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Catalytic Degradation of Organic Substances by Activated Hydrogen Peroxide

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ABSTRACT

This research work compares between catalytic activity of metal iron (II), iron (III) and cobalt (II) to decompose hydrogen peroxide which promoting the oxidative degradation of organic compounds, and to evaluate the catalyst function and study of the effect of the pH on the reaction constants (k). The research plan is to create models of waste water by adding a known amount of organic substances and then removing these substances by catalytic oxidation, studying the effect of change catalyst type, pH and calculating the reaction rate of the reactions in each.The selected organic substances are *crystal violet and toluidine blue* (organic dyes), then calculating the change of their concentrations (change in absorption) with time in different catalysts and pHs. The obtained results showed the optimum pH to activate hydrogen peroxide varies between 8 and 9. It is also found that cobalt (II) catalyst is more active than iron (II), iron (III) which generates hydroxyl radical from hydrogen peroxide promoting the oxidative degradation. It confirmed by HPLC that cobalt (II) (at pH 8) catalyzed hydrogen peroxide and completely degrade crystal violet.

المستخلص

البحث يقارن بين النشاط التحفيزي لايونحديد ((II، III)) وكوبالت (II) لتحلل بيروكسيد هيدروجين الذي يقوم بالاكسده الحفزية و يعمل لكي يحلل المركبات العضوية، وتقييم وظيفة الحفاز ودراسة تأثير درجة الحمضية على ثوابت التفاعل (k)، وتهدف خطة البحث عمل تخليق نماذج من مياه الصرف الصحي عن طريق إضافة مواد عضوية معلومة ومن ثم إزالة هذه المواد عن طريق الأكسدة الحفزية ودراسة تأثير تغيير المحفزات ودرجة الحمضية وحساب معدل التفاعل في كل منهما، والمواد العضوية التي اختيرت لهذه التجارب هي كريستال بنفسجي وأزرق تولويدين (أصباغ عضوية)، وحساب التغيير في التركيز (التغيير في الامتصاص) مع مرور الزمن في محفزات ودرجات حمضية مختلفة. أظهرت النتائج التي تم الحصول عليها ان درجة الحمضية الامثل لتفعيل بيروكسيدهيدروجين تتراوح بين 8 و 9 ، وكذلك وجد ان كوبالت (II) أكثر فاعلية من حديد (II، III) لتوليد جذر الهيدروكسيل من بيروكسيد هيدروجين الذي يحفز التحلل التحفيزي، وأيضا أثبت أن كوبالت (II) (في درجة الحمضية 8) حفز بيروكسيد هيدروجين الذي حلل كريستال بنفسجي تماما ووضوح بكروماتوقرافيا الضغط العالي للسائل.

KEYWORDS: Catalytic degradation, hydroxyl radical, metal ion catalysis, crystal violet, toluidine blue

INTRODUCTION

Hydrogen peroxide is environment friendly, efficient, easy to use, and suitable for application in the remediation of contaminants. However, hydrogen peroxide alone is not an excellent oxidant of most organic substances so the activation of hydrogen peroxide is needed. Transition metal ions, such as iron ions, are widely employed to catalyze hydrogen peroxide, generating the very reactive hydroxyl free radical [1]. The mixture of iron(II) salts and hydrogen peroxide is known as Fenton's reagent:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^-$$
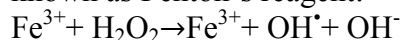
Application of Fenton's reagent in the degradation of organic compounds is limited by the slurry system because it produces a significant amount of ferric hydroxide sludge, which requires further separation and disposal. Iron oxides have been recently applied for the degradation or mineralization of organic contaminants with hydrogen peroxide [2-5]. The major advantages of iron oxides are that they are economical and easy to activate. As heterogeneous catalysts, they can also be easily separated from treated wastewater. Various types of iron oxides exhibit various chemical activities. Additionally, hydrogen peroxide, which is activated by iron oxide, is usually related to the Fenton-like system:

$$Fe^{3+} + H_2O_2 \rightarrow Fe(OOH)^{+2} + H^+ \quad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet \quad (3)$$
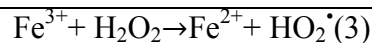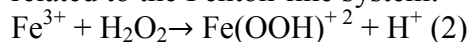
Fe(II) ion can be slowly generated by reactions (2) and (3). However, the consumption rate of H_2O_2 does not equal the generation rate of hydroxyl radical, because hydrogen peroxide can be decomposed to water and oxygen via non radical producing pathways by iron oxides. Therefore, some effective iron oxides that can transform hydrogen peroxide to generate the hydroxyl radical must be present.[6] The degradation of H_2O_2 occurs through many methods one of the methods was conducted by using Cu(II)-aminoacidcomplexes (glycine, alanine, and lysine) withquin-aldine blue as an oxidant. Parameters such as pH and concentration of cu(II), hydrogen peroxide, and amino acid are examined to understand the activation mechanism of hydrogen peroxide. The oxidation rate is also substantially enhanced in Cu(II)/amino acid /H_2O_2 system with increasing pH from 6 to 9, fig (1) shows the effect of pH and plots of oxidation rate of quinaldine blue and the formation rate of $OH^\bullet$ versus pH. The oxidation rate increased exponentially as the pH was varied from 6.0 to 8.5 as shown in fig (1). The oxidation rate of quinaldine blue correlates markedly with the formation rate of $OH^\bullet$. The trend is consistent with the formation of $OH^\bullet$, the formation which is favored under alkaline condition
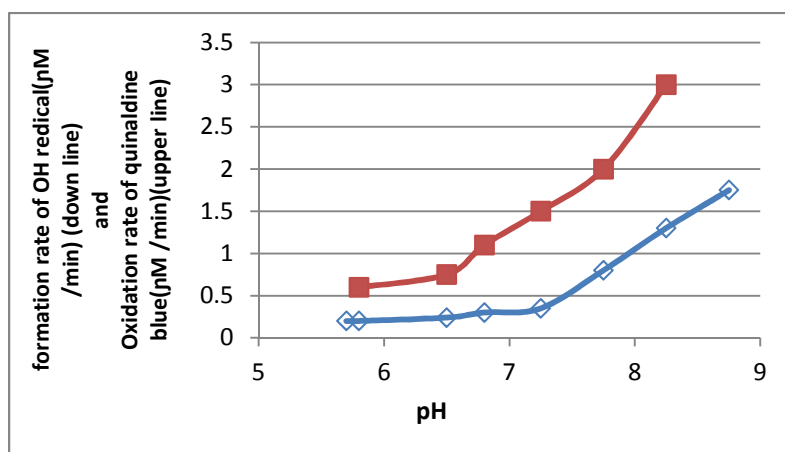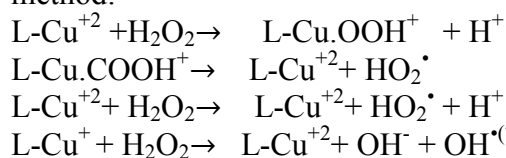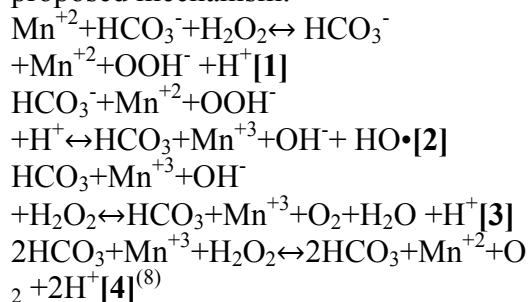
Figure 1: The oxidation rate of quinaldine blue(down line) and formation of hydroxyl radical (upper line)

The proposed mechanism for this method:

$L-Cu^{+2} + H_2O_2 \rightarrow L-Cu.OOH^+ + H^+$

$L-Cu.COOH^+ \rightarrow L-Cu^{+2} + HO_2^\bullet$

$L-Cu^{+2} + H_2O_2 \rightarrow L-Cu^{+2} + HO_2^\bullet + H^+$

$L-Cu^+ + H_2O_2 \rightarrow L-Cu^{+2} + OH^- + OH^{\bullet (7)}$

Another method is by using manganese (II) which decomposes H_2O_2 in order to catalyze the oxidation of NADH. Strikingly, these processes were found to depend on the simultaneous presence of both CO_2 andHCO_3^-, and the proposed mechanism:

$Mn^{+2} + HCO_3^- + H_2O_2 \leftrightarrow HCO_3^- + Mn^{+2} + OOH^- + H^+$ **[1]**

$HCO_3^- + Mn^{+2} + OOH^- + H^+ \leftrightarrow HCO_3 + Mn^{+3} + OH^- + HO\bullet$ **[2]**

$HCO_3 + Mn^{+3} + OH^- + H_2O_2 \leftrightarrow HCO_3 + Mn^{+3} + O_2 + H_2O + H^+$ **[3]**

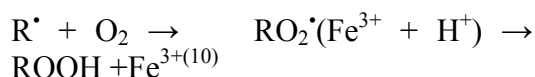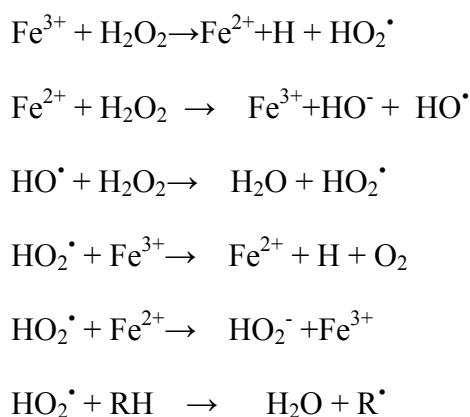$2HCO_3 + Mn^{+3} + H_2O_2 \leftrightarrow 2HCO_3 + Mn^{+2} + O_2 + 2H^+$ **[4]** [8]

Also it has been reported that the oxidation of organic compounds with hydrogen peroxide can be accelerated by selenium dioxide catalyst, but the mechanism of this reaction has not yet been clarified satisfactory. [9]

Recently Iron (III) was also used to activate the hydrogen peroxide and generate the hydroxyl radical. This is called (Fenton process) which can easily deg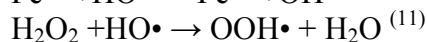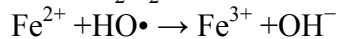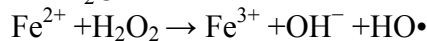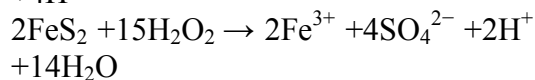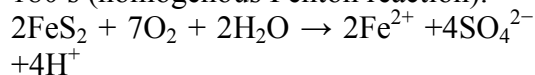rade the organic substances; in this study added substrates, acetone and t-butyl alcohol, strongly retard the decomposition of H_2O_2 brought about ferric (EDTA) at pH 8-9.5. Their relative effectiveness and the kinetic form of the retardation are consistent with their interruption of hydroxyl radical chain that is propagated by HO• attack upon both H_2O_2 and on complex.

The reaction was considered to involve the steps:-

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H + HO_2^\bullet$

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^\bullet$

$HO^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet$

$HO_2^\bullet + Fe^{3+} \rightarrow Fe^{2+} + H + O_2$

$HO_2^\bullet + Fe^{2+} \rightarrow HO_2^- + Fe^{3+}$

$HO_2^\bullet + RH \rightarrow H_2O + R^\bullet$

$R^\bullet + O_2 \rightarrow RO_2^\bullet (Fe^{3+} + H^+) \rightarrow ROOH + Fe^{3+(10)}$

Another Fenton reaction was conducted using pyrite as heterogeneous catalyst to degrade diclofenac by the pyrite Fenton system. The appropriate pH of (3- 4) completely degrade of diclofenac within

120 s, while only 65% of diclofenac was removed by classic Fenton system in 180 s (homogenous Fenton reaction).

$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$

$2FeS_2 + 15H_2O_2 \rightarrow 2Fe^{3+} + 4SO_4^{2-} + 2H^+ + 14H_2O$

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

$Fe^{2+} + HO\bullet \rightarrow Fe^{3+} + OH^-$

$H_2O_2 + HO\bullet \rightarrow OOH\bullet + H_2O$ [11]

In a recent study a new catalyst was used to activate the hydrogen peroxide.The decomposition was catalyzed by a mixed ligand cobalt(II) and nickel (II) complexes as heterogeneous catalysts and adsorbed on alumina has been investigated by measuring the evolution of oxygen at different time intervals between 35-60°C. The effect of variation in the concentration of hydrogen peroxide and in the quantity of catalysts on the extent of disproportionation has also been studied. Enhanced activity has been observed in presence of alumina-adsorbed complexes. The reaction rate is found to increase with increase in temperature and quantity of the catalyst. The effect of stereochemical aspects of the complexes on the kinetics of decomposition of hydrogen peroxide has also been studied [12]

In this study a comparison was carried out between the catalytic activity of iron (II), iron (III) and cobalt (II) metal ions to decompose the hydrogen peroxide to degradecrystal violet and toluidine blue at different pH values.

MATERIALS and METHODS
Chemicals

All chemicals used were of analytical-grade

Crystal violet$[C_{25}H_{30}ClN_3]$ (90.0%)was purchased from Central Drug House "CDH" ,Toluidine blue $[C_{15}H_{16}N_3S.Cl]$(85%) ,was obtained from Sigma-Aldrich ,and Hydrogen peroxide (50%w/w) was obtained from Scharlau , the catalysts Fe(III) [Ferric chloride 96.0%], Fe(II)[Ferrous ammonium sulphate 99.0%] and Co(II)[Cobalt Chloride hexahydrate98%] from CDH, Buffer solution [pH 2.0 (Citrate), 7.0 (Phosphate), 9.0 (Borate) from CDH, pH 8.0 (Phosphate)from Fisher Scientific], Acetonitrile was purchased from Scharlau.

Instruments
pH/ ion meter Pinnacle -555-JENWAY.
Spectrophotometer - 6300 - JENWAY.
High performance liquid chromatograph(HPLC) - SHIMADZU -Auto sampler with PDA detector

Procedure for spectrophotometer
1 cm^3 of the dye (0.00245 M) was added to 50cm^3 of the buffer solution (to adjust the pH of the reaction), 1cm^3 of the catalyst (0.000245M) was added and 4 cm^3 of hydrogen peroxide (50%) added to the reaction solution, the reaction was monitored with time using spectrophotometer by measuring the absorption of the dye at its maximum absorption. The logarithm of absorption was represented against time according to the relation below.

$$ln(a-x)=-kt+lna$$

Procedure for HPLC
1 cm^3 of the crystal violet (0.00245M) was added to the 50cm^3 of phosphate buffer solution (pH 8) and 1cm^3 of cobalt (II) catalyst (0.000245M) was added and 4 cm^3 of hydrogen peroxide (50%) added to the reaction solution. After period of time the solution was totally colorless, 1cm^3 of the solution was transferred in a vial and injected in the HPLC.

Chromatographic condition for crystal violet:
The mobile phase (A: phosphate buffer pH= 8 , B: acetonitrile) at flow rate 1.75 cm^3/ min , at room temp, as detector spectrophotometer set at (590nm) , the column type and size C18 , 3- 6 X 150nm.[13]

Note: All experiments were conducted at room temperature

Results and discussion
Spectrophotometer results
Toluidine blue results

Degradation kinetics under different catalysts [Fe (II), Fe (III), and Co (II)] at pH [2, 8, and 9] showed in figures 2 to 4
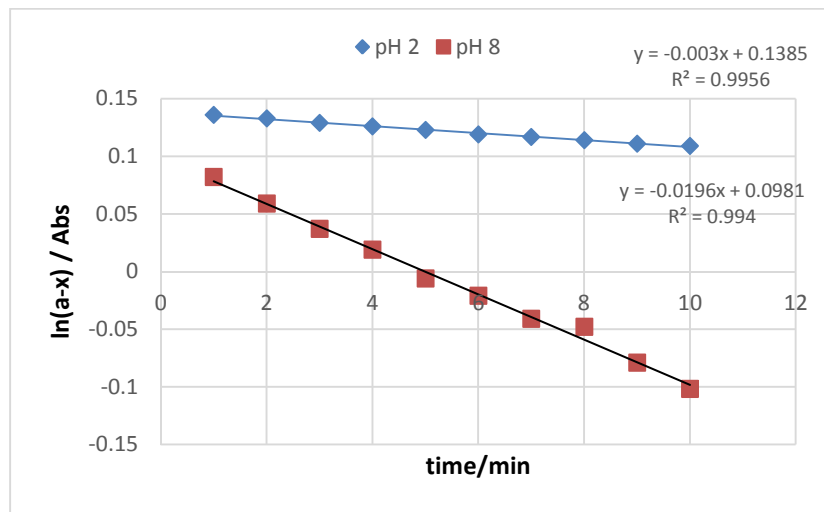

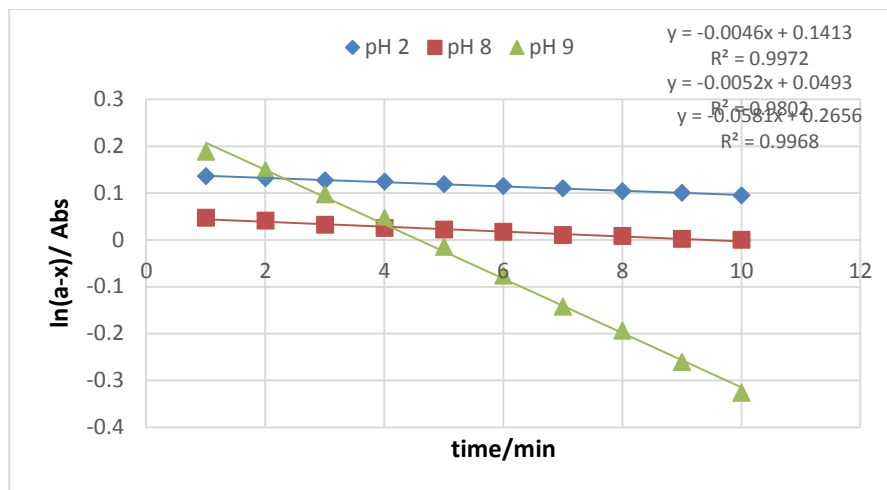**Figure 2: Degradation of Toludine blue using Co(II) as catalyst in pH 2 & 8**

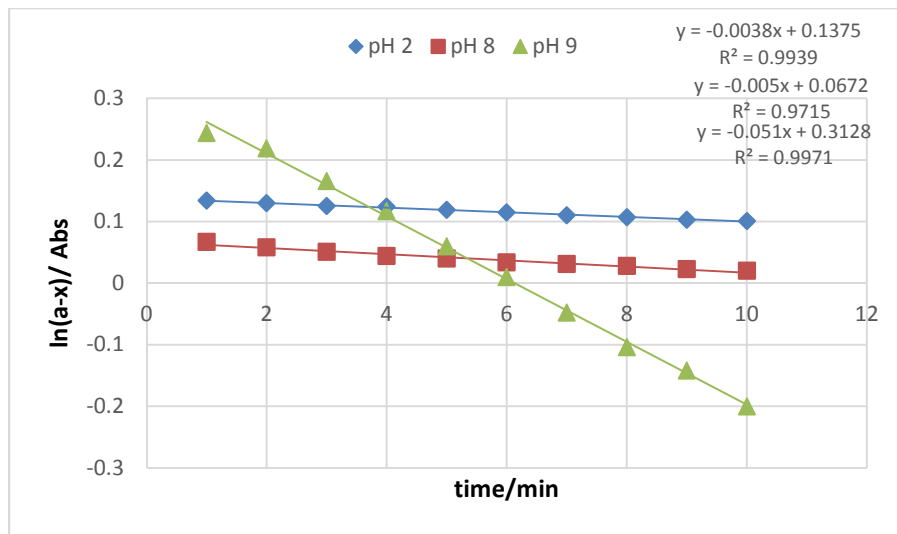**Figure 3: Degradation of Toludine blue using Fe (II) as catalyst in pH 2, 8 & 9**

Figure 4: Degradation of Toludine blue using Fe (III) as catalyst in pH 2, 8 & 9

Crystal Violate results:

Degradation kinetics under different catalyst [Fe (II), Fe (III), and Co (II)] and pH [2, 7, and 8] showed in figure 5 to 7
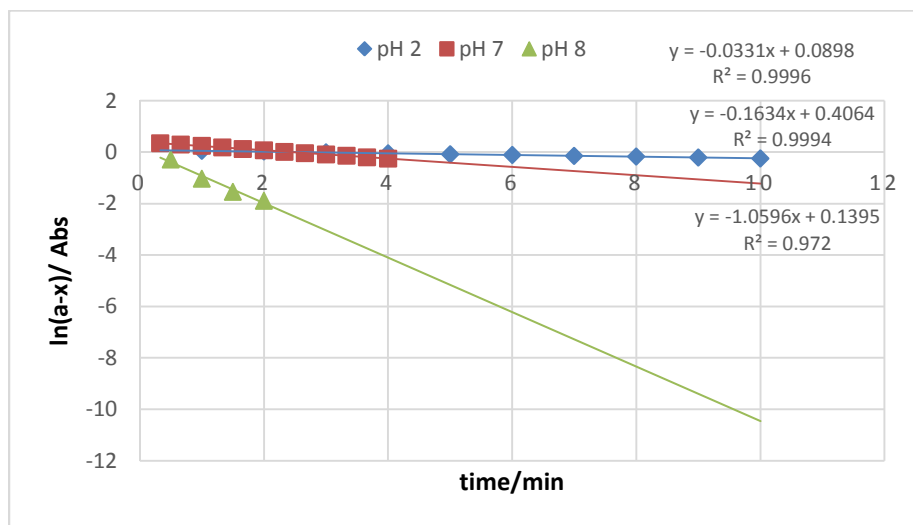

Figure 5: Degradation of Crystal violet using Co (II) as catalyst in pH 2, 7, & 8
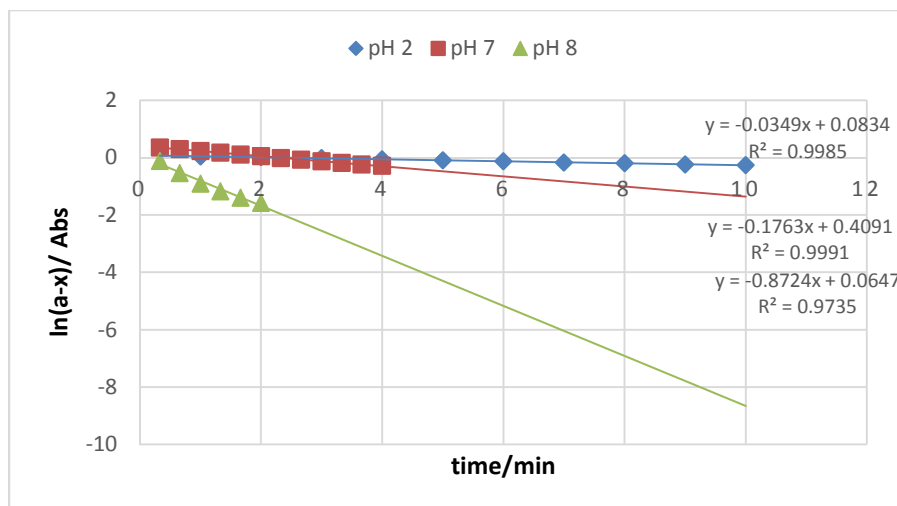
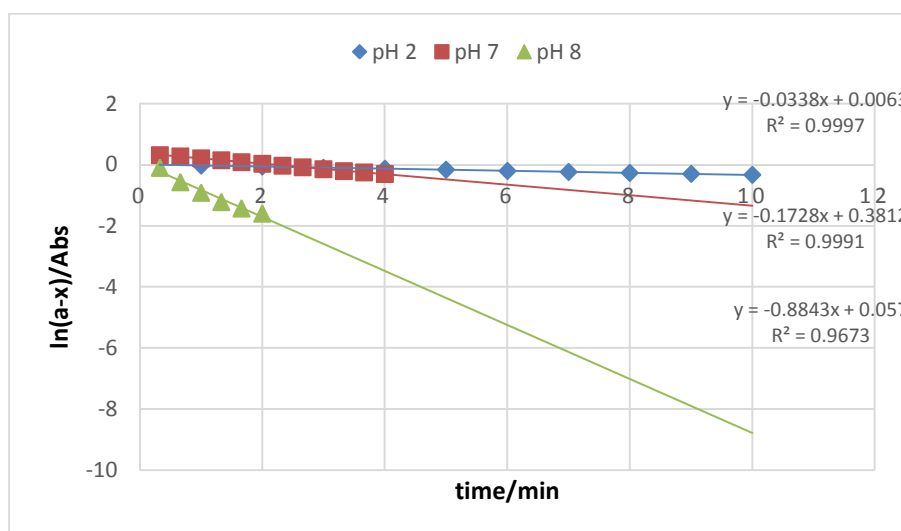**Figure 6: Degradation of Crystal violet using Fe (II) as catalyst in pH 2, 7, & 8**

Figure 7: Degradation of Crystal violet using Fe (III) as catalyst in pH 2, 7, & 8

Comparison between rates of reactions
Toluidine blue

Table 1: Comparison between rates of the degradation for the toludine blue at different **catalysts and pH**

| Catalyst	Co(II) min^{-1}	Fe(II) min^{-1}	Fe(III) min^{-1}
pH 2	0.0030	0.0046	0.0038
pH 8	0.0196	0.0052	0.0050
pH 9	OFF	0.0581	0.0510

Crystal violet

*Table 2: Comparison between rates of the degradation for the Crystal violets at differ**ent catalysts and pH***
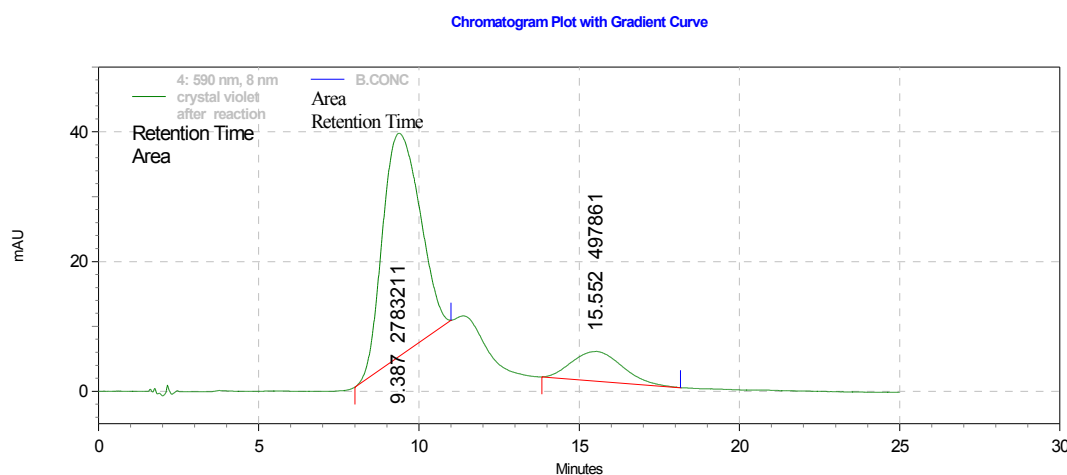
Catalyst	Co(II) min^{-1}	Fe(II) min^{-1}	Fe(III) min^{-1}
pH 2	0.0331	0.0349	0.0338
pH 7	0.1634	0.1763	0.1728
pH 8	1.0596	0.8724	0.8843

HPLC results

HPLC spectra showing degradation of crystal violet
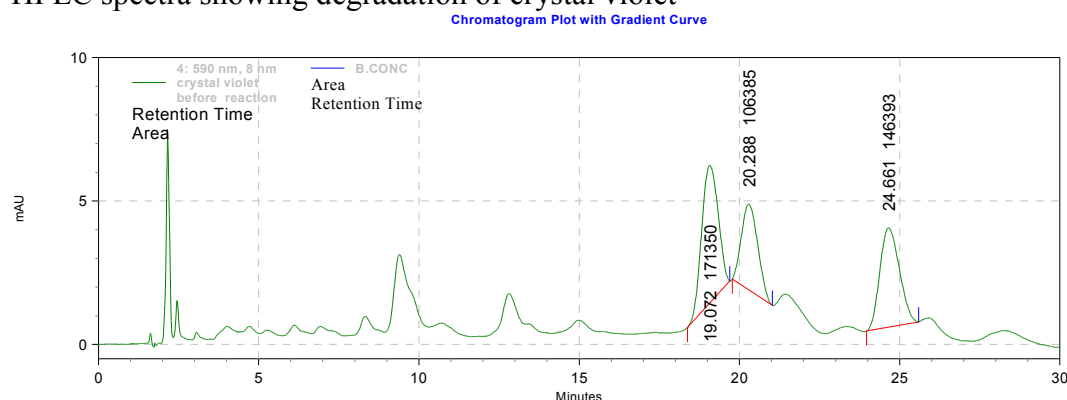
Figure 8: Chromatogram before reaction (all components without catalyst)

Figure 9: Chromatogram after reaction

DISCUSSION

The optimum pH to activate hydrogen peroxide varying between 8 and 9, that is due to the formation of hydroxyl radical (OH$^\bullet$), the formation of which is stable in alkaline solutions , and is responsible of the oxidation of organic compounds .

According to the results, three facts can be taken in consideration, first the acidic medium is not a suitable medium to hydroxyl radical (OH$^\bullet$) formation. Second-

ly hydrogen peroxide is highly stable in acidic medium. Thirdly the organic substances in lower pH values retard the decomposition.

Study of the reaction at pH 9 and above 9 is very unlikely, because of the interference between crystal violet and alkaline solution. Toluidine blue reaction at pH 9 is stable but the hydrogen peroxide is dissociate in at 10 and above.

The cobalt(II) catalyst is more active than iron(II), iron(III) for the decomposition of hydrogen peroxide what promotes the oxidative degradation of organic compounds in neutral and alkaline medium. In acidic media the Iron(II), iron(III) show better reactivity than cobalt(II).

It is also demonstrated that cobalt-catalyzed hydrogen peroxide can completely degrade crystal violet (HPLC Data graph). At pH 8 , we can see in figure (1) the retention time of crystal violetis around 19 to 20 min , nevertheless , in figure (2) the peak disappeared due to the catalytic degradation in that retention time.

CONCLUSION

The conditions for catalytic degradation were optimized and the best pH was between 8-9 for iron(II), iron (III) and cobalt (II) which gives the highest rate of degradation for the toludine blue 0.058, 0.51 and 0.0196 min^{-1}consecuti-vely and for crystal violet was about 0.6 min^{-1} for the three catalysts. It was obvious that the optimum pH was at high pH, because the formation of hydroxyl radical is high and it is highly stable.The degradation was proven also using the high performance liquid chromatography, because the peak of the crystal violet disappeared after the addition of hydrogen peroxide to the catalyst.

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