Removal Color Study of Azo dye (4-4/-antipyriyl azo 4-Amino Phenol) from Aqueous Solution by using Photo – Fenton Oxidation

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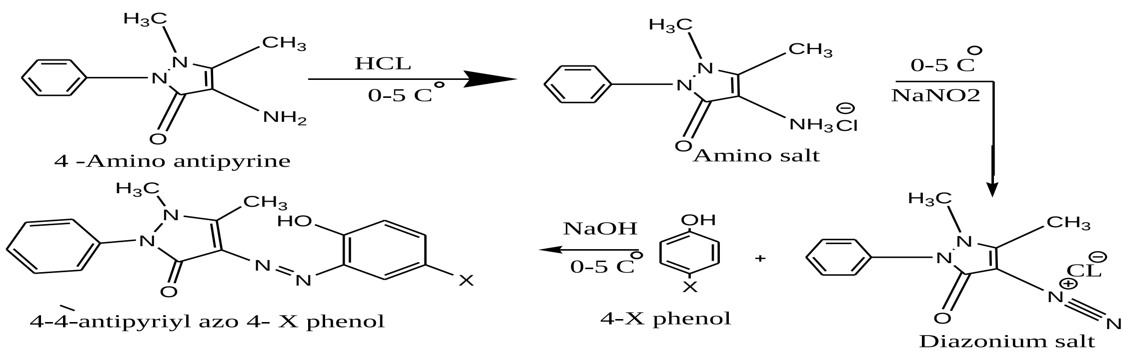
Abstract

Advanced oxidation processes are extensively used for the removal of organic constituents from water and wastewater. The aim of this study was to show the parameters the effects of initial dye concentration, hydrogen peroxide dosage, pH, and Fenton reagent of azo dye. It has been found that the removal rate increased as the initial concentration of H_2O_2 and ferrous ion increase to optimize value. The degradation with UV/H_2O_2/ Fe^{2+} system was the fastest. The degradation is fast with UV/H_2O_2/ Fe^{2+} system. The best results were obtained from photo Fenton's reagent with efficiency more than 99% at pH= 6.5, [H_2O_2] = 300 mg/L, [Fe^{2+}] = 150 mg/L. The concentration of undegraded dye was detected by using parameters at λ_{max}=391 nm.

Key words: Photo – Fenton Oxidation, Removal, Azo dye, UV-Visible.

1- Introduction

The environmental the danger of the liquid waste of Textile and yarn factories wastewater industry are the major source of water and contaminants in groundwater. Azo dyes constitute the largest class of dyes which is used in several industries[1], as well as for colored solvents, inks, paints, food, paper, plastic, rubber, varnishes, cosmetics, and drugs [2]. One of these risks is vehicles that carry high colors, high level of COD, large ranges of pH neutral, and which resist natural degradation. For instance fabric dying disposed 100- 170 L of colored effluents per Kg of cloth processed[3]. Due to high efficiency in the removal of the most poisonous in particular environmental pollutants used Photo-oxidation technique for that purpose [4].The development of advanced oxidation processes (AOPs) is an attempt to take advantage of the speed and time at work, the nonselective reactivity of the (·OH). AOPs are defined as those techniques that include the generation of highly reactive radical intermediates, particularly the (·OH) at ambient temperature. The advantages of AOP_S are their high treatment capability, rapid reaction rates, hence relatively small reactors, high elasticity and the possibility of mixing them into water recycling processes [5], [6] Generation of hydroxyl radicals (· OH) from hydrogen peroxide this process is called Fenton reaction and is based on an electron transfer between H_2O_2 and iron ions conduct as homogeneous catalyst[7],[8]. This method provides effective hydroxyl radical at the lowest cost, using easy-to-handle reagents. Some industrial wastewater contains aromatic amines and Fenton reagent an effective way to treat these substances [9], a wide range of dyes [10], and many other substances, such as. Repeller[11],[12] and corrosion inhibition [13],[14]. The antipyrine azo dyes (Table 1) was prepared according to the equations[15] (scheme1). Using various advanced oxidation processes various reaction conditions under UV light.



X = Br , CL , NH2

Scheme (1) :preparation of dyes.

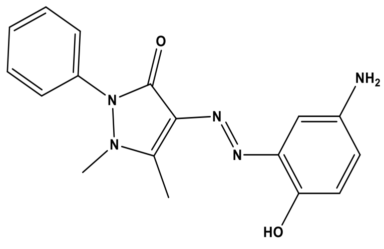
4-4′-antipyriyl azo 4-Amino Phenol (4AANH$_2$) (E)-4-((5-amino-2-hydroxyphenyl) diazenyl)-1,5-dimethyl-2-phenyl-1,2-dihydropyrazol-3-one	
λ_{max} **= 391 nm**	**Molar mass= 323 g / mol**

Table 1 : antipyrine azo dyes

2- Materials and methods

2.1 Materials and Reagents

All chemicals were used without further purification. Ferrous chloride($FeCl_2$), Hydrogen peroxide($H_2O_2$30%w/v),Hydrochloric acid(HCL) and sulphuric acid H_2SO_4 Sodium hydroxide and (NaOH) were supplied from BDH. Distilled water is used to prepare all the chemicals and solutions.

2.2 Instruments

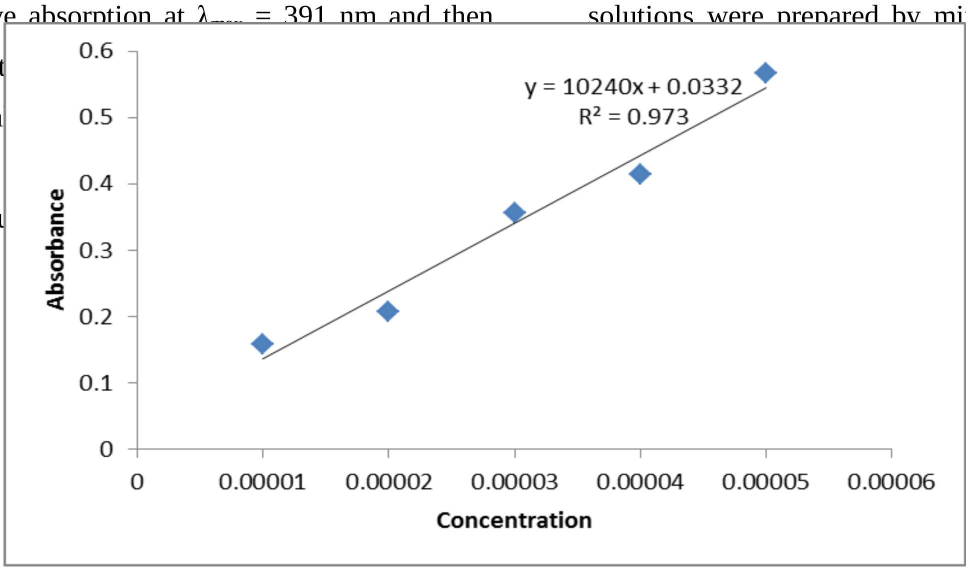
UV-Visible 7804 C spectrophotometer (Sunny, China) was used to measure the maximum absorbance of dye solutions at (391nm).

UV-Visible 1650 spectrophotometer (Shimadzu ,Japan) was used to recording the absorption spectra of aqueous solutions of dye. The temperature was adjusted by using regulator water bath WB (Optima). The pH was measured by using a microprocessor pH meter 211, (Hanna ,Romania) instruments.

2.3 Irradiation of dye solutions

All dye solutions were irradiated for duration of 80 minutes (the most of dye molecules were 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} = 391 nm and then the det the ca shows spectr

Ferrous ion at the range (20-100 mg/L) at the pH equal of 6.5 and 298K . Another series of solutions were prepared by mixing Fe^{+2} (100) at pH equal of



Figure(2): Calibration curve for $4AANH_2$ dye concentration $1x10^{-5}$ M at pH=6.5 , T=298 K

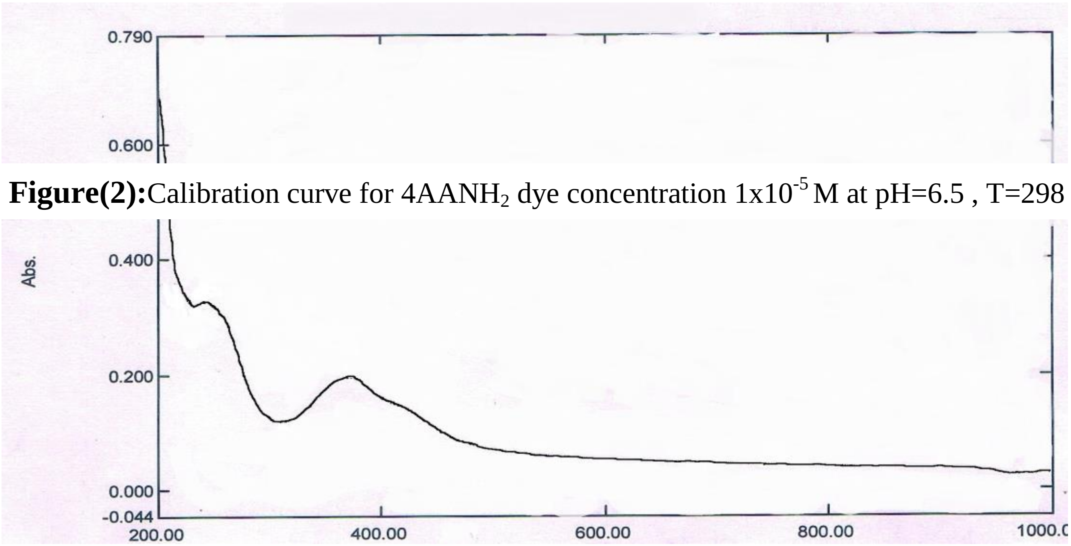


Figure (3): UV-Visible spectrum of aqueous solution of $4AANH_2$ dye concentration $1x10^{-5}$ M, pH=6.5 , T=293K.

2.4 Fenton's system

A series of Fenton's solutions were prepared by mixing H_2O_2 (100 mg/L) and solution were prepared by using Fe^{+2}(150 mg/L) and H_2O_2(100 mg/L) at pH=(1-8) and 298K. In all the above solutions, the dye concentration was $3x10^{-5}$M. All the solutions were irradiated for **80** minutes [16],then measuring the concentration was determined by measuring the dye absorbance at λ_{max}= 391 nm.

Figure(5): Relationship between Log R and Log C from ox pH=6.5 , T=298K.

3- RESULTS AND DISCUSSION

3.1 The effect of initial dye concentration

In Figure (4) for 4AANH2 dye at pH= 6.5 show effect of different dye concentrations on the degradation of azo dye using UV irradiation for 80 minutes, T=298K. It has found that increasing the initial concentration from $1x10^{-5}$M to $5x10^{-5}$M and because of decreasing penetration of photons entering into the solution and lowering the formation of hydrox color r

The obtained results proved are reactions of first order with respect to dye concentration that the photooxidation reactions to the $4AANH_2$ dye .The law empirical method used to calculate the rapidity of reaction can be related with the absorption of the dye [18]. To calculate the order of reaction, the drawing was between Log R and Log C and show in Figure(5) To calculate the order of reaction, the

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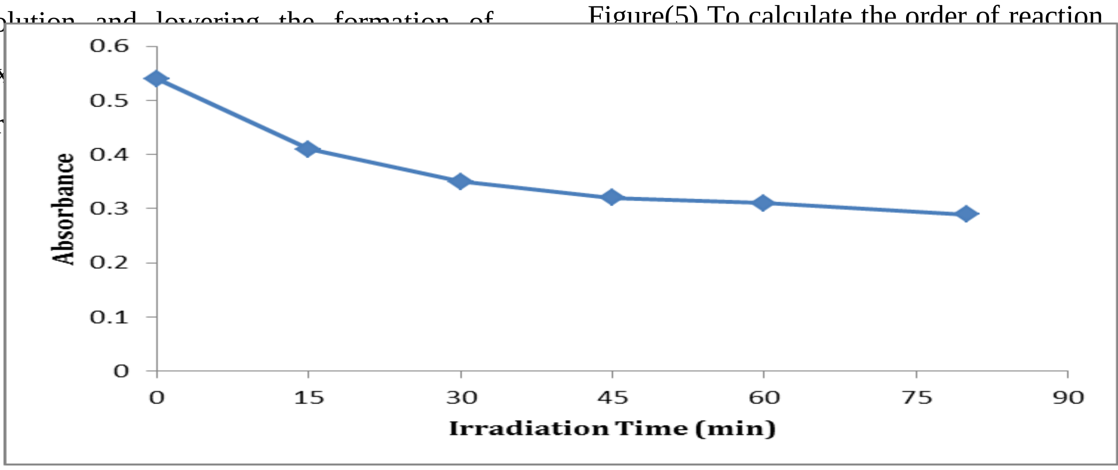
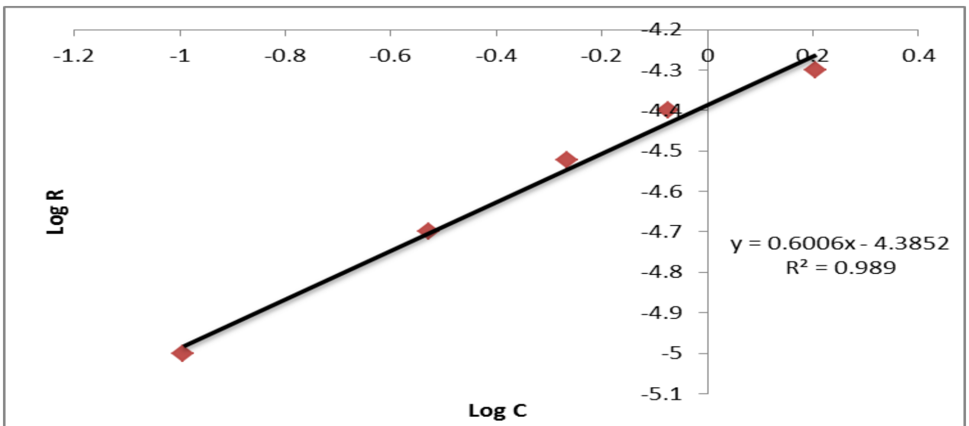


Figure(4): Effect of Irradiation time on Color removal , [4AANH2] =$3x10^{-5}$ M , pH=6.5 , T=298K



Figure(6): Effect of different Fe^{+2}concentration on the color removal time.[4AANH$_2$]=1X10^{-5}M,[H_2O_2]=(300mg/L), pH= 4, T=298K by usi

3.2 Fenton's system

3.2.1 Effect of initial Ferrous ion concentration

The rate of the degradation by H_2O_2 alone is very low for many dyes ,especially azo dyes, addition of Fe^{+2} fast the generation of hydroxyl radical ($^{\cdot}OH$) [19].Figure (6) shows the effect of photo Fenton's reagent on the decolourization of azo dyes as a function of UV irradiation time for various concentrations of ferrous ion in the range 50-150 mg/L in the presence of a fixed concentration of H_2O_2 (300 mg/L) for **80** minutes. The best finding was reached **97.8%** of color removal by Fe^{+2} /H_2O_2/UV used [H_2O_2]= 300mg/L,[Fe^{2+}]=150 mg/L, with the increasing concentration of Fe^{+2}, H_2O_2 the percent of color removal increased after 80 minutes of reaction time. The mechanism of the Fenton process is reported below[20],[21].

$Fe^{2+}+H_2O_2 \rightarrow Fe^{3+}+OH^{-}+HO^{\bullet}$ (1-2)

$Fe^{3+}+H_2O_2 \rightarrow Fe^{2+}+H^{+}+HO_2^{\bullet}$ (1-3)

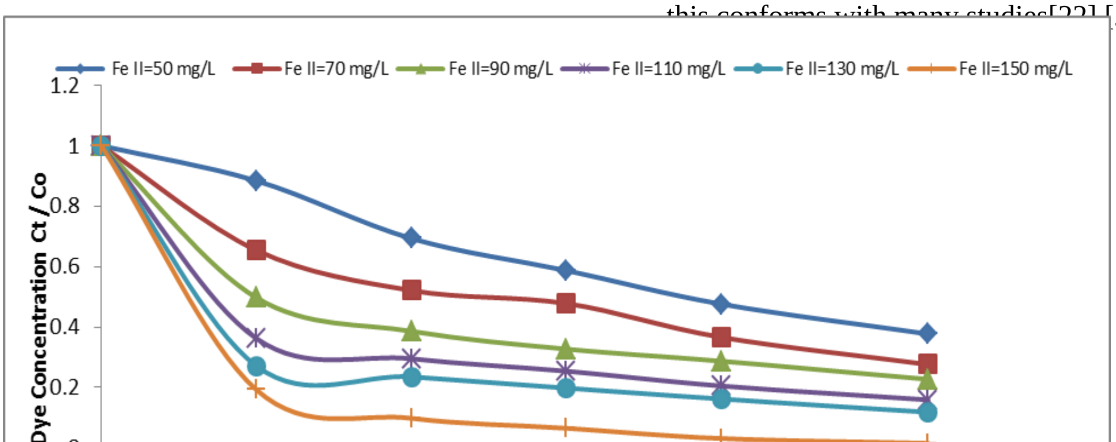
$2H_2O_2 \rightarrow HO^{\bullet}+HO_2^{\bullet}+H_2O$ (1-4)

conditions is due to more hydroxyl radical $^{\bullet}OH$ generate, because Fe^{+2} ions rapidly oxidized to Fe^{+3} ions formation $Fe(OH)_3$ the color removal at basic conditions is low**.**

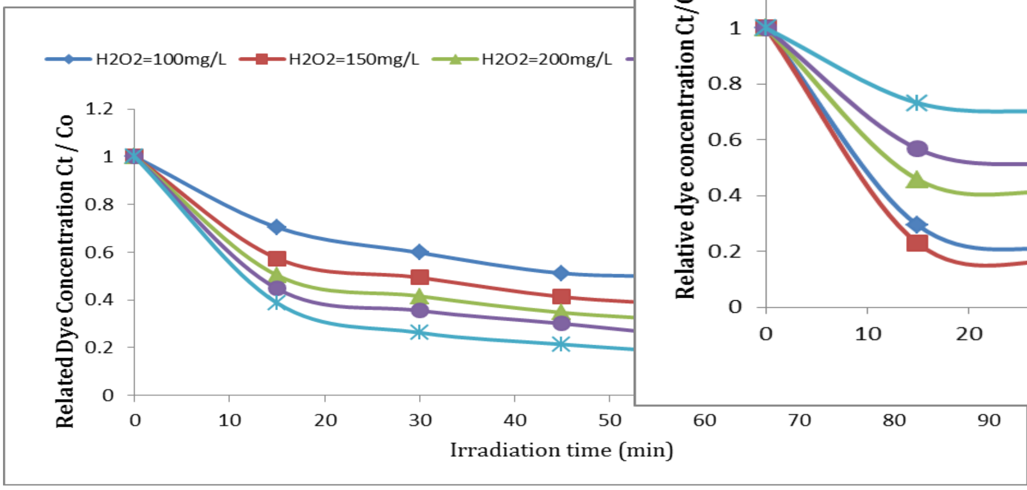
3.2.2 Effect of initial H_2O_2 concentration

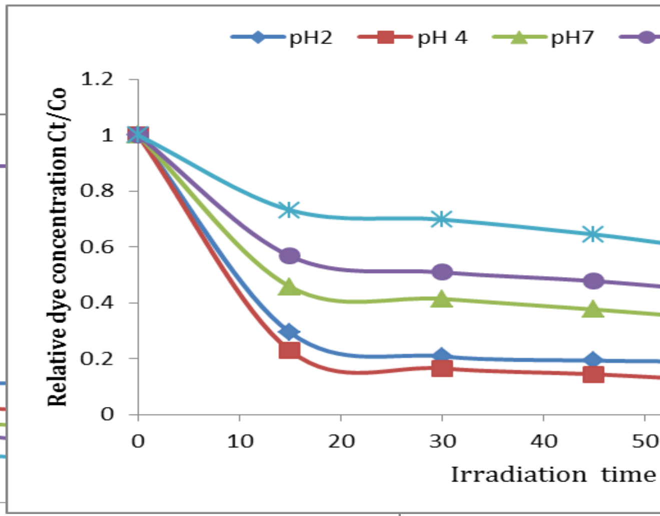
The concentration of hydrogen peroxide H_2O_2 in Fenton systems has an important role in the degradation of azo dye. As it observed through experiments that were carried out using changing concentrations of H_2O_2 ranging (100–300 mg/L) at a constant concentration of ferrous ion (150 mg/L).Also, the H_2O_2 dosages increasing the removal percentage of color increased from 97.5 % to 99.1% .

Figure (7) shows the color removal of 4AANH$_2$ as a function of UV irradiation time for various initial H_2O_2 dosages. Therefore the increasing of hydrogen peroxide concentration the ratio of degradation of pollutants increases because of increase quantity of generating hydroxide radicals and this conforms with many studies[22],[23].



decreased as the pH value increased under UV irradiation.





Figure(7): Effect of different initial H_2O_2 concentration on the color removal from $4AANH_2 = 1X10^{-5}$ M, $[Fe^{+2}]$=(150mg/L) ,$[H_2O_2]$=(300mg/L), pH= 4, T=298k by using UV/ H_2O_2 / Fe^{+2} method.

3.2.3 Effect of initial pH

The higher ratio color removal of $4AANH_2$ dye was obtained under acidic media at pH=4 under UV light and decreasing the ratio in basic media. The low color removal in basic conditions (due to $Fe(OH)_3$ formation) because Fe^{+2} ions rapidly oxidized to Fe^{+3} ions formation $Fe(OH)_3$ and this conforms with many studies and high color removal was obtained under acidic media (due to more ·OH adical generation)[24],[25]. Figure(8) refers the relation dye concentration Ct/Co was

initial dye concentration .

2. The study showed the speed of degradation is reduced when the increasing the concentration of the dye, due reduce the ability of light penetration when high concentrations of the dyes and lead to reduce the speed of the degradation and the color removal of dyes.
3. In the presence of Fenton's reagent and at pH media (6.5) were achieved Higher efficiencies in color removal, and high capacity were observed by increasing the concentration of Fe^{+2}.

Figure(8): Effect of different pH value of color removal from azo dye as a function of irradiation time, [4AANH$_2$]=1X10^{-5}M , [Fe^{+2}]=(150mg/L) ,[H$_2$O$_2$]=(300mg/L) , pH=4 , T=298K , using UV / H$_2$O$_2$ / Fe^{+2}method.

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الخلاصة

أحدى طرق ازالة الملوثات العضوية الموجودة في مياه التصريف للمعامل الصناعية تتم بإستخدام عمليات الأكسدة المتقدمة (AOP 'S) . في هذه الدراسة تم دراسة تأثير التركيز الإبتدائي للصبغة ، pH المحلول ، جرعة بيروكسيد الهيدروجين المستخدمة ، كاشف فنتون . في هذه الدراسة لوحظ ان سرعة الإزالة للصبغة تزداد بزيادة تركيز بيروكسيد الهيدروجين H_2O_2 المستخدم . كما ان استخدام نظام فنتون $UV/\ H_2O_2\ /\ Fe^{2+}/$ فأن التجزئة الضوئية تكون أسرع حدوثاً . تم الحصول على افضل النتائج بإستخدام نظام فنتون الضوئي حيث كانت كفاءةالازالة أكبر من 99% عند pH =6.5، بوجود $[H_2O_2]$ =300 ملغم\لتر ، $[Fe^{2+}]$ =150 ملغم\لتر . تم استخدام المطياف لغرض قياس تركيز الصبغة غير المتحطمة وذلك عند امتصاص محلولها المائي الأعظم (λ_{max} =391 نانومتر) .