Optimization of Degradation Crystal Violet Utilizing Photocatalyst ZnO/UV Light.

إيجاد الظروف المثلى لتحطيم صبغة البنفسجي البلوري باستعمال الحفاز الضوئي ZnO تحت ضوء UV.

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ABSTRACT

Decolorization of Crystal Violet (CV) cationic dye was studied using photocatalyst process. This catalyst was show to be more effective for photodegradation of many structural classes of temperature, and photocatalyst used ZnO were examined to find out the optimum operating conditions of the treatment processes.Generally it has been found that the rates of photodegradation was completed in the comparatively shortened time of 75 minutes irradiation. The photocatalytic bleaching of the dye was observed Spectrophotometer at λmax = 565nm The photodegradation reaction of dye under UV obeys the pesedu first order kinetics .

الخلاصة .

في هذا البحث تم دراسة إزالة صبغة (CV) بأستعمال عمليات الأكسدة المحفزة بأستعمال السطح ZnO وتقنية UV. وتم ايضاح تأثير العامل المحفز على التجزئة الضوئية لبعض الأصناف التركيبية من الأصباغ العضوية في محاليلها المائية . هذه الدراسة تضمنت دراسة تأثير تركيز الصبغة الابتدائي ، pH المحلول ، درجة الحرارة ، والتحفيز الضوئي باستخدام ZnO لمعرفة الظروف المثلى في عمليات المعالجة . تم التوصل الى عملية التجزئة الضوئية قد تحققت في فترة زمنية قصيرة نسبيا لمدة 75 دقيقة من التشعيع . تم استخدام المطياف لغرض قياس تركيز الصبغة غير المتحطمة وذلك عند امتصاص محلولها المائي الأعظم (λmax 565nm) =نانومتر) أشارت حركية التجزئة ان سرعة التجزئة الضوئية لصبغة البنفسجي البلوري تتبع حركيات من المرتبة الأولى الكاذبة .

1.Introduction

The environmental risks by effluents of textile wastewater industry are the major source of water and ground water pollution. These risks include highly colored compounds, high level of COD(means measuring chemical oxygen consumer), wide range of pH natural, and resistance to the natural degradation[1,2,3] . Major pollutants in textile wastewaters are high acidity, heat and other soluble substances main pollution in textile wastewater came from dyeing and finishing processes [4,5] . Photo-oxidation technique is one of the important techniques that is used in many fields which was high efficiency in the removal of the toxic effects of the environmental pollutants [6] . After the dyeing process, a lot of non-bonded dyes are released into the wastewater, which can also be treated by Advanced Oxidation Processes (AOP) in order to destroy the dye molecule and to decolorize the wastewater and reduce organic pollution It is well-known that under the experimental conditions of such methods, which can be very useful because of the short-time of treatment, hazardous compounds can be formed due to formed radicals such as hydroxyl radicals ($^{\bullet}OH$) [7,8]. It is necessary to develop a photo catalytic system which can be applied under visible and / or solar light irradiation [9,10] .TiO_2 photocatalyst initiates upon absorbing UV photons with generation conduction band (CB) electron and valence band (VB) holes within the particle .The hydroxyl radicals in particular , generated through the reaction of VB holes account for the strong oxidizing power of the TiO_2 photocatalyticsystem. Water treatment produces organic and mineral sludges

from filtration and sedimentation. Textile industry produces large amounts of liquid by-products [11,12]. Different treatment processes included physical , chemical, and biological have been employed to treat various municipal [13,14]. In the case of dye solutions, it is used in a combination with chemical or biological methods producing particles containing dye or dye degradation products with coagulation/precipitation or with some other chemical methods, or adsorption on various materials [15]. In some of the processes ZnO has been reported to be more economical for the treatment of industrial effluents and more efficient than TiO_2 [16,17] Crystal violet is an organic compound that is used as a dyestuff .It is traditionally used as a dye for materials such as silk, leather, and paper .The present study was carried out to investigate to remove cationic dye Fig(1) using various advanced oxidation processes various reaction conditions under UV light.

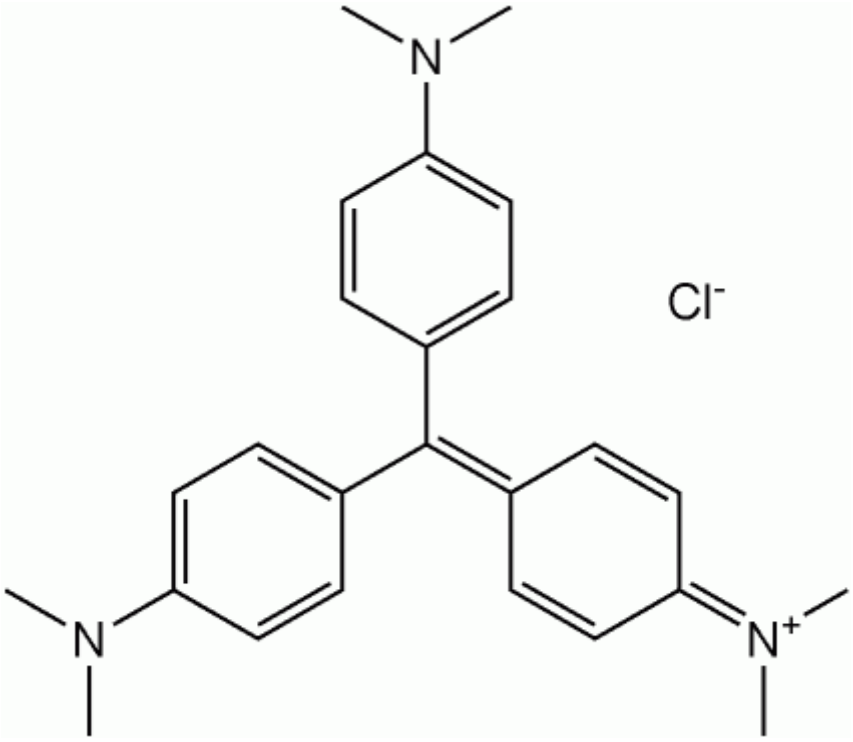


Fig (1): Structural formula of crystal violet dye.

2. Materials and methods

2.1. Materials

All chemicals were used without further purification. Sodium hydroxide (NaOH) and hydrochloric acid(HCl) were supplied from BDH. Crystal Violet is known high solubility in water($C_{25}H_{30}N_3Cl$),other name(Basic violet 3) was purchased from Aldrich . The photocatalyst ZnO was purchased from Merck (99% purity). All the other chemicals and solution s were prepared with distilled water.

2.2. Instruments

UV-Visible 1650 spectrophotometer (Shimadzu) was used to recording the absorption spectra of aqueous solutions of dye. Centrifugation of ZnO suspensions was performed by using CORP Triup International , Italy instrument . Photo reactor was setup for the experiments with UV- light is generated from UV lamp low pressure mercury lamp supplied from (Poland) in batch mode operation was used. All Photolysis experiments were performed in photolysis Pyrex cell (1L).

2.3. Photodegradation Experiment

All photodegradation experiments were performed by irradiating the aqueous suspension of dye by UV-Visible light emitted from low pressure mercury lamp . Aqueous ZnO suspensions were prepared by adding 0.80 gm of powder to 1L of ZnO aqueous dye solution (concentration of all dyes was $1X10^{-5}$ M) and dye solutions were irradiated for a period of 75 minutes (the primary experiments indicated that the most of dye molecules are degraded or become colorless at the time near to this period). Within this time samples were taken by syringe for measuring the dye absorption at λ_{max} =565nm by using spectrophotometer after removal the ZnO particles by centrifugation and recording the results . Determination of dye concentration by using the calibration curve shown in Fig(2). Fig(3) shows the UV-Visible absorption spectrum of dye.

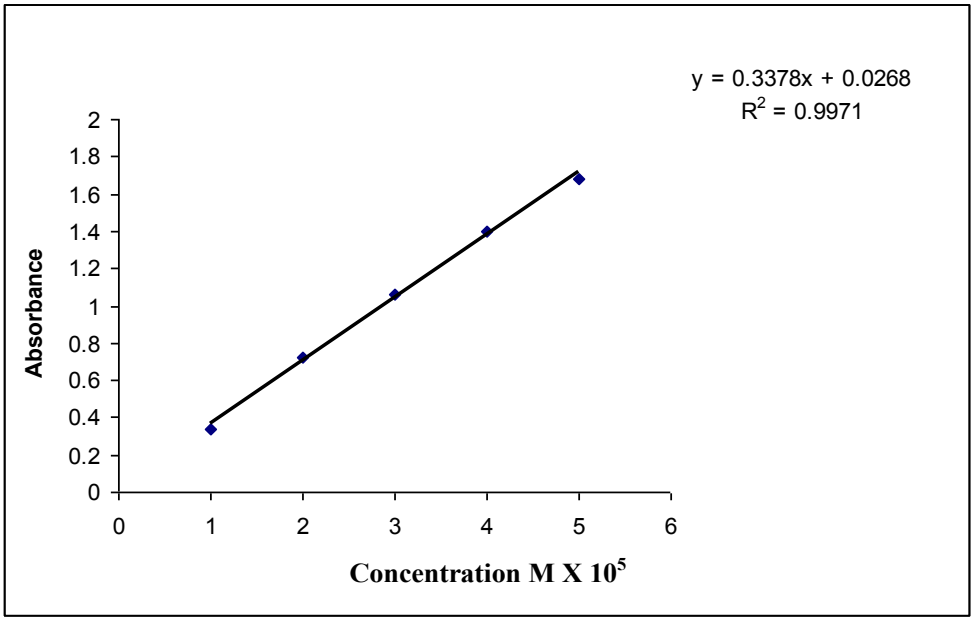


Fig (2):Calibration curve for Crystal Violet dye at pH=6,T=298K

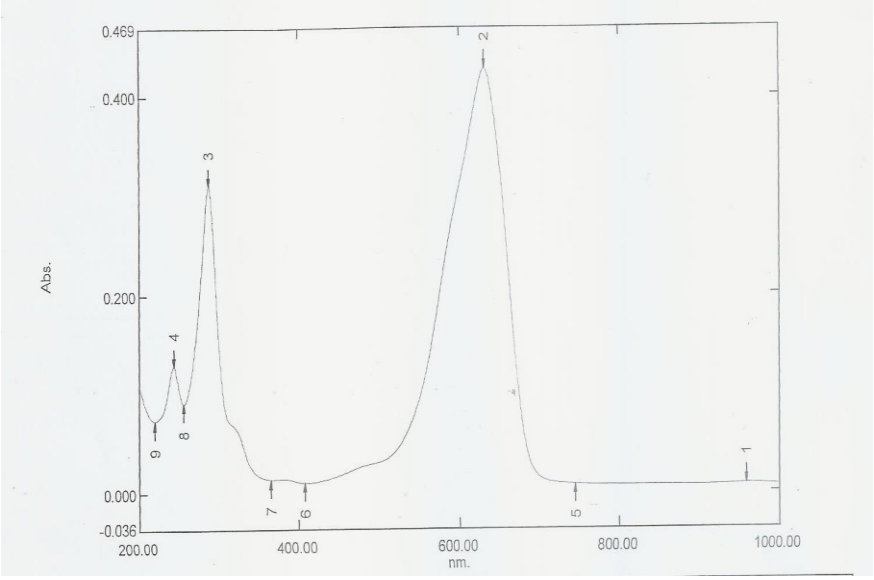
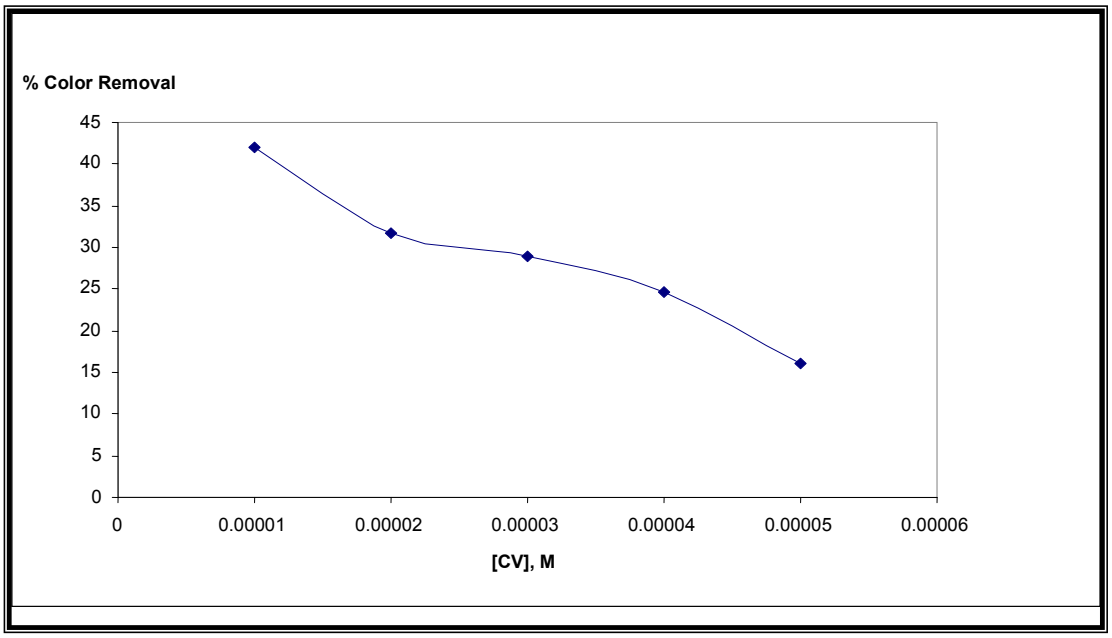


Fig (3): UV-Visible absorption spectrum for CV dye solution

3. Results and Discussion

3.1 Influence of primary Dye Concentration

In this study, the effect of various initial dye concentration in the range $1x10^{-5}$-$5x10^{-5}$M on the degradation of Crystal Violet dye was investigated by using UV irradiation for 75 minute . This study, shows the ratio of removal color of dye was examined by measuring the absorbance of the solution at the suitable wave length (λ_{max}) with time for all the component. The results are shown in Fig (4) clear that the percent of color removal decreases from 42.3% to 16% with increasing the concentration of dye from $1x10^{-5}$M to $5x10^{-5}$M in presence of UV irradiation the relationship between absorbance and irradiation time. It is clear that dye concentration decreases as long as the time increases , high removal rate was achieved during the time of 75 minutes . The obtained results proved that the photooxidation reactions of the Crystal Violet dye is reactions of first order with respect to dye concentration. Fig (5) refer the relationship between Log R and Log C to produced order reaction.



Fig(4):Effect of dye concentrations on color removal at pH=6,T=298K.

Extremely concentrations of increased the UV absorption radiation, subsequently lowering the UV light availability for the reaction , so decreasing the formulation free radicals of hydroxyl in the solution [18].

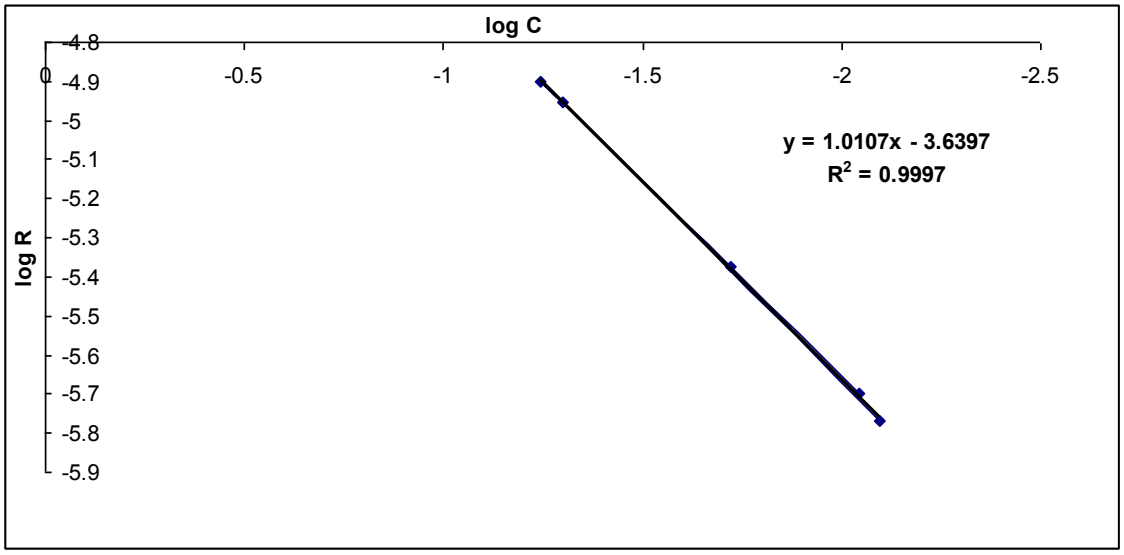


Fig (5): Relationship between Log R and Log C of oxidation of [CV] dye =1x10^{-5} M by using UV at pH=6, T=298K.

3.2. Photolysis of ZnO

In the present work the ZnO/Dye system shows a good efficiency, the photodegradation of dye in presence of ZnO at 75 min of the irradiation time were showed in Fig (6). The color removal rate was increased significantly by increasing the amount of ZnO .The increasing in the amount of catalyst increases the number of active sites of the ZnO surface and the means increases the number of $^{\cdot}OH$ and O_2 radicals [19] . To optimize the amount of ZnO needed for the highest degradation rate the following quantities were used starting from 0.1 to 1.0gl^{-1}[20] . This increase in the rate of bleaching may be attributed to increase in the exposed surface area of the semiconductor. But after certain limit (0.8 g), if the amount of zinc oxide is increased further, there will be no increase in the exposed surface area of the photocatalyst . In previous studies [21,22,23] , it has been that titanium dioxide and zinc oxide have good photocatalytic properties nominated both catalysts to and be promising substrates for photodegradation of water pollutants and show the appropriate activity in the range of visible irradiation . Efficiency of photocatalytic degradation processes was determined from the equation (1) [21].

Degradation (%) = $(C_o - C_t) / C_o$ X 100 ……(1)

Where C_o is the initial value of dye solution at t=0 min and C_t is the final value of dye solution during different periods of time of photocatalysis processes in presence of ZnO .

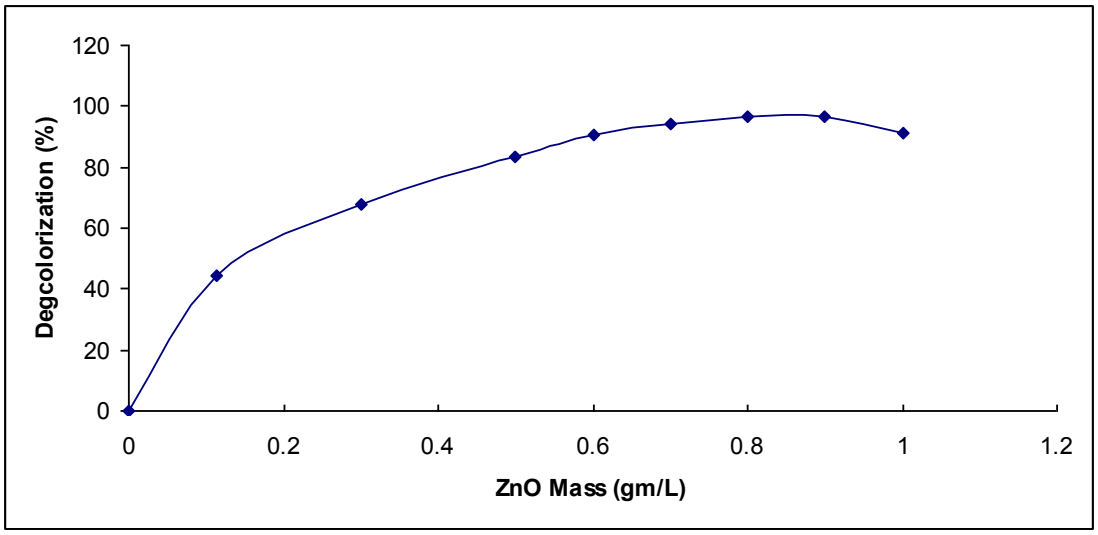


Fig (6): Mass effect of ZnO on decolorization% of [CV] dye= 1 X10^{-5} M T=298K.

3.3. Effect of pH

The effect of different pH media was investigated (2,3,4,5,7,9,10 and 12) on the color removal of Crystal Violet dye by using the UV/ ZnO method . Fig (7) refer this results deduced that the high color removal was 97.4% under acidic medium at pH= 4 from Crystal Violet . The experiments are conducted at 1x10^{-5} M dye concentration . The increase of the rate of removing the color in low pH value to more •OH radical generation changes in the structure of the molecular because of having a free hydrogen atom which makes the dye molecule exposed for attack by the hydroxyl radical in acidic medium [24].

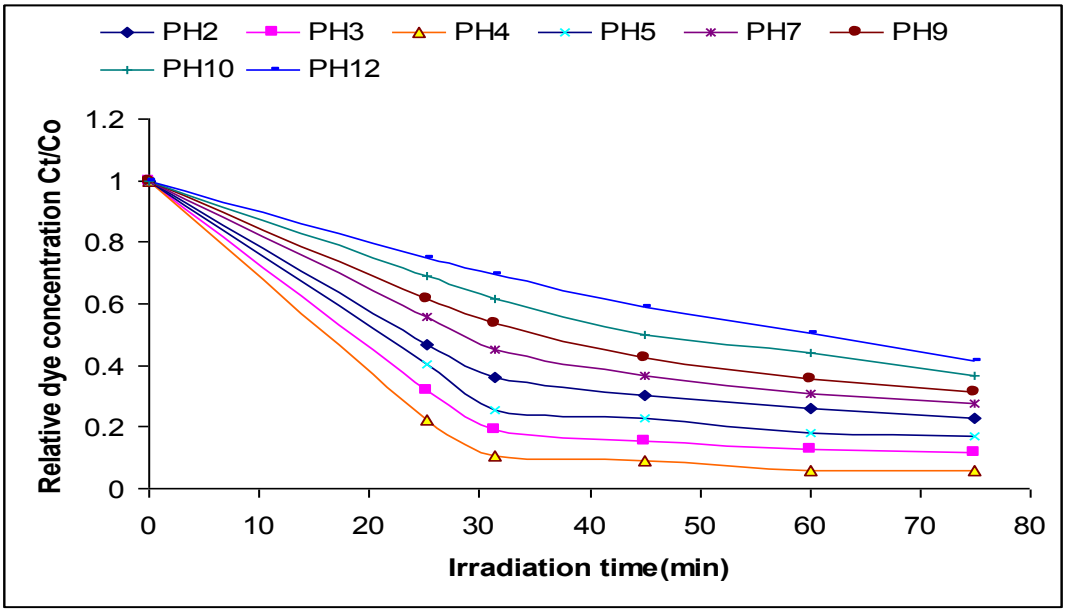


Fig (7):Effect of different pH value on color removal of Crystal Violet as function of irradiation time using UV/ ZnO method, [CV]=1X10^{-5},T=298k .

3.4. Effect of Temperature

Temperature is an important kinetic factor on enhancing the color removal percentage . The dye removal rate by using the UV method increased with increasing temperature of the system. Also, high temperature increases the generation rate of $^{\bullet}$OH or directly affects the reaction rate with the dye molecule [25]. The experiments were carried out in a range between 298-318K and the results are clarified in the Fig (8). The Arrhenius equation is used to describe the relationship between rate constants and temperature and draw this equation as in the Fig (9) from Crystal Violet .

$$\log k = \log A - Ea/RT \qquad \ldots\ldots\ldots\ldots (2)$$

where: k : rate constant, A : frequency factor, Ea : activation energy, R : ideal gas constant. T : the absolute temperature.

The activation energy calculated from the diagram was equal to 61.14 kJ/mole for Crystal

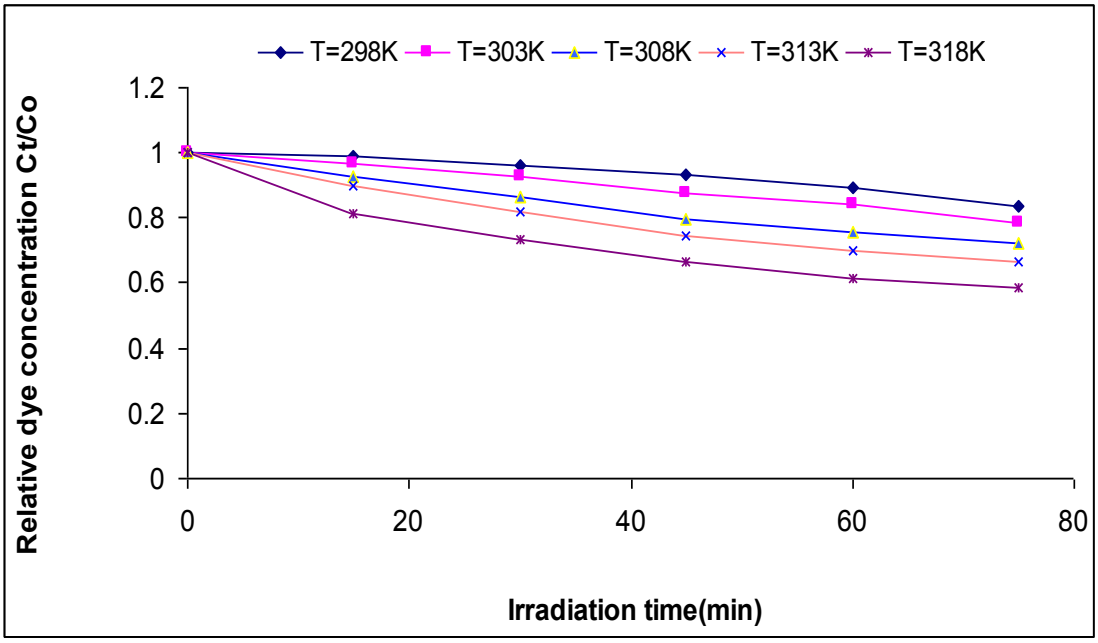


Fig (8): Effect of different temperature on the color removal of [CV]=1x10^{-5}M at pH=6 using UV method .

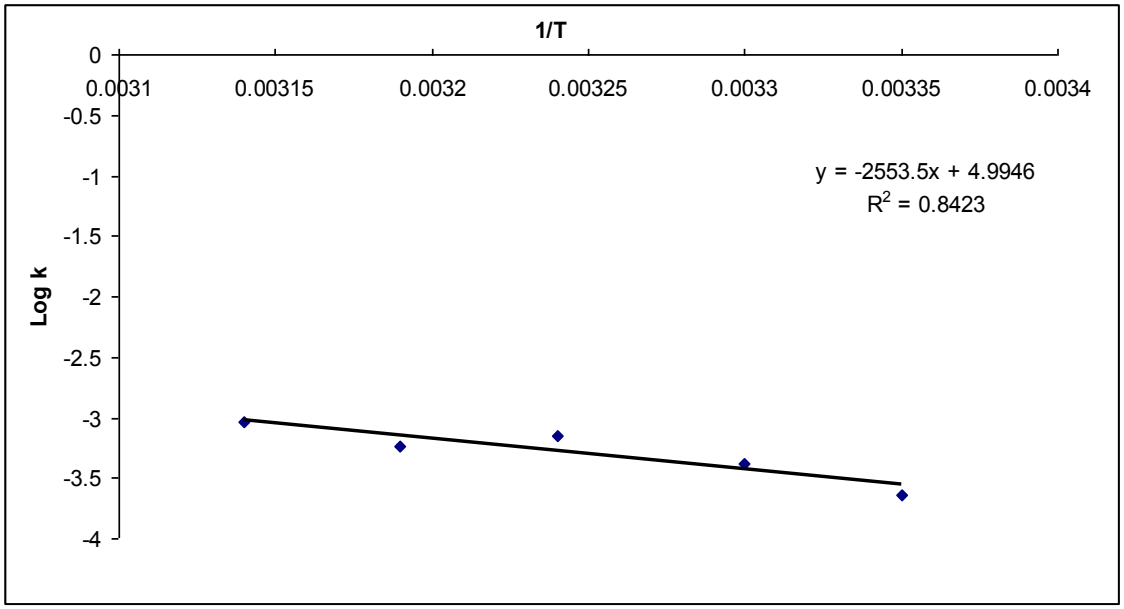


Fig (9): Arrhenius plot of color removal of dye [CV]= 1x10^{-5} M, pH=6.

3.4. Conclusions

1-The photocatalyst of Crystal Violet dye is more effective in an acidic medium with the amount of ZnO needed for the highest degradation rate limit (0.8 g) .

2- The degradation was strongly influenced by various parameters, particularly the initial dye concentration, pH and amount of semiconductor .

3- The uses of amount semiconductor oxides as photocatalyst in presence UV light has been established in case of bleaching of Crystal Violet dye. Solar energy has been proved more efficiency for removal the dyes .

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