

Removal Color Study of Toluidine Blue dye from Aqueous Solution by using Photo-Fenton Oxidation

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Abstract

The degradation of Toluidine Blue dye in aqueous solution under UV irradiation is investigated by using photo-Fenton oxidation (UV/H₂O₂/Fe⁺). The effect of initial dye concentration, initial ferrous ion concentration, pH, initial hydrogen peroxide dosage, and irradiation time are studied. It is found put that the removal rate increases as the initial concentration of H₂O₂ and ferrous ion increase to optimum value ,where in we get more than 99% removal efficiency of dye at pH = 4 when the [H₂O₂] = 500mg / L, [Fe⁺ 2 = 150mg / L]. Complete degradation was achieved in the relatively short time of 75 minutes. Faster decolonization is achieved at low pH, with the optimal value at pH 4 .The concentrations of degradation dye are detected by spectrophotometer at $\lambda_{\max} = 626$ nm. The order of photo degradation reaction under UV is the first order kinetics. The photo-Fenton degradation process was monitored by UV-visible spectrophotometer.

Key words: Photo-Fenton Oxidation, Removal, Toluidine Blue dye ,UV-Visible.

Introduction

Major pollutants in textile wastewaters have high acidity, heat and other soluble substances main pollution in textile wastewater comes from dyeing and finishing processes [1-4]. Over the last few years the ten dyes have been to carry out chemical oxidation in the presence of catalyst that serves as a generator of hydroxyl radicals. The most dyes can be easily treated if the conventional treatment methods are incorporated with the advanced

oxidation processes which can break the complex structure of the dye and make it more amenable to bio-degradation [5]. The environmental risks by effluents of textile wastewater industry are the major source of water and ground water pollution. Textile industry is one of the most famous complicated industries among manufacturing industry [6]. Photo-oxidation technique is one of the important techniques that is used in many fields, it has a high efficiency in

the removal of the toxic effects of the environmental pollutants [7]. The degradation of these synthesised dyes has been extensively investigated by different technological and chemical processes such as photocatalytic degradation SiO_2 , TiO_2 , ZnO [8-10], chemical methods ozonation [11-12], chlorination [13]. Many researchers suggested that the potential exists for the use of highly concentrated sunlight in the removal of dyes from wastewater [14-15]. Industrial facilities take clean water from nature and re-contaminated water into water sources where these industrial pollutants effect the physical properties of natural water such as the intensity, color and taste, etc. [16]. The natural water contains a certain concentration of many organic and inorganic materials soluble and non-soluble and suspending material, different type of these material and focus greatly. Another important problem of textile industry wastewater is the colored effluent because of the usage of large amounts of dyestuffs during the dyeing stages of the textile-manufacturing process and contains visible pollutants [17-18]. In this work the photo-Fenton oxidation is used to removal Toluidine Blue dye. The relative dye concentration % and decolorization ratios, effect of Fe^{+2} concentrations, effect of H_2O_2 concentration, and effect of pH were

measured with spectro-photometric technique.

Materials and Methods

All chemicals are used without further purification. Hydrogen peroxide (H_2O_2 30% w/v), ferrous chloride (FeCl_2), sodium hydroxide (NaOH) and hydrochloric acid (HCl) and sulphuric acid H_2SO_4 are supplied from BDH. Toluidine Blue dye (product of USA.MSDS) Figure 1, is purchased from Omega. All the other chemicals and solutions are prepared with double distilled water.

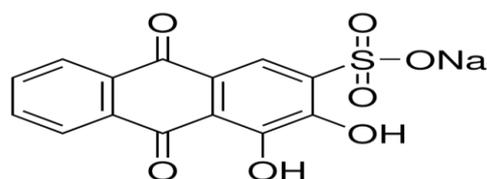


Fig. (1): Structural Formula of Toluidine Blue Dye.

Spectroscopic Measurements

UV-Visible spectra of aqueous solutions of dye was recorded by Shimadzu UV-Visible 1650 spectrophotometer, UV-Visible 7804 C spectrophotometer (SUNNY) is used to measure absorbance of dye solutions at λ_{max} . The pH is measured by using microprocessor pH meter 211, HANNA instruments. The temperature is adjusted by using regulator water bath WB 710M (Optima). Figure(2) shows the UV-Visible spectrum of aqueous solution of 1×10^{-5} M of TB dye. The $\lambda_{\text{max}} = 626$ nm.

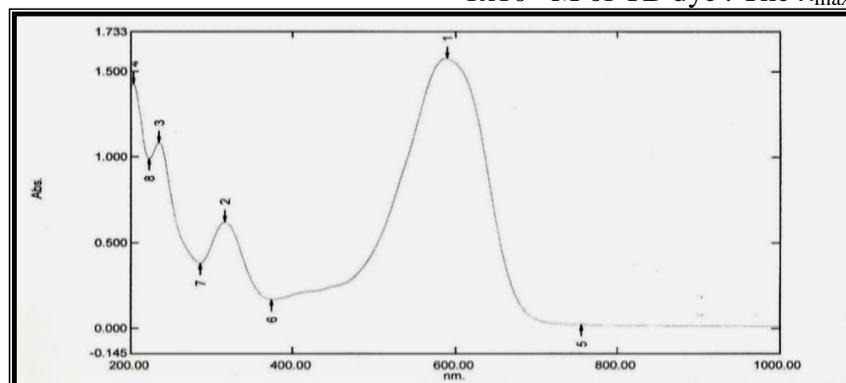


Fig. (2): UV-Visible Spectrum of Aqueous Solution of 1×10^{-5} M of TB Dye, pH=6, T=298K

Experimental Procedure

The operating irradiation time for all experiments is fixed at 75 min, due to the primary experiments indicating that the dye molecules are degraded and the dye solution become colorless at the time near to this period. The pH is adjusted to the desired value using 0.1N of sodium hydroxide and hydrochloric acid[19]. Control experiments are carried out under UV irradiation in the solutions with H₂O₂. In all experiment the lamp is warming on for 10 mins prior to initiation of reaction. Determination of the dye concentration is carried out by using the calibration curve as shown in Fig (3). The absorbance of dye is measured at maximum absorption at=626nm .

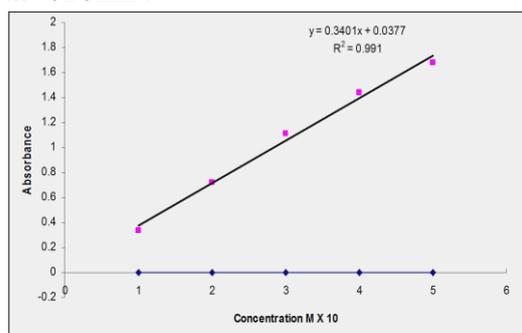


Fig. (3): Calibration Curve of TB Dye at pH=6, T=298K .

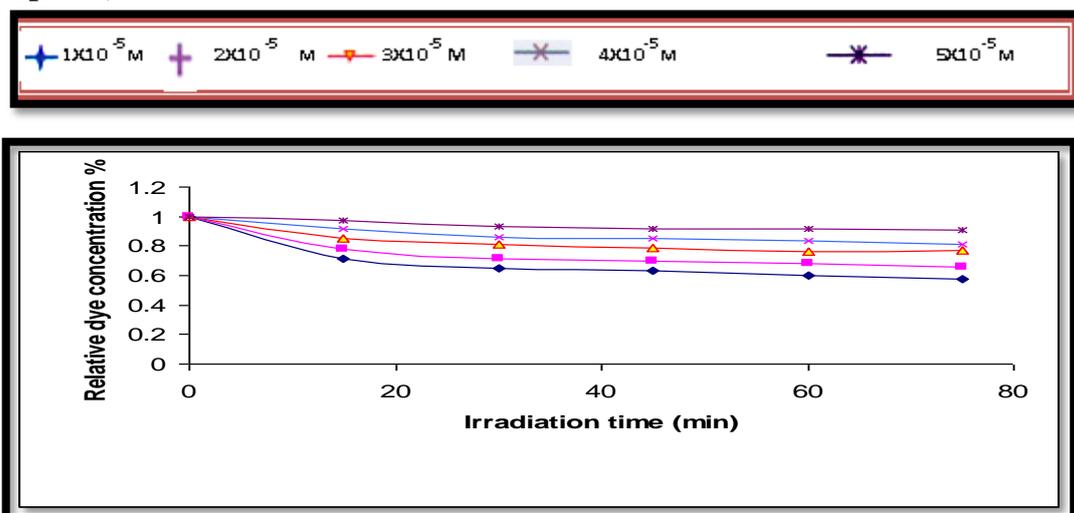


Fig. (4): Effect of Different Initial of TB Dye Concentration on the Color Removal as a function of Irradiation Time , at pH=6, T=298K.

Results and Discussion:

Effect of Initial Dye Concentration

Various initial dye concentrations in the range (1×10^{-5} - 5×10^{-5} M) are exposed to UV irradiation. It has been found out that any increasing in the initial concentration of the dye leads to the decreasing the color removal, because of decreasing penetration of photons entering into the solution and lowering the formation of hydroxyl free radicals [20]. It is clear that the dye concentration decreases as long as the time increases, high removal rate is achieved during the time of 75 minutes. The results are shown in Figure (4)

Study of Order Reaction

The obtained results prove that the photo oxidation reactions of the TB dye are reactions of the first order with respect to dye concentration; the coincident of the rapidity of reaction can be related with the absorption of the dye and calculated by using the law is called an empirical method [21]. Figure(5) .shows the relationship between Log R and Log C to determining order reaction. Also, the total order of reaction is calculated by :

Rate₁/ Rate₂ =k [Dye]₁^x [H₂O₂]₁^Y / k [Dye]₂^x [H₂O₂]₂^Y lead to this order x equal (0.8) .

Log R= log k + n log C Where:

C: concentration of dye, n: order reaction, R: reaction rate, k: reaction rate constant.

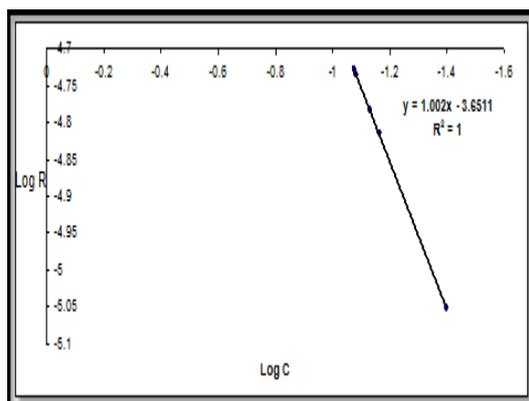


Fig. (5): Relationship between Log R and Log C of Oxidation of TB dye =1x10⁻⁵M , pH=6, T=298K.

Fenton's System.

Effect of Initial Ferrous Ion Concentration.

Fenton reaction on dye TB concentration (1x10⁻⁵M) under the same condition by using various concentration of ferrous ion in the range 50- 150m g/L in the presence of fixed concentration of H₂O₂ (500mg/L). Higher dosages of Fe⁺² lead to a high level of removal because a large amount of Fe⁺² can promote the formation of ·OH [22]. Figure(6) shows the

decolonization of TB as a function of UV irradiation time for various concentration of ferrous ion.

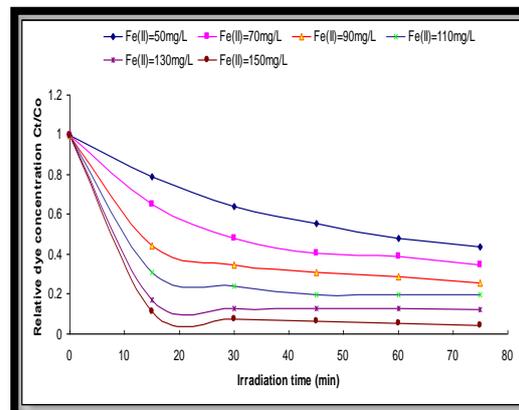


Fig. (6): Effect of Different Fe⁺² Concentration on the Color Removal of TB Dye as a Function of Irradiation Time.[TB]=1X10⁻⁵M, [H₂O₂]=(500mg/L), T=298K.

Effect of Initial H₂O₂ Concentration

Concentration of hydrogen peroxide has an important role in the degradation of TB dye in Fenton systems, as observed through experiments that carried out by using changing concentration of hydrogen peroxide ranging 100 – 500 mg/L at constant concentration of ferrous ion (150mg/L). The increasing of concentration of hydrogen peroxide effects in the reaction rate , this is obvious through the results ratio of color removal dye TB at 1X10⁻⁵M of increasing from 97 % to 99.1% under UV light . Therefore as same of hydrogen peroxide increased the ratio of degradation of pollutants increases due to increase the quantity of generated hydroxide radicals and this conforms with many studies[23-25]. Figure (7), shows the color removal of TB dye as a function of UV irradiation time for various initial H₂O₂ dosages.

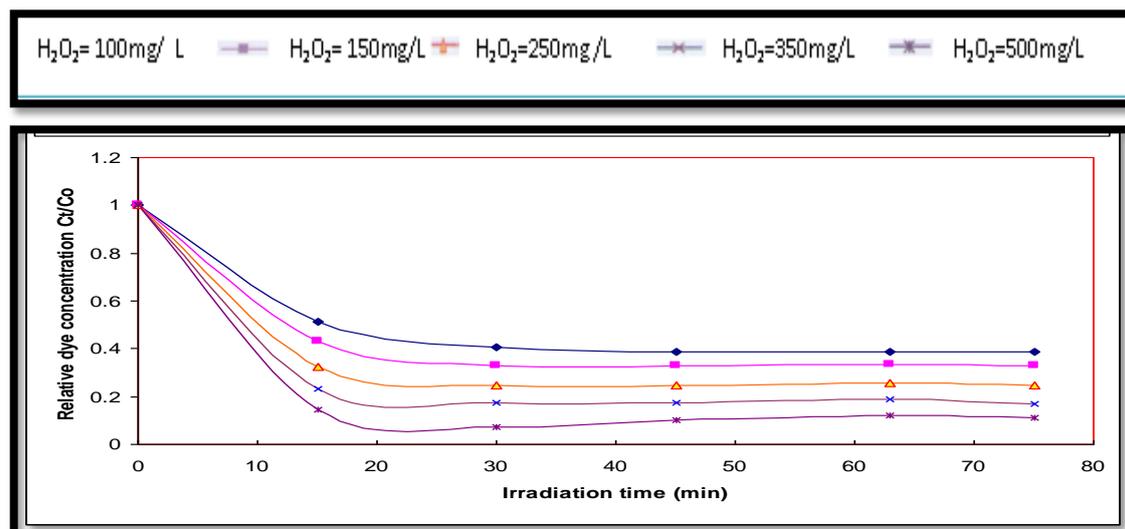


Fig. (7): Effect of Different Initial H_2O_2 Concentration on the Color Removal From $[TB]=1 \times 10^{-5}$ M $[Fe^{+2}]=(150\text{mg/L})$, $T=298\text{K}$ by using UV/ H_2O_2 / Fe^{+2} method

Effect of Initial pH

The results show a clear effect of initial pH in oxidation reaction of TB dye. The high color removal is obtained under acidic media (due to more $\cdot OH$ radicals generation) and low color removal in basic conditions (due to $Fe(OH)_3$ formation)[26]. The higher ratio color removal of TB dye is obtained under acidic media at $pH=4$ under UV light and decreasing ratio in the basic media. The higher decolorization rate demand reduces pH value because of the change in molecular structure. Figure (8). It has been found and that during 75 minutes of UV irradiation, the decolorization rates under UV/ H_2O_2 should decrease with increasing pH. The results improve that the highest ratio at the initial $pH = 4$ by the photo - Fenton oxidation process must be adjusted either by HCl or NaOH at $pH= 4$ acidic medium. This pH is consistent with some previous works [27].

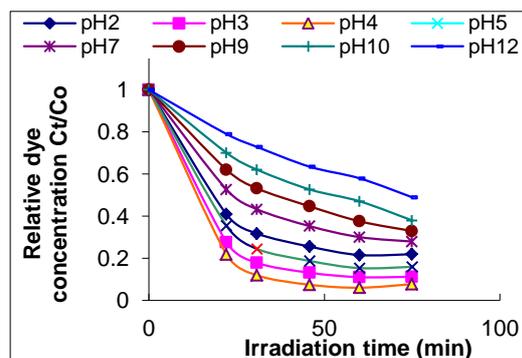


Fig (8): Effect of Different pH Value on Color removal from TB Dye as Function of Irradiation time, $[TB]=1 \times 10^{-5}$ M, $[Fe^{+2}]=(150\text{mg/L})$, $[H_2O_2]=(500\text{mg/L})$, $T=298\text{K}$ using UV/ H_2O_2 / Fe^{+2} method.

Conclusions

The degradation is strongly influenced by various parameters, particularly the initial H_2O_2 dosage and pH as well as irradiation time. The study shows that when carrying out reactions of Fenton's on Toluidine Blue dye the percentage removal increases with increasing the concentration of hydrogen peroxide and the concentration of ferrous ion in presence of UV light. Also, the presence of constant concentration of hydrogen peroxide and ferrous ion increases at $pH=4$.

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دراسة ازالة صبغة التلودين الازرق من محلولها المائي بواسطه استخدام تقنية الفنتون

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الخلاصة

تم التحري عن صبغة تولدين الازرق باستعمال عمليات الأكسدة المتقدمة التي تتضمن تقنية الفنتون UV /H₂O₂ /Fe⁺². تضمنت هذه الدراسة تأثير تركيز الصبغة الابتدائي، pH المحلول، كاشف فنتون، جرعة بيروكسيد الهيدروجين المستخدمة و زمن التشعيع على سرعة إزالة اللون. وجد إن سرعة الإزالة تزداد بزيادة تركيز بيروكسيد الهيدروجين وايون الحديدوز للوصول إلى القيمة المثلى. أن التجزئة الضوئية باستعمال UV/H₂O₂/Fe⁺² أسرع والنتائج أفضل حيث حصل على كفاءة أكثر من 99% عند pH= 4 عندما يكون [Fe⁺²]= 150mg/L، [H₂O₂]=500mg/L. تم تحديد الطول الموجي لصبغة تولدين بلو باستعمال جهاز Spectrophotometer وكان الطول الموجي الأعظم يساوي 626nm. أوضحت نتائج التجارب الحركية إن تفاعل درجة التحطم الضوئي بتأثير الأشعة فوق البنفسجية هي من الدرجة الأولى بوجود الصبغة فقط.

الكلمات المفتاحية: اكسدة الفوتو-فنتون، الازالة، صبغة التلودين الازرق