

Removal of Titan Yellow GR from Water Using Advanced Oxidation Process (AOP) in the Presence of Suspended ZnO as a Catalyst

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Abstract

UV/ZnO process was used to degrade titan yellow GR indicator which is the type of azo dyes., The effect of some parameters in the photocatalytic degradation of dye by UV/ZnO process such as: UV irradiation time, pH, the concentrations of both dye, bromate anion and ethanol were examined. First order reaction rate constant was calculated and it was found to be to $9 \times 10^{-3} \text{ min}^{-1}$. It was observed that the increasing in the irradiation time increased dye removal while the increasing in the concentrations of both dye in the range from 20 to 70mg/L and ethanol in the range from 1 to 7mM decreased the efficiency of photoreaction. The effect of pH (from 1 to 11) on the photodegradation process of dye was studied and the maximum efficiency of the degradation was at neutral pH (pH=7). It was found that the increasing in the dye removal was regular when the concentration of bromate anion increased from 1 — 3 mM. While at the higher concentrations of bromate anion (above 4 mM), the decreasing in the dye removal was also regular and the maximum dye removal was at 4mM. Also the adsorption isotherms such as: Langmuir and Freundlich were studied and were identical with the Langmuir model.

1-Introduction :-

Azo dyes are a class of colored organic compounds that have largely used in industry for many applications such as textiles, papers, leathers, additives and analytical chemistry ⁽¹⁾. During dye production and textile manufacturing process, a large quantity of wastewater containing dye stuffs with intensive color and toxicity are introduced into the aquatic bc systems ⁽²⁾. In such cases, it is important to remove color from wastes, because the presence of even small amounts of dye (below 1 ppm) is clearly visible and influences water environment considerably .The degradation of azo dyes has been reported in many papers. ⁽³⁻⁷⁾

Lately, very extensive studies done by researchers on many photocatalytic systems (UV/ semiconductor) , which they have been found to be very effective in degrading various organic dyes .They are able to photosensitizes the compete mineralization of a wide range of compounds like dyes, phenols and pharmaceutical drugs, without producing harmful by-products at near room temperature and pressure ⁽⁸⁻¹²⁾.

One of the wastewater treatment methods is advanced oxidation process (AOP) defined by Glaze et al. ,which present a suitable alternative to remove color from water ^(13,14) .Common AOP involves Fenton , Fenton-like , photo- Fenton process , azonation , photochemical and electrochemical oxidation, photolysis with H₂O₂ and O₃ , high voltage electrical discharge (corona) process , semiconductor photocatalysis , radiolysis , wet oxidation , water solutions treatment by electronic beams ⁽¹⁵⁻¹⁹⁾ .

The principle of AOP is the generation of very reactive species such as hydroxyl radicals ($\cdot\text{OH}$)⁽²⁰⁾, which have a high oxidation potential ($E_0=+2.80\text{ v}$). Hydroxyl radicals rapidly oxidize a wide range of organic pollutants⁽²¹⁾.

Many researchers consider TiO_2 as the best photocatalyst that has the ability to treat water from a number of organic pollutants⁽²²⁻²⁴⁾. On the other hand, it has been proven similar efficiency of photocatalytic between ZnO and TiO_2 . ZnO has been reported to be a better substitution to TiO_2 in some applications, thus ZnO can be a suitable alternative for TiO_2 ⁽⁸⁻¹⁰⁾.

In this work, various parameters influenced the removal efficiency of titan yellow GR such as: irradiation time, pH, the concentration of dye and ethanol and bromate anion were investigated. The kinetics of photoreaction and the adsorption of dye on to the surface of ZnO particles were also examined.

2- Experimental

The photo cell was consisted of 100 ml three neck round bottom flasks as reactor placed onto magnetic stirrer hotplate (obtained from GalenKamp) to make the homogeneous mixing and controlled temperature at 20C° for all experiments. Commercial mercury lamps (CAC 220 /240v 50/60 Hz 11 WCE with power of 160 w) were used as a source of light. To prevent another irradiations to reach the reactor, the last was surrounded by cubic box of aluminum with equal lengths about 50cm. The distance between the lamps and reactor was 10 cm. In each experiment, 50 ml of dye solution with 0.25 g of ZnO was irradiated at a period of time, and then centrifuged by centrifuge (supplied from Truip International Corp. 120 cycle/ min.). The electronic spectra and measurements of dye concentration (supplied from Shimadzu Uv-vis. 1650 Spectrophotometer) were done. The conversion fraction of dye was calculated using the equation 1:

$$X = (C_0 - C) / C_0 = 1 - (C / C_0) \dots\dots\dots (1)$$

Where x is conversion fraction, C_0 and C (mg/L) are initial dye concentration and dye concentration at time t respectively. Batch equilibrium studies were carried out by adding a fixed amount of titan yellow GR 0.25g into 100-mL Erlenmeyer flasks containing 50mL of different initial concentrations (10 — 60 mg/L) of dye solution. The flasks were agitated in an isothermal water-bath shaker at 120rpm and 20C° for 24 h until equilibrium was reached. The pH was adjusted by adding a few drops of diluted 0.1M NaOH or 0.1M H_2SO_4 . The amount of equilibrium adsorption, Q_e (mg/g), was calculated by equation 2:

$$Q_e = (C_0 - C_e)V/W \dots\dots\dots (2)$$

Where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V (L) is the volume of the solution and W (g) is the mass of dry adsorbent used.

NaOH, H_2SO_4 , ZnO and ethanol were from Merck. Titan yellow G.R and potassium bromate were from Aldrich. Cyclohexane used as a solvent of the dye in all experiments was from Fluka.

3. Discussion

3.1. The determination of calibration curve

Various concentrations of titan yellow GR (which have the structural formula as illustrated in fig.1) at the range between (10-70) mg/L were prepared using cyclohexane as a solvent.

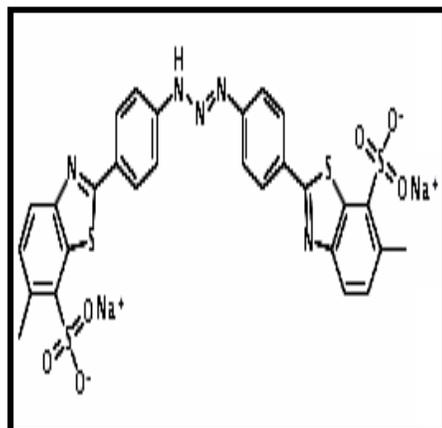


Fig.1: The structural formula of titan yellow GR.

The spectrum of titan yellow GR was shown in fig.2, the wave length at 410nm was selected to monitor the photodegradation of dye.

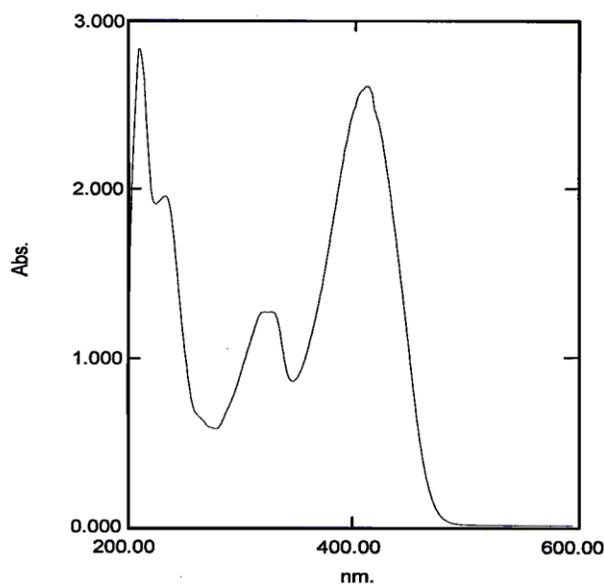


Fig.2: The electronic spectrum of titan yellow GR .

The calibration curve of dye was determined by plot the values of absorbance at 410nm versus the values of concentration. The calibration curve in the concentration range that falls in the region of applicability of Beer-Lambert's law were employed. (fig.3).

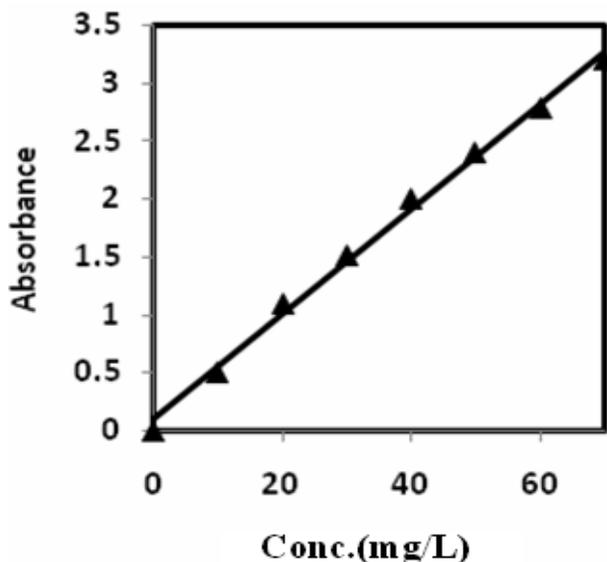


Fig.3: The calibration curve of titan yellow GR at 410 nm.

3.2 The effect of irradiation time

Fig.4 shows the effect of irradiation time on dye removal efficiency. It can be seen that the conversion fraction of the dye increases when the irradiation time increases and after 180 min. the conversion fraction remains constant. This is because of increasing the excited ZnO particles with time and therefore increasing the number of produced $\cdot\text{OH}$ radicals and positive holes⁽²⁵⁾.

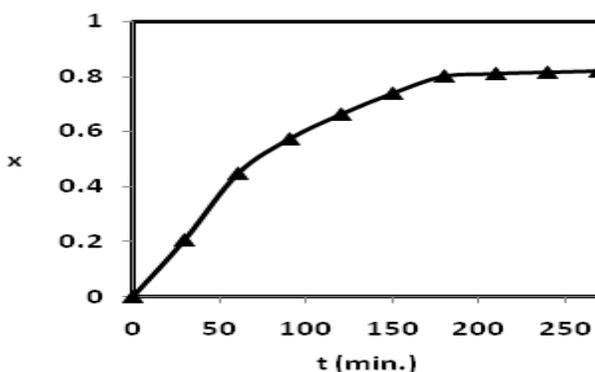


Fig.4: The effect of irradiation time on the removal of dye

[dye]=50mg/L, [ZnO]=0.25g/50ml,
pH=7, temp. =20C°.

3.3 The determination of reaction order.

Using the data, which have been reported in section 3.2, it can be seen that the plot of LnC vs. irradiation time (min.) was linear (30-150 min) and therefore the reaction belonged to first order rate system (fig. 5) and k value was calculated from slope(-k) and it is found to be equal to $9 \times 10^{-3} \text{ min.}^{-1}$ according to equation 3⁽²⁶⁾.

$$\text{LnC} = \text{LnCo} - kt \dots\dots\dots (3)$$

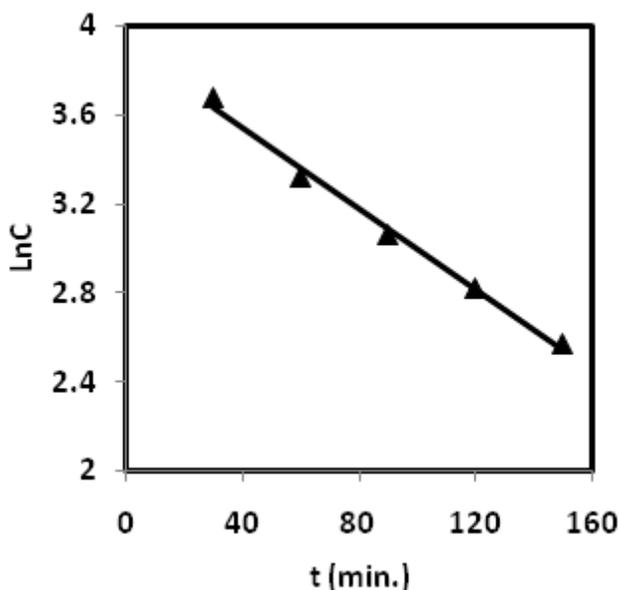


Fig.5: Plot of first order reaction of the dye

3.4 The effect of dye concentration.

The pollutant concentration is a very important parameter in wastewater treatment .The effect of various initial dye concentrations on the photo degradation has been investigated from 20 to 70 mg/L as illustrated by electronic spectra (fig. 6).

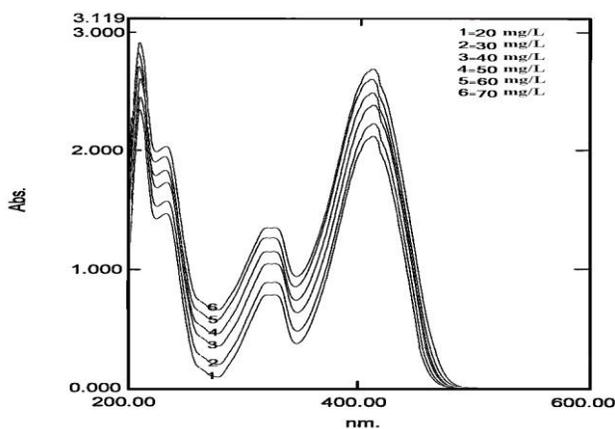


Fig.6: The electronic spectra of dye at different concentrations. [ZnO]=0.25g/50mL, pH=7, temp.=20C°, time=150min.

It is found from the results in fig .7 that the increase in the dye concentration from 20 to 70 mg/L decreases the removal efficiency of dye .When the dye concentration increases, the amount of dye adsorbed on the catalytic surface increases. This affects the catalytic activity of ZnO. The increasing in dye concentration also decreases the path length of photo entering the dye solution. At high dye concentration a significant amount of solar light may be absorbed by dye molecules rather than the catalyst and this may also reduce the catalytic efficiency ⁽²⁷⁾.

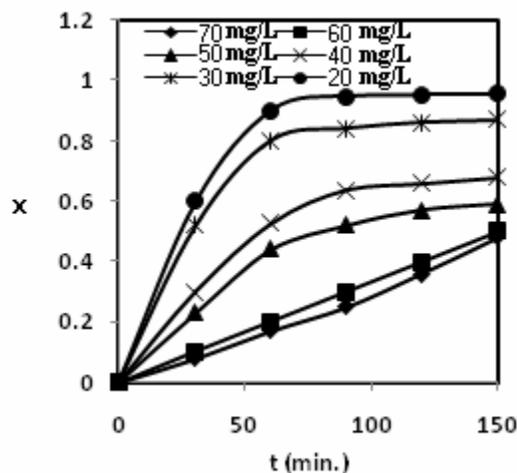


Fig.7: The effect of dye concentration on its removal efficiency. [ZnO]=0.25g/50mL, pH=7, temp.=20C°, time=150min.

3.5. The effect of pH.

Fig .8 shows the electronic spectra of dye at different pH values.

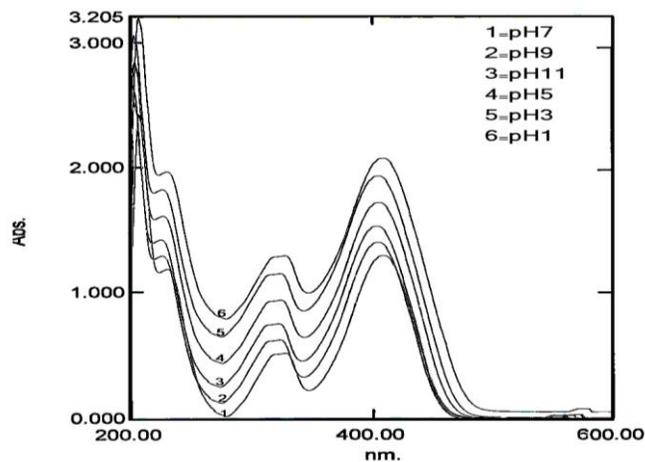


Fig.8: The electronic spectra of dye at different pH. [dye]=20mg/L, [ZnO]=0.25g/50mL, temp.=20C°, time=150min.

It can be seen from fig.9 that the removal efficiency was maximum at neutral pH. At acidic pH values, ZnO is dissolved as Zn^{+2} and has not any photocatalytic properties, at basic pH values, ZnO particles have negative surface charge and repulse dye anion molecules. Negative charges on dye molecules ordinate from SO_3 group substituted on aromatic ring ⁽²⁵⁾.

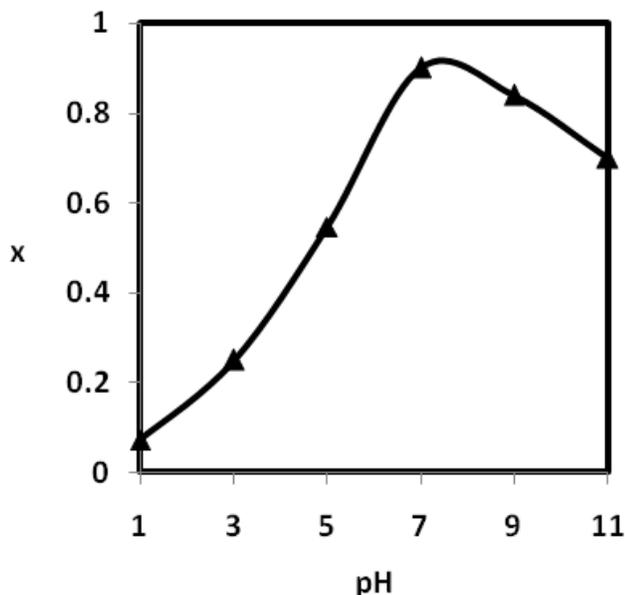


Fig.9: The effect of pH on the dye removal efficiency.[dye]=20mg/L,[ZnO]=0.25g/50mL,temp.=20C°,time=150min.

3.6. The effect of ethanol concentration.

The electronic spectra of dye at different ethanol concentrations are illustrated in fig.10.

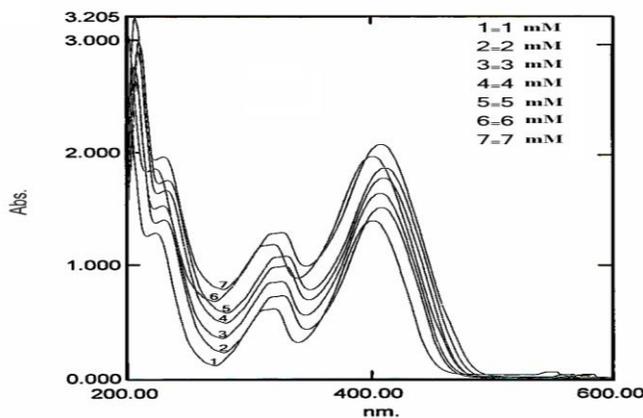


Fig.10: The electronic spectra of dye at different ethanol concentrations .[dye]=20mg/L,[ZnO]=0.25g/50mL,pH=7,temp.=20C°,time=150min.

Fig.11 shows inhibitory effect of ethanol on dye removal efficiency .It can be seen that increasing ethanol concentration decreased the efficiency of dye removal, because ethanol quenches OH radicals ⁽²⁸⁾.

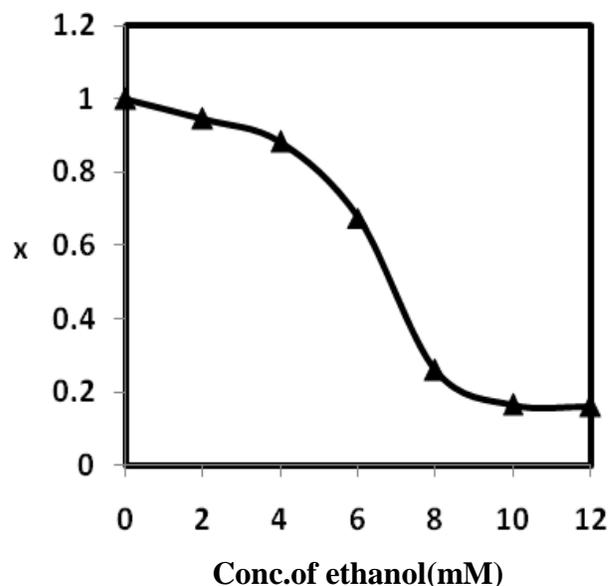


Fig.11: The effect of ethanol concentration on the dye removal efficiency [dye]=20mg/L, [ZnO] =0.25g/50mL, pH=7, temp. =20C°, time=150min.

3.7. The effect of bromate anion concentration.

KBrO₃ is an efficient electronic acceptor and used as an additive to enhance photocatalytic degradation rate .Fig 12 shows the electronic spectra of dye at different bromate anion concentration.

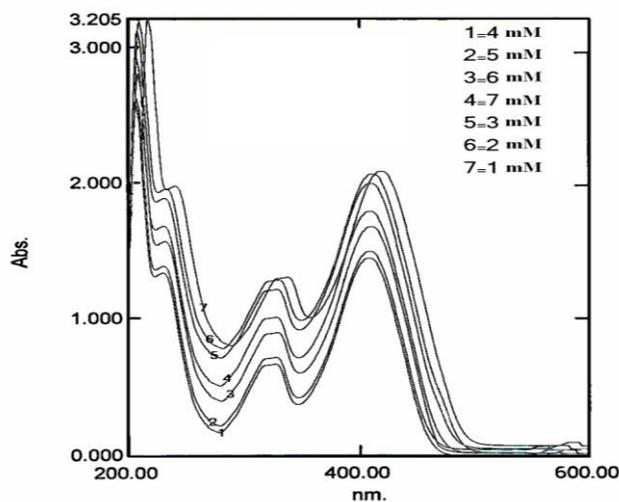
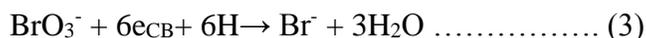


Fig.12: The electronic spectra of dye at different bromate anion concentrations .[dye]=20mg/L,[ZnO]=0.25g/50mL,temp.=20C°,time=150min.

From fig .13 it can be seen that the addition of KBrO_3 in the range of 1 to 3 mM increase the removal efficiency of dye regularly .The enhancement of the removal rate is due to the reaction between BrO_3^- anion and conduction band electron (Eq.2) which reduces the recombination of electron-hole.



The further increase of KBrO_3 concentration from 5 to 7 mM, decrease the removal efficiency of dye. This is due to adsorption effect of Br^- ion on ZnO surface which affects the catalytic activity of ZnO⁽²⁹⁾.

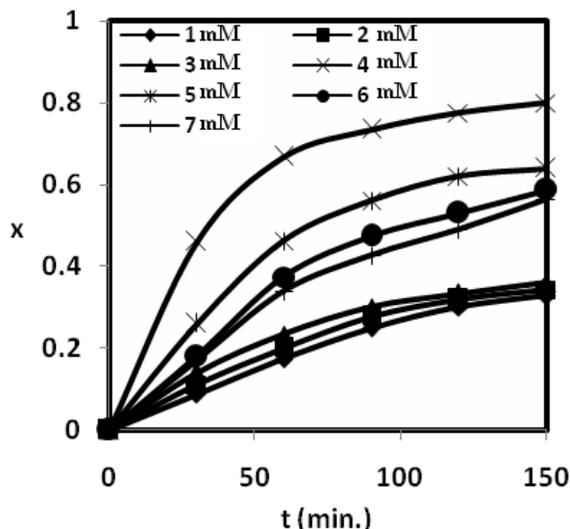


Fig.13: The effect of bromate anion concentration on the dye removal efficiency. [dye]=20mg/L, [ZnO] =0.25g/50mL, pH=7, temp. =20C°, time=150min

3.8. The adsorption studies.

In heterogeneous photocatalytic degradation process, the adsorption of dye onto the catalytic surface is the primary step of the reaction. The experimental data of adsorption were described by using the Langmuir and Freundlich isotherms⁽³⁰⁾ The Langmuir isotherm (fig.14) can be expressed as follows:

$$C_e/Q_e = 1/Q_m b + C_e/Q_m \dots\dots\dots (4)$$

Where C_e (mg/L) is the concentration of dye at equilibrium, Q_e is the amount adsorbed at equilibrium (mg /g), and Q_m and b are Langmuir constants related to adsorption efficiency and energy of adsorption respectively.

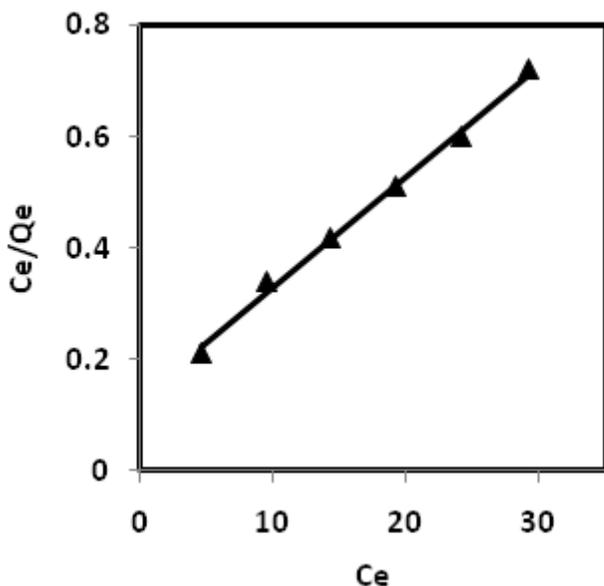


Fig.14: Linearized Langmuir isotherm of dye adsorption on ZnO surface
While Freundlich isotherm (fig.15) can be given by the following equation:

$$\log Q_e = \log k_f + 1/n \log C_e \dots\dots\dots (5)$$

Where Q_e is the amount of dye adsorbed (mg /g), C_e is the equilibrium concentration of dye in solution (mg/L), k_f and n are constants related to adsorption capacity and intensity of adsorption respectively.

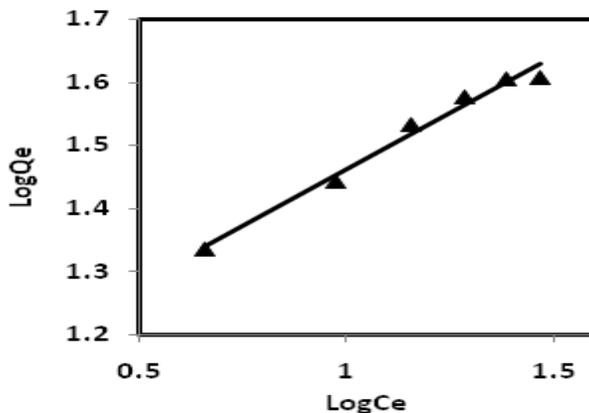


Fig.15: Linearized Freundlich isotherm of dye adsorption on ZnO surface

The Langmuir and Freundlich constants are illustrated in table 1. From the results, it can be seen that the adsorption of dye onto ZnO surface was fitted with Langmuir isotherm due to the largest value of R^2 and the value of n ($n < 2$). This means that the adsorption was chemisorption

Table 1: The Langmuir and Freundlich constants for dye adsorption.

Langmuir	Q_m	b	R^2
	52.632	0.143	0.995
Freundlich	k_f	n	R^2
	12.618	1.786	0.983

4- Conclusions.

The photodegradation experiment showed that the dye removal efficiency increased with increasing irradiation time. The kinetics of photodegradation reaction expressed the pseudo first order reaction. The increasing of both dye and ethanol concentrations decreased dye removal efficiency. The maximum efficiency of dye removal was at neutral pH (pH = 7). The concentration of bromate anion from 1 to 3 mM increased the photodegradation reaction, while the further increasing of bromate anion above 4 mM decreased the efficiency of reaction. Also the adsorption studies showed the appearance of adsorption isotherm with Langmuir model.

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إزالة Titan Yellow GR من الماء باستخدام عملية الأكسدة المتقدمة (AOP) بوجود عالق ZnO كعامل مساعد

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الخلاصة:-

استخدمت عملية UV/ZnO لتجزئة كاشف Titan yellow GR الذي هو من نوع اصباغ الازو. وتم دراسة تأثير بعض للعوامل في التفكك الضوئي المحفز بعملية UV/ZnO مثل: زمن التشعيع بالاشعة المرئية وفوق البنفسجية و الـpH و تراكيز كل من الصبغة وانيون البرومات والايثانول. تم حساب ثابت السرعة لتفاعل المرتبة الاولى ووجد انه كان مساويا الى 10×9^{-3} دقيقة⁻¹. لوحظ ان الزيادة في زمن التشعيع تزيد من ازالة الصبغة بينما الزيادة في تراكيز كل من الصبغة في المدى كم 20 الى 70/ملغم/لتر والايثانول في المدى من 1 الى 7 مليمولاري يقلل من كفاءة التفاعل الضوئي. درس تأثير الـpH (من 1 الى 11) على عملية التجزئة الضوئية للصبغة وكانت الكفاءة القصوى للتجزئة عند الـpH المتعادل (pH=7). وجد بان الزيادة في ازالة الصبغة كانت منتظمة عندما يزداد تركيز انيون البرومات من 1 الى 3 مليمولاري. اما عند التراكيز العالية لانيون البرومات (فوق 4 مليموري) فان النقصان في ازالة الصبغة كان منتظما ايضا وكانت اعلى ازالة للصبغة عند 4 مليمولاري. كذلك تم دراسة ايزوثيرمات الامتزاز مثل لانكماير وفريندلج وكانت متطابقة مع نموذج لانكماير.