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Degradation of Methylene Blue Dye by Using TiO_2/Fe_2O_3 Nanocomposite and Study the Effect of Ultrasonic Spectroscopy

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Abstract: The aim of this research is to remove the organic dye (methylene blue) by prepared the nanocomposie (TiO_2/Fe_2O_3) in precipitation method and study the effect of pH and temperature in degradation process. ultrasonic spectroscopy used to decrease the particle size of nanocomposie (from 127.9 to75.7 nm) measured the surface area by Atomic force microscope (AFM) lead to increase the percentage of the degradation. The best pH to degradation process is {7} the % degradation increased with increased temperature.
Keywords: Nano TiO_2, AFM, TiO_2/Fe_2O_3 composite, methylene blue, Fenton's reaction

I. Introduction

Advanced oxidation process (AOP) is the chemical reaction generating oxidizing agent ability to oxidized and cracking the contamination [1].AOP is useful to generate the radicals such as ($OH^{\cdot}$, $SO_4^{\cdot}$). The radical can react with contaminate to degrade the toxic organic compounds (dye) in present the aqueous solution.These radicals with organic compounds include [hydrogen abstraction from aromatic rings,addition to double bonds, electron transfer and aliphatic carbon] [2]. Many process give hydroxyl radicals such as(O_2/light , H_2O_2/light , TiO_2/light , Electrolysis , sonolysis , H_2O_2 , O_3 , and photo Fenton) [3].

Fenton reagent is "a homogeneous catalytic oxidation process which is the mixture of an oxidizing agent (hydrogen peroxide) and a catalyst (an oxide or metal salt, usually iron) to give hydroxyl radicals" [4,5]. the equation for the generation of $OH^{\cdot}$ is [6]:

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

The rate of Fenton reaction is strongly in the presence of UV/visible light in aqueous solution lead to accumulate the Fe^{3+} and consumedFe^{2+} lead to stop the reaction [7].

Photo catalyst classifies to [(Homogeneous photo catalysis: the reactant and photo catalyst exist as the same phase [8]) (Heterogeneous photo catalysis: which depend on the photo excitation of semiconductor solid and absorbed the radiation. Semiconductor material excited near the UV irradiation by photons processing energy to give conductive band electrons and valence band holes [9].

Atomic force microscope [AFM] is the one of the imaging tools. Collect the information by the (feeling) between the surfaces with mechanical probe [10]. The AFM consist of a probe (sharp tip) in the end with a cantilever that is used to scan the surface. The cantilever is formed from (silicon nitride or silicon with a tip radius of curvature on the order of nanometers). The transported of tip into surface of the sample formed the forces between(the tip and the sample), after that lead to a deflection of the cantilever according to Hooke's law [11].

Atomic force microscope "is the topographical scan of a glass surface & can be operated in a number of modes according to the application"[12].

Ultrasonic spectroscopy used a frequency to determination the particle size distribution and concentration of a colloidal dispersion "analyze particle sizes between about 10 nm and 1000 nm". The particle size distribution depending on being (able to measure the frequency and the ultrasonic velocity and/or attenuation coefficient)[13,14].

Methylene blue (MB) is a crystalline or dim green powder, which is used usually as a stain. These dyes are carcinogenic which cause various health problems, such as causes (vomiting, shocks, cyanosis, tissue necrosis in human being, jaundice and heart failure etc). Photosynthesis of plants is affected by the presence of the methylene blue dye by preventing sunlight from reaching it [15].

II. Experimental Parts:

1. Preparation of TiO_2/Fe_2O_3nanocomposite:

An aqueous solution of TiO_2 was prepared by adding 10g of TiO_2 to 500 mL H_2O under vigorous stirring for 3 h at 298 K .Sodium carbonate was added slowly as powder into a vigorously stirred 0.2 M solution of iron nitrate for 3h. 500 mL solution obtained from the second step was added drop by drop into the dispersion of TiO_2 prepared in the first step under vigorous stirring. The suspension was stirred for 3h followed by ageing at 100°C in an autoclave for 48h. 1000 ml of TiO_2 /Fe_2O_3 composite suspension was obtained and ready for coating.. Stainless steel pipe with (4 cm diameter and 15 cm length) 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 or HCL to make the inner surface rough and able to pick up the coating, secondly the cell or photo react filled with TiO_2 /Fe_2O_3 Nano composite suspension for 10 minutes to allow forming stable coating layer, then the suspension evacuate from the reactor. To calcinated the catalyst TiO_2 /Fe_2O_3 layer, the photo reactor exposed to 500°C until the inner surface by compact with TiO_2 /Fe_2O_3 composite, by tested the transparency of distilled water when filled with it.

Figure (1) explain the degradation cell used in this research .

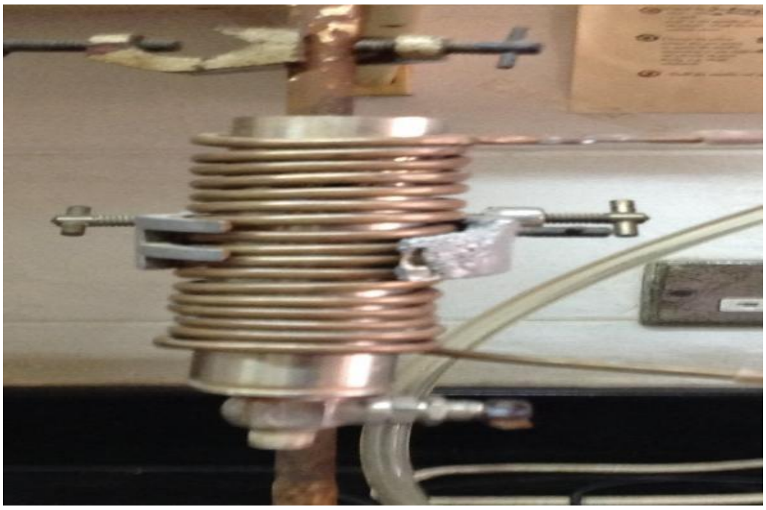


Figure 1: Show the degradation proces

2. **Calculate the percentage degradation :**

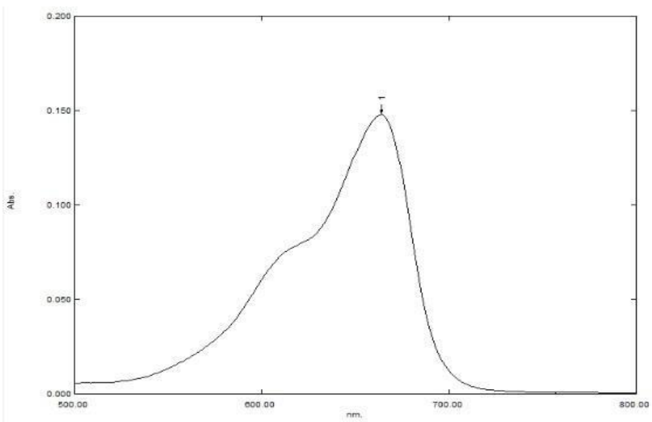
$$\%\boldsymbol{deg.} = \frac{C_o - C_e}{C_o} * \mathbf{100} \quad \ldots\ldots\ldots\ldots(2)$$

Where:) Co: Initial concentration of M.B, Ce: Concentration of M.B after different radiation times) [16-17].

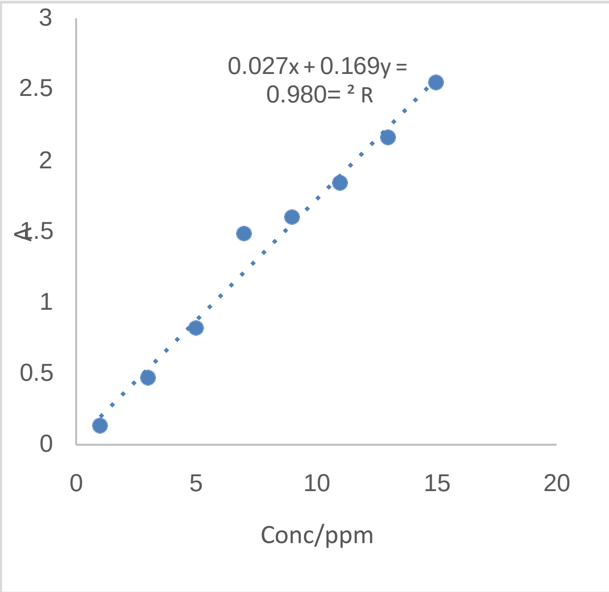
$$\mathbf{C_e} = \frac{A-Intercept}{Slope} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Where :A: Absorbance of Methylene blue after different times [18].

Figure (2) explain the wave length of Methylene blue dye (664nm) and calibration curve.



(A)



(B)

Figure.2 : A: UV-Visible absorption spectrum for Methylene blue dye. B: calibration curve of Methylene blue dye.

3. Preparation of Methylene blue solutions

Six concentrations of M.B solutions (15, 20, 25, 30) ppm were prepared in 100 ml from stock solution (1000 ppm M.B), which will be used in degradation processes.

4. Hydrogen peroxide

From 0.1M hydrogen peroxide prepared (0.005M) H2O2 concentrations were prepared by dilution with Distilled Water (D.W).

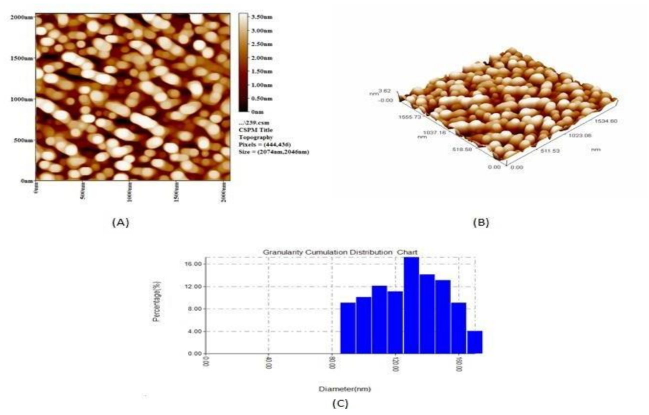
III. Results and Discussions:

Table (1): Granularity cumulating distribution and average diameter of TiO_2/Fe_2O_3Before Ultrasonic process

Avg. Diameter:122.85 nm	<=10% Diameter:90.00 nm
<=50% Diameter:120.00 nm	<=90% Diameter:150.00 nm

Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation (%)
90.00	9.09	9.09	120.00	11.11	42.42	150	13.13	86.87
100.00	10.10	19.19	130.00	17.17	59.60	|00	9.09	95.96
110.00	12.12	31.31	140.00	14.14	73.74	160.00	4.04	100.00
						170.00		

Figure.3: A-granularity cumulating distribution chart of TiO_2/Fe_2O_3 B&C views of AFM image of TiO_2/Fe_2O_3 before Ultrasonic process



Table(2): Granularity cumulating distribution and average diameter of TiO_2/Fe_2O_3 After ultrasonic Prosess

Avg. Diameter:75.7 nm	<=10% Diameter:0 nm
<=50% Diameter:160.00 nm	<=90% Diameter:250.00 nm

Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)
30.00	0.34	0.34	65.00	10.51	42.71	100.00	3.05	83.05
35.00	1.36	1.69	70.00	8.14	50.85	105.00	5.42	88.47
40.00	2.03	3.73	75.00	6.78	57.63	110.00	6.78	95.25
45.00	4.75	8.47	80.00	6.44	64.07	115.00	4.07	99.32
50.00	4.41	12.88	85.00	5.42	69.49	120.00	0.68	100.00
55.00	9.83	22.71	90.00	5.76	75.25			
60.00	9.49	32.20	95.00	4.75	80.00			

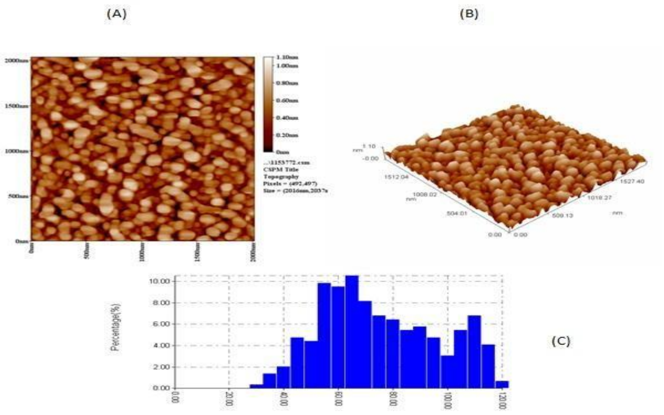


Table 3: %deg. of (10, 25, 35, 50) ppm M.B in the presence of TiO_2/Fe_2O_3 composite & H_2O_2 (0.005M) at 298K, pH=7 before & after ultrasonic

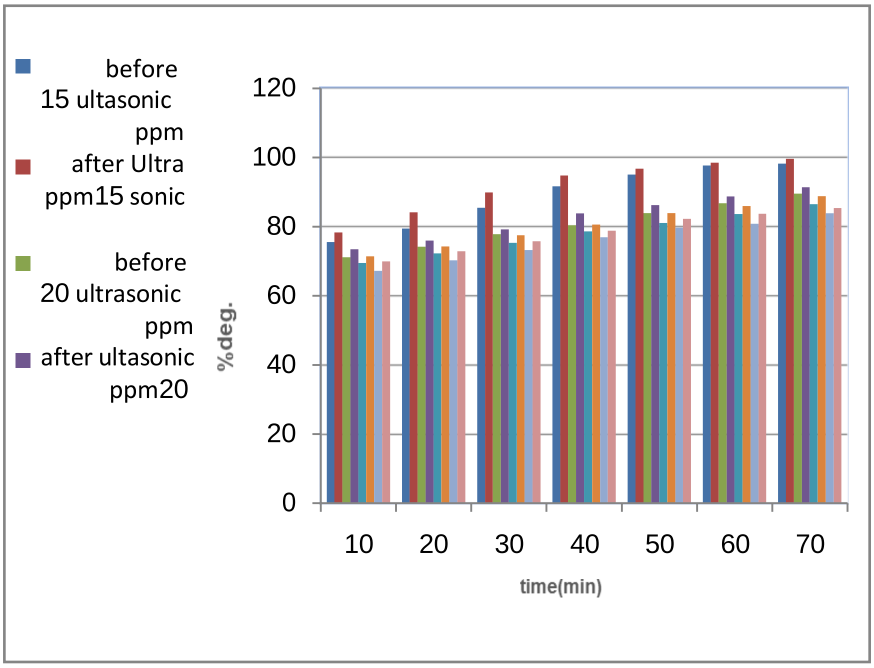


Figure 4.A-granularity cumulating distribution chart of TiO_2/Fe_2O. B&C: views of AFM image of TiO_2/Fe_2O_3 after Ultrasonic process

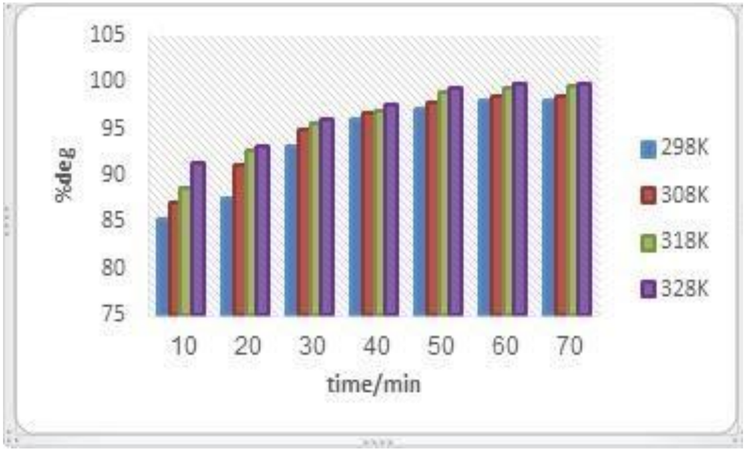


Fig. 5: %deg. vs. time for M.B by TiO_2 before and after treating with ultrasonic

Table (4)& (5) shows the effect of pH and temperature in degradation process.

Table (4): %deg. of 25 ppm M.B by the TiO_2composite with different pH and 0.005 M H_2O_2

pH	%deg. NPS-TiO_2
3	80.4
4	85.6
5	91.7
6	94.8
7	97.0
8	95.2
9	92.4

T/ Min	%deg. TiO_2/Fe_2O_3							
	15ppm M.B Bef.	15ppm M.B Aft.	20ppm M.B Bef.	20ppm M.B Aft.	25ppm M.B Bef.	25ppm M.B Aft.	30ppm M.B Bef.	30ppm M.B Aft.
10	75.6	78.3	71.1	73.4	69.4	71.4	67.2	69.9
20	79.4	84.2	74.2	75.9	72.2	74.3	70.3	72.9
30	85.5	89.9	77.8	79.2	75.3	77.5	73.2	75.7
40	91.7	94.8	80.4	83.8	78.6	80.6	76.9	78.8
50	95.1	96.8	83.9	86.2	81.0	83.9	79.7	82.2
60	97.7	98.5	86.8	88.7	83.6	85.9	80.8	83.7
70	98.2	99.6	89.5	91.4	86.5	88.8	83.9	85.4

Fig.(7): %deg. of 25 ppm M.B vs time by the NPS- TiO_2/Fe_2O_3 composite at different temperature

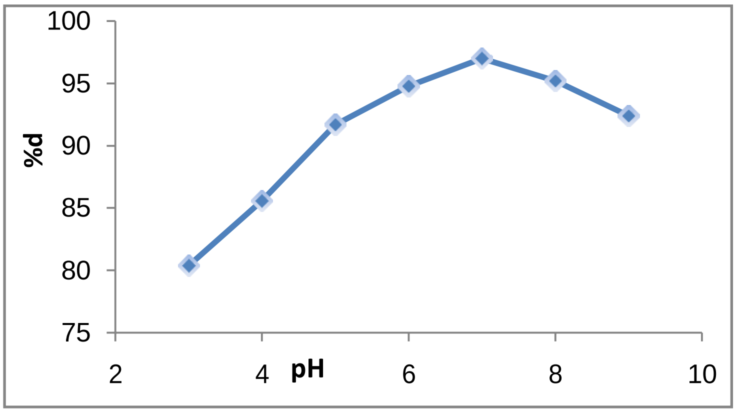


Fig.(6): Variation of 25ppm M.B %deg. With

NPS TiO_2/Fe_2O_3 composite and 0.005 M H_2O_2 with different pH

The degradation process was high rates at neutral ranges of pH, neutral pH are favorable 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 favorable and hence spontaneous".The rate of Photocatalytic degradation also increases [19].

Table (5):Effect the temperature on the %deg. of 25 ppm M.B in the presence of NPS-ZnO/Fe_2O_3 composite & H_2O_2 (0.005M

T /min	%deg. NPS-TiO_2/Fe_2O_3			
	298K	**308K**	**318K**	**328K**
10	85.4	87.1	88.6	91.3
20	87.6	91.2	92.6	93.2
30	93.2	94.8	95.5	95.9
40	96.1	96.6	97.0	97.6
50	97.2	97.9	98.8	99.3
60	98.0	98.4	99.4	99.8
70	98.1	98.5	99.5	99.8

The [•OH radical] may be played a dominant role in the decomposition process due to its high oxidizing power and its responsible for the decomposition of (H_2O_2)at higher temperature, which in turn contributes to the degradation of M.B. The [•OH radical] is similar to decompose methylene blue at a high reaction rate in the high temperature range [20].

The % degradation of Methylene blue dye increased after using ultrasonic spectroscopy process because increased the surface area of TiO_2/Fe_2O_3 measured by Atomic force microscope.

The hydroxyl radicals are formed in Fenton process to remove the contaminants.The hydroxyl radical is "a strong and non-selective chemical oxidant and works very quickly to attack most organic chemical compounds".The reaction between contaminants and hydroxyl radical depending on the nature of the species 1st: the hydroxyl radical can abstract the hydrogen atom from the water as in alkanes and alcohol. 2nd: it can add itself to contaminants as in olefins, methylene blue dye and aromatic compounds.

The hydroxyl root in the presence of oxygen attacks the contaminants with a series of oxidative reactions leading to the mineralization of organic compounds. Pollutant removal depends on the (proportion of the fixed rate contaminated with the hydroxyl root) [21].

IV. Conclusion:

The particle size of nanoTiO_2/Fe_2O_3 (measured by atomic force microscope) after ultrasonic process smallest lead to increase the % degradation of methylene blue dye. High temperature lead to faster formation of free radical to attack the organic dye lead to increased % degradation in the presence of H_2O_2 and Uv light.

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