Decolorization and Degradation of Reactive Red Dye-238 by using ZnO

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Abstract

Removal of reactive red dye (Cibacron Red FN-R) from simulated wastewater has been investigated as a function of solar advanced oxidation process. The photocatalytic activity using ZnO as a photocatalyst has been estimated. Different parameters affected the removal efficiency, including pH of the solution; initial dye concentration and H_2O_2 concentration were evaluated to find out the optimum value of these parameters. The results proved that, the optimal pH value was 8 and the most efficient H_2O_2 concentration was 100mg/L. Reduction of organic content for effluent solution was also monitored by measuring chemical oxygen demand (COD) to assess the degradation process. This treatment method was able to strongly reduce the organic content of reactive red dye-238 to 90% while the colour removal was 99%. It can be concluded, from these experiments, that the using of ZnO as a photocatalysis was exhibited as economical and efficient treatment method to remove reactive red dye-238 from aqueous solution by reducing its colour and COD value. Results were properly fitted to LH model.

Key Words: photocatalysis, reactive dye, zinc oxide, azo dye.

ازالة اللون و تحلل الصبغة الفعالة الحمراء -238 بأستخدام اوكسيد الخارصين

د.رياض الانباري د.عبد الحميد العبيدي ايمان عبد

الخلاصة

تم دراسة عملية ازالة اللون لصبغة الازو الحمراء (Cibacron Red FN-R) من مياه مخلفات مصنعة في المختبر باستخدام عملية الاكسدة المتقدمة بالطاقة الشمسية. تم تقييم كفاءة التحفيز الضوئي لاوكسيد الخارصين عند استخدامها كعوامل مساعدة ومن ثم تقييم تأثير عدة عوامل والتي تشمل قيمة الاس الحامضي- للمحلول وتركيز الصبغة الاولي وتركيز بيروكسيد الهيدروجين المضاف وذلك لإيجاد أفضل قيم لهذه العوامل . لقد تم التوصل الى ان أفضل قيمة للاس الحامضي- للمحلول كانت 8 وأفضل تركيز لبيروكسيد الهيدروجين المضاف كانت 100 ملغم/لتر.تمت مراقبة نسبة الانخفاض في المحتوى العضوي للمحلول الخارج من المعالجة وذلك من خلال قياس المتطلب الكيميائي للاوكسجين COD لتقييم عملية تحلل الصبغة. وكانت هذه المعالجة قادرة على تقليل المحتوى العضوي للصبغة الفعالة الحمراء -238 بدرجة كبيرة تصل الى 90% بينما كانت نسبة ازالة اللون بحدود 99% . من التجارب العملية تم التوصل الى ان استخدام اوكسيد الخارصين كعامل مساعد لعملية التحفيز الضوئي يمثل طريقة معالجة كفوءة واقتصادية لازالة الصبغة الحمراء الفعالة-238 من المحلول المائي من خلال تقليل شدة اللون وقيم COD . كانت النتائج متطابقة مع موديل LH .

1. Introduction

Dyes are common industrial residues present in wastewater of different industries, ordinarily in the textile dyeing process, inks, and photographic industries, among others (Saha, 2012).Textile industry produces large volume of colored dye effluent, which are toxic and non-biodegradable

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(Kansal *et al*., 2009).

Dyes contained two types of group, namely chromophore (chromophore is an electron withdrawing group) and auxochromes (are electron releasing groups) which are responsible for their color. The most important chromophores are the azo (-N = N-), carbonyl (C = O), methine (-CH=), and nitro (NO_2) groups (Ling, 2009).

Among the different types of dyes used in textile industry, 60–70% is azo compounds (Kansal *et al*., 2009).Due to their synthetic nature and structure mainly aromatic, most dyes are non-biodegradable, having carcinogenic action or causing allergies, dermatitis, skin irritation or different tissular changes. Moreover, various azo dyes, mainly aromatic compounds, show both acute and chronic toxicity. High potential health risk is caused by adsorption of azo dyes and their breakdown products (toxic amines) through the gastrointestinal tract, skin, lungs, and also formation of hemoglobin adducts and disturbance of blood formation (Anjaneyulu *et al*., 2005)

There are several available methods to treat this wastewater such as: adsorption, coagulation and precipitation, aerobic and anaerobic process, and others (Khataee *et al*., 2009). One difficulty with these methods is that they are not destructive but only transfer the contamination from one phase to another. Therefore, a new and different kind of pollution is faced and further treatments are deemed necessary (Saien and Khezrianjoo, 2008). An alternative to conventional methods, "advanced oxidation processes" (AOPs) have been developed based on the generation of very reactive species such as hydroxyl radical. The generated hydroxyl radical can oxidize a broad range of organic pollutants quickly and non-selectively (Ibhadon and Fitzpatrick, 2013).

A photocatalyst is defined as a substance, which is activated by adsorbing a photon and is capable of accelerating a reaction without being consumed; these substances are invariably semiconductors (Sanayei et al., 2009).

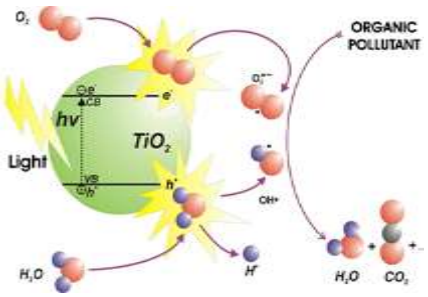

Figure 1. Schematic of semiconductor excitation (Transito, 2015)

The photocatalytic reaction mechanism shown in Figure 1 can be described by equations (1) to (7) as shown below (Montano, 2007):

$$\text{Photocatalysts} + h\nu \rightarrow e^- + h^+ \quad (1)$$

$$h^+ + H_2O \rightarrow H^+ + OH^\bullet \quad (2)$$

$$h^+ + OH^- \rightarrow OH^\bullet \quad (3)$$

$$e^- + O_2 \rightarrow O_2^- \quad (4)$$

$$2e^- + O_2 + 2H^+ \rightarrow H_2O_2 \quad (5)$$

$$e^- + H_2O_2 \rightarrow OH^\bullet + OH^- \quad (6)$$

$$\text{Organic} + {}^\bullet OH + O_2 \rightarrow CO_2 + H_2O \quad (7)$$

The present study was concerned to monitor the decolorization of the reactive red dye-238 (Cibacron red FN-R) in solution by using ZnO as a photocatalysis under solar light radiation instead of UV-lamp. The effects of important parameters including pH and concentration of H_2O_2 were examined with respect to the highest efficiency of decolorization of reactive red dye. Reduction in toxicity of azo dye was also monitored during the treatment process.

2. Experimental Set-up and Materials

2.1. Materials

The reactive red dye-238 RR had been supplied from AL-Kut textile factory south of Baghdad, (Department of Dying and Printing). Simulated solutions were prepared by dissolving a defined amount of dye in the required volume of distilled water. The chemical formula for this dye is $C_{29}H_{15}O_{13}S_4ClFN_7Na_4$ and the colour index number is CI Reactive Red 238 (Nunez *et al.*, 2007).
Analytical grade reagents of ZnO, H_2SO_4, NaOH and H_2O_2 were used as such without further purification.

2.2. Experimental set-up

Advanced oxidation processes were carried out by preparing a suspension of simulated synthetic solution containing reactive red dye and the selected photocatalysis was ZnO. This suspension was kept in an absence of light for about 15 min to achieve the equilibrium of adsorption, after that the degradation was accomplished under sunlight and the average intensity of sunlight was measured by using UV-radiometer (UV-340A, Lutron, USA). The heat up of the solution was not much and the temperature varied within ± 6 °C between starting and ending point of reaction.
Samples were withdrawn from effluent at regular time interval and filtered by using 0.45 μm membrane filter then the dye concentration was measured by UV-spectrophotometer (UV-1800 Shimadzu) at a spectrum length of 541nm.
The concentrations of H_2O_2 added were 0, 100, 200, 300 and 400 mg.L^{-1}. The initial concentration of reactive red dye chosen was 25, 50, 75 and 100 mg.L^{-1}. To study the effect of pH, the values of 2,4,6,8 and 10 were selected as initial pH value of the solution.

2.3. Kinetic analysis

The most suitable model used to describe photocatalytic processes is the Langmuir–Hinshelwood (LH), which is described by the following mathematical relationship:

$$r = -\frac{dc}{dt} = K_{LH}\frac{KC}{1+KC} \quad (8)$$

Where: r (mg $L^{-1}s^{-1}$) represents the reaction rate, C (mg L^{-1}) the pollutant concentration at time t during degradation, K (mg^{-1}L) the equilibrium constant for pollutant adsorption onto catalyst and k LH (mg $L^{-1}s^{-1}$) the reaction rate constant at maximum coverage. Under certain experimental conditions, KC<<1, so that the LH model is usually closer to first-order reaction kinetics and equation (8) will simplified to:

$$r = \frac{dc}{dt} = -K_{LH}.KC = -K_{\circ}C \quad (9)$$

Where, $K_{\circ}$ (min^{-1}) =K_{LH} K is the pseudo-first-order rate constant (Transito *et al.*, 2015).
The intensity of solar irradiance was never constant and could not be controlled due to multiple environmental influences (i.e., time of day or atmospheric conditions) and in order to normalize data collected at different solar light intensity and exposure time was used (Montano, 2007).

$$t_{30W,n} = t_{30W,n-1} + (t_n - t_{n-1})\frac{UV}{30}\frac{V_i}{V_T} \quad (10)$$

In equation (10), t_n is the experimental time for each sample, UV the average solar ultraviolet radiation measured during tn, and t_{30W} is the "normalized illumination time". In this case, time refers to a constant solar UV power of 30 W/m^2 (typical solar UV power on a perfectly sunny day around noon), V_i is the irradiate volume and V_T the total volume (Vargas and Nunez, 2010). In that way, photocatalytic process could be evaluated as a function of time taking into account environmental conditions (Montano, 2007).

3.Results and Discussion

3.1 Effect of pH

The pH value of the aqueous solution is a key parameter for photocatalytic process. The aqueous solution of dye having 25mg.L^{-1}concentration were treated by varying the initial pH of solution from pH=2 to 10. The pH value was justified by using 0.1N H_2SO_4 or 0.1N NaOH as required.

Figure 2 shows the effect of pH on the removal efficiency of reactive red dye. It can be concluded from this figure that the photocatalytic efficiency was maximized when solution pH reached to 8 .

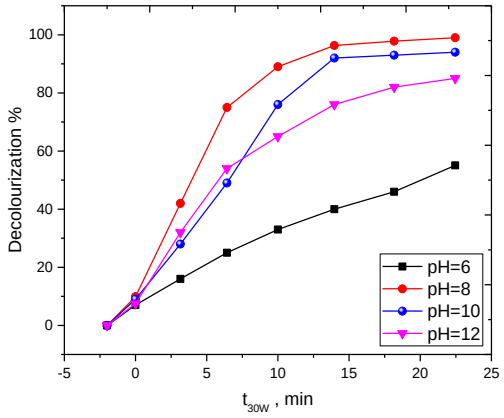

Figure 2. Removal efficiency of reactive red dye at different initial pH .

This behaviour can be explained by the surface charge of catalyst. Each catalyst have point of zero charge (pHpzc) at this pH where the net charge on catalyst surface is equal zero (Zuafuani and Ahmed, 2015) and catalyst surface is positively charged at pH< pHpzc whereas it is negatively charged for pH > pHpzc (Khezrianjoo and Revanasiddappa, 2013).

The point of zero charge (pHpzc) for ZnO was cited in literatures at pH=8.9 (Zuafuani and Ahmed, 2015).

3.2 Effect of H_2O_2 concentration

The addition of H_2O_2 has a major effect on the photocatalytic process; this additive increases the rate of reaction by improvement the formation of hydroxyl radical. This is due to inhibition the recombination of the electron–hole in present of H_2O_2. The decolorization rate of reactive red dye can be accelerated by increasing the concentration of OH radicals by the addition of oxidant like H_2O_2 (Kavitha and Palanisamy, 2011). As illustrated in Figure 3, the results show that the decolorization percent increases when the concentration of H_2O_2 increased, the percentage removal becomes maximum at 100 mg/l and after that begin declining with further increase in H_2O_2 concentration.

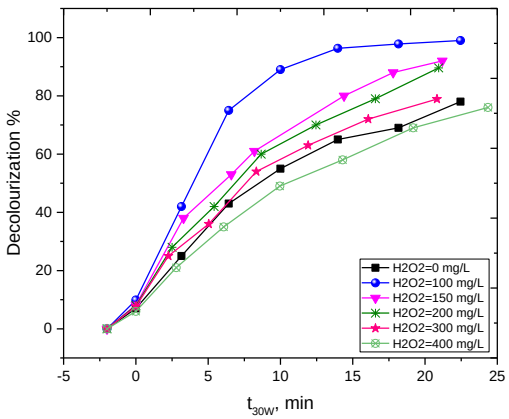

Figure 3. The effect of H_2O_2 concentration on decolorization percent of reactive red dye

This effect is due to the fact that at a higher H_2O_2 concentration, scavenging of OH radicals will take place (Kalantary *et al*., 2014).

3.3 The effect of initial concentration of dye

The effect of initial concentration of reactive dye was evaluated by chosen different initial concentration (25, 50, 75 and 100 mg/L) and the others operation conditions was kept constant.

Figure 4 shows, as the concentration of reactive red bye was increased, the decolorization percent decreased. The increase in the initial concentration of reactive red dye will reduce the transparency of solution which finally effect on the penetration of sunlight through the solution. Another reason is that: increasing in the initial concentration of dye lead to increase the number of molecules that must be treated while the active catalytic sites still constant and this cause the decrease in the decolorization rate.

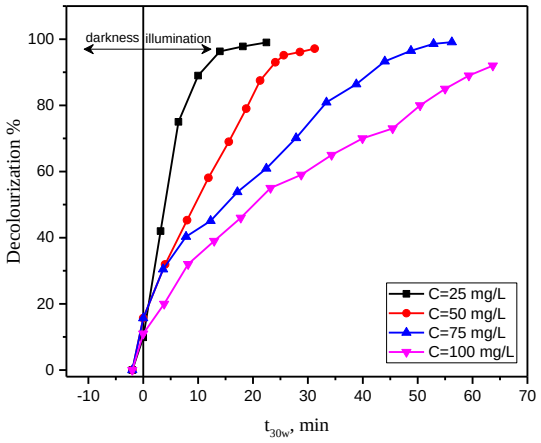

Figure 4.The effect of initial concentration of blue dye on decolorization percent of reactive red dye.

The kinetics for photocatalytic process under solar light was predicted at various dye concentrations (25, 50, 75, and 100 mg/L) and the data were fitted the LH model (Figure 5).

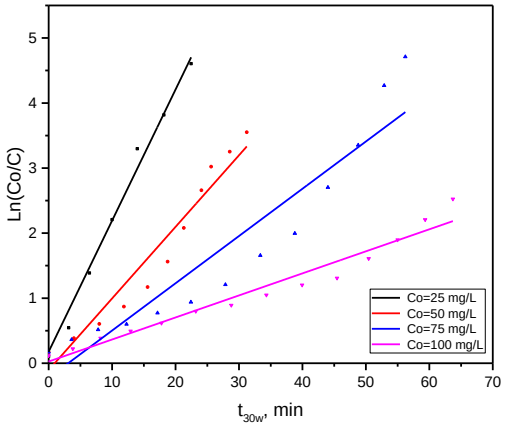

Figure 5. The LH models for reactive red dye.

The rate constant ($K_{\circ}$) for reactive red dye was estimated from the slope of the linear plots of Ln (C_o/C) vs. t_{30W} .The variation of ($1/K_o$) as a function of initial concentration of reactive dye are given in Figure 6. The equation and correlation coefficient were estimated and tabulated in Table (1).

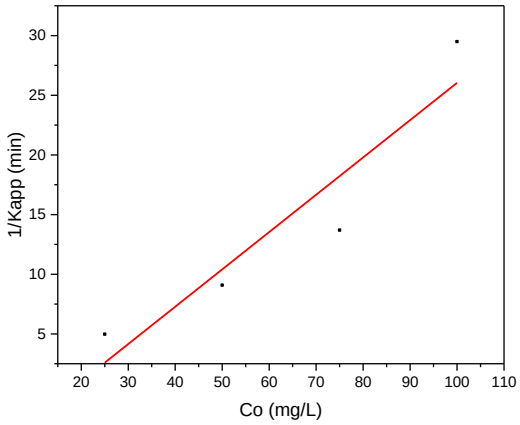

Figure 6. Variation of $1/K_0$ vs. C_0 of reactive red dye

Table 1. The kinetic analysis data

Catalysis	Equation for linear fitting	Correlation coefficient R^2
ZnO	Y= -5.229+0.3127X	0.83

3.4 Variation of COD values

The great part of the study on the photocatalytic degradation of dyes relies only on the monitoring of solution decolorization. In this study and in order to assess the degree of degradation for reactive dyes during the photocatalytic treatment, degree of degradation for reactive dyes was evaluated by determination of chemical oxygen demand during the photocatalytic process. The COD and colour removal rates for reactive red dye solution were shown in Figure7.

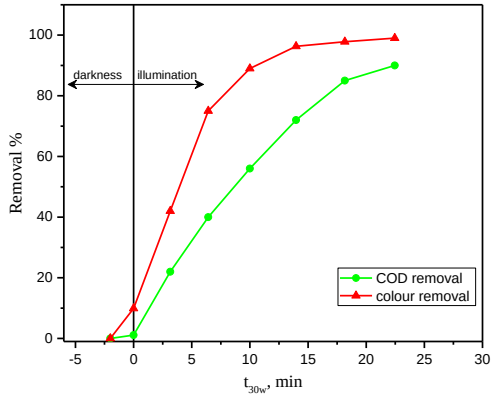

Figure 7: Variation of COD and colour removal rate with time for reactive red dye

Figure 7 indicates that the color removal efficiency was much faster than COD removal efficiency. The fast decolorization of the dye solution appears to suggest a sequenced oxidation mechanism in which hydroxyl radical preferably attacks the chromophore center of dye molecules (i.e., the azo groups, -N=N-) that resulted in fast decolorization of solution (Montano, 2007) The same trend of results was concluded by Montano(2007) and Singh *et al*. (2013).

Figure 7 demonstrates that the reduction in COD value for reactive red dye solution were up to 90 % while the color removal efficiency was 99 %.

4.Conclusions

Photocatalytic process of reactive red dye was carried out by using ZnO under solar light irradiation. The optimum conditions for decolorization were obtained to be: pH=8, H_2O_2

concentration =100mg/L and initial concentration of dye=25 mg/L.

It was observed that the degradation process was strongly affected by pH value and the concentration of H_2O_2 added. COD value of dye solution was clearly decreased during the reaction time. Reduction in colour and COD values reached to 99% and 90% respectively. The decolorization process could be fitted to L-H model and the reaction kinetics was estimated.

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