin has been done in this work . Irradiation of reaction mixture carried out by sunlight ,and ultraviolet light from mercury vapor lamp. the reaction was followed spectrophotometrically by Infrared ,and ultraviolet-Visible spectrophotometer .The remaining quantity of the acid was determined by spectrophotometric method ,by using a suitable calibration curve .The calibration curve was obtained by using a standard solutions of the acid ,the absorbance is measured at 320 nm .the investigated result showed that, sensitized zinc oxide was more active than its naked for in this reaction . under irradiation with sunlight and using RF/ZnO ,The represented result of the reaction was more active according to activation energy equal to $30.88 \text{ kJ mol}^{-1}$ respective than naked ZnO under the same conditions of reaction.

الخلاصة :

تم اجراء دراسة التجزوء الضوئي المحفز لحمض الساليسليك بواسطة استخدام عالق اوكسيد الزنك المجرد والمحسس بصبغة الرايبوفلافين . تم تشيع مزيج التفاعل باستخدام ضوء الشمس الاعتيادي والاشعة فوق البنفسجية المنبعثة من مصباح زئبقي . تم متابعة التفاعل طيفيا بواسطة مطيافية الأشعة تحت الحمراء والأشعة المرئية وفوق البنفسجية . تم تقدير كمية الحامض المتبقي من التفاعل طيفيا بواسطة استخدام منحنى معايرة قياسي يتضمن تراكيز قياسية من محلول حامض الساليسليك وبطول موجي مقداره 320 نانوميتر . بينت النتائج ان اوكسيد الخارصين المحسس بصبغة الرايبو فلافين ذو كفاءة أعظم , وبطاقة تنشيط تساوي 30.88 كيلو جول لكل مول واحد مقارنة بالعامل المساعد المجرد لنفس تفاعل تجزئة حامض الساليسليك و بنفس الظروف المستخدمة.وكذلك تبين ان استخدام العامل المساعد المجرد مع ضوء الشمس يعطي نتائج سلبية مقارنة باستخدامه مع صبغة الرايبو فلافين.

Introduction :

Heterogeneous photocatalysis systems can be defined as type of photoreactions which are carried into different phases usually liquid/solid phase. In this type of reaction semiconductors play a main role in the reaction as a photocatalysts⁽¹⁾. Usually reaction started by irradiation the particles with light of a proper energy ,that's equal to ,or greater than band gap energy of these photocatalyst⁽²⁾. Many methods are used in order to reduce the rate of recombination reaction which is commonly occurs when used naked photocatalast⁽³⁾ . One of the most importantly methods which are used to prevent back electron transfer ,is the used of photosensitizers which are an organic dyes absorbing light with high efficiency at wide range of solar spectrum. Excited state of the dye (D^*) inject electron in the conduction band of the photocatalyst⁽⁴⁾ as in Figure (1).

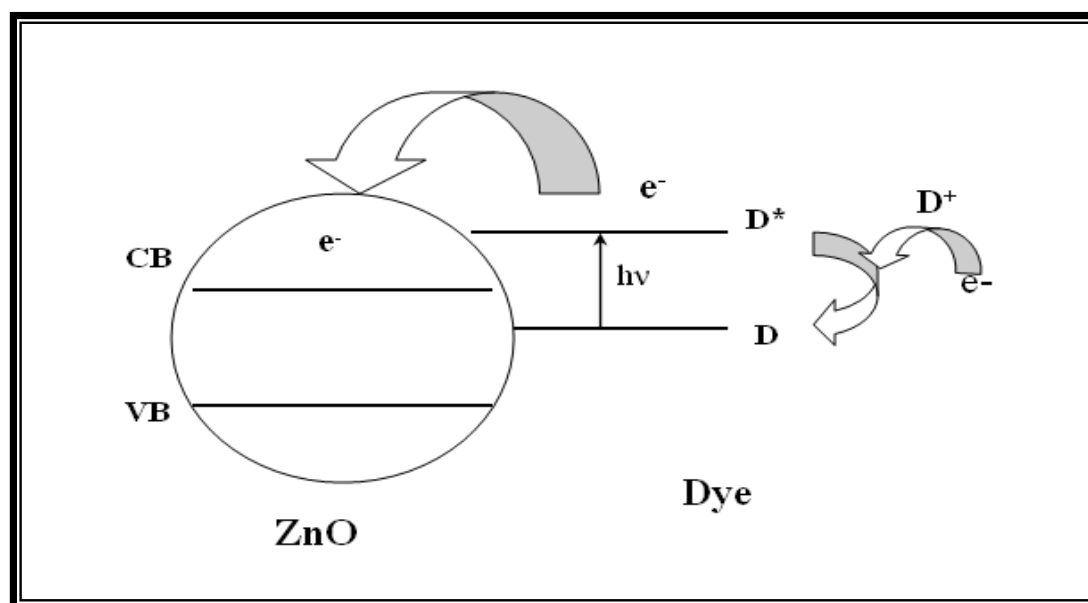


Figure (1) Electron injection from excited dye molecules into the conduction band of catalyst.

The used photosensitizer can extend photoresponse of semiconductor particles into the visible region of solar spectrum. Also this process can reduce recombination reaction between conduction band electron and valence band hole, the recombination reaction commonly occurs when used naked photocatalyst^(5,6).

The present work involved photocatalytic degradation of salicylic acid over ZnO, and RF/ZnO under illumination with solar energy and ultraviolet light, using mercury vapor lamp at different temperatures.

Experimental

Zinc Oxide (99.97% BDH) has been used as photocatalyst⁽⁷⁾. Unit cell of reaction compartment was made from Pyrex, which is provided with quartz window. This window is fitted with mercury vapor lamp. Also the cell has connections for passing air over reaction, and for water circulation around reaction cell in order to keep temperature at desired value. The reaction units are represented in Figure (2).

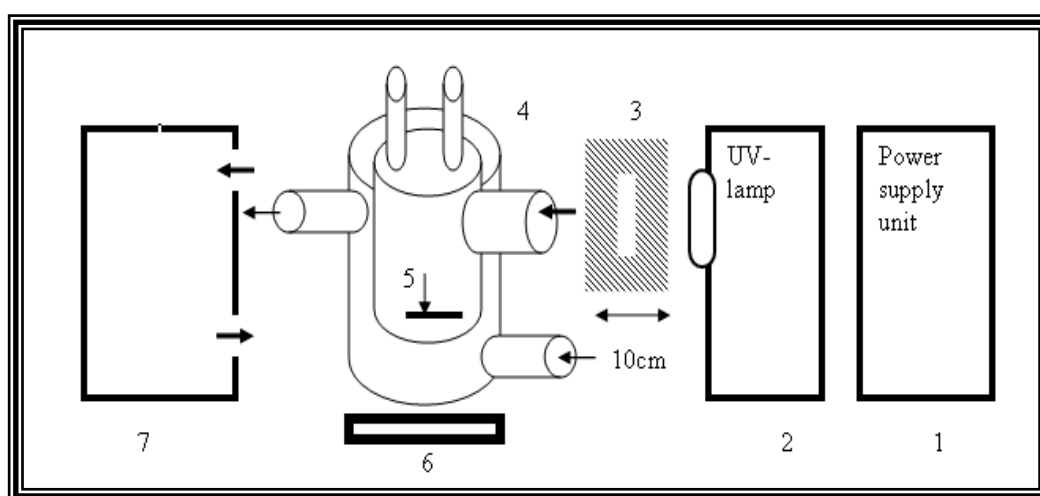


Figure (2) Apparatus setup for the reaction system.

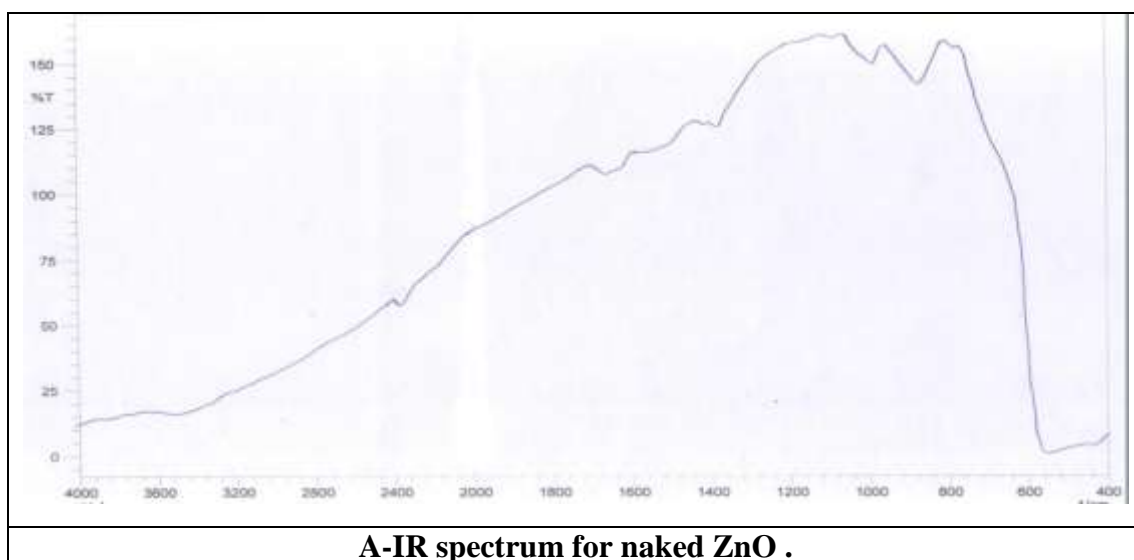
- | | |
|-----------------------|--|
| 1- Power supply unit. | 5- Mixing Plate |
| 2- UV-Light Source. | 6- Magnetic stirrer. |
| 3- Lens. | 7- Thermostats and water Circulating unit. |
| 4- Photo cell. | |

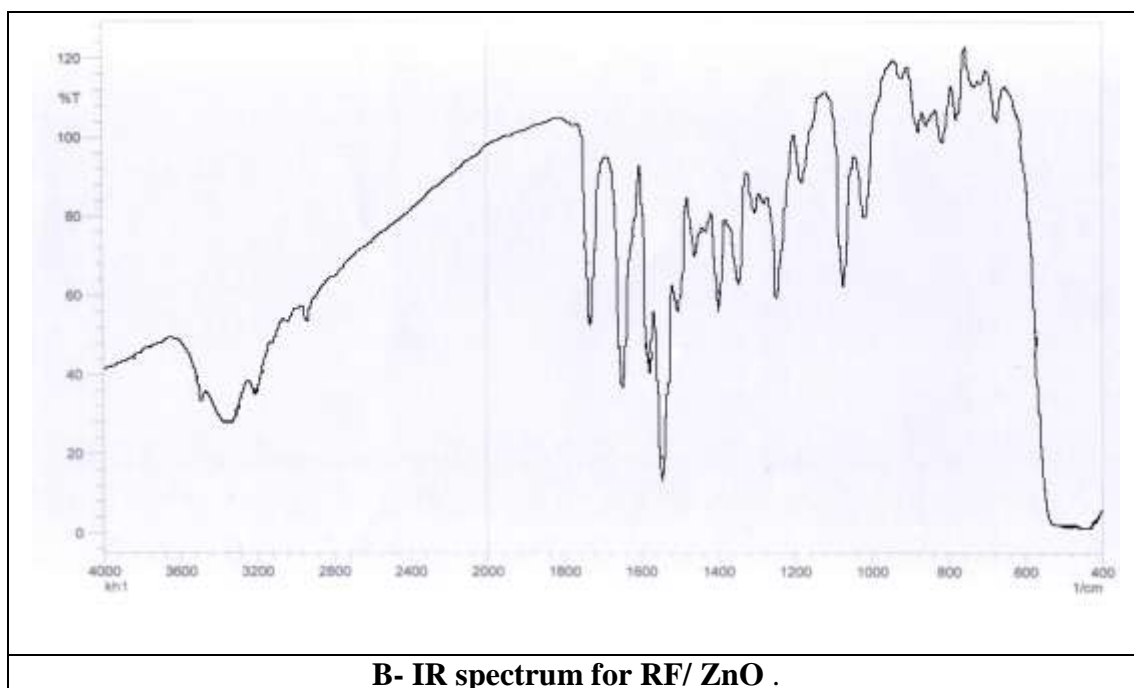
In each experiment 0.14 gm of ZnO powder was suspended in 30 mL of 0.08 mol.dM⁻³ of a salicylic acid solution. The solution has been kept homogenous by continuous stirring with magnetic stirrer. periodically ,samples of 2mL of reaction mixture were with drawing by using syringe . These solutions are centrifuged in order to remove a solid catalyst.

The absorbance of supernatant liquid is measured at 320nm by using ultraviolet visible spectrophotometer(SP21). The concentrations of remaining salicylic acid with reaction time was determined by calibration curve . the calibration curve was obtained by using standard solution of salicylic acid .sensitization of ZnO with riboflavin was done by impregnation method .According to this method ZnO was add in 1%to alcoholic solution of dye 1×10^{-5} M of propanol with passing air at $20 \text{ cm}^3 \text{ min}^{-1}$ with continuous stirring at 298K for 120 mint. The product has been centrifuged and washed with ethanol to remove weakly adsorbing dyes on the surface. The samples then dried at 328K into four hours.

Results and Discussion:

This work involve photocatalytic degradation of salicylic acid over naked ZnO ,and its sensitized form with riboflavin as a photosensitizer . Also the reaction was carried out in the irradiation with sun light and UV light. The loading of photocatalyst with riboflavin was followed spectrophotometer by using FT-IR and for ZnO and RF/ZnO respectively .these results are shown in Figure (3).





Figure(3) FT-IR spectrums of semiconductor catalyst with out and with the sensitized pigments .

The results of the photocatalytic degradation of salicylic acid over naked ZnO and irradiation with solar energy and UV light are shown in table (1).

Table (1) photocatalytic degradation of Salicylic acid over ZnO under irradiation with sun light and ultraviolet light at 303K.

Source of light	Salicylic acid concentration (mol.dM ⁻³)				
Sun light					
Time (hour)	0	4	8	12	16
concentration	0.080	0.078	0.077	0.076	0.074
UV light					
Time (min)	0	15	30	45	60
concentration	0.080	0.075	0.069	0.065	0.058

The investigation from above results tends to presence efficient reaction, which is more active by using UV light radiation with respect to use sun light under some conditions for the reaction. This feature is related to the energy that's required in the excitation of ZnO particles ($E_g = 3.020 \text{ eV}$). The wave length which is provided this energy fall in the ultraviolet region of solar spectrum⁽⁸⁾. The ratio of UV-light in solar spectrum is about 10% this small ratio give a low intensity of radiation as it compared with UV-light from industrial source which is supplied 125 Wcm^{-2} intensity of radiation in UV-region⁽⁹⁾. According to the first law of photochemistry only one particle of ZnO is excited by absorbing one photon. The excited particles of photocatalyst are contributed in the photocatalytic degradation of the used acid⁽¹⁰⁾, irradiation with solar energy have been low efficiency as comparing with mercury vapor lamp energy under same reaction conditions .

Results of photocatalytic degradation of salicylic acid over sensitized ZnO with (RF)under irradiation with sunlight and UV light from mercury vapor lamp are shown in table (2).

Table (2) Photocatalytic degradation of salicylic acid over ZnO and RF/ZnO under irradiation with solar energy at 303K.

Catalyst	Salicylic acid concentration (mol.dM ⁻³)				
ZnO					
Time (hour)	0	4	8	12	16
concentration	0.080	0.078	0.077	0.076	0.074
RF/ZnO					
Time (min)	0	15	30	45	60
concentration	0.080	0.070	0.060	0.052	0.043

Table (3)Photocatalytic degradation of salicylic acid over ZnO and RF/ZnO under irradiation with UV-light energy at 303K.

Catalyst	Salicylic acid concentration (mol.dM ⁻³)				
ZnO					
Time (min)	0	15	30	45	60
concentration	0.080	0.078	0.077	0.076	0.074
RF/ZnO					
concentration	0.080	0.070	0.060	0.052	0.043

From above results ,its clearly that using sunlight in the irradiation ZnO gives low efficiency of reaction. This feature may be attributed to the band gap energy of ZnO(3.22ev)this energy lies in the range of UV-light ($\lambda < 400\text{nm}$)⁽¹¹⁾. Using of riboflavin as a photosensitizer with ZnO gives a good results ,because dye molecules absorb light strongly in visible region of solar spectrum ⁽¹²⁾ . the absorption of light by dye molecules generates excited state of the dye , either singlet or triplet ⁽¹³⁾ .

Excited state of dye injects electron into the conduction band of the photocatalyst . this process prevents back electron transfer ,which is commonly occurs in recombination reaction when used naked ZnO as shown in Figure (1).

So that reduction rate of recombination reaction by used sensitized photocatalyst can give a high efficiency for the reaction .the high efficiency for reaction in this case is due to contribution of electron in conduction band in the redox reaction of the adsorbed species on the surface of the photocatalyst ⁽¹⁴⁾ .

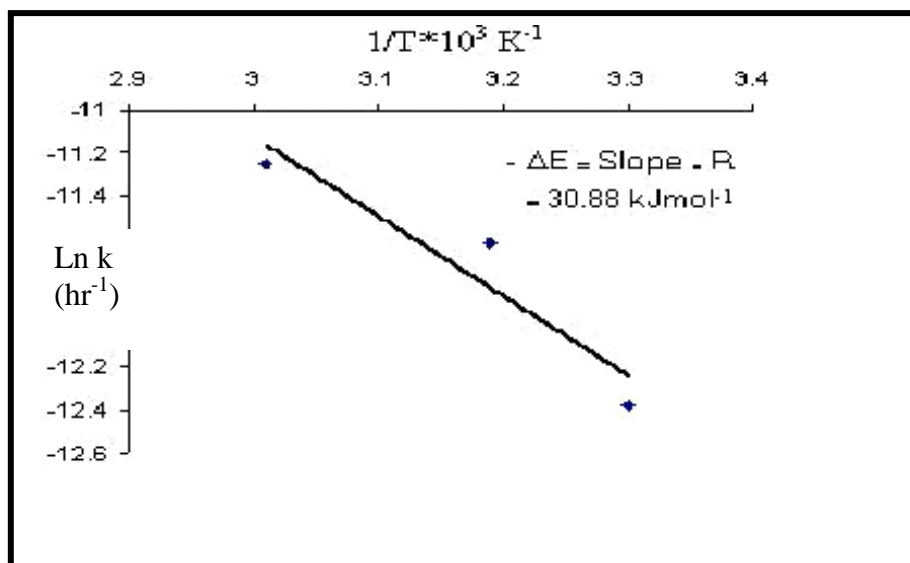
Effect of temperature on the reaction rate

Temperature effect on reaction rate have been carried out by using a range of temperature degrees to photocatalytic degradation of salicylic acid .the results of temperature effect are shown in table(4).

Table (4) Effect of temperature on the reaction rate of photocatalytic degradation of salicylic acid.

T/K	Salicylic acid concentration (mol.dM ⁻³)				
	Time (hour)				
	0	15	30	45	60
303	0.080	0.076	0.070	0.065	0.058
313	0.080	0.070	0.062	0.060	0.052
323	0.080	0.062	0.055	0.051	0.041

Generally ,the conductivity of the semiconductor are directly proportional with the number of electrons in the conduction band which in turn depends on the Boltzman factor as a function of temperature ($e^{-\Delta E/RT}$).So that conductivity of semiconductor increases exponentially with temperature, therefore the reaction rate of salicylic acid degradation increased as temperature raising ⁽¹⁵⁾ .Figure (4)represent the relation between rate constant and temperatures degree of reaction, were activation reaction equal to 30.88 kJ mol⁻¹.



Figure(4)relation of rate constant with temperature degree for photo reaction salicylic acid.

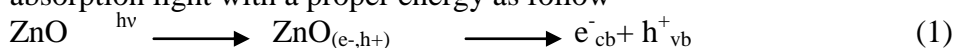
Temperature effect on reaction also resulted from the process which are occurred on the surface of photocatalyst such as adsorption of reacted species into the active sites on the surface and the adsorption of products from the surface. These process are strongly effected by change of temperature ⁽¹⁶⁾.

These steps are not rate determining step in photocatalytic reaction. the rate determining step in this type of reaction is the electron transferring from valance band into the conduction band of the photocatalyst ⁽¹⁷⁾.

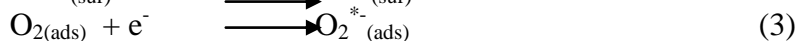
Reaction Mechanism

1- using naked ZnO

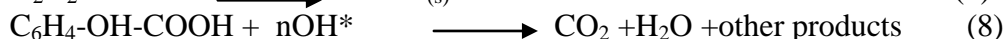
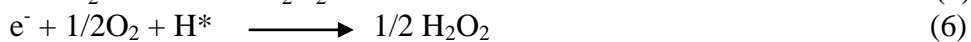
the first step in this reaction mechanism is the excitation of semiconductor particles by absorption light with a proper energy as follow



Positive holes are trapped by surface hydroxyl group, while electrons are trapped by absorbing oxygen as follow



These radicals are contributed in many reaction produced peroxide and hydroxide radicals as follow

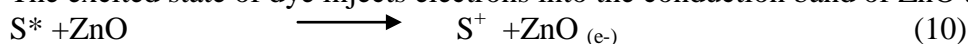


2- Used photosensitizers

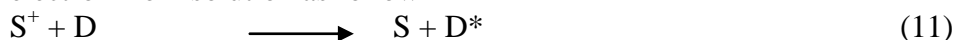
The first step in this case is the excitation of dye molecule as follow



The excited state of dye injects electrons into the conduction band of ZnO as



These electrons are used in the reduction of adsorbed oxygen molecules as reported in previous mechanism. The difference in this mechanism is the absence of the positive hole (h^+) which appears when used naked ZnO . this feature can lead to prevent recombination reaction which gives high efficiency for the reaction . the oxidized state of dye (S^*) returns to its initial state by received electron from solution as follow



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