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Synthesis of ZnO/Fe_2O_3 Composite from Different Source of ZnO and its Use in Degradation of Methylene Blue

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Abstract: ***The purpose of this research is to prepare and compare the ZnO composite/Fe_2O_3 which prepared from different sources(normalZnO , ZnO as waste from shaheed factory of copper and brass industry , nanoZnO)and their impact on the degrade of pollution as an example(methylene blue dye) in the aqueous solution with presence of UV irradiation and H_2O_2as a Fenton's reaction at different temperature and dye concentration. The different products of ZnO/Fe_2O_3 composite was prepared by precipitation method,and the threecomposites were identify by AFM(Atomic Force Microscope) to find out the particle size and scan its morphology.***

Keywords: NanoZnO, AFM, ZnO/Fe_2O_3 composite , methylene blue , Fenton's reaction

1. Introduction

Photocatalysis using semiconductor oxides have been used to solve pollution problems, and its proves to be effective degradation of great number of contaminants[1].ZnO appears to be a suitable alternative to TiO_2 since its photodegradation mechanism has been proven to be similar to that of TiO_2 .ZnO has been reported, sometimes, to be more efficient than TiO_2[2]. In heterogeneous photocatalysis system, when a suspension of a particular semiconductor is irradiated with a natural or artificial light, with an energy equals to or larger than the band gap, the electrons will be promoted to the conduction band (C.B.), leaving positive holes in the valence band (V.B.). If the electrons and holes are in a reaction, a steady state will be reached when the removal of electrons and holes equal the rate of generation by illumination[3-5] Zinc oxide is an excellent photocatalytic oxidation material. It has been widely used to deal with wastewater, such as pharmacy wastewater, printing and dyeing wastes, papermaking wastewater[6].

Zinc oxide (ZnO) Nanoparticles are low cost and can be produced widely[7].

ZnO having lot of desirable properties such as high electron mobility, wider band gab, and exhibits luminescence at room temperature. The wide band gab of 3.3ev find use in varied application such as electronic device,bio medical field and sensor field [8]

(AOP)"are promising technologies which can be used todecolorization and mineralization to many kinds of dyes and transform dyes into biodegradable orharmless products" [9]. The Photo Fenton's oxidation "is a homogeneous catalytic oxidation process using a mixture of ferrous ionsand hydrogen peroxide" .Byusingartificial light or UV into Fenton's process lead to accelerate dye decolorizationand formation of (•OH) radicals. The main reactions in the photo-Fenton process for the formation of (•OH) radical includephoto reduction of ferric ion &photolysis of hydrogen peroxide, this processes shows in following equations respectively [10].

$$Fe^{+2} + H_2O_2 \xrightarrow{UV} Fe^{+3} + OH^- \quad (1)$$

$$H_2O_2 \xrightarrow{UV} 2\,\bullet OH \quad (2)$$

$$Fe^{+3} + H_2O_2 \xrightarrow{UV} \bullet OH + Fe^{+2} + H^+ \quad (3)$$

A dye is a synthetic chemical compound used to transfer color to materials. Dyes are carbon based organic compounds, mostly include heavy toxic metals [11].

In the dye molecules, there are two important components : chromosphere which are responsible for producing the color; and auxochromes which reinforced the convergence of dye towards fiber[12-13].At all events, the dyes used in the textile industry are basic dyes, acid dyes, reactive dyes, direct dyes, azo dyes, mordant dyes, vat dyes, disperse dyes, and sulfur dyes [14-16].There are three types for dyes: firstly, cationic dyes, are widely used in acrylic, wool, nylon. These dyes include different chemical structures based on substituted aromatic group[17].Secondly, Anionic dyes, depend on a negative ion. They include many compounds from the most varied classes of dyes, which exhibit characteristic differences in structure (e.g., azoic, anthraquinone, nitro dyes) [18]. Thirdly, Nonionic dyes, are colorants with low water solubility that, in their disperse colloidal form, are suitable for dying and printing hydrophobic fibers and fabrics[19].

Methylene Blue or tetramethylthioninechloride ($C_{16}H_{18}N_3SCl$) (MB) "is one of the high consuming materials in the dye industry and was selected as a model organic pollutant and its degradation was studied in the presence of Magnetite under UV" (Fig. 1). It behaviors as cationic thiazine dye with deep blue colorthat absorb @ 664 nm in the oxidized state while the reduced form of MB (i.e., leukomethylene blue-LMB) is colorless. In addition, MB has widely been used in environmental analysis such as wastewater discoloration [20]

Figure 1: Chemical formula of methylene blue

2. Experimental Section

1) Determination of Maximum Adsprption (λ_{max}) :

Wavelength values utilize for estimation of quantity of compound are 664nm for Methylene blue

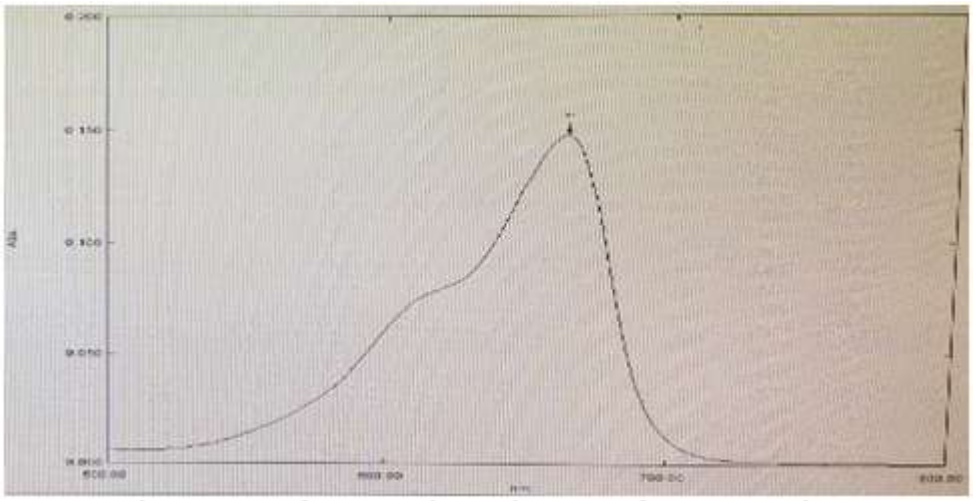

Figure 2: UV-Visible absorption spectrum for Methylene blue dye

2) Calibration Curve

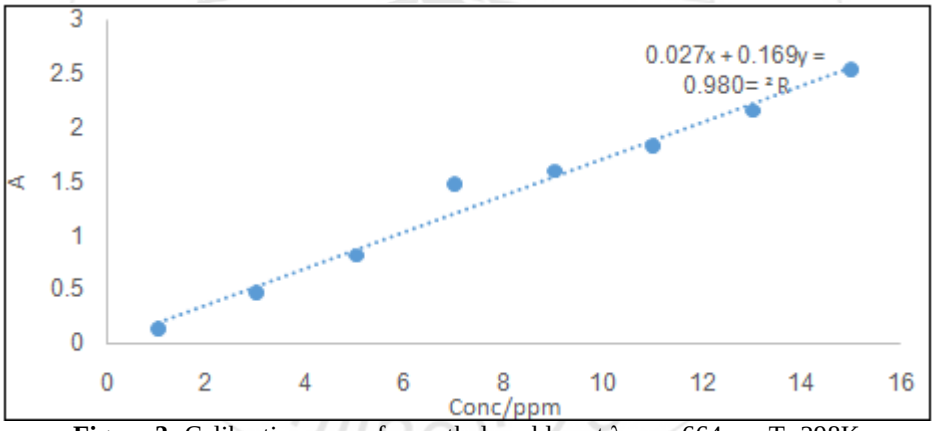

Figure 3: Calibration curve for methylene blue at λ_{max} = 664 nm,T=298K

3) Preparation of ZnO/Fe2O3 composite

The ZnO/Fe_2O_3 composite was prepared through the following steps: firstly, an aqueous dispersion of nomalZnO was prepared by adding 5g of normal ZnO to 250 mL H_2O under vigorous stirring for 3 h at 298 K. Secondly, sodium carbonate was added slowly as powder into a vigorously stirred 0.2 M solution of iron nitrate for 3h. Thirdly, 250 mL solution obtained from the second step was added drop by drop into the dispersion of ZnO prepared in the first step under vigorous stirring. Fourthly, the suspension was stirred for 3h followed by ageing at 100°C in an autoclave for 48h. Finally 500 ml of ZnO/Fe_2O_3composite suspension was obtained and ready for coating. Repeat the previous steps by using nanoZnO and shaheed ZnO (waste).

Stainless steel pipe with 4 cm diameter and 15 cm length figure (2) was supplied with copper coil surrounded the outer cell surface and connected to the water bath for controlling the reactor solution temperature and lamp .

Inner cell surface firstly treated with concentrated HF acid to make the inner surface rough and able to pick up the coating, secondly the cell or photo react filled with ZnO/Fe_2O_3 Nanocomposite suspension for 10 minutes to allow forming stable coating layer, then the suspension evacuate from the reactor. To calcinated the catalyst ZnO/Fe_2O_3 layer, the photo reactor exposed to 500°C until the inner surface by compact with ZnO/Fe_2O_3 composite, by tested the transparency of distilled water when filled with it.

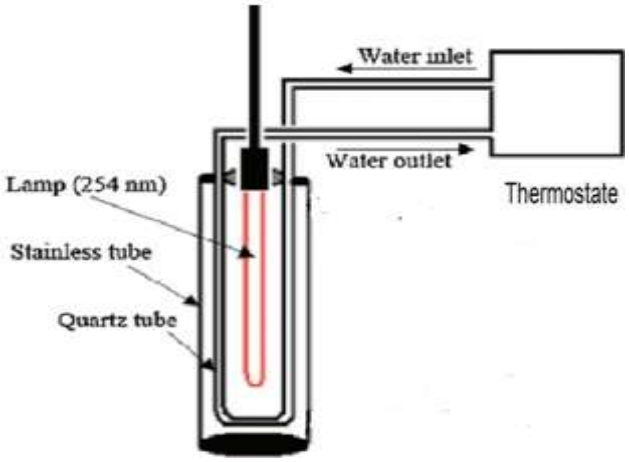

Figure 4: Complete system set up for photo degradation

3. Result and Discussion

1) Characterization of ZnO

Atomic Force Microscope:

The AFM analysis provides the measurements of average grain size (and the granularity cumulating distribution for both normal ZnO /Fe_2O_3composite, ZnO Shaheed factory/Fe_2O_3 and nano ZnO /Fe_2O_3 composite. The average diameter is 122.85nm,107.72 nm and 73.08 nm for normal ZnO /Fe_2O_3 composite, shaheed factory ZnO /Fe_2O_3 and nano ZnO /Fe_2O_3 composite respectively

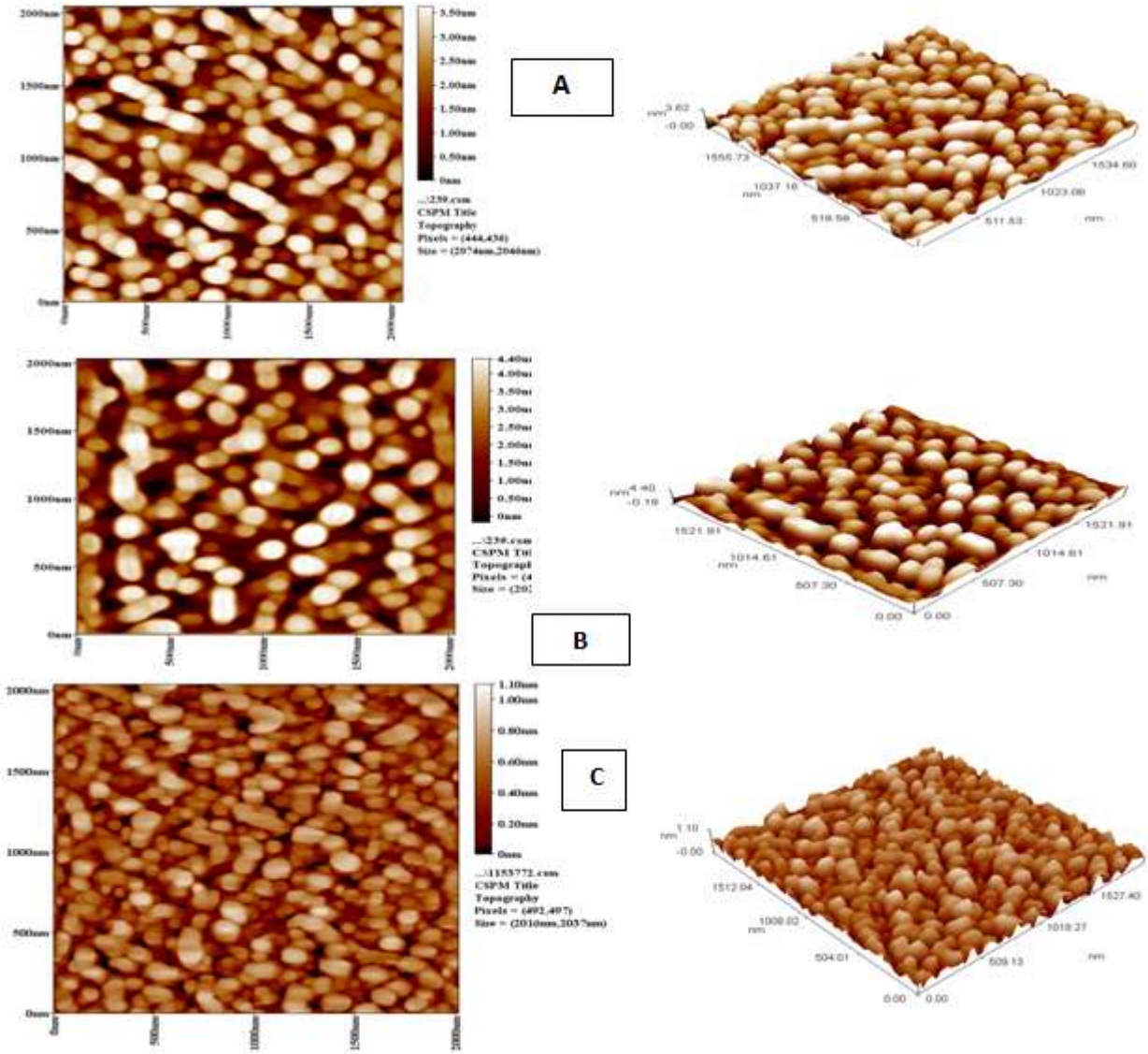

Figure 5: Atomic force microscope image for: A- normal ZnO /Fe_2O_3 composite, B- Shaheed factory ZnO /Fe_2O_3 ,C-nanoZnO /Fe_2O_3 composite

2) Effect the H_2O_2 concentration in the Degradation process

Different H_2O_2 concentration were listed to investigate its effect on the M.B degradation percentage as show in table (1) and fig.6.

Table 1: M.B percentage degradation by different ZnO/Fe_2O_3 composite using different H_2O_2 concentration

Conc./M	*% deg. normal ZnO*	*% deg. Shaheed ZnO*	*% deg. Nano ZnO*
0.0005	85.04	91.32	94.64
0.001	88.28	93.48	96.96
0.005	91.6	95.8	98
0.01	91.84	95.88	98.08
0.015	92.08	96.04	98.24
0.02	92.1	96.1	98.3

It is clear that the suitable H_2O_2concentration in the degradation process is 0.005 M.

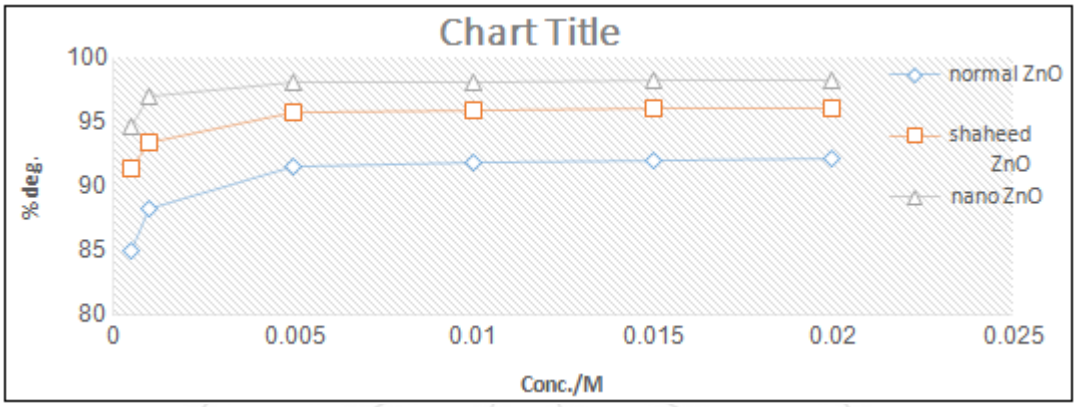

Figure 6: Variation of %deg. With H_2O_2 concentration for the three ZnO composite

Nano ZnO/Fe_2O_3lead to the best %deg. and the %deg. increase with H_2O_2 concentration increasing.

3) Effect of ZnO sources on %deg. :

Percentage degradation (%deg.) was calculated from the following equation :

$$\%deg. = \frac{Co-Ce}{Co} * 100[21] \quad (4)$$

Where:

C_0: Initial concentration of Methylene blue

C_e: Concentration of Methylene blue after different radiation times.

Table (2) shows the variation of %deg. with time using the three types of prepared composites.

Table 2: %deg. for 25 ppm M.B at (different sources) ZnO /Fe_2O_3at 298K and 0.005M H_2O_2

t/min	%deg. Normal ZnO	%deg. saheed ZnO	%deg. Nano ZnO
10	79.1	84.6	85.4
20	82.5	86.8	87.6
30	85.8	92.4	93.2
40	88.1	93.7	96.1
50	90.1	94.4	97.2
60	91.6	95.8	98.0
70	91.7	95.9	98.1

It is clear that %deg. increase with time for all sources of ZnO but %deg. by nano ZnO>%deg. by shaheed ZnO> %deg. by normal ZnO dependent on average diameter for this compound shows in AFM.

Fig.7 shows the variation of %deg. with time for M.B by different ZnO sources.

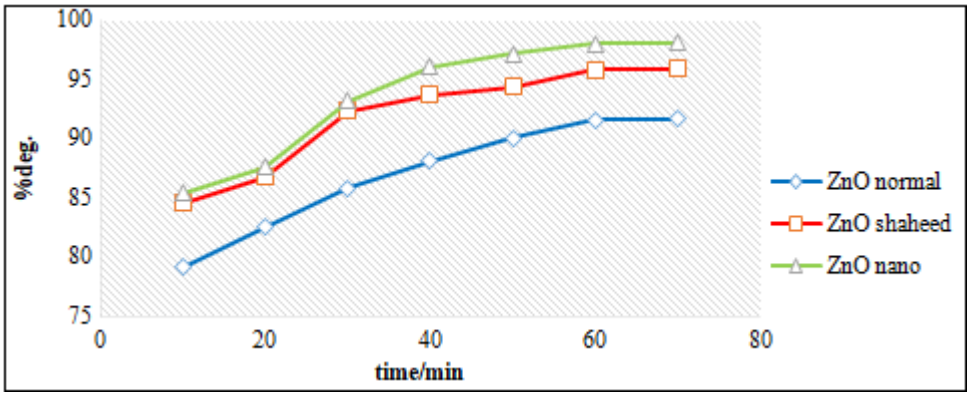

Figure 7: Variation of %deg. with different sources of ZnO

4) Effect of Temperature

The effect of temperature on the %deg. for the composites prepare from different sources of ZnO were listed in table 4 and fig 8.

Table 4: %deg. for25 ppm M.B at (different sources) ZnO /Fe_2O_3 at time 70 min, and 0.005M H_2O_2

T/K	%deg. normal ZnO	%deg. shaheed ZnO	%deg. nano ZnO
298	91.7	95.9	98.1
308	93.9	96.5	98.5
318	95.4	96.9	99.5
328	96.4	97.8	99.8

It is clear that increase %deg. with increase temperature for the three sources of ZnO and %deg. by nano> %deg. by shaheed> %deg. by normal.

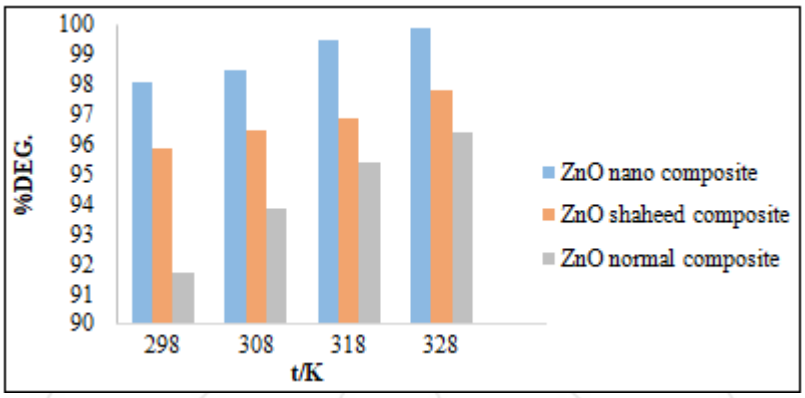

Figure 8: Variation of M.B %deg. by the three ZnO composite at different temperature

5) Effect of the pH on % degradation of 25 ppm M.B in the presence of different ZnO composite and H_2O_2(0.005M) and t= 60 min.

Table 5.and Fig.9 shows the effect of pH on %deg. by the different ZnO composite.

Table 9: %deg. of 25 ppm M.B by the three composite with different pH and 0.005 M H_2O_2

pH	%deg. normal ZnO	%deg. shaheedZnO	%deg. nanoZnO
3	71.2	79.2	82.6
4	79.2	85.0	88.9
5	88.0	90.3	95.3
6	89.9	93.9	96.9
7	91.6	95.8	98.0
8	90.4	92.9	94.4
9	89.0	91.0	93.1

The photodegradation reaction was also carried out under varying pH conditions from (3 to 9), by adjusting with HCl and NaOH [22], with ZnO kept at constant amounts of dye solutions (Fig. 9). The reaction was found to have low rates at neutral ranges of pH. While at higher and lower cases it was found to increase. This implies that alkaline as well as acidic conditions are favourable towards the formation of the reactive intermediates that is hydroxyl radicals is significantly enhanced, which further help in enhancing the reaction rate. On the other hand in neutral medium conditions the formation of reactive intermediates is relatively less favourable and hence less spontaneous.

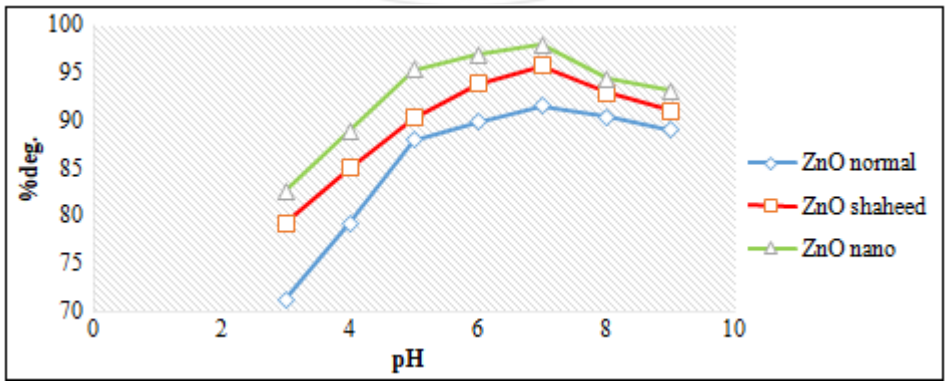

Figure 9: Variation of %deg. of 25ppm M.B with different pH by the three ZnOcomposite and 0.005 M H_2O_2

6) Thermodynamic degradation study

The following first order equation were applied for the degradation of 25 ppm M.B and 0.005 M H_2O_2 by normal ZnO, shaheed ZnO and nanoZnO:

$$\text{Ln } C_e = \text{Ln } C_0 - kt \quad (5)$$

Where:

C_0: initial concentration of M.B

C_e: Concentration of M.B after exposing to UV at time t

The Arrhenius equation is the following:

$$k = Ae^{-Ea/RT}\text{[23]} \quad (6)$$

$$Lnk = Ln\ A - E_a/RT \quad (7)$$

Alternatively, the equation may be expressed as:

$$k = Ae^{-Ea/kbT} \quad (8)$$

where

- k is the rate constant.
- kb is the Boltzmann constant
- T is the absolute temperature (in kelvins)
- A is the pre- exponential factor
- E_a is the activation energy for the reaction (in K.J mol^{-1})
- R is the universal gas constant.

Calculate the $\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$ from the following equations :

$$A=KbT/h*e^{\Delta S\#/R}*e^{-\Delta H\#/RT} \quad (9)$$

$$LnA=LnKbT/h+\Delta S^{\#}/R-\Delta H^{\#}/RT \quad (10)$$

$$\Delta G^{\#}=-RT\ lnk \quad (11)$$

Table 6 and fig.10 represent the kinetic parameter for M.B degradation percentage by normal ZnO composite.

Table 6: The Relationship between LnCe and t for 25ppm M.B , H_2O_2 (0.005M) andnormal composite at different temperature

Time (min)	Ln Ce (298K)	Ln Ce (308K)	Ln Ce (318K)	Ln Ce (328K)
10	1.77	1.64	1.38	1.31
20	1.59	1.37	0.78	0.74
30	1.33	1.24	0.61	0.53
40	0.80	0.70	0.47	0.44
50	0.73	0.57	0.40	0.30
60	0.69	0.65	0.16	0.01

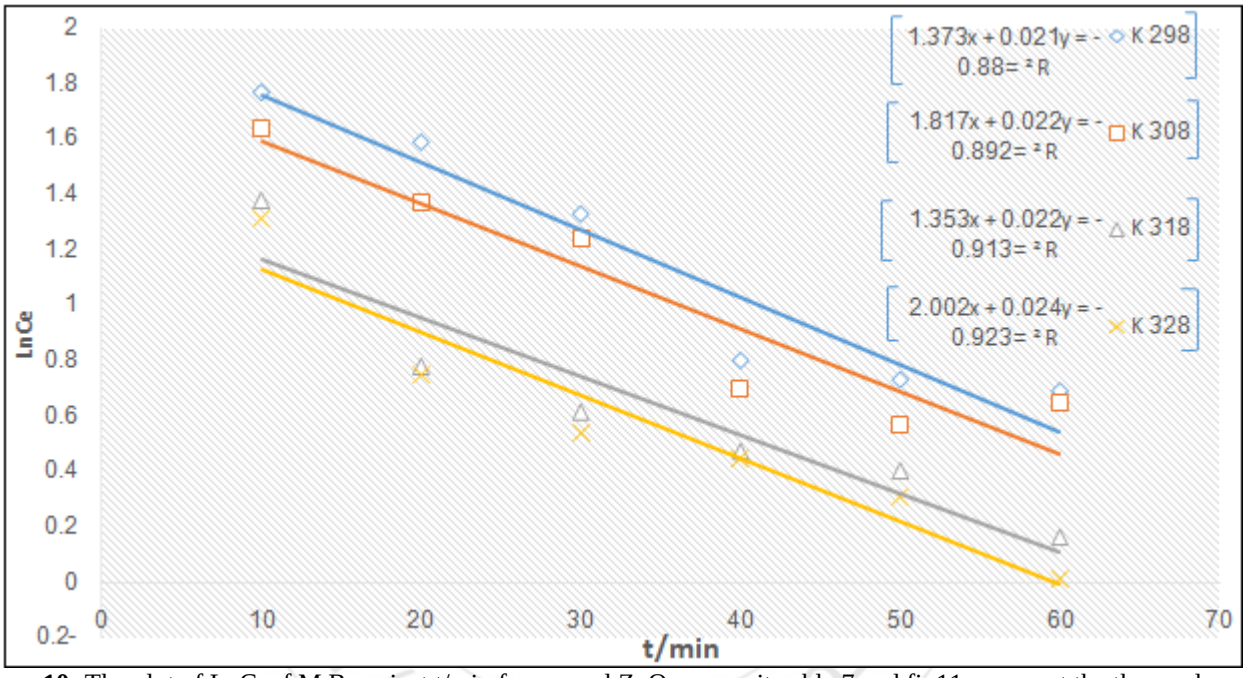

Figure 10: The plot of LnCeof M.B against t/min for normal ZnO composite able 7 and fig11 represent the thermodynamic function for M.B degradation percentage by normal ZnO composite

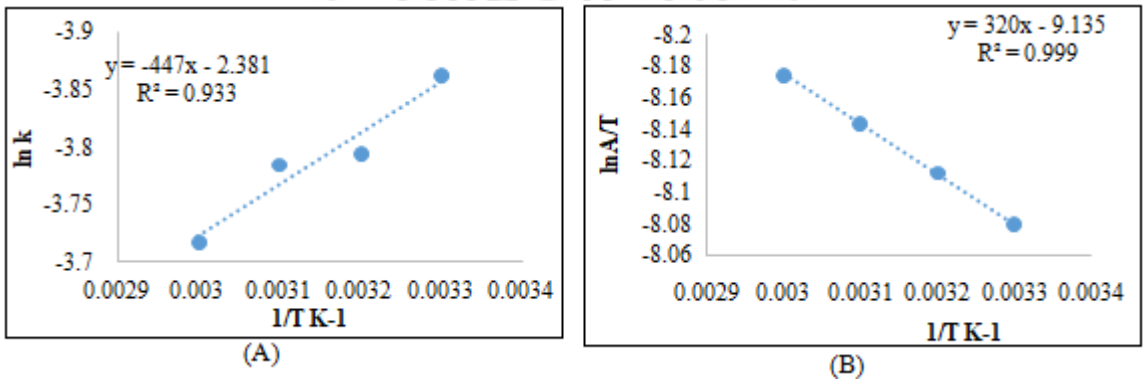

Figure 11: The plot of: A- Ln k against 1/T, B- Ln A/T against 1/T for normalZnO composite

Table 7: The Thermodynamic function fornormalZnO composite at 298K and 0.005M H_2O_2

T(K)	K(min^{-1})	Ln k	Ea($kJ.mol^{-1}$)	A(S^{-1})	Ln A/T	1/T(K^{-1})	$\Delta H^{\#}$($kJ.mol^{-1}$)	$\Delta S^{\#}$($kJ.mol^{-1}K^{-1}$)	$\Delta G^{\#}$($kJ.mol^{-1}$)
298	0.021	-3.717	3.716	0,0923	-8.079	0.0033	-2.66	-0.205	92.09
308	0.0225	-3.785			-8.112	0.0032			96.92
318	0.0227	-3.794			-8.144	0.0031			100.30
328	0.0243	-3.863			-8.175	0.0030			105.34

The energy of (E_a) was calculated from the slope of the plot. Therefore, otherparameters for thermodynamic such as entropy, free energy of activation &enthalpy were also evaluated. The positive energy of activation refer to the reaction is less energy intensive. This could be because the activated state is a good solvated structure formed between the dye molecules and the reaction intermediate that is hydroxyl radical which is also supported by positive entropy of activation.

The rate of reaction (k) increase with increase temperature .Therefore, the %deg. increase with increase temperature and helps to acceleration the velocity of both the dye molecules and hydroxyl radicals to interact to each other. The degradation of M.B dye with ZnO occur as the following equation :

$$ZnO + h\upsilon \longrightarrow ZnO^* \quad (12)$$

$$ZnO^* + H_2O \longrightarrow ZnO^* + H^+ + {}^{\bullet}OH \quad (13)$$

$${}^{\bullet}OH + \text{dye molecules} \longrightarrow \text{intermediates} + \text{mineral salts} \longrightarrow CO_2 \uparrow H_2O \quad (14)$$

Table 8 and fig.12 represent the kinetic parameter for M.B degradation percentage by shaheed factory ZnO composite.

Table 8: The Relationship between LnCe and t for 25ppm M.B, H_2O_2 (0.005M) and shaheed factory ZnO composite

Time (min)	Ln Ce (298K)	Ln Ce (308K)	Ln Ce (318K)	Ln Ce (328K)
10	1.62	1.62	1.20	1.01
20	1.43	1.26	0.53	0.50
30	0.90	0.83	0.49	0.44
40	0.64	0.49	0.28	0.21
50	0.53	0.40	0.16	0.09
60	0.44	0.35	0.02	-0.04

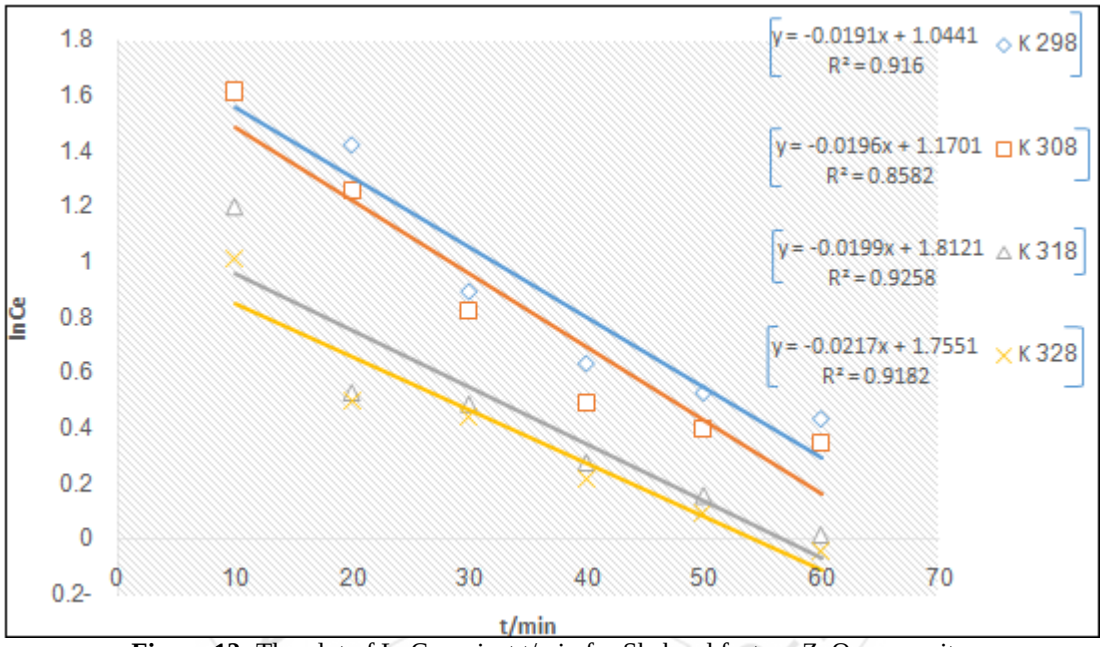

Figure 12: The plot of LnCeagainst t/min for Shaheed factory ZnO composite

Table 9 and fig13 represent the thermodynamic function for M.B degradation percentage by shaheed factory ZnO composite.

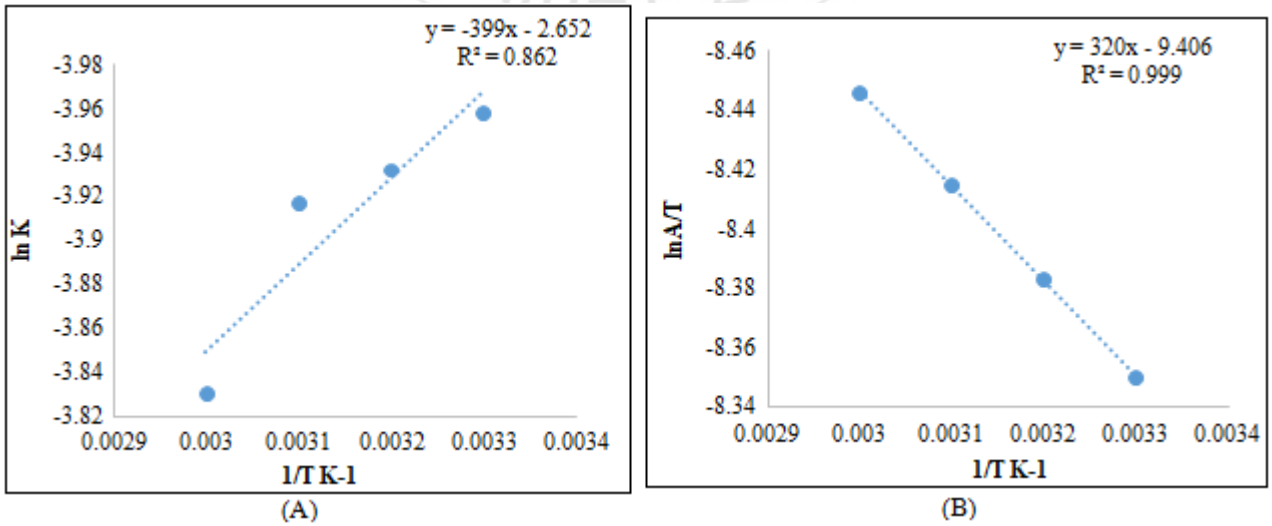

Figure 13: The plot of : A- Ln k against 1/T, B- Ln A/T against 1/T for Shaheed factory ZnO composite

Table 9: The Thermodynamic function for Shaheed factory ZnO composite at 298K and 0.005M H_2O_2

T(K)	K(min^{-1})	Ln k	Ea($kJ.mol^{-1}$)	A(S^{-1})	Ln A/T	1/T(K^{-1})	$\Delta H^{\#}$($kJ.mol^{-1}$)	$\Delta S^{\#}$($kJ.mol^{-1}K^{-1}$)	$\Delta G^{\#}$($kJ.mol^{-1}$)
298	0.0191	-3.958			-8.350	0.0033			98.06
308	0.0196	-3.932			-8.383	0.0032	-2.66	-0.207	100.68
318	0.0199	-3.917			-8.415	0.0031			103.55
328	0.0217	-3.830	3.317	0.0704	-8.446	0.003			104.44

Table 10 and fig.14 represent the kinetic parameter for M.B degradation percentage by nanoZnO composite.

Table 10: The relationship between LnCe and t for 25ppm M.B , H_2O_2 (0.005M) and nanoZnOcomposite

Time (min)	Ln Ce (298K)	Ln Ce (308K)	Ln Ce (318K)	Ln Ce (328K)
10	1.27	1.20	1.05	0.87
20	0.83	0.78	0.50	0.41
30	0.65	0.57	0.40	0.33
40	0.40	0.37	0.25	0.02
50	0.24	0.19	0.02	-0.06
60	0.14	0.13	-0.05	-0.16

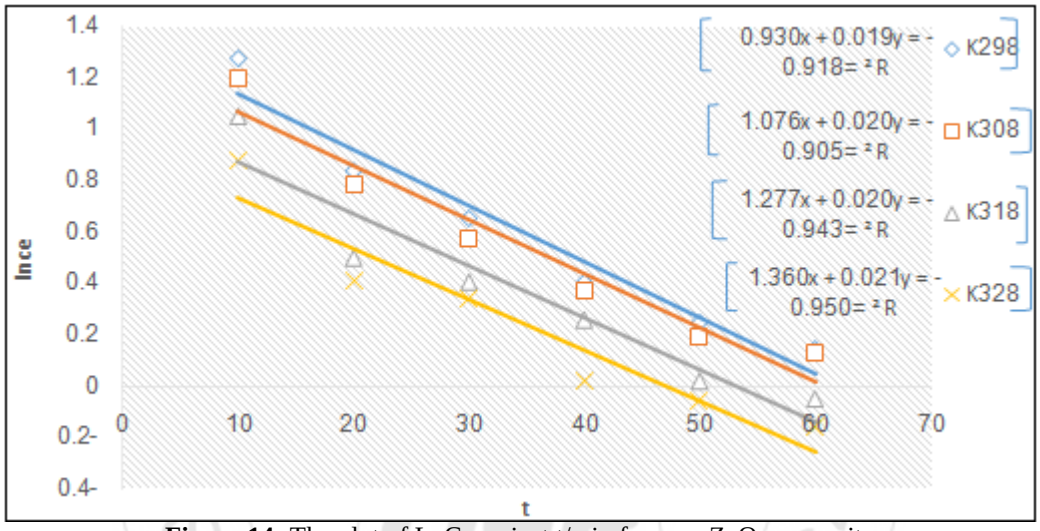

Figure 14: The plot of LnCeagainst t/min for nanoZnO composite

Table 11and fig15 represent the thermodynamic function for M.B degradation percentage by nano ZnO composite.

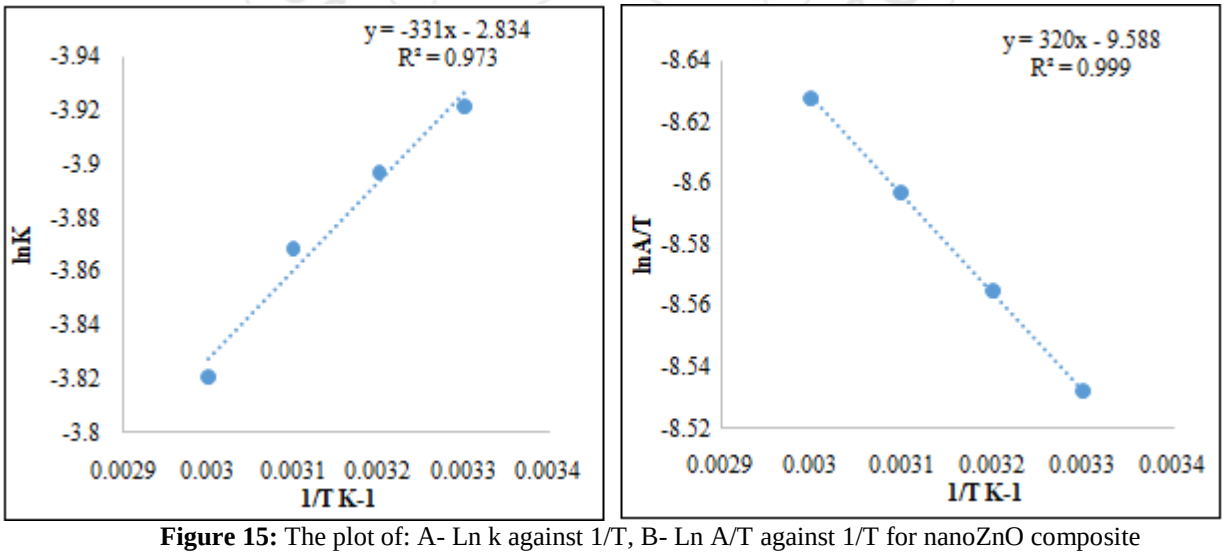

Figure 15: The plot of: A- Ln k against 1/T, B- Ln A/T against 1/T for nanoZnO composite

Table 11: Show the thermodynamic function for Nano ZnO composite at 298K, 0.005M H_2O_2

T(K)	K(min^{-1})	Ln k	Ea($kJ.mol^{-1}$)	A(S^{-1})	Ln A/T	1/T(K^{-1})	$\Delta H^{\#}$($kJ.mol^{-1}$)	$\Delta S^{\#}$($kJ.mol^{-1}K^{-1}$)	$\Delta G^{\#}$($kJ.mol^{-1}$)
298	0.0198	-3.922			-8.532	0.0033			97.17
308	0.0203	-3.897			-8.565	0.0032	-2.66	-0.209	99.79
318	0.0209	-3.869			-8.597	0.0031			102.29
328	0.0219	-3.821	2.751	0.0587	-8.628	0.003			104.19

4. Conclusion

In this work ZnO/Fe_2O_3 composite were synthesized from different source of ZnO by precipitation method characterization of composite such as average diameter and morphology were achieved by AFM to compare between the three composites.

The average diameter were obtained for nanoZnO /Fe_2O_3 composite<shaheed factory ZnO/ Fe_2O_3 composite < normal ZnO/Fe_2O_3 composite, therefore the %deg. increase with decrease the average diameter and increase with increase temperature .In addition, this study refer to advantage of the shaheed ZnO and can be turned it to a useful compound in dye removal by introducing it in the preparation of composite based on comparing the AFM value before and after the composite preparation. E_a for: nano ZnO>shaheed ZnO> normal ZnO , therefore the degradation for nano composite is easily from shaheed composite and the latter is easily degradation from normal composite.

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