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Technical Report

Effect of Three Operating Variables on Degradation of Methylene Blue by ZnO Electrodeposited: Response Surface Methodology

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There are several studies on the morphology of zinc oxide (ZnO) in the photocatalytic elimination of organic pollutants, but few studies focus on the simultaneous effect of different operating parameters. Most studies have been carried out by unifactorial experiments, which is inefficient. For this reason, in this study, ZnO thin films were prepared by electrodeposition and the response surface methodology (RSM) was applied to evaluate the effect of variables such as: concentration of methylene blue dye (MB), pH and air flow involved on the photocatalytic degradation of methylene blue. The results showed that the RSM is a suitable technique to determine the operating conditions favorable for the degradation of MB within a determined range of study.

Keywords: MB photodegradation, operating variables, response surface.

1. INTRODUCTION

The Mexican textile industry contributes around 3% of industrial discharges and occupy 7th place in water pollution[1]. To remedy this problem; the chemical, physical, physicochemical or electrochemical processes are used today, thus helping to eliminate at least the most dangerous pollutants.

Several methods for tertiary treatment of waste water have been developed in order to reuse the water without pollutants, some of these methods include: UV radiation, ozonation and reverse osmosis, between others. Ozonation is one of the best methods for the removal of dye from textile wastewater, however, is not economically viable. This has prompted a search for alternative methods which can be economic and efficient, it finding that the zinc oxide is an alternative. The interest in ZnO is because it is relatively inexpensive, non toxic, can be activated by UV light and has a high oxidizing power [2].

Several authors point out that the photocatalytic properties of ZnO depend strongly on their morphology, which in turn depends on the conditions of preparation, for example, in electrochemical deposition are: substrate temperature, substrate material, heat treatment, voltage, deposition time, additives and equalization of the lattice parameter between the semiconductor and the substrate [3-8]. On the other hand, adequate control of the operating conditions for the degradation of organic pollutants by ZnO is necessary for optimal performance of the photocatalyst. Some of the more important operating conditions affecting the photocatalytic process are: organic pollutant concentration, concentration of the photocatalyst, UV light intensity, pH and oxygen flow [9, 10]. ZnO has been little studied for purposes of catalysis because it exhibits photocorrosion in aqueous solutions at very low or very high pH value, which leads to decreasing its photocatalytic efficiency [10]. However, there are reports of minimal photocorrosion to optimum working pH [11] and by increasing the crystallinity of ZnO [12].

In order to know the individual and combined effects of operating variables: methylene blue concentration, pH and air flow over the photocatalytic process of methylene blue by ZnO, it was proposed the experimental design 2^3 with center point as it is presented in the Table 1.

Table 1. Experimental Design 2^3 proposed for the methylene blue photodegradation by ZnO.

Variable codes	Factor	Low level (-1)	Center points (0)	High level (+1)
A	MB concentration	10 ppm	15 ppm	20 ppm
B	pH	2.8 pH	5.8 pH	8.8 pH
C	Air flow	0.94 mL/s	1.17 mL/s	1.36 mL/s

2. EXPERIMENTAL

ZnO samples for the experimental design were prepared by potentiostatic deposition method from an aqueous solution of zinc nitrate ($Zn(NO_3)_2$) 0.1 M. The deposition parameters were: voltage between the electrodes V= -1.5 V, temperature T = 65 ° C and deposition time t = 18 min.

A three electrode glass cell was used it, a graphite electrode of 0.9 cm x 1.3 cm x 0.2 cm, silver chloride electrode and a graphite electrode of 1.2 cm x 2.0 cm x 0.2 cm as the working, reference and counter electrodes, respectively.

The chemical equations of the reaction are the following [13].

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$$
$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$$
$$Zn(OH)_2 \rightarrow ZnO + H_2O$$

The electro-deposits were characterized using a BRUKER D8 DISCOVER diffractometer in order to identify the crystalline phase. The surface morphology was observed by mean to a JEOL-JSM 6610LV scanning electron microscope (SEM).

The methylene blue photodegradation was performed according to the random list of experimental treatments generated with STATGRAPHICS plus 4.1, which it is presented in the Table 2. The solution pH was adjusted by adding a small amount of HCl or NaOH.

Table 2. Experimental treatments generated with STATGRAPHICS plus 4.1

Treatments	pH	MB concentration ppm	Air flow mL/s
1	-1.0	1.0	-1.0
2	0.0	0.0	0.0
3	1.0	1.0	-1.0
4	-1.0	-1.0	-1.0
5	1.0	1.0	1.0
6	1.0	-1.0	1.0
7	-1.0	-1.0	1.0
8	-1.0	1.0	1.0
9	1.0	-1.0	-1.0
10	-1.0	1.0	-1.0
11	0.0	0.0	0.0
12	1.0	1.0	-1.0
13	-1.0	-1.0	-1.0
14	1.0	1.0	1.0
15	1.0	-1.0	1.0
16	-1.0	-1.0	1.0
17	-1.0	1.0	1.0
18	1.0	-1.0	-1.0

Figure 1 shows a schematic diagram of the experimental setup to perform the photocatalytic degradation. The system consists of a wooden box, in which it was placed a beaker (on a Jack) containing 25 mL of methylene blue solution, where the ZnO/graphite system was introduced. The housing has an opening on the top where a Mineralight xenon UV lamp (6 mW/cm^2) was mounted, the air flow was introduced through a hole on the wall of the box. Photodegradation of Methylene Blue was monitored by a UNICAM V-2 UV-Vis spectrophotometer.

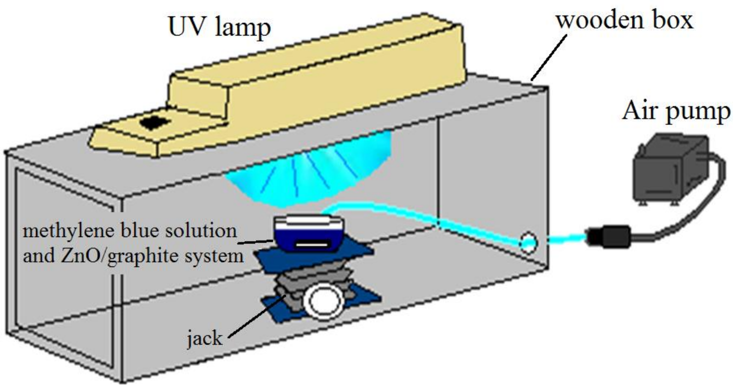

Figure 1. Schematic diagram of the system used for the methylene blue degradation.

3. RESULTS AND DISCUSSION

3.1 Characterization by X-ray diffraction.

Figure 2 shows the characterization by X-ray diffraction for the ZnO/graphite system. The diffractogram shows peaks corresponding to ZnO polycrystalline in the hexagonal phase (labeled with black asterisk) according to JCPDS crystallographic table, also other peaks were identified (labeled with red asterisk), corresponding to the graphite substrate. The zero overlap between the diffraction peaks corresponding to graphite and ZnO indicates no interdiffusion between the deposit and substrate, which means that no new substance is formed.

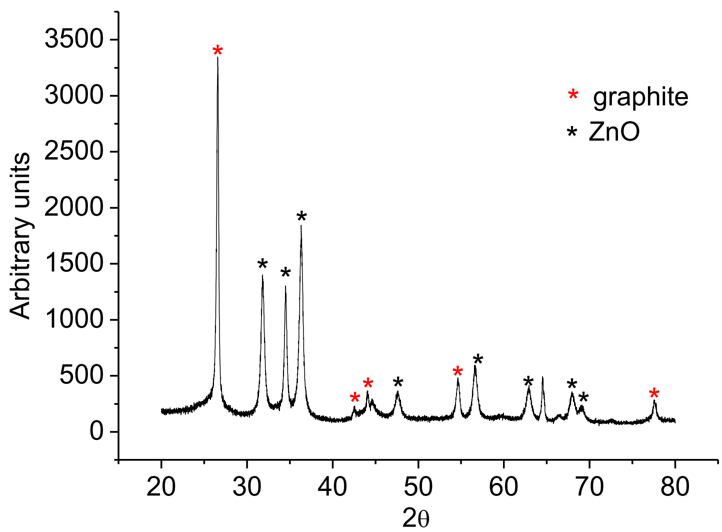

Figure 2. Diffractogram of the ZnO/graphite system.

3.2 Characterization by Scanning Electron Microscopy

Figure 3 shows the morphology of the ZnO samples obtained by SEM. The pores in the substrate are related to the effect of hydrogen adsorbed on the surface of the graphite during ZnO electrodeposition process.

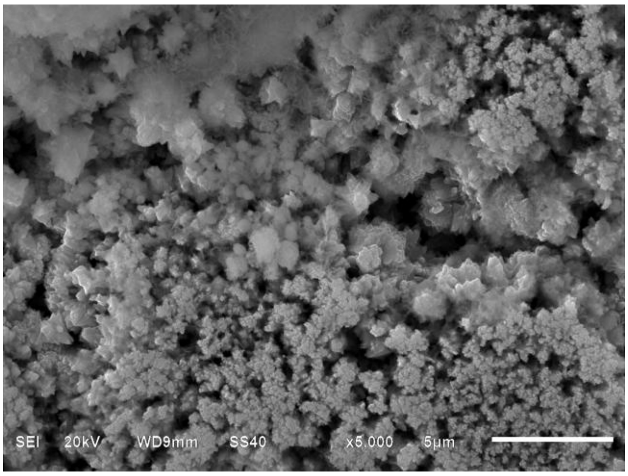

Figure 3. Micrograph of the ZnO/graphite system obtained by SEM.

3.3 Photodegradation of the Methylene Blue solution

Figure 4 shows the evolution absorption spectrum of the MB depends on the illumination time for a representative sample. In general, it appears that as greater is the illumination time of Methylene Blue solution, the intensity of the peak located at 664 nm is reduced, which it demonstrating the MB photodegradation [14].

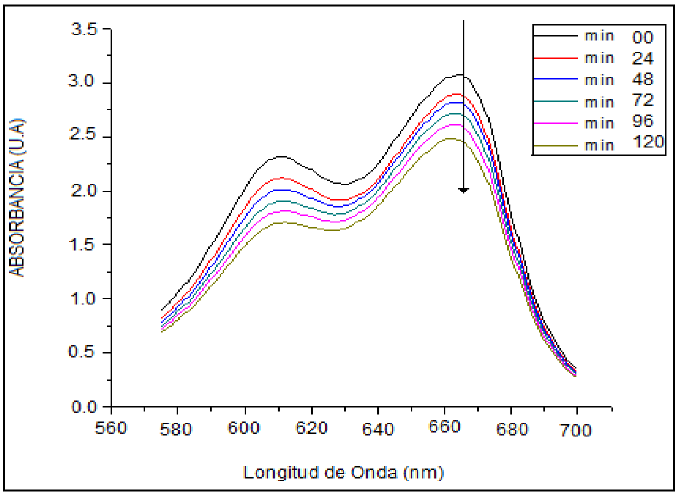

Figure 4. Variation of absorption spectrum of methylene blue depends on the illumination time.

The photocatalytic activity of ZnO films was monitored from MB photodegradation, the results are presented in the Table 3 and are used for the statistical analysis of the response variable presented below.

Table 3. Results of the photocatalytic decolorization of methylene blue according to experimental design.

	factors			Real factors			Response Variables	Replication
Treatments	A	B	C	pH	MB concentration ppm	Air flow mL/s	Percentage degradation of MB	Percentage degradation of MB
1	-1	-1	-1	2.8	10	0.94	44.55	47.09
2	1	-1	-1	8.8	10	0.94	34.92	42.6
3	-1	1	-1	2.8	20	0.94	15.99	20.74
4	1	1	-1	8.8	20	0.94	24.84	21.94
5	-1	-1	1	2.8	10	1.36	23.61	31.61
6	1	-1	1	8.8	10	1.36	47.37	51.51
7	-1	1	1	2.8	20	1.36	21.41	19.28
8	1	1	1	8.8	20	1.36	19.95	21.91
Center points	0	0	0	5.8	15	1.17	26.89	22.64

3.4 Statistical analysis for response variable (MB degradation)

The effects are plotted in a Standardized Pareto chart (Figure 5), because it is easy to decide if the different categories of factors affect the response variable to a confidence level of 95%, so if the bar representing an effect is greater than the critical value represented by the vertical line, then the effect is statistically different from zero and affect the response [15]. The preliminary interpretation of Standardized Pareto chart indicates that the factor B affects the response variable to a significance level of 95%.

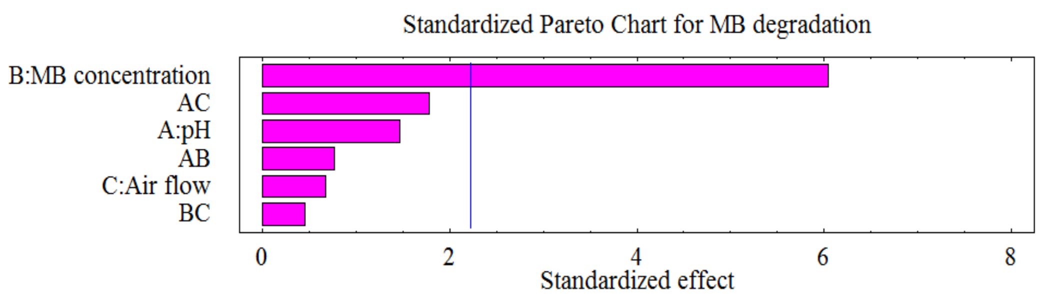

Figure 5. Standardized Pareto chart for the response variable (MB degradation) of the experimental design.

To corroborate this, a statistical study was carried out by an analysis of variance (Table 3). If an effect has a p-value less than 0.05, then the effect influences on the response and as the smaller the p-value, the more significant is this effect.

Table 3. Analysis of variance for MB degradation.

Analysis of Variance for MB degradation

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
A:pH	94.09	1	94.09	2.17	0.1718
B:MB concentration	1583.24	1	1583.24	36.45	0.0001
C:Air flow	20.205	1	20.205	0.47	0.5107
AB	25.7049	1	25.7049	0.59	0.4595
AC	137.71	1	137.71	3.17	0.1053
BC	9.21123	1	9.21123	0.21	0.6550
blocks	17.6616	1	17.6616	0.41	0.5380
Total error	434.364	10	43.4364		
Total (corr.)	2322.19	17			

R-squared = 81.2951 percent
R-squared (adjusted for d.f.) = 71.0924 percent

The preliminary interpretation of the results indicates that the factor B only affects the response to a significance level of 95%. However, there are factors that have a p-value closer to 0.05, which are A and AC. To clarify if this factors really influence on the response variable, only significant effects are included in the Standardized Pareto chart, Figure 6. As we can see in the figure 5, the effects C, AB and BC have little influence on the response variable because it have a high p-value (0.5107, 0.4595 and 0.6550 respectively) and hence practically does not contribute to the value of adjusted R^2, for what they were not considered.

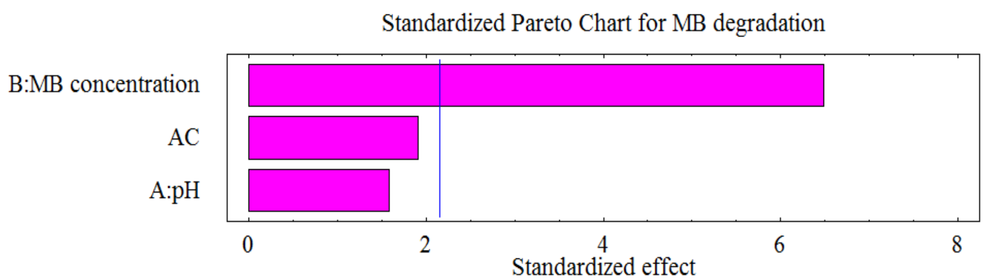

Figure 6. Standardized Pareto chart for grain number showing only significant effects

The standardized Pareto diagram clearly shows that statistically the effect B influences the response variable to a confidence level of 95%. Figure 7 shows the effect B and according to this, it is possible to consider the higher Methylene Blue degradation is obtained at a concentration of 10 ppm, because of a lower methylene blue concentration allows that more UV light passes through the solution, leading to the activation of more active catalytic sites which help to degrade more methylene blue solution.

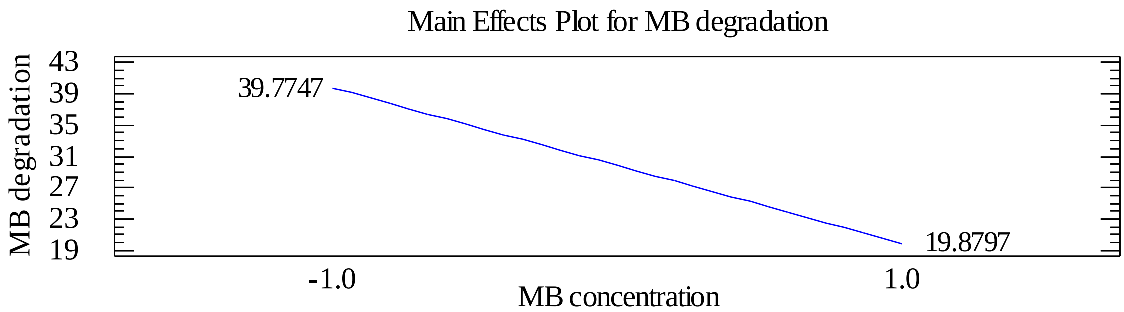

Figure 7. Representation of the effect B.

On the other hand, as it was observed in the figure 6, the A and AC effects also influences the response variable, because of the bars representing the effects are near the critical value. Since interactions have priority over the effects, then we interpret the interaction AC through its response surface, which it shows in the Figure 8. The general trend is that MB degradation increases as pH and high air flow increased it. This may be due to the greater oxygen flow increases the degradation capacity [16]. On the other hand, since the pH of the zero point of charge (pHzpc) is 9.0,then the surface of the catalyst is positive below this value, thereby to pH = 8.8 the ZnO surface it is less positive, which it facilitates the electrostatic attraction between the catalyst and the cationic dye and increase both adsorption and the degree of photodegradation [10].

The adjusted model of the response variable in the experimental region was obtained by the important factors and is:

MB degradation = 29.8272 + 2.425*pH - 9.9475*MB concentration +2.93375*pH*Air flow

The twist in the response surface indicates a possible minimum.

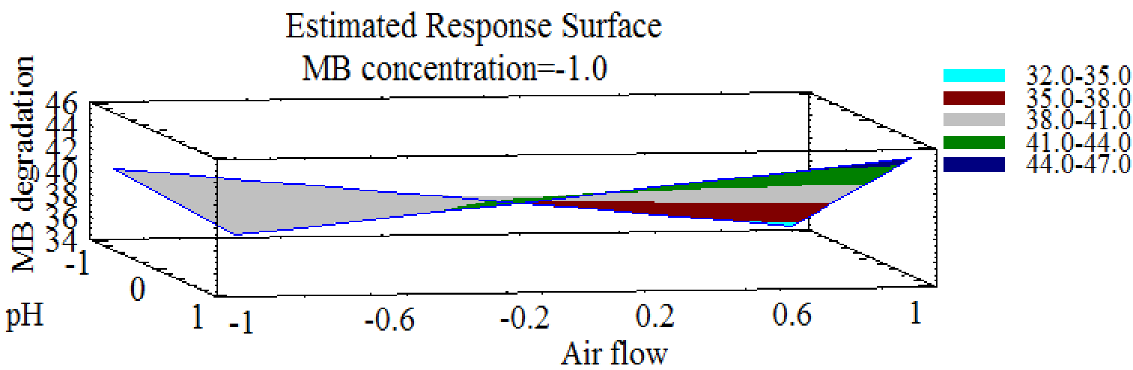

Figure 8. Estimated response surface of the factors A (pH) and C (air flow).

Based on this, it can be concluded that the optimum conditions for the MB degradation are: 10 ppm of MB solution, pH=8.8 and air flow=1.38 mL/s.

4. CONCLUSIONS

Statistical analysis of experimental design is appropriate to determine the operating conditions favorable for the degradation of MB by photocatalysis method, where operating conditions favorable are to a high pH (8.8), low MB concentration (10 ppm) and high air flow (1.38 mL/s).

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