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Photocatalytic degradation of indigo carmine by ZnO photocatalyst under visible light irradiation

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Abstract

In this work, the photocatalytic degradation of indigo carmine (IC) using zinc oxide suspension was studied. The effect of influential parameters such as initial indigo carmine concentration and catalyst loading were studied with the effect of Vis irradiation in the presence of reused ZnO was also investigated. The increased in initial dye concentration decreased the photodegradation and the increased catalyst loading increased the degradation percentage and the reused-ZnO exhibits lower photocatalytic activity than the ZnO catalyst. It has been found that the photocatalytic degradation of indigo carmine obeyed the pseudo-first-order kinetic reaction in presence of zinc oxide. This was found from plotting the relationship between ln (C_0/C_t) and irradiation the rate constant of the process.UV- spectrophotometer was used to study the indigo carmine photodegradation.

Key words: photodegradation; Indigo Carmine; Zinc oxide.

Introduction:

Environmental pollution has become the most important subject in the last few years due to uncontrolled use of hazardous chemicals in agriculture, disappearing water bodies, unplanned urbanization with rapid deforestation and speedy industrialization with inadequate waste dealing and disposal [1]. This has given rise to unhealthy living conditions and increase in life threatening diseases .The organic dyes are related to one of the most familiar and large group of contaminants in waste waters from dye manufacturing, textile industries and numerous other industrial processes such as food and paper manufacture, cosmetics pharmaceuticals, and etc. The worldwide dye production is more than 7×10^5 tons per year .The losses in waste waters at different stages of industrial and during application are about 10-15% of the total production amount [2]. Organic dyes can go through transformation in aquatic media and can form harmful carcinogenic and mutagenic intermediates, this way cause a serious risk for survival of microorganisms[3,4] , marine life and environmental media-water and soil. The influence of such infections on human health may be unpredictable hazardous inflicting diverse diseases like immune -suppression, neurobehavioral disorders presage as allergy, irritation and respiratory, central nervous, and even lung edema[5].

Materials and Methods:

Materials

Indigo Carmine dye was obtained from Al- Hila Textile Factory, photocatalyst ZnO purity (99%) from BDH, Hydrogen peroxide purity (50%) from LTD, Sodium chloride purity (99.5%) from BDH.

Methods

A stock solution of indigo carmine was prepared (1000 ppm) by diluting 0.1 gm of indigo carmine in 100 ml deionize water and then the required concentrations were prepared by diluting (10, 14.5, 25, 30, 35, 20, 40, 55, 60 ppm). Table (1) shows the concentrations with absorbance. Figure (1), (2) shows the spectra of the best concentration for indigo carmine.

Table (1) shows the concentration of indigo carmine and its absorbance.

Concentration of indigo carmine ppm	ABS.
10	0.993
14.5	1.143
25	1.325
30	1.462
35	1.578
40	1.662
45	1.734
55	1.943
60	2.042

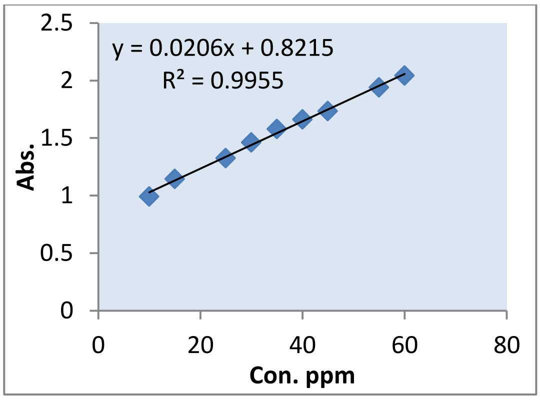


Fig. (1). calibration curve of indigo carmine.

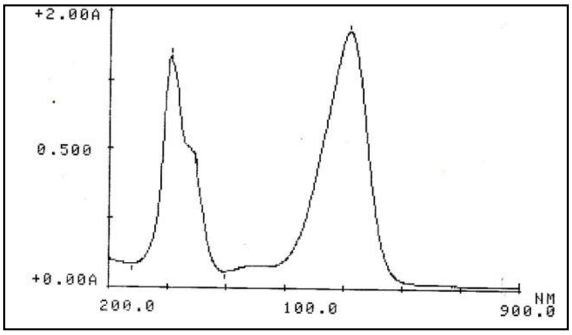
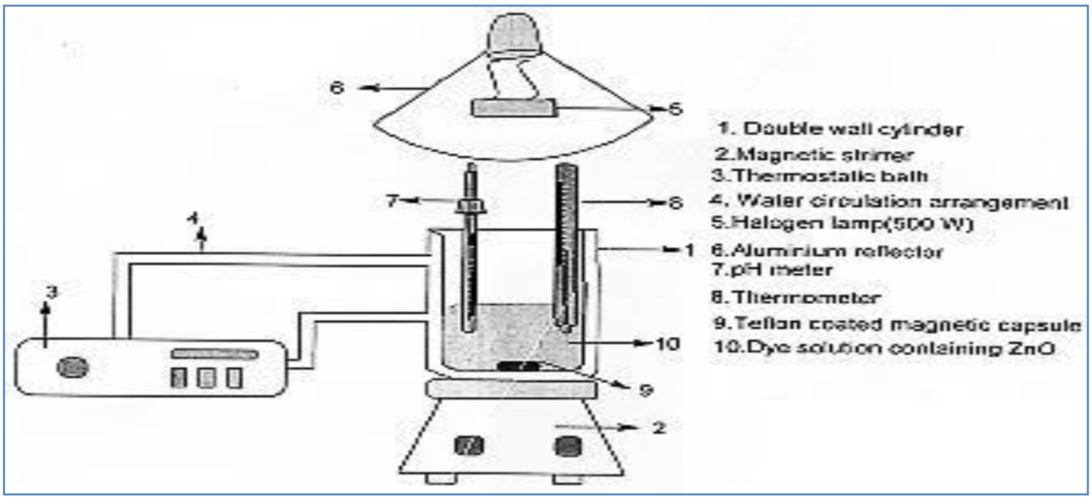


Fig. (2). UV –Vis spectra for indigo carmine (60 ppm).

Sodium chloride solutions were prepared by dissolving (5 gm,10 gm) from Nacl with 1000 ppm/100 ml of indigo carmine respectively. Hydrogen peroxide (1.67 M)0.28 ml of hydrogen peroxide (M.Wt= 34.01g/mole, density= 1.20 g/ml) was diluted in deionize water to 50 ml; then 0.2 ml of hydrogen peroxide added to 60 ppm/100 ml of indigo carmine and making the final volume 50 ml.

Control Experiments:

Added 50 ml of indigo carmine solution to the double – well Pyrex photocell as shown in Figure (3). This was followed by the addition of 0.1 gm/50 ml of the catalyst zinc oxide. In all experiments, the solution was stirred by a magnetic stirrer to keep the solution homogeneous. The reactions temperature was controlled by water circulating thermostat. The photocell was covered by aluminum foil to avoid any release of radiation. The photocell suspension solutions were irradiated in the photocell from the top of the photocell. The mixture of solution is visible irradiation irradiated by halogen lamp (50W) placed in the top of photocell for visible irradiation decision time.



Results and Discussion:

The Effect of Catalyst Loading

The influence of catalyst loading on photodegradation of indigo carmine was investigated by varying the 584 amount from 0.05 to 0.2 gm/50 ml for indigo carmine to found the effect of photocatalyst loading and to avoid needless excess photocatalyst , keeping all parameters fixed. The results in Figures (4) show that the maximum % was done at 0.1 gm of photocatalyst . This may be due to the fact that increasing the amount of photocatalyst increases the number of effective sites and thus leads to enhanced of OH• radicals or super oxide O_2^{-2}. Furthermore, the number of adsorbed indigo carmine molecules increased owing to an increase in the number of photocatalyst particales, which results in increasing photodegradation[6]. When the mount of photocatalyst was enhanced beyond optimum, the photodegradation was not increased [7]. The decreased efficiency beyond the optimum photocatalyst loading may be attributed to the screening effect of excess photocatalyst particles in the solution. Moreover, agglomeration and sedimentation of photocatalyst particles is also probable. In such a condition, a part of the photocatalyst surface probably becomes unavailable for photon absorption and dyes adsorption, thus bringing little stimulation to the photocatalytic reaction[8].

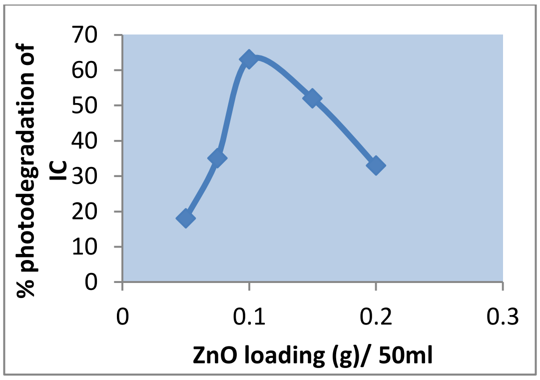


Fig. (4) shows influence of catalyst loading on indigo carmine (60ppm) photodegradation, ZnO=0.1 gm/50ml, T=298.15K.

The Effect of Initial Concentration of dye

The photocatalytic degradation of various indigo carmine concentrations (60, 75, 90 ppm) were studied as shown in Figure (5). With an increase in the concentration of indigo carmine photodegradation percentage was decreased. The concentration of 60 ppm for indigo carmine degraded totally, with an increase in the concentrations of dye photodegradation percentage was decreased [9]. For higher dye concentration, the presumption is that active sites are covered by dye and its intermediates can cause reduced generation of e--h+, which reduces photodegradation efficiency[10]. The other possibility is that as the initial dye concentration increases but the mass of photocatalyst and the intensity of light and illumination time are constant, then the •OH and O_2^{-2} species formed on the surface of photocatalyst are constant, so that the relative ratio of the •OH and O_2^{-2} for attacking indigo carmine decreases and the photodegradation% decreases. Another factor which may be responsible for the decrease in photocatalytic degradation rate is the competition between adsorbed dye and H_2O molecules for photodegraded h+ and the dye start acting as filter for the incident light and they do not permit the desired light intensity to reach the semiconducting particales and thus, decreasing the rate of photocatalytic bleaching of dye[11].

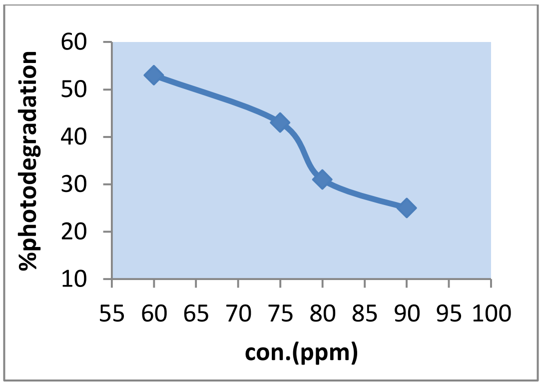


Fig. (5) shows the photodegradation of indigo carmine at various initial concentration, ZnO=0.1 gm/50 ml, pH=7 and T=298 K.

A comparison of ZnO and reused- ZnO Degradation

To compare the efficiency, reused- ZnO catalyst was tried under the similar process conditions. Figure (6) is for indigo carmine which shows the rate of photodegradation. They show that reused- ZnO catalyst displays lower photocatalytic activity than the ZnO catalyst, and the clarification is that as the active groups of reused- ZnO catalyst decrease, the equilibrium adsorption of dye and adsorption of OH^- on the catalyst surface active sites also decrease, which means a lower degradation efficiency [12].The rate constant for indigo carmine is 0.0096 min^{-1} Figures (7) show the kinetics and R^2 values. Figures (8) show the UV-Vis spectra change for the dye. Tables (2) show the rate of photodegradation for the dye.

Table (2) shows the rate of photodegradation at different times of 60ppm indigo carmine and 0.1 gm ZnO reused.

t (min)	ABS	C_t	ln C_t
15	1.746	44.8	3.802
30	1.711	43.1	3.763
45	1.672	41.2	3.718
60	1.448	30.4	3.414
75	1.351	25.7	3.246
90	1.310	23.7	3.166

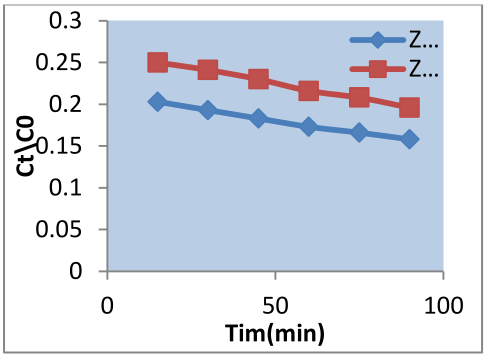


Fig. (6) shows the rate of photodegradation of indigo carmine 60ppm with 0.1 gm ZnO reused.

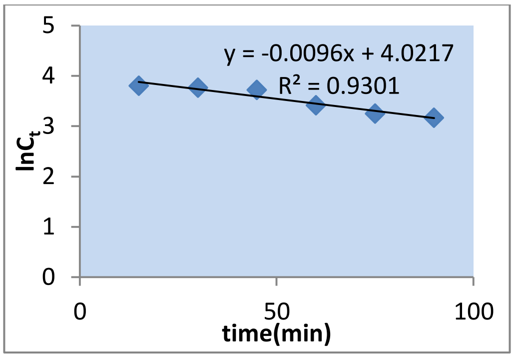


Fig. (7) shows the kinetics of degradation of indigo carmine 60ppm with 0.1 gm ZnO reused.

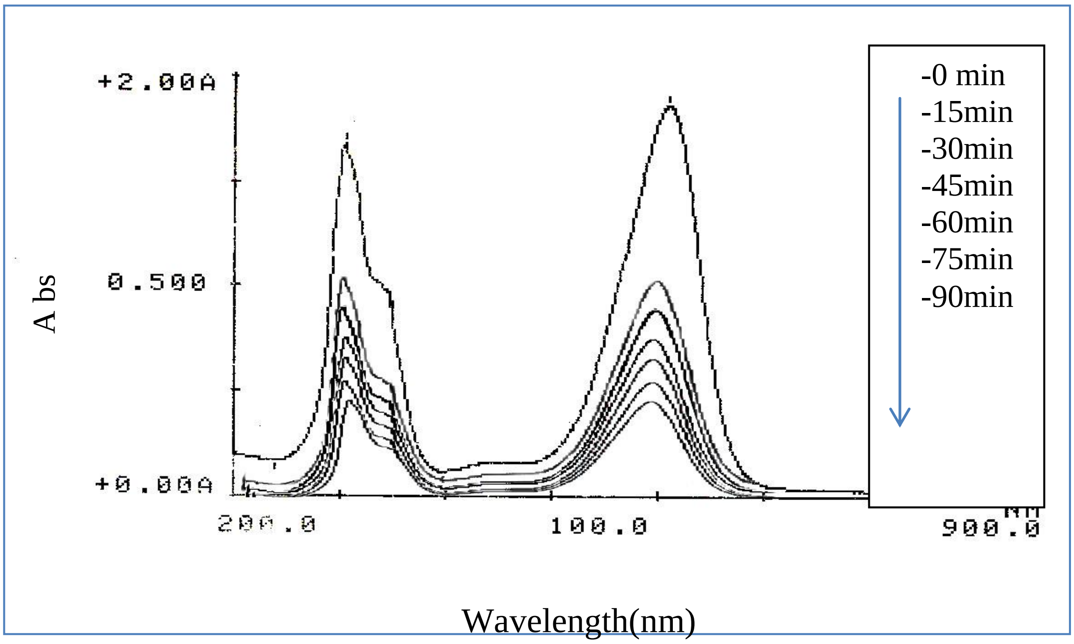


Fig. (8) UV-Vis spectra shows the change of degradation for indigo carmine (60ppm), T=298.15 K with different irradiation time by using ZnO reused =0.1 gm.

Conclusion:

1- Indigo carmine degraded totally by using ZnO under Vis irradiation.

2- The photocatalytic degradation efficiency decreased with increasing the dye concentration.

3- The photocatalytic degradation increased with increasing the ZnO loading and the optimum load was 0.1 gm.

4- The reused- ZnO catalyst exhibits lower photocatalytic activity than the ZnO catalyst.

5- The photocatalytic degradation of dye followed a pseudo- first-order kinetic model.

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التجزئة الضوئية لصبغة Indigo carmine بأستخدام عامل مساعد فعال ضوئيا ZnOتحت تأثير الضوء المرئي

علي سلمان الطائي **هبه مجيد ضاحي**

قسم الكيمياء، كلية العلوم للبنات، جامعة بغداد، بغداد، العراق.

الخلاصة

تم من خلال البحث الحالي دراسة التجزئة الضوئية المحفزة لبعض الملوثات بوجود اوكسيد الخارصين بوصفه محفزا ضوئيا . كما تمت دراسة تاثير العوامل المؤثرة في التفاعل مثل التركيز الابتدائي لهذه الملوثات وكمية المادة المحفزة. لقد تبين ان زيادة تركيز المادة الملوثة تقلل من النسبة المئوية للتجزئة وزيادة تركيزالمادة المحفزة تزيد من النسبة المئوية للتجزئة. كما وجد ان التجزئة الضوئية لهذه الملوثات تتبع تفاعلات المرتبة الاولى الكاذبة بوجود العامل المحفز ZnO اذ تم رسم العلاقة$\ln(C_0/C_t)$ وزمن التشعيع فكانت العلاقة خطيه . جرى تتبع هذه النتائج بوساطة مطيافية UV-Vis لدراسة التجزئة للصبغةindigo carmine

الكلمات المفتاحية: التحلل الضوئي، صبغة indigo carmine، أكسيد الزنك.