USE OF ZnO NANOPARTICLES IN TREATMENT OF DYE-POLLUTED WATER

By

Ehsan K. Ismaeel[1] and Aghareed M. Tayeb[2]*
[1]El-Minya High Institute for Engineering and Technology
[2]Faculty of Engineering, Minia University
Minia, Egypt
***Contact author: aghareed1@yahoo.com**

ABSTRACT:

In the present work photocatalytic oxidation is used for treating a dye-polluted water solution using ZnO (in the nano scale form) as a photocatalyst. The variables studied are: initial concentration of dye, catalyst dosage and pH value. Experiments are run using dye solutions of 5, 10, 15, 30 and 50 ppm dye concentration and the percentage dye degradation is determined periodically with time. Results indicated that for a dye solution with pH value of 2.2 and catalyst concentration of 0.1 g/l of solution, the percentage dye degradation was 54, 52.7, 49.87, 29.17 and 13.06% for dye concentrations of 5, 10, 15, 30 and 50 ppm, respectively. Thus the percentage dye degradation is higher for more diluted solutions. The corresponding values, for percentage dye degradation, when using catalyst concentration of 0.2 g/l were: 56.6, 55.3, 52.40, 34.6 and 13.42% for the same sequence of initial dye concentration of 5, 10, 15, 30 and 50 ppm. Thus, an increase in percentage dye degradation is recorded for increasing catalyst dosage (increased to 0.2 gm/l as compared to 0.1 g/l earlier). The values determined when using catalyst concentration of 0.3 g/100 ml were 59.4, 57.3, 53.8, 37.6 and 15.04%. Still higher values for percentage dye concentration were recorded when increasing catalyst concentration to 0.4 g/l of dye solution with the highest value of 62.0% percentage degradation for catalyst concentration of 0.4 g/100 ml and 5ppm dye solution. For a 5 ppm dye solution and 0.4 g/l catalyst dosage, the percentage dye degradation was 74.6% at pH 7.2, while the maximum value was 97.6% and it was recorded for 5 ppm dye solution with catalyst dosage of 0.4 g/l dye solution and pH value of 12.2. Thus, the study showed that increasing both catalyst concentration and pH value have positive effect on percentage dye concentration, while initial dye concentration has a negative effect.

Keywords:
Nanoparticles, Methylene blue (MB), Photocatalysis, Water Pollution, Tratment

1. INTRODUCTION:

Water pollutants can come from several industrial streams. An example is the pollution caused by dyes from textile industries and other commercial dyestuffs.

Dye pollution is considered one of the most problematic groups of pollutants because they can be easily identified by the human eye and are not easily removed. The removal of such dyes from industrial effluents is very difficult because dyes show resistance to many chemicals, oxidizing agents, light and heat and are biologically non-degradable [1, 2].

AOPs include photocatalytic systems such as a combination of a semiconductor (TiO_2, ZnO, etc.) and UV light [3-5]. Photo- catalytic oxidation is cost effective and capable of degrading any complex organic chemicals when compared to other purification techniques [3]. ZnO has been reported to be more efficient than TiO_2.

During recent years there has been an increasing public awareness and concern regarding environmental pollution. Most pollutants in the waste water effluents from industrial or domestic sources comprise some organic chemicals and pathogens which must be removed or destroyed before discharge into the water. The main sources

of colored organic reagents which are called dyes are the textile industry and other chemical industries. The wastes released from these industries are in highly complex state causing difficulty in handling for further treatment. Most modern synthetic dyes are fairly stable even to sunlight, with some of them being carcinogenic [6, 7]. Thus waste water from a textile industry essentially needs an efficient treatment technology which can overcome all the aforesaid challenges giving ultimately clean water for safe disposal. Various conventional methods have been pressed into practice, in the decolourization and degradation of dyes in the waste namely: biological treatment methods, coagulation, filtration, adsorption by activated carbon, reverse osmosis [8]. Low cost methods such as adsorption by activated charcoal, amongst these have been proven to be effective but incomplete in that they produce large amounts of solid wastes for further disposal thus adding to further pollution and environmental hazards. The other methods which have been proved efficient are not cost-effective [9]. Thus these methods either produce large amount of toxic sludge causing disposal problems or fail to accomplish the complete degradation.

Therefore, there is a need to develop a novel treatment method that is more effective in eliminating dyes from the wastewater. Recently, there are alternative techniques for destructing dyes in industrial water. These techniques are called advanced oxidation processes (AOPs). They were developed to face the increasing demand of an effective wastewater treatment process. These technologies are based on the generation of highly reactive intermediates (principally the hydroxyl radical), which are capable of attacking the organic pollutants, and initializing their oxidation and mineralization. The complete mineralization of pollutants leads to harmless end products (CO_2+H_2O). Semiconductor photocatalysis are newly developed AOPs and can be applied to degrade dyes conveniently [10]. One of the most commonly used semiconductors in photocatalytic processes is ZnO.

The photocatalytic decolorization of a dye is believed to take place according to the following mechanism: when a catalyst is exposed to UV radiation, electrons are promoted from the valance band to conduction band and an electron- hole pair is produced (equation 1) [11].

$$\text{Catalyst} + h_\nu \rightarrow e^-_{cb} + h^+_{vb} \quad (1)$$

Where, e^-_{cb} and h^+_{vb} are the electrons in the conduction band and the electron vacancy in the valence band, respectively. Both these entities can migrate to the catalyst surface, where they can enter in a redox reaction with other species present on the surface. In most cases, h^+_{vb} can react easily with surface bound H_2O to produce $OH^\bullet$ radicals, whereas, e^-_{cb} can react with O_2 to produce superoxide radical anion of oxygen (equations 2 and 3) [11].

$$H_2O + h^+_{vb} \rightarrow OH^\bullet + H^+ \quad (2)$$

$$O_2 + e^-_{cb} \rightarrow O_2^{-\bullet} \quad (3)$$

This reaction prevents the combination of the electron and the hole which are produced in the first step. $OH^\bullet$ and $O_2^{-\bullet}$, can then react with the dye to form other species and are thus responsible for the decolorization of the dye (equations 4 - 7).

$$O_2^{-\bullet} + H_2O \rightarrow H_2O_2 \quad (4)$$

$$H_2O_2 \rightarrow OH^{2\bullet} \quad (5)$$

$$OH^\bullet + \text{dye} \rightarrow \text{dye}_{ox} \quad (6)$$

$$\text{dye} + e^-_{cb} \rightarrow \text{dye}_{red} \quad (7)$$

The advantage of using semiconductor- based materials as photoactive catalysts in the detoxification of pollutants is the complete mineralization into environmentally friendly products, without generation of waste, which is not possible in the case of any other treatment method [12]. Other advantages include easy regeneration, reusability and activity under easily available UV-visible photolight. Among the various semiconductor

photocatalysts, ZnO appears to be a highly promising photocatalyst. One of the emerging technologies is nano photocatalysis using nanostructured semiconductors due to its high catalytic efficiency.

The main focus of the present work is to use commercially available nano structured ZnO in the photocatalytic decolourization and degradation study of methylene blue dye (MB).

2. EXPERIMENTAL PART:

2.1. Experimental setup and instrumentation:

The experiments were performed using a UV Tubular reactor, which uses a UV lamp for the photodegradation of the MB dye used as a pollutant. Fig. (3.1) shows the experimental setup

The UV lamp is 10 cm diameter and 40 cm long. It has a wavelength of 400 nm and 15watts. A pump is used for circulating the polluted water. It is a peristaltic (dosing) pump, supplied by Cole Parmer Instrument Company System, Model No 7521-10, giving a maximum flow rate of 580 ml/ min. A magnetic stirrer is used to ensure good mixing of ZnO with the polluted water. It is a product of B&T Company, having a maximum velocity of 100 rpm. A centrifuge is used to separate the catalyst particles from the solution before carrying up the measurement on the spectrophotometer. It is an auto bench centrifuge (80- 2) having a maximum speed of 4000 rpm. Dye concentration is followed along the test period using a UV-Vis spectrophotometer (PG Instruments LTD, Model T80).

2.2. Materials

***Pollutants*:**

Methylene Blue dye (λ= 664 nm) is used as a model pollutant throughout the experiments. It has the formula: $C_{16}H_{18}N_3SCl.3H_2O$. It is kindly supplied by Ciba Giegy

***Catalyst*:**

ZnO nano particles with particle size <100nm and average particle size ≤ 40nm are used as catalysts for the degradation of the pollutant, Methylene Blue dye, in the synthetic wastewater. The catalyst was prepared by Beni-Suef University.

Hydrochloric Acid:

HCl is used for adjusting the pH of the polluted water. It is supplied by Elnasr Pharmaceutical Chemicals Co., Egypt.

Sodium Hydroxide:

NaOH (98% purity; molecular weight 40) is used for adjusting the pH of the polluted water. It is kindly supplied by Oxford Laboratory.

Water:

Distilled water is used for preparing artificially polluted effluents.

2.3. Parameters Studied:

The parameters studied in the present work are:
Initial dye concentration: Solutions with concentrations 5, 10, 15, 20, 30 and 50 ppm were used.

Catalyst concentration: catalyst dosage with the values of 0.1, 0.2, 0.3 and 0.4 g/l were tested.

pH value: pH was changed with the values of 2.2, 7.2 and 12.2

3. RESULTS AND DISCUSSION:

The concentration of dye in the solution is followed through periodic readings on the spectrophotometer and these readings are used for calculating the percentage dye degradation along the test period.

3.1. Effect of initial dye concentration:

Solutions with initial dye concentration os 5, 10, 15, 30 and 50 ppm were tested with different values of catalyst concentration and different values of pH. Sample results are given in Figs. 1, 2 for relatively dilute (5, 10 and 15 ppm) solutions and relatively concentrated (30 and 50 ppm) solutions, respectively at catalyst loading of 0.1 g/l and pH value 2.2.

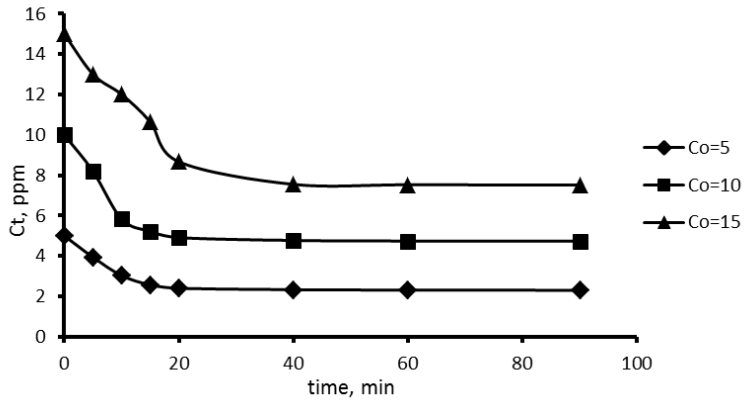

Fig. 1: Effect of initial concentration of pollutant on its degradation, C_o=5, 10, 15 ppm, at 0.1 g ZnO/l and pH=2.2

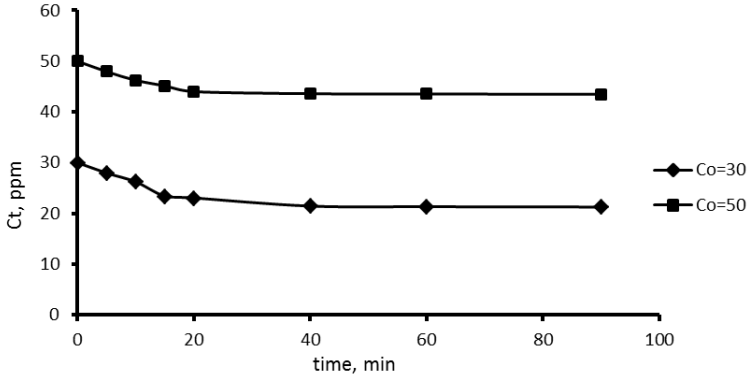

Fig. 2: Effect of initial concentration of pollutant on its degradation, C_o=30, 50 ppm, at 0.1 g ZnO/l and pH=2.2

Figures 1, 2 show that the rate of degradation is higher in the initial period of the reaction and it decreases afterward. After 90 minutes of reaction, the percentage dye degradation was calculated to be 54, 52.7, 49.87, 29.17

and 13.06% for solutions with dye conentrations of 5, 10, 15, 30 and 50 ppm, respectively. Thus the percentage dye degradation is higher with lower dye concentration in the solution. This result agrees with the work of Sampa Chakrabarti [13]. The corresponding results for 0.4 g/l catalyst dosage and pH 12.2 are shown in Figs. 3 and 4.

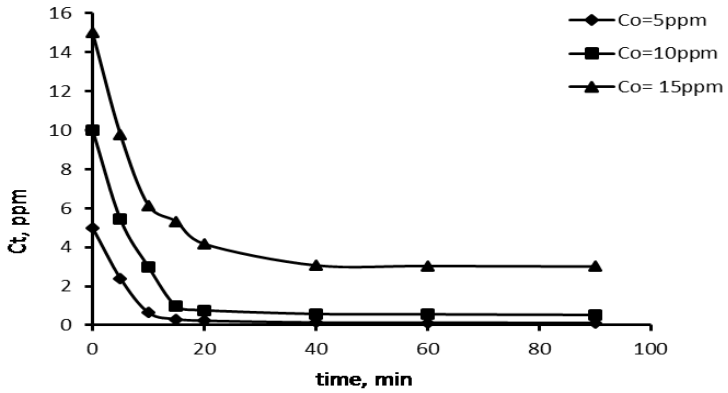

Fig. 3: Effect of initial concentration of pollutant on its degradation, C_o=5, 10, 15 ppm, at 0.4g ZnO/l and pH=12.2

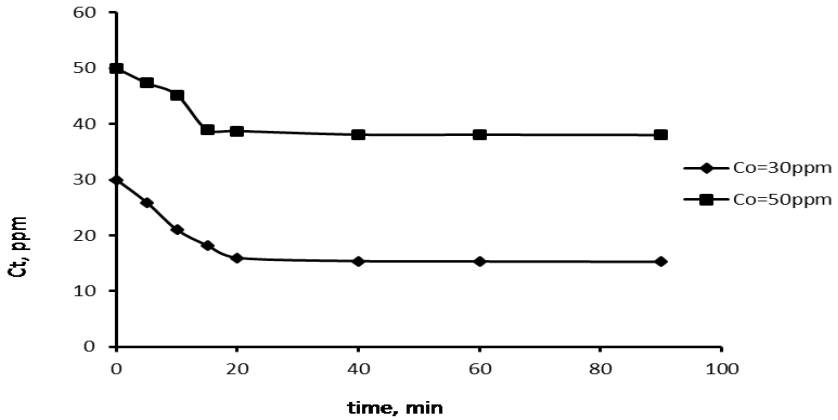

Fig. 4: Effect of initial concentration of pollutant on its degradation, C_o=30, 50 ppm, at 0.4g ZnO/l and pH=12.2

The values of dye concentration measured at different times, Ct, are used to calculate the percentage dye degradation at these particular times and the calculated values for percentage dye degradation are given in Table 1.

Table 1: Percentage dye degradation for different initial dye concentration at pH 12.2 and 0.4g/l ZnO

time	Pollutant Concentration (Ct), ppm									
	5ppm		10ppm		15ppm		30ppm		50ppm	
	Ct	% deg	Ct	% deg	Ct	% deg	Ct	% deg	Ct	% deg
0	5	0.00	10.00	0.00	15.00	0.00	30.00	0.00	50.00	0.00
5	2.4	52.00	5.43	45.70	9.78	34.80	25.92	13.60	47.36	5.28
10	0.65	87.00	3.00	70.00	6.15	59.00	21.01	29.97	45.21	9.58
15	0.31	93.80	0.97	90.30	5.33	64.47	18.20	39.33	38.92	22.16
20	0.23	95.40	0.77	92.30	4.17	72.20	15.98	46.73	38.74	22.52
40	0.14	97.20	0.58	94.20	3.07	79.53	15.38	48.73	37.11	24.78
60	0.13	97.40	0.56	94.40	3.04	79.73	15.32	48.93	37.08	25.84
90	0.12	97.60	0.53	94.70	3.01	79.93	15.26	49.13	37.07	25.86

Examination of the figures in Table 1 shows that the highest percentage dye degradation, 97.6%, is obtained from a 5 ppm dye polluted solution at pH value 12.2, using a catalyst dosage of 0.4 g/l.

3.2. Effect of catalyst dose:

Catalyst dosage of 0.1, 0.2, 0.3 and 0.4 g/l ZnO nanoparticles/l of dye solution was used and tests were run on solutions with different concentrations; 5, 10, 15, 30 and 50 ppm and different pH values; 2.2, 7.2, and 12.2. Sample results are presented in Figs. 5-7, for 5 ppm dye solution at pH values 2.2, 7.2 and 12.2, respectively.

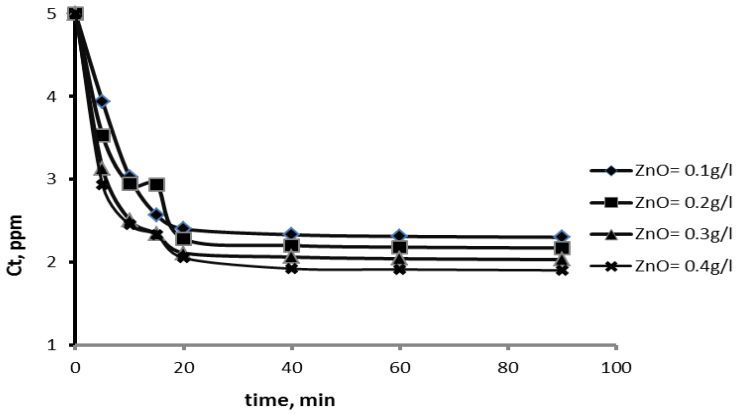

Fig. 5: Effect of amount of ZnO catalyst on degradation at C_o=5 and pH=2.2 at ZnO= 0.1, 0.2, 0.3 and 0.4g/l

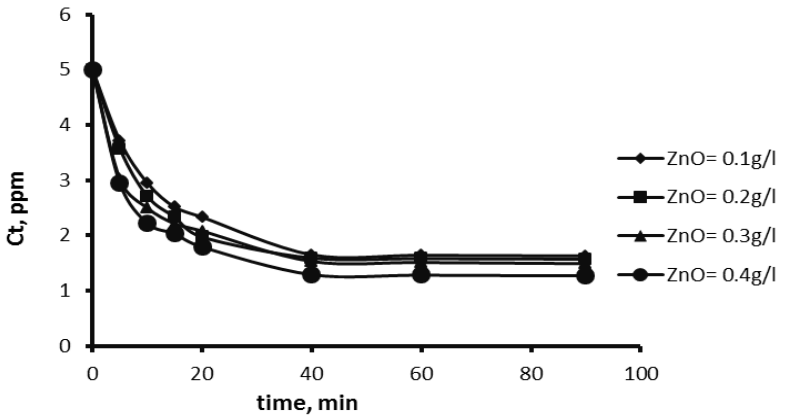

Fig. 6: Effect of amount of ZnO catalyst on degradation at C_o=5 and pH=7.2 at ZnO= 0.1, 0.2, 0.3 and 0.4g /l

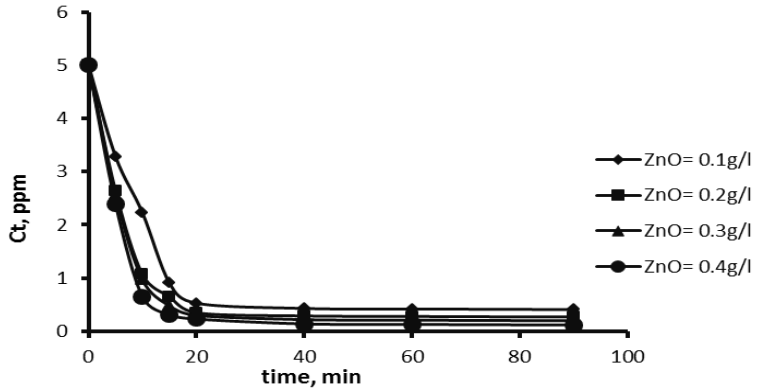

Fig. 7: Effect of amount of ZnO catalyst on degradation at C_o=5ppm and pH=12.2 at ZnO= 0.1, 0.2, 0.3 and 0.4g /l

Examination of these figures clarifies that the same trend for the effect of catalyst dosage – increasing rate of dye degradation with increasing catalyst dose- is shown even with changing the pH value. The values calculated for the percentage dye degradation at pH value 12.2 and different catalyst dosages are shown in Table 2. Examination of the figures in Table 2 indicates that the highest percentage dye degradation, 97.6%, is obtained when using catalyst concentration 0.4 g/l at pH value 12.2. This is followed by 96.0, 94.6 and 91.86% for catalyst concentrations 0.3, 0.2 and 0.1 g/l, respectively.

Table 2: Percentage dye degradation for different doses of catalyst at pH 12.2 and 5 ppm MB

Time, Min	Pollutant Concentration (Ct), ppm							
	0.1g ZnO/l		0.2g ZnO/l		0.3g ZnO/l		0.4g ZnO/l	
	C_t	% deg.	C_t	% deg.	C_t	% deg.	C_t	% deg.
0	5	0	5	0	5	0.00	5	0.00
5	3.29	34.52	2.64	47.20	2.57	48.60	2.4	52.00
10	2.23	55.43	1.07	78.60	0.97	80.60	0.65	87.00
15	0.91	81.79	0.65	87.00	0.48	90.40	0.31	93.80
20	0.53	89.22	0.35	93.00	0.30	94.00	0.23	95.40
40	0.43	91.37	0.29	94.20	0.22	95.60	0.14	97.20
60	0.42	91.61	0.28	94.40	0.21	95.80	0.13	97.40
90	0.41	91.86	0.27	94.60	0.20	96.00	0.12	97.60

The corresponding values at pH 2.2 are given in Table 3; also for 5 ppm dye solution and different catalyst concentrations. Examination of the figures in Table 3 shows that increasing catalyst concentration increases percentage dye degradation. However, relatively lower values for percentage dye degradation are obtained as compared to those values obtained at pH 12.2 (in Table 2).

Table 3: Percentage dye degradation for different doses of catalyst at pH 2.2 and 5 ppm MB concentration

Time, min	Pollutant Concentration (Ct), ppm							
	0.1g ZnO/l		0.2g ZnO/l		0.3g/l ZnO		0.4g ZnO/l	
	C_t	% deg.	C_t	% deg.	C_t	% deg.	C_t	% deg.
0	5	0	5	0	5	0	5	0
5	3.94	21.2	3.53	29.4	3.13	37.4	2.93	41.4
10	3.03	39.4	2.94	41.2	2.51	49.8	2.45	51.00
15	2.57	48.6	2.93	41.4	2.34	53.2	2.33	53.4
20	2.4	52.00	2.28	54.4	2.11	57.8	2.05	59.00
40	2.33	53.4	2.2	56.00	2.06	58.8	1.92	61.6
60	2.31	53.8	2.18	56.4	2.04	59.2	1.91	61.8
90	2.3	54.00	2.17	56.6	2.03	59.4	1.9	62.00

3.3. Effect of pH value:

Experiments were run on dye solutions 5, 10, 15, 30 and 50 ppm concentration with catalyst concentrations 0.1, 0.2, 0.3 and 0.4 g/l at different pH values of 2.2, 7.2 and 12.2. Sample results are given below.

Table 4 and figure 8 show the experimental results for a dye polluted solution of 5 ppm concentration and 0.1 g/l catalyst at different values of pH. After 90 minutes of reaction time, a solution with an initial dye concentration of 5 ppm reached 0.41 ppm with a percentage degradation of 91.86% at pH value 12.2 and 0.1 g/l catalyst concentration. This percentage corresponds to 67. 4 and 54.0% at pH values of 7.2 and 2.2, respectively. Thus, increasing the pH value of the solution increases the percentage degradation of the dye.

Table 4: Percentage dye degradation for 5pmm MB solution, 0.1g/l ZnO and different pH values

Time, min	Pollutant Concentration (Ct), ppm					
	2.2 pH		7.2 pH		12.2 pH	
	Ct	% deg.	Ct	% deg.	Ct	% deg.
0	5	0	5	0	5	0
5	3.94	21.2	3.71	25.80	3.29	34.52
10	3.03	39.4	2.95	41.00	2.23	55.43
15	2.57	48.6	2.51	49.80	0.91	81.79
20	2.4	52.00	2.33	53.40	0.53	89.22
40	2.33	53.4	1.65	67.00	0.43	91.37
60	2.31	53.8	1.64	67.20	0.42	91.61
90	2.3	54.00	1.63	67.40	0.41	91.86

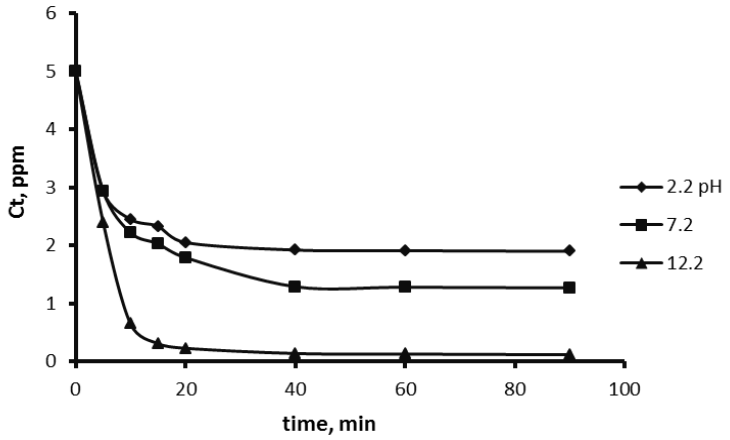

Fig. 8: Effect of pH values on dye degradation at C_o=5ppm and ZnO = 0.1g/l and pH= 2.2, 7.2 and 12.2

For a solution 10 ppm concentration and at the same catalyst concentration of 0.1 g/l, the corresponding values of percentage degradation were 52.7, 62.75 and 86.90% at pH values 2.2, 7.2 and 12.2, respectively. Thus the results in this test have the same trend as the earlier ones at 5 ppm solution but with relatively lower values for percentage dye degradation. The results of this test are shown in Table 5.

Table 5: Percentage dye degradation for 10ppm MB, 0.1g/l ZnO and different pH values

Time, min	Pollutant Concentration (Ct), ppm					
	2.2 pH		7.2 pH		12.2 pH	
	Ct	% deg.	Ct	% deg.	Ct	% deg.
0	10	0	10	0	10.00	0.00
5	9.02	18	7.2	28	7.01	29.90
10	7.26	41.7	5.83	41.7	5.21	47.90
15	6.02	47.8	5.22	47.8	3.12	68.80
20	5.57	50.9	4.91	50.9	1.95	80.50
40	4.91	52.3	3.77	62.3	1.34	86.60
60	4.84	52.6	3.74	62.6	1.33	86.70
90	4.83	52.7	3.73	62.7	1.31	86.90

For a dye solution of 5 ppm concentration and 0.4 g/l catalyst concentration, the highest percentage degradation was 97.6% at pH 12.2. This is to be compared with 74.6 and 62.0% at pH values 7.2 and 2.2, respectively. The results of this test are shown in Table 6. The attitude of these results agrees with the previous work of Gajbhiye, 2012 [14]. Furthermore, for a solution 50 ppm dye concentration and 0.4g/l catalyst concentration, the results are shown in Table 7. The results have the same trend as the previous test, i.e., increasing percentage dye concentration with increasing pH value. A percentage dye degradation of 25.86 was achieved at pH value 12.2 as to be compared with 21.2 and 17.26% at pH values of 7.2 and 2.2, respectively.

Table 6: Percentage dye degradation for 5pmm MB solution, 0.4g/l ZnO and different pH values

Time, min	Pollutant Concentration (Ct), ppm					
	2.2 pH		7.2 pH		12.2 pH	
	Ct	% deg.	Ct	% deg.	Ct	% deg.
0	5	0	5	0	5	0.00
5	2.93	41.4	2.94	41.20	2.4	52.00
10	2.45	51.00	2.22	55.60	0.65	87.00
15	2.33	53.4	2.03	59.40	0.31	93.80
20	2.05	59.00	1.79	64.20	0.23	95.40
40	1.92	61.6	1.29	74.20	0.14	97.20
60	1.91	61.8	1.28	74.40	0.13	97.40
90	1.9	62.00	1.27	74.60	0.12	97.60

Table 7: Percentage dye degradation for 50ppm MB, 0.4g/l ZnO and different pH values

Time, min	Pollutant Concentration (Ct), ppm					
	2.2 pH		7.2 pH		12.2 pH	
	Ct	% deg.	Ct	% deg.	Ct	% deg.
0	50	0	50.00	0.00	50.00	0.00
5	45.02	9.96	45.09	9.82	47.36	5.28
10	43.83	12.34	43.51	10.98	45.21	9.58
15	43.41	13.18	41.56	16.88	38.92	22.16
20	42.51	14.98	40.83	18.34	38.74	22.52
40	41.55	16.9	39.62	20.76	37.11	24.78
60	41.49	17.02	39.46	21.08	37.08	25.84
90	41.37	17.26	39.40	21.20	37.07	25.86

Thus, when studying the effect of pH value, it is noticed that higher pH values result in higher percentage degradation. This is valid at different values of catalyst concentration and for different values of initial dye concentration.

CONCLUSION:

The following conclusions could be made from the present study:

- The rate of dye degradation is higher as the initial dye concentration is lower.
- Higher percentage dye degradation is achieved by lower concentration dye solutions, e.g., a percentage dye degradation of 97.6% is achieved by a dye solution 5 ppm concentration at pH 12.2 and 0.4 catalyst concentration as compared to 25.86 % for 50 ppm dye solution at the same values of pH and catalyst concentration.
- Increasing the catalyst dose has a positive effect on the percentage dye degradation. Values of percentage dye degradation using 0.4 g/l catalyst concentration were noticeably higher than its corresponding's when catalyst doses of 0.3, 0.2 or 0.1 g/l were used. A 10 ppm dye solution showed a percentage dye degradation of 94.7 when using 0.4 g/l catalyst at pH 7.2, while the same solution showed 68.3, 66.2 and 62.7% degradation when using catalyst concentration 0.3, 0.2 and 0.1 g/l, respectively at the same pH value.

- Increasing the pH value increases the rate of dye degradation and its percentage degradation. A percentage dye degradation of 97.6 was achieved with a 5 ppm dye solution at pH value 12.2 when using 0.4 g/l catalyst dose and this corresponds to 74.6 and 62% at pH values of 7.2 and 2.2, respectively, keeping other parameters constant.

REFERENCES

1. Akar, T., et al., Biosorption potential of Neurospora crassa cells for decolorization of Acid Red 57 (AR57) dye. Journal of Chemical Technology and Biotechnology, 2006. **81**(7): p. 1100-1106.
2. . Kargi, F. and S. Ozmıhcı, Biosorption performance of powdered activated sludge for removal of different dyestuffs. Enzyme and Microbial Technology, 2004. **35**(2): p. 267-271.
3. Daneshvar, N., D. Salari, and A. Khataee, Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO 2. Journal of Photochemistry and Photobiology A: Chemistry, 2004. **162**(2): p. 317-322.
4. Kuo, W. and P. Ho, Solar photocatalytic decolorization of methylene blue in water. Chemosphere, 2001. **45**(1): p. 77-83.
5. Legrini, O., E. Oliveros, and A. Braun, Photochemical processes for water treatment. Chemical Reviews, 1993. **93**(2): p. 671-698.
6. Hamza, A. and M. Hamoda, 35th Purdue industrial waste congress. West Lafayette, IN, USA, 1980.
7. Souther, R. and T. Alspaugh, Textile waste treatment studies. Journal of the Water Pollution Control Federation, 1957. **29**: p. 804.
8. Beydoun, D., et al ،.Role of nanoparticles in photocatalysis. Journal of Nanoparticle Research, 1999. **1**(4): p. 439-458.
9. Matthews, R., Photocatalysis in water purification: Possibilities, problems and prospects. Photocatalytic Purification and Treatment of Water and Air, 1 .**121-993**.
10. Sobczyński, A. and A. Dobosz, Water purification by photocatalysis on semiconductors. Polish journal of environmental studies, 2001. **10**(4): p. 195-205.
11. Jeni, J. and S. Kanmani, Solar nanophotocatalytic decolorisation of reactive dyes using titanium dioxide. Iranian Journal of Environmental Health Science & Engineering, 2011. **8**(1): p. 15.
12. Dieckmann, M.S. and K.A. Gray, A comparison of the degradation of 4-nitrophenol via direct and sensitized photocatalysis in TiO 2 slurries. Water Research, 1996. **30**(5): p. 1169-1183.
13. Chakrabarti, S. and B.K. Dutta, Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst. Journal of hazardous materials, 2004. **112**(3): p. 269-278.
14. Gajbhiye, S.B., Photocatalytic degradation study of methylene blue solutions and its application to dye industry effluent. Int. J. Mod. Eng. Res, 2012. **2**(3): p. 1204-1208.

الملخص العربى

في هذه الدراسة ، تم دراسة التحلل الضوئي لصبغة الميثيلين الأزرق . وذلك باستخدام أكسيد الزنك فى الصورة المتناهية الصغر (النانو) حيث يعتبر شكل معدل من أكسيد الزنك فى الصورة العادية. طبقات اكسيد الزنك المتناهية الصغر تمتلك المسافات البينية المرنة و قدرة التبادل الكاتيوني تكون عالية وايضا مساحة سطح عالية كما انها لها كثافة عالية من مجموعة الهيدروكسيل على السطح. وبالتالي، فإنها تعتبر حافزا واعدا لإزالة الصبغة.

هنا يتم استخدام اكسيد الزنك فى الحالة المتناهية الصغر (النانو) كمحفز ضوئى لتدمير صبغة الميثلين الزرقاء الموجودة بالمحلول.

العوامل التى تمت دراستها هى: التركيز الابتدائى للصبغة (خمس قيم تم اختبارها ٥، ١٠، ١٥، ٣٠، ٥٠ جزء فى المليون) وتركيز العامل الحفاز ،اكسيد الزنك كمادة متناهية الصغر (اربع قيم تم اختبارها ٠,١، ٠,٢، ٠,٣، ٠,٤ جم/لتر من المحلول) وايضا تمت دراسة وسطية المحلول من حيث الأس الهيدروجينى (ثلاث قيم تم اختبارها ٢,٢، ٧,٢، ١٢).

التحلل الضوئى باستخدام أكسيد الزنك فى الصورة المتناهية الصغر (النانو):

دراسة تأثير التركيز الابتدائى للصبغة داخل المحلول اظهرت التالى:

- ✓ كلما قل التركيز الابتدائى كلما زاد معدل التدهور او التحلل للصبغة.
- ✓ الكمية الأنسب من العامل الضوئى الحفازهى عند التركيز ٠,٤جم/لتر من المحلول مقارنة بالكميات الاقل (٠,١، ٠,٢، ٠,٣جم/لتر).
- ✓ عمليات التحفيز الضوئى تعمل بشكل افضل فى الوسط القاعدى عنها فى الوسط الحامضى او المتعادل بمعنى ان القيمة الانسب للأس الهيدروجينى للمحلول هو ١٢.

دراسة (Optimization):

وقد اجريت دراسة الأبتمة باستخدام برنامج (RSM) وذلك لتحديد القيم الأنسب للعوامل المؤثرة على عملية التحلل الضوئى والتى تؤدى إلى أعلى نسبة لتحلل الصبغة. وفى هذا الجزء تمت دراسة تأثير معدل السريان، كمية العامل الضوئى الحفاز وقيم الأس الهيدروجينى للمحلول وكانت الظروف الأمثل هى:

- ✓ معدل السريان عند ٣٥٨,٢٧٢ ملليلتر/دقيقة.
- ✓ قيمة الأس الهيدروجينى عند ١١,١٦٦٧.
- ✓ كمية العامل الحفاز الضوئى عند ٠,٤٩٨٢جم/لتر من المحلول.

وهذا يوضح توافق النتائج المعملية ونتائج الأبتمة الى حد كبير