



## Application of Nano-Copper – Substituted Lead Zirconate as Surface Catalyst for Oxidative Degradation of Organic Dye

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### ABSTRACT

The oxidative decomposition reactions of fuchsine dye on the surface of nano-catalyst  $\text{Cu}_{0.5}\text{Pb}_{0.5}\text{ZrO}_3$  were studied carefully in an aqueous solution in the presence of  $\text{H}_2\text{O}_2$  under condition of pseudo-first order reaction. The catalyst was prepared by solid state route using pure nominal composition of metal oxides. The structural and micro-structural properties of the catalyst were characterized well by XRD, SEM and AFM respectively. Many of the kinetic parameters were investigated in this article, results obtained indicated that, the rate of oxidative degradation of acid fuchsine dye was found to be pH-dependent. The mechanism was proposed and the activation parameters were calculated.

**Keywords:** Cu-doped-PLZ; Kinetics; SE-microscopy; X-ray Diffraction; oxidative Degradation; Fuchsine dye

## 1. INTRODUCTION

Textile dyes and many other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger [1,2]. One of the novel technologies for treating polluted water and wastewater is the advanced oxidation processes (AOPs), by which hydroxyl radicals (-OH) are generated to degrade organic pollutants [3].

Throughout the 20th century, the mechanisms, kinetics, and products of the AOPs using hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), ozone (O<sub>3</sub>), UV or ultrasonic irradiation, titanium dioxide (TiO<sub>2</sub>), and Fenton's reagent, which is a combination of ferrous ions and H<sub>2</sub>O<sub>2</sub>, were investigated extensively. These treatments were studied separately or in various combinations [4-7].

Acid fuchsine dye is one of the most important derivatives of fuchsine or rosaniline hydrochloride, acid fuchsine is a mixture of homologues of basic fuchsine, modified by addition of sulfonic groups.

While this yields twelve possible isomers, all of them are satisfactory despite slight differences in their properties. Acid fuchsine is an acidic magenta dye with chemical formula C<sub>20</sub>H<sub>17</sub>N<sub>3</sub>Na<sub>2</sub>O<sub>9</sub>S<sub>3</sub> [8,9] {see Fig. (1)}.

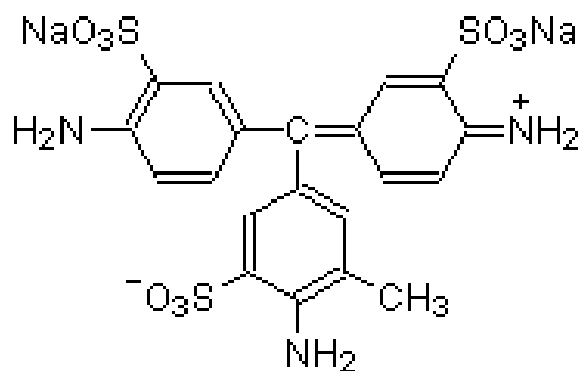


Fig. 1. The structure of acid fuchsine dye.

Some authors gave some interest for the oxidative degradation of azo fuchsine such as J. Wang *et al.* [10] that used nanometer rutile titanium dioxide (TiO<sub>2</sub>) powders as sonocatalysts for the degradation of acid fuchsine; they reported that, the method of sonocatalytic degradation of organic pollutants in the presence of TiO<sub>2</sub> powder was an advisable choice for treating organic wastewaters for non-or low-transparent and fuscous dye wastewater.

Recently, a numerous numbers of authors have been investigated using of copper oxide as individual catalyst or supported on other oxide mixture for promoting its catalytic activity having many chemical formula, such as CuO/Pt/Al<sub>2</sub>O<sub>3</sub>, CuO/MgO, CuO/ZnO, Cu/Ce/MgO, CuO/CeO<sub>2</sub> and CuO/ZrCeO<sub>4</sub> catalysts [11-21]. Also, copper used in catalysis process as La-Eu-Cuprate [22,23].

The essential goal of present article is describing a new trend for application of Cu- lead zirconate regime as an active surface catalyst for oxidative degradation of acid fuchsine dye.

## 2. EXPERIMENTAL

### 2. 1. Preparations

#### 2. 1. 1. Catalyst synthesis

The Cu-doped lead zirconate sample with general formula ( $\text{Pb}_{1-x}\text{Cu}_x\text{ZrO}_3$ ) where ( $x = 0.5$  mole) was prepared by the conventional solid state reaction route and sintering procedure using appropriate amounts of  $\text{Pb}_3\text{O}_4$ ,  $\text{ZrO}_2$  and  $\text{CuCO}_3$  each of purity  $>99\%$ . The mixture was ground in an agate mortar for 1h. Then the finely ground powder were subject to firing at  $800^\circ\text{C}$  for 20 hrs and reground and finally pressed into pellets with ( thickness 0.2 cm & diameter 1.2 cm ).

Sintering process was carried out at  $850^\circ\text{C}$  for 48 hrs. Then the furnace is cooled slowly down to room temperature. 10% more off-stoichiometric  $\text{Pb}_3\text{O}_4$  were used in order to compensate lead deficient which is due to its sublimation during sintering process.

#### 2. 1. 2. Dye Solutions

A commercial dyestuff of deep red colour was supplied from (El-Mehalla textile dyeing factory-Egypt). The dye was investigated carefully spectrophotometrically and established as being pure Acid fuchsine dye which is one of the most important derivatives of Fuchsine dyes with  $\lambda_{\text{max}}$  546 nm (Fig. 2). All dye solutions were prepared immediately before use in distilled water.

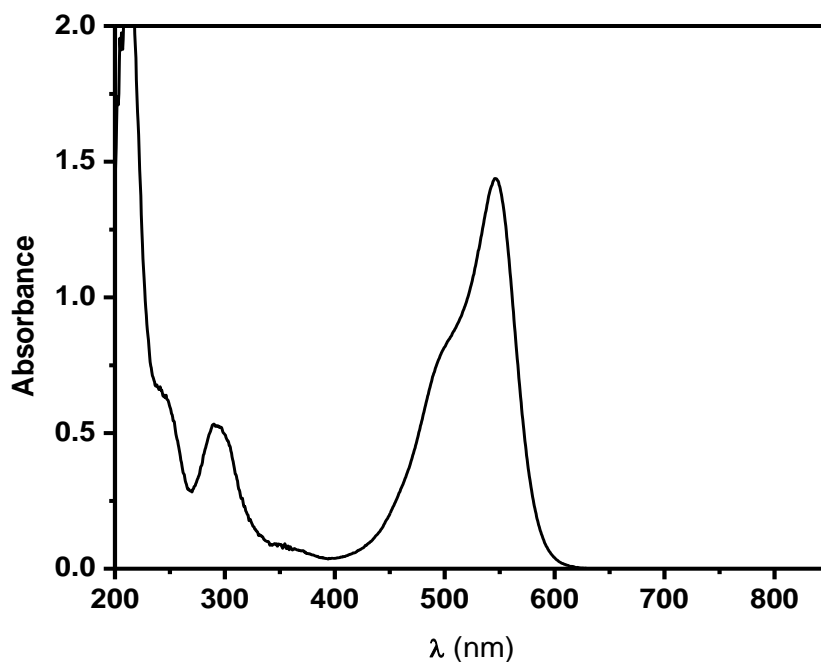


Fig. 2. Estimation of  $\lambda_{\text{max}}$  for acid fuchsine dye.

## 2. 2. Catalyst Characterization

### 2. 2. 1. The X-ray diffraction

The X-ray diffraction measurements (XRD) were carried out at room temperature on the fine ground samples on the range ( $2\theta = 15-75^\circ$ ) using Cu- $K_\alpha$  radiation source and a computerized [Shimadzu (Japan)] X-ray diffractometer with two theta scan technique. The analysis of the corresponding  $2\theta$  values and the interplanar spacings  $d(\text{\AA})$  by using computerized programme proved that, the Cu-doped lead zirconate mainly belongs to orthorhombic crystal structure (Fig. 3). The unit cell dimensions were calculated using the parameters of the most intense X-ray reflection peaks.

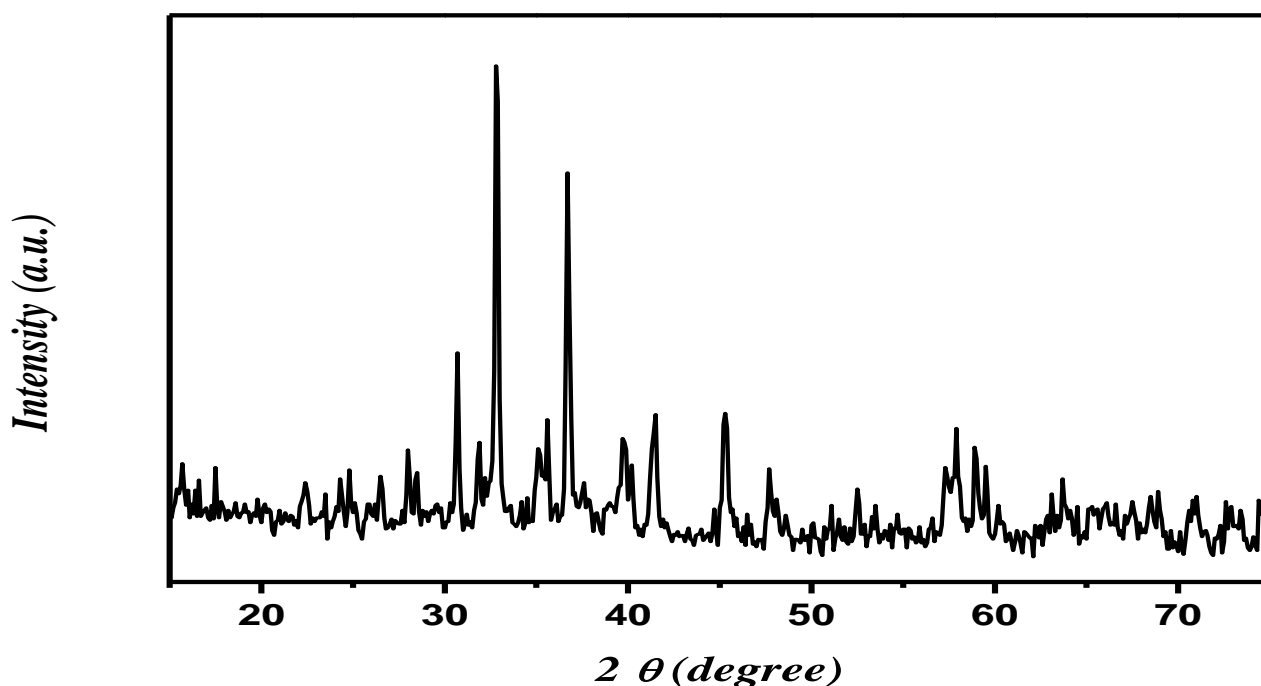
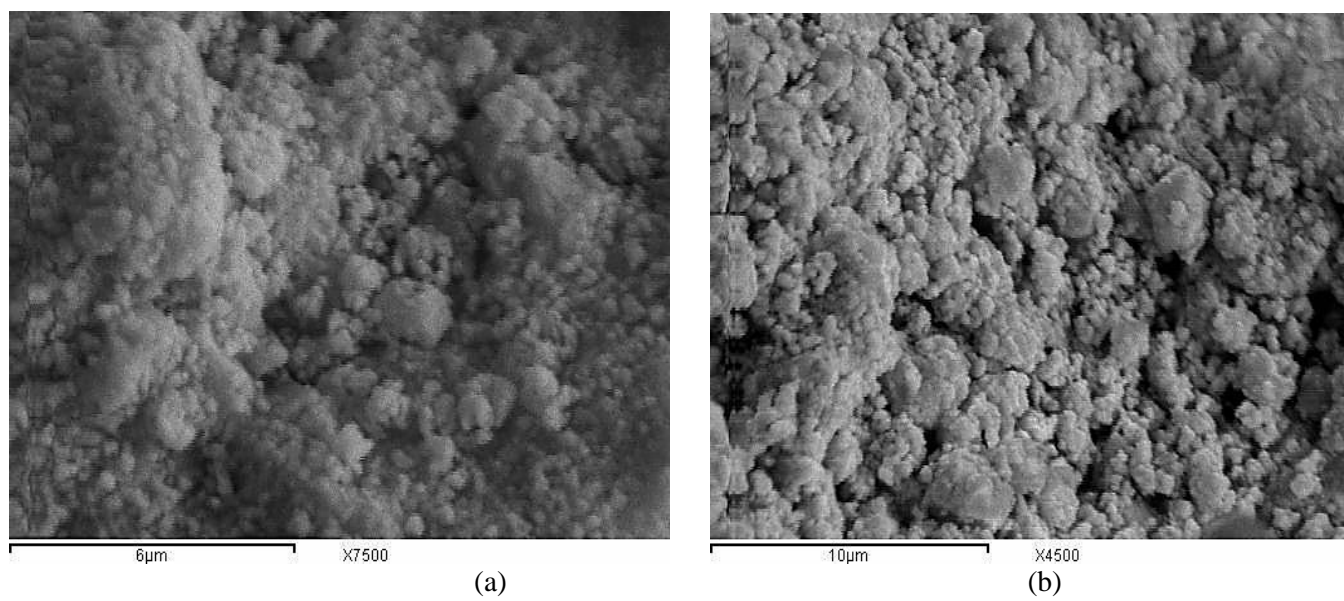


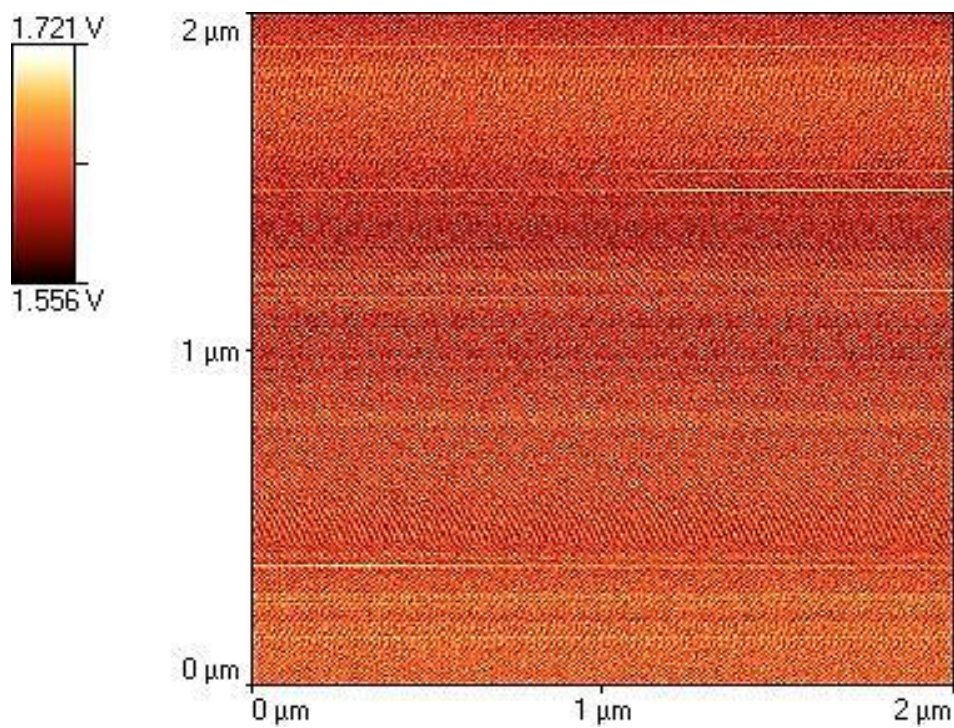
Fig. 3. The X-ray diffraction pattern for  $\text{Pb}_{0.5}\text{Cu}_{0.5}\text{ZrO}_3$  regime.

### 2. 2. 2. Scanning electron microscope (SEM)

Scanning electron microscope (SEM) measurements were carried out using small pieces of the prepared samples on different sectors to be accurate to the actual molar ratios by using "JXA-840A, JEOL-Japan". Fig. 4(a,b) shows the SEM of the catalyst surface. The average grain size was calculated and found in between 80 and 150 nm which is fully consistent with literature [24,25]. Fig. 4c shows AFM-image applying non-contact tapping mode. The analysis of image indicated that the particle size  $\sim 6-11$  nm and the average of grain size was compatible with results obtained from SEM recording 88 nm.



**Fig. 4(a,b).** SE-micrographs for pure  $\text{Pb}_{0.5}\text{Cu}_{0.5}\text{ZrO}_3$  with two different amplification factors **4a**: 6  $\mu\text{m}$  and **4b**:10  $\mu\text{m}$  respectively.



**Fig. 4(c).** AFM-image for copper-lead zirconate nano-catalyst.

### 2. 3. Kinetic measurements

The kinetic measurements of the reaction were carried out using UV-VIS spectronic 601 spectrophotometer at  $\lambda_{\max}$  546 nm for the oxidized acid fuchsine dye

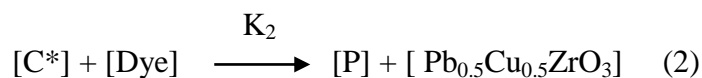
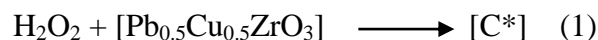
The run was carried out according to the following sequence; 0.025 gm of the catalyst was added carefully to a certain concentration of  $\text{H}_2\text{O}_2$  then the solution of the dye was added. At different time intervals the reaction mixture was quenched through  $\text{cm}^{-1}$  optical path length and the concentration of the dye was recorded and monitoring spectrophotometrically at  $\lambda_{\max}$  546 nm.

## 3. RESULTS AND DISCUSSION

### 3. 1. Mechanism and order of reaction

The mechanism of oxidative degradation of acid fuchsine dye was proposed in our investigations as two step process. The first step, is the fast one which includes the reaction between hydrogen peroxide and lead zirconate solid surface irreversibly with a rate constant  $K_1$  (Eq. 1) to form intermediate activated complex  $C^*$ , but this step is the fast one and irreversible.

The second step is the rate-determining step (slow step) includes the reaction between activated complex  $C^*$  with the acid fuchsine dye with a rate constant  $K_2$  (Eq. 2).



where [P] is decoloured oxidative dye.

The mechanistic sequences may describes as follow: the addition of  $\text{H}_2\text{O}_2$  to the catalyst ( $\text{Pb}_{0.5}\text{Cu}_{0.5}\text{ZrO}_3$  surface) which includes different oxidation states of different ions but generally we will use symbol  $M^{n+}$  which indicate to all positive cations on the catalyst surface ( $\text{Pb}^{2+}$ ,  $\text{Zr}^{4+}$  and  $\text{Cu}^{2+}$ ) which reacts with  $\text{H}_2\text{O}_2$  forming  $\mu^2$  bound peroxide, which stabilized by hydrogen bonding [26,27] forming activated complex  $[\text{C}^*]$  that finally reacts rapidly reversibly with substrate dye oxidizing it as described in equation (2).

Robbins *et al.* [26] studied the activation of hydrogen peroxide for oxidation of quinaldine blue indicator by using copper II complexes and they reported that, using of metal redox mechanisms [28] for activation of  $\text{H}_2\text{O}_2$  decomposition but, in their mechanism of activation  $\text{H}_2\text{O}_2$  coordinates fastly with copper II with out any change in its oxidation state.

### 3. 2. Order of the reaction

The order of reaction is evaluated by application the conditions of pseudo-first order reaction by keeping  $\text{H}_2\text{O}_2$  in large excess and consequently, the overall reaction can be expressed as shows in Eq. (3)



Hence the rate of oxidation depends only on the concentration of acid fuchsine dye and can be expressed as follows:

$$\text{Rate} = K_{\text{true}} [\text{H}_2\text{O}_2] [\text{Pb}_{0.5}\text{Cu}_{0.5}\text{ZrO}_3] [\text{dye}] \quad (4)$$

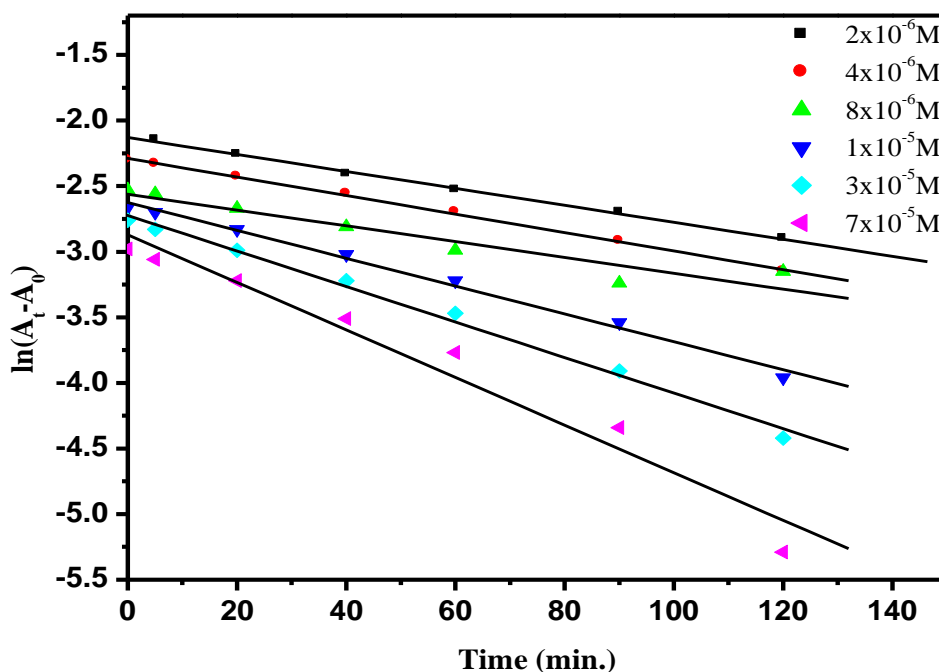
where  $K_{\text{true}}$  is the true rate constant but,

$$[\text{Pb}_{0.5}\text{Cu}_{0.5}\text{ZrO}_3] \text{ and } [\text{H}_2\text{O}_2] \gg \gg [\text{dye}]$$

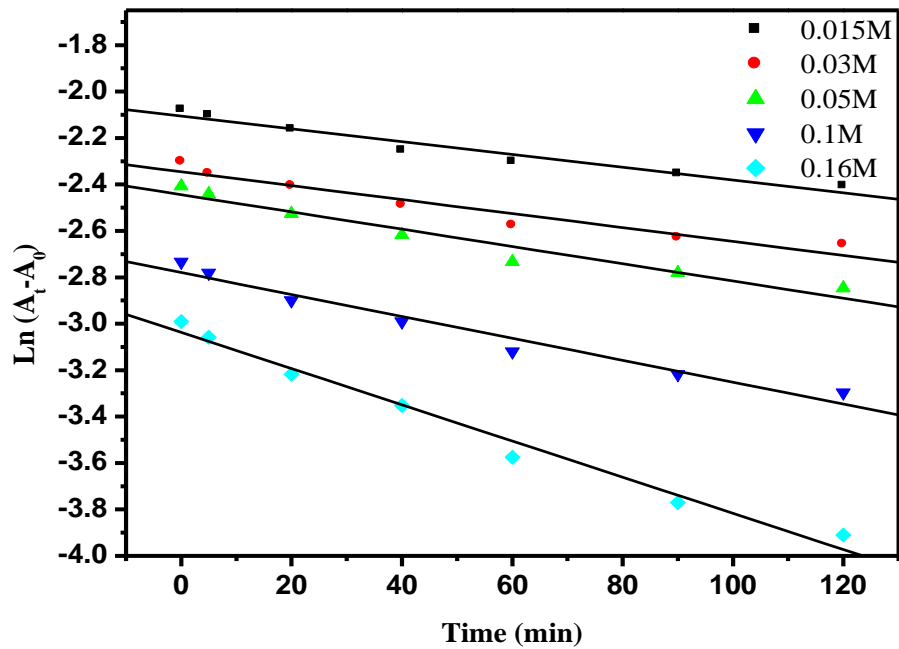
Thus, rate =  $K_{\text{obs.}}$  [Dye], where

$$K_{\text{obs.}} = K_{\text{true}} [\text{H}_2\text{O}_2] [\text{Pb}_{0.5}\text{Cu}_{0.5}\text{ZrO}_3] \quad (5)$$

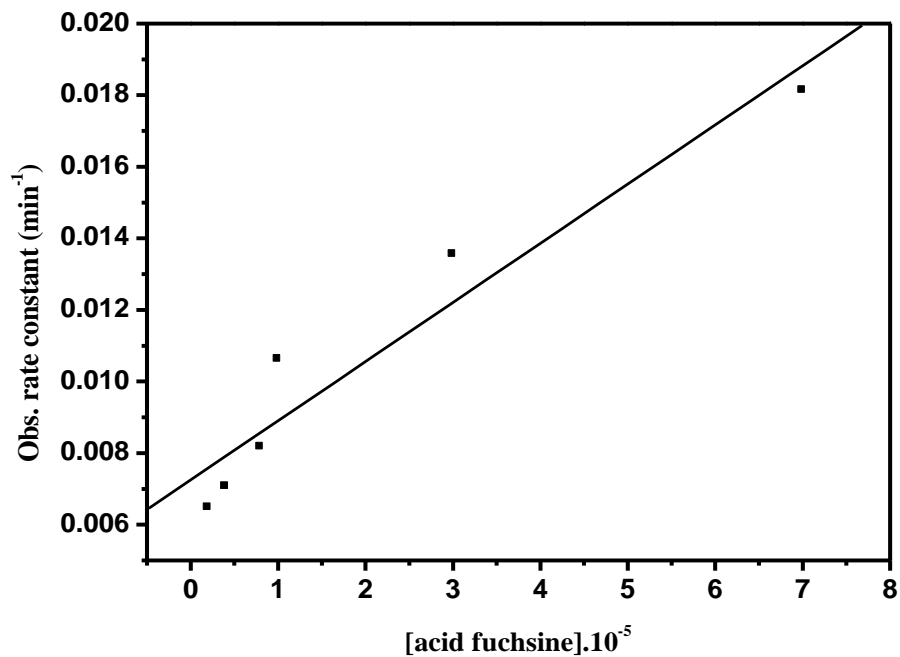
According to the first order reaction condition a plot between  $\ln(A_t - A_0)$  and time was constructed giving straight lines (Fig. 5a,b) with slop equal to observed rate constant  $K_{\text{obs.}}$  and hence, the true rate constant  $K_{\text{true}}$  can be easily evaluated by knowing [catalyst] and  $[\text{H}_2\text{O}_2]$ . In this respect,  $A_t$  and  $A_0$  are the absorbance of the dye at time t and infinity, respectively.



**Fig. 5(a).** The oxidative reaction of acid fuchsine dye different concentrations with lead zirconate catalyst = 0.025 gm in presence of  $[\text{H}_2\text{O}_2] = 0.01$  M, Temp. 30 °C and pH = 7.



**Fig. 5(b).** The oxidative reaction of [acid fuchsine dye] =  $4 \times 10^{-6}$  M with lead zirconate catalyst = 0.025 gm, Temp. 30 °C and pH = 7 at different concentrations of H<sub>2</sub>O<sub>2</sub>.



**Fig. 6(a).** The variation of observed rate constant ( $K_{obs}$ ) versus acid fuchsine dye concentrations.



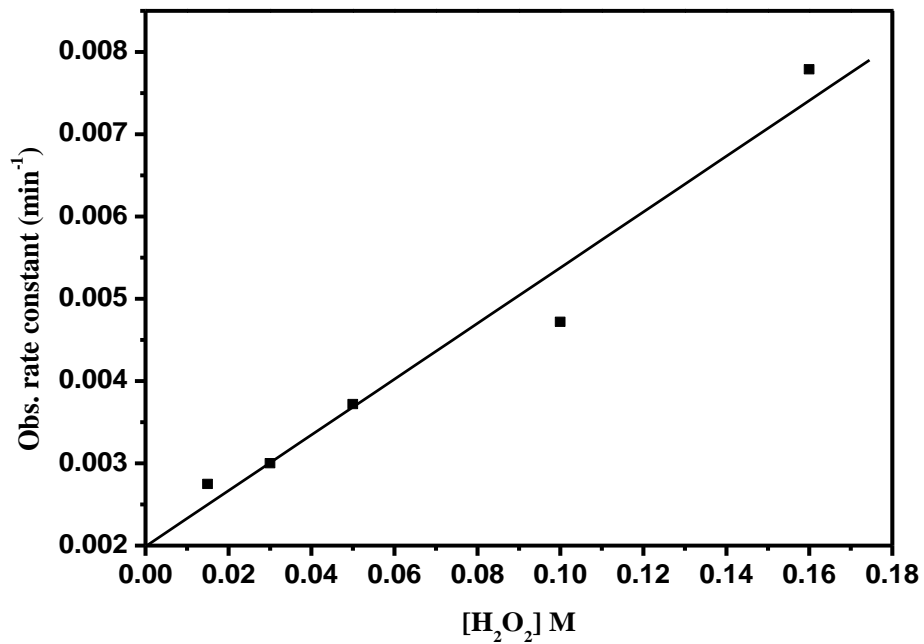


Fig. 6(b). The variation of observed rate constant ( $K_{obs.}$ ) versus  $H_2O_2$  concentrations.

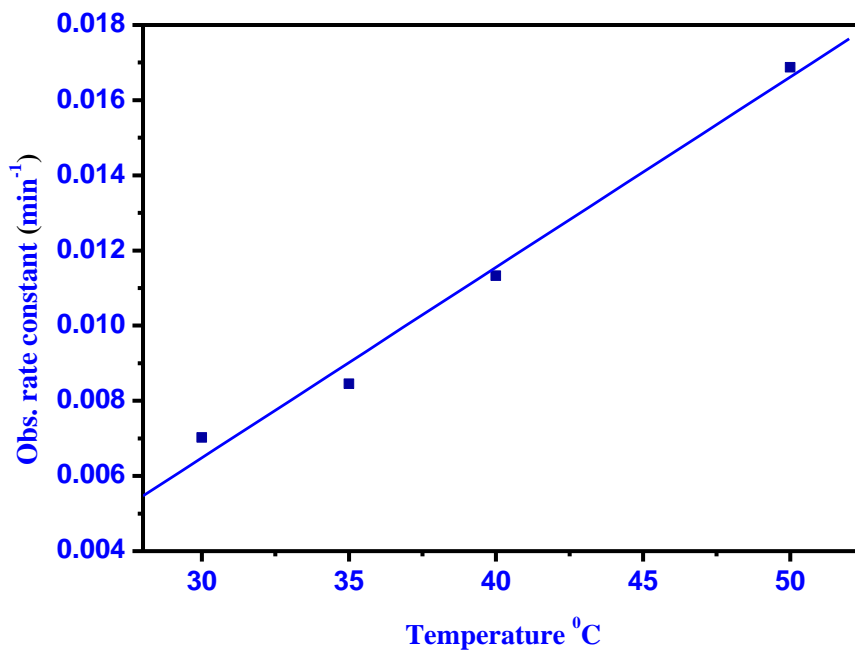


Fig. 7. The variation of observed rate constant ( $K_{obs.}$ ) versus temperatures.

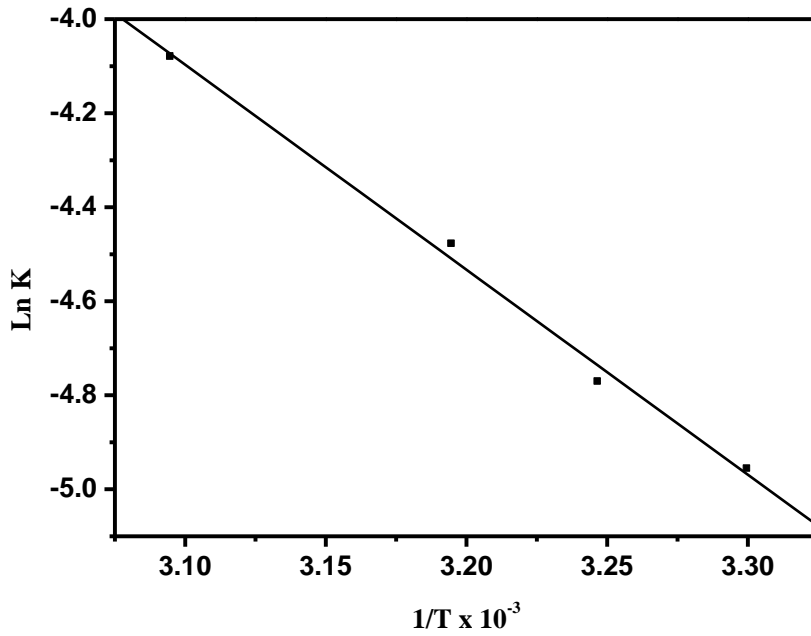


Fig. 8. Arrhenius plot for oxidative decomposition of acid fuchsine dye with Cu-doped lead zirconate.

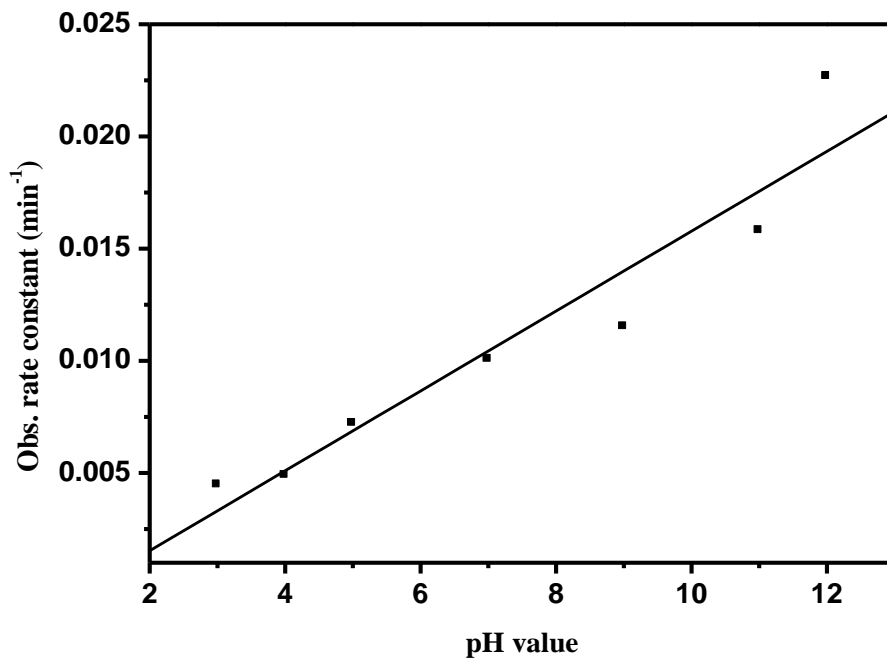


Fig. 9. The variation of observed rate constant ( $K_{obs.}$ ) versus pH values.

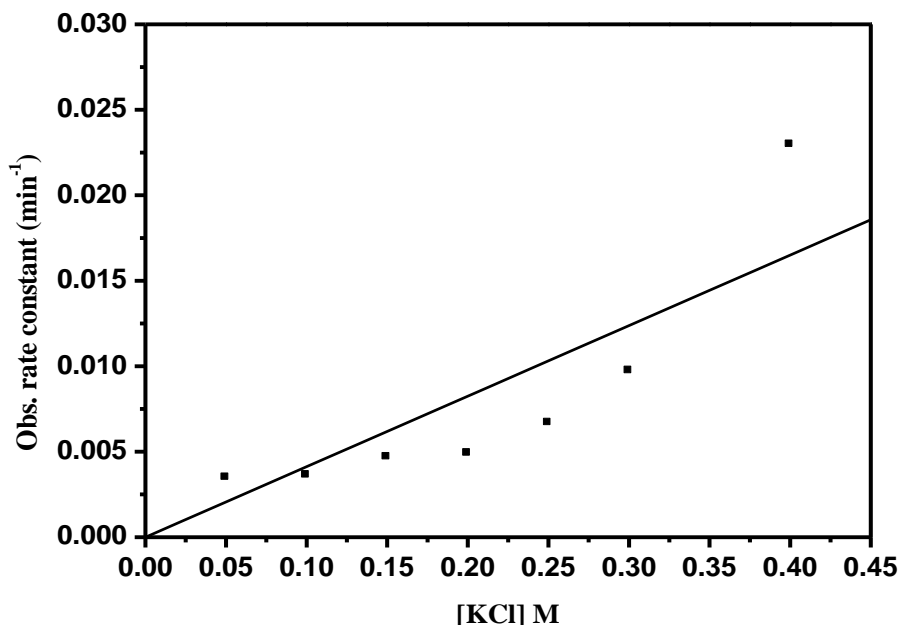


Fig. 10. The variation of observed rate constant ( $K_{obs.}$ ) versus KCl concentrations.

### 3. 3. Dye concentration effect

Fig. 6(a,b) display the relation between the concentration of acid fuchsine dye and  $H_2O_2$  respectively with the evaluated rate constant ( $K_{obs.}$ ) and it is clear that, the values of rate constant increase with increasing both of dye concentration and hydrogen peroxide confirming that the oxidative degradation of fuchsine dye is a first order reaction under these conditions and hydrogen peroxide dependent .

According to Eq. 1 and Eq. 2 both of  $H_2O_2$  and fuchsine dye play an important role in the reaction sequence since the hydrogen peroxide initially attacks the active centers on the catalyst surface forming  $\mu^2$  bound peroxide, which stabilized by hydrogen bonding [26,27] forming activated complex  $[C^*]$  that finally reacts rapidly and reversibly with substrate dye oxidizing it as described in equation (2). And by the same the increasing in the substrate dye concentration must leads to correspondence increase in the reaction rates.

### 3. 4. Temperature effect

Fig. 7, shows the effect of temperature on the reaction rate of degradation of the dye. The reaction between [acid fuchsine dye] =  $4 \times 10^{-6}$  M with 0.025 gm of the catalyst at pH = 7 was carried out at different temperatures. It is clear that, the rate of oxidative degradation of acid fuchsine dye with Cu-doped lead zirconate catalyst increases with increasing the temperature. In our view the increasing of temperature causes an activation to the surface area of the cu-doped PZ catalyst that already reacted to reform new one and consequently the numbers of active centers will be raised remarkably yielding to correspondence increase on the reaction rate of degradation process.

### 3. 5. Determination of the activation parameters

Fig. 8, shows the Arrhenius plot of  $\ln K$  versus  $1/T$ , where  $T$  is the absolute temperature at which the reaction proceeds and  $K$  is the observed reaction rate constant at this temperature in accordance with the Eyring-Polanyi equation [29].

$$K = k_b T / h \cdot e^{\Delta G^* / RT} \quad (6)$$

where  $k_b$  and  $h$  are the Boltzmann's and Plank's constants, respectively.

From this plot, the activation enthalpy was found to be  $\Delta H^* = 36.25$  KJ/mol &  $\Delta G^* = 59.80$  KJ/mol and  $\Delta S^* = -197.56$  J/mol K.

These thermodynamic activation parameters help to understand and support the proposed catalytic oxidative mechanism enhancing us to estimate how much the ease of such these reaction to occur spontaneously.

### 3. 6. Buffer effect (pH)

The oxidative degradation of acid fuchsine dye was carried out at different pH-values using universal buffer. From Fig. 9, it can be easily seen that, the rate of oxidative degradation of fuchsine dye increases as pH-value increases. These results are in full agreement with those reported by Robbins et al. [26] and Khaled M. Elsabawy et al. [30] due to the concentration of hydro peroxide anion  $[HO_2]^-$  species is maximum in alkaline medium and consequently according to our mechanistic proposal pathway the formation of activated complex  $[C^*]$  is maximum in alkaline medium. That means rate of oxidation for acid fuchsine dye is pH dependent and oxidation efficiency on Cu-doped lead zirconate surface catalyst is maximum in alkaline medium.

### 3. 7. Salt effect

Fig. 10, shows the effect of the  $[KCl]$  salt on the oxidation reaction rate of the dye. It is clear that, the increasing of salt concentration yields to corresponding increase in the total ionic strength in the reaction medium and consequently increasing the adsorption of the substrate dye on the catalyst surface. These results are in full agreement with numerous reported articles like [31-35] in which the kinetics investigations on the degradation of hazardous materials dyes, and organic substrates ) were performed in presence of hydrogen peroxide and metal oxide surface catalyst. Most of reported investigation [33-35] unified in one result which is theses kind of photo-catalytic reactions are mainly belong to pseudo-first order reaction and all of them are pH-dependent.

## 4. CONCLUSIONS

The kinetics of oxidative decomposition of fuchsine dye using selected Cu-doped lead zirconate was studied carefully in an aqueous solution in the presence of  $H_2O_2$  under condition of pseudo-first order reaction and proved that:

- (1) Cu-doped lead zirconate exhibits as a reasonable surface catalytic activity towards the oxidative degradation of fuchsine dye.

- (2) The active centers on the catalyst surface have an important role in the H<sub>2</sub>O<sub>2</sub> activation process through the formation of activated complex that stabilized by hydrogen bonding.
- (3) The rate of oxidative degradation of fuchsine dye with Cu-doped lead zirconate catalyst increases with increasing the concentration of the dye as well as increasing the temperature.
- (4) The rate of oxidation of fuchsine dye is pH dependent and the oxidation efficiency on Cu-doped lead zirconate surface catalyst is maximum in alkaline medium.

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