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Hydrothermal synthesis of Cr_2O_3/ZnO nanocomposite for environmental applications

Karam Khadhim, Hazim Y. Al-gubury*

Department of Chemistry, College of Science for Women, University of Babylon, Hilla, Iraq

** Corresponding author's Email: h.yahya40@yahoo.com*

ABSTRACT

This article uses a produced nanocomposite and a solar lamp to explore the photocatalytic breakdown process of the acid fuchsin dye. Hydrothermal techniques were used to create the Cr_2O_3/ZnO nanocomposite. The characteristics of nanocomposite were studied using various techniques such as "X-ray diffraction (XRD)", "scanning electron microscopy (SEM)", and diffuse reflectance spectra to calculate the band gap found to be 2.77eV. The particle size of synthesized Cr_2O_3/ZnO nanocomposite was calculated using the Scherer equation (47.62 nm). Using 0.13 g 100^{-1} mL of nanocomposite, dye degradation was carried out in irradiation aqueous suspension solutions with various dye concentrations. The influence of the mass of the nanocomposite, the concentration of Acid Fuchsin dye, and the effect of temperature were examined to determine their effects on the photocatalytic degradation process of this dye. Calculations showed that the activation energy is 31.67 kJ $mole^{-1}$. Using a UV-Vis spectrophotometer, the irradiated solutions were investigated.

Key words: Degradation, Photocatalysis, Nanocomposite, Acid Fuchsin Dye, Zinc Oxide, Chromium Oxide.
Article type: Research Article.

INTRODUCTION

Water contamination as a result of population growth and industrial expansion has detrimental impacts on the environment and human health (Ahmed *et al.* 2018). Waste products from industrial sectors such the paper and pulp, pharmaceutical, dyeing, and textile dyeing industries are the main suppliers of organic and inorganic chemicals leading to water pollution. In particular, organic dyes emitted by companies have the ability to fade resistant, are poisonous, unbreakable, bio-recalcitrant, mutagenic, and carcinogenic. To prevent these organic contaminants from being discharged into the environment, suitable removal techniques are required. Photocatalysis is one of the ways for wastewater treatment that is both effective and efficient. The procedure is inexpensive, safe for the environment, and results in the total mineralization of organic contaminants in wastewater. Heterogeneous semiconductor-based catalysts have been investigated and described as effective and efficient treatment options among the photocatalysts that have been promised (Fardood *et al.* 2018). Semiconductors, which feature a valence band (with a full electron) and a conduction band (with a higher energy and no electron) with a distinct band gap, are the most important photo catalytic materials. When a ZnO catalyst is exposed to photons from a light source with energy greater than or equal to the band gap energy of the catalyst, electrons are stimulated from the valence band to the conduction band area, leaving holes in the valence band (V_B). This is the primary mechanism underlying the photocatalytic reaction. This creates electron hole ($e^-\backslash h^+$) pairs. AOPs are technologies that remove various organic contaminants from dirty water to provide clean water for human use, including drinking and other domestic purposes (Sharma *et al.* 2018). Researchers are interested in accelerated oxidation processes (AOPs), which facilitate antibiotic degradation. The Fenton procedure has been widely used to clean wastewater because of its low cost and high removal efficiency. A so-called advanced oxidation processes (AOPs) are a group of related, however, distinct technologies rely partly (but not only) on the creation of highly reactive hydroxyl radicals. AOPs include wet oxidation processes, homogeneous and

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heterogeneous photocatalysis, Fenton and Fenton-like processes, ozonation, ultrasound, microwaves, and g-irradiation (Dewil *et al.* 2017; Khan *et al.* 2020; Radhy & Jasim 2021). AOPs are utilized in wastewater treatment systems to successfully remove bio recalcitrant micro-pollutants, in water treatment facilities that generate drinking water, and in disinfection methods (including photo-assisted ones). These processes rely on the production of strong reactive species, usually radicals, which are capable of attacking and mineralizing almost all oxidizable substances (Marco *et al.* 2021).

Fuchsin acid

Dyes are organic colorants that are often composed of water-soluble compounds. Its application in many sectors across the world has increased. One of the contaminants present in industrial wastewater is the dye carbol fuchsin (CF), which has the molecular formula $C_{20}H_{17}N_3Na_2O_9S_3$. CF Combining phenol and basic fuchsin (BF), a common red dye used for biological staining and for colouring a range of materials like leather, paper, and cotton Typically, cation-exchange membranes are used to remediate dye-contaminated water (Abu Zurayk *et al.* 2021).

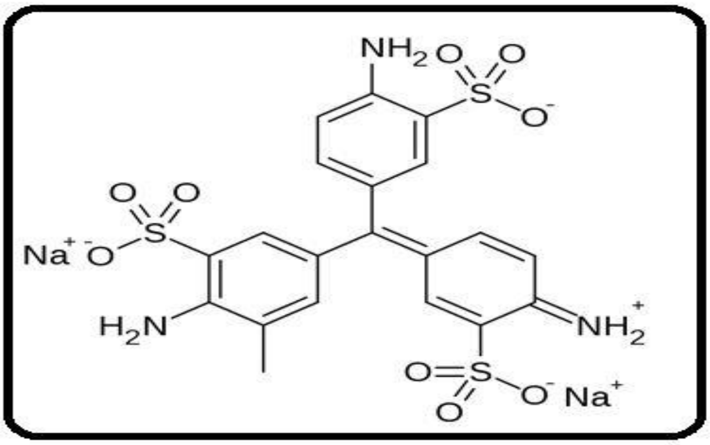

Fig. 1. Chemical structure of Acid Fuchsin dye.

Experimental section

Chemicals

a) Zinc acetate dehydrate, were provided by Fluka.
b) Oxalic acid, were provided by Fluka (Buchs, Switzerland)
c) Zinc oxide, supplied by Fluka AG, purity (99%), particle size (100 mesh).
d) Chromium oxide was purchased from Sigma-Aldrich (St. Louis, USA)
e) Acid Fuchsin dye is a product of Sigma-Aldrich.
f) Ethanol was provided by Fluka.

All chemicals were employed without any further purification.

Synthesis of Cr_2O_3/ZnO nanocomposite

Hydrothermal method is a synthesis technique for growing single crystals from an aqueous solution in an autoclave (a thick-walled and sealed vessel) at high temperature and pressure. Nanocomposite of Cr_2O_3/ZnO has been created using this method. Initially, 50 mL distilled water and 5 g zinc acetate dehydrate were combined and swirled constantly for 15 min. Next, 50 mL distilled water was used to dissolve 3 g oxalic acid while stirring for 15 min. Lastly, zinc oxide nanoparticles were produced by combining the two solutions with thread. After the mixture of zinc oxide nanoparticles was homogenous, 1 g Cr_2O_3 was added after being dissolved in 100 mL distilled water. The stainless steel autoclave was filled with the finished mixture (a thick-walled and sealed vessel). For 12 h, the hydrothermal synthesis was kept at 180 °C. The precipitate was removed from the autoclaves at room temperature and repeatedly cleaned with deionized water and ethanol to eliminate any contaminants. All of the finished products were then filtered and baked in a vacuum oven at 60 °C for an extended period of time. To create Cr_2O_3/ZnO composites, the mixture powders were calcined at 600 °C in the air for 2 h.

Photocatalytic degradation processes of Acid Fuchsin dye using Cr_2O_3/ZnO composites.

Cr_2O_3/ZnO nanocomposite was used as a photo catalyst in photocatalytic degradation tests for the breakdown of Acid Fuchsin dye in aqueous solution under solar light irradiation. The entire experiment, which consists of two phases, was completed using a specially built photo reactor. By running cooling water through the first one, the suspension solution was cooled. The second component contained a suspension solution for the dye degradation with a 100 mL capacity. Distilled water was used to create a 100-ppm stock solution of Acid Fuchsin dye solutions. Stirring was used to create a suspension solution combination for each colour concentration. 100 mL of each colour were combined with 0.13 g Cr_2O_3/ZnO nanocomposite, and then the mixture was stirred. A benchtop ultraviolet light source was used to irradiate the respective suspension solution combination. Every ten min, 2-3 mL of each sample were drawn using a syringe, spun at 3000 rpm for ten min, and the UV-Vis spectrophotometer was used to assess each sample's absorption.

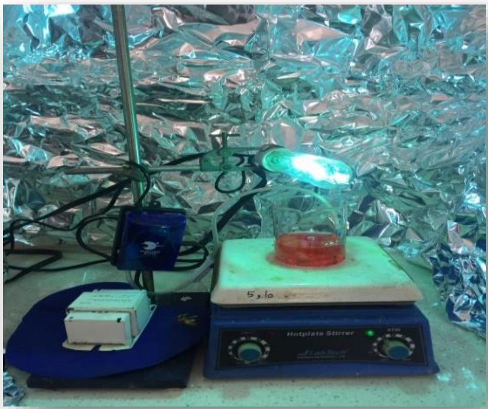

Fig. 2. The primary elements of the photocatalytic cell that were used to photocatalytically degrade acid fuchsin dye.

RESULTS AND DISCUSSION

Characterization Cr_2O_3/ZnO nanocomposite

X-Ray Diffraction analysis for Cr_2O_3/ZnO nanocomposite at 600 °C

X-ray diffraction technique was used to study crystallinity of synthesized Cr_2O_3/ZnO nanocomposite as a catalyst, and measure the particles size of the synthesized catalyst. XRD analyses of the prepared nanocomposite were carried out using XRD 6000, Shimadzu, Japan. The measuring parameters were set with 45 Cu Kα radiation (λ = 1.54056 Å) at 40 kV, 30 mA with a rate of 5 deg / min. The average crystallite sizes of synthesized Cr_2O_3/ZnO nanocomposite were measured according to the Scherer equation. The calculated value was 47.62 nm.

As shown in Fig. 3, the distinguishing peaks of synthesized nanocomposite sintered at 600 °C, were detected at 2θ (30.31º, 35.71º, 43.40º, 53.87º, 57.41º, 63.06º, 71.52º and 74.65º, respectively), which are corresponding to the crystallographic planes [100 (ZnO), 110 (Cr_2O_3), 113 (Cr_2O_3), 116 (Cr_2O_3), 110 (ZnO), 103 (ZnO), 004 (ZnO), and 202 (ZnO)] respectively.

1-2. Scanning electron microscopy (SEM) for Synthesized Cr_2O_3/ZnO nanocomposites at 600 ºC

Scanning electron microscopy techniques was used to study the morphology of Cr_2O_3/ZnO nanocomposites sintered at 600 ºC in order to obtained useful information about the structure of the synthesized nano composite using SEM images. The morphology of Cr_2O_3/ZnO nanocomposites at 600 ºCare illustrated in Fig. 4. SEM micrograph analysis was appeared as irregular distributed aggregated along with aspherical shape.

Band Gap Energy of Cr_2O_3/ZnO Nanocomposite at 600 ºC

The band gap of the synthesized Cr_2O_3/ZnO nanocomposite was calculated using Kubelka–Munk relation with the help of diffuse reflectance spectra of sample, by plot of $F(R) \times hU^{2}$ versus photon energy, and then extrapolating the straight line. The absorption spectrum of the Cr_2O_3/ZnO nanocomposite at 600 °C was studied by diffuse reflectance spectroscopy (DRS; Fig. 5). The obtained absorption band edge was at approximately 350 and 400 nm. Bonding between ZnO and Cr_2O_3 led to a shift the band gap of the ZnO nanoparticle from 3.37 eV to 2.77 eV.

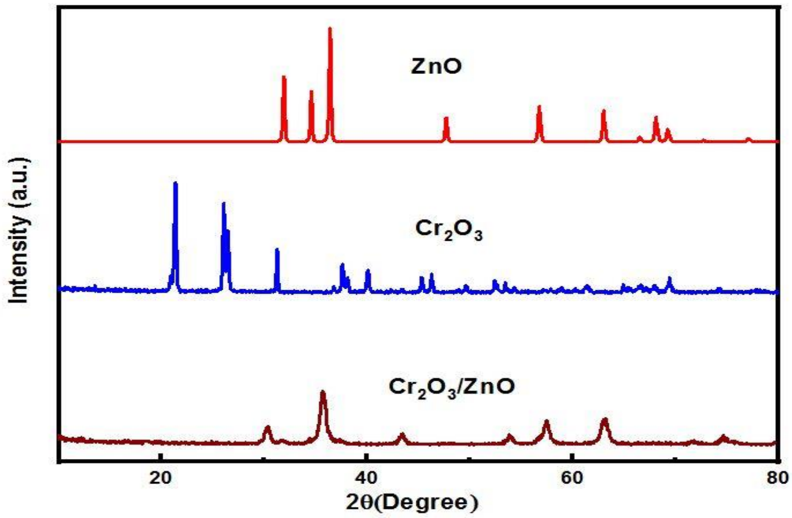

Fig. 3. XRD patterns of Cr_2O_3/ZnO nanocomposite at 600 °C.

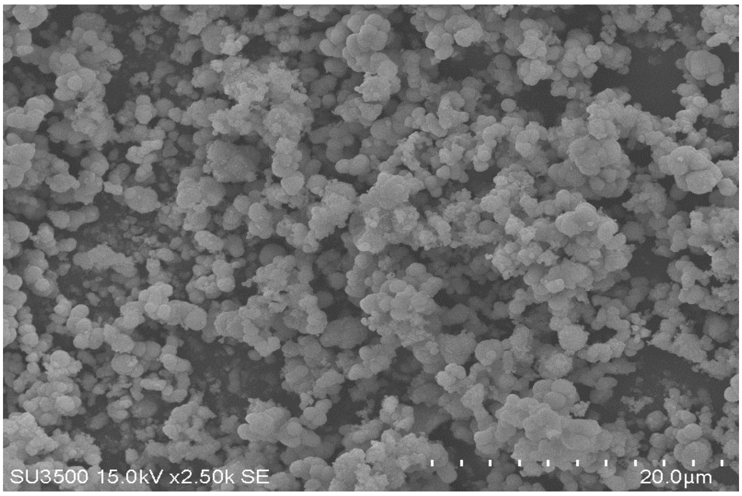

Fig. 4. SEM pattern of Cr_2O_3/ZnO nanocomposite at 600 ºC.

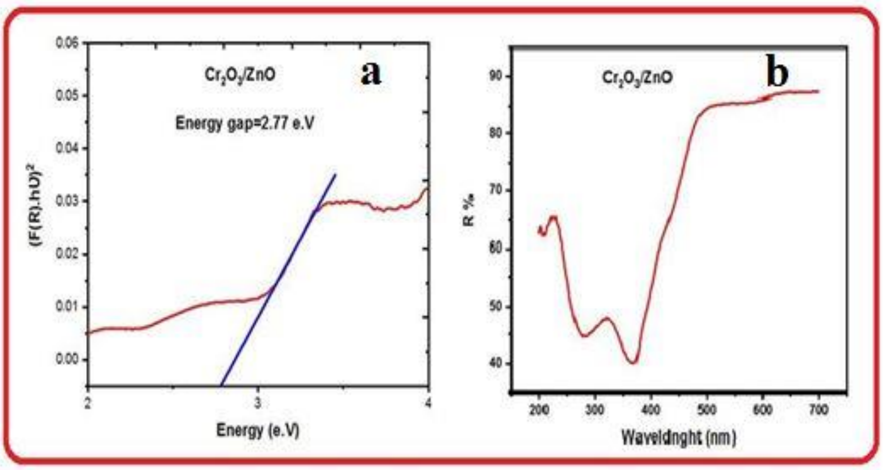

Fig. 5. (a) Kubela-Munk Plots for Cr_2O_3/ZnO nanocomposite at 600 ºC; and (b) Diffuse-reflectance UV-visible spectrum of Cr_2O_3/ZnO nanocomposite at 600 ºC.

Effect of mass of Cr_2O_3/ZnO nanocomposite on photo catalytic degradation of the Acid Fuchsin dye

The effect of mass of Cr_2O_3/ZnO nanocomposite on photocatalytic degradation of Acid Fuchsin dye, was studied using 20 ppm of dye, flow rate of air 10 mL/min at room temperature. When the masses of Cr_2O_3/ZnO nanocomposite increases until reach to the mass 0.13 g /100 mL, the photo catalytic degradation of Acid Fuchsin dye, gradually upraises, then gradually decreases (Fig. 6). When the mass of Cr_2O_3/ZnO nanocomposite (0.13 g /100 mL). The semiconductor has the capacity to absorb the most light. The initial layers of Acid Fuchsin dye will only experience a reduction in photodegradation efficiency caused by light absorption at Cr_2O_3/ZnO nanocomposite masses higher than 0.13 g/100 mL; additional layers of solution will not be exposed to light photons. Many workers studied this effect (Chakrabarti & Dutta 2004; Hu *et al.* 2010; Ashwin *et al.* 2017; Al Gubury *et al.* 2017). When the loading mass of Cr_2O_3/ZnO nanocomposite is less than the ideal value of 0.13g/100 mL, the rate of photo degradation of Acid Fuchsin dye also drops due to the mass of Cr_2O_3/ZnO nanocomposite's surface area declining, resulting in a reduction in the amount of light that Cr_2O_3/ZnO nanocomposite can absorb.

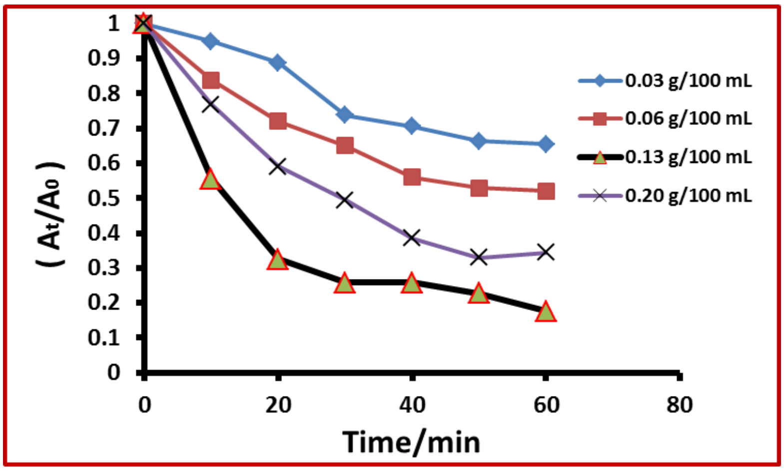

Fig. 6. Variation in (A_t / A_0) with the produced dye's irradiation time at 20 ppm.

When Acid Fuchsin concentration was sufficient, the high photo degradation efficiency (82.32%) was 20 ppm. Fig. 7 depicts the photocatalytic degradation efficiency (PDE), which was determined at various Acid Fuchsin concentrations.

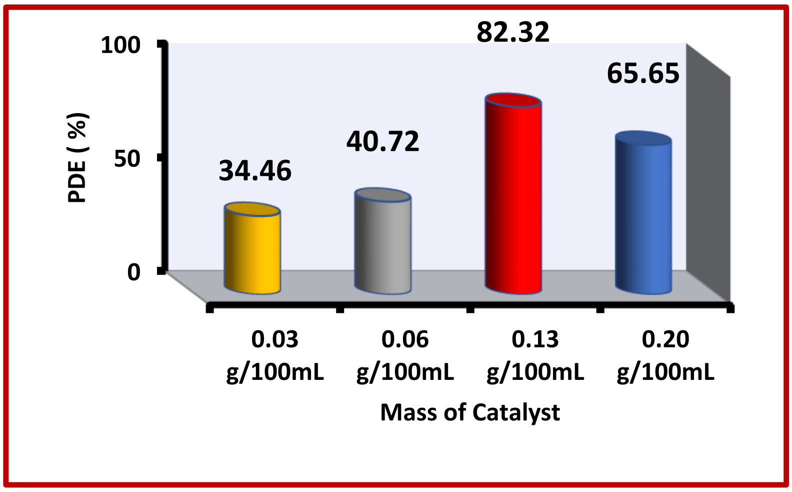

Fig. 7. Efficiency of photocatalytic degradation utilizing 20 ppm of Acid Fuchsin dye and 0.13g/100 ml Cr_2O_3/ZnO nanocomposite.

Effect of Acid Fuchsin dye initial concentration on the photocatalytic degradation process

The effect of Acid Fuchsin dye concentration solution were investigated by maintaining the same circumstances throughout the rest of the experiment and the breadth of photocatalytic degradation processes (20-70 ppm). Fig. 9 displays the outcomes in a plot. Our findings showed that as initial dye concentration was elevated, photocatalytic degradation rate dropped. As the initial concentration of Acid Fuchsin dye declines, the lengthening of the photon's path once entering the solution, increases the number of photons that reach the catalyst surface, and as a result, the rate at which the super oxide ions and hydroxyl radicals are formed, which in turn, elevates the rate at which materials degrade (Rattan *et al.* 2008; Aljeboree *et al.* 2020; Kazm *et al.* 2023).

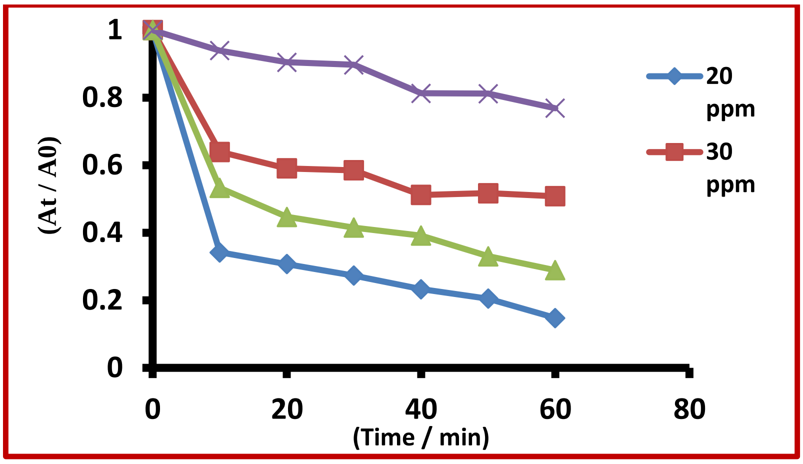

Fig. 8. Changes in (A_t / A_0) with time and irradiation at various dye concentrations.

Effect of temperature on photocatalytic degradation of acid fuchsin dye

Using a series of tests, it was determined how temperature affected the photocatalytic degradation of Acid Fuchsin dye in the 288–303-k range. By an initial Acid Fuchsin-dye concentration of 20 ppm, manufactured Cr_2O_3/ZnO catalyst dose was 0.13 g/100 cm^3, keeping all testing settings unchanged. The degradation of the dye rapidly increased as the temperature elevated (Fig. 10). This might be as a result of the presence of more reactive hydroxyl radicals (Chen *et al.* 2014; Al Gubury 2016). By plotting ln k vs 1/T, the activation energy associated with dye photodegradation was determined using the Arrhenius equation, yielding a value of 31.67 1 kJ mol^{-1}.

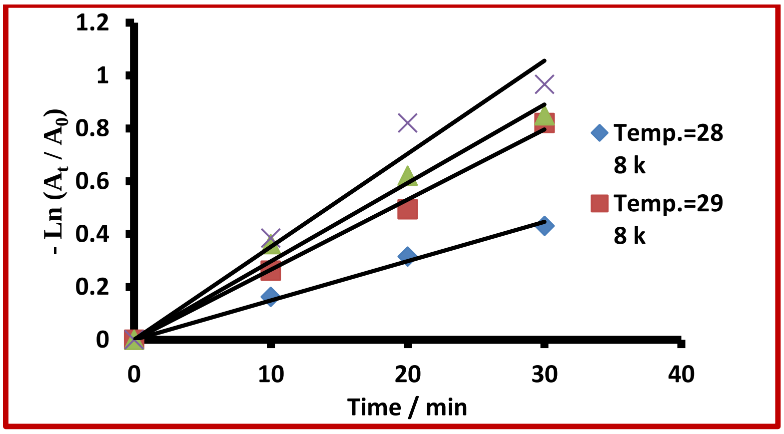

Fig. 9. The variation - ln (A_t / A_0) with UV radiation exposure time and temperature, with initial Acid Fuchsin dye concentrations of 20 ppm and photocatalyst amounts of 0.13 g/100 cm^3.

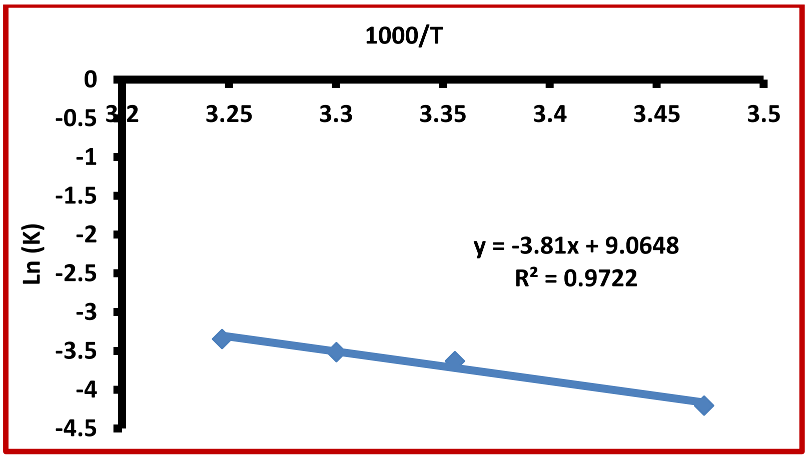

Fig. 10. Arrhenius plot of acid Fuchsin Dye.

CONCLUSION

This study used a hydrothermal approach to create a nanocomposite of chromium oxide over zinc oxide. The mean crystallite size for the prepared Cr_2O_3/ZnO nanocomposite was calculated using the Scherer equation, exhibiting that the average crystallite size were 47.62 nm according to XRD. Acid Fuchsin's photocatalytic degradation processes were dependent on the catalyst dosage, with 0.13 g of Cr_2O_3/ZnO nanocomposite per 100 cm^3 being the ideal value. The ideal value of acid Fuchsin Dye (20 ppm) was researched in terms of the impact of dye concentration. When the concentration of Acid Fuchsin increased, the photocatalytic degradation slowed down, since there was less OH^- adsorbed on the catalyst surface. The photocatalytic breakdown of Acid Fuchsin had an efficiency of 82.32%. Calculations showed that the activation energy is 31.67 kJ $mol^{-1.}$

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